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

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Supplementary Information for

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

Theodore D. Matson, Katalin Barta, Alexei V. Iretskii, Peter C. Ford*

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Scheme S1. Reaction network leading to HAE production from cellulose

Table S-1 : Conversion of pine sawdust to liquids as a function of reaction time^a

| Catalyst | time (h) | Solids (mg) | conversion (%) |
|-----------|----------|-------------|------------------|
| Cu20-PMO | 0.16 | 145 | 55 |
| Cu20-PMO | 0.33 | 135 | 65 |
| Cu20-PMO | 0.5 | 123 | 76.6 |
| Cu20-PMO | 1.0 | 100 | >99 ^b |
| Cu20-PMO | 2.0 | 98 | >99 |
| Cu20-PMO | 4 | 103 | >99 ^b |
| Cu20-PMO | 6 | 104 | >99 ^b |
| Cu20-PMO | 8 | 103 | >99 |
| Cu20-PMO | 10 | 104 | >99 ^b |
| Cu20-PMO | 12 | 101 | >99 |
| None | 0.5 | 60 | c |
| None | 2 | 14 | c |
| None | 24 | 9 | c |
| Mg/Al-PMO | 24 | 115 | c |

^a Each experiment involved the reaction of sawdust (100 mg), catalyst (100 mg) and MeOH (3.0 mL) in a 10 mL mini-reactor at 320 °C, except where noted. ^b full conversion of sawdust was additionally verified by solubilization of the residue in HNO₃. ^cProducts not identified; liquid phase products showed little volatility.

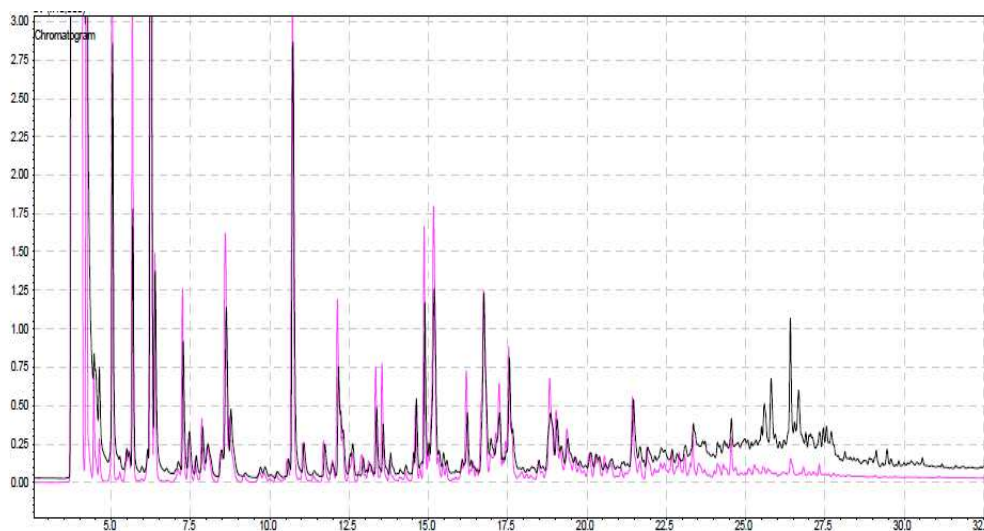


Figure S-1 Comparison of the FID traces obtained for the liquid products from the treatment of pine sawdust (200 mg) in MeOH (3 mL) with Cu20PMO (100 mg) in a 10 mL mini-reactor for 8 h at 320 °C (black) and an analogous run with cellulose (purple.). (GC-FID recorded on a Shimadzu AOC-20i instrument with a SHRXI-5MS column 30 m x 0.25 mm ID). *Note:* The vertical axis is FID signal intensity; the horizontal axis is retention time in minutes.

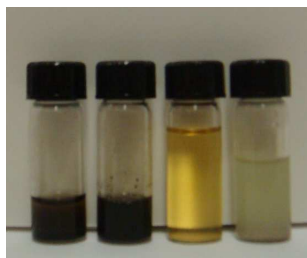


Figure S-2. Photograph of liquids resulting from digestion of residual solids by aq. HNO₃. The two on the left showing black char were prepared by "dissolving" solid residues of the 2 h reaction of pine sawdust (100 mg) in sc-MeOH (320 °) without catalyst (far left) and 24 h reaction of pine sawdust in the presence of Mg/Al PMO not containing any copper (middle left). The two on the right were prepared by dissolving residuals of analogous reactions with Cu20-PMO present. The sample displaying the yellow color was for a sample allowed to react for only 0.33 h, while that on the far right is typical of samples where the reaction has gone to completion. These samples were from runs designated in Table S-1 with the footnote *b*.

Table S-2. Effects of reaction time and substrate loading on cellulose solubilization^a

| cellulose (mg) | time (h) | Remaining solids (mg) | conversion (%) |
|-------------------|-------------|--------------------------|-------------------|
| 200 | 0.5 | 180 | 60 |
| 200 | 2 | 95 | >99 |
| 200 | 4 | 102 | >99 |
| 200 | 8 | 101 | >99 |
| 100 | 8 | 99 | >99 |
| 400 | 8 | 99 | >99 |
| 600 | 8 | 100 | >99 |
| 200 ^b | 8 | 98 | >99 |

^a Each experiment involved the reaction of cellulose, Cu20-PMO catalyst (100 mg) and MeOH (3.0 mL) in a 10 mL mini-reactor at 320 °C, except where noted. ^b 280°C

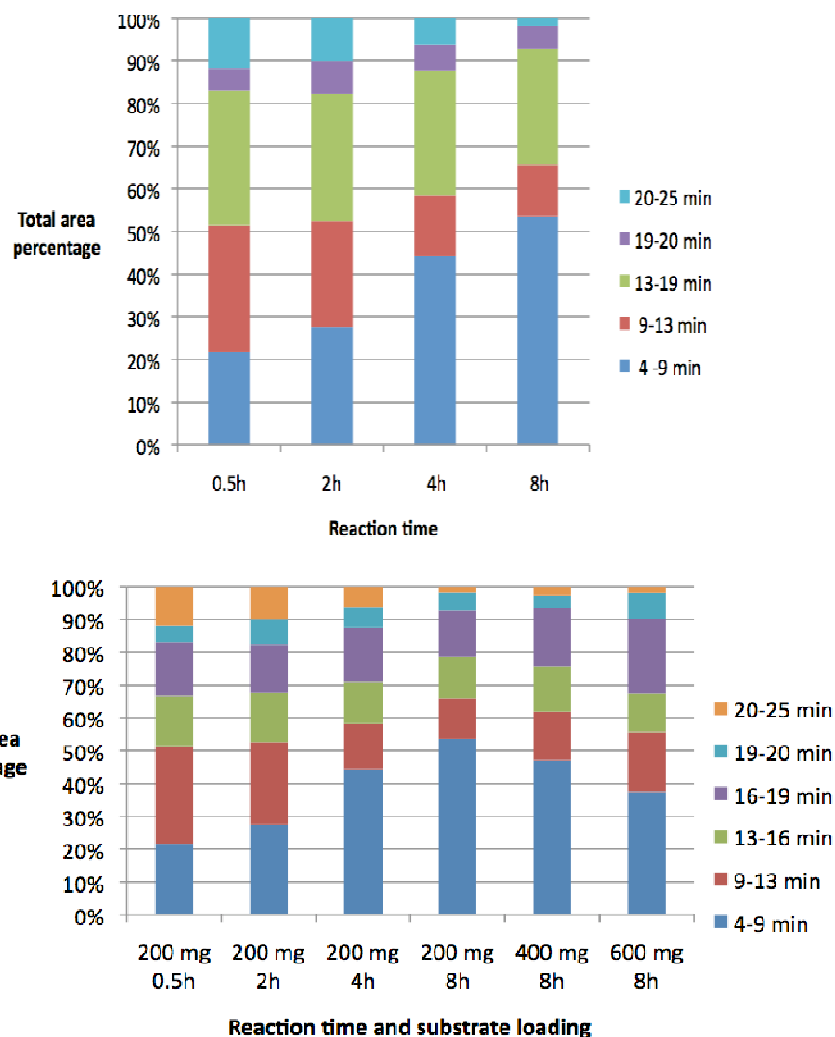


Figure S-3: (*Top*) Holistic evaluation of temporal product distributions for the reaction of cellulose (200 mg), methanol (3 mL) and Cu20-PMO (100 mg) in a 10 mL micro-reactor at 320 °C for 0.5 h, 2h, 4h and 8h. The liquid phase of each run was analyzed with GC-FID in order to compare their chemical composition using a Shimadzu GC equipped with an FID detector and a SHRXI-5MS column (30 m x 0.25 mm ID). The chromatograms were integrated over defined retention time regions: R₁ (4-9 min, dark blue), R₂ (9-13 min, red), R₃ (13-19 min, green), R₄ (19-20 min, purple) and R₅ (20-25 min, light blue). Under these conditions, retention times of isopropanol, butanol, pentanol, 2-hexanol were 5.3, 8.42, 12.8 and 14.07 min., respectively. In this context, R₁ roughly corresponds to C₂-C₄ alcohols, R₂ to C₅ alcohols, R₃ to C₆ and possibly C₇ longer chain alcohols, while retention times longer than 20 min. would involve alcohols with C₈ and longer chain length. These results show that after only 0.5 h reaction time, where solubilization of solid cellulose is not yet complete, the composition of the liquid phase is similar to the mixture obtained after longer reaction times, suggesting that the liquid phase reactions of the solubilized monomeric units are rapid. Systematic differences between the shorter and longer runs are that the lighter species (R₁) progressively grow at the expense of heavier fractions. Notably, the number of species increases with increasing chain length, thus producing larger numbers of smaller peaks. (*Bottom*) Similar holistic analysis of temporal product distributions from analogous reaction of pine sawdust under analogous conditions.

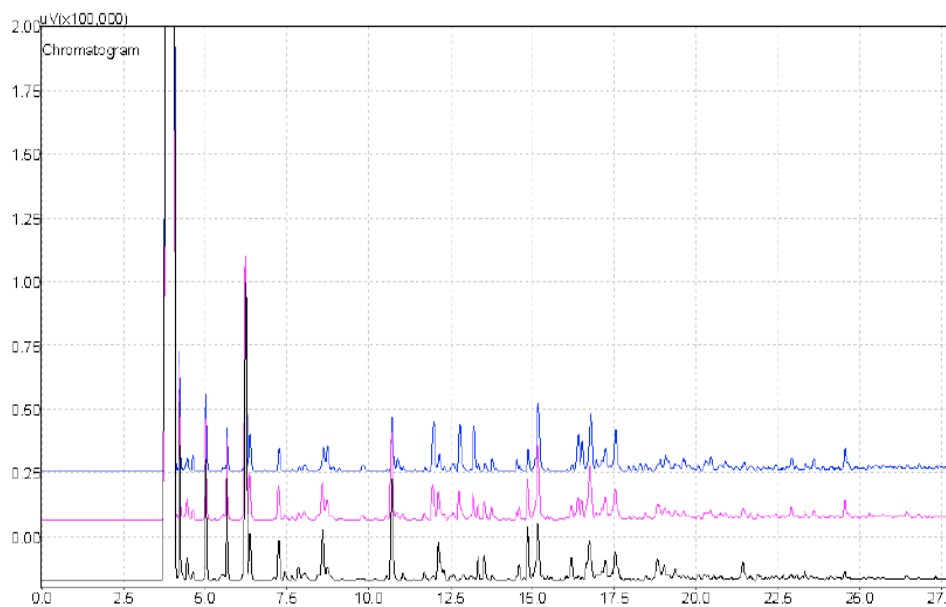


Figure S-4 Comparison of the FID traces obtained for the liquid products from the treatment of cellulose in MeOH (3 mL) with Cu₂₀PMO (100 mg) in a 10 mL mini-reactor for 8 h at 320 °C. Substrate loading 200 mg (black), 400 mg (purple) and 600 mg (blue). (GC-FID recorded on a Shimadzu AOC-20i instrument with a SHRXI-5MS column 30 m x 0.25 mm ID). *Note:* The vertical axis is FID signal intensity; the horizontal axis is retention time in minutes.

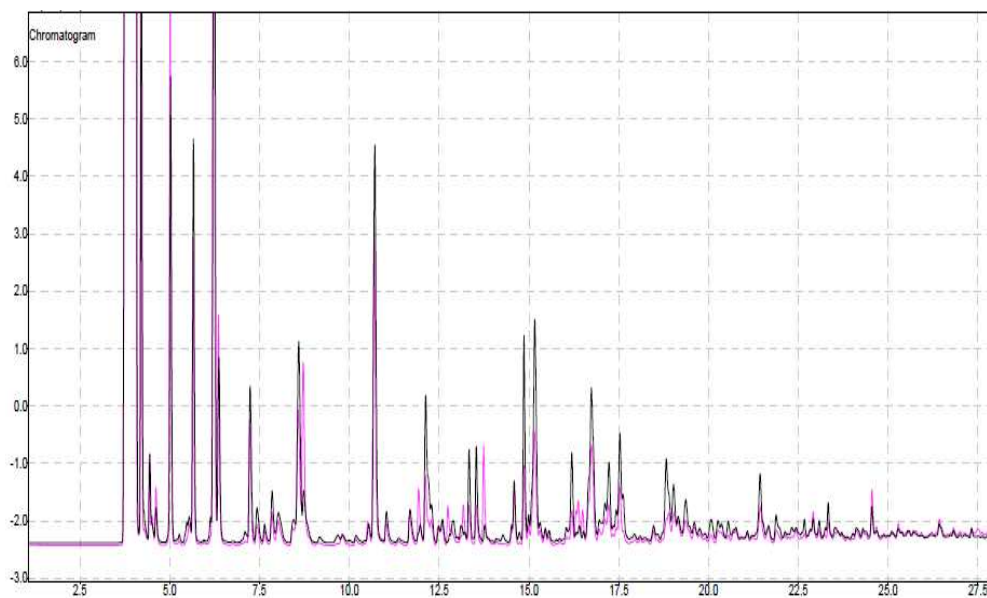


Figure S-5 FID traces obtained for the liquid products from reaction of glucose (200 mg), MeOH (3 mL) and Cu₂₀-PMO (100 mg) for 8 h at 320 °C (purple) and an analogous run with cellulose (black). (GC-FID recorded on a Shimadzu AOC-20i instrument with a SHRXI-5MS column 30 m x 0.25 mm ID). *Note:* The vertical axis is FID signal intensity; the horizontal axis is retention time in minutes.

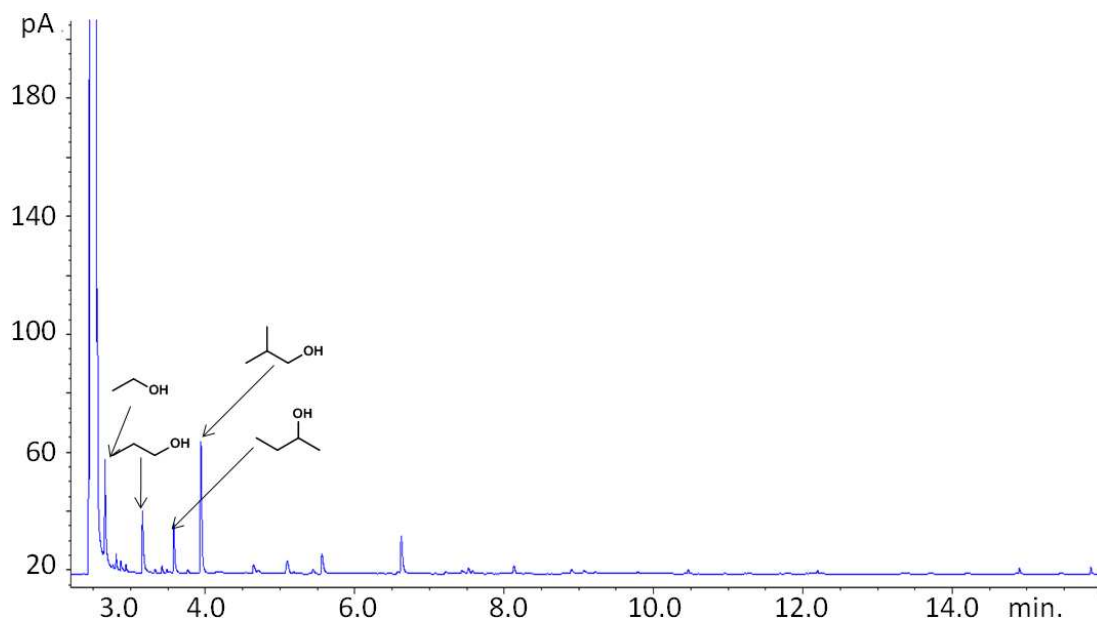


Figure S-6: GC-FID of the liquid phase from a control reaction in a mini-reactor (no substrate) (2.4 g CH_3OH , 100 mg Cu20-PMO, 320 °C, 8 hr.). Products are a mixture of 0.3 wt% HAE and 0.3 wt% DME in MeOH. (Recorded on a Agilent model 6890 GC with a 30 m DB-5 column). *Note:* The vertical axis is FID signal intensity; the horizontal axis is retention time in minutes.

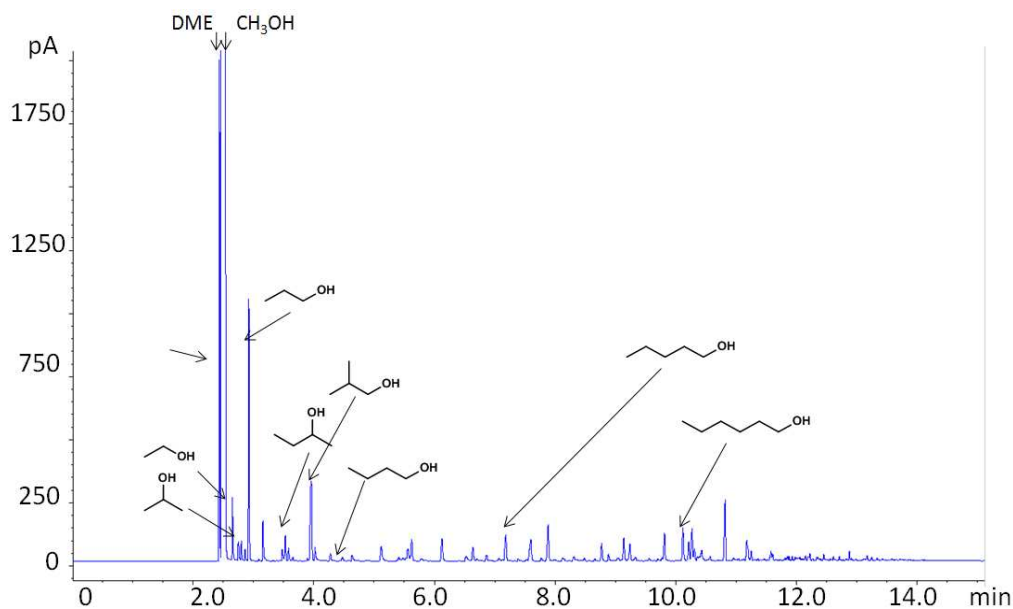


Figure S-7: GC-FID trace of the distilled liquids from the treatment of eucalyptus chips. (Recorded on a Agilent model 6890 GC with a 30 m DB-5 column). *Note:* The vertical axis is FID signal intensity; the horizontal axis is retention time in minutes.

Table S-3: Specific components of the products identified in Figure S-6.

| Compound | Retention Time (min.) | Weight % |
|----------------|-----------------------|----------|
| dimethyl ether | 2.44 | 3.1 |
| ethanol | 2.66 | 0.4 |
| isopropanol | 2.76 | 0.2 |
| propanol | 2.93 | 1.9 |
| isobutanol | 3.96 | 1.2 |
| butanol | 4.64 | 0.1 |
| pentanol | 7.18 | 0.4 |
| hexanol | 10.27 | 0.4 |
| others | | 9.4 |
| MeOH | 2.53 | 82.9 |

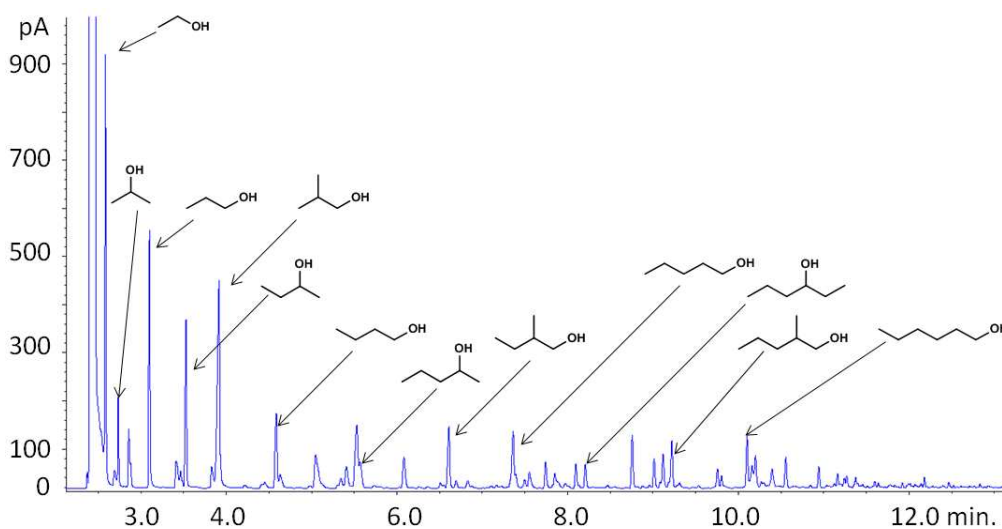


Figure S-8. GC-FID trace of liquid products from the larger scale cellulose reaction. (Recorded on a Agilent model 6890 GC with a 30 m DB-5 column). *Note:* The vertical axis is FID signal intensity; the horizontal axis is retention time in minutes.

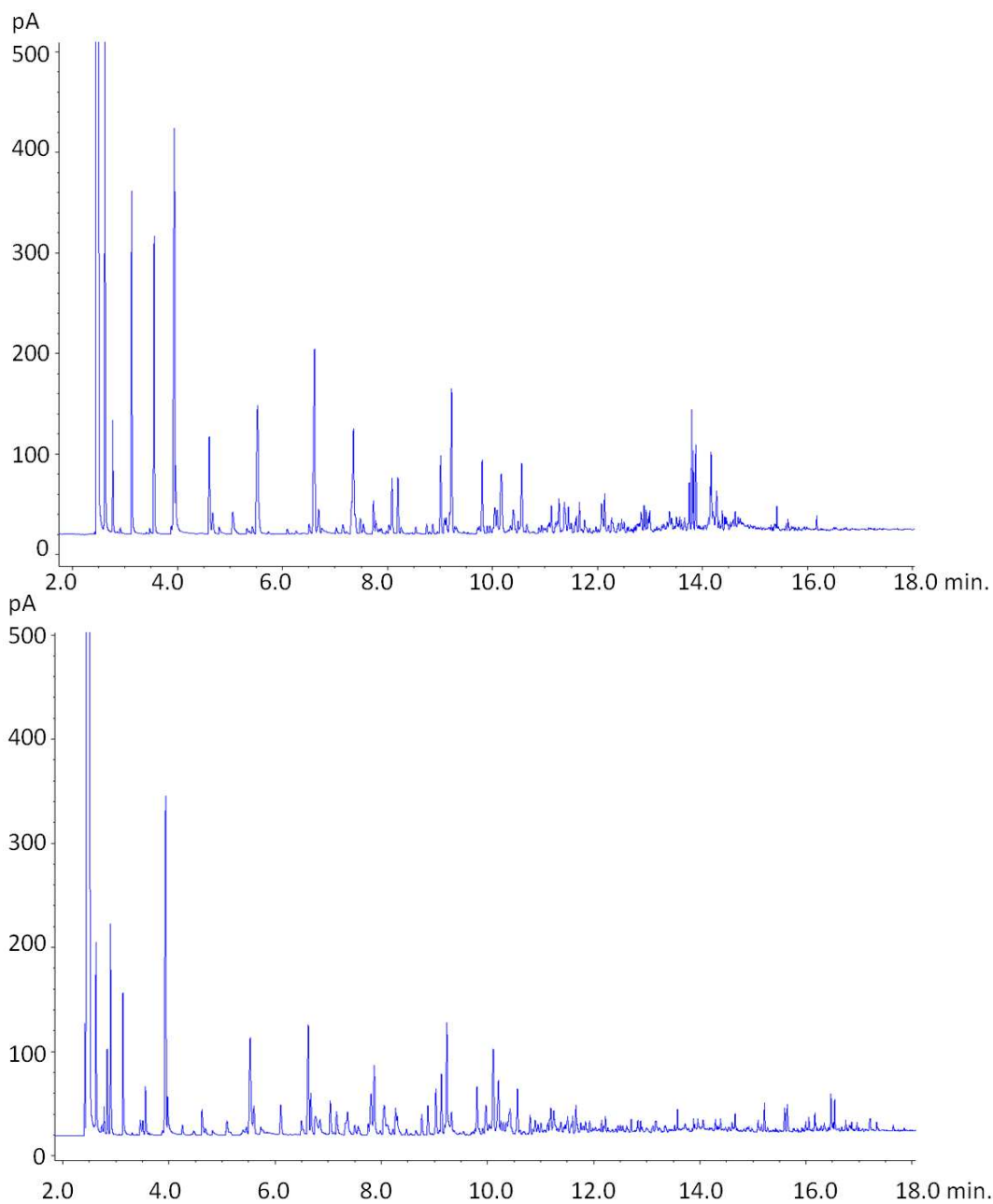
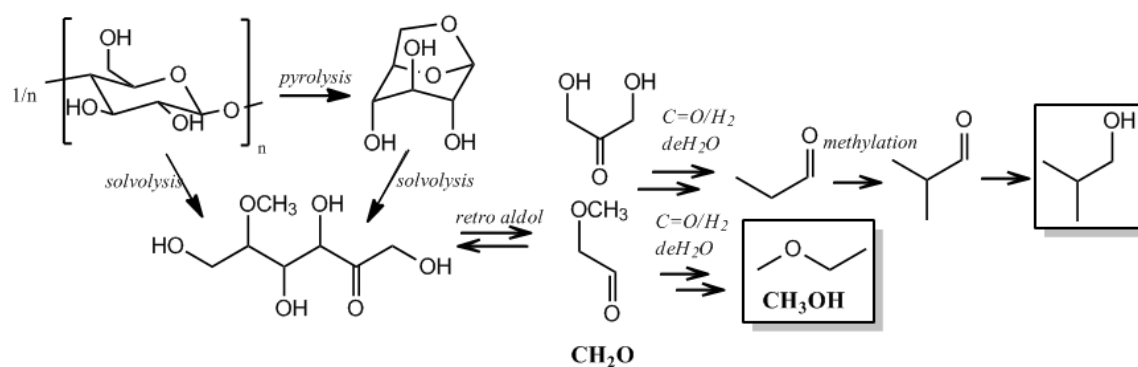


Figure S-9. GC-FID traces of run 1 of 4 sequential runs with eucalyptus chips (upper) and run 3 of the same series reusing the catalyst in each of the runs. (Recorded on a Agilent model 6890 GC with a 30 m DB-5 column). *Note:* The vertical axis is FID signal intensity; the horizontal axis is retention time in minutes.

Table S-4. Inorganic elemental analyses for catalyst, ash, and calcinate solids following conversion of 5 x 400 mg eucalyptus (“calcinate”).

| Element | Cu20-PMO (wt%) | Ash (wt%) | Calcinate (wt%) | % Leached ($\times 10^{-3}$) |
|---------|----------------|-----------|-----------------|--------------------------------|
| Cu | 19.6 | n.d. | 17.3 | n.d. |
| Mg | 27.3 | 6.0 | 22.6 | n.d. |
| Al | 12.6 | 0.2 | 9.3 | 0.001 |
| Na | 0.5 | 2.2 | 1.0 | 0.003 |
| K | n.d. | 5.0 | 0.5 | 0.001 |
| Ca | n.d. | 24.5 | 1.9 | n.d. |
| Fe | n.d. | 0.2 | n.d. | n.d. |

n.d. = none detected. The percent leached is relative to the calculated total mass of the individual elements in the calcinate. The following emission lines had good linearity for between 0.1 and 50 ppm of the listed element: Al (167.0 nm); Ca (422.6 nm); Cu (224.7 nm); Fe (239.5 nm).



Scheme S1: Reaction network leading to HAE production from cellulose