Green Chemistry

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c4gc01911c

A synergistic biorefinery based on catalytic conversion of lignin prior to cellulose starting from lignocellulosic biomass†

Trenton Parsell,‡[a,b] Sara Yohe,‡[b,c] John Degenstein,‡[b,c] Tiffany Jarrell,[a,b] Ian Klein,[a,b] Emre Gencer,[b,c] Barron Hewetson,[b,d] Matt Hurt,[a,b] Jeong Im Kim,[b,e] Harshavardhan Choudhari,[b,c] Basudeb Saha,[a,b] Richard Meilan,[b,f] Nathan Mosier,[b,d] Fabio Ribeiro,[b,c] W. Nicholas Delgass,[b,c] Clint Chapple,[b,e] Hilkka I. Kenttämaa,[a,b] Rakesh Agrawal*[b,c] and Mahdi M. Abu-Omar*[a,b,c]

Received 1st October 2014,
Accepted 1st December 2014

DOI: 10.1039/c4gc01911c

www.rsc.org/greenchem

Current biomass utilization processes do not make use of lignin beyond its heat value. Here we report on a bimetallic Zn/Pd/C catalyst that converts lignin in intact lignocellulosic biomass directly into two methoxyphenol products, leaving behind the carbohydrates as a solid residue. Genetically modified poplar enhanced in syringyl (S) monomer content yields only a single product, dihydroeugenol. Lignin-derived methoxyphenols can be deoxygenated further to propylcyclohexane. The leftover carbohydrate residue is hydrolyzed by cellulases to give glucose in 95% yield, which is comparable to lignin-free cellulose (solka floc). New conversion pathways to useful fuels and chemicals are proposed based on the efficient conversion of lignin into intact hydrocarbons.

Significance statement

Renewable fuels are of great interest because of depleting fossil fuel reserves and climate change caused by increased CO_2 emissions. The component of biomass known as lignin hinders our ability to convert cellulose to ethanol and is currently wasted. Here we present a chemical method for converting lignin in two steps to fuels and chemicals while making the cellulosic carbohydrates more accessible. The described synergies should improve carbon utilization in the future biorefinery.

Introduction

Production of liquid fuels and chemicals from lignocellulosic biomass is an integral part of the solution to the energy grand challenge.[1] Biorefinery concepts for the production of liquid fuels and chemicals from biomass have been developed and some commercially implemented.[2–4] However, any renewable platform must provide both liquid fuels and commodity chemicals on a large scale. For example, in 2012 the U.S. consumed ~4.6 billion barrels of liquid fuels and produced greater than 90 Mton of organic commodity chemicals, respectively (including ~8 Mton of benzene).[5–7] Cellulosic conversion methods to ethanol and other liquid fuels make use of only the carbohydrate components of biomass (~50–60% by weight).[8–10] In comparison, the lignin component (20–30% by weight but accounting for ~37% of the carbon in biomass) inhibits the conversion of cellulose and constitutes a major waste stream that is burned for its heat value in most applications.[11] Therefore, lignin represents an opportunity for meeting the demand for a renewable platform of aromatic fuels and commodity chemicals (*e.g.* benzene, toluene, xylene (BTX), styrene, and cumene). As a result, methods for the selective conversion of lignin are important.[11]

The concept of lignin utilization to produce high-value products is not new.[12,13] However, actual reaction schemes to effectively convert lignin with high yield to useful end-products

---

[a] *Brown Laboratory and Negishi Brown Institute, Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907, USA*
[b] *The Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio), Discovery Park, Purdue University, West Lafayette, IN 47907, USA. E-mail: agrawalr@purdue.edu, mabuomar@purdue.edu*
[c] *School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA*
[d] *Laboratory of Renewable Resources Engineering and Department of Agricultural and Biological Engineering, Purdue University, West Lafayette, IN 47907, USA*
[e] *Department of Biochemistry, Purdue University, West Lafayette, IN 47907, USA*
[f] *Department of Forestry and Natural Resources, Purdue University, West Lafayette, IN 47907, USA*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4gc01911c

‡ Contributed equally to this work.

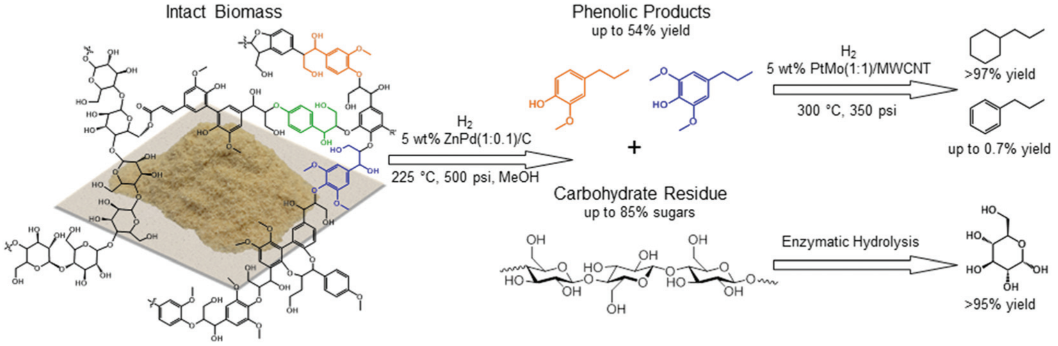


Fig. 1 Selective depolymerization and hydrodeoxygenation (HDO) of lignin first from wood biomass to give a lignin-derived hydrocarbon platform and glucose from the carbohydrate residue.

remains a significant challenge. There are processes that produce organosolv lignin separating it from hemicellulose and cellulose, but the resulting organosolv lignin fraction is an extremely complex mixture, which upgrading to a reasonable number of products in any significant yields is yet to be demonstrated.[14] Currently one of the few notable commercial processes utilizes lingo-sulfonate lignin derived from sulfite pulping to produce vanillin at a maximum yield of only 7.5% by mass.[15] Even though new catalysts have been reported for the cleavage of ether C–O bonds and hydrodeoxygenation (HDO) of lignin model compounds, only limited successes have been reported with lignin or biomass.[16–23] Heterogeneous Ni catalysts have been used recently with lignosulfonate to give a mixture of phenolic compounds and dimeric lignin fragments with removal of the sulfur as H_2S.[22] Ford and coworkers have reported a catalytic method in supercritical methanol at 300–320 °C and 160–220 bar of H_2 that converts the lignified components of biomass to hydrogenated cyclic alcohols.[23] A recent report has appeared on the conversion of birch sawdust to phenolic compounds utilizing a Ni/C catalyst.[24,25] Previously we reported on a catalytic system that could cleave the β-O-4 linkages found in lignin dimeric and polymeric model compounds with high selectivity and yields.[26]

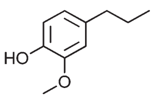
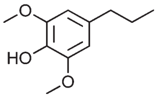
Here we present the use of a bimetallic catalyst based on Zn and nanoparticulate Pd in a selective conversion process compatible with diverse species of intact woody biomass. The catalyst produces a single lignin-derived product stream in high yields, leaving essentially all polysaccharide components of the biomass as a solid residue, which we have demonstrated undergoes enzymatic hydrolysis, resulting in high yields of glucose (Fig. 1). In addition to several wild type species of poplar, conversion of genetically modified poplar that contain high S type lignin is described.[27] This type of bioengineering offers a method to control the potential products from reactions involving biomass. Furthermore, methoxypropylphenols similar to those produced during this catalytic reduction of lignin can be converted quantitatively in a second step using a bifunctional Pt–Mo catalyst to hydrocarbon fuel or propylbenzene. The latter serves as a platform for production of aromatic chemicals.

Selective catalytic conversion of lignin

Our biomass conversion process is accomplished *via* a bimetallic catalytic system composed of Zn^{II} sites and metallic Pd nanoparticles (3–4 nm) dispersed on a carbon support. This bimetallic system has been shown previously to have a synergistic effect that cleaves β-O-4 linkages found in model compounds more effectively than either component alone.[26] For this catalytic process the biomass was first milled to pass through a 40 mesh screen then washed consecutively with water and ethanol *via* soxhlet extraction. Three different types of pretreated wild-type (WT) poplar (species within the genus *Populus*) wood were reacted with the Zn/Pd/C catalyst in methanol (MeOH) at 225 °C and 500 psig of H_2 which resulted in 40–54% of the available lignin being converted to two products: 2-methoxy-4-propylphenol (dihydroeugenol) and 2,6-dimethoxy-4-propylphenol (Table 1, entries 1, 3, and 4, and Fig. 2A). Based on our experimental results, Zn, Pd, and H_2 are all required for catalysis. Control reactions with poplar biomass using Zn alone gave minimal conversion to multiple oxygenated products and no products were generated in the absence of H_2. Reactions of poplar wood with Pd/C alone gave low yields of more highly oxygenated methoxypropylphenol products. To facilitate separation and recycling (shown in Table S1†) of the Zn/Pd/C catalyst, we ran the reaction employing a microporous cage (325 mesh) to separate the Pd/C from the biomass. Such a cage allows the solvent and solute to access the catalyst and leaves behind a cellulosic biomass residue that is Pd/C free. This result is also consistent with the mechanism proposed in our previous study with model compounds where the Zn can be desorbed from the carbon surface and is free to pass in and out of the microporous cage.[26]

The described preparation/pretreatment of biomass is minimal and all the steps are scalable, an important prerequisite of any process for large-scale application in a biorefinery. The two products reflect guaiacyl (G) and syringyl (S) lignin components present in WT poplar and illustrate the applicability of our catalysis to variants within the genus *Populus*. Following our single-step catalytic conversion, the starting biomass is fractionated into two forms, the first is a solid

Table 1 Conversion of lignin starting with intact lignocellulosic biomass over Zn/Pd/C catalyst

Biomass type	%G lignin[a]	%S lignin[a]	% Lignin content[b]	Selectivity 	Selectivity 	Yield[c] (wt%)
Poplar WT-717	44	51	19	31	69	40
Poplar 717-F5H	20	73	20	17	83	36
Poplar WT-NM-6	40	55	18	28	72	44
Poplar WT-LORRE	49	47	19	45	55	54
WT-white birch	44	49	16	31	69	52
WT-eucalyptus	34	65	24	30	70	49
WT-lodgepole pine	100	0	31	100	NA	19

[a] Lignin composition as determined by DFRC (derivatization followed by reductive cleavage) analysis. [b] Lignin content as determined by ABSL (acetyl bromide-soluble lignin) lignin analysis. [c] Yield is calculated using the initial mass of lignin and the mass of the products, factoring in the loss of two atoms of oxygen for each mole of product produced.

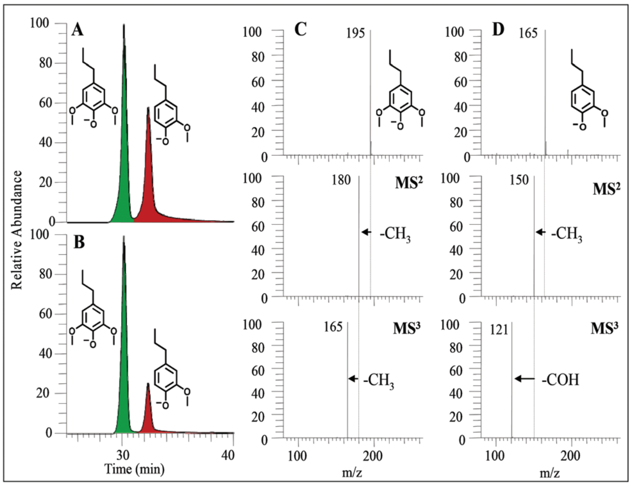


Fig. 2 Single ion monitoring ESI(−)/HPLC/MS of lignin products (*m/z* 165 and *m/z* 195) from (a) WT-717 poplar and (b) 717-F5H, a high-S transgenic line. CAD MS/MS of (c) deprotonated 2,6-dimethoxy-4-propyl phenol and (d) deprotonated dihydroeugenol derived from WT-717 poplar.

residue that is easily filtered and the second consists of products that are soluble in MeOH. The MeOH liquid-phase contains the methoxypropylphenol products shown in Table 1 and a small amount of soluble sugars that mostly originate from hemicellulose (Tables S2 and S5†). An additional phenolic product of methylparaben was detected and quantified from the reaction with the poplar species (Table S1†). This product is extracted in various quantities from all reactions using poplar, even those without catalyst present, and its exact origin is unknown as the amounts of H lignin found in the poplar species is very low (Table S3†). There is no evidence that the solvent, MeOH, is consumed during this reaction and its volatility makes it easy to separate from both the phenolic products and sugar residue. Upon removal of methanol, dihydroeugenol and 2,6-dimethoxypropylphenol can be extracted from the remaining residue using diethylether. NMR spectra of this extract confirm it consists of mainly two products with small amounts of unidentified impurities (Fig. S2 and S3†). The non-ether soluble fraction was also analyzed *via* NMR and gave spectra with features consistent with sugars and aromatic lignin fragments suggesting that a portion of our unaccounted for lignin is present in the methanol solution (Fig. S4†). This fraction was then subjected to analysis for carbohydrates and found to contain a majority of xylans with smaller amounts of glucans and arabinans (Table S5†).

In comparison to the Pd–Zn catalytic process described above for intact wood biomass, organosolv lignin contains hundreds of compounds,[15] rendering its conversion to a reasonable number of products extremely difficult (Fig. S1c†).

Carbohydrate residue retains its value

To determine the composition of the leftover carbohydrate residue it was digested by acid hydrolysis, which produced mainly glucose (Table S6†). This leftover carbohydrate residue was subjected to cellulase enzyme digestion, giving 95% of the theoretical glucose yield.[28] In comparison, intact poplar wood released only 11% of theoretical glucose from cellulase enzyme digestion over the same time period. These results are consistent with those reported in the literature showing that cellulose can be hydrolyzed by enzymes once lignin is removed, as lignin deactivates cellulase enzymes.[29] The sugars from hydrolysis as well as the sugars present in the MeOH phase were analyzed allowing mass balance closure of 74% of the starting biomass weight in quantified products (Fig. 3). Our results illustrate the positive impact of lignin conversion by the Zn/Pd/C catalyst on enhancing sugar yields from poplar. Furthermore, the released sugar can be upgraded by known biological and chemical catalytic conversion processes that have been developed independently for pure carbohydrates.[30,31]

The availability of the leftover carbohydrate residue for direct conversion was demonstrated by subjecting the sample to analytical fast pyrolysis in a pyroprobe/mass spectrometer developed previously for the determination of primary pyro-

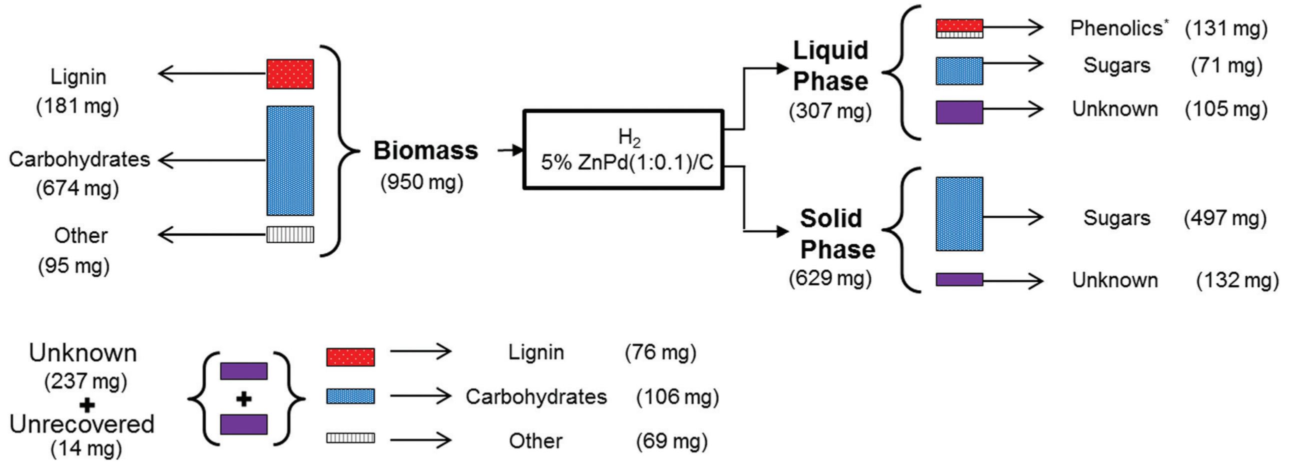


Fig. 3 Mass balance after catalytic cleavage and HDO of WT poplar lignin over Zn/Pd/C catalyst. *Mass of phenolic products includes all quantified phenolics and also accounts for the loss of O into H_2O during HDO. Liquid phase sugars were quantified by HPLC analysis. The solid phase residue was hydrolyzed with acid. Then glucose, arabinose, and xylose were quantified by HPLC analysis.

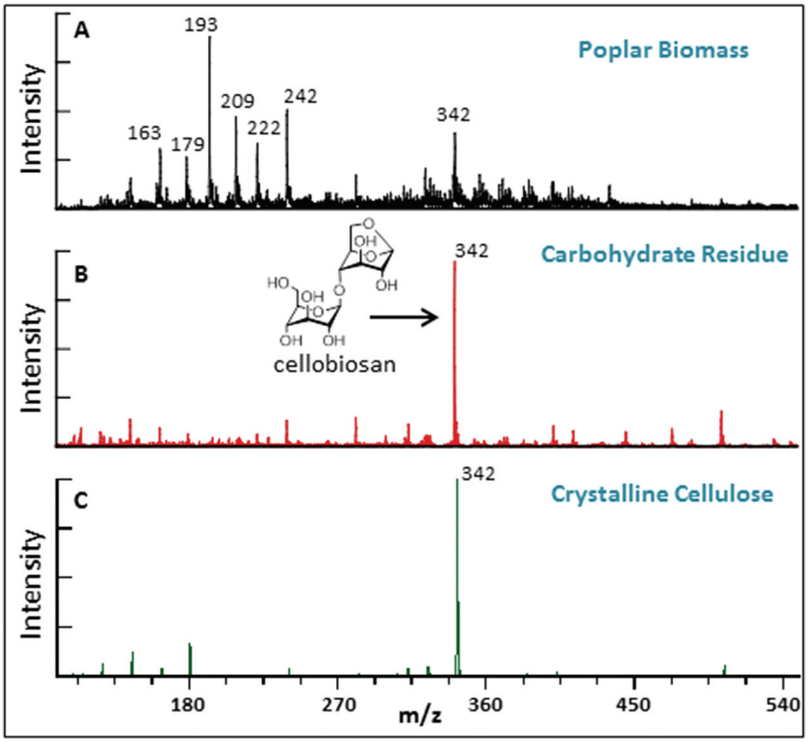


Fig. 4 Positive mode ammonium attachment atmospheric pressure chemical ionization mass spectra measured for fast pyrolysis[32] products of (a) WT-LORRE poplar, (b) carbohydrate residue from WT poplar after our one-step catalytic conversion of lignin over Zn/Pd/C, and (c) pure crystalline cellulose.

lysis products.[32] The results obtained for pure cellulose and the leftover carbohydrate residue derived from woody biomass are compared in Fig. 4, together with fast-pyrolysis products of raw woody biomass. The solid residue behaved similarly to pure cellulose, yielding a similar product distribution, the main product of which was cellobiosan. This result is in sharp contrast to the highly complex mixture obtained upon fast pyrolysis of the lignified raw biomass (Fig. 4A).

Genetic variants control products

Lignin is made by radical polymerization of *p*-hydroxyphenyl (H), G, and S monomeric units to give various linkage types (Fig. 1). The most ubiquitous is the β-O-4 linkage. H, G, and S subunit abundance in lignin varies depending on the plant species, and the availability of different monomers can be manipulated genetically.[33,34] To evaluate whether such engineered lignins can be successfully converted using our process, we employed a genetically engineered line (717-F5H) with high-S lignin (Table 1, entry 2).[27,35] Unmodified WT-717 poplar gives a ~1 : 2 ratio of dihydroeugenol to 2,6-dimethoxy-4-propylphenol. In comparison the high-S line gives a greater yield of 2,6-dimethoxy-4-propylphenol with a final product distribution of 1 : 6 (Fig. 2B). The results from this experiment demonstrate how tailoring biomass through genetic control can affect the product distribution.

Wood from other tree species, such as pine, white birch, and eucalyptus, can also be broken down by our catalyst (Table 1, entries 5–7). Pine contains exclusively G lignin and has very high lignin content (30% by weight). Pine gave exclusively dihydroeugenol as the phenolic product but with lower yield compared to poplar and birch, presumably due to the high degree of cross-linking in G lignins. Although the lignin content of white birch is only 16% by weight, it gave an impressive yield (52%) (Table 1, entry 6); whereas, the combination of high lignin content (24% by weight) and high yield 49% from eucalyptus produced the greatest overall yield of products from a mass standpoint (~12% of the total biomass converted to the two phenolic products).

Lignin-derived fuel and chemical platform

While the methoxypropylphenol products have value as chemicals, we have also developed novel catalysis for their conversion to the high-octane liquid fuel propylbenzene (Fig. 1). When dihydroeugenol; 2,6-dimethoxy-4-propylphenol; or a mixture of the two was reacted with H_2 over a Pt–Mo bimetallic catalyst at 300 °C and 342 psig H_2, propylcyclohexane and propylbenzene were obtained in >97% and ~0.7% yield, respectively (Table S8a†). This is the highest reported yield of hydrocarbons from the continuous, vapor-phase reaction of lignin-derived methoxypropylphenols to date. The propylcyclohexane can be aromatized *via* a dehydrogenation reaction to give additional propylbenzene and return 3 equivalents of the H_2 used in the hydrogenation of methoxypropylphenols over the Pt–Mo catalyst.[36,37] Current work is aimed at the direct production of propylbenzene from methoxypropylphenols.

The effective lignin processing demonstrated here opens a new direction for biorefinery configurations and synergies. The catalytic depolymerization of lignin into methoxypropylphenols employs the lignin portion of biomass first, while simultaneously leaving behind an essentially intact solid-carbohydrate fraction that can be further processed *via* traditional biorefinery methods. Utilization of all components of lignocellulosic biomass feedstock (lignin, cellulose, and hemicellulose) is critical for maximizing fuel and chemical yield per acre. The selective production of two methoxypropylphenols and their further conversion to the hydrocarbon propylcyclohexane/propylbenzene platform reported here enables many options for the conversion of the natural aromatic structure of lignin into currently used aromatic chemicals that were previously not viable. In addition, we envision a biorefinery that encompasses multiple synergies (as opposed to conventional biorefineries involving only one processing method) designed to minimize chemical bond breaking by making products that exploit the natural structure of biomass.

The lignin-derived methoxypropylphenols can be used in the fragrance industry (*i.e.* dihydroeugenol), as well as be catalytically upgraded to a variety of fuels (*e.g.* propylbenzene, toluene, *etc.*) and chemicals (*e.g.* propane, methanol, benzene, cumene, *para*-xylene, ethylbenzene, styrene, phenol, and

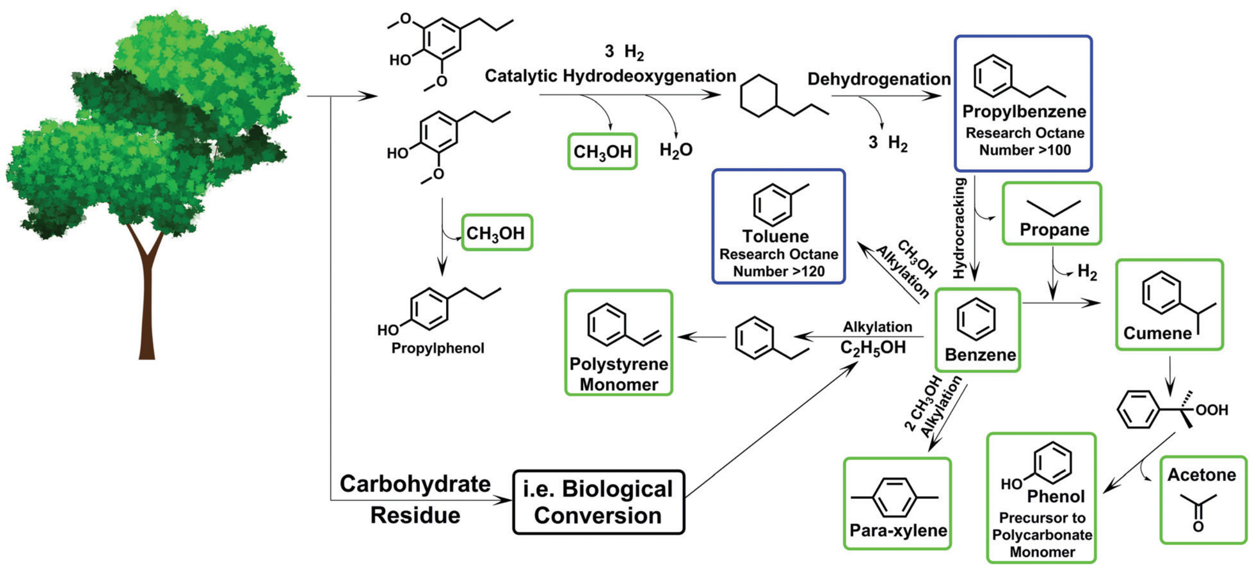


Fig. 5 Pathways for the production of renewable fuels (in blue) and chemicals (in green) from the lignin portion of biomass. Methoxypropylphenols can be used as is for the fragrance industry (dihydroeugenol), or can be catalytically tailored to fuels (such as propylbenzene and toluene) or used for the production of chemicals (such as propane, methanol, benzene, cumene, *para*-xylene, ethylbenzene, styrene, phenol, and acetone).

acetone) as shown in Fig. 5. We have demonstrated high-yield production of the hydrocarbon propylcyclohexane from lignin. Propylcyclohexane can be converted *via* dehydrogenation to propylbenzene, which can be hydrocracked subsequently to benzene and propane.[38] Benzene can be used as a chemical building block for production of fuels and chemicals *via* a variety of known and practiced conversions, such as: alkylation of benzene with co-produced propane (propylene after dehydrogenation) to form cumene, alkylation with co-produced MeOH to form toluene or xylenes, or alkylation with ethanol or ethylene to form ethylbenzene and styrene.[39,40] The propane produced can be dehydrogenated and employed for polymer production or converted further to acetone; which when reacted with phenol forms the polycarbonate monomer, bisphenol-A.[41]

The solid carbohydrate fraction can be further processed to fuels and chemicals by currently employed chemistries such as liquid-phase (catalytic) processing and biological conversion such as fermentation, or thermochemical processes such as fast hydropyrolysis or gasification followed by further catalytic upgrading.[42] Additionally, the waste from some steps, such as carbonaceous residue or char, can be utilized by feeding to a thermo-chemical unit (fast-pyrolysis or gasification) for conversion into a variety of intermediate products that can be upgraded.

New synergies emerge from integration of lignin and carbohydrate chemistries. For example, in Fig. 5, we show alkylation of benzene with methanol to form *para*-xylene (an important chemical) or alkylbenzene molecules as fuels. The methanol can be sourced from cleavage of the methoxy groups of methoxypropylphenols or produced from the breakdown of the carbohydrate fraction. Additionally, methanol derived from the biomass itself can be used as the solvent for the lignin depolymerization step with the aforementioned Zn/Pd/C catalyst. Styrene can be produced through an integrated pathway involving alkylation of benzene using ethylene or renewable ethanol produced from sugar fermentation.

In addition to the pathways discussed above, the development of new and more-direct pathways are immediately recognizable, utilizing the natural aromatic lignin structure (aromatic ring, alkyl and oxygen substituents) and minimizing the number of conversion steps to generate renewable commodities. For example, cumene could be synthesized directly from propylbenzene *via* isomerization of the propyl substituent, and hydrocracking of propylphenol could afford a direct route to phenol and propane. Some of these transformations present the need to develop new chemistries starting from a variety of different intermediate chemicals that go beyond "traditional" chemistry used in the petrochemical industry.

Conclusion

Catalytic conversion of lignin to discrete phenolic molecules was achieved with good yields utilizing a process that produces a clean carbohydrate residue. This was accomplished under reasonable conditions (225 °C, 500 psi H_2) using a synergistic Pd/C and Zn system that cleaves and deoxygenates the β-O-4 linkages in native lignin. These lignin-derived methoxypropylphenols can be further converted to a variety of valuable aromatic fuels and chemicals. This new approach to utilization of lignin enables the future biorefinery to obtain higher yields of fuels and chemicals. The newfound ability to utilize lignin-first for fuels and chemicals presents a new paradigm for biofuel production in which lignin is potentially more valuable than cellulose and provides opportunity for plant biologists to tailor biomass that contains more lignin. Mapping of products based on the natural structure of lignin identifies new chemical transformations and catalysis that will stimulate target driven fundamental research.

Material and methods

Chemicals

Pd/C (5 wt%) was purchased from Strem Chemicals (Newburyport, MA). 4-Allyl-2,6-dimethoxyphenol (98% purity) was purchased from Alfa Aesar (Ward Hill, MA). Isoeugenol, eugenol, 2-methoxy-4-propylphenol (all >98% purity) and ammonium formate (>99% purity) were purchased from Sigma-Aldrich (St. Louis, MO). 2-Methoxy-4-methylphenol (98% purity) and methylparaben (>99% purity) were obtained from TCI America (Portland, OR). High-performance liquid chromatography-mass spectrometry (HPLC-MS) grade water and acetonitrile were purchased from Fisher Scientific (Pittsburgh, PA). All chemicals were used without further purification. A Zorbax SB-C18 column (4.6 × 250 mm, 5 μm particle size) was purchased from Agilent Technologies (Santa Clara, CA). 2,6-Dimethoxy-4-propylphenol was synthesized as outlined below.

Feedstock

Poplar genotype NM-6 (*Populus nigra* × *P. maximowiczii*, WT-LORRE) was provided by Adam Wiese of the USDA Northern Research Station in Rhinelander, Wisconsin.[43] Hybrid aspen INRA 717-1B4 (*P. tremula* × *P. alba*, WT-717), Poplar (*P. nigra* × *P. maximowiczii*) WT-NM-6, the genetically engineered line 717-F5H and WT-White Birch (*Betula papyrifera*) were provided by Purdue University's Department of Forestry and Natural Resources Department. The WT lodgepole pine (*Pinus contorta*) was provided by Mr Jerry Warner (COL, U.S. Army Ret.), Managing Director of Defense LifeSciences, LLC (Alexandria, VA). The WT-Eucalyptus (*Eucalyptus grandis* × *E. urophylla*) was provided by William H. Rottman, ArborGen, Inc (Ridgeville, SC).

Preparation of 2,6-dimethoxy-4-propylphenol

2,6-Dimethoxy-4-propylphenol was synthesized through the hydrogenation of the side chain of 4-allyl-2,6-dimethoxyphenol. 4-Allyl-2,6-dimethoxyphenol was dissolved in a suspension of Pd/C (5 wt%, 105 mg) in 15 mL MeOH (1.945 g, 10.1 mmol). The reaction mixture was placed in a stainless steel Parr reactor, pressurized with 500 psig H_2 and heated at 60 °C for 3 hours. Pd/C was removed by filtration and methanol was removed *in vacuo* to yield 2,6-dimethoxy-4-propylphenol as a colorless oil. The reaction product was further purified on a silica-gel column with a mobile phase of 17% ethyl acetate and 83% hexanes. [^{1}H]NMR ($CDCl_3$) δ 0.93 (t, 3H, CH_3), 1.61 (s, 2H, CH_2), 2.50 (t, 2H, CH_2), 3.85 (s, 6H, OCH_3), 5.42 (s, 1H, OH), 6.39 (s, 2H, ArH).

Biomass preparation

Biomass was first milled to pass through a 40 mesh screen using a Mini Wiley Mill (Thomas Scientific, Swedesboro, NJ). Biomass was washed consecutively with water and ethanol soxhlet using the LAP Determination of Extractives in Biomass procedure.[44] Following soxhlet extraction, the biomass was dried and evaluated using a moisture analyzer (Halogen model HB43-S, Mettler-Toledo LLC, Columbus, OH).

General *in situ* generated catalyst reactions

In a typical experiment, 1.0 g of biomass, 0.10 g Pd/C (5 wt%), $ZnCl_2$ (5–10 wt%), methanol (30 mL), and glass stir bar were added to a stainless steel Parr reactor, which was subsequently sealed. While stirring the mixture was purged with UHP grade H_2 for ~1 min, then pressurized with H_2 (500 psig, 34 bar). The mixture was heated to 225 °C. This temperature was maintained for *ca.* 12 hours. The reaction was terminated by removing the heat and cooling the reactor to room temperature (WARNING! use caution when handling and venting the reactor; Pd/C is pyrophoric). The reaction mixture was filtered to remove Pd/C and remaining solid biomass residue. This Pd/C/biomass mixture was washed with additional MeOH and the filtrate was collected and diluted in a volumetric flask. This solution was analyzed by GC-FID and HPLC/MS as described below to determine amounts of methoxypropylphenols.

Author contributions

TP, SY, and JD performed experiments, analyzed data and wrote the paper. TJ, MH, and HIK designed and performed MS analyses. EG performed calculations for the synergistic biorefinery concept. IK, BH, and BS performed experiments and analyzed data. JIK performed ABSL and DFRC analyses. HC provided technical assistance on experiments with the PtMo catalysis. RM, CC, and NM supervised and provided technical knowledge on biomass handling and analyses. FR, WND, RA, and MMAO designed experiments, analyzed data, and wrote the paper. All authors provided comments on the paper.

Conflict of interest

MMAO has equity interests with Spero Energy, Inc., a start up company focused on making specialty chemicals from renewable sources. NM acts as a consultant for Spero Energy. Activities with Spero Energy have been disclosed to Purdue University in accordance with Purdue Policy on Conflicts of Commitment and Reportable Outside Activities (http://www.purdue.edu/policies/ethics/iiib1.html).

Acknowledgements

This work was supported as part of the Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio), an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award no. DE-SC0000997. The work by JD and the purchase of the Pyroprobe were supported by the National Science Foundation Emerging Frontiers in Research and Innovation (EFRI) under Award no. 0938033. SY was supported by the National Science Foundation Graduate Research Fellowship Program (#DGE-1333468).

Notes and references

1 R. F. Service, *Science*, 2013, **339**, 1374–1379.
2 D. J. Hayes, *Catal. Today*, 2009, **145**, 138–151.
3 M. Wellisch, G. Jungmeier, A. Karbowski, M. K. Patel and M. Rogulska, *Biofuels, Bioprod. Biorefin.*, 2010, **4**, 275–286.
4 M. G. Mandl, *Biofuels, Bioprod. Biorefin.*, 2010, **4**, 268–274.
5 M. McCoy, M. Reisch, A. Tullo, J. Tremblay, P. Short, J. Tremblay and W. Storck, *Chem. Eng. News*, 2005, **83**, 67–76.
6 M. Bomgardner, M. McCoy, M. Reisch, A. Tullo, A. Scott and J. Tremblay, *Chem. Eng. News*, 2013, **91**, 41.
7 Statistical Review of World Energy, BP, 2013.
8 G. W. Huber, J. W. Shabaker and J. A. Dumesic, *Science*, 2003, **300**, 2075–2077.
9 S. K. Hanson, R. T. Baker, J. C. Gordon, B. L. Scott, A. D. Sutton and D. L. Thorn, *J. Am. Chem. Soc.*, 2009, **131**, 428–429.
10 A. J. Crisci, M. H. Tucker, M. Y. Lee, S. G. Jang, J. A. Dumesic and S. L. Scott, *ACS Catal.*, 2011, **1**, 719–728.
11 J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599.
12 J. E. Holladay, J. F. White, J. J. Bozell and D. Johnson, *Top Value-Added Chemicals from Biomass-Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin*, Pacific Northwest National Laboratory (PNNL), Richland, WA (US), 2007.
13 F. Cherubini and A. H. Strømman, *Biofuels, Bioprod. Biorefin.*, 2011, **5**, 548–561.
14 T. M. Jarrell, C. L. Marcum, H. Sheng, B. C. Owen, C. J. O'Lenick, H. Maraun, J. J. Bozell and H. I. Kenttämaa, *Green Chem.*, 2014, **16**, 2713–2727.
15 H.-R. Bjørsvik and F. Minisci, *Org. Process Res. Dev.*, 1999, **3**, 330–340.
16 A. G. Sergeev and J. F. Hartwig, *Science*, 2011, **332**, 439–443.
17 Z. Strassberger, A. H. Alberts, M. J. Louwerse, S. Tanase and G. Rothenberg, *Green Chem.*, 2013, **15**, 768–774.

18 A. L. Jongerius, R. Jastrzebski, P. C. A. Bruijnincx and B. M. Weckhuysen, *J. Catal.*, 2012, **285**, 315–323.

19 W. Xu, S. J. Miller, P. K. Agrawal and C. W. Jones, *ChemSusChem*, 2012, **5**, 667–675.

20 R. N. Olcese, G. Lardier, M. Bettahar, J. Ghanbaja, S. Fontana, V. Carré, F. Aubriet, D. Petitjean and A. Dufour, *ChemSusChem*, 2013, **6**, 1490–1499.

21 A. C. Atesin, N. A. Ray, P. C. Stair and T. J. Marks, *J. Am. Chem. Soc.*, 2012, **134**, 14682–14685.

22 Q. Song, F. Wang and J. Xu, *Chem. Commun.*, 2012, **48**, 7019–7021.

23 T. D. Matson, K. Barta, A. V. Iretskii and P. C. Ford, *J. Am. Chem. Soc.*, 2011, **133**, 14090–14097.

24 Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu and J. Xu, *Energy Environ. Sci.*, 2013, **6**, 994–1007.

25 C. Li, M. Zheng, A. Wang and T. Zhang, *Energy Environ. Sci.*, 2012, **5**, 6383–6390.

26 T. H. Parsell, B. C. Owen, I. Klein, T. M. Jarrell, C. L. Marcum, L. J. Haupert, L. M. Amundson, H. I. Kenttämaa, F. Ribeiro, J. T. Miller and M. M. Abu-Omar, *Chem. Sci.*, 2013, **4**, 806–813.

27 S. D. Mansfield, K.-Y. Kang and C. Chapple, *New Phytol.*, 2012, **194**, 91–101.

28 M. Selig, N. Weiss and Y. Ji, *Enzymatic Saccharification of Lignocellulosic Biomass: Laboratory Analytical Procedure*, National Renewable Energy Laboratory, 2008, issue date, 3/21/2008.

29 Y. Kim, E. Ximenes, N. S. Mosier and M. R. Ladisch, *Enzyme Microb. Technol.*, 2011, **48**, 408–415.

30 E. I. Gürbüz and J. A. Dumesic, in *Catalysis for the Conversion of Biomass and Its Derivatives*, ed. M. Behrens and A. K. Datye, Open Access, 2013, pp. 293–359.

31 G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446–1450.

32 M. R. Hurt, J. C. Degenstein, P. Gawecki, D. J. Borton II, N. R. Vinueza, L. Yang, R. Agrawal, W. N. Delgass, F. H. Ribeiro and H. I. Kenttämaa, *Anal. Chem.*, 2013, **85**, 10927–10934.

33 N. D. Bonawitz and C. Chapple, *Annu. Rev. Genet.*, 2010, **44**, 337–363.

34 R. Vanholme, K. Morreel, C. Darrah, P. Oyarce, J. H. Grabber, J. Ralph and W. Boerjan, *New Phytol.*, 2012, **196**, 978–1000.

35 R. Franke, C. M. McMichael, K. Meyer, A. M. Shirley, J. C. Cusumano and C. Chapple, *Plant J.*, 2000, **22**, 223–234.

36 S. Hama, X. Li, K. Yukawa and Y. Saito, *Chem. Lett.*, 1992, **21**, 2463–2466.

37 R. T. Baker, A. P. Sattelberger and H. Li, *US* 8524963 B2, 2013.

38 C. L. Russell, M. T. Klein, R. J. Quann and J. Trewella, *Energy Fuels*, 1994, **8**, 1394–1400.

39 S.-S. Chen and Updated by Staff, *Styrene in Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 2000.

40 K. H. Chandawar, S. B. Kulkarni and P. Ratnasamy, *Appl. Catal.*, 1982, **4**, 287–295.

41 J. Wallace and Updated by Staff, *Phenol in Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 2000.

42 D. Mohan, C. U. Pittman and P. H. Steele, *Energy Fuels*, 2006, **20**, 848–889.

43 C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch, Y. Y. Lee, C. Mitchinson and J. N. Saddler, *Biotechnol. Prog.*, 2009, **25**, 333–339.

44 A. Sluiter, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton, *Determination of extractives in biomass*, National Renewable Energy Laboratory, 2005, vol. 1617, issue date, 7/17/2005.