An Integrated Strategy for the Conversion of Cellulosic Biomass into γ-Valerolactone

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Materials and Methods

Levulinic acid, cellulose, sulfuric acid, octyl ether, 2-methyltetrahydrofuran, gamma valerolactone and ethanol were purchased from Sigma Aldrich. All chemicals were used without further purification. Raney Nickel was acquired in packed stainless steel cartridges (70 x 4 mm) from ThalesNano. Milled beech wood was kindly prepared and provided by the group of Dr. Roberto Rinaldi (Max Planck Institut für Kohlenforscher) according to previously published methods.[1] Wood composition was also previously reported.[2]

HPLC analysis was performed using Agilent 1200 series equipped with a Phenomenex Rezex ROA-Organic Acid H+ (8 % cross-linked sulfonated styrene-divinylbenzene; length 300 mm, 7.8 mm i.d., flow 0.4 mL/min) using isocratic aqueous H_2SO_4 (5 mM) as eluent and UV as detector (wavelength: 210 nm). Citric acid was used as standard for quantification of levulinic acid. The calibration curve was prepared using levulinic acid solutions at different concentrations and showed linearity (r^2 = 0.998) between the range of concentrations of interest. ^{1}H- and ^{13}C-NMR spectra were acquired using a Bruker Spectrospin 400 MHz Ultrashield Spectrometer in deuterated solvents. FT-IR spectra were measured on a Varian1000 FT-IR spectrometer. GC-MS analyses were performed using an Agilent Technologies 5975 gas chromatograph equipped with a MS detector and a capillary column (HP-5MS, 30 m, 0.25 mm, 0.25 micron). The temperature program started with an isothermal step at 50 °C for 2 min, in a second step the temperature was increased to 300°C (rate of 30 °C/min) and then kept for 1 min. Reactions were carried out multiple times and showed good reproducibility. Quantification of GVL was done via GC chromatography using GVL calibration curves in the concentration range of 10–100 mM and octyl ether as the internal standard.

Hydrolysis reactions

The acidic hydrolysis of the biomass was performed following literature known procedures without further optimizations. Briefly, glucose (or alternatively cellulose or milled beech wood, 540 mg) was loaded in a Teflon lined, stainless steel autoclave

purchased from Parr Instruments (45 ml volume) followed by 0.5 M H_2SO_4 (15 mL). The autoclave was placed into an oven and the reaction was heated up to 220 °C for 8 hours, then allowed to cool to room temperature. The solution was filtered and the volume of the solution was measured. An analytical sample was thus analyzed by HPLC using isocratic aqueous H_2SO_4 (5 mM) as the eluent as described above.

Recycling Hydrolysis Reactions

For recycling experiments we followed the previously described procedure "Hydrolysis reactions" and the final water phase was extracted with 2-MeTHF. The two phases were separated followed by a new quantification of the levulinic acid content in the aqueous phase by HPLC. The acidic aqueous phase was then used for further hydrolysis reactions without purifications. At the end of the reaction an oil is formed on top of the water phase, which is separated, while the formation of precipitates is not observed. The aqueous phase is thus reused after extractions with 2-MeTHF for further iterative cycles.

Reduction reactions

All the reactions were performed using a H-Cube Pro™ reactor[3] equipped with a hydrogen feed (with a flow rate of 60 mL min^{-1}) and a liquid feed (0.3–1.0 mL min^{-1}). Solutions of the starting materials at the desired concentration were pumped through a 70mm column packed with Raney Nickel (0.9 g, wet) using a HPLC pump. The residence time was controlled by adjusting the flow rate. The hydrogen produced in situ is mixed with the eluent at 12 bars before reaching the packed cartridge. The Raney Nickel particles in the packed column cause a low pressure drop (<2 bar). After equilibrating the system at the desired temperature over a period of 20 minutes, samples from the eluate were collected and analyzed by GC-MS.

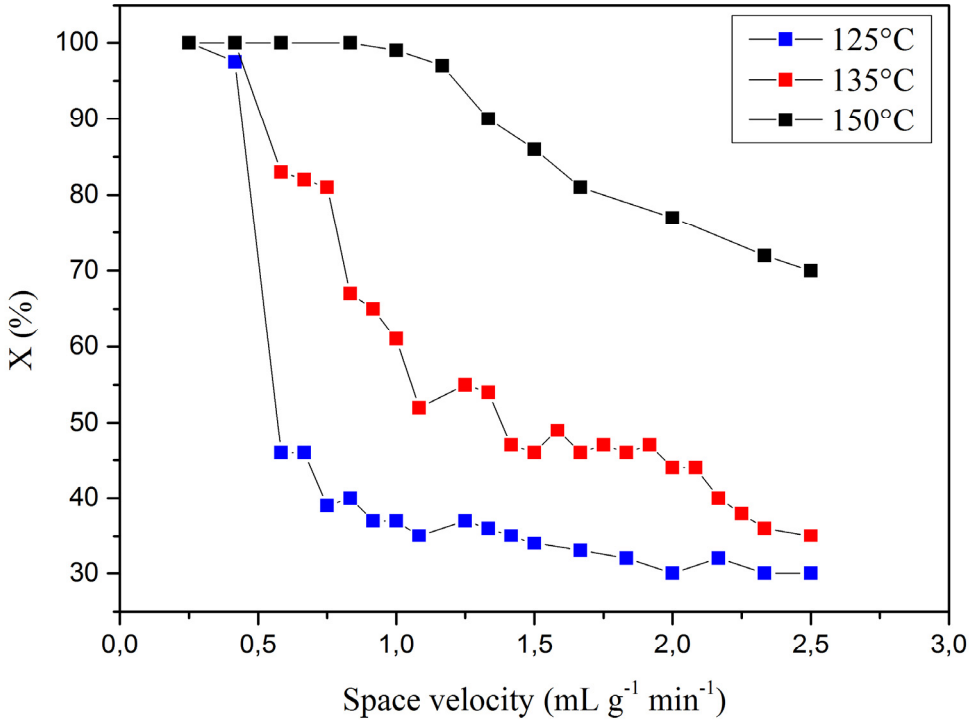

Figure SI 1 Conversion VS space velocity for the conversion of LA into GVL at different temperatures.

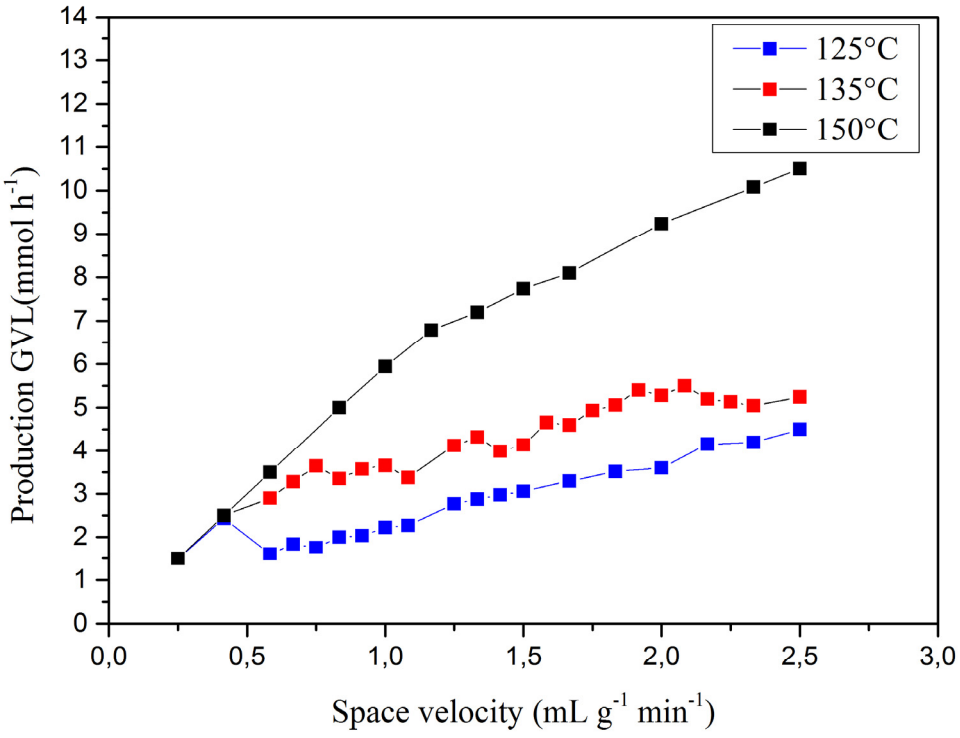

Figure SI 2 Production VS space velocity for the conversion of LA into GVL at different temperatures.

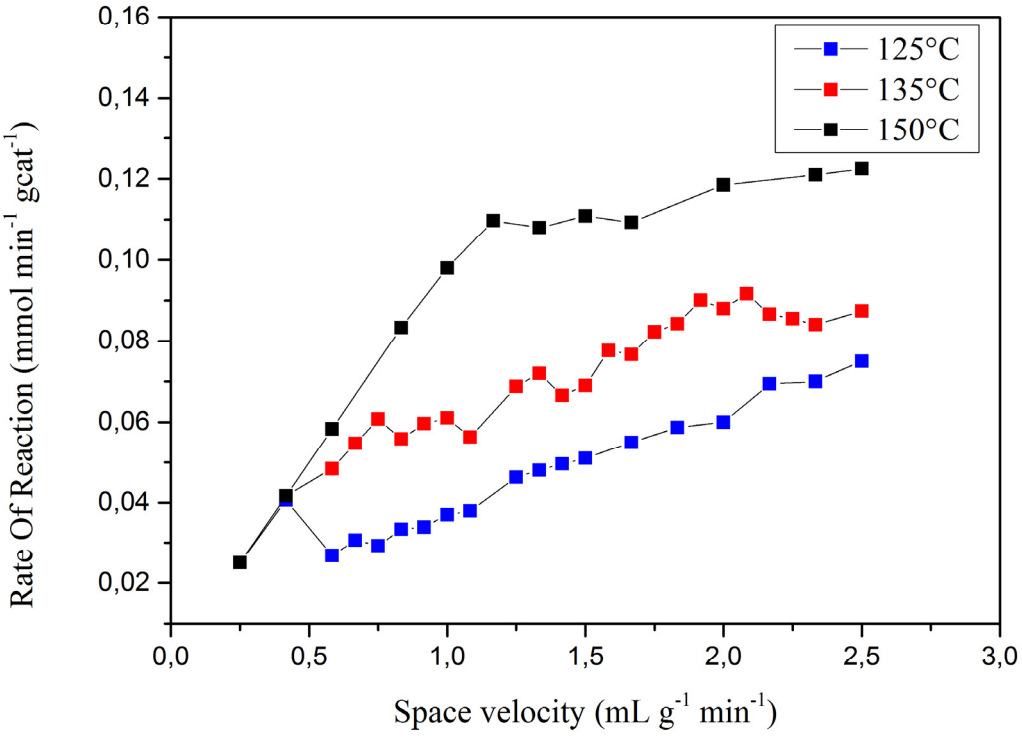

Figure SI 3 Rate of reaction VS space velocity for the conversion of LA into GVL at different temperatures.

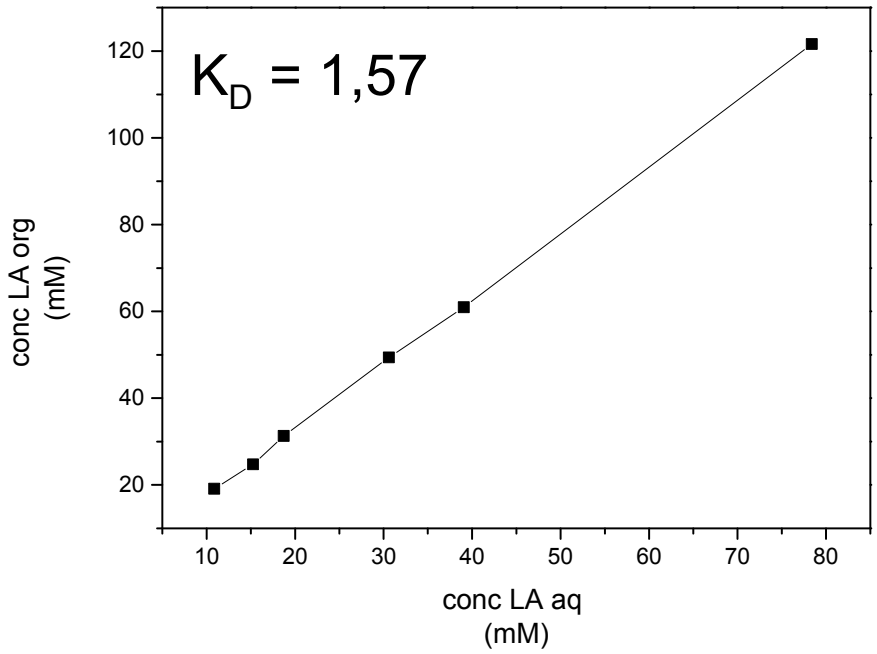

Figure SI 4 Partition ratio of levulinic acid in 2-MeTHF/H_2SO_{4aq} (0.5 M). The value was calculated by extracting different water solutions of levulinic acid (20 mL) at known concentrations with 2-MeTHF (20 mL) and measuring the corresponding final concentrations by HPLC analysis (water phase) and GC-MS analysis (organic phase).

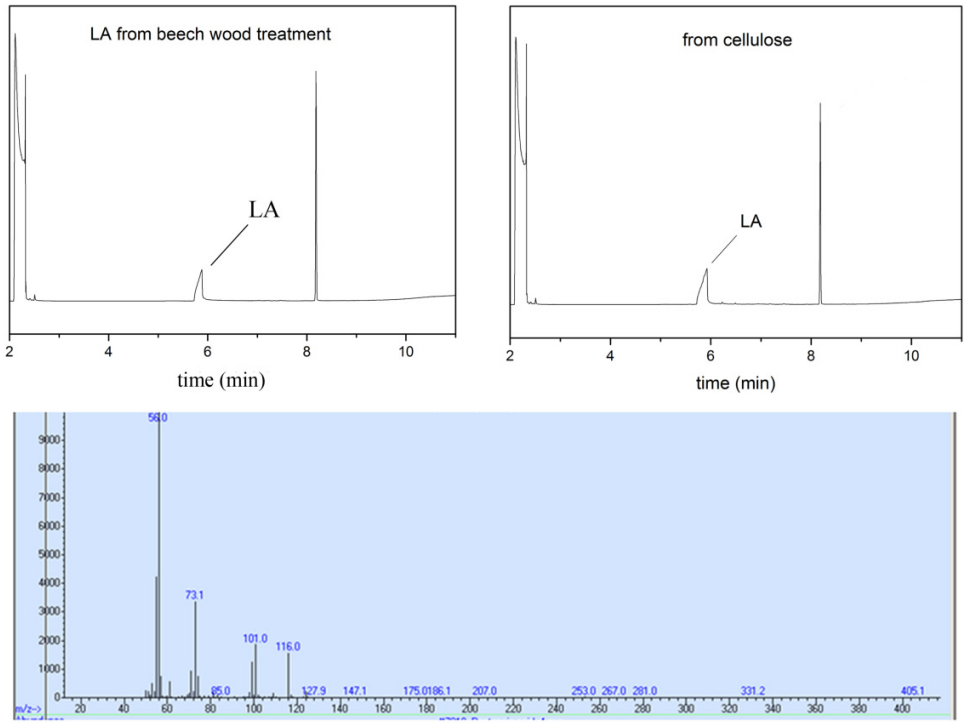

Figure SI 5 GC chromatogram with the corresponding EI-mass spectrum of LA produced from beech wood and cellulose (peak at ~8 min = Butylhydroxytoluol stabilizer for 2-MeTHF).

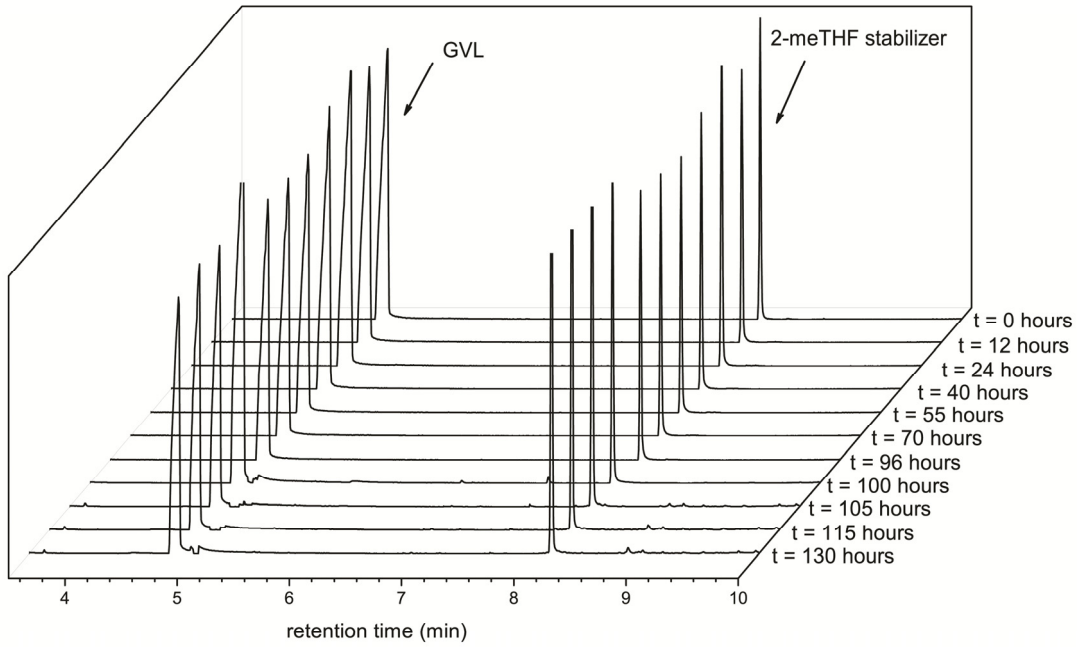

Figure SI 6 GC chromatograms for the reduction of biomass derived LA over Raney nickel as a function of the time on stream; 117 mmol of LA are converted using 0.9g of wet RaNi.

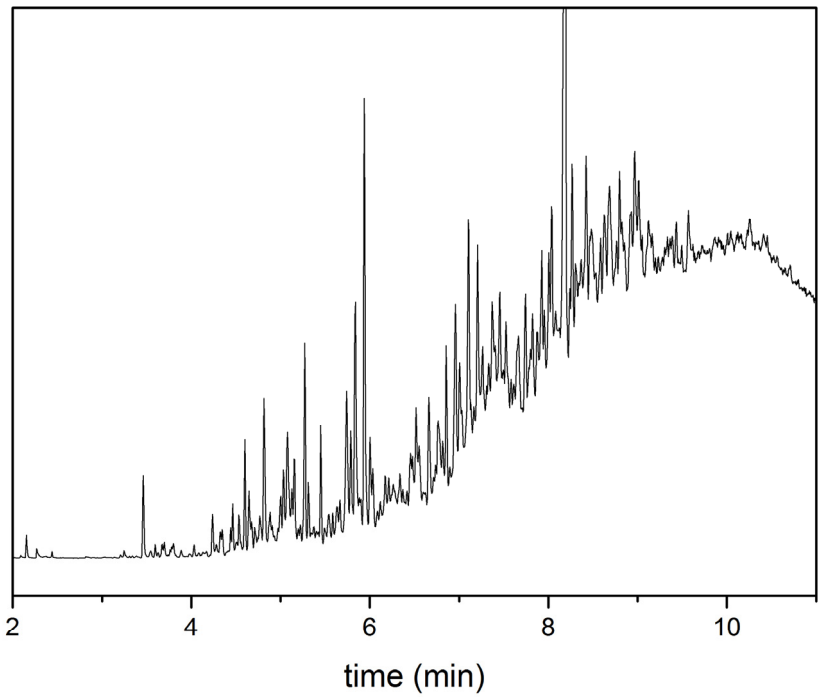

Figure SI 7 GC chromatogram of bio-oil obtained after biomass hydrolysis with $H_2SO_{4\ aq}$ in the presence of 2-MeTHF.

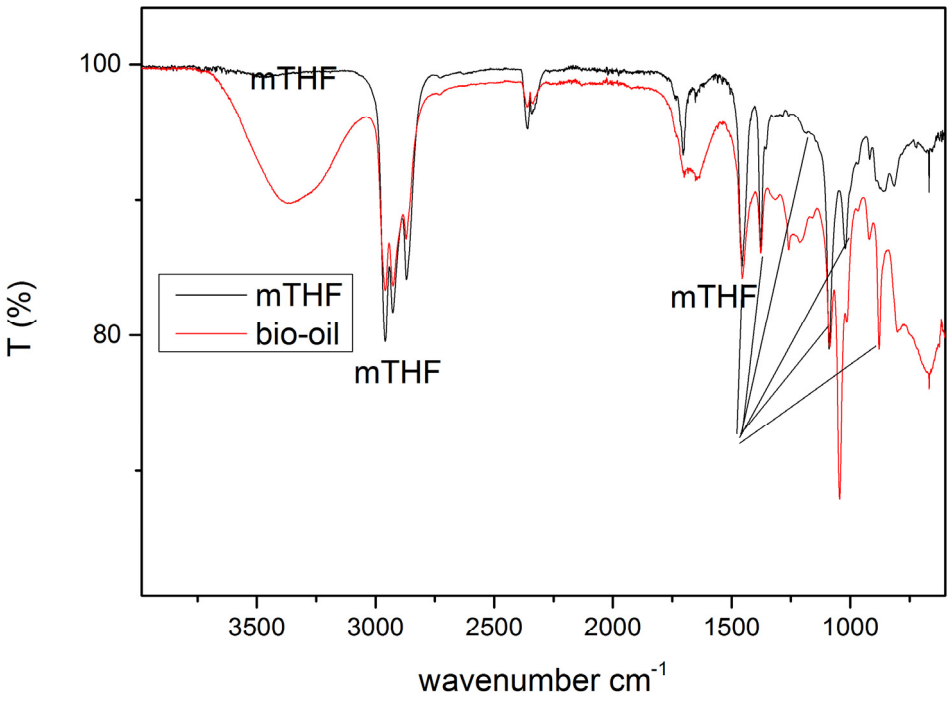

Figure SI 8 FTIR of bio-oil made after first circle of biomass treatment of $H_2SO_{4\ aq}$.

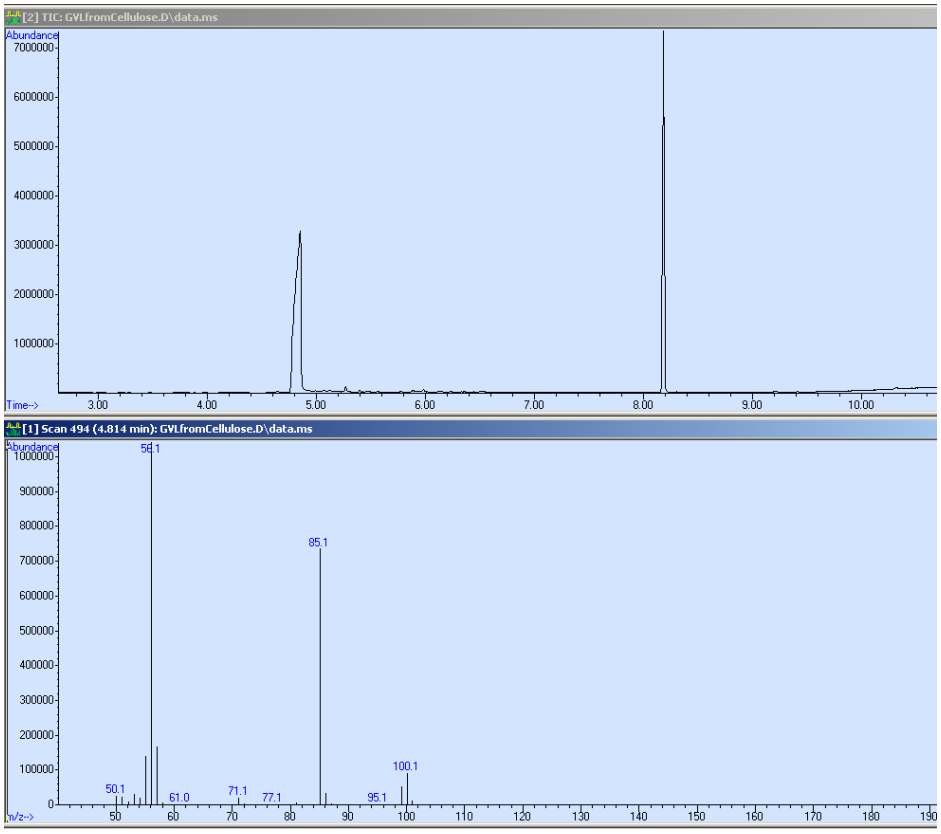

Figure SI 9 GC chromatogram and corresponding EI-mass spectrum of GVL obtained after reduction (peak at ~8 min = Butylhydroxytoluol stabilizer for 2-MeTHF).

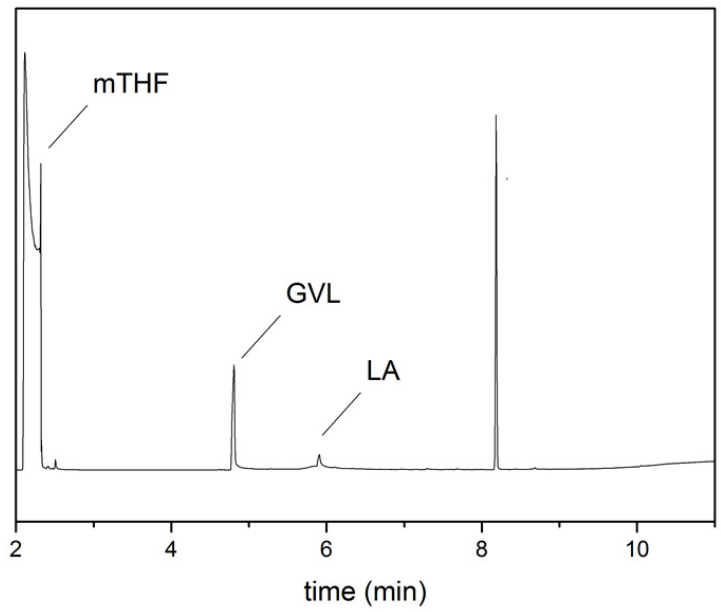

Figure SI 10 GC-chromatogram for the reduction of LA produced from beech wood into GVL at 125°C, 0.7 mL min^{-1} (peak at ~8 min = Butylhydroxytoluol stabilizer for 2-MeTHF).

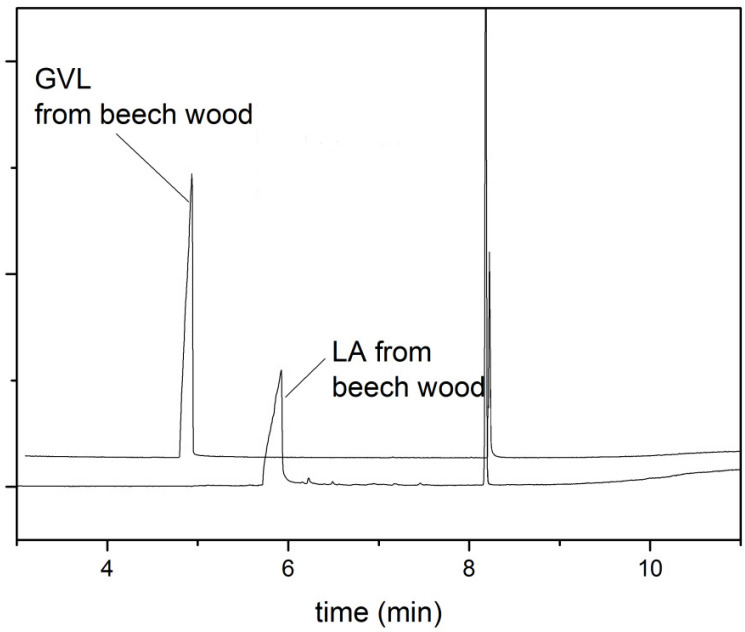

Fig. SI 11 Reference GC-chromatograms of GVL produced from beech wood and levulinic acid from beech wood (peak at ~8 min = Butylhydroxytoluol stabilizer for 2-MeTHF).

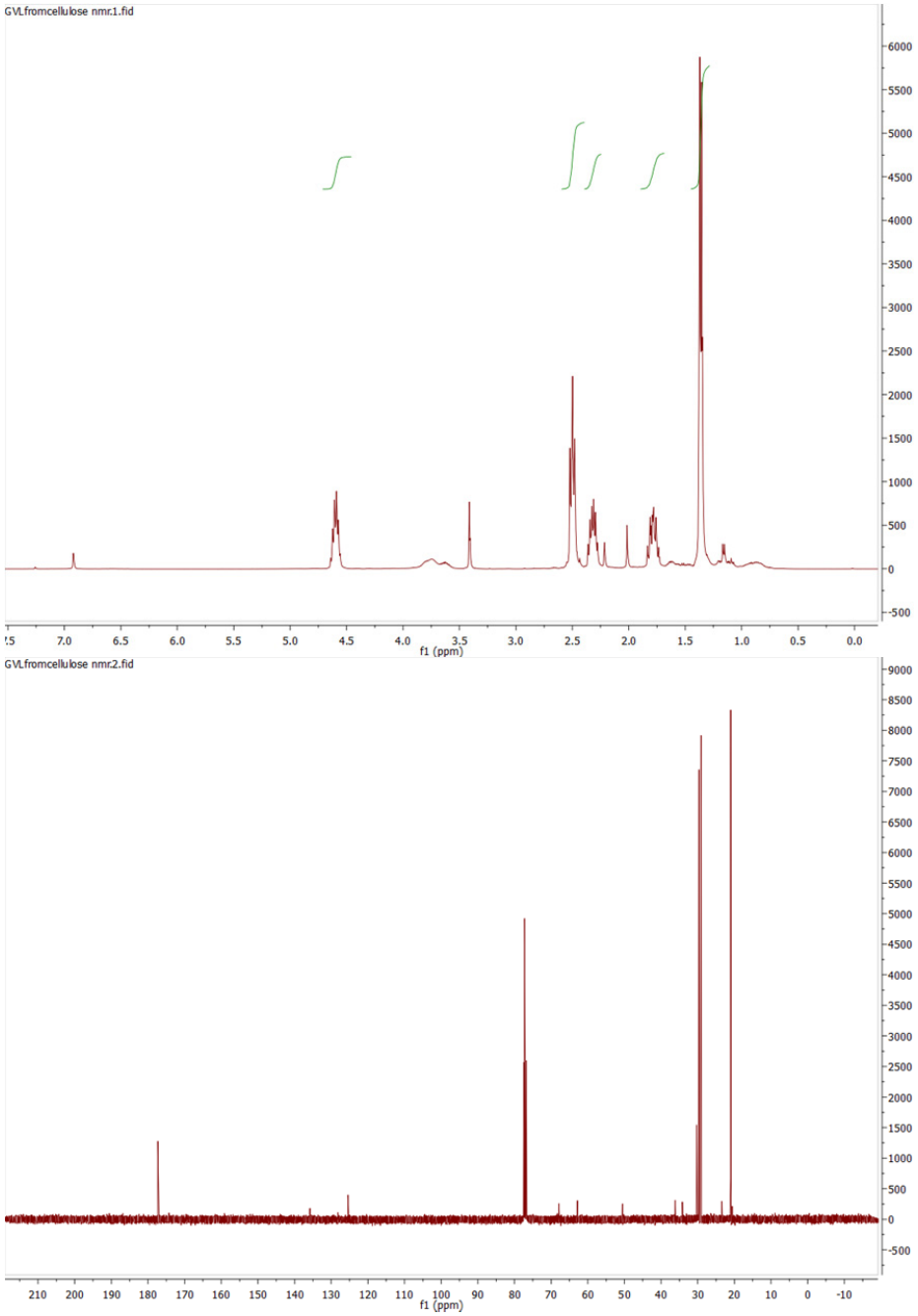

Fig. SI 12 ^{1}H-NMR and ^{13}C-NMR of crude GVL produced from cellulose; in the spectra, the signals of residual 2-MeTHF and the Butylhydroxytoluol stabilizer are also visible.

1. J. Hilgert, N. Meine, R. Rinaldi and F. Schuth, *Energy Environ. Sci.*, 2013, **6**, 92-96.
2. R. Carrasquillo-Flores, M. Käldström, F. Schüth, J. A. Dumesic and R. Rinaldi, *ACS Catal.*, 2013, **3**, 993-997.
3. http://www.thalesnano.com/products/H-Cube%20Pro.