

Production of Renewable Alcohols from Maple Wood using Supercritical Methanol Hydrodeoxygenation in a Semi-continuous Flowthrough Reactor

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Number of figures: 3

Number of tables: 4

Table S1. Weight percent and composition of maple wood solubilized at 190, 230, 270, 300, and 330°C. Conditions: 190-330°C, 2-6 hours, 0.6 g maple wood, 0.3 mL min⁻¹ methanol flowrate for 190-230°C points and 0.18 mL min⁻¹ for 270-330°C points to maintain liquid residence time in reactor at varying density.

| Temperature (°C) | Reaction time (h) | Biomass remaining (wt%) | Unsolubilized holocellulose (wt%) | Char/coke (wt%) |
|------------------|-------------------|-------------------------|-----------------------------------|-----------------|
| 190 | 2 | 71.2 | 59.3 | 11.8 |
| 230 | 2 | 53.7 | 39.6 | 14.2 |
| 230 | 6 | 53.3 | 45.7 | 7.6 |
| 270 | 2 | 48.7 | 32.2 | 16.5 |
| 300 | 2 | 30.5 | 13.0 | 17.4 |
| 300 | 6 | 19.6 | 2.0 | 17.6 |
| 330 | 2 | 22.5 | 0.0 | 22.5 |
| 190+300 | 2+2 | 36.4 | 26.1 | 10.3 |
| 230+330 | 2+2 | 18.7 | 2.4 | 16.3 |
| 190+230+300+330 | 1+1+1+1 | 14.0 | 6.6 | 7.3 |

Table S2. Composition of C2-C6 products in biomass conversion with catalyst regeneration.

| | Mol C% of C2-C6 products | | | | | |
|------------------------------------|--------------------------|------|------|------|------|------|
| | Bed1 | Bed2 | Bed3 | Bed4 | Bed5 | Bed6 |
| <u>Alcohols</u> | | | | | | |
| ethanol | 16.4 | 15.7 | 16.3 | 14.9 | 16.8 | 13.4 |
| 1-propanol | 10.1 | 9.5 | 9.8 | 9.2 | 0.5 | 8.8 |
| 2-propanol | 2.6 | 2.8 | 2.6 | 2.3 | 2.3 | 2.1 |
| 1-butanol | 3.8 | 3.6 | 3.8 | 3.3 | 4.0 | 3.1 |
| 2-butanol | 9.5 | 9.4 | 9.3 | 8.7 | 9.2 | 8.1 |
| isobutanol | 11.5 | 11.9 | 12.9 | 13.0 | 14.9 | 12.9 |
| 1-pentanol | 1.2 | 0.9 | 1.0 | 1.0 | 1.4 | 1.1 |
| 2-pentanol | 4.3 | 4.2 | 4.3 | 3.7 | 4.0 | 3.5 |
| 3-pentanol | 3.5 | 3.4 | 3.5 | 3.0 | 3.2 | 2.8 |
| 2-methyl-1-butanol | 9.9 | 9.9 | 9.9 | 10.5 | 16.6 | 14.0 |
| 1-hexanol | 0.5 | 0.5 | 0.5 | 0.6 | 0.6 | 0.7 |
| 2-hexanol | 1.4 | 1.3 | 1.3 | 1.1 | 1.3 | 1.1 |
| 3-hexanol | 2.8 | 3.2 | 3.0 | 3.0 | 3.0 | 3.0 |
| 2-methyl-1-pentanol | 3.9 | 3.8 | 4.1 | 3.9 | 4.5 | 4.0 |
| <u>Esters, Ethers, and ketones</u> | | | | | | |
| methyl acetate | 4.6 | 5.1 | 4.6 | 6.8 | 5.1 | 6.5 |
| methyl propanoate | 3.5 | 3.3 | 2.9 | 4.1 | 2.2 | 3.7 |
| methyl butyrate | 2.1 | 2.3 | 2.0 | 2.5 | 1.0 | 2.6 |
| 2-methoxy ethanol | 3.6 | 4.4 | 4.6 | 4.9 | 4.9 | 5.1 |
| 1-methoxy 2-propanol | 4.4 | 4.8 | 3.7 | 3.6 | 4.5 | 3.5 |

Table S3. Composition of C2-C6 products in multi-temperature catalyst bed reaction.

| | Mol C% of C2-C6 products | | | | | |
|-----------------------------|--------------------------|------|------|------|------|------|
| | Bed1 | Bed2 | Bed3 | Bed4 | Bed5 | Bed6 |
| Alcohols | | | | | | |
| ethanol | 19.6 | 18.1 | 17.8 | 17.7 | 16.3 | 15.9 |
| 1-propanol | 10.5 | 9.5 | 9.3 | 9.1 | 9.2 | 8.6 |
| 2-propanol | 3.2 | 3.2 | 3.3 | 3.4 | 2.9 | 3.0 |
| 1-butanol | 5.6 | 4.8 | 4.7 | 4.7 | 4.8 | 4.1 |
| 2-butanol | 8.8 | 8.9 | 9.0 | 9.0 | 8.4 | 8.5 |
| isobutanol | 12.3 | 12.5 | 12.5 | 12.3 | 13.5 | 13.6 |
| 1-pentanol | 4.3 | 4.0 | 3.8 | 3.6 | 3.8 | 3.0 |
| 2-pentanol | 3.6 | 3.7 | 3.5 | 3.6 | 3.6 | 3.6 |
| 3-pentanol | 3.0 | 3.2 | 2.9 | 2.6 | 3.1 | 2.8 |
| 2-methyl-1-butanol | 7.6 | 8.2 | 8.0 | 7.8 | 9.0 | 9.2 |
| 1-hexanol | 1.5 | 1.4 | 1.5 | 1.2 | 1.4 | 1.3 |
| 2-hexanol | 1.0 | 1.0 | 1.0 | 1.0 | 1.1 | 1.0 |
| 3-hexanol | 2.3 | 2.4 | 2.4 | 2.3 | 2.7 | 2.6 |
| 2-methyl-1-pentanol | 2.8 | 2.5 | 2.4 | 2.3 | 2.6 | 2.3 |
| Esters, Ethers, and ketones | | | | | | |
| methyl acetate | 5.1 | 5.9 | 6.7 | 7.4 | 6.2 | 7.8 |
| acetone | 0.5 | 0.6 | 0.6 | 0.6 | 0.5 | 0.0 |
| methyl propanoate | 2.1 | 2.3 | 2.4 | 2.6 | 2.5 | 3.0 |
| methyl butyrate | 2.1 | 2.3 | 2.4 | 2.7 | 2.4 | 2.7 |
| 2-methoxy ethanol | 3.9 | 4.8 | 5.1 | 5.5 | 5.3 | 6.0 |
| 1-methoxy 2-propanol | 0.3 | 0.9 | 0.9 | 0.9 | 0.9 | 1.0 |

Table S4. Composition of C2-C6 products from batch reactions at varying biomass loading.

| | Mol C% of C2-C6 products | | | | |
|-----------------------------|--------------------------|-------|--------|--------|-----------|
| | 4 wt% | 8 wt% | 10 wt% | 20 wt% | 10+10 wt% |
| Alcohols | | | | | |
| ethanol | 20.0 | 19.6 | 19.7 | 20.4 | 20.5 |
| 1-propanol | 8.9 | 9.3 | 10.0 | 10.3 | 9.6 |
| 2-propanol | 3.3 | 3.2 | 3.0 | 2.9 | 3.3 |
| 1-butanol | 4.7 | 5.1 | 5.5 | 6.3 | 5.8 |
| 2-butanol | 10.3 | 10.2 | 9.7 | 8.7 | 9.0 |
| isobutanol | 11.8 | 11.8 | 11.9 | 13.1 | 11.8 |
| 1-pentanol | 4.3 | 4.9 | 5.3 | 6.4 | 5.8 |
| 2-pentanol | 4.0 | 4.0 | 3.6 | 3.6 | 3.7 |
| 3-pentanol | 3.2 | 3.0 | 3.1 | 2.7 | 2.8 |
| 2-methyl-1-butanol | 6.3 | 6.4 | 6.6 | 7.4 | 6.4 |
| 1-hexanol | 3.2 | 3.5 | 3.3 | 2.4 | 3.3 |
| 2-hexanol | 2.1 | 2.1 | 1.8 | 1.5 | 1.8 |
| 3-hexanol | 3.2 | 3.0 | 2.7 | 2.6 | 3.1 |
| 2-methyl-1-pentanol | 2.2 | 2.3 | 2.6 | 2.6 | 2.3 |
| Esters, Ethers, and ketones | | | | | |
| methyl acetate | 3.3 | 2.5 | 2.5 | 1.6 | 2.2 |
| acetone | 0.9 | 1.0 | 0.6 | 0.3 | 0.6 |
| methyl propanoate | 1.3 | 1.3 | 1.4 | 1.0 | 1.1 |
| methyl butyrate | 2.0 | 2.1 | 2.0 | 1.5 | 2.2 |
| 2-methoxy ethanol | 4.3 | 3.7 | 3.5 | 3.5 | 3.4 |
| 1-methoxy 2-propanol | 0.6 | 0.9 | 1.4 | 1.0 | 1.5 |

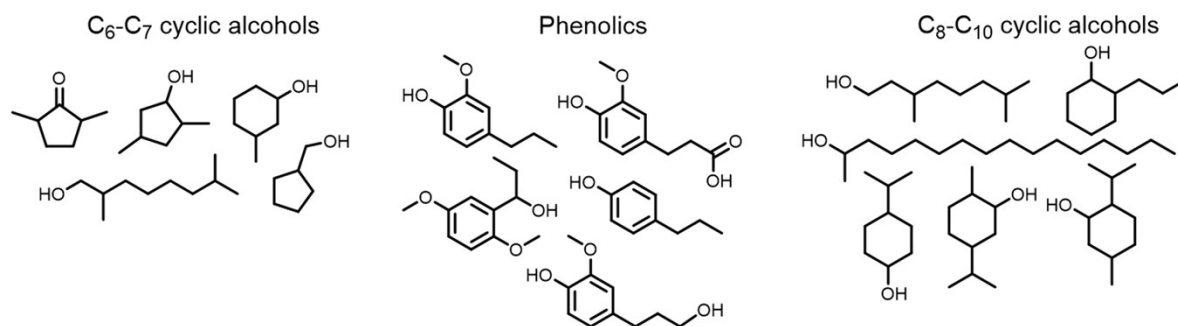


Figure S1. Product types of high boiling compounds from close matches in a Shimadzu GC-2010 MS after SCM-DHDO of maple wood.

190-230°C products

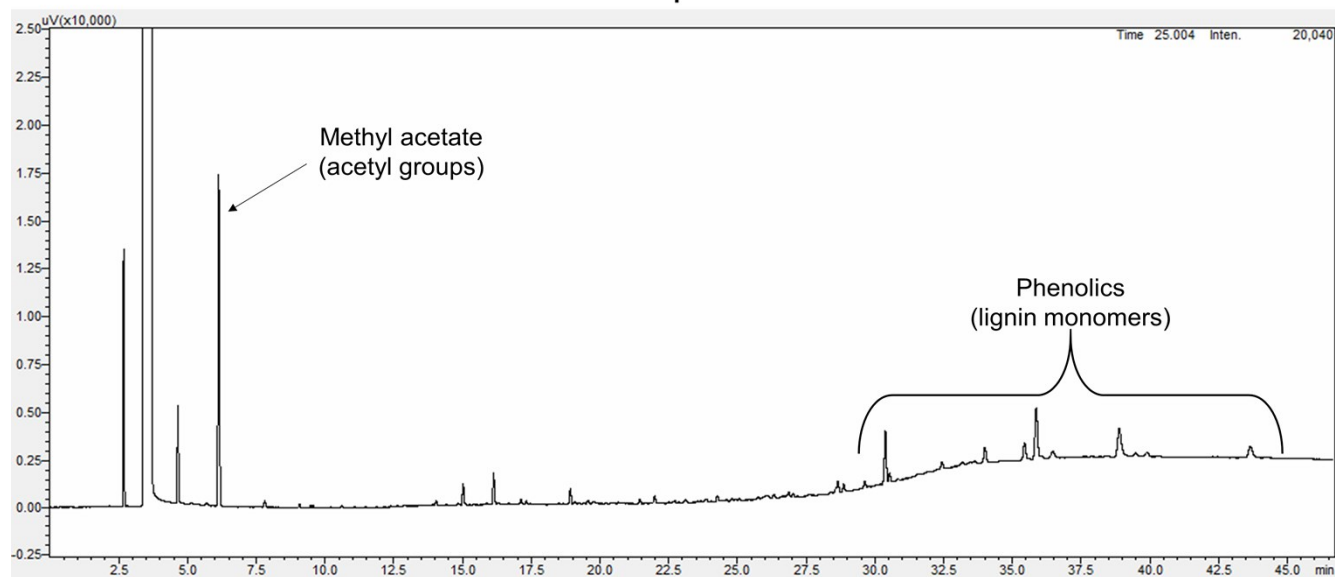


Figure S2. 190-230°C products from multi-temperature catalyst bed reaction with maple wood.

300-330°C products

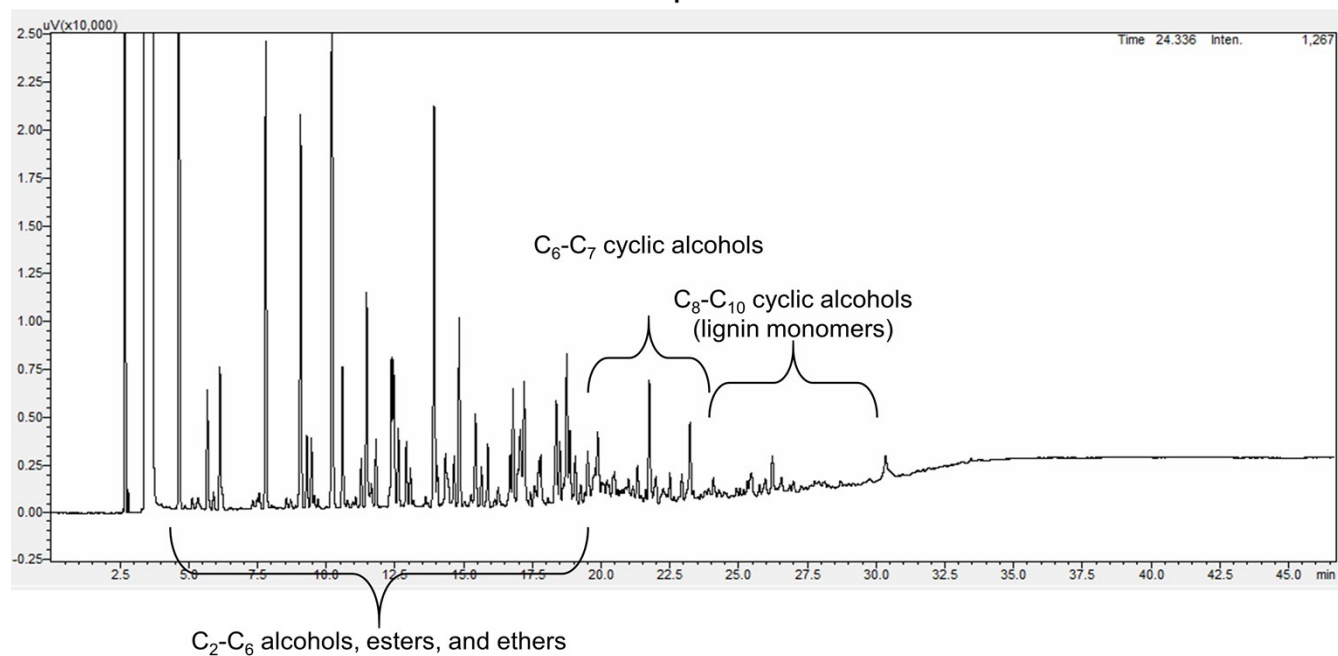


Figure S3. 300-330°C products from multi-temperature catalyst bed reaction with maple wood.