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Catalytic Conversion of Nonfood Woody Biomass Solids to Organic Liquids

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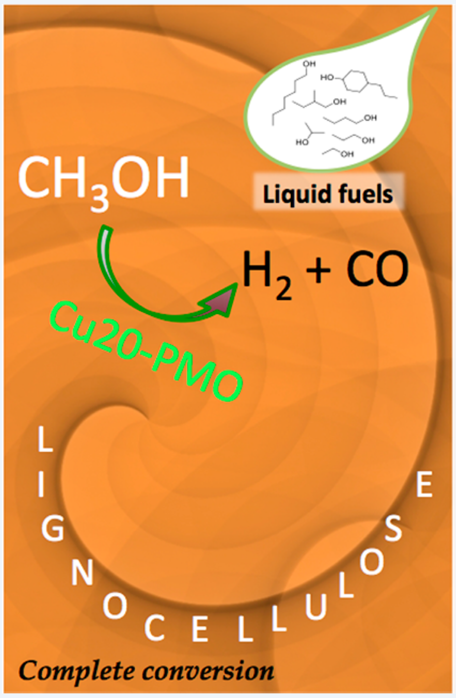

CONSPECTUS: This Account outlines recent efforts in our laboratories addressing a fundamental challenge of sustainability chemistry, the effective utilization of biomass for production of chemicals and fuels. Efficient methods for converting renewable biomass solids to chemicals and liquid fuels would reduce society's dependence on nonrenewable petroleum resources while easing the atmospheric carbon dioxide burden. The major nonfood component of biomass is lignocellulose, a matrix of the biopolymers cellulose, hemicellulose, and lignin. New approaches are needed to effect facile conversion of lignocellulose solids to liquid fuels and to other chemical precursors without the formation of intractable side products and with sufficient specificity to give economically sustainable product streams.

We have devised a novel catalytic system whereby the renewable feedstocks cellulose, organosolv lignin, and even lignocellulose composites such as sawdust are transformed into organic liquids. The reaction medium is supercritical methanol (sc-MeOH), while the catalyst is a copper-doped porous metal oxide (PMO) prepared from inexpensive, Earth-abundant starting materials. This transformation occurs in a single stage reactor operating at 300−320 °C and 160−220 bar. The reducing equivalents for these transformations are derived by the reforming of MeOH (to H_2 and CO), which thereby serves as a "liquid syngas" in the present case. Water generated by deoxygenation processes is quickly removed by the water−gas shift reaction. The Cu-doped PMO serves multiple purposes, catalyzing substrate hydrogenolysis and hydrogenation as well as the methanol reforming and shift reactions. This one-pot "UCSB process" is quantitative, giving little or no biochar residual.

Provided is an overview of these catalysis studies beginning with reactions of the model compound dihydrobenzofuran that help define the key processes occurring. The initial step is phenyl−ether bond hydrogenolysis, and this is followed by aromatic ring hydrogenation. The complete catalytic disassembly of the more complex organosolv lignin to monomeric units, largely propyl-cyclohexanol derivatives is then described. Operational indices based on ^{1}H NMR analysis are also presented that facilitate holistic evaluation of these product streams that within several hours consist largely of propyl-cyclohexanol derivatives. Lastly, we describe the application of this methodology with several types of wood (pine sawdust, etc.) and with cellulose fibers. The product distribution, albeit still complex, displays unprecedented selectivity toward the production of aliphatic alcohols and methylated derivatives thereof. These observations clearly indicate that the Cu-doped solid metal oxide catalyst combined with sc-MeOH is capable of breaking down the complex biomass derived substrates to markedly deoxygenated monomeric units with increased hydrogen content. Possible implementations of this promising system on a larger scale are discussed.

■ INTRODUCTION

The transformation from a petroleum-based infrastructure to one where sustainable biomass-derived feedstocks have a more important role in the economy will require profoundly new approaches.[1,2] Current methodologies for organic resource utilization are predominantly hydrocarbon oriented with a principal goal of adding functionality to simpler structures to obtain value-added chemicals. Biomass, in contrast, is highly functionalized with nearly every carbon atom oxidized, and such functionality needs to be removed to gain useful products. New catalysts, reactions, and mechanistic insights will be necessary to develop methods for chemically disassembling biopolymers and for selective deoxygenation of the resulting fragments.[3−6] Figure 1 illustrates the conceptually different approaches needed for a chemical economy drawing upon renewable feedstocks rather than petroleum.

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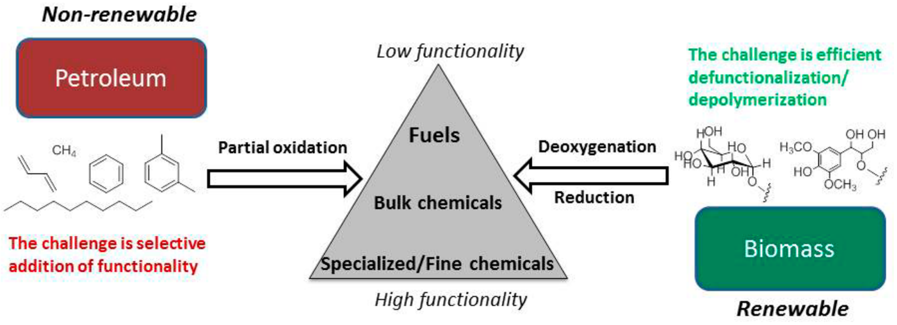


Figure 1. Contrasting challenges in the conversion of petroleum and biomass based feedstocks.

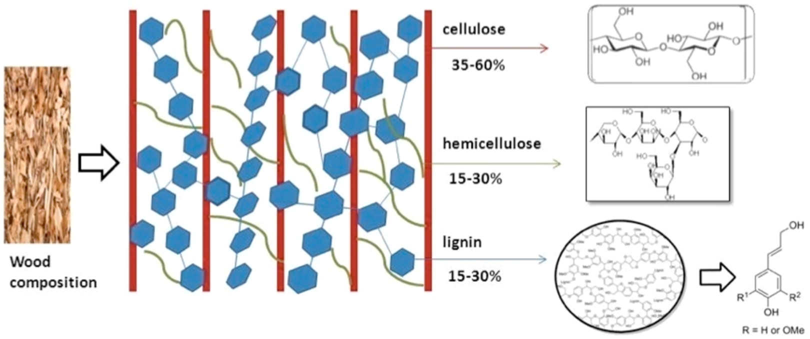


Figure 2. Main components of woody biomass and their chemical structures.

Initial exploratory efforts in biomass utilization at UCSB were concerned with developing catalysts for the transesterification of triglycerides with methanol to give the fatty acid methyl esters typically used as biodiesel fuels. The goal was to reduce formation of soapy byproducts by employing porous metal oxide (PMO) solid bases prepared by calcining transition metal-doped hydrotalcites. We successfully demonstrated that iron doped PMOs were particularly effective at catalyzing the transesterification pathway.[7] However, concern about whether food (vegetable oils) should be converted to fuels led us to focus on a different challenge, namely developing chemical pathways for converting lignin and lignocellulose to organic liquids.

Lignocellulose constitutes the woody cell walls of dry plant matter, is composed of the biopolymers cellulose, hemicellulose, and lignin (Figure 2), and is generally not considered to be part of the food reserves. As the most abundant source of renewable carbon on the planet, it is an obvious target for catalytic conversion to liquid transportation fuels or platform industrial chemicals. Potential sources of this "carbon-neutral" feedstock include forests and farms as well as municipal, agricultural, and forest waste products.[8] Current approaches to converting woody biomass to liquid fuels include gasification, and pyrolysis.[9] In gasification, high temperature (>700 °C) partial oxidation converts plant biomass to a gaseous mixture composed of CO, H_2, and CO_2. The syngas thus derived can be converted to liquid fuels by Fischer–Tropsch chemistry, although a key problem is the need to clean such biomass-derived syngas owing to the sensitivity of F–T catalysts to impurities.[10] On the other hand, fast pyrolysis of woody biomass directly gives a liquid product, pyrolysis oil (sometimes called "bio-oil"). However, this material has limited direct application as transportation fuel owing to its water content, corrosive nature, low vapor pressure, and instability.[11] As a consequence, methods for chemically upgrading bio-oil are drawing considerable attention.[12,13]

Lignin, which constitutes 15–30% of dry woody biomass, provides mechanical and chemical stability to plant tissues, since it is very difficult to degrade biologically. It has the highest carbon content among biomass components, and while aromatics can be derived by catalytic cracking of biomass derived oxygenates,[12] lignin represents a potentially very important, renewable source of aromatic chemicals.[14−16] However, chemical conversion of lignin to liquid fuels and other higher value chemicals has been problematic owing to its complex and diverse structure (Figure 3) and resistance of phenolic ethers toward hydrolysis.[14−16] Historically, lignin has been separated from the more easily processed carbohydrate components[17−23] and either discarded or burned for its heat content.

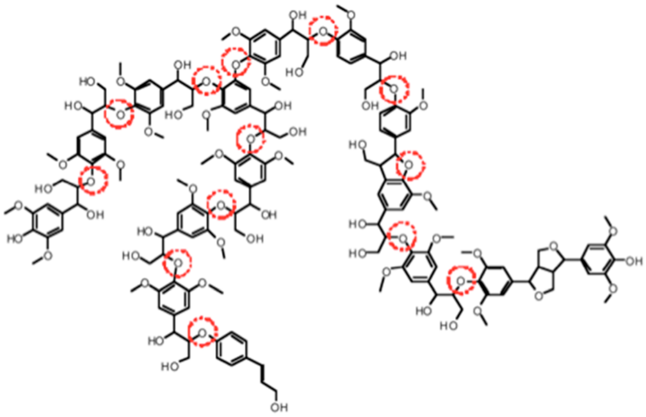


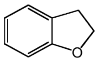
Figure 3. Model for organosolv lignin from poplar softwood (drawing based on a structure suggested in ref 24). Phenolic ethers indicated by circles.

To address these issues, we have developed a one-pot procedure for disassembling lignin and lignocellulose that relies on inexpensive, Earth-abundant materials as catalysts and affords complete conversion of woody biomass solids to organic liquids, without the formation of intractable chars. Dubbed the "UCSB process", this involves a combination of hydrothermal and catalytic processing, while product analysis is largely based on holistic methods.

CATALYTIC STUDIES WITH A LIGNIN MODEL COMPOUND

Characteristic lignin units are methoxylated and hydroxylated 4-propylphenols coupled as ethers and occasionally cross-linked with carbon−carbon bonds (Figure 3). The relatively few biological pathways for lignin degradation are oxidative;[25] however, alternative strategies for chemical disassembly include hydrolysis or hydrogenolysis of the ether linkages.[14,26] An advantage of hydrogenolysis is the increased fuel value from added H_2 equivalents. An earlier report[27] described the degradation of lignin and various models by stoichiometric excess KOH in 300 °C methanol, above the supercritical temperature (239.6 °C) of that solvent.[7] While stoichiometric consumption of KOH would not appear to be practical, we envisioned that analogous reactivity could be effected catalytically by the use of solid bases. Such bases were already in hand, namely, the PMOs prepared by calcining various transition metal-doped hydrotalcites that we had investigated as catalysts for biodiesel production[7] and as reversible CO_2 sorbants.[28] Hydrotalcites are double-layered clay minerals consisting of Mg^{2+} and Al^{3+} hydroxycarbonates.[29] Synthetic hydrotalcites derived by varying the M^{2+}/M^{3+} ratio and replacing some of the Mg^{2+} or Al^{3+} ions with other metal ions offer widely variable catalyst compositions. Upon calcination, the resulting PMOs have large surface areas, while long-range order characteristic of the hydrotalcite structure is lost.[7]

Our exploratory studies[30] in this regard used dihydrobenzofuran (DHBF) as a very simple model for lignin. The advantage of DHBF is that the carbon framework remains intact, thereby making the products easier to track. A series of PMOs derived by calcining metal ion doped Mg−Al hydrotalcite precursors were screened for catalytic reactivity toward DHBF in supercritical methanol (sc-MeOH). The most active were those we designated as Cu10-PMO and Cu20-PMO, where 10% or 20% of the Mg^{2+} ions were replaced in the 3:1 Mg/Al hydrotalcite precursors with Cu^{2+} ions. The high-pressure reactions were largely studied using the minireactors pictured in Figure 4. Solvent MeOH, catalyst, and substrate were added to the minireactors, which were sealed and heated to a specific temperature. After a defined time period, the reactions were quenched by rapid cooling. Upon opening, reactors containing the PMO catalysts were under pressure, so the gas was collected, and the volume was measured and analyzed by gas chromatography with thermal conductivity detection (GC-TCD). Prior to reaction, the Cu-doped PMOs were green, but afterward they were reddish, a color change apparently accompanied by Cu^{II} reduction to Cu^{I} or Cu^{0}, as evidenced by X-ray photoelectron spectroscopy.[30,33]



DHBF

The resulting gas phase was composed of H_2, CO, and CO_2 consistent with the operation of the Cu catalyzed methanol reforming and water−gas shift reaction described in Scheme 1.

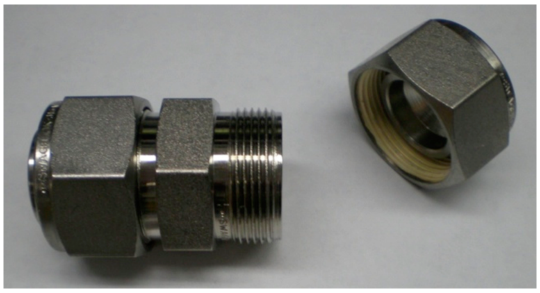
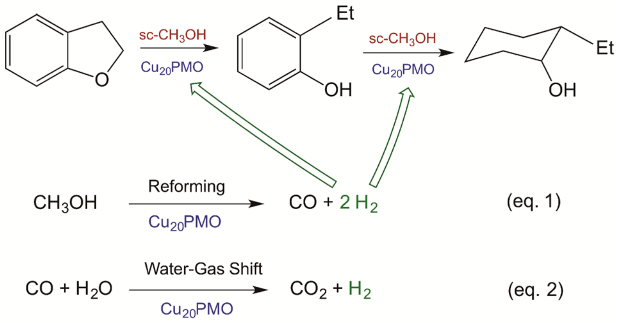


Figure 4. Photograph of 10 mL minireactors built from Swagelok junctions.

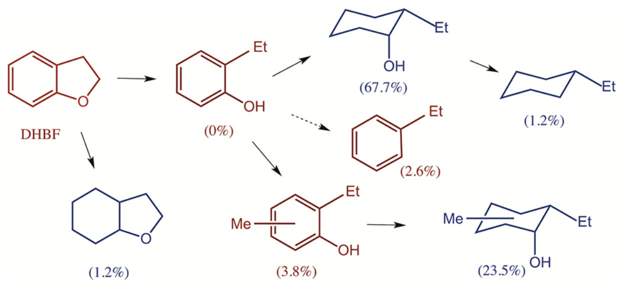
Scheme 1. Key Steps in DHBF Reaction with a Cu20-PMO Catalyst in sc-MeOH



Thus, MeOH is functioning as a liquid syngas precursor.[31,32] Small amounts of methane, likely from the undesired hydrogenation of MeOH, were also present. No gases were formed in the absence of catalyst, while a control reaction with fresh catalyst in MeOH alone gave, after 8 h at 320 °C, a gas mixture with 27 mmol H_2, 4 mmol CO, 5 mmol CO_2, and 1 mmol CH_4.[35] Based on the gas phase carbon products, the predicted amount of H_2 would have been ~22 mM (three H_2 per CO_2 plus two per CO minus one per CH_4). A likely explanation for the higher-than-estimated value of H_2 found is the capture of some CO_2 by the catalyst as the system was quenched prior to analysis since these hydrotalcite-derived PMOs are solid bases,[7] effective in reversible capture of carbon dioxide.[28] Out of the 2.4 g of methanol used in a typical minireactor experiment, ~0.6 g (~19 mmol) was not recovered. About 12 mmol of this can be attributed to the reforming reactions and the remainder to handling losses.[35]

When a series of such reactions were run with DHBF under identical conditions but for various times, a temporal product profile was created based on GC-MS analysis of the liquid products using an unreactive internal standard (dodecane) to quantify the products using GC and GC-MS methods.[30] After 1 h, about 12% of the DHBF was consumed, and the principal product was 2-ethylphenol (~90% of the DHBF consumed), but at longer reaction times, the 2-ethylphenol concentration was also depleted to give (primarily) 2-ethylcyclohexanol. This is consistent with the key steps being hydrogenolysis of the ether linkage, followed by aromatic ring hydrogenation of the intermediate phenol (Scheme 1). The reducing equivalents for the hydrogenolysis and hydrogenation steps are derived from CH_3OH reforming (eq 1) and the water−gas shift (eq 2), both catalyzed by the Cu-doped PMO. A notable side reaction was aromatic ring methylation, very likely also via the phenolic intermediate. Under these conditions, the DHBF was fully consumed within 8 h, and (within experimental uncertainties) good mass

Scheme 2. Products from Cu20-PMO Catalyzed Reaction of DHBF in 300 °C sc-MeOH[a]



[a]Yields after 13 h based on GC-MS data using an internal standard (n-dodecane) are indicated (as reported in ref 30).

balance of the products was obtained. Scheme 2 shows the product distribution at long reaction times.

QUANTITATIVE CONVERSION OF ORGANOSOLV LIGNIN

Since the studies with DHBF clearly indicated that the combination of sc-MeOH and copper-doped Mg/Al PMO readily cleaved phenyl ether linkages, we anticipated that this system should be effective in depolymerizing the more challenging target, lignin.[34] However, two issues were of concern. The first was whether a process involving the heterogeneous catalyst (Cu-doped PMO) and a heterogeneous substrate would indeed be effective. The second was the recognition that the complexity of lignin combined with the multiplicity of products found even from the simple substrate DHBF would make product analysis especially difficult.

The first concern was addressed by using "organosolv lignin", obtained by extracting poplar wood sawdust with acidic methanol according to a published procedure.[26] This material has an average molecular weight of 2.5 × 10^3 g/mol, according to gel permeation chromatography (GPC),[34] and is sufficiently complex to illustrate the chemical transformations taking place during processing. Furthermore, its solubility makes it possible to assess principal structural features by solution-phase NMR spectroscopy. The second concern was addressed by taking a holistic approach to analysis using proton NMR.

A typical experiment consisted of heating a deep brown solution of organosolv lignin (100 mg) in methanol (3 mL) at 300 °C with the Cu20-PMO catalyst (100 mg) in a closed mini-reactor. All product phases, solid, liquid and gas, were analyzed by various techniques (Figure 5).

Two important outcomes were immediately apparent. The liquid phase upon removal of solvent delivered a transparent oily material (58 ± 2 mg). Moreover, essentially no char formed, as evidenced by negligible weight gain of the reddish colored solids recovered from the reactor. The latter point was reinforced in experiments with lignocellulose composites (see below) by the absence of residue after dissolving the PMO solids in nitric acid.[35] In contrast, a control reaction run with substrate (100 mg) but no catalyst gave a black, char-like residue (~40 mg) and little liquid product. The gas phase produced during the organosolv lignin experiments was similar to that obtained with DHBF substrate and consisted mainly of hydrogen.

Analysis focused largely on the oily liquid products after removal of volatiles. The mass of this material (58 mg) corresponded to ~86% yield, if one were to make the simplistic assumption that propylcyclohexanol is the sole product of lignin disassembly and reduction. GPC analysis gave an average molecular weight (191 g mol^{-1}, polydispersity 1.48) within the range of the monomer and dimer units (186−387 g mol^{-1}) that might be derived from the hypothetical structure shown in Figure 3. There was no indication that any organosolv lignin remained.

Holistic NMR Analysis

Given the complexity of potential products, we wanted a relatively fast analysis that gave a holistic view of the temporal reaction progress as we surveyed different substrates, catalysts, reaction conditions, and time. Proton NMR provides the opportunity to look through this murky window, since different spectrum regions, which can be integrated, allow one to assess quantitatively the protons in different chemical environments. In this context, we proposed the operational indices H, O, and A to provide metrics for classifying the chemical transformations in this and other biomass conversions.[34] These are summarized in Scheme 3, where the subscripts "T" and "E" indicate theoretical and experimental indices.

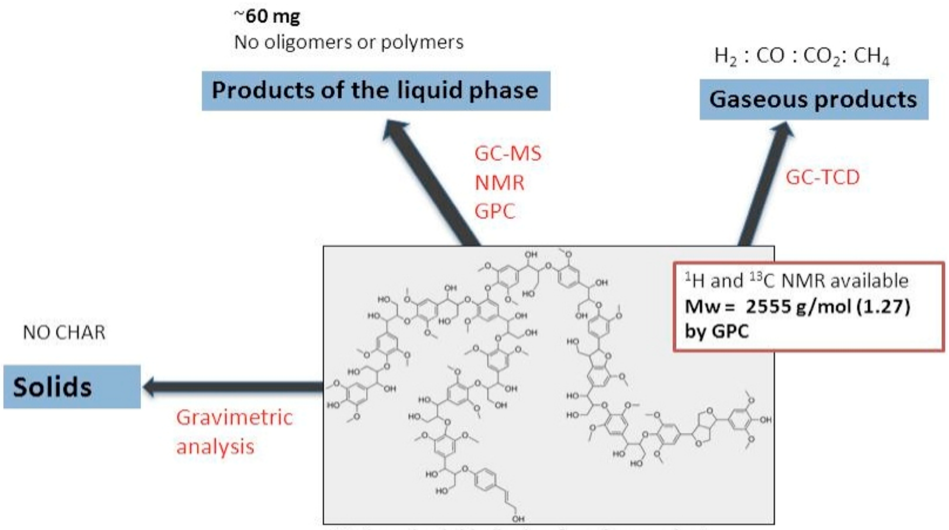


Figure 5. Reaction methodology for assessing product streams from organosolv lignin substrate.

Scheme 3. Indices for Holistic Evaluation of Transformations in the Catalytic Disassembly of Lignin Using Proton NMR[a]

$$H_T = \{N_H / (N_A + N_O + N_H)\} \times 100 \; ; \; H_E = \{R_H / (R_A + R_O + R_H)\} \times 100$$

$$A_T = \{N_A / (N_A + N_O + N_H)\} \times 100 \; ; \; A_E = \{R_A / (R_A + R_O + R_H)\} \times 100$$

$$O_T = \{N_O / (N_A + N_O + N_H)\} \times 100 \; ; \; O_E = \{R_O / (R_A + R_O + R_H)\} \times 100$$

[a] N_A, N_O, and N_H are the numbers of aromatic protons, of those on carbons bearing an oxygen (including −OH), and of aliphatic protons, respectively. R_A, R_O, and R_H are integrated areas of resonances in the chemical shift ranges 7.2−5.0, 5.0−3.0, and 3.0−0.3 ppm, respectively.

Theoretical indices are determined by anticipating the product distribution (see below) and simply counting the various types of protons. Experimental indices are determined by integrating the various ^{1}H NMR chemical shift regions described in Scheme 3 in spectra recorded for a $CDCl_3$ solution of the liquid product (e.g., Figure 6). Comparing the experimental indices provides an overview of the temporal composition of the complex mixtures generated during catalytic processing. There is some ambiguity in determination of aliphatic and aromatic −OH protons, since these sometimes appear outside the 5−3 ppm range. However, control measurements of product mixtures treated with D_2O confirmed that these mobile protons do not affect the results strongly.

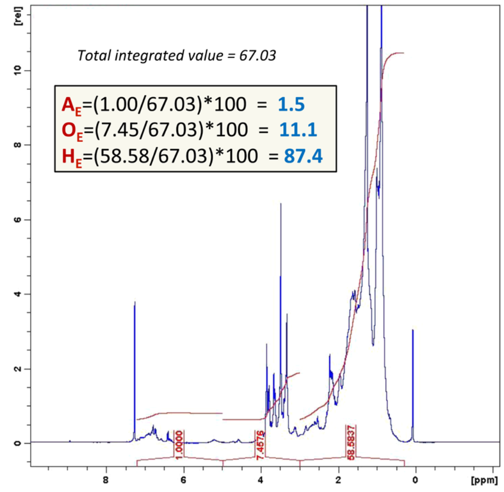


Figure 6. The ^{1}H NMR spectrum of a $CDCl_3$ solution of the liquids from the reaction of organosolv lignin for 12 h under standard conditions. The A_E, O_E, and H_E values determined according to Scheme 3 are 1.5, 11.1, and 87.4, respectively (redrawn from data in ref 34).

To support this analysis, we envisioned a series of hypothetical reactions of the poplar lignin structure proposed by Brunow[24] consisting of 15 aromatic units (Figure 3) with a molecular weight (~3.1 × 10^3) just a bit larger than that determined for our organosolv lignin. The first reaction set would involve hydrogenolysis of the phenyl ether linkages to give compounds **1**−**5** (Scheme 4). In a second set, compounds **1** and **2** would undergo partial deoxygenation via H_2O elimination coupled to hydrogenation to give **6**, **7**, and **8** (Scheme 5). Hydrogenation of the aromatic rings would then lead to **9**−**11**. More extensive deoxygenation/hydrogenation would lead to **12** and **13**.

Similar processes are envisaged for the reactivity of dimeric structures **4** and **5**. Accordingly, the products would become more uniform with each stage of functionality removal, resulting in the simple propylcyclohexyl skeleton of reduced lignin. (This analysis ignores the methylations observed when DHBF was the substrate.) Based on these scenarios, the compounds formed in different reaction stages can be collected into groups A−E according to aromatic character and oxygen content (Table 1), although they might not be formed in the sequence proposed.

In Figure 7, theoretical indices for each of the compound classes in Table 1 are depicted graphically. Since the H index reflects the extent of hydrogen transfer to the organosolv lignin, it is at a minimum for unmodified substrate. The hypothetical lignin model structure shown in Figure 3 has an H_T of 1.0, an O_T of 80.4, and an A_T of 18.5. Complete transformation of lignin to alkanes (group E) would give H_T = 100.

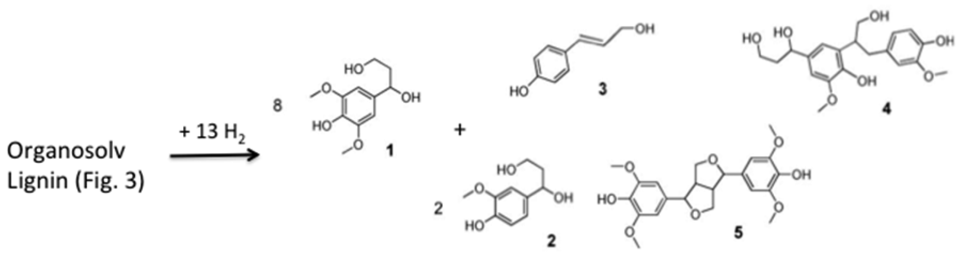
Time Course for Lignin Disassembly

Figure 8 illustrates the temporal progression of A_E, O_E, and H_E during the reaction of organosolv lignin in sc-MeOH at 300° using Cu20-PMO catalyst. After 2 h, the A_E value dropped from 12.9 for the substrate to 4.3 in the product mixture, while O_E decreased from 74.3 to 17.2, and H_E increased markedly from 12.9 to 78.6. The O_E/H_E is about that expected for the theoretical indexes described for group D, although a residual of aromatic protons remain. These were essentially entirely consumed at longer reaction times. GC-mass spectral (GC-MS) analysis of the liquid product revealed a relatively complex mixture of compounds that appeared to consist mainly of functionalized propylcyclohexanols as evidenced by MS fragmentation patterns.

The expected solvent-to-substrate hydrogen/deuteron transfer was demonstrated by conducting a catalysis experiment in methanol-d_4. The ^{2}H NMR spectrum revealed deuteration of the cyclohexyl rings as well as extensive exchange between substrate aromatic protons and the reactive solvent.

These observations clearly indicated that the Cu-doped solid metal oxide catalyst combined with sc-MeOH is capable of breaking down the complex, but soluble, oligomer organosolv lignin to monomeric units. In these studies, the sc-MeOH is both the reaction medium and the source of reducing equivalents. However, the question remained whether analogous reactivity might be expected for a solid substrate such as lignocellulose in the UCSB process, since one might expect such highly oxygenated

Scheme 4. Hydrogenolysis of Phenyl Ethers As Hypothetical First Step in Organosolv Lignin Disassembly



Scheme 5. Prospective Reactions of Compounds Formed by Lignin Hydrogenolysis (Scheme 4)

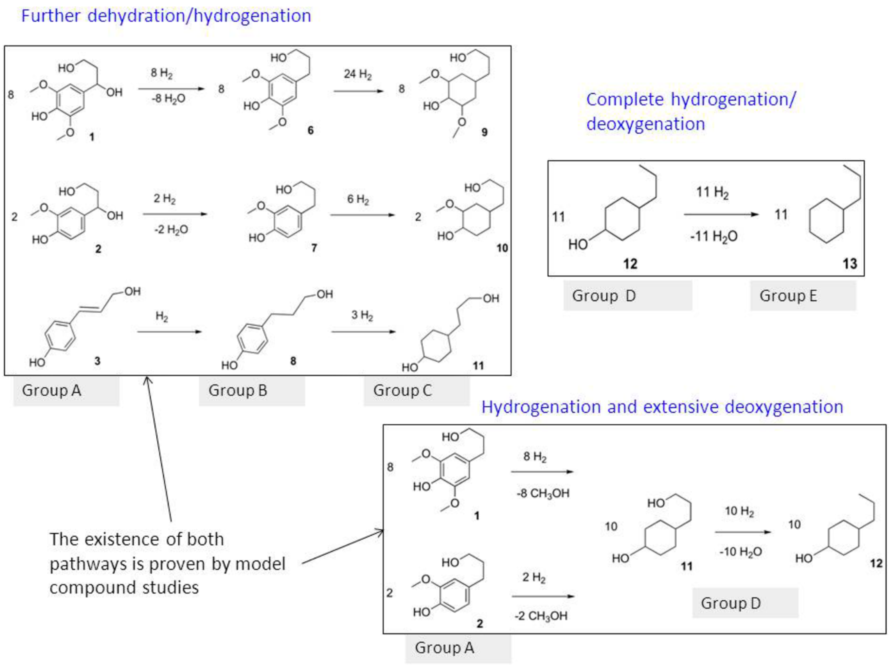


Table 1. Grouping of Hypothetical Products from Sequential Reductive Disassembly of Organosolv Lignin

group	description	sample compounds[a]
A	products of lignin hydrogenolysis	**1−5**
B	products of single dehydration/hydrogenation	**6−8**
C	products of aromatic ring hydrogenation	**9**, **10**
D	products of extensive deoxygenation	**11**, **12**
E	products of total deoxygenation	**13**

[a]Dimers not shown.

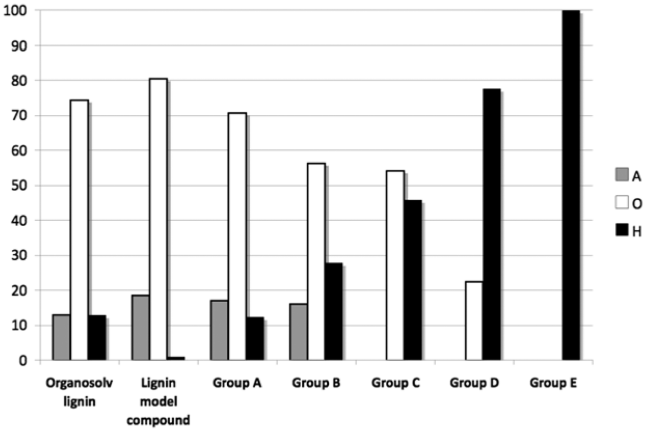


Figure 7. Indices of H_T, O_T, and A_T as measures of aliphatic, oxygen, and aromatic content for organosolv lignin (assuming Figure 3) and product groups in Table 1, assuming the stoichiometries of Schemes 4 and 5 (redrawn from data in ref 34).

feedstocks to form intractable chars and tars through uncontrolled dehydration pathways.

■ WOODY BIOMASS MATERIALS AS SUBSTRATES

Our next step was to apply this promising one-pot method to the conversion of wood particles. Nagging questions were: Would

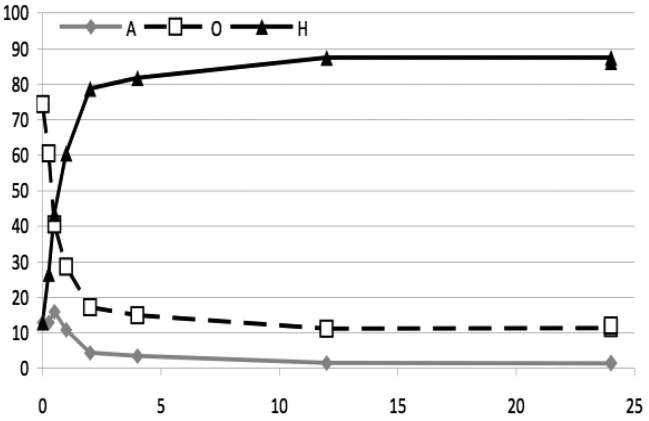


Figure 8. Temporal evolution of A_E (diamonds), O_E (squares), and H_E (triangles) for the catalyzed reaction of organosolv lignin in sc-MeOH at 300 °C (redrawn from data in ref 34).

such solids react at all? Would they turn to char? Or would they behave in a more dynamic fashion to give the desired result? The outcome exceeded our expectation; nearly quantitative conversion of wood to liquids occurred.

Initial experiments[35] were done using the 10 mL minireactors (Figure 4). Typically, a solid substrate (100−600 mg), catalyst (100 mg), and MeOH (2.4 g) were sealed in one of these units and allowed to react for a prescribed time at a specified temperature. After rapid cooling, the resulting gases were collected and analyzed by GC-TCD, and liquid products were separated from the solids and analyzed by NMR and by GC with flame ionization detection (GC-FID). The solids were collected by filtration, dried, and weighed and were dissolved in aq. nitric acid, and the resulting solution was filtered to probe the formation, if any, of insoluble organic residue, that is, char.

The substrates thus explored included pine flour, pine and maple sawdusts, eucalyptus chips, powdered torrefied wood, and cellulose fibers. The gaseous products were the typical mixes of H_2 (~2/3), CO_2, CO, and CH_4. The liquid phase products fell mostly into two groups based upon GC retention times: monomeric higher alcohols and ethers (generally C_2 to C_6) designated as HAEs and a higher molecular weight component (largely C_9-C_{12}) mostly composed of substituted cyclohexyl alcohols and ethers and designated collectively as CAEs (Figure 9). A number of the major species, especially those falling in the HAE category, were identified by comparison of GC retention times with standards and by GC-MS. The NMR for the liquid products from the pine sawdust substrate gave $A_E \approx 0\%$, $O_E \approx 10\%$, and $H_E \approx 90\%$. None of these substrates gave significant organic char residues.

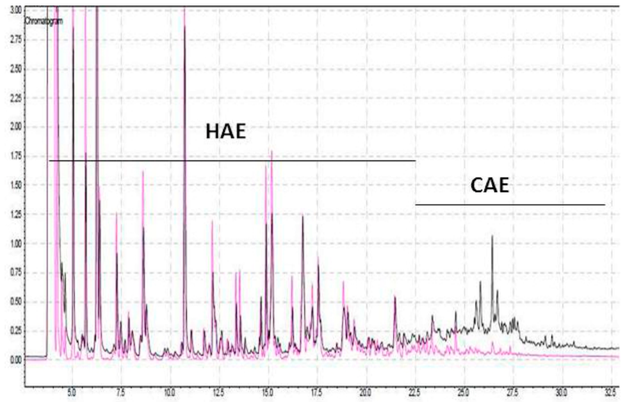


Figure 9. GC-FID traces from solubilization of sawdust (black) and cellulose (purple) via the UCSB process (100 mg substrate, 100 mg Cu20-PMO, 3 mL of MeOH, 320 °C).

The reaction time required for this transformation was probed in a series of experiments where mixtures of pine sawdust (100 mg), Cu20-PMO (100 mg), and MeOH (3.0 mL) were heated at 320 °C from 10 min to 12 h. Wood solubilization was determined to be ~75% within 30 min and essentially complete within an hour, although the solution remained slightly colored (Figure 10). Within 2 h, the product mixture was colorless. At shorter times, some unreacted wood was present, but this was nearly all solubilized at longer times with no detectable residue or char as confirmed by weighing residual solids. Studies with maple sawdust also gave similar results. The PMO catalyst was reused at least 5 times with pine sawdust without significant loss of activity or changes in the product distribution.[35] However, a control reaction with pine sawdust under analogous conditions but using a copper-free PMO, prepared by calcining 3/1 Mg/Al hydrotalcite, led to only ~40% solubilization of the substrate plus considerable char formation.

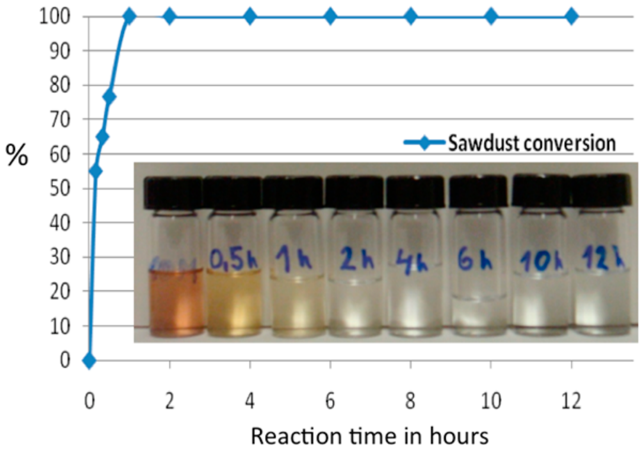


Figure 10. Solubilization of pine sawdust as described in text. Inset: Photograph of liquid phases as a function of reaction time. Adapted from ref 35. Copyright 2011 American Chemical Society.

Similar solubilization of cellulose fibers was observed under analogous conditions. The GC-FID trace for the resulting liquid products showed a pattern of HAE species similar to that for the products from pine sawdust but displayed only traces of the CAE species (Figure 9), consistent with the latter being largely derived from the lignin component of lignocellulose. Qualitatively this was confirmed by subjecting the product solution obtained from a reaction with cellulose substrate to rotary evaporation at 40 Torr. Virtually no higher boiling components (<2 mg) remained. Analogous treatment of the product from pine sawdust gave ~20 mg of higher boiling residue.[35]

The catalyst could be reused multiple times both for cellulose and wood substrates, and ICP analysis of the liquid phase confirmed no significant leaching of inorganic material. After multiple runs with eucalyptus chips, ICP analysis of the recovered catalyst showed a Cu/Mg/Al weight ratio approximately the same as the initial catalyst but showed increased amounts of Na^+, K^+, and Ca^{2+} consistent with the small amount of inorganic ash characteristic of this substrate.[35]

Larger-scale batch reactions in a stirred Parr reactor also showed effective conversion.[35] For example, when a mixture of eucalyptus wood chips (6.6 g) and Cu20-PMO (1.0 g) in methanol (15.8 g) was heated for 4.5 h at 300 °C, 77% conversion of biomass to liquids (and gases) was observed, the remainder being in the residual solids. Further processing converted much of this residual, although for this mixture small amounts of char remained. The major product was a pale yellow liquid collected by room temperature vacuum distillation (0.1 Torr) containing 2.8 g of HAE and 0.8 g of CAE. A similar reaction using cellulose (0.79 g) gave liquid products, mostly HAE (0.69 g) with a small amount (0.08 g) of higher boiling products.

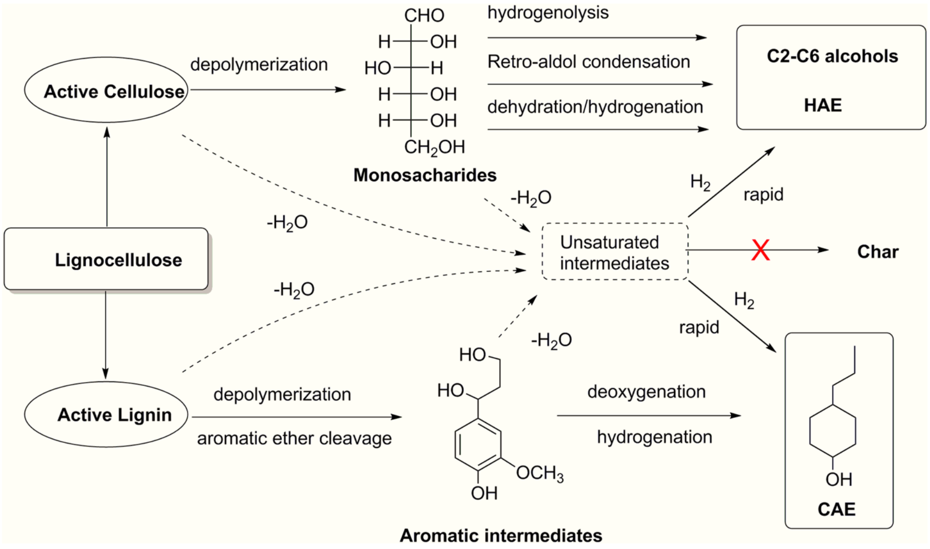
Lastly, preliminary Parr reactor experiments to which mixtures of H_2 and CO gas were added demonstrated that part of the reducing equivalents necessary can be derived directly from syngas rather than from the methanol.[35] This is a topic that will be explored in greater detail. On the other hand, attempts to replace the sc-MeOH with sc-ethanol as the reaction medium were complicated by formation of oligomers derived from reactions of the ethanol itself.[36]

Mechanistic Considerations

Catalyst free control experiments with cellulose and with organosolv lignin in sc-MeOH lead to substantial char formation under the conditions of the UCSB process.[34,35] Similarly while sc-MeOH is known to partially solubilize wood, char formation occurs in the absence of catalyst. This undesired byproduct is absent in nearly every case for the reactions with the Cu-doped porous metal oxides described here. Thus, for the UCSB process, it is likely that unsaturated intermediates, formed during dehydration pathways under these hydrothermal conditions,[37] undergo catalytically hydrogenation more rapidly than polymerization steps leading to these undesired products. The hydrogen equivalents for such reduction are generated by the methanol reforming and water−gas shift catalyzed by the copper-doped PMO.

Scheme 6 represents a hypothetical scenario where hydrothermal processes lead to smaller, soluble fragments that we will refer to as "active cellulose"[37] and "active lignin".[38] The active

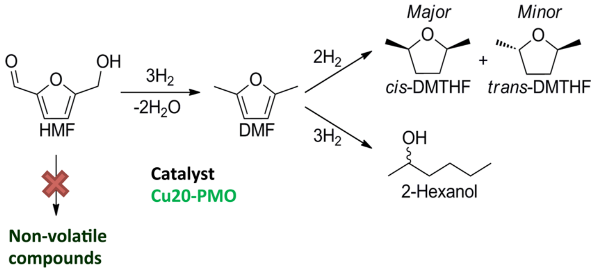
Scheme 6. Mechanistic Model for Solubilization of Sawdust



lignin is depolymerized by aryl ether hydrogenolysis and then undergoes aromatic ring hydrogenation.[34] Solubilized cellulosic components undergo hydrogenolysis, dehydrations, and retro-aldol condensations coupled to catalytic hydrogenation of unsaturated intermediates. Notably the products derived from an analogous treatment of glucose are very similar to those derived from cellulose, suggesting that the latter undergoes depolymerization to monosaccharides[39] prior to the sequential processes leading to formation of HAEs. Cellulose depolymerization to monosaccharide units prior to further chemical conversion has been observed in various systems,[40] including hydrogenation by supported copper catalysts.[41]

This view derives support from the activity of the Cu20-PMO/sc-MeOH system in the deoxygenation and hydrogenation of hydroxymethylfurfural (HMF), which is a hexose sugars-derived intermediate of considerable interest as a potential platform chemical.[19,21,42,43] At 300 °C, HMF is quickly and completely converted without forming involatile side products giving principally dimethylfurfual (DMF), dimethyl-tetrahydrofuran (DMTHF), and 2-hexanol plus a collection of other volatiles that GC-MS studies indicated to be various aliphatic alcohols plus furan and THF derivatives[44] (Scheme 7). Without the copper catalyst, a brownish tar-like residue resulted. The valorization of HMF could further be broadened by devising a tunable and highly selective system in ethanol with added H_2 gas. Here, 2,5-furan-dimethanol was obtained in 97% isolated yield using Cu20-PMO. Notably this catalyst could be recycled up to 8 times. The combined DMF and DMTHF selectivities reached 84% with a new catalyst composition, containing small amounts of ruthenium dopants besides copper.[45]

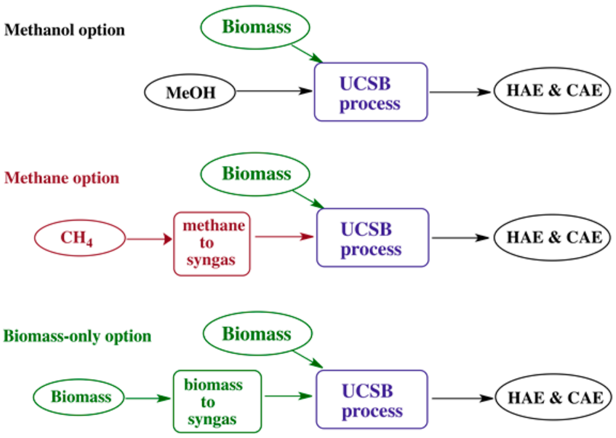
Scheme 7. The Reduction of HMF via the Cu20-PMO/sc-MeOH System at 300 °C



Potential Implementation

Transportation costs limit the range over which woody biomass can be economically collected, so processing of such geographically dispersed feedstocks would best be accomplished at moderate-sized facilities centered in regions where lignocellulose wastes or crops are generated.[2] In this context, Scheme 8 envisions three variations of how the UCSB process might be implemented. The first is direct extension that utilizes MeOH both as the reaction medium and as the principal source of the reducing equivalents. This approach should be the most easily scaled and implemented from current technology and fits well with the proposed "methanol economy".[46] The second would use methane-to-syngas reforming to generate the reducing equivalents as syngas. However, while methane reforming is well-established, this step obviously adds to the complexity of the necessary facility. A third option combines existing technology biomass-to-syngas conversion[47] with the biomass-to-fuels process and should have an even lower CO_2 footprint. With the latter two options, the methanol reaction medium could be generated internally.

Scheme 8. Possible Implementation of UCSB Process To Produce Biomass-Based Fuels. Adapted from ref 35. Copyright 2011 American Chemical Society.



WHERE NEXT?

While the above potential implementations may prove valuable in biomass to fuels applications, greater specificity will be needed to produce platform chemicals from such renewable feedstocks. In this context, ongoing studies in both of our laboratories are focused on exploring the fundamental mechanisms of reactions catalyzed by the metal-doped hydrotalcite-based PMOs with the expectation that better defining these pathways will provide guidelines for improved selectivity. In collaboration with others, we are also characterizing the short-range structure of the Cu-doped PMOs, both before and after use as catalysts in the sc-MeOH system,[48] and are exploring the activities and selectivities of related metal-doped PMOs with various substrates in order to "fine-tune" the chemistry of these systems to desired outcomes.[49]

For example, an important goal is to formulate a system for the production of low molecular weight aromatic precursors from lignins, a task that has long been a "holy grail" of biomass conversion. While this was not achieved in the above studies, a recent experiment by Barta et al.[50] demonstrated that the ethyl acetate soluble fraction of the organosolv lignin from candlenut shells (MW ≈ 1130) is converted by Cu_{20}-PMO to mixtures of aromatic compounds (various monomeric catechols) with high selectivity at milder temperatures (140−220 °C) using added H_2 (4 MPa at RT) as the reductant. This is very promising, and ongoing studies are probing related systems to determine whether this selectivity is due to the character of candlenut shell lignin (low syringyl content) or to the milder conditions. Further study with the higher molecular weight (~2450 g/mol) ethyl acetate insoluble fractions of candlenut shell organosolv lignin showed that disassembly to mixtures of oligomers and monomers requires higher temperatures (~310 °C) where the methanol is supercritical.[51] Reactions of this substrate catalyzed by $Cu_{20}La_{20}$PMO (with La^{3+} replacing 20% of the Al^{3+} in the 3:1 hydrotalcite precursor) gave greater yields of aromatic products than did reactions with Cu_{20}PMO, possibly because the La dopant appears to partially suppress the alcohol reforming process.

CONCLUDING REMARKS

We have described the development of a process using reusable catalysts prepared from inexpensive, Earth-abundant materials that can quantitatively convert lignocellulose solids to combustible liquids via a one-pot reaction in supercritical methanol. Under most conditions, little or no char is formed. These results plus the observation that the Cu-based catalyst is reusable suggest that this system may be modified to be compatible with high yield, continuous operation. Ongoing studies are focused on characterizing and optimizing the catalysts used in this process, on elucidating key mechanistic issues, and on evaluating how the reaction variables control the yields and selectivity in product streams. Successful development of economically viable processes for converting renewable biomass feedstocks to fuels and to chemical precursors for industrial products has the potential for reducing the atmospheric CO_2 burden without compromising food supplies.

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Notes

The authors declare no competing financial interest.

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