Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary information

One-pot catalytic conversion of beech wood and organosolv lignin over NiMo/γ-Al_2O_3

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Composition analysis of beech wood

The composition analysis of the beech wood was outsourced to the commercial company Celignis. The procedure for determination of biomass constituents is briefly presented as follows:

The biomass is acid hydrolyzed by mixing 300 mg of the sample with 3 mL of 72% H_2SO_4 in a pressure tube and keeping at 30 °C for 1 hour, followed by addition of 84 mL water for a second-stage-hydrolysis and heating to 121 °C in an autoclave for another 1 hour. After this specific time and cooling down to the ambient temperature, the solution is filtered. The residual solid fraction is considered as acid insoluble residue. The acid soluble lignin is determined by analysis of the filtrate with a UV-Visible transmission spectrum and based on absorbance value at 205 nm. The Klason lignin content is determined by deducing the acid insoluble ash from acid insoluble residue content. The acid insoluble ash is measured by combusting the acid insoluble residue in a ramp temperature program heated up to 575 °C (180 min). The total sugar content is calculated by summing up the glucose, xylose, mannose, arabinose, galactose and rhamnose content. The content of each sugar is determined by HPLC analysis of the hydrolysate (filtrate phase) using the representative standards as reference.

For a detailed instruction please check Celignis's website:

https://www.celignis.com

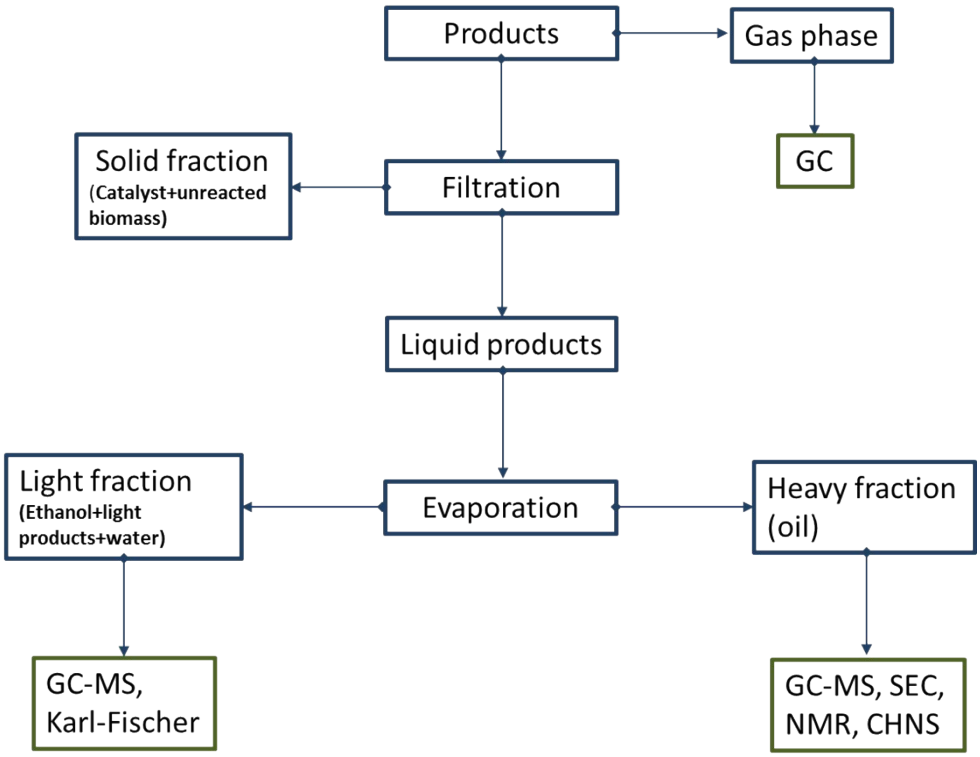

Figure S1 Diagram of the workup procedure employed at the end of each reaction

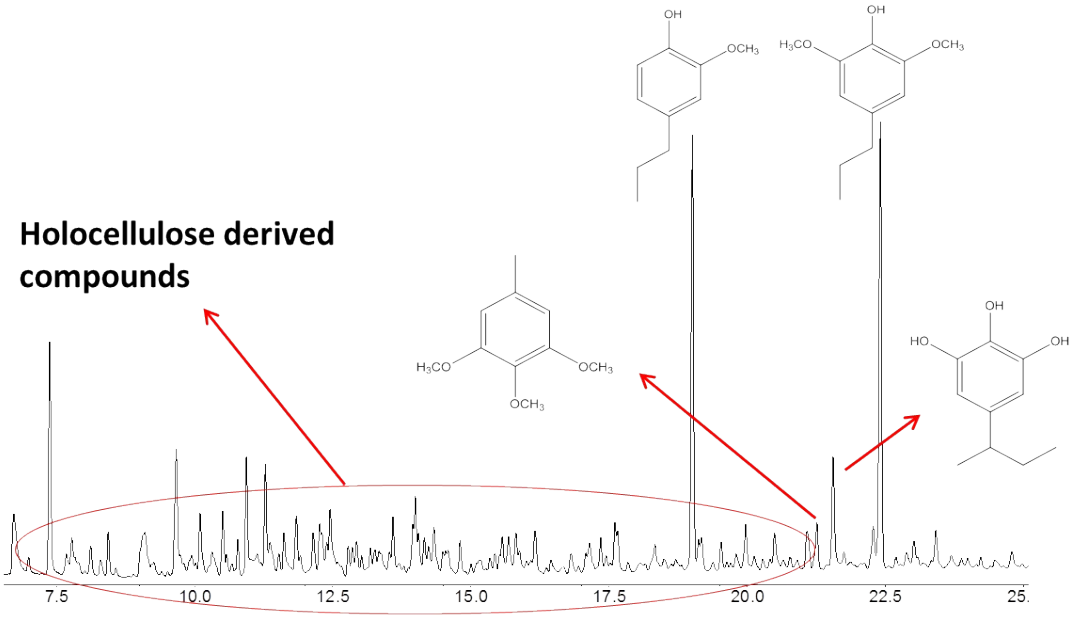

Figure S2 GC chromatogram of the heavy fraction obtained from conversion of beech wood at 300 ˚C and the main identified monomers; 4-propyl guaiacol (RT:19.1), 1,2,3-trimethoxy-5-methyl benzene (RT:21.3), 5-sec-butyl-1,2,3-benzenetriol (RT:21.6), and 4-propyl syringol (RT:22.4). Reaction condition: 1 g NiMo/γ-Al_2O_3 catalyst: 10 g beech wood, 100 ml ethanol, 26 bar H_2 (loaded at RT), 3 hours.

Table S1 The main identified products in the light fraction from catalytic conversion of beech wood at 300 ˚C and the representative area percent of each compound in the light fraction. 1 g NiMo/γ-Al_2O_3 catalyst: 10 g beech wood, 100 ml ethanol, 26 bar H_2 (loaded at RT), 3 hours.

Compound	Area %	Holocellulose[a]	EtOH[a]
Alcohols			
1-Propanol	0.20	*	*
Butanol	1.01	*	*
Propylene glycol	0.06	*	*
2,4-dimethyl 1-Heptanol	0.20	*	*
1-Nonanol	0.06	*	-
Aldehydes			
Acetaldehyde	1.8	*	*
Esters			
Propanoic acid ethyl ester	0.43	*	*
Butanoic acid ethyl ester		*	*
2-Propanol, 1-(2-methylpropoxy)	0.05	*	*
Pentanoic acid ethyl ester	0.12	*	-
Acetic acid, ethoxy-, ethyl ester	0.02	*	*
Ethers			
Ethanol, 2-ethoxy	0.09	*	-
1,1-diethoxy ethane	1.13	*	*
1-ethoxy, 2-propanol	0.04	*	*
1-ethoxy, butane	0.19	*	*
2-ethoxy, pentane	0.04	*	*
Ethylene glycol monovinyl ether	0.03	*	*
4-ethoxy 1-butanol	0.01	*	*
2-ethoxy, butane	0.03	*	-
1,1-diethoxy butane	0.07	*	*
1-ethoxy, 3-pentanol	0.02	*	*
1-(1-ethoxyethoxy), butane	0.03	*	*
2-Ethoxypentane	0.05	*	*
Ketones			
2-Pentanone	0.20	*	-
3-Hexanone	0.10	*	-
2-Hexanone	0.21	*	-
2-Methyl, cyclopentanone	0.18	*	-
3-Methyl, cyclopentanone	0.04	*	-
4-Heptanone	0.05	*	-
2-Octanone	0.03	*	-
Cyclopentanone	0.09	*	-
4-Octanone	0.02	*	-
Furans			
2,5-Dimethylfuran	0.23	*	-
Furanmethanol-tetrahydro	0.19	*	-

[a] It is specified by * whether the compounds were detected from conversion of holocellulose or ethanol

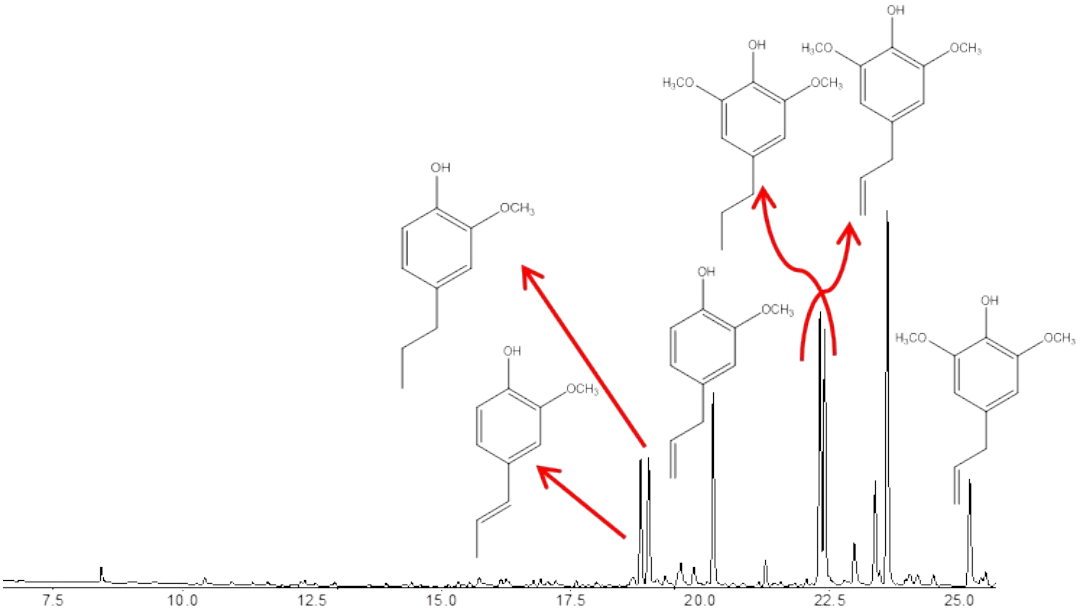

Figure S3 GC chromatogram of the heavy fraction obtained from conversion of beech wood at 200 ˚C and the main identified monomers; 2-methoxy-4-(2-propenyl) phenol (RT:18.9), 4-propyl guaiacol (RT:19.1), 2-methoxy-4-propenyl phenol (RT:20.3), 2,6-dimethoxy-4-(2-propenyl) phenol (RT:22.3, 23.6 & 25.2), and 4-propyl syringol (RT:22.4). Reaction condition: 1 g NiMo/γ-Al_2O_3 catalyst: 10 g beech wood, 100 ml ethanol, 26 bar H_2 (loaded at RT), 3 hours.

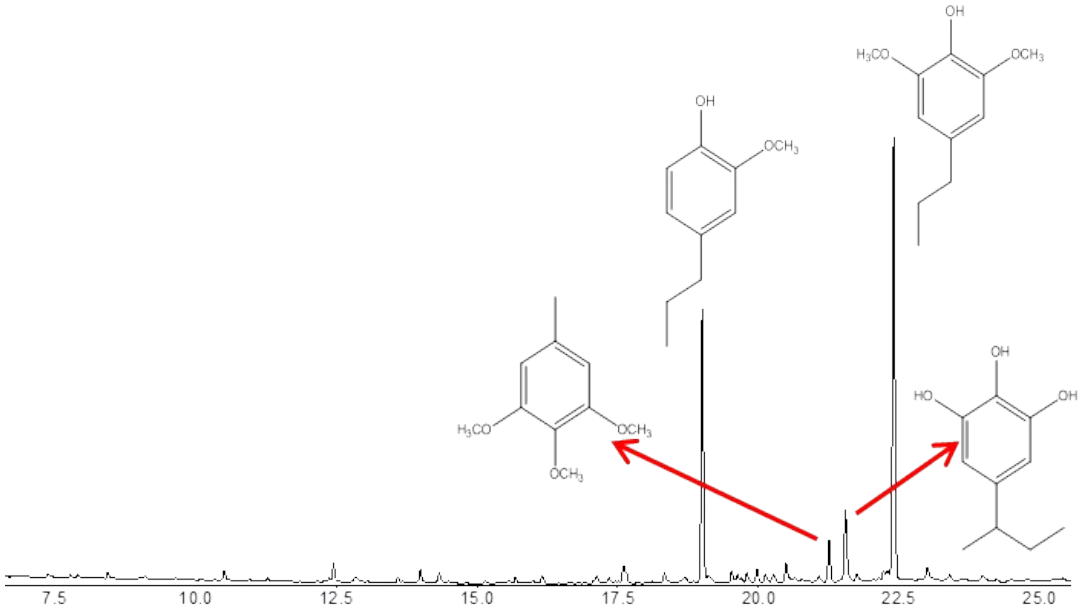

Figure S4 GC chromatogram of the heavy fraction obtained from conversion of beech wood at 260 ˚C and the main identified monomers; 4-propyl guaiacol (RT:19.1), 1,2,3-trimethoxy-5-methyl benzene (RT:21.3), 5-sec-butyl-1,2,3-benzenetriol (RT:21.6), and 4-propyl syringol (RT:22.4). Reaction condition: 1 g NiMo/γ-Al_2O_3 catalyst: 10 g beech wood, 100 ml ethanol, 26 bar H_2 (loaded at RT), 3 hours.

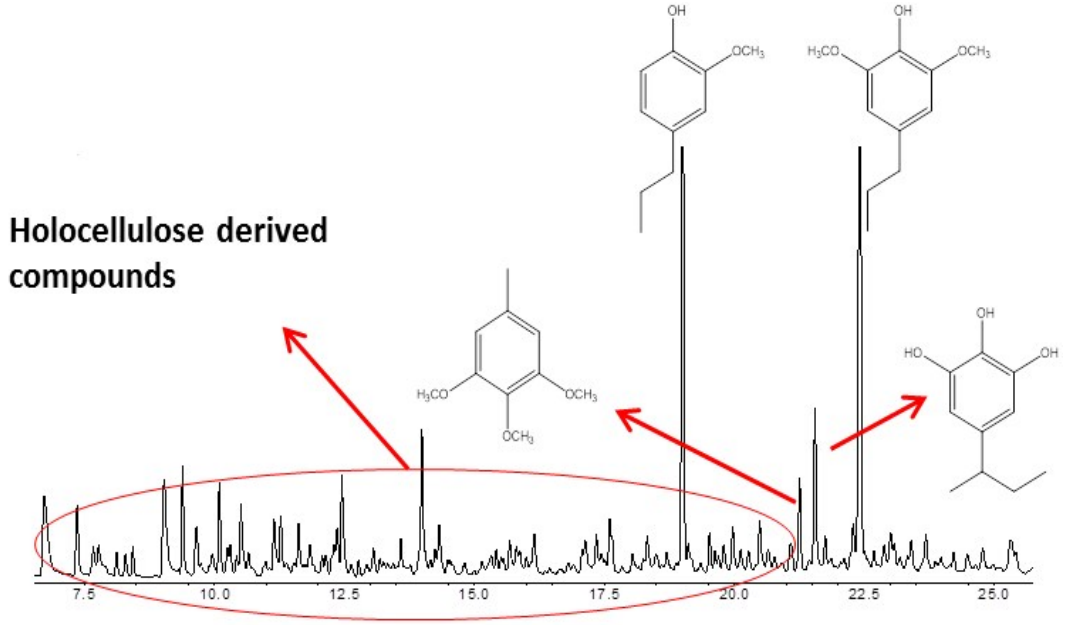

Figure S5 GC chromatogram of the heavy fraction obtained from conversion of beech wood at 280 ˚C and the main identified monomers; 4-propyl guaiacol (RT:19.1), 1,2,3-trimethoxy-5-methyl benzene (RT:21.3), 5-sec-butyl-1,2,3-benzenetriol (RT:21.6), and 4-propyl syringol (RT:22.4). Reaction condition: 1 g NiMo/γ-Al_2O_3 catalyst: 10 g beech wood, 100 ml ethanol, 26 bar H_2 (loaded at RT), 3 hours.

Table S2 Elemental analysis, atomic O/C and H/C ratio and HHV of beech wood and the oil fractions from conversion of beech wood over sulfided NiMo/γ-Al_2O_3. Reaction condition: 1 g NiMo/γ-Al_2O_3 catalyst: 10 g beech wood, 100 ml ethanol, 26 bar H_2 (loaded at RT), 3 hours.

Sample	**C wt%**	**H wt%**	**N wt%**	**S wt%**	**O wt%**	**Atomic O/C ratio**	**Atomic H/C ratio**	**HHV (MJ/kg)**
Beech wood	53.0	5.8	0.1	-	41.0	0.58	1.32	18.9
Oil at 200 ˚C	59.2	7.5	0.4	2.0	30.9	0.39	1.52	25.2
Oil at 260 ˚C	59.0	7.4	0.4	1.3	31.9	0.41	1.51	24.8
Oil at 280 ˚C	61.4	8.4	0.4	-	29.8	0.36	1.64	27.4
Oil at 300 ˚C	60.9	8.2	0.3	1.0	29.6	0.36	1.61	26.9

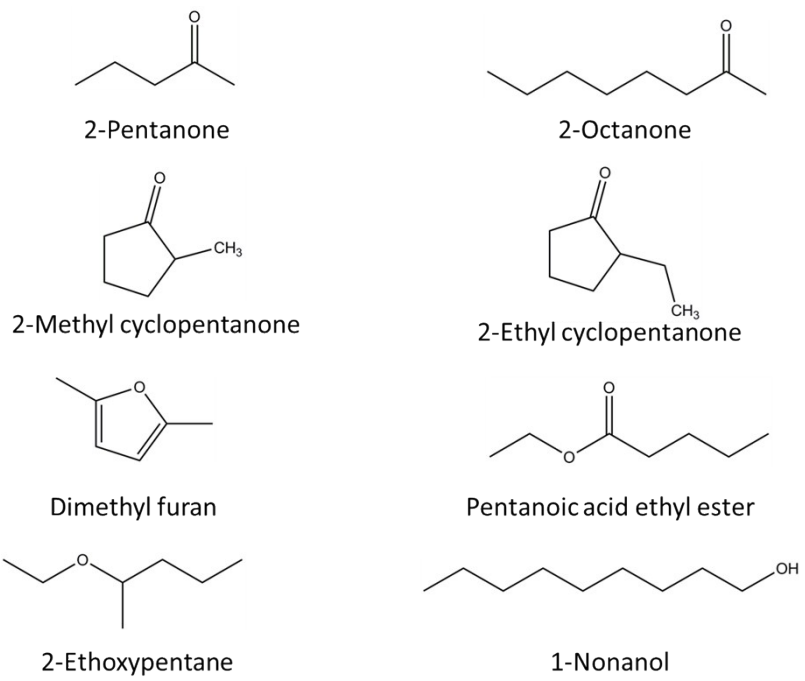

Figure S6 Structure of sugar derived compounds from conversion of beech wood over sulfided NiMo/γ-Al_2O_3 in ethanol.