One-Pot Catalytic Conversion of Cellulose and of Woody Biomass Solids to Liquid Fuels

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Ⓢ Supporting Information

ABSTRACT: Efficient methodologies for converting biomass solids to liquid fuels have the potential to reduce dependence on imported petroleum while easing the atmospheric carbon dioxide burden. Here, we report quantitative catalytic conversions of wood and cellulosic solids to liquid and gaseous products in a single stage reactor operating at 300–320 °C and 160–220 bar. Little or no char is formed during this process. The reaction medium is supercritical methanol (sc-MeOH) and the catalyst, a copper-doped porous metal oxide, is composed of earth-abundant materials. The major liquid product is a mixture of C_2–C_6 aliphatic alcohols and methylated derivatives thereof that are, in principle, suitable for applications as liquid fuels.
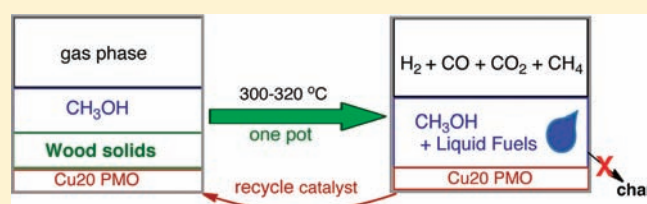
■ INTRODUCTION

With the goal of reducing anthropogenic CO_2, we have developed a clean, single-stage, high-yield conversion of biomass solids to combustible liquids. Woody biomass, primarily a matrix of the biopolymers lignin, cellulose, and hemicellulose, is a renewable feedstock for sustainable energy production that does not compromise the world food supply. Efficient methodologies for its utilization in the production of liquid fuels or chemicals can reduce societal dependence on fossil-carbon based energy. Two types of approaches have historically received consideration for the transformation of wood to liquid fuels: (a) acid pretreatment and separation followed by fermentation or liquid phase processing, and (b) high temperature conversion such as gasification or pyrolysis to bio-oils.[1] Each has specific problems relevant to efficient conversion of lignocellulose carbon to value-added products. For (a), the lignin fraction, comprising up to 30% of the carbon content, is often simply burned,[2] although there has been recent effort into feedstock pretreatment[3−5] and better utilization of aqueous sugars[6,7] and lignin byproducts.[8,9] For (b), a significant fraction of the feedstock is transformed into intractable carbonaceous waste (i.e., "char"),[10] and refinery-scale infrastructure is needed for processing. Moreover, the geographically dispersed nature of biomass feedstocks both makes forest-to-refinery transport a key economic consideration and therefore limits the size of processing units.[11] We offer a unique alternative, the methanol-mediated, catalytic conversion of woody biomass and of cellulose solids to liquids and gases (Scheme 1). This process is quantitative (little or no char) and

should be compatible with operation scales that match the transportation limitations of biomass feedstocks. Furthermore, the catalyst is based on earth-abundant elements.

Simple chemical conversion of lignocellulosic biomass is challenged by the complexity of this material; indeed, many of the studies of new biomass conversion methodologies have focused on simpler molecular models, especially for lignin. Effective utilization requires depolymerizing cellulose and lignin, the latter being nearly refractory toward hydrolysis of its phenolic ether linkages, and substantially reducing overall oxygen content without producing chars. We have previously addressed the issue of lignin depolymerization by demonstrating that the simple model dihydrobenzofuran[12] and the more complex organosolv lignin[13] undergo catalytic hydrogenolysis of phenolic ether linkages in supercritical methanol in the presence of a copper-doped porous metal oxide (Cu20-PMO).

The Cu20-PMO also catalyzes methanol reforming (eq 1)

$$CH_3OH \rightleftharpoons 2H_2 + CO \tag{1}$$

and the water gas shift (eq 2).

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{2}$$
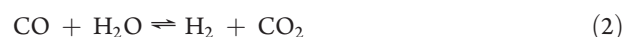
The resulting H_2 provides the reducing equivalents necessary both to cleave the aromatic ethers and for further reduction and deoxygenation. We now show that this single-stage process also

Scheme 1. Conversion of Lignocellulose Solids to Liquid Fuels As Mediated by sc-MeOH and Copper-Doped Hydrotalcite Based Porous Metal Oxides
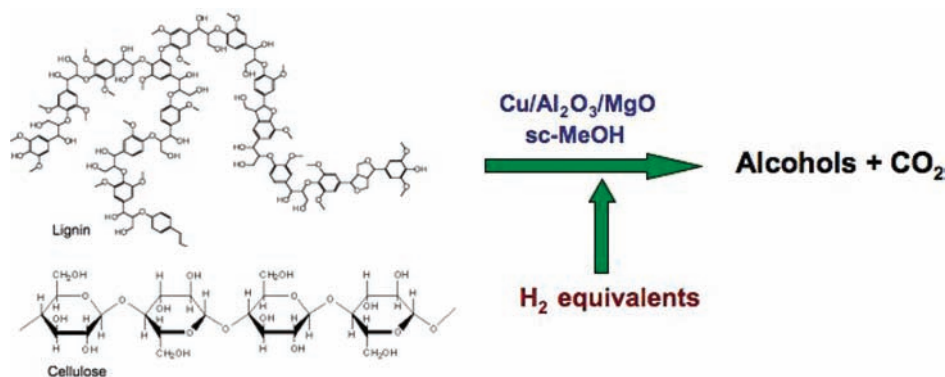
depolymerizes and reduces cellulose and converts much more complex lignocellulose composites, various finely divided wood particles, to a mixture of alcohols potentially usable as liquid fuels.

■ EXPERIMENTAL SECTION

Materials. Sawdust samples were obtained by sanding oven-dried woods followed by sifting through a screen of a predetermined mesh or were used as provided from commercial sources. Coniferous wood ponderosa pine flour (140 mesh maximum) was purchased from American Wood Fibers. Powdered torrefied wood was used as provided by Energy Institute of The Netherlands. Cellulose fibers were purchased from Aldrich (#C6288). The Cu20-PMO catalyst typically used has a 15/60/25 Cu/Mg/Al molar ratio and was prepared by calcining a copper-doped hydrotalcite as previously reported.[12,13]

Small-Scale Batch Reactions. In a typical run, a finely divided substrate (wood or cellulose), catalyst (usually Cu20-PMO), and methanol (3.0 mL) were added to a 10 mL stainless steel, Swagelok union minireactor.[13] The reactor was sealed, shaken, and placed in a preheated aluminum block at the desired temperature (T) and allowed to react at the specified T for a prescribed period. For analysis, the reaction was quenched by rapid cooling, after which the reactor was weighed to ensure that no leakage had occurred. (Any sample deviating >10 mg from the prereaction weight was discarded.) The gaseous products were collected and the volume measured by displacement of water in a specially designed volumetric displacement apparatus equipped with sampling port. (WARNING: These minireactors develop high internal pressures during a catalysis run and must be handled and opened with care.) A sample of 500 μL of gas was analyzed by GC–TCD according to the methods described below. The liquid products were separated by filtration or by centrifugation from the remaining solids, which were dried and weighed after washing with methanol and ether. Approximately 1.0 μL sample of this liquid was analyzed by GC–FID as described below. In several cases, the solids were further treated with ~10 mL of MeOH and the filtrate was analyzed by GC–FID to verify that the concentrate obtained initially was representative of the bulk liquid.

Gas Analysis. Gas phase samples were obtained with a gas tight syringe, then injected into a programmable Agilent model 6890 GC with a 10 m Carbosieve packed column and a thermal conductivity detection (TCD). The injector was maintained at 290 °C. The carrier gas was helium at a flow of 7.3 mL min^{-1}. The column was maintained at 50 °C for 5 min, raised at 40 °C min^{-1} to 250 °C and held for 10 min, then finally raised at 10 °C min^{-1} to 290 °C and held for 45 min. The gases H_2, CO, CH_4, CO_2, C_2H_6, and C_3H_8 are well resolved with this configuration and detected by a thermal conductivity detector. Quantification was achieved by comparison to calibration curves determined for each gas.

Liquids Analysis. At UCSB, liquid phase samples were obtained with a microliter syringe and injected into a programmable Agilent model 6890 GC with a 30 m DB-5 column equipped with a 10 m guard column and a flame ionization detector (FID). The injector was maintained at 290 °C. The carrier gas was helium at a flow of 20 mL min^{-1}. The column was maintained at 30 °C for 5 min, raised at 10 °C min^{-1} to 90 °C, then raised at 25 °C min^{-1} to 250 °C and maintained for 20 min. Identification of the alcohols was achieved by retention time comparison to standards. In some cases, samples were mixed with authentic standards and analyzed with two different temperature programs to obtain positive identification. Mass fraction was determined by integration.

At Yale, the GC–FID analyses used a Shimadzu GC equipped with an FID detector and a SHRXI-5MS column of 30 m × 0.25 mm i.d. The carrier gas was helium at a total flow of 19.6 mL/min. Split injection mode was used with a split ratio of 15.2. The oven program maintained T at 40 °C for 10 min, heated at 10 °C/min to 90 °C where it paused for 5 min, then heated at 15 °C/min to 260 °C where it paused for 5 min, then finally heated at 25 °C/min to 290 °C.

Solids Analysis. Solids were washed extensively with methanol and water, and then slurried in ~20-fold excess by weight H_2O. Concentrated nitric acid was added dropwise with stirring and a flow of air was maintained to remove evolved gases. At a nominal concentration between 10 and 12 M HNO_3, complete oxidation and dissolution of copper was obtained. The contents of the vial (10 mL for a 100 mg sample of solid) were transferred to a flask and further treated with 40 mL of 5 M HNO_3. The contents of the flask were then gravity filtered on a pretared medium porosity frit and washed with 10 × 10 mL of H_2O, 3 × 10 mL of MeOH, and 3 × 10 mL of Et_2O. The frit was then dried in vacuo and the extent of conversion determined by mass difference.

Elemental analyses of dissolved catalysts, ash, and other residues were accomplished using a Thermo iCAP Model 6300 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP).

Larger-Scale Batch Reactions. Runs were also carried out in a Parr series 5500 compact reactor equipped with a stirrer and a 100 mL base (total volume 113 mL) or a 25 mL base (38 mL). Inorganic catalyst and organic material were added to the reactor base with a weighed quantity of methanol. The reactor was then sealed and raised to the designated temperature over 20–30 min. Stirring was maintained at 1000 rpm. After the time period designated for the reaction, the reactor was cooled. Volatile species were collected in a 5 L Tedlar gas bag equipped with a septum sampling port. The reactor was opened, and liquid and solid contents were discharged onto a medium porosity frit. The filtrate was analyzed by GC–FID, and the contents of the gas bag were analyzed by GC–TCD and GC–FID (VOC's).

Table 1. Summary of Minireactor Experiments[a]

substrate (amount)	conditions: T (°C), time (h)	conversion (%)	gases (mmol) H_2, CO, CO_2, CH_4	HAE (wt %)	CAE (wt %)
maple sawdust (100 mg)	320, 8	99	22, 6.1, 4.7, 0.9	5.9	2.0
maple sawdust (100 mg)	320, 8 (second run)	99	20, 5.8, 6.0, 1.1	5.7	2.0
maple sawdust (100 mg)	300, 24	∼100	not determined	4.6	1.8
pine flour (207 mg)	320, 8	96[b]	not determined	9.1	4.0
torrefied wood (100 mg)	320, 8	89	21, 4.5, 4.8, 0.8	5.8	1.4
cellulose fibers (100 mg)	320, 8	98[c]	23, 3.7, 6.2, 0.9	8.6	0.4
no substrate	320, 8		27, 4.0, 5.0, 1.5	0.3	0

[a] Runs carried out in 10 mL Swagelok union reactors with methanol (2.4 g) and 100 mg of solid catalyst. The gas and liquid compositions were determined by GC–TCD and GC–FID techniques, respectively, while conversion was based on the amount of solid residues not soluble in aq HNO_3 solution. [b] The 9 mg residue after dissolution in HNO_3 was visually assessed to be unreacted wood. [c] The 2 mg residue was a white powder presumed to be cellulose.

■ RESULTS AND DISCUSSION

Small-Scale Reactions with Sawdust. Typically, substrate (100−600 mg), catalyst (100 mg), and MeOH (2.4 g) were sealed in 10 mL minireactor, heated to specified T for a prescribed period, then quenched by cooling. Gaseous products were collected and analyzed by GC–TCD, and liquid products were separated from the remaining solids and analyzed by GC–FID. The solids were dried and weighed, then dissolved in aq HNO_3, and the resulting mixture was filtered to measure quantitatively any insoluble organic residues.

We applied this procedure to several wood sawdusts, to powdered torrefied wood, and to cellulose fibers and have identified and quantified the major components in the gas and liquid phases in each case. The liquid products fall largely into two groups of monomeric alcohols and ethers: HAE (higher alcohols and ethers), which are C_2−C_6 species, and CAE (substituted cyclohexyl alcohols and ethers), which are largely C_9−C_{12} components.[14] No organic char residues were observed in these experiments.

In one such experiment, a minireactor was charged with maple sawdust (100 mg, <63 μm), Cu20-PMO (100 mg), and MeOH (2.4 g), purged with argon, sealed, weighed, and heated at 300 °C for 24 h. Upon opening the reactor, H_2, CO, CO_2, CH_4 and other volatiles were expelled. Analysis by GC–FID showed the clear, colorless liquid product (1900 mg) to contain unreacted methanol and dimethyl ether and a mixture of HAE and CAE corresponding to 4.6 and 1.8 wt % of this solution (∼87 and ∼34 mg) in a ratio roughly consistent with the origins of these components being cellulose and lignin, respectively. We note that these amounts are somewhat more than expected purely from lignocelluloses; increases in mass can be attributed to the incorporation of some methanol-derived carbon into the products (see below).

The solids were collected quantitatively by filtration and washed with MeOH, diethyl ether, and pentane, and then dried to give a blackish-red material weighing 96 mg. After treating this with aq HNO_3 to dissolve the copper and inorganic oxides, the remainder was a colorless, flocculent solid weighing <1 mg. Thus, the substrate was converted to MeOH-soluble or volatile products without formation of intractable organic waste (char).

Nearly identical results were obtained for an analogous run conducted at 320 °C for 8 h (Table 1). The liquid products were a mixture of HAE and CAE in methanol according to GC–FID analysis (Figure 1). The solids recovered were washed with methanol and directly recycled into a second run with maple sawdust. Analogous products were observed, and acid digestion of the remaining solids showed that overall conversion was >98%. Thus, the copper-doped PMO catalyst can be used in multiple runs (see below).

Similar observations were made with pine sawdust and powdered torrefied wood, although only 89% conversion was found for the latter substrate (Table 1). In each case, a H_2, CO, CO_2, CH_4 gas mixture was generated while the liquid fraction contained HAE and CAE in a ratio consistent with cellulose/hemicellulose and lignin origins, respectively.

The reaction time required for solubilization of the biomass solid 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 in minireactors for the various time intervals: 0.17, 0.33, 0.5, 1.0, 2, 4, 6, 8, 10, and 12 h. The extent of solubilization was determined by weighing the solid residues after the reaction, and these data (summarized in Figure 2 and Supporting Information Table S-1) show this to be ∼75% within 30 min and essentially complete within an hour. GC–FID analysis of the liquid products from an 8 h experiment with pine sawdust is reported in SI Figure S-1. After 20 min, the liquid fraction, once separated from the solids, was a bright orange, which suggested the presence of organosolv lignin. However, after only 1 h reaction, the color changed to a light yellow then after 2 h it became completely colorless (Figure 3). The solids were additionally subjected to the nitric acid test to establish the extent of conversion. The inorganic fraction of the solid residues quickly dissolved, while the remaining unreacted biomass did not, and no char was observed in samples where the remaining solid weighed 100 ± 5 mg. GC–FID results of these samples are further reported in the Supporting Information.

SI Table S-1 also summarizes control reactions where a pine sawdust sample (100 mg) was subjected to analogous conditions for 0.5, 2, and 24 h *without catalyst*. The behavior was markedly different from those with added Cu20-PMO. For example, only about 40% of the substrate was solubilized after 30 min and the 60 mg solid organic residue was visually assessed to be a mixture of unreacted biomass and char (SI Figure S-2). Furthermore, significant amounts of char remained after longer reaction times. Qualitatively, the liquid phases obtained were strongly colored in every case, and when analyzed by GC–FID, only a small fraction proved to be volatile. When a sawdust sample was treated similarly for 24 h with a Mg/Al hydrotalcite derived PMO (100 mg) *not containing copper*, the system behaved similarly to the control reaction without any catalyst (SI Table S-1). Additionally, the initially white PMO was black after filtration, washing and drying, showing char formation when Cu was not present.
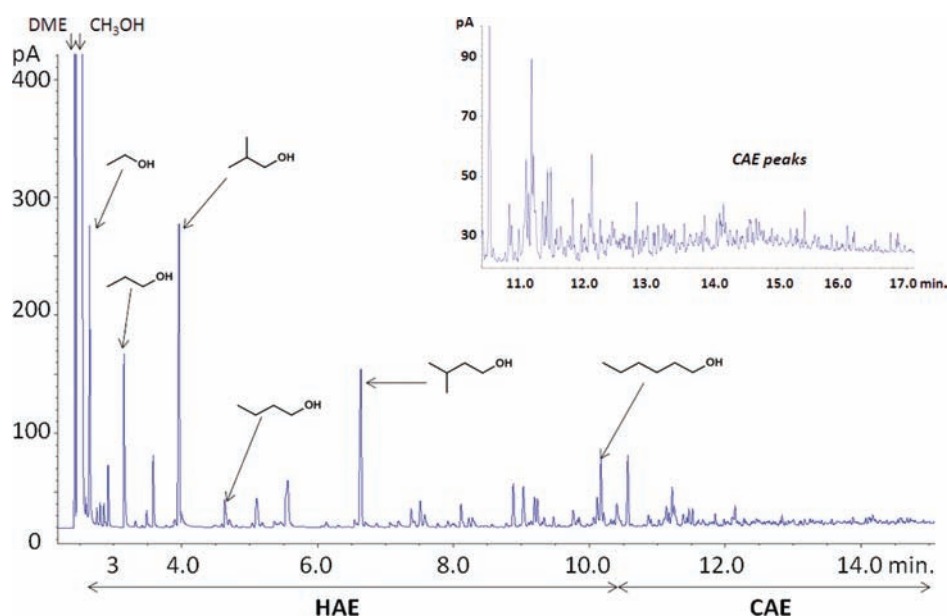
Figure 1. GC–FID trace of the liquids from the reaction of maple sawdust and Cu20-PMO in a 10 mL minireactor at 320 °C for 8 h, noting some key chemical entities, identified by comparison to standard samples. (Recorded on a Agilent model 6890 GC with a 30 m DB-5 column.) (DME is dimethyl ether. *Note:* The vertical axis is FID signal intensity; the horizontal axis is retention time in minutes.).
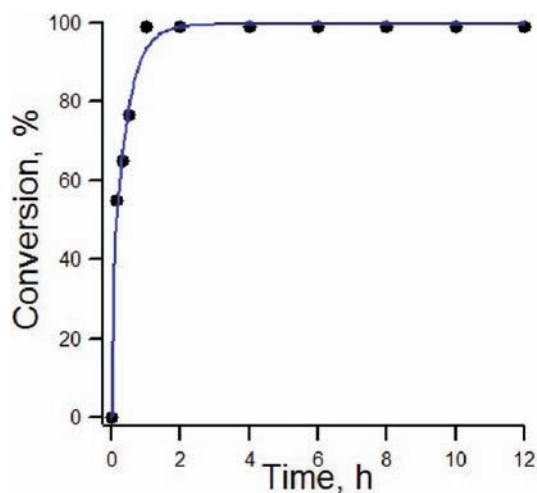

Figure 2. Temporal solubilization of pine sawdust for mixtures of substrate (100 mg), Cu20-PMO (100 mg), and MeOH (3.0 mL) heated at 320 °C in minireactors.
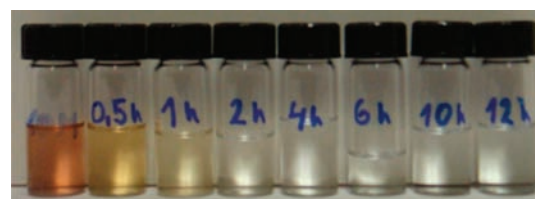

Figure 3. Photograph of liquid phases from experiments probing the temporal solubilization of pine sawdust in the presence of Cu20-PMO catalyst in experiments detailed in SI Table S-1. The strongly colored sample at the left is after 10 min reaction at 320 °C in a 10 mL minireactor.

Small-Scale Reactions with Cellulose. The reactivity of cellulose alone was verified by heating cellulose fibers (100 mg), Cu20-PMO (100 mg), and MeOH (2.4 g) in a minireactor for 8 h at 320 °C. Conversion was ~98%, and the standard gas mixture of H_2, CO, CO_2, and CH_4 was observed. Most significantly, the methanolic liquid collected was 8.6 wt % HAE with only a trace of CAE (0.4%) (Figure 4). We attribute formation of small quantities of C_7+ alcohols and ethers from cellulose to condensation and/or hydroformylation of reactive intermediates generated by dehydration/hydrogenation under the processing conditions as well as possibly some polymethyl glycosides or their partially reduced/deoxygenated forms.[15]

When the liquid phase product from an analogous cellulose conversion (100 mg) was subjected to rotary evaporation at 40 Torr, virtually no higher boiling components (<2 mg) remained.[24] In contrast, analogous treatment of the liquid product from a pine sawdust (100 mg) reaction gave ~20 mg of higher boiling residue. GC–FID analysis of this residue corresponded to CAE, consistent with it being of lignin origin. GC–FID traces for analogous runs with pine sawdust and with cellulose are shown in SI Figure S-1, illustrating the much greater quantity of the CAE component in the former.

Reactions with cellulose (200 mg) and Cu20-PMO (100 mg) were also carried out at different reaction times (0.5–8 h). At 0.5 h, 60% solubilization of cellulose was achieved, and this was complete within the first 2 h (SI Table S-2). Interestingly, the product stream, as evaluated by GC–FID, continued to evolve during this time sequence with the lighter components becoming more prominent and components having the longest retention times becoming less so (see Figure S-3) presumably as the latter undergo further processing via retro-Aldo and dehydration processes (see below). Full solubilization of cellulose was also obtained after 8 h reaction at a lower temperature (280 °C). Additionally, the effect of different cellulose loadings (100, 200, 400, and 600 mg) at the same catalyst loading was probed for an 8 h reaction time at 320 °C (SI Table S-2). All experiments resulted in approximately 100% conversion of cellulose to methanol soluble
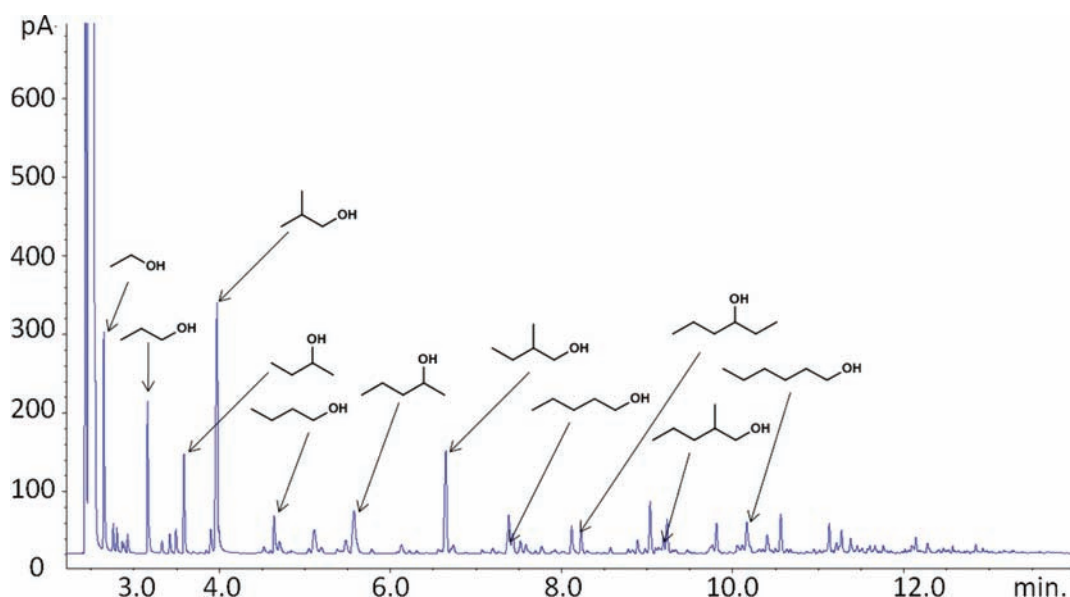
Figure 4. GC−FID trace of the liquids from the reaction of cellulose fibers and Cu20-PMO and methanol in a minireactor at 320 °C for 8 h. (Recorded on a Agilent model 6890 GC with a 30 m DB-5 column). *Note:* The vertical axis is FID signal intensity; the horizontal axis is retention time in minutes.

species, and the GC−FID chromatograms of the liquid phase products were nearly the same (SI Figure S-4).

Reaction with Glucose. A minireactor experiment with glucose (200 mg), MeOH (2.4 g), and Cu20-PMO (100 mg) at 320 °C for 8 h was carried out. GC−FID analysis showed the liquid products to be similar to those obtained by analogous treatment of cellulose (SI Figure S-5), suggesting that cellulose may be first converted to monosaccharide units under these conditions.

In a control reaction, methanol and Cu20-PMO were heated in a minireactor at 320 °C for 8 h in the absence of substrate. The liquid products were HAE (0.3 wt %) and dimethyl ether (DME, 0.3 wt %) in MeOH (SI Figure S-6). The quantity of HAE thus formed is minor compared to that found when a biomass-derived substrate is present.

Larger-Scale Batch Reactions. These experiments demonstrated that the liquid products can be readily separated into lighter and heavier fractions. Excellent mass balances were observed. For example, the reaction of eucalyptus wood chips (6.6 g, 1.4−2.0 mm size range), Cu20-PMO (1.0 g), and MeOH (15.8 g) for 4.5 h at 300 °C in the larger reactor led to an autogenous pressure of 180 bar. Product workup gave: (a) the gases H_2, CO, CO_2, and CH_4 (134, 4.6, 67, and 15.1 mmol, respectively, ~3.6 g total) plus volatile organics (0.5 g), which were collected by room temperature, atmospheric distillation into a gas collection bag; (b) a pale yellow liquid (15.6 g) collected by room temperature vacuum distillation (0.1 Torr); (c) methanol-soluble organics (0.8 g) recovered by washing; and (d) residual solids (2.5 g). GC−FID analysis of the liquid distillate found methanol, HAE (2.8 g), and CAE (0.8 g) (SI Figure S-7 and Table S-3). On the basis of the mass of the residual solids, the above reaction gave 77% conversion in 4.5 h. When these solids were subjected to further processing with methanol for 8 h at 320 °C, half the unreacted biomass was solubilized; however, acid digestion of the inorganic components suggested that the remainder of the organic residue contained some char.

A Parr reactor (38 mL) run with cellulose (0.79 g) gave a mixture of liquid products (SI Figure S-8) mostly HAE (0.69 g)

as seen with the minireactors but with a measurable quantity of CAE (0.08 g). Conversion to liquid products was >98%.

We also probed the effect of added syngas on reaction patterns. The Parr reactor was charged with pine flour (1.0 g), Cu20-PMO (0.5 g), MeOH (7.8 g), CO (133 mmol), and H_2 (40 mmol) to an initial pressure of 52 bar. The mixture was heated for 2.0 h at 320 °C and then for 4.0 h at 300 °C, during which a maximum pressure of 194 bar was observed. Analysis found H_2, CO, CO_2, and CH_4 (139, 116, 33, and 2.3 mmol, respectively) in the gases released and 10.0 wt % HAE and 5.8 wt % CAE in the liquid methanol phase. Conversion was ~85%. Thus, it appears that CO/H_2 mixtures may, at least partially, supplant reducing equivalents from CH_3OH.

Catalyst Stability Studies. Minireactor runs were carried out in which the catalyst was recycled and mixed with fresh MeOH and solid substrate. Each run was 3.0 h at 320 °C. Initially, MeOH (2.4 g) and Cu20-PMO (220 mg) were heated without substrate, the liquids and gases collected and the solids washed with MeOH (~10 mL). The solids were dried, weighed, and returned to the same reactor with fresh MeOH (2.4 g) plus cellulose fibers (400 mg), and the process was repeated four times with new substrate. The mass of solid (catalyst and unreacted substrate) recycled to the reactor was ~255−275 mg, and it was estimated that ~3−5 mg of solids were lost each time due to handling. The product solution for each cycle with substrate was analyzed by GC−FID, and the run-to-run product distributions were essentially indistinguishable with <1% deviation in relative intensities of individual peaks (Figure 5). Following the 5 cycles (4 with substrate), a 50 mg portion of the remaining solid (265 mg total) was titrated with aq HNO_3; the insoluble fraction was 5 mg of a white, flocculent solid. Thus, we estimated that ~27 mg of cellulose was carried over between runs. The remaining solid (215 mg) plus MeOH (2.4 g) was returned to the reactor at 320 °C for 3 h and the residue (190 mg) was completely soluble in aqueous HNO_3, indicating that overall substrate conversion was >99%.

This process was duplicated with eucalyptus chips (<250 μm) with an ash content of 0.9 wt % determined by published procedures.[16] Cu20-PMO (320 mg) was first treated with pure

MeOH (2.4 g) for 3.0 h at 320 °C, while the subsequent five cycles contained eucalyptus chips (400 mg) and MeOH (2.4 g). The mass of solids recycled to the reactor was ~425−440 mg (after washing with MeOH and drying) with 3−5 mg lost between runs due to handling. Compared to the cellulose reactions, a greater run-to-run variability was observed in the GC−FID analyses of product liquids from the eucalyptus chips (SI Figure S-9) with greater quantities of heavier products being detected in the later runs. After 6 cycles (5 with substrate), a 75 mg sample of the solid (430 mg total) was titrated with nitric acid and found to contain ~10 mg of a dark brown, flocculent solid. We estimated that organic residue carried over between runs was ~57 mg. When the remaining solid was heated in MeOH (2.4 g) at 320 °C for 3 h, the organic material was fully converted to soluble products; thus, total conversion was >99%. Therefore although apparent changes occur with continued conversion of lignocellulose by the UCSB Process (in contrast with pure cellulose), the conversion of solid biomass to liquids remains highly efficient.

The washed and dried solids (260 mg) from the multiple eucalyptus chips runs were calcined at 450 °C for 5 h to obtain a very dark green material (240 mg). A 100 mg sample was dissolved in aq HNO_3 and subjected to ICP elemental analysis. Notably, the Cu/Mg/Al weight ratio was approximately the same as that of the initial catalyst. However, the composition of the recovered solid reflected collection of some wood ash as evidenced by increased sodium, potassium, and calcium (SI Table S-3). ICP analysis of product solutions, combined washes, and so forth, showed extremely small quantities of Na, K, and Al, and essentially no Cu, Mg, or Ca; hence, the catalyst is resistant to leaching by the medium.

Mechanistic Interpretation. Conversion of lignin and cellulose to liquid fuels requires reduction of these highly functionalized biopolymers. The process described here uses catalytic methanol reforming to provide the necessary reducing equivalents R, although the introduction of syngas may also serve this purpose. If we define the 1-electron reducing equivalents provided by the system as n_R, then $n_R = 6n_{MeOH} + 2n_{H_2} + 2n_{CO}$. For example, in the larger-scale conversion of cellulose described above, n_R equaled 720 mmol at the beginning of the reaction and 610 mmol at completion. The difference ($\Delta n_R = 110$ mmol) is consistent with the reduction of the cellulose (4.9 mequiv of $C_6(H_2O)_5$) to a mixture of C_2−C_6 alcohols such as in the simplified model illustrated in eq 3.

$$1/y\{C_6(H_2O)_5\}_y + 24R \rightarrow 2C_2H_5OH$$
$$+ C_4H_9OH \ (+2H_2O, \text{ assuming } 24R = 12H_2) \qquad (3)$$
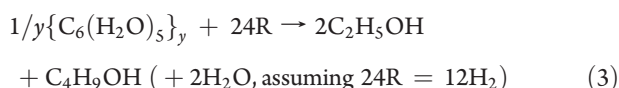
Cellulose has been shown to form char under vacuum[17] and in sc-MeOH[18] at the temperatures utilized in the present studies. Similarly, organosolv lignin forms chars in sc-MeOH in the absence of catalyst.[13] Since this undesired byproduct is absent in nearly every case when cellulose or woody materials are treated in the process described here, chemical pathways under these conditions must intercept the unsaturated intermediates that would otherwise polymerize to such wastes. Scheme 2 proposes a model for this transformation of an insoluble lignocellulose matrix to liquids.

Key roles for the copper/metal oxide catalyst include methanol reforming[19] to give the necessary reducing equivalents, hydrogenation[20] of unsaturated intermediates generated by dehydration, and the water gas shift.[21] The sc-MeOH medium
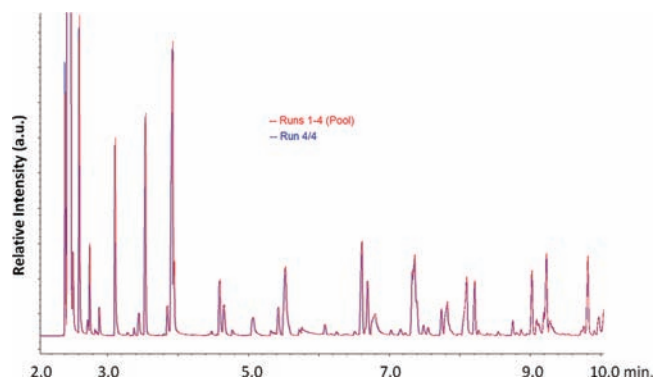

Figure 5. GC−FID trace showing liquid products of a single cellulose conversion experiment (blue) compared to the pool of liquid products from the four cellulose conversion experiments (red). (Recorded on a Agilent model 6890 GC with a 30 m DB-5 column). *Note:* The vertical axis is relative FID signal intensity; the horizontal axis is retention time in minutes.

provides conditions suitable for solubilizing constituent polymers to give "active cellulose" and "active lignin".[17] Depolymerization of the solubilized cellulosic components would be followed by sequential dehydrations and retro-aldol condensations[22] coupled to catalytic hydrogenation of unsaturated intermediates. The "active lignin" component is depolymerized by aryl ether hydrogenolysis followed by aromatic ring hydrogenation.[12,13] Successive dehydration and catalytic hydrogenations would lead to propylcyclohexanol derivatives, the latter step being faster than competitive polymerizations of reactive intermediates to chars. The fact that glucose and cellulose display qualitatively similar product suites suggests that rapid solvolysis or hydrogenolysis of cellulose to monosaccharide units is the first step. More specific proposals regarding transformations of cellulosic components to HAE are offered in Scheme S-1 of the Supporting Information.

The treatment of lignin models by the process described here also led to considerable ring methylation of the eventual products.[12,13] Analogous methylation of unsaturated intermediates is a likely source of branched alcohols in the HAE products from the treatment of cellulose.

Copper/metal oxide are also proficient catalysts for carbonyl hydrogenation,[20] aryl ether hydrogenolysis, and aromatic ring hydrogenations,[12] but are not Fischer−Tropsch catalysts. Thus, the combination of *in situ* reduced Cu20-PMO and the sc-MeOH medium appear to be ideally suited for facilitating the complex set of physical processes and chemical reactions required to convert lignocellulose composites to liquid fuels.

Potential Implementation. Transportation costs limit the range over which biomass solids can be collected and moved to a processing facility.[11] We envision that biomass conversion via the process described here would occur at moderate-sized facilities located where lignocellulose wastes or crops are generated. Three variations of this methodology are described in Scheme 3.

The "methanol option" involves utilizing MeOH both as the reaction medium and as a "liquid syngas" for reducing biomass components. This option should be the most easily scaled from the current technology. The "methane option" uses CH_4-to-syngas reforming to generate the necessary reducing equivalents. In the United States, an advantage of the latter option is that the methane distribution network is already extensive, including areas in the Midwest that would be major suppliers of biomass feedstocks.[23] The disadvantage would be the addition of another process to the

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Scheme 2. Model for Converting Lignocellulose Solids to Fluid Alcohols by the UCSB Process[a]
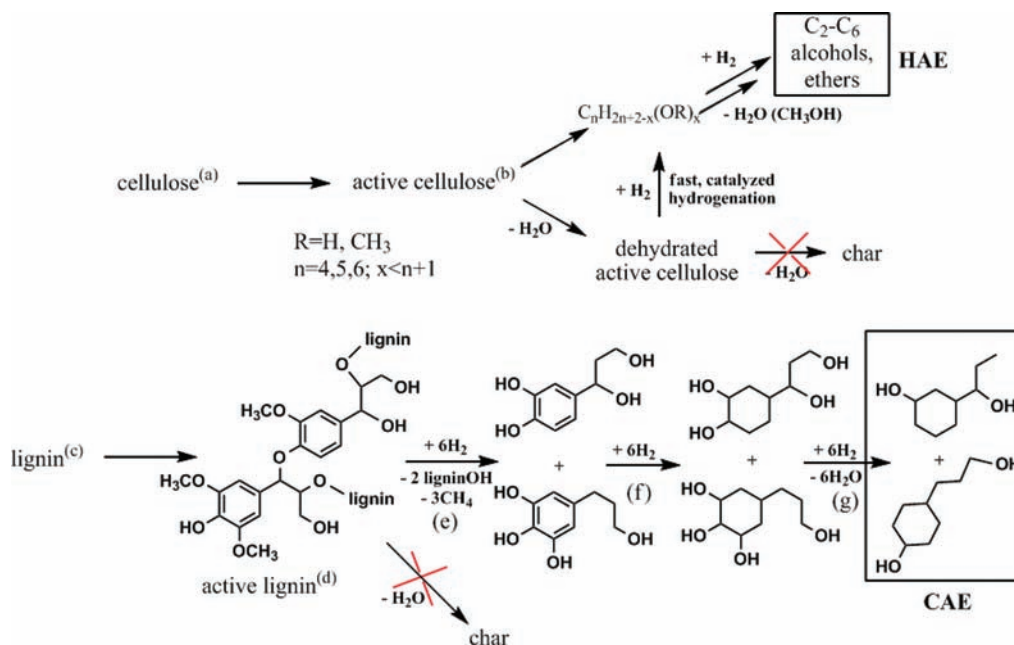
[a] (a) "Cellulose" refers to cellulose, hemicellulose, and the cellulosic component of lignocellulose; (b) "active cellulose" consists of soluble oligomers and methylated monomers; (c) "lignin" refers to the lignified component; (d) "active lignin" refers to solubilized lignified material or lignin oligomers; (e) depolymerization and demethoxylation by hydrogenolysis; (f) aromatic hydrogenation; (g) dehydration-hydrogenation.

Scheme 3. Options for Biomass Conversion via the UCSB Process (Material Inputs and Outputs Indicated by Ovals)
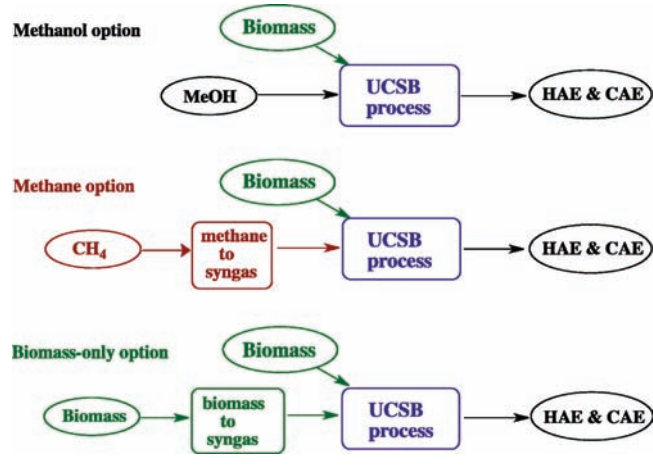
front end of this process, although methane reforming is well-established technology. The "biomass-only option" uses a biomass-to-syngas conversion at the front end of the biomass-to-fuels process. The advantage would be an even lower CO_2 footprint combining an existing technology (biomass-to-syngas)[25] with a new one (the UCSB process), and in the long run would clearly be a desirable goal. With the latter two options, the methanol utilized as the reaction medium could be generated internally.

In summary, we have described the quantitative conversion of lignocellulose solids to combustible liquids via a unique single stage, methanol mediated process. Little or no char is formed, and this result plus the observation that the copper-based metal oxide catalyst can be reused suggests that this process is compatible with high yield, continuous operation. Successful utilization of renewable biomass solids via this process would have the potential of reducing the CO_2 burden from liquid fuel utilization without compromising food supply. Ongoing studies are focused on characterizing and optimizing the earth-abundant catalysts used in this process, on elucidating key mechanistic issues, and on evaluating how the reaction variables control yields and selectivity in product streams. For example, one approach may be to develop simple deoxygenation procedures to generate clean mixtures of alkanes.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Tables and figures describing the temporal conversion of substrates, displaying GC–FID data for additional experiments and summarizing analyses of catalysts before and after reactions. Scheme of hypothetical reaction network leading to products from cellulose. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Operationally, the HAE are defined as those eluting during the first 10.3 min including 1-hexanol (10.26 min) of the GC–FID program using the Agilent Gas Chromatograph described in the Experimental Section. Major peaks were confirmed by comparison to authentic samples. Similarly, CAE are defined as those eluting after 10.3 min and correspond to materials of the type identified by GC–MS experiments as being formed from lignin precursors (ref 13). Analyses using the GC–FID program of Shimadzu GC (see Experimental Section) gave very similar product patterns but with longer retention times.

(15) (a) Comparable results were obtained with cellulose when the Cu20-PMO was replaced by a Cu/Zn/Al metal oxide catalyst (100 mg) with 27/53/20 molar ratio (Cu/ZnO/Al$_2$O$_3$), prepared according to literature procedures (ref 15b) and known to be active for methanol reforming and the water gas shift. (b) Herman, R. G.; Klier, K.; Simmons, G. W.; Finn, B. P.; Bulko, J.l B.; Kobylinski, T. P. *J. Catal.* **1979**, *56*, 407–429.

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