Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Continuous flow process for the production of 2,5-dimethylfuran from fructose using (non-noble metal based) heterogeneous catalysis

Max Braun, Markus Antonietti*

Max-Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, 14424 Potsdam, Germany.

Corresponding Author:

*email: max.braun@mpikg.mpg.de

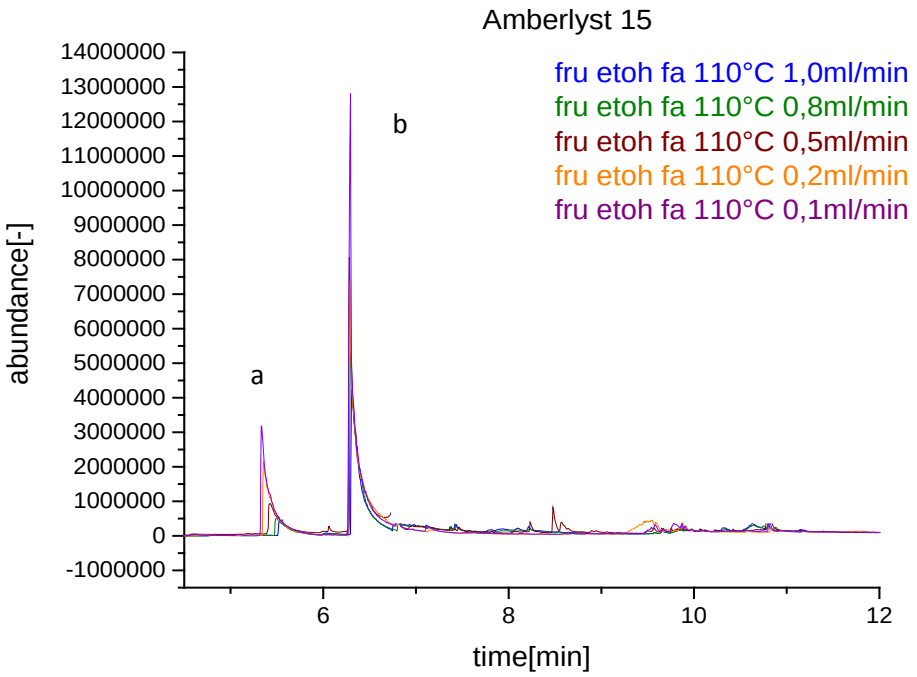


Figure S1: GC-MS Chromatogram of product solution of 0.05 M fructose/ethanol/0.5 M formic acid solution after a run over Amberlyst 15 in 250 mm column; exemplary at different flow rates; peak a) represents the ethyllevulinate, peak b) the HMF derivatives, mainly 5-ethoxymethylfurfural.

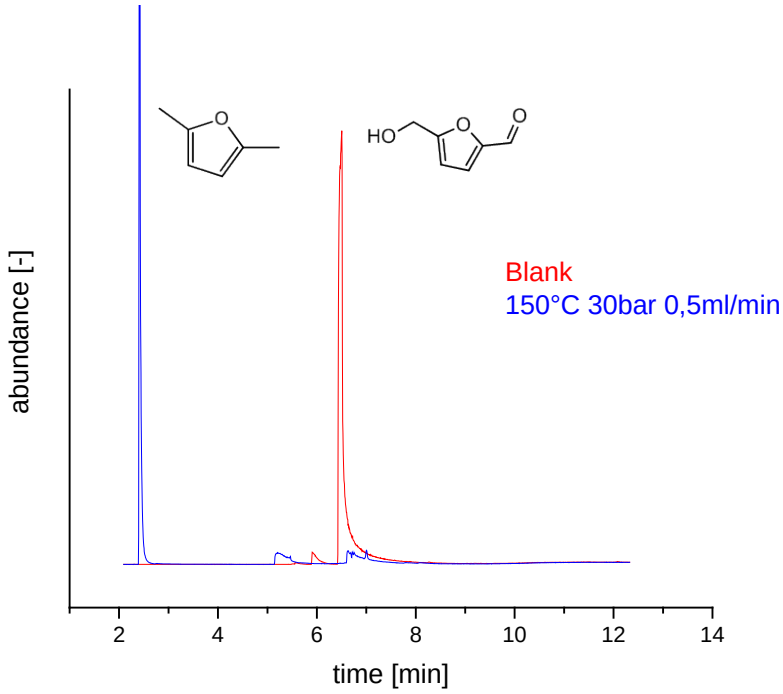


Figure S2: Conversion of 0.05 M HMF in ethanol solution using 150 °C, 30 bars and 0.5 mL min^{-1}. The blank is shown in red and was almost fully converted to DMF (blue). 1,68 g of 10 wt % Ni@WC was used in a 70 mm cartridge, using hydrogen from in situ electrochemical water-splitting in the H CUBE Pro itself.

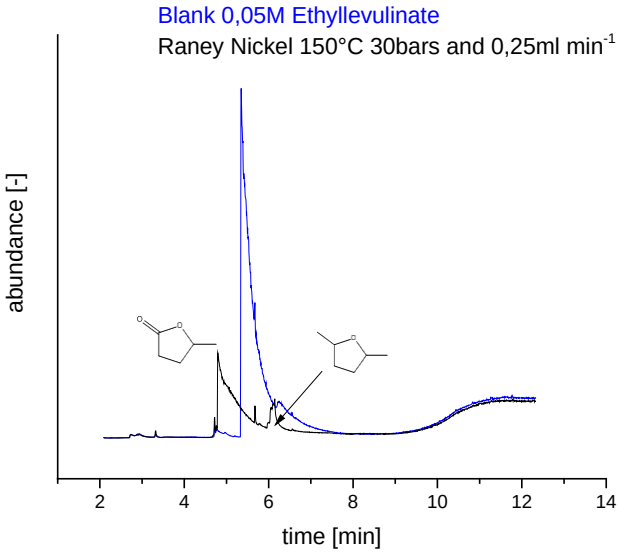


Figure S3: Conversion of 0.05 M ethyllevulinate ethanol solution using 150 °C, 30 bars and 0.25 mL min^{-1}. The blank solution was fully converted and the products were identified with a mass spectrometer connected to the GC. Raney nickel showed main selectivity to γ-valerolactone and the fully hydrogenated product 2,5-dimethyltetrahydrofuran.

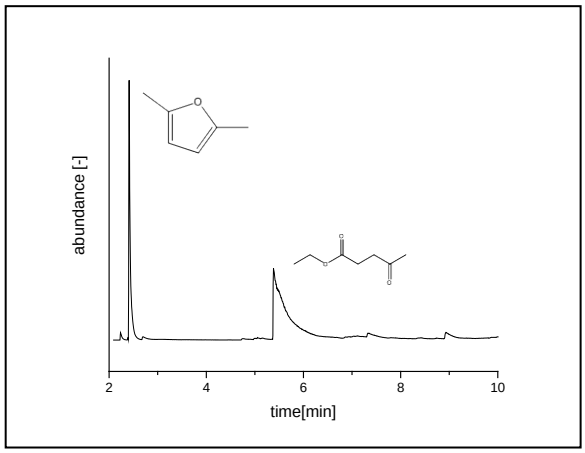


Figure S4: Qualitative GC –MS chromatogram of reaction products directly produced in a single run from fructose in solution in the combined system using Amberlyst 15 and Ni@WC with 30 bar and 0.25 mL min^{-1}.

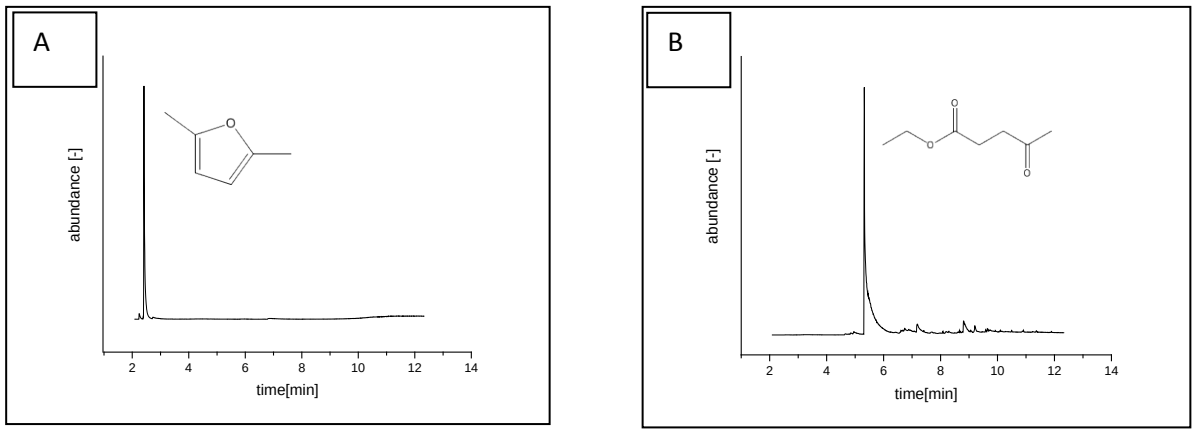


Figure S5: Qualitative GC –MS chromatogram of reaction products directly produced in a single run from fructose in solution in the combined system using Amberlyst 15 and Ni@WC after distillation. This reaction mixture was evaporated in the rotary evaporator and analyzed by GC-MS afterwards. The distillate (DMF) is shown in A. The slurry, what stayed in the bottom of the flask is represented by B (ethyllevulinate). The rotary evaporation conditions are: 55 °C water bath, 150 mbar reduced pressure.

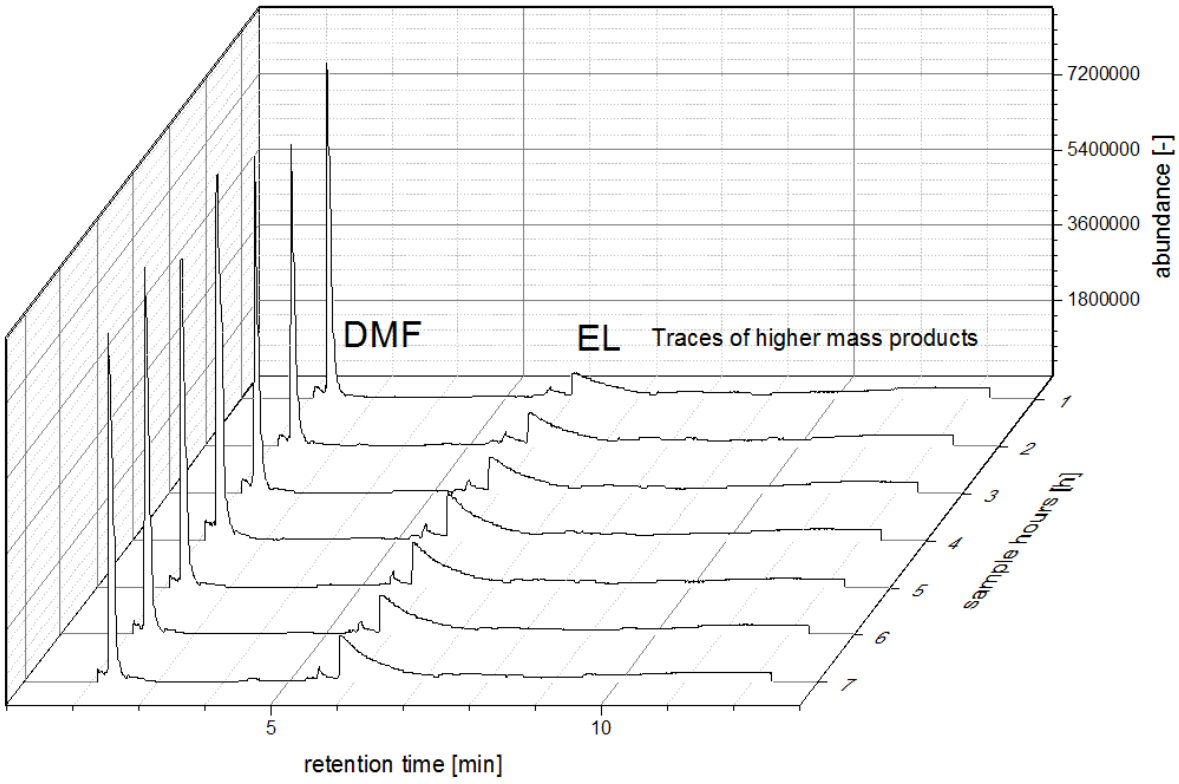


Figure S6: GC-MS chromatogram of the results during a 7 h continuous run using Amberlyst 15 and Ni@WC in series. The reaction parameters are as follows: 2.4 g Amberlyst 15 at 110 °C, 30 bar and 0.25 mL min^{-1} in a 250 mm x 4.6 mm column. The residence time in the column was about 16.6 minutes. Furthermore the flow was directed into the 1.68 g Ni@WC column at 150 °C with additional hydrogen input. The residence time in here was about 3 minutes.

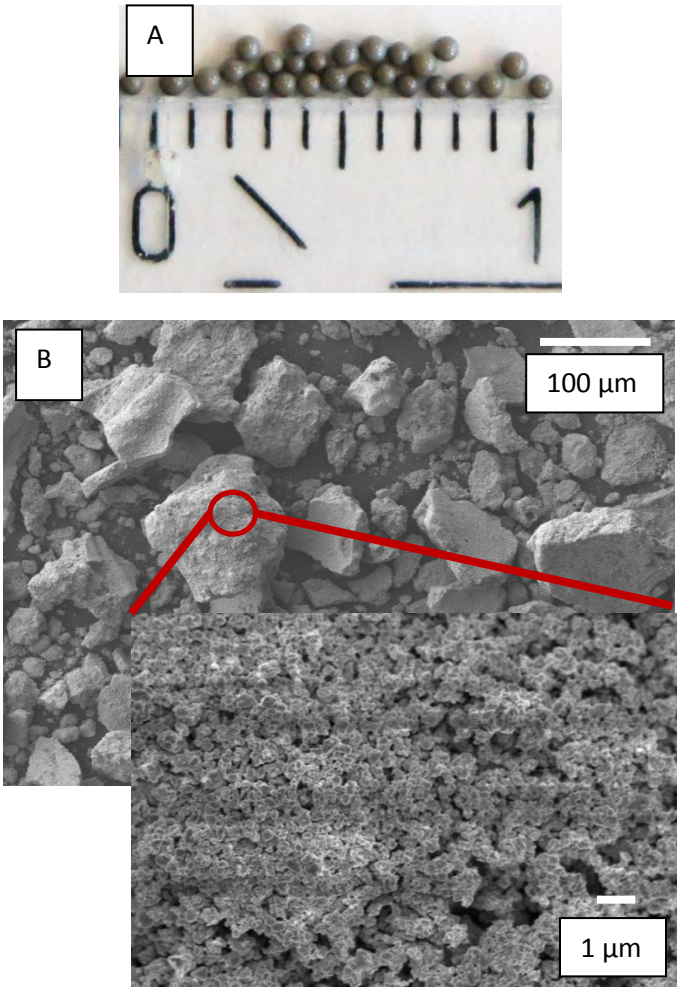


Figure S7: A: Amberlyst 15 spheres derived from Sigma Aldrich.(Sigma Aldrich CAS Number 12070-12-1) B: Ni@WC powder in different magnification. Nickel is deposited on top of commercial tungsten carbide (Sigma Aldrich CAS Number 39389-20-3), which agglomerates the structures to porous micrometer blocks.

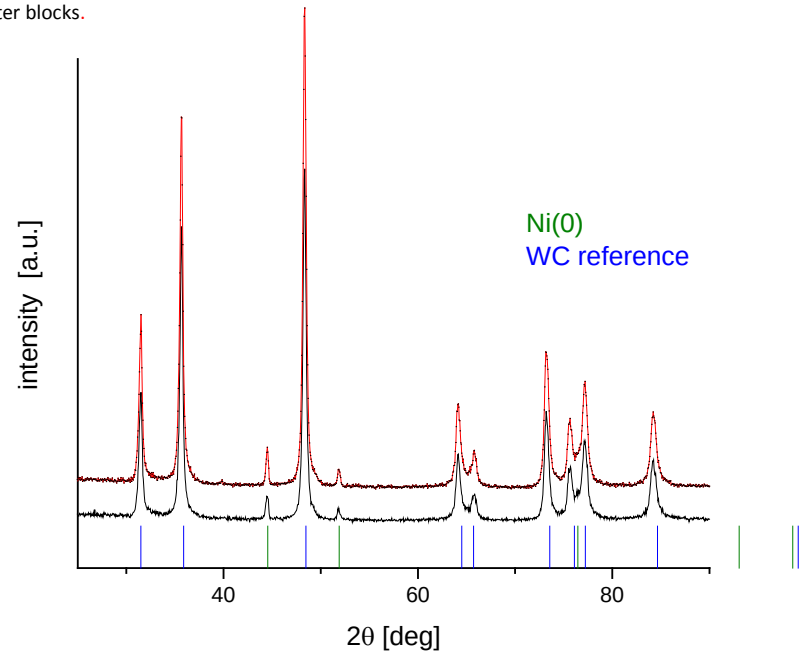
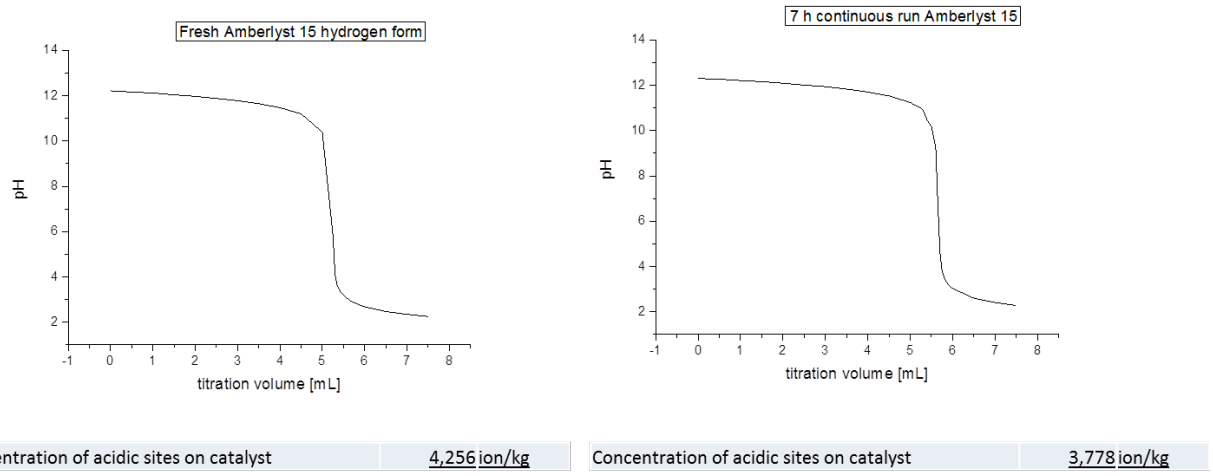


Figure S8: XRD results before (black) and after 7 hours (red) of reaction. The nickel is shown in green, whereas the tungsten carbide peaks are labeled in blue. Black is before the reaction and red is after the 7 h run with 150 °C, 30 bar and 0.25 mL min^{-1}. (Reference pattern PDF4 database: Ni 00-004-0850; WC 01-077-4389)

Table T1: Elemental Analysis of fresh Amberlyst 15 before reaction and 7 hours used Amberlyst 15 with 110 °C in a 250 mm x 4.6 mm column with 0.05 M fructose conversion. Additionally the black colored 7 hours Amberlyst 15 catalysts from the entrance of the column (Figure 3C) is analyzed. A sulfur to carbon ratio is given.

Elemental Analysis	C [%]	S [%]	S/C
Fresh Amberlyst 15	47.2	14.6	0.31
7 h Amberlyst 15	42.6	12.6	0.29
7 h Amberlyst 15 (Figure 3C)	50.3	10.4	0.21



Concentration of acidic sites on catalyst	4,256 ion/kg

Concentration of acidic sites on catalyst	3,778 ion/kg

Figure S9: Titration of the solid acid catalyst Amberlyst 15. Before reaction and after a 7 h continuous run. The resulting values are referring to mol equivalent per kg.

Table T2: ICP-OES analysis of fresh Ni@WC and catalyst used for 7 h.

ICP Analysis	Ni wt %
fresh Ni@WC	8.3
7 h used Ni@WC	8.5