Catalytic disassembly of an organosolv lignin *via* hydrogen transfer from supercritical methanol†

Katalin Barta,[a] Theodore D. Matson,[a] Makayla L. Fettig,[a,b] Susannah L. Scott,[a,c] Alexei V. Iretskii*[a,b] and Peter C. Ford*[a]
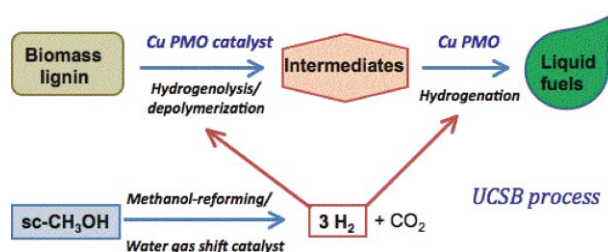
A novel approach to disassembling biomass-derived lignin into processible units is described. This transformation is achieved in supercritical methanol, using a Cu-doped porous metal oxide as the catalyst, at a relatively mild temperature (300 °C). Hydrogen transfer from methanol to an organosolv lignin results in the complete hydrogenolysis of phenyl ether bonds, coupled with the hydrogenation of aromatic rings. The product is a complex mixture composed principally of monomeric substituted cyclohexyl derivatives with greatly reduced oxygen content and negligible aromatics. Notably, no char formation was observed. We also describe operational indices based on the ¹H NMR spectra that facilitate holistic evaluation of the product distribution in this and other biomass transformations.

Introduction

Non-food biomass is an increasingly significant, renewable resource that has been estimated as having the potential to produce the annual equivalent of 3 billion barrels of liquid transportation fuel in the US alone.[1] Thus, developing chemical approaches for transforming the lignocellulose component of this carbon-neutral energy source to liquid transportation fuels would have significant economic and environmental impacts.[2] The two most plentiful biopolymers making up herbaceous biomass are cellulose and lignin. The latter is a complex material consisting largely of oxygenated 4-propylphenolic units cross-linked *via* phenyl ether bonds, as well as by C–C and other C–O bonds. Lignin serves to provide mechanical stability to plant tissues, and is very difficult to degrade by biochemical or chemical means.[3] It makes up 15–30% of lignocellulose, and among biomass components has the highest carbon content potentially usable as liquid fuel. The difficulty in transforming lignin to liquid fuels originates mostly from its highly complex and diverse structure, as well as from the refractory behavior of phenolic ethers toward hydrolysis. Thus developing methods for the chemical processing of lignins is of crucial importance to effective utilization of biomass.

Reductive lignin disassembly has the advantage of increasing the fuel value of the product by adding H_2 equivalents. Lignin hydrogenation was first described many decades ago by Harris *et al.*, in high pressure/high temperature experiments,[4] and it continues to be investigated for the conversion of lignins to fuel precursors.[5] More recently explored reductive methods include pyrolysis with formic acid at temperatures above 350 °C to give bio-oils with significantly lower O/C ratios than the starting lignins.[6] Similar results have been obtained in multi-step processes utilizing noble-metal catalysts,[7] and Lercher *et al.*[8] have demonstrated hydrodeoxygenation of bio-oil phenolic fractions to alkanes and methanol using a combination of a hydrogenation catalyst and a strong acid. These observations suggest that viable pathways for the production of liquid fuels and/or chemical precursors from lignins are becoming accessible, although multi-step processes and precious metal catalysts are generally involved.
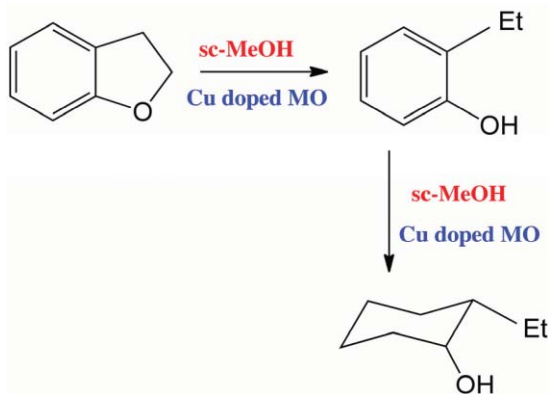

We have developed a single-step approach using a non-precious metal catalyst for the hydrogenolysis-depolymerization of lignin and subsequent hydrogenation of aromatics. This method is based on our recent report of a process for the hydrogenolysis of phenyl ether bonds and subsequent aromatic ring hydrogenation, as demonstrated with the lignin model dihydrobenzofuran (DHBF, Scheme 1).[9] The UCSB process utilizes supercritical methanol (sc-MeOH) as the reaction medium and is catalyzed by a copper-doped porous metal oxide (PMO) derived from an easily-prepared hydrotalcite precursor. The reducing equivalents for both steps originate from the solvent itself, which

*[a] Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara CA, 93106-9510, USA.
E-mail: ford@chem.ucsb.edu*
*[b] Department of Chemistry and Environmental Sciences, Lake Superior State University, Sault Sainte Marie, MI, 49783, USA.
E-mail: airetski@lssu.edu*
*[c] Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara CA, 93106, USA.
E-mail: sscott@engineering.ucsb.edu*

† Electronic supplementary information (ESI) available: Illustration of syringyl and guaiacyl units (1 fig.) and expanded descriptions of experimental procedures, including (a) preparation of HTC, (b) extraction and molecular weight characterization of organosolv lignin (1 figure, 1 table), (c) NMR evaluation of organosolv lignin (2 figures), and (d) product analyses (13 figures, 5 tables). See DOI: 10.1039/c0gc00181c

Scheme 1 Principal steps in the hydrogenolysis/hydrogenation of the lignin model compound dihydrobenzofuran (DHBF) by sc-MeOH in the UCSB process.

can be viewed as a "liquid syngas". Here we show that a more realistic model, organosolv lignin, can be fully disassembled into monomeric components using this process. We further describe a holistic approach for evaluating the resulting complex product mixture that may have general applicability to product streams derived by other methods for processing biomass substrates.

Results and discussion

Key structural properties of lignins are the aromatic ether linkages that are relatively refractory toward hydrolysis. Based on the behavior of DHBF under analogous conditions, we anticipated that lignin reactions catalyzed by the copper-doped metal oxide in sc-MeOH would lead first to hydrogenolysis of the ether linkages to give largely aromatic monomers.[9] Some C–C cross-linked dimers are also likely to form. These smaller aromatic components would then undergo ring hydrogenation. The DHBF reaction also gave a small amount of ethylcyclohexane, which likely arose from dehydration of ethylcyclohexanol to an alkene, followed by hydrogenation. If sufficient dehydration–hydrogenation pathways were available to the cyclic polyols produced in lignin hydrogenation/hydrogenolysis, the final products would have a low enough oxygen content for use as a fuel additive. We emphasize that no hydrogen gas is directly introduced; instead, the hydrogen equivalents are derived exclusively from the solvent, *via* the methanol reforming and water gas shift activity of the multifunctional heterogeneous catalyst.

The model substrate

The composition and structure of lignin varies depending on the source and the method of extraction.[10] The substrate chosen for these studies is "organosolv lignin", extracted from poplar sawdust with methanol according to the method of Adkins *et al.* (see Experimental Section).[4] This material is sufficiently complex to illustrate the generality of the chemical transformations taking place during processing, but its solubility makes it possible to assess principal structural features by solution-state NMR spectroscopy. Elemental analysis of the organosolv lignin showed it to contain 60.7% C; 6.1% H and 0.3% N (O not determined).

The organosolv lignin obtained in this manner has an average molecular weight of *ca.* 2.5×10^3 g mol^{-1} and a polydispersity of 1.3, according to gel permeation chromatography (GPC) measurements in THF (Supporting Information, Figure S-1†). This molecular weight is consistent with the high solubility of organosolv lignin in various organic solvents, including methanol at room temperature, and is similar to that of the hypothetical structure depicted in Fig. 1 (3.1×10^3 g mol^{-1}, 15 aromatic units).

For NMR spectral analysis, 100 mg organosolv lignin was fully dissolved in 0.7 mL CDCl$_3$. The ^{1}H NMR and ^{13}C APT NMR spectra of this solution (Supporting Information, Figures S-2 and S-3†) show resonances characteristic of lignins.[13] There are at least ten types of bonds present in a typical lignin structure.[11] As a starting point for the further discussion of NMR spectra and assessment of product streams from our reductive disassembly, we selected a hypothetical model for poplar lignin based on that proposed by Brunow.[12] It consists of syringyl and guaiacyl units, cross-linked mostly through β-*O*-4 linkages (see Supporting Information, Figure S-4, for the structures of such units).

Stoichiometry considerations

Ideally, a series of hydrogenolysis, hydrogenation and dehydration reactions will convert lignin exclusively to hydrocarbon products. The hydrogen equivalents originate from methanol by reforming (CH$_3$OH → CO + 2 H$_2$) and water-gas shift (CO + H$_2$O → CO$_2$ + H$_2$) of the resulting CO with any H$_2$O present to give three equivalents of H$_2$ per methanol consumed. Assuming sufficient water is formed or added, about half the methanol needed to generate the required H$_2$ would be formed in the reaction shown in eqn (1). If no C–C bonds are cleaved, one mole (3.14 kg) of the lignin model (Fig. 1) requires *ca.* 18 moles additional CH$_3$OH (0.58 kg) to produce 11 moles (1.64 kg) C$_9$ hydrocarbon and 2 moles (0.47 kg) C$_{18}$ hydrocarbon.

$$C_{159}H_{192}O_{65} + 126 \ H_2 \rightarrow 11 \ C_9H_{18} + 24 \ CH_3OH + 41 \ H_2O + 2 \ C_{18}H_{34} \qquad (1)$$
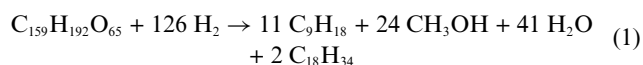
Model reactions in lignin disassembly

We propose the following hypothetical series of reactions for the stepwise reductive disassembly of lignin. In the first step, compounds **1–5** (Scheme 2) are created by selective hydrogenolysis of four β-*O*-4 linkages, one diphenyl ether-type linkage, and one dihydrobenzofuran unit. For compounds **1**, **2** and **4**, the alcohol group in the position alpha to the aromatic ring is likely to undergo dehydration to form a double bond that is conjugated with the aromatic system. In a reducing atmosphere, this double bond will be hydrogenated. Upon dehydration/hydrogenation of **1** and **2**, compounds **6** and **7** are formed (Scheme 3), while compound **3** undergoes hydrogenation to **8**. Compounds **6–8**, upon hydrogenation of their aromatic rings, give the functionalized propylcyclohexanols **9–11**.

If compounds **6** and **7** were to instead undergo loss of methoxy groups and hydrogenation of their aromatic rings, both would result in 4-(1-hydroxypropyl)-cyclohexanol (**11**). This could undergo subsequent dehydration/hydrogenation (Scheme 4) to form 4-propyl-cyclohexanol (**12**), as suggested
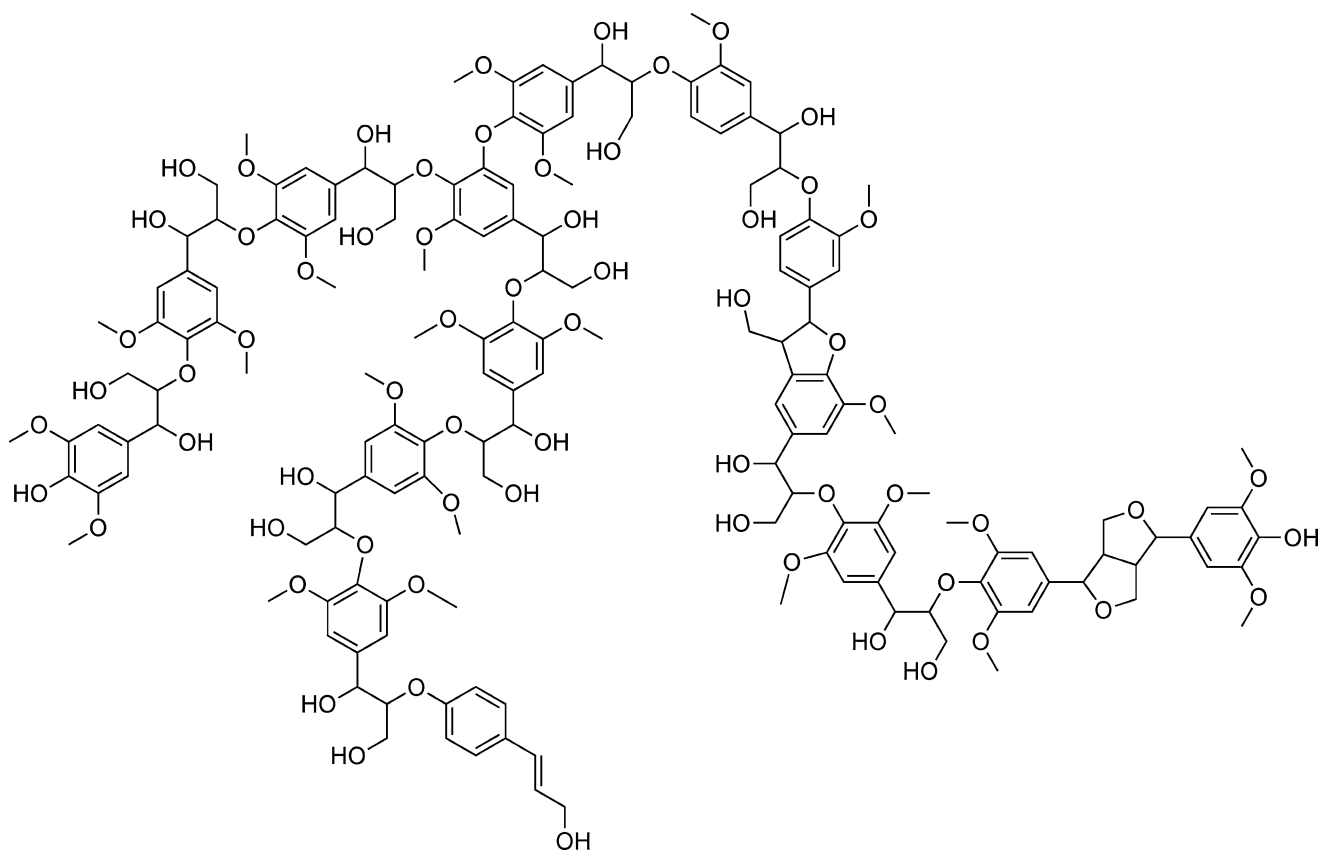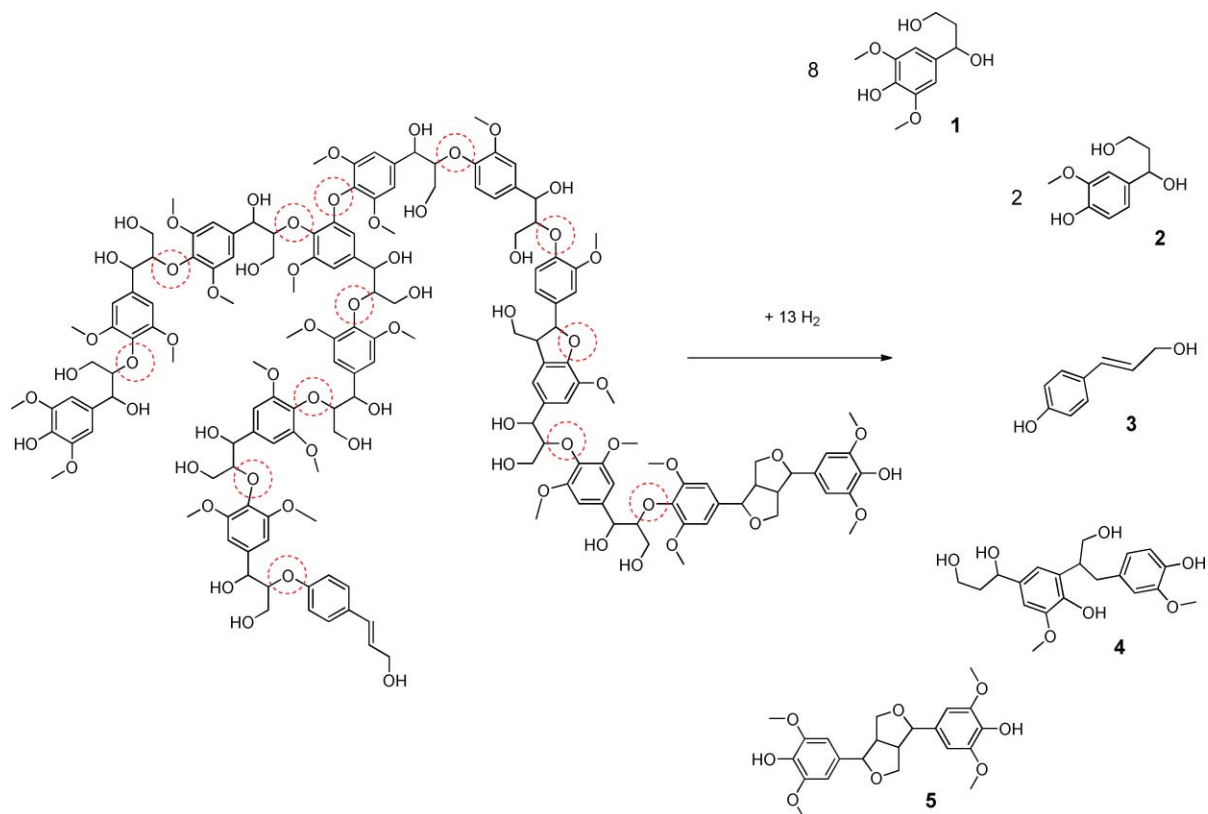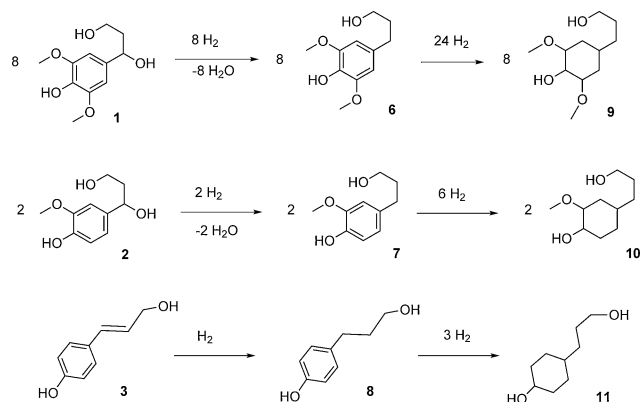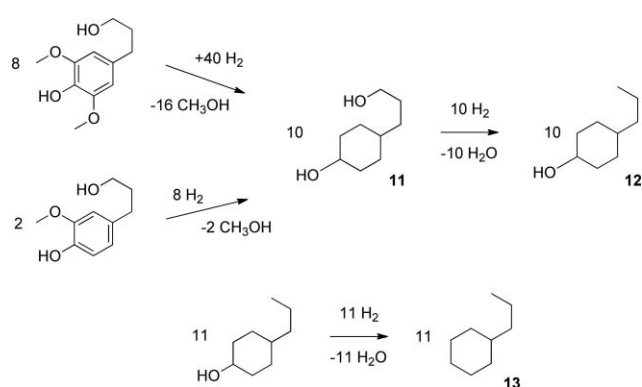
Fig. 1 Hypothetical structure for organosolv lignin derived from poplar sawdust.

Scheme 2 Selective hydrogenolysis of aromatic ether linkages in lignin.

Scheme 3 Potential dehydration and hydrogenation reactions of aromatic monomers.

Scheme 4 Products of extensive hydrogenation of aromatics **6** and **7**, coupled with methoxy loss, dehydration and further hydrogenation.

by the appearance of methyl resonances at *ca.* 0.9 ppm in the ^{1}H NMR spectra (see below). Both **11** and **12** are saturated alcohols with low oxygen content, and could be used as fuel additives. The coexistence of both pathways (methoxy-loss and hydrogenation) is suggested by the reaction of guaiacol (2-methoxyphenol), which under these reaction conditions gives phenol, dihydroxybenzene and the corresponding ring hydrogenation products (see Supporting Information†). Dehydration/dehydrogenation of **12** gives propylcyclohexane, **13**.

Accordingly, the products become more uniform with each stage of functionality removal, resulting eventually in the simple propylcyclohexyl skeleton of reduced lignin. Similar processes are envisaged for the reactivity of **4** and **5**, as qualitatively proposed in Scheme 5.

Based on these scenarios, the compounds originating from different stages of these processes can be grouped according to their aromatic character and oxygen content, Table 1. (We note that they will not necessarily be formed in an easily identifiable sequence such as shown in the proposed steps.)

Definitions of operational indices

Owing to the complexity of the reaction product mixtures, we created a set of numerical indices to provide metrics for classifying the chemical transformations in this and other biomass conversions.

$$H = \{N_H / (N_A + N_O + N_H)\} \times 100$$

Table 1 Groups of lignin-derived compounds based on their chemical structure

Group	Description	Compounds
A	Products of lignin hydrogenolysis	1–5
B	Products of single dehydration/hydrogenation	6–8 and 14
C	Products of aromatic ring hydrogenation	9–10 and 15–16
D	Products of extensive dehydration/hydrogenation	11–12 and 17–19
E	Products of total dehydration/hydrogenation	13 and 20–21
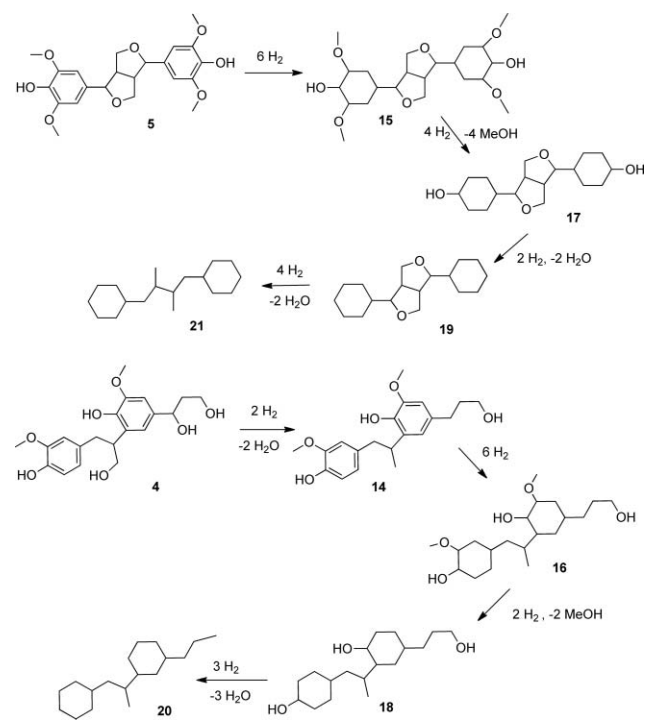
Scheme 5 Possible pathways for transformation of dimers to alkanes.

$$A = \{N_A / (N_A + N_O + N_H)\} \times 100$$

$$O = \{N_O / (N_A + N_O + N_H)\} \times 100$$

where N_A is the number of aromatic protons; N_O is the number of protons on carbons that bear an oxygen (including –OH); and N_H is the number of aliphatic protons. Thus, H represents the fraction of protons bound to aliphatic carbons, A the fraction at aromatic sites and O those that are adjacent to or bonded to oxygen. The subscript "T" indicates theoretical values (*i.e.*, H_T, A_T and O_T), calculated simply by counting the various types of protons in the model compounds. Table 2 summarizes the values of the H_T, A_T and O_T indices for the hypothetical lignin model and for each of the compound classes in Table 1.

The subscript "E" designates experimentally determined values: H_E, A_E and O_E. These were defined as shown from the ratios of the integrations of specific chemical shift regions (R_i) in

Table 3 Indices for liquid reaction products, defined operationally and obtained from ^{1}H NMR measurements. For each experiment, 50 mg substrate and 50 mg $Cu_{20}PMO$ catalyst were heated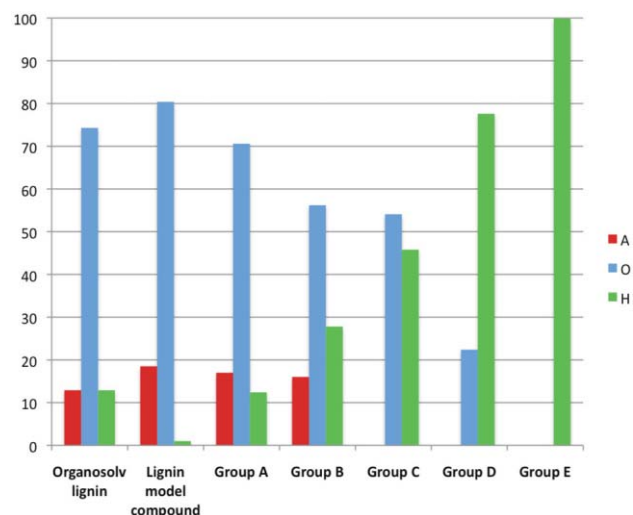 to 300 °C in 3 mL CH_3OH in a 10 mL volume minireactor for a specific time period, and the liquid products were separated and analyzed by ^{1}H NMR. No insoluble char was formed except in experiment 10

Experiment	time/h	A_E	O_E	H_E	H_E/O_E	H_E/A_E
organosolv lignin	0	12.9	74.3	12.9	0.17	1.0
1	0.25	12.9	60.5	26.6	0.44	2.1
2[a]	0.5	16.0	40.4	43.5	1.1	2.7
3	1	10.9	28.6	60.5	2.1	5.6
4	2	4.3	17.2	78.6	4.6	18.5
5	4	3.5	14.9	81.6	5.5	23.4
6	12	1.5	11.1	87.4	7.9	58.6
7	24	1.4	11.3	87.3	7.7	61.2
8	24	1.6	12.1	86.2	7.1	53.9
9 (D_2O)[b]	24	1.8	11.6	86.6	7.5	48.1
10 Uncatalyzed[c]	24	12.7	41.1	46.2	1.1	3.6

[a] This solution was somewhat inhomogeneous. [b] Data for experiment 9 was generated from the sample used in experiment 8, which was shaken with a small amount of D_2O in order to evaluate its content of readily-exchanged protons. [c] Reaction conducted under analogous conditions but with 100 mg substrate and without catalyst; 40 mg insoluble "char" was also formed.
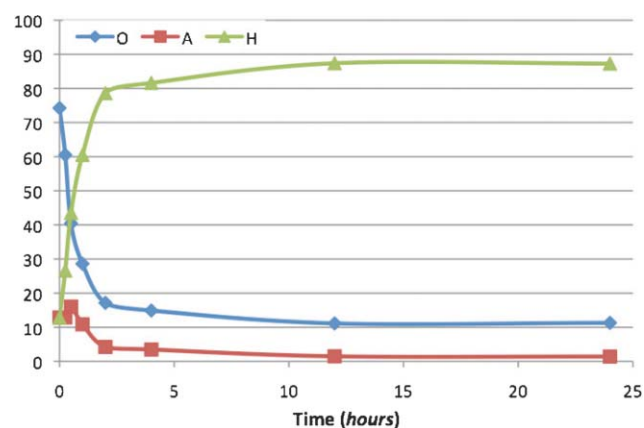

Fig. 4 Temporal evolution of the A_E, O_E and H_E indices during organosolv lignin hydrogenolysis/hydrogenation under standard conditions.

has been largely disassembled, with most of its aromatic rings hydrogenated and significant deoxygenation having already taken place. Longer reaction times lead to a slow increase in H_E, to 86.2 after 24 h, and further declines in A_E and O_E to 1.5 and 11.8, respectively. The 24 h values represent the average of runs 7 and 8, the reasonable agreement of which (Table 3) provides a measure of the technique's reproducibility. In experiment 9, the liquid product of experiment 8 was shaken with D_2O to evaluate the content of readily exchangeable product protons. The differences between the results for experiments 8 and 9 are minor (Figures S-13 and S-14†) suggesting that surprisingly few exchangeable O–H protons remain.

The elevated H_E index of the final product mixture, compared to the H_T index for Group **D**, suggests that ring alkylation may occur concurrently with the reduction; methylated byproducts were seen previously in the analogous reactions of DHBF.[10] The temporal evolution of the H_E/A_E and H_E/O_E ratios (Table 3) emphasizes the markedly increasing fraction of aliphatic (vs. aromatic) protons, and the decreasing oxygen content of the

products. The reproducibility of the behavior in Table 3 and Fig. 4 was demonstrated by an independent series of experiments with another sample of organosolv lignin (Supporting Information, Table S-5 and Figure S-15†).

Mass balance

A more detailed investigation of the product mixture, including gases, was conducted to evaluate the mass balance. Each experiment consisted of a deep brown solution of 100 mg organosolv lignin with 100 mg $Cu_{20}PMO$ in 3 mL methanol, heated to 300 °C for 24 h. After quenching by rapid cooling, the gas phase was collected and analyzed by gas chromatography. The liquid phase was then recovered quantitatively and centrifuged. The resulting colorless solution was decanted and the solid catalyst residue dried in vacuo at room temperature for several days.

The gas phase (550 mL at room temperature, ambient pressure) obtained after 24 h reaction consisted of H_2 (18.2 mmol), CH_4 (1.8 mmol), CO (2.0 mmol) and CO_2 (0.89 mmol). The H_2 and CO originate largely from catalytic methanol reforming ($CH_3OH \rightarrow 2H_2 + CO$), while the CO_2 results from water-gas shift ($CO + H_2O \rightarrow CO_2 + H_2$). The amount of water generated is apparently insufficient to give complete conversion of CO to CO_2. There are several likely sources for the methane, including hydrogenolysis of O–CH_3 linkages in the organosolv lignin and hydrogenation of one of the C_1 components of the system, including CH_3OH. Based on the model in Fig. 1, a maximum of 1 mmol CH_4 can originate from the substrate itself, therefore the larger observed value implies that C_1 hydrogenation is significant.

The originally green catalyst was purple when recovered from the reactor. When the used catalyst was dissolved in nitric acid, the resulting solution contained no black particulates. The absence of char or other insoluble materials was demonstrated by gravimetric analysis of the residual solid. Its average weight after reaction was (102 ± 5) mg (Supporting Information, Table S-3†); thus, there was negligible weight gain.

The colorless solution phase was further treated by removing methanol and other low-boiling volatiles in vacuo. The remaining oily material weighed (58 ± 2) mg (Supporting Information, Table S-4), and was further analyzed by NMR spectroscopy, GC-MS and gel permeation chromatography. Notably, if that the sole product were a propylcyclohexanol, the yield would be 68 mg; the recovered liquid product represents 86% of that quantity. For GPC analysis, the crude mixture was dissolved in 1 mL THF. Less than 2% of the original 100 mg substrate remained, based on a lower detection limit of ca. 1 mg polymer per mL. The observed average molecular weight (191 g mol^{-1}, polydispersity 1.48) corresponds to the monomer-dimer range of 186–387 g mol^{-1} (Supporting Information, Figure S-5).

GC-MS analysis revealed a relatively complex mixture of compounds (Supporting Information Figure S-15†). Several components were identified qualitatively by their fragmentation patterns to be cyclohexanols (Supporting Information, Figure S-16). GC-MS results after 2, 4, 12 and 24 h reaction times confirm that, although the product composition evolves, cyclohexyl-derivatives are present. There are only modest changes after the first 4 h, consistent with the behavior seen with the NMR indices.

A control reaction with 100 mg catalyst and 3 mL methanol but no substrate was carried out under analogous conditions. However, no higher boiling liquid products were detected by GC-MS analysis.

Fig. 5 compares the ^{1}H NMR spectrum of the liquid phase after 24 h reaction to that of the original organosolv lignin. The result for a control reaction performed under the same conditions but without added catalyst is also shown. In the aliphatic chemical shift region, the spectra suggest that the majority of the protons occur in methylene groups (1–2 ppm), consistent with formation of cyclohexyl rings. There is significant intensity below 0.9 ppm, characteristic of aliphatic methyl groups, possibly the termini of propyl chains or methyl substituents on cyclohexyl rings. The latter may arise by aromatic methylation, as seen previously with the model compound DHBF.[9] The relatively low intensity in the 5–3 ppm region indicates that most methoxy groups in the original lignin structure are lost during the reaction.
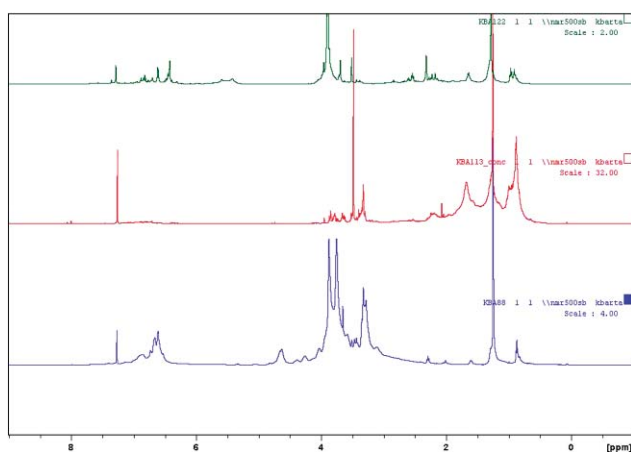

Fig. 5 Comparison of ^{1}H NMR spectra (CDCl$_3$) for organosolv lignin (bottom), after reaction over the catalyst for 24 h (middle), and a control reaction carried out for 24 h without catalyst (top).

A control reaction run with 100 mg substrate but no catalyst led to the formation of *ca.* 40 mg of a black, char-like material. This material is insoluble in all common organic solvents. Elemental analysis showed it contains 69.3% C; 4.3% H and 0.4% N (O not determined). This composition was not dramatically different from that of the organosolv lignin itself, so we conclude that the "char" is largely polymerized lignin. The liquid phase was separated, methanol removed and the brown oily product analyzed by ^{1}H NMR. From its spectrum (Fig. 5, top), it is clear that although some transformations had taken place, little aromatic ring hydrogenation had occurred (A$_E$ = 12.7, Table 3).

The expected solvent-to-substrate hydrogen/deuteron transfer was demonstrated by conducting an experiment in methanol-d_4. Fig. 6 shows the ^{1}H and ^{2}H NMR spectra of the liquid product mixture. In the ^{1}H spectrum, there is little change in the aliphatic proton region (3.0–0.3 ppm) from that of unprocessed organosolv lignin (Fig. 5, bottom). However, the same aliphatic region of the ^{2}H NMR spectrum of the same sample reveals extensive deuteration, strongly suggesting that the cyclohexyl rings generated by aromatic ring hydrogenation
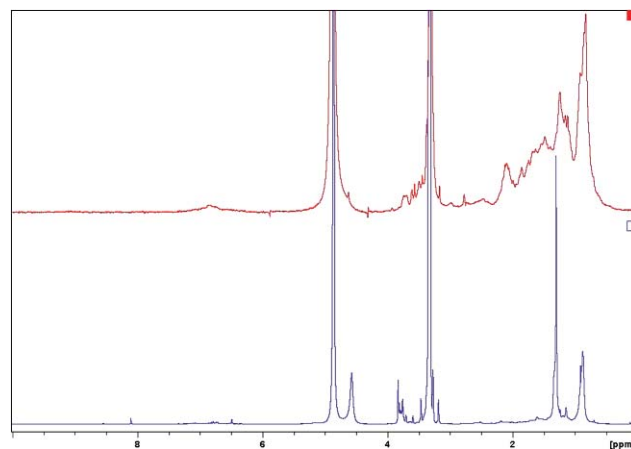

Fig. 6 Comparison of the ^{1}H NMR spectrum (bottom) and ^{2}H NMR spectrum (top) for the reaction products, both in CD$_3$OD.

(deuteration) also underwent extensive exchange between the aromatic protons of the substrate and the reactive solvent medium.

Summary

The bio-oligomer organosolv lignin is disassembled to monomeric units with little or no formation of insoluble char by hydrogen transfer from supercritical methanol. The process is catalyzed by a copper-doped porous metal oxide, and the products contain virtually no aromatics and have greatly reduced oxygen content. Such products may be further processed to give liquid hydrocarbon fuels or fuel additives. A scheme for rationalizing lignin disassembly is discussed, and operational indices based on ^{1}H NMR properties that describe the progressive transformation from oxygenated aromatics to aliphatic alcohols are introduced. It should be emphasized that the exact structure of the lignin model utilized has only modest influence on the overall conclusions since the use of the indices focuses on the holistic nature of the transformations rather than the specific products formed.

While there is increasing interest in utilizing supercritical fluids, including sc-MeOH, for biomass solubilization,[15] a key advantage of doing so in the presence of a reforming catalyst is the absence of accompanying char formation. Hydrotalcite-derived PMOs doped with Earth abundant metals are air- and moisture-stable catalysts and are ideal candidates for optimization. We are extending the application of this promising system to other biomass materials.

Experimental section

Materials

Organosolv lignin was extracted from sanded poplar sawdust (100 g) with 800 mL methanol (containing 1% HCl) following literature procedures.[4] The 20% Cu-doped hydrotalcite catalyst precursor was prepared and characterized as described previously,[9] with slight modifications described in the Supporting Information.† This material was calcined at 460 °C for 24 h to give the catalyst used in these experiments.

Catalysis procedures

In a typical run, the organosolv lignin substrate (100 mg) was dissolved in methanol (3 mL) and combined with the metal oxide catalyst (100 mg) in a 10 mL stainless steel bomb. After purging the vessel with argon, the microreactor was sealed. It was placed in a heating block and heated to 300 °C for the indicated reaction time, after which it was rapidly cooled by immersing in a water bath. Once the pressure was released, the solid and liquid contents of the reactor were transferred to a centrifuge tube and centrifuged at 7000 rpm for 5 min. The liquid phase, containing the reaction products, was decanted. The solid was washed 3 times with methanol, centrifuged, and the methanol washings were collected. The remaining solid was dried *in vacuo* and weighed. The methanol solvent was removed from the liquid phase by rotary evaporation at room temperature. The remaining, higher boiling liquid was weighed and then further analyzed by NMR, GC-MS and GPC methods.

Instrumentation

GPC measurements were carried out using a Waters 2690 Separation Module instrument equipped with a 2414 Differential Refractometer and a Waters 2998 Photodiode Array Detector, with DMF as the solvent. GC-MS experiments were carried out on a programmable Agilent 5890 GC-MS instrument with splitless injector, 30 m DB-5 capillary column and quadruple MS detector, using suitably diluted samples. Product identification was accomplished by analysis of the mass fragments. NMR measurements were performed on a Bruker AVANCE500 instrument.

Elemental analyses were carried out by the UCSB Marine Science Analytical Laboratory.

Acknowledgements

References

1 (*a*) M. Paster, J. L Pellegrino and T. M. Carole, *Industrial Bioproducts: Today and Tomorrow*, 2003 Available electronically at http://www1.eere.energy.gov/biomass/products.html; (*b*) Energy Information Administration *Official Energy Statistics- International Data Projections*, US Department of Energy, 2008, online at http://www.eia.doe.gov/oiaf/ieo/pdf/ieoreftab_1.pdf.

2 (*a*) J. E. Holladay, J. F. White, J. J. Bozell, D. Johnson "Top Value-Added Chemicals from Biomass" DOE Report PNNL-16983 (website: http://chembioprocess.pnl.gov/staff/staff_info.asp?staff_num = 390); (*b*) A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484–489; (*c*) J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164–7183.

3 J. Ralph, K. Lundquist, G. Brunow, F. Lu, H. Kim, P. F. Schatz, J. M. Marita, R. D. Hatfield, S. A. Ralph, J. H Christensen and W. Boerjan, *Phytochem. Rev.*, 2004, **3**, 29–60.

4 E. E. Harris, J. D'Ianni and H. Adkins, *J. Am. Chem. Soc.*, 1938, **60**, 1467–1470.

5 M. Nagy, K. David, G. J. P. Britovsek and B. A. J. Ragauskas, *Holzforschung*, 2009, **63**, 513–520.

6 G. Gellerstedt, J. Li, I. Eide, M. Kleinert and T. Barth, *Energy Fuels*, 2008, **22**, 4240–4244.

7 N. Yan, C. Zhao, P. J. Dyson, C. Wang, L.-t. Liu and Y. Kou, *ChemSusChem*, 2008, **1**, 626–629.

8 (*a*) C. Zhao, A. A. Lemonidou, X. Li and J. A. Lercher, *Angew. Chem., Int. Ed.*, 2009, **48**, 3987–3990; (*b*) C. Zhao, Y. Kou, A. A. Lemonidou, X. Li and J. A. Lercher, *Chem. Commun.*, 2010, **46**, 412–414.

9 G. S. Macala, T. D. Matson, C. L. Johnson, R. S. Lewis, A. V. Iretskii and P. C. Ford, *ChemSusChem*, 2009, **2**, 215–217.

10 (*a*) M. Lawoko, G. Henriksson and G. Gellerstedt, *Biomacromolecules*, 2005, **6**, 3467–3473; (*b*) K. H. Holtman, H-M. Chang and J. F. Kadla, *J. Wood Chem. Technol.*, 2007, **27**, 179–200.

11 (*a*) H. Nimz and K. Das, *Chem. Ber.*, 1971, **104**, 2359–2380; (*b*) L. B. Davin and N. G. Lewis, *Curr. Opin. Biotechnol.*, 2005, **16**, 407–415.

12 G. Brunow, "Methods to Reveal the Structure of Lignin" pp. 89–116 in M Hofrichter and A Steinbuchel (eds) *Lignin, Humic Substances and Coal*, Vol. 1. Wiley-VCH, Weinheim, 2001.

13 (*a*) H. L. Luedemann and H. Nimz, *Biochem. Biophys. Res. Commun.*, 1973, **52**, 1162–1169; (*b*) L. L. Landucci, *Holzforschung*, 1991, **45**, 425–432; (*c*) M. Bunzel and J. Ralph, *J. Agric. Food Chem.*, 2006, **54**, 8352–8361; (*d*) J. Zhou, X. Sui and H. Shi, *BioResources*, 2009, **4**, 979–985.

14 N. Itagaki, M. Kimura, T. Sugahara and Y. Iwabuchi, *Org. Lett.*, 2005, **7**, 4185–4188.

15 (*a*) for example: C. Schacht, C. Zetzl and G. Brunner, *J. Supercrit. Fluids*, 2008, **46**, 299–321; (*b*) A. J. Soria, A. G. Mc Donald and S. R. Shook, *Holzforschung*, 2008, **62**, 402–408.