SUPPORTING INFORMATION

Mitigation of the cation exchange resins deactivation in the one pot conversion of fructose to methyl levulinate

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1. Chemicals

All reagents and solvent were used as received from commercial suppliers (unless otherwise indicated). All cation exchange resins have been kindly provided by SEPROSYS.

Table S1. List, purity and origin of chemicals used

Name	CAS number	Purity	Supplier
Fructose	57-48-7	99 %	Sigma-Aldrich
Methanol	67-56-1	97 %	Carbo erba
Ethanol absolu	64-17-5	99%	Carbo Erba
Butanol	71-36-3	98%	Sigma-Aldrich
5-Hydroxymethylfurfural	67-47-0	99%	Sigma-Aldrich
Levulinic acid	123-76-2	98%	Sigma-Aldrich
5-Methoxymethylfurfural	1917-64-2	95%	Manchester organics limited
Methyl levulinate	624-45-3	98%	Sigma Aldrich
Ethyl levulinate	539-88-8	99%	Sigma Aldrich
Butyl levulinate	2052-15-5	98%	Sigma Aldrich
Sulfuric acid	7664-93-9	96%	Sigma Aldrich

Table S2. List and characterization of cation exchange resins studied in the main article

Name	Proton exchange capacity (mmol H^+/g)	Matrix	Humidity	Supplier
Amberlyst® 45	2.95	Macroporous	51-55%	Dow
Amberlyst® 40	5.2	Macroporous	44-53%	Dow
Amberlyst® 31	4.8	Gel	63-67%	Dow
Amberlyst® 35 (WET)	5.4	Macroporous	52-57%	Dow
Amberlyst® 36 (WET)	5.40	macroporous	51-57%	Dow
Amberlyst® 119	4.9	Gel	49-55	Dow
Amberlyst® 16	4.7	Macroporous	52-58%	Dow
Amberlyst®15	4.80	Macroporous		Dow
Purolite C124SH	5.01	Gel	65-70%	Purolite
Purolite CT251	5.2	Macroporous	54-59%	Purolite
Purolite CT124	5.2	Gel	60-65%	Purolite
Treverlyst CAT400	3.00	Macroporous	45-55%	Chemra
Treverlite XS129700	2.46	Macroporous	45-55%	Chemra
Treverlite XS134400	3.91	Macroporous	52-58%	Chemra

2. Analytical section

^{1}H NMR was recorded on a Bruker Ultrashield 500 plus (500MHz). All spectra were internally referenced to residual proton solvent signals. Data for ^{1}H NMR are reported as chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad signal), coupling constants (Hz) and integration.

Gas chromatography (GC) analysis: samples were analyzed on a Scion 436-GC equipped with a FID detector, a HP5MS column (30 m x 0.25 mm x 0.5 Micron, -60 to 325/350 °C) using with a flow front of 1 mL/min and with a split ratio of 40:1. The temperature at the injector is 275 °C and the injected volume is 5 µL. The heating ramp of the GC column was set as follow: 80°C to 100 °C (10°C/min), 1 min at 100°C, 100°C to 200°C (65°C/min), 1 min at 200°C, 200°C-300°C (10°C/min) and 1 min at 300°C.

Ultra High Performance Liquid Chromatography (UHPLC) coupled to High Resolution Mass Spectrometry (HRMS): UHPLC-HRMS analyses were performed at 30°C on a Thermo scientific Ultimate 3000 coupled with a Bruker impact HD Series Quadrupole-Time of Flight (QTOF) MS equipped with an Electrospray (ESI) ion source. The LC column was a Hypercarb, 50 x 2.1 mm using mixtures of ultra-pure water and acetonitrile, containing 0.1 % of formic acid, as a mobile phase (0.4 mL min^{-1}). After injection of 10 µL of sample, the gradient was programmed as presented in Table S3.

Table S3. Program used for HPLC analysis

Time (min)	%ultrapure water	% acetonitrile
0	1.0	99
2	1.0	99
6	40.0	60.0
7	60.0	40.0
12	100	0
16	100	0
16.01	1.0	99
20	1.0	99

For the HRMS, ESI source operated in positive polarity and its parameters were as follows: gas temperature 200 °C; drying gas 8.0 L min^{-1}; nebulizer 2.1 Bar, capillary 2500 V; the mass range was from 50 to 1000 m/z. The ESI source operated also in negative polarity and its parameters were as follows: gas temperature 200 °C; drying gas 8.0 L min^{-1}; nebulizer 2.1 Bar, capillary 3000 V; the mass range was from to 1000 m/z.

High Performance Liquid Chromatography (HPLC): HPLC analyses were performed on a Shimadzu LC -20ADSP at 40°C. The LC column was a ICSep ICE-COREGEL 107H column 300 x 7.8 mm using a 7 mM aqueous sulfuric acid solution as a mobile phase(flow of mobile phase: 0.8 $mL.min^{-1}$). Detection by refractive index was performed on a Shimadzu RID-20A.

Table S4. HPLC retention times of reagents and products used in this work

Reagent/product name	Retention time
Levulinic acid	11.856
Formic acid	10.500
5-(hydroxymethyl)furfural	23.664
Fructose	8.100
Methyl levulinate	18.864
Methyl formate	10.516

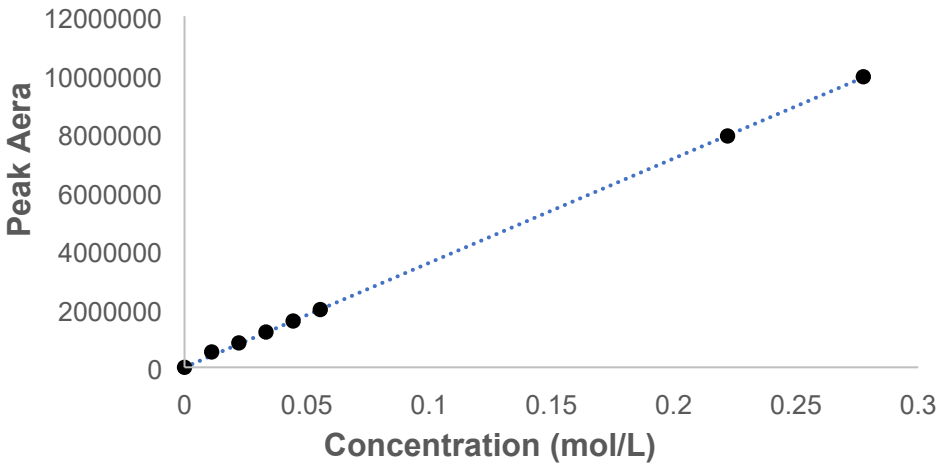


Figure S1 Calibration curve of fructose

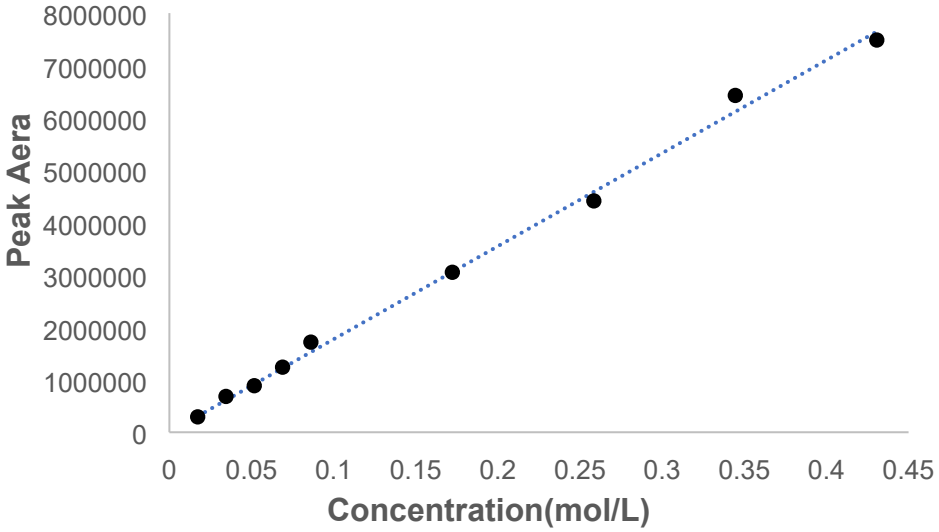


Figure S2 Calibration curve of levulinic acid

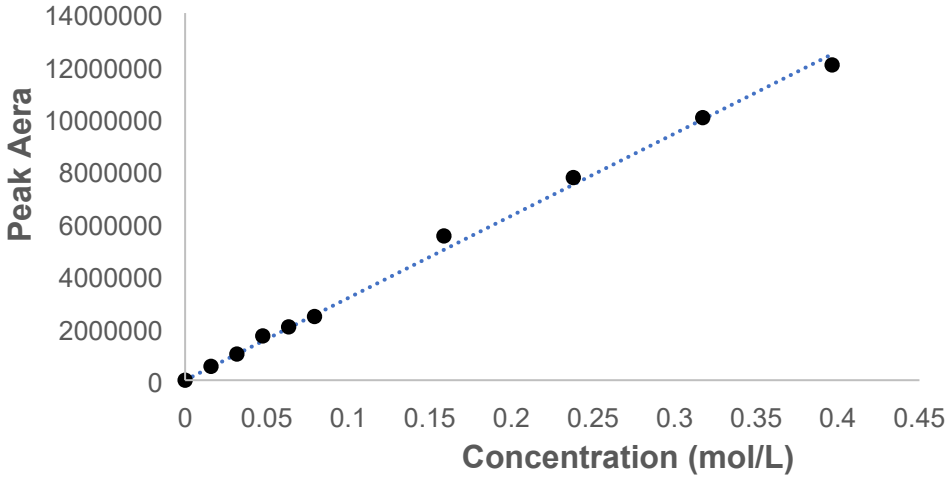


Figure S3 Calibration curve of HMF

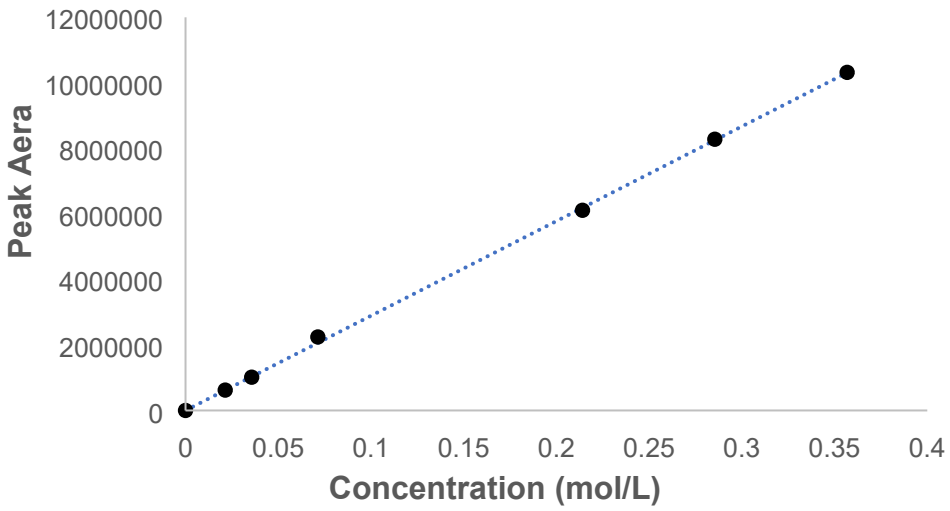


Figure S4 Calibration curve of MMF

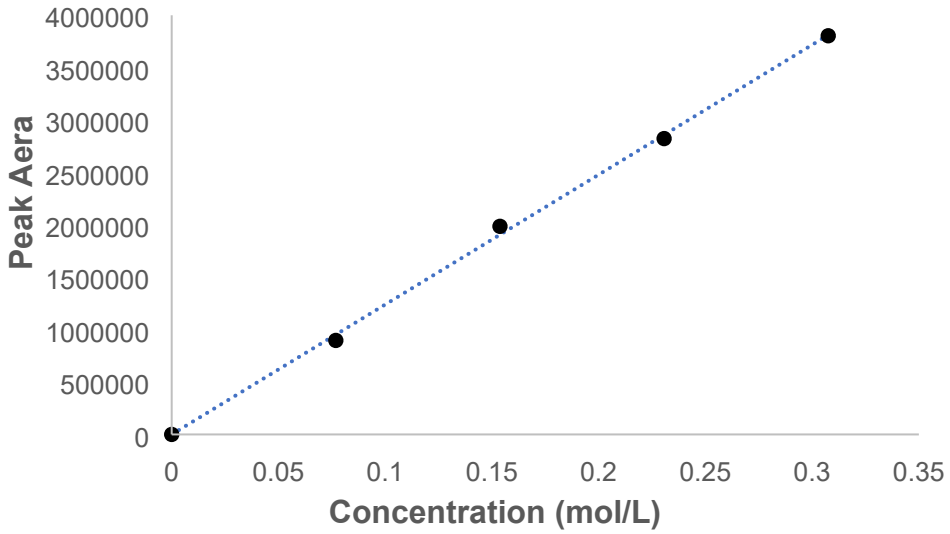


Figure S5 Calibration curve of methyl levulinate

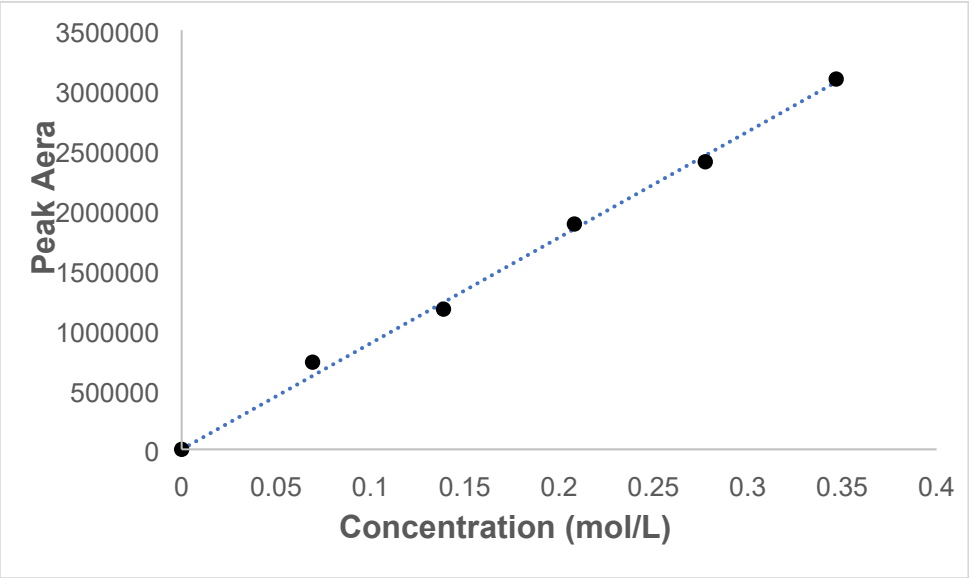


Figure S6 Calibration curve of ethyl levulinate

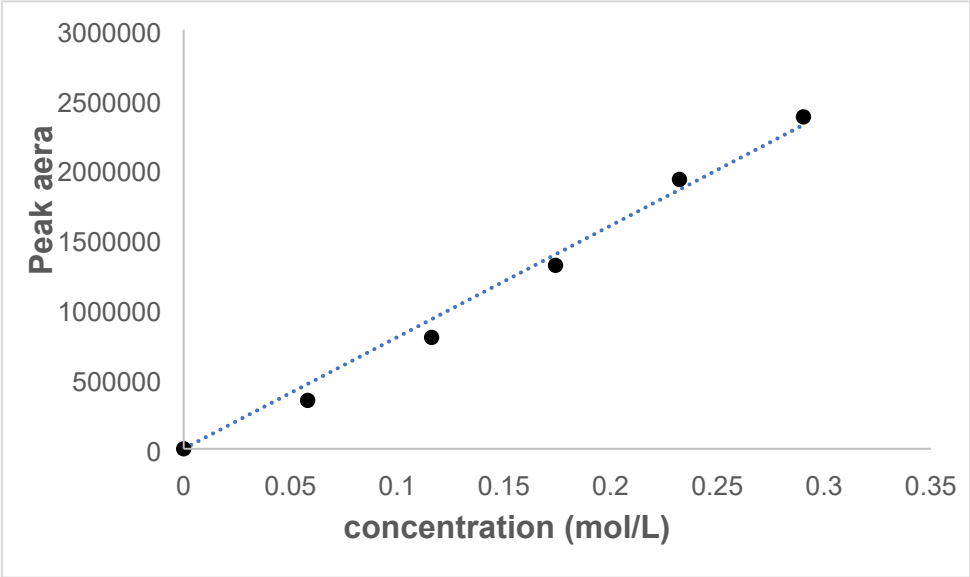


Figure S7 Calibration curve of *n*-butyl levulinate

Solubility of fructose in alkyl alcohols

The solubility of fructose in different alkyl alcohols (methanol, ethanol, and *n*-butanol) was determined by HPLC. Typically, 0.09g of fructose was added to 2 mL of the desired alkyl alcohols and stirred for 1 hour at 25°C with a magnetic stirring bar. The suspension was then filtered to remove the excess of undissolved fructose and the recovered solution was analyzed by HPLC to determine the amount of fructose solubilized (*i.e*. amount of fructose dissolved in 2 mL of alkyl alcohols)

Acid-base titration of cation exchange resins: 0.08 g of cation exchange resin was stirred for 2 hours in a 10 mL solution of 0.05 M sodium hydroxide. The cation exchange resin was then filtered and 5 mL of the alkaline solution was titrated with a 0.05 M aqueous HCl solution. The equivalent volume was used to determine the quantity of acid site per gram of (dry) cation exchange resin.

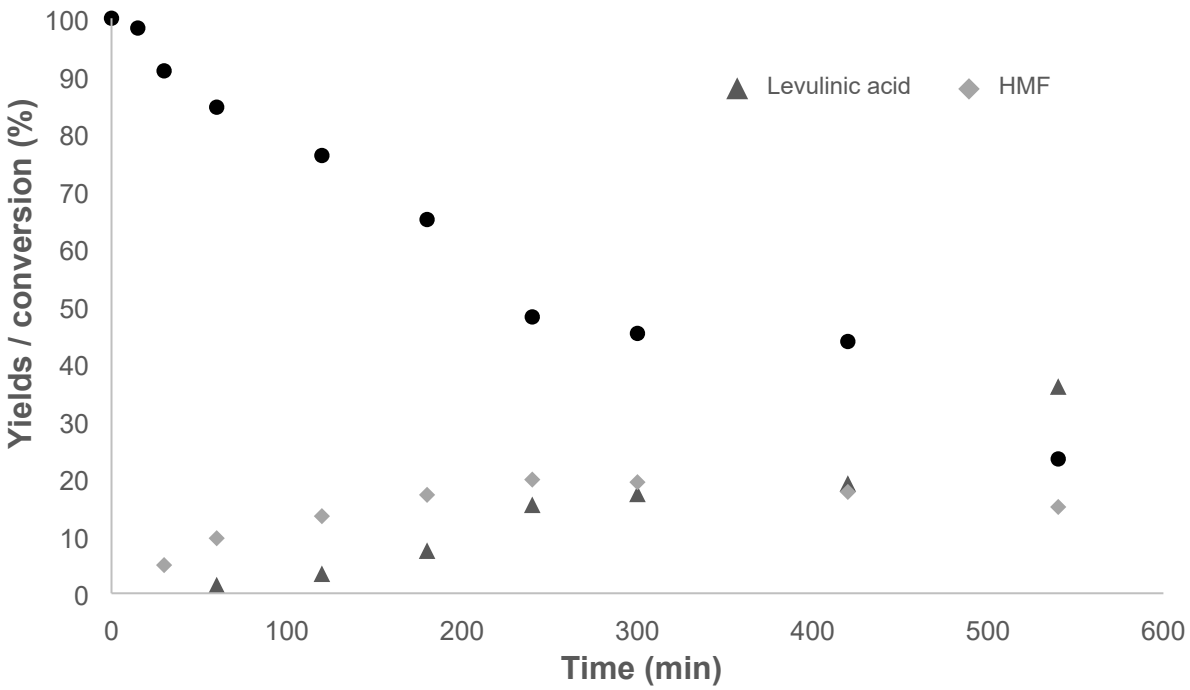


Figure S8 Plot of the fructose conversion and levulinic acid/HMF yield as a function of the reaction time in the presence of 0.665M H_2SO_4 (100°C, 5 wt% fructose in water)

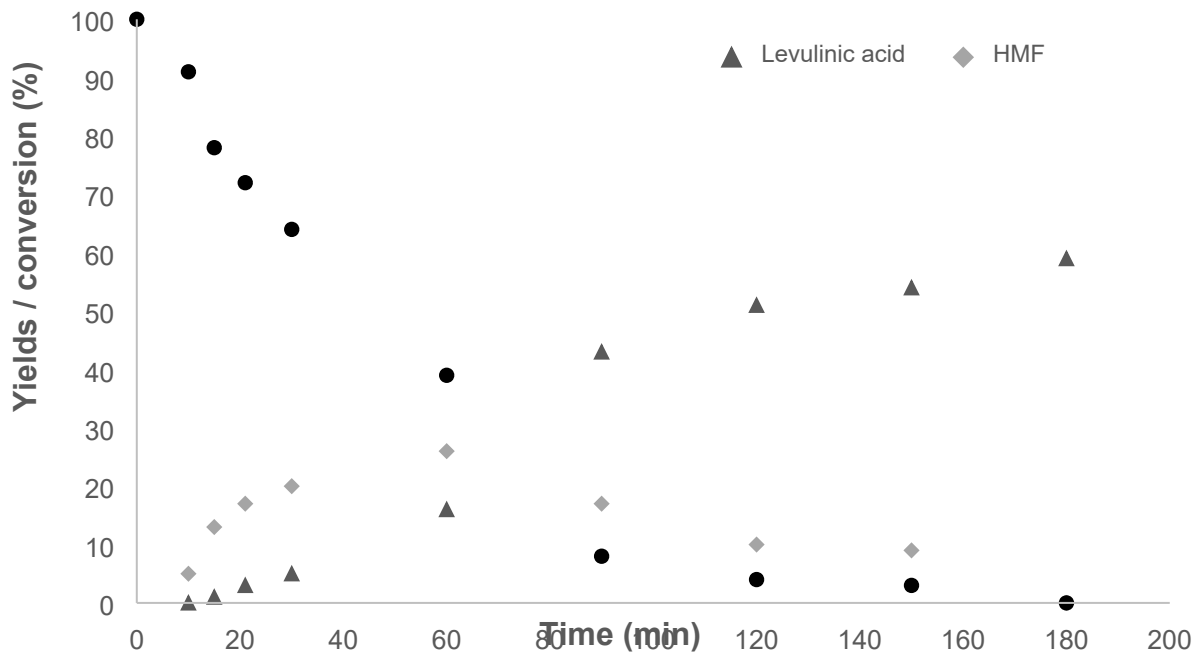


Figure S9 Plot of the fructose conversion and levulinic acid/HMF yield as a function of the reaction time in the presence of 0.665M H_2SO_4 (120°C, 5 wt% fructose in water)

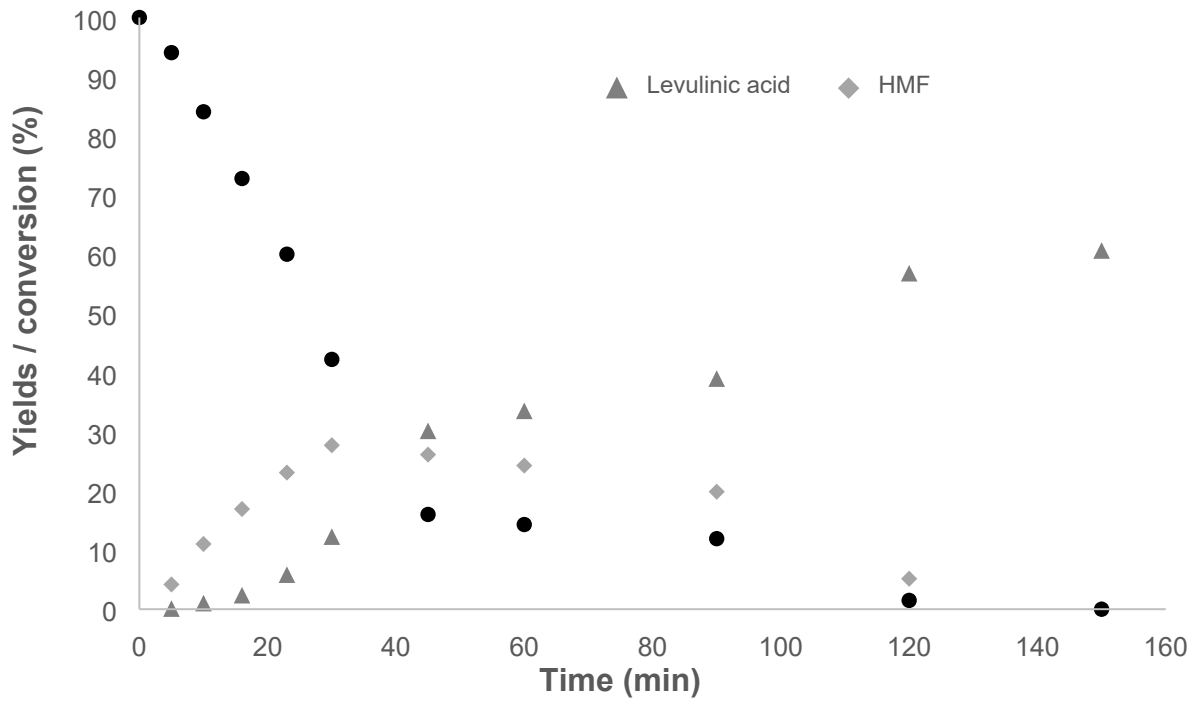


Figure S10 Plot of the fructose conversion and levulinic acid/HMF yield as a function of the reaction time in the presence of 0.665M H_2SO_4 (130°C, 5 wt% fructose in water)

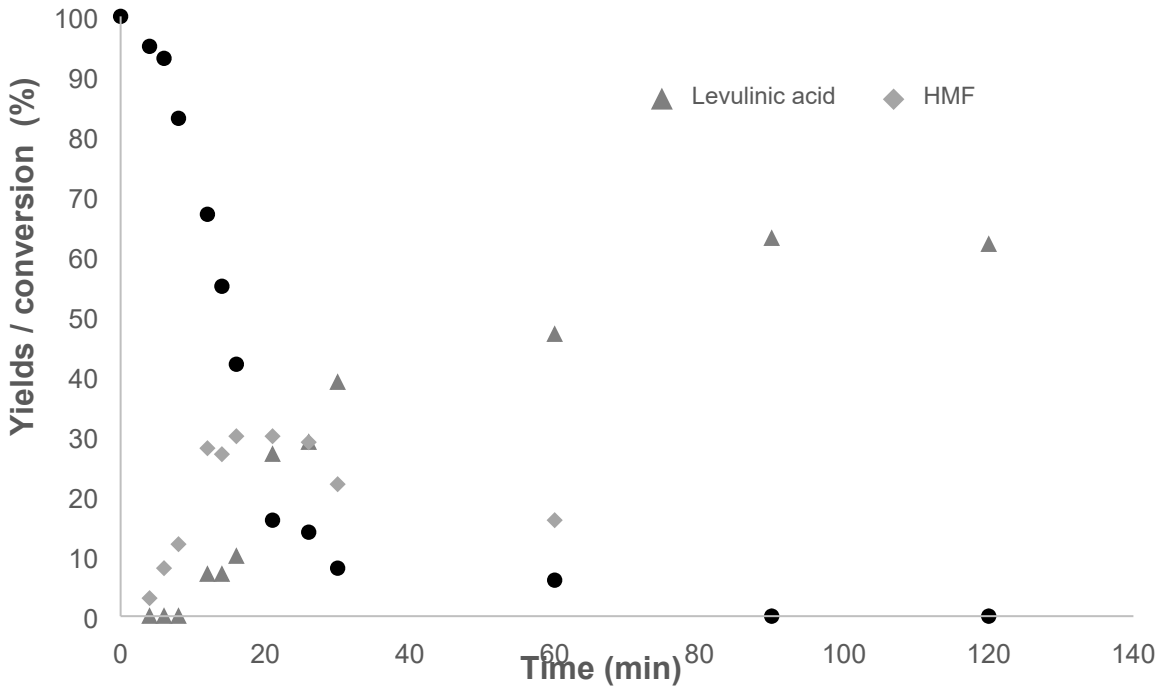


Figure S11 Plot of the fructose conversion and levulinic acid/HMF yield as a function of the reaction time in the presence of 0.665M H_2SO_4 (140°C, 5 wt% fructose in water)

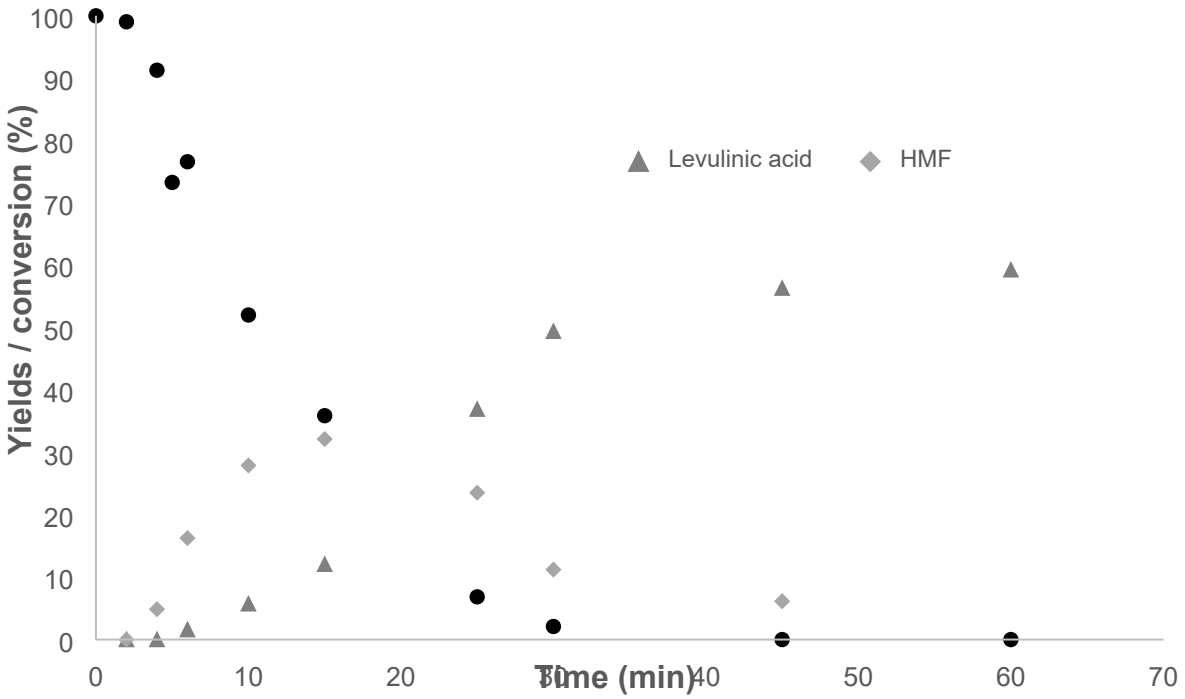


Figure S12 Plot of the fructose conversion and levulinic acid/HMF yield as a function of the reaction time in the presence of 0.665M H_2SO_4 (150°C, 5 wt% fructose in water)

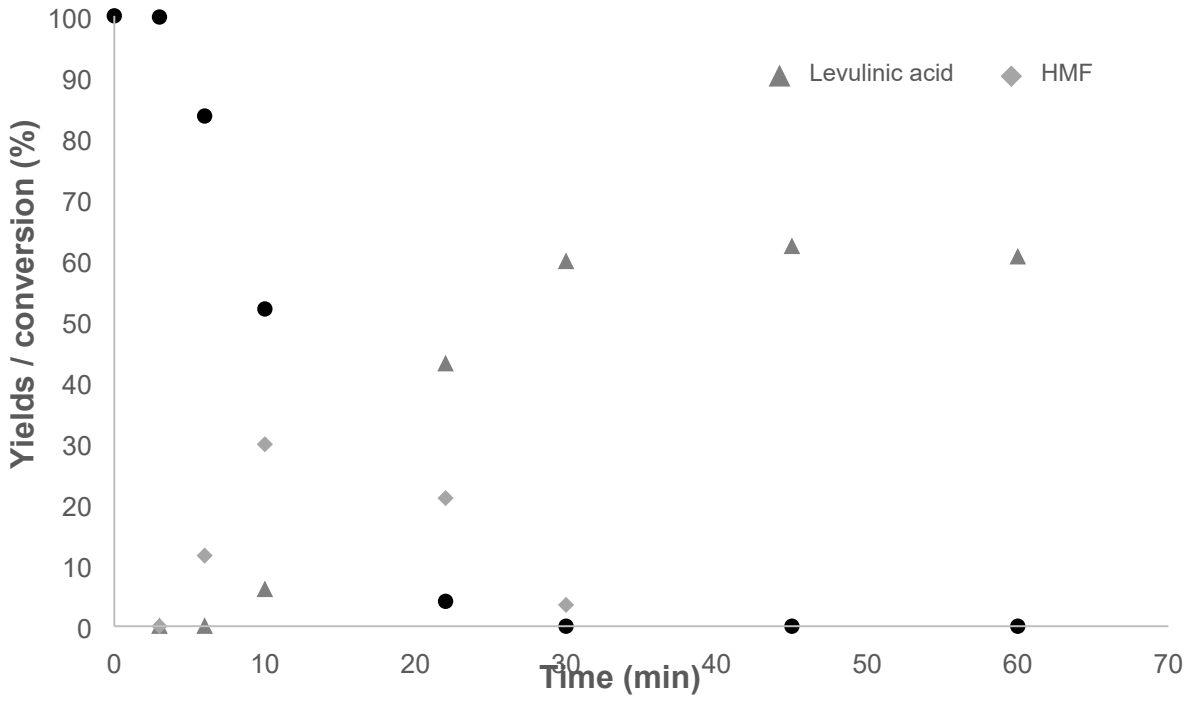


Figure S13 Plot of the fructose conversion and levulinic acid/HMF yield as a function of the reaction time in the presence of 0.665M H_2SO_4 (160°C, 5 wt% fructose in water)

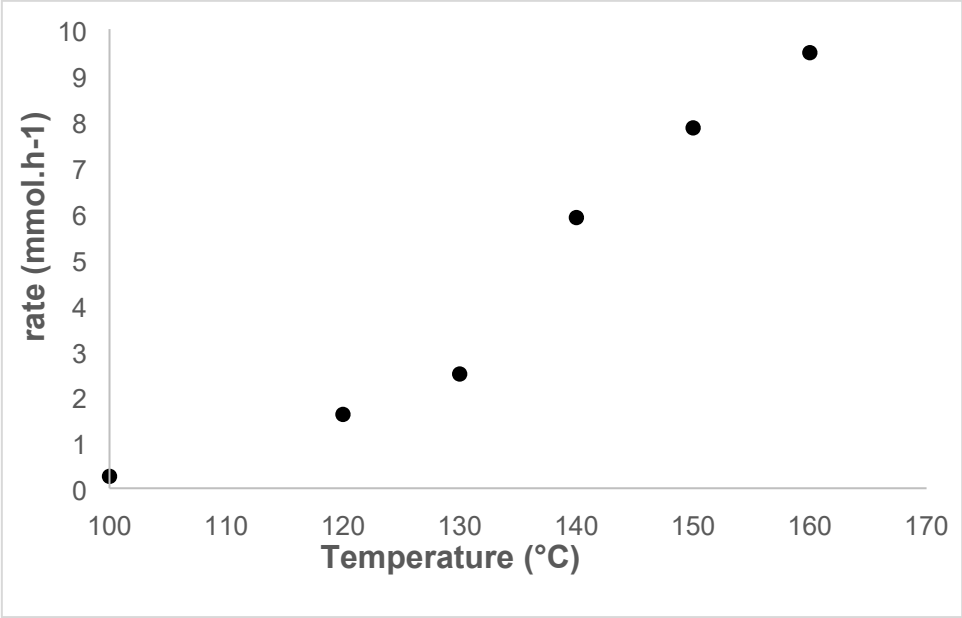


Figure S14 plot of the reaction rate as a function of the reaction temperature (5 wt% fructose in water)

Figure S15. Photo of humins filtrated at 100°C (left, 40% conv. of fructose) and 140°C (right, 20% conv. of fructose)

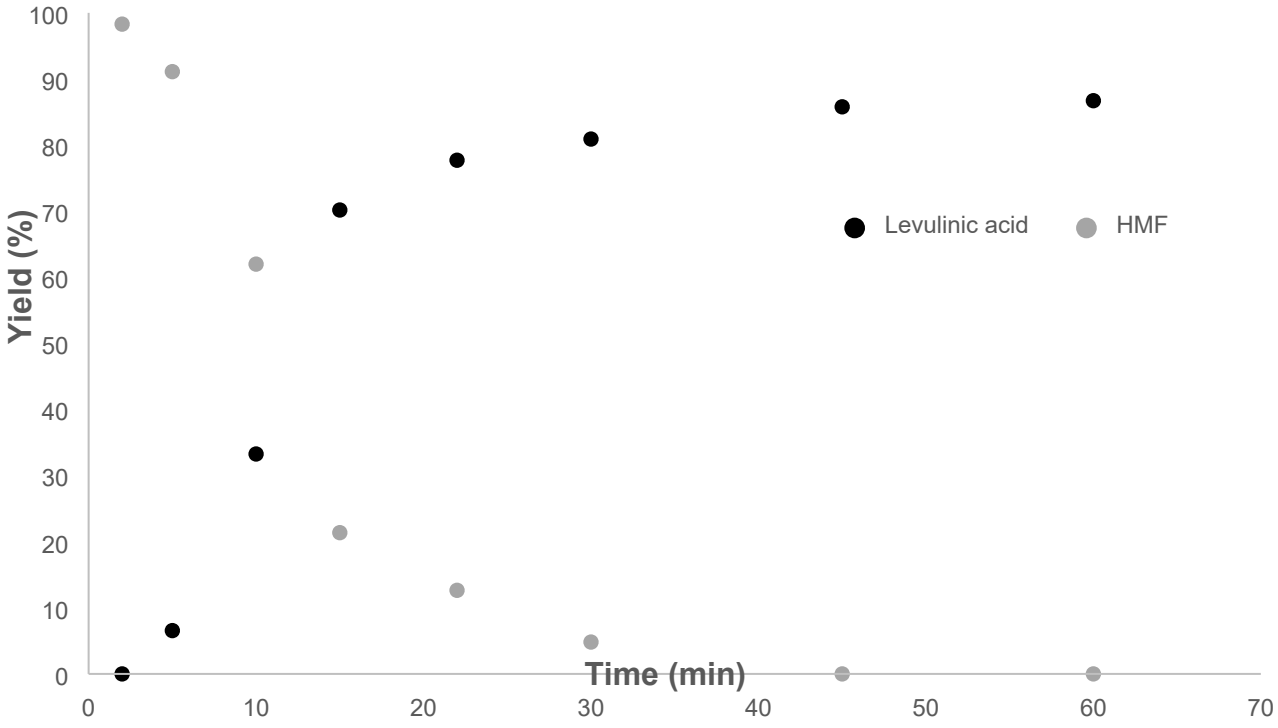


Figure S16 Plot of the HMF conversion and LA yield as a function of the reaction time in the presence of 0.665M H_2SO_4 (160°C, 5 wt% HMF in water)

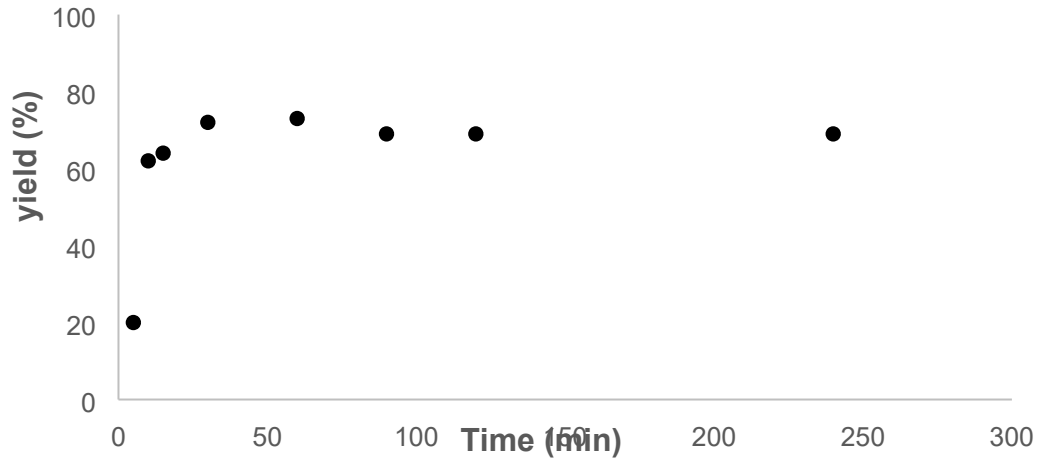


Figure S17 Plot of the ethyl levulinate yield as a function of the reaction time (160°C, 5 wt% of fructose in a 0.065 M ethanolic solution of H_2SO_4)

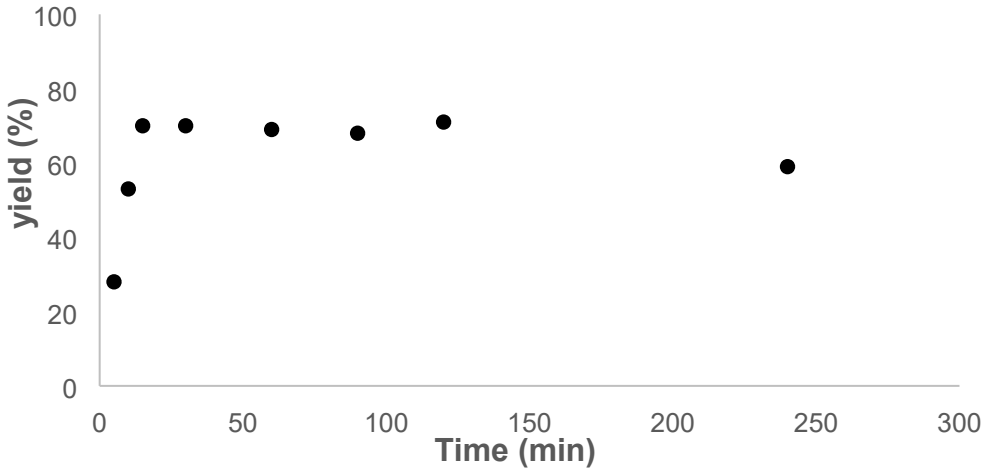


Figure S18 Plot of the *n*-butyl levulinate yield as a function of the reaction time (160°C, 5 wt% of fructose in a 0.065 M *n*-butanolic solution of H_2SO_4)

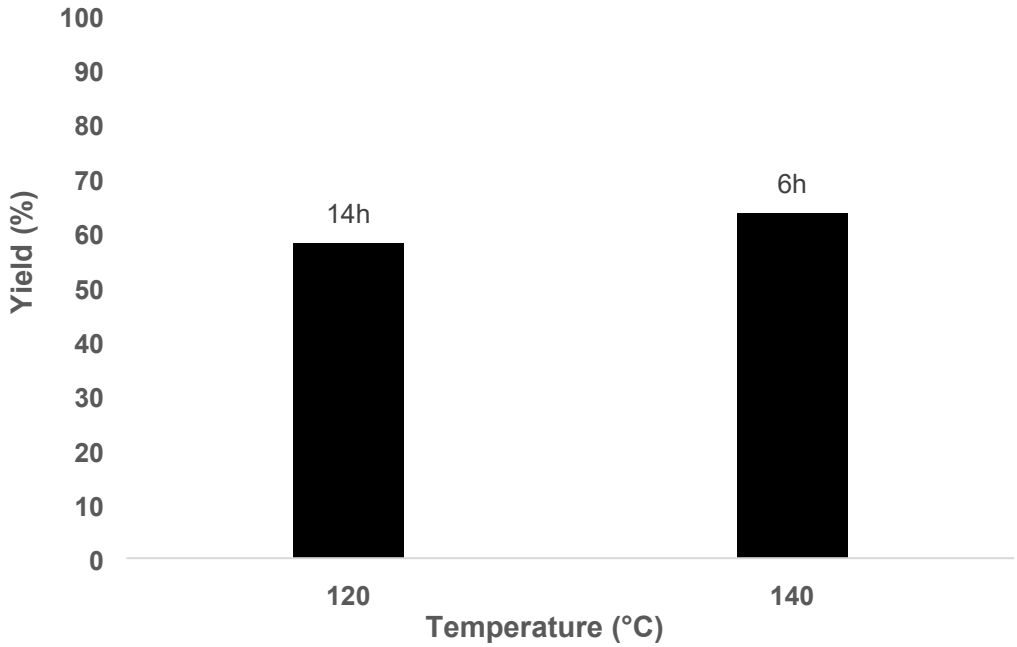
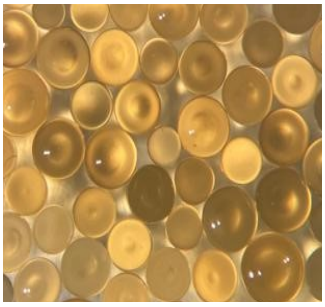
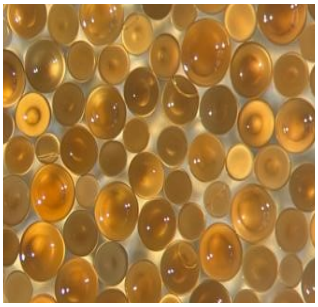


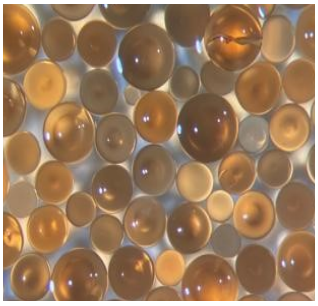
Figure S19 Yield in LA at 120 and 140°C (5 wt% fructose in water)



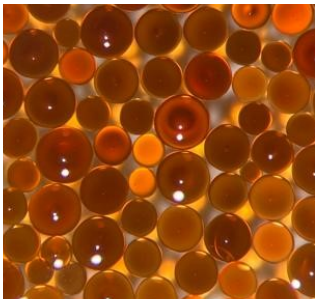
5 min LA yield : 0 %



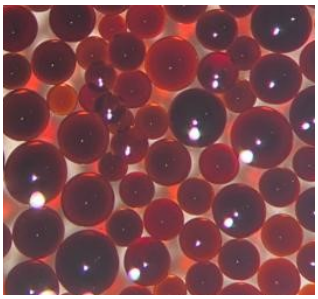
10 min LA yield : 0%



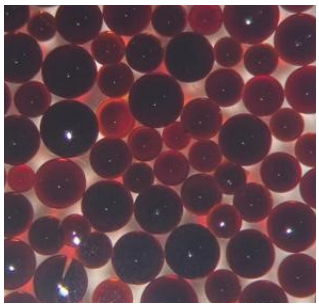
15 min LA yield : 2%



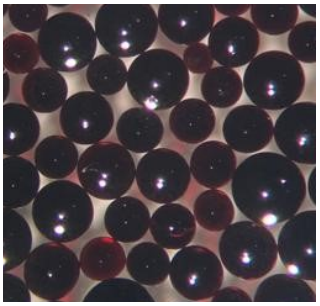
30 min LA yield : 10%



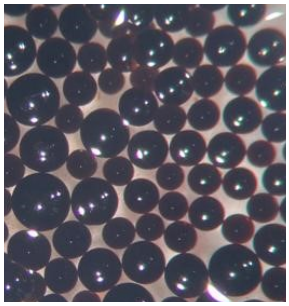
1 h LA yield : 23%



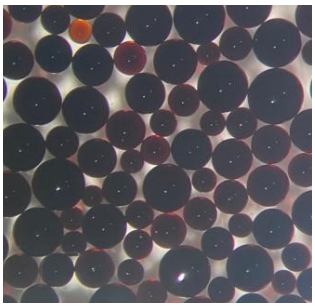
2 h LA yield : 44%



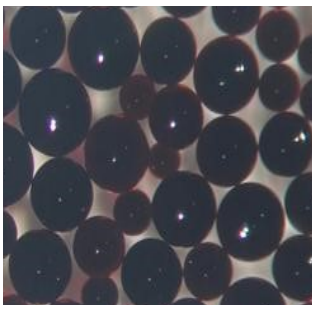
3 h LA yield : 61%



4 h LA yield : 66%



5 h LA yield : 70%



6 h LA yield : 64%

Figure S20 Visual aspect of the Purolite C124-SH as a function of the reaction time in water (140°C, 5 wt% in water)

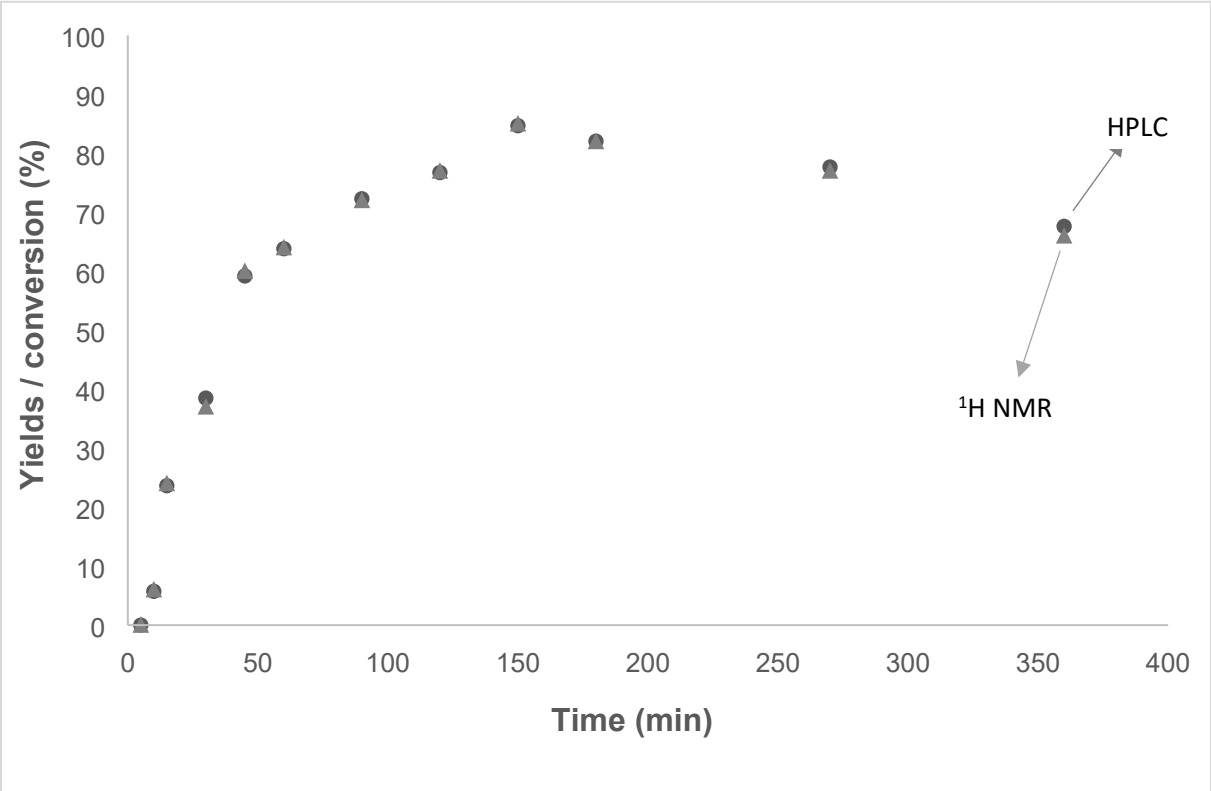
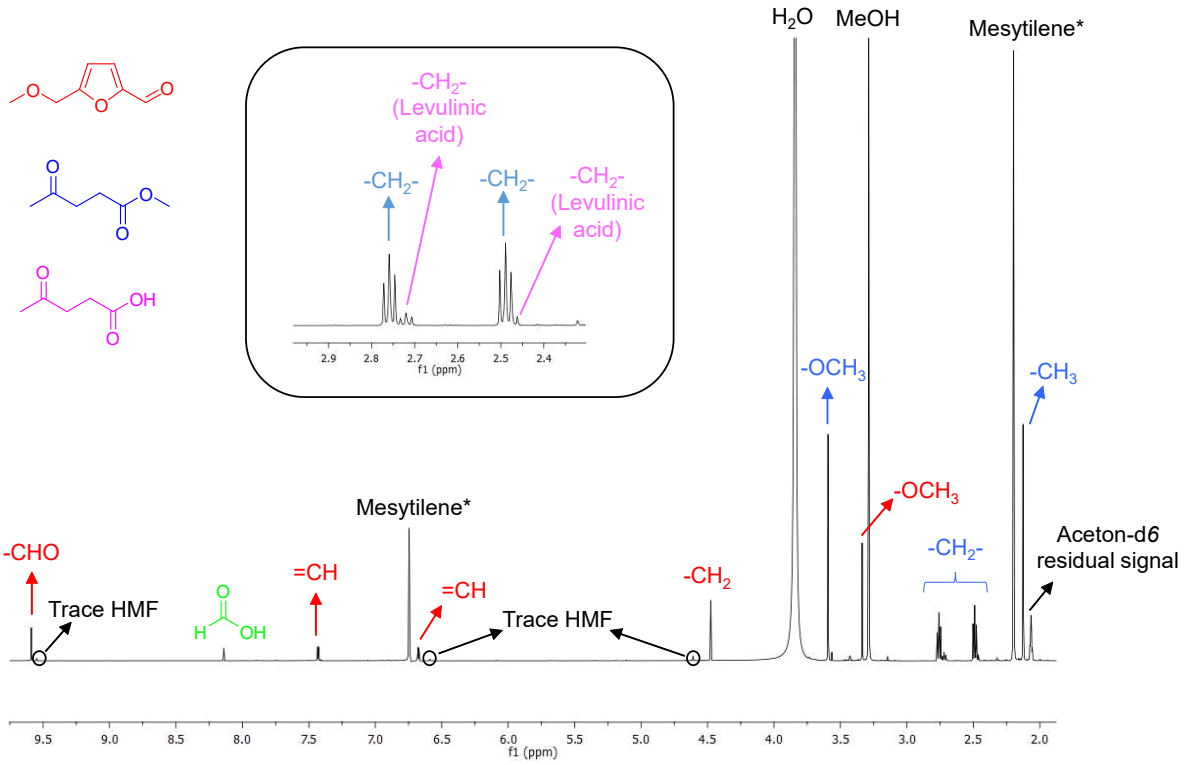


Figure S21 Plot of the methyl levulinate yield as a function of the reaction time in the presence of Purolite C124 SH followed by HPLC and ^{1}H NMR (circle HPLC and triangle ^{1}H NMR) (160°C, 5 wt% fructose in methanol)



* Mesytilene was used as an internal standard

Figure S22 ^{1}H NMR of the crude reaction media in $(CD_3)_2CO$ (methyl formiate was removed during the distillation of methanol under vacuum and was thus not present on the ^{1}H NMR spectrum). ^{1}H NMR collected after 1h of reaction (5 wt% fructose in methanol, 160°C, Purolite C124 SH (0.05 mmol H^+).

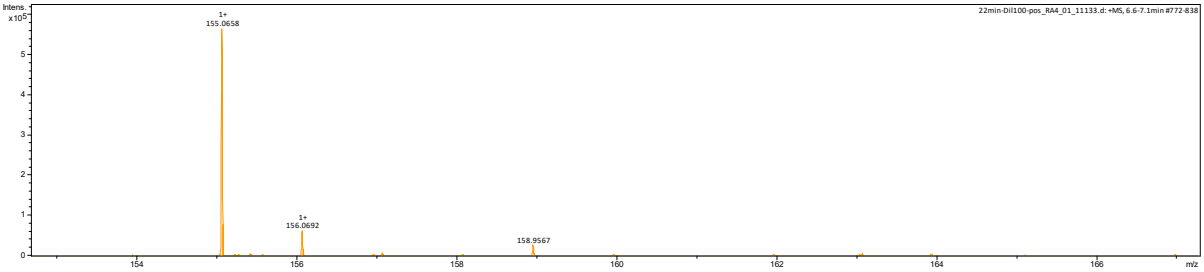


Figure S23. Mass spectrum of the suspected ester between HMF and formic acid (positive mode m/z=155.0657 amu $[M+H]^+$.

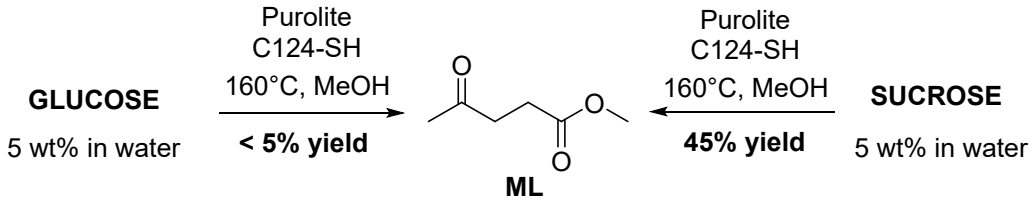


Figure S24: Transposition to glucose and sucrose (5 wt% sugar in MeOH, 160°C, 5 mmol H^+ Purolite C124 SH)

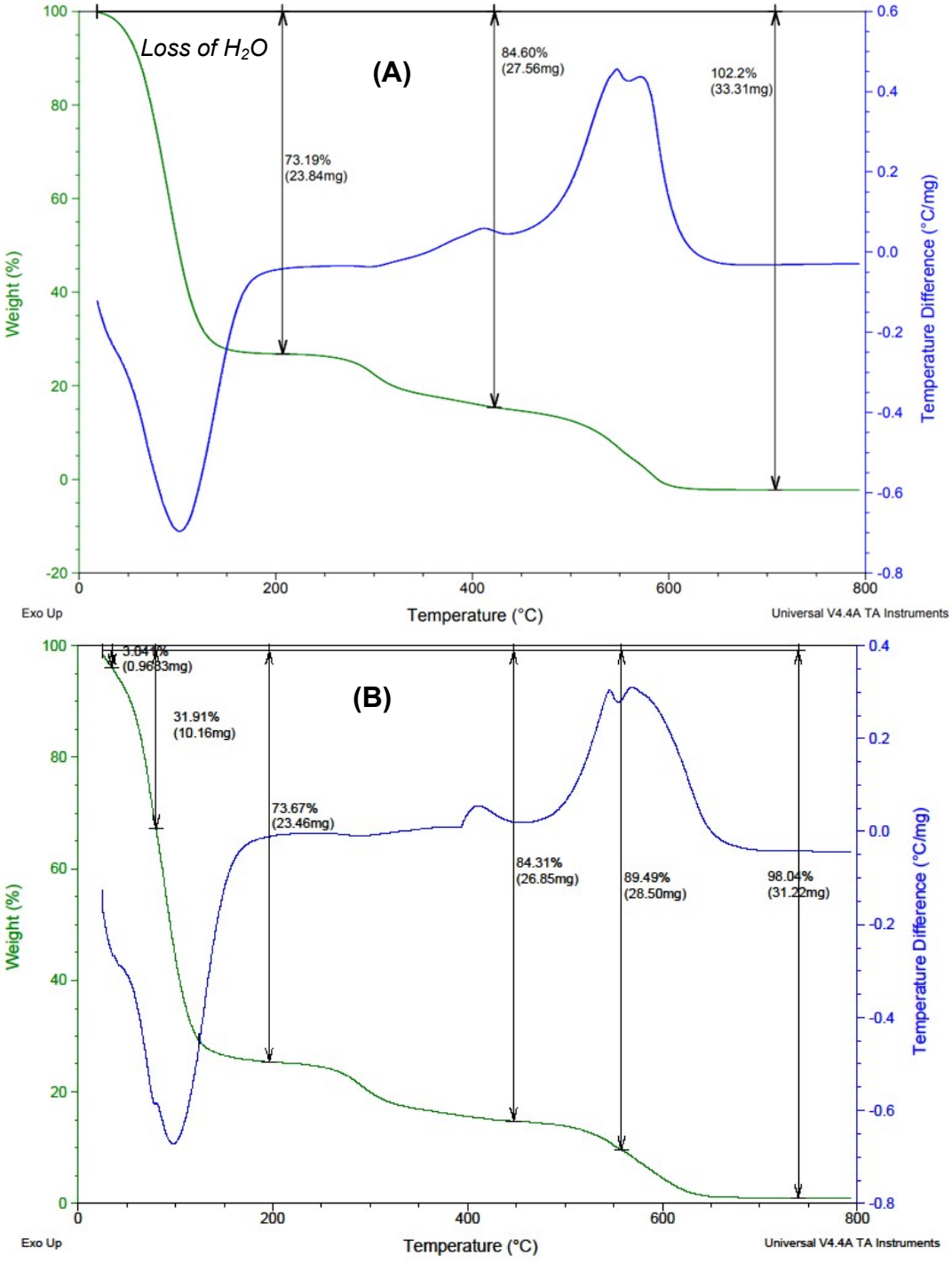


Figure S25: TDA/TGA of (A) fresh and (B) spent Purolite C124 SH performed un air (heating ramp 10°C/min, air flow 100 mL/min)

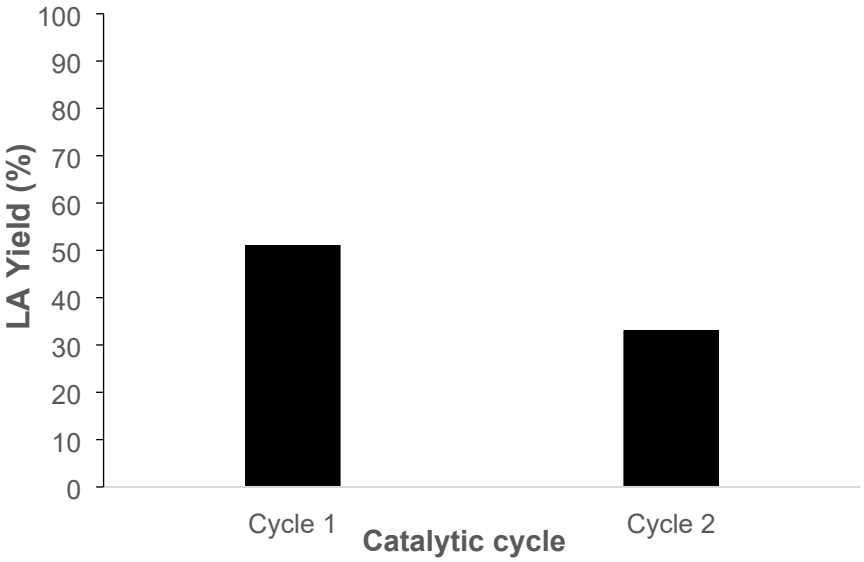


Figure S26 Catalytic recycling of the Amberlyst 119 at 140°C in water (5 wt% fructose, 2 h)

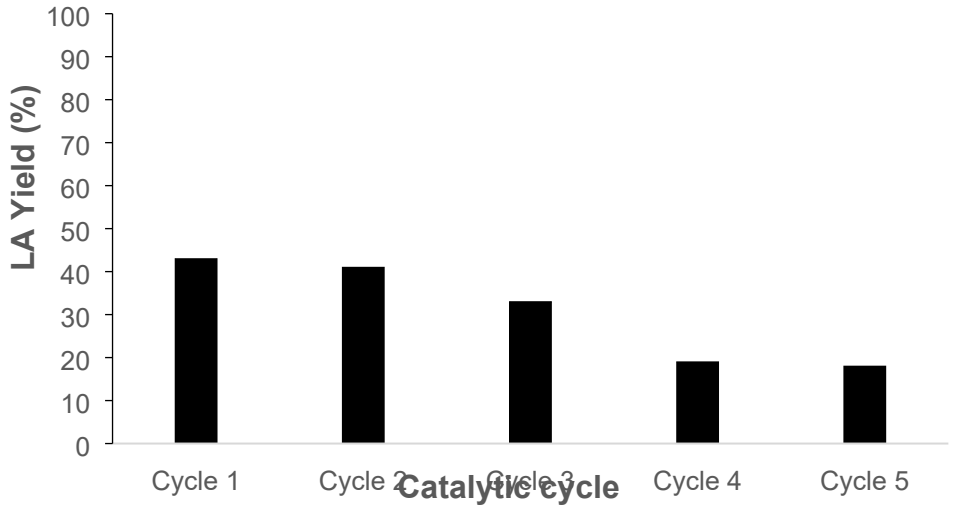


Figure S27 Catalytic recycling of the Amberlyst 16 at 140°C in water (5 wt% fructose, 2 h)

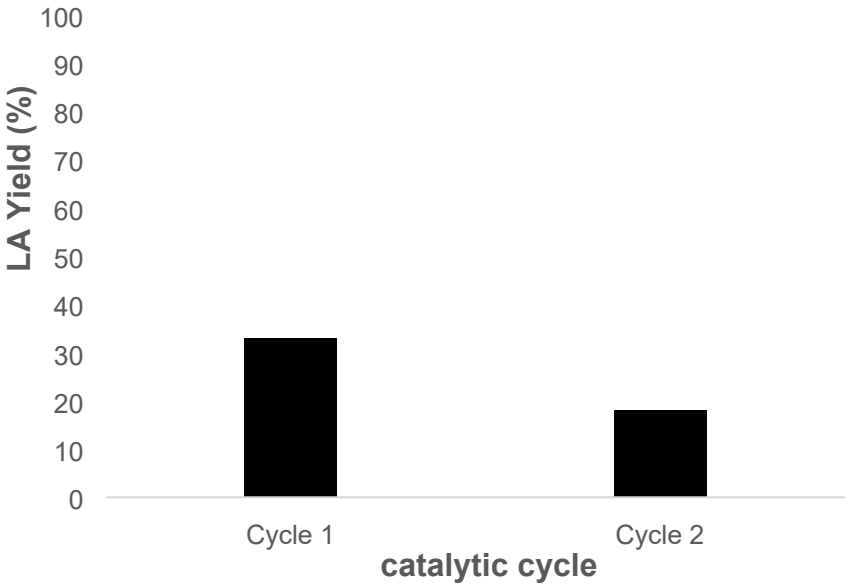


Figure S28 Catalytic recycling of the Amberlyst 36 at 140°C in water (5 wt% fructose, 2 h)

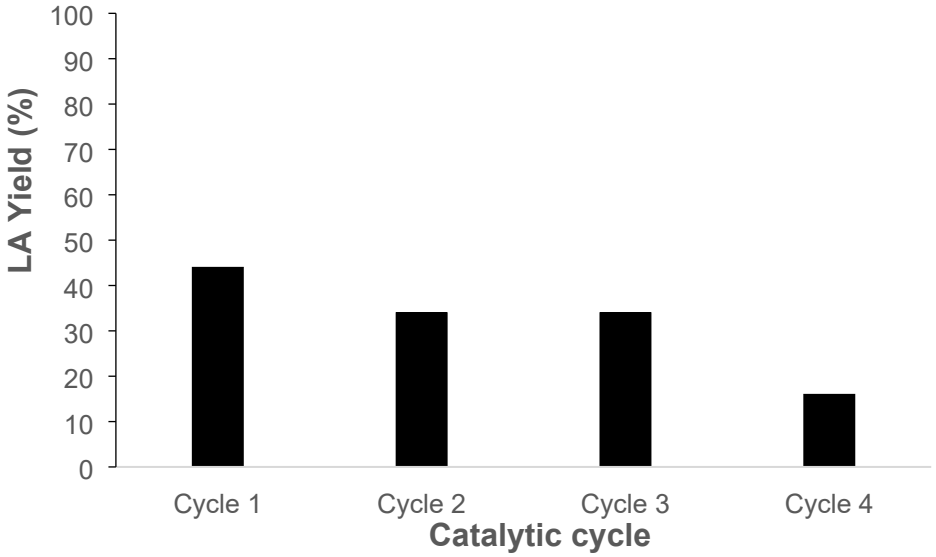


Figure S29 Catalytic recycling of the Amberlyst 45 at 140°C in water (5 wt% fructose, 2 h)

Note: Unfortunately, it was not possible to test the recycling of the Amberlyst 31 cation exchange resin mentioned in the article text. Indeed, Amberlyst 31 was mechanically not stable in water in our conditions, it was rapidly crushed during the stirring once the first catalytic cycle.

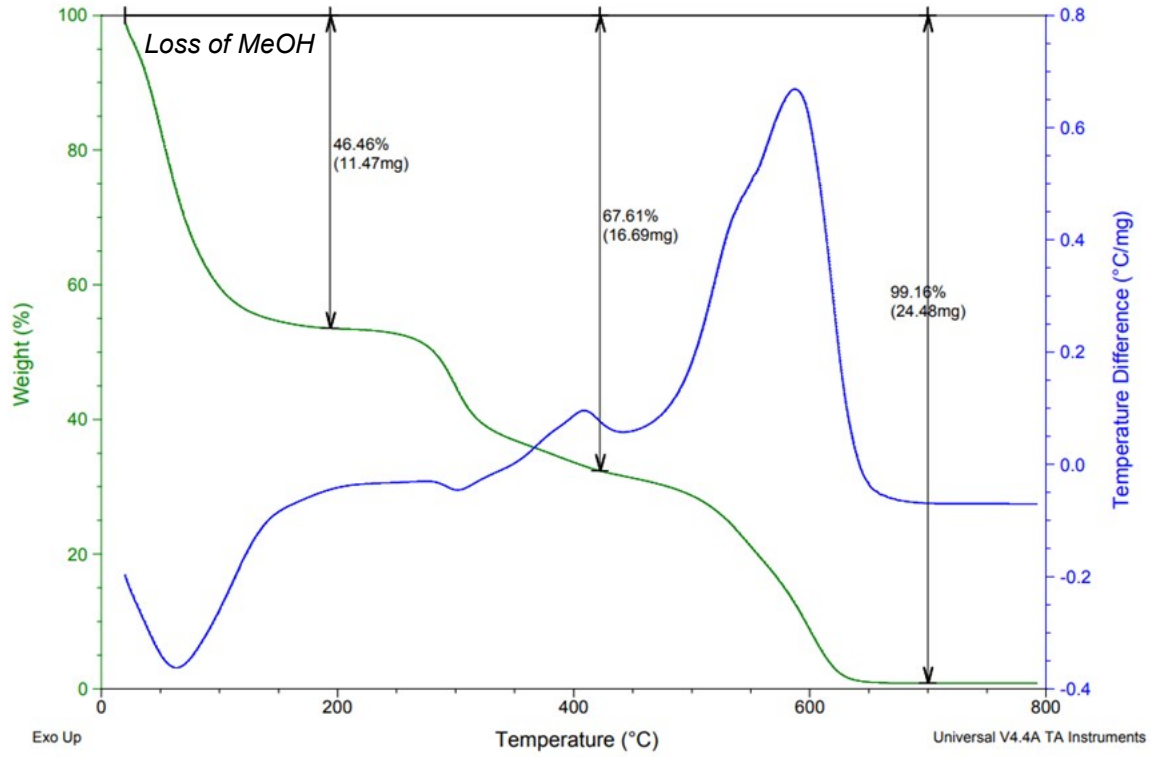


Figure S30: TDA/TGA of Purolite C124 SH after several washing with methanol (heating ramp 10°C/min, air flow 100 mL/min).

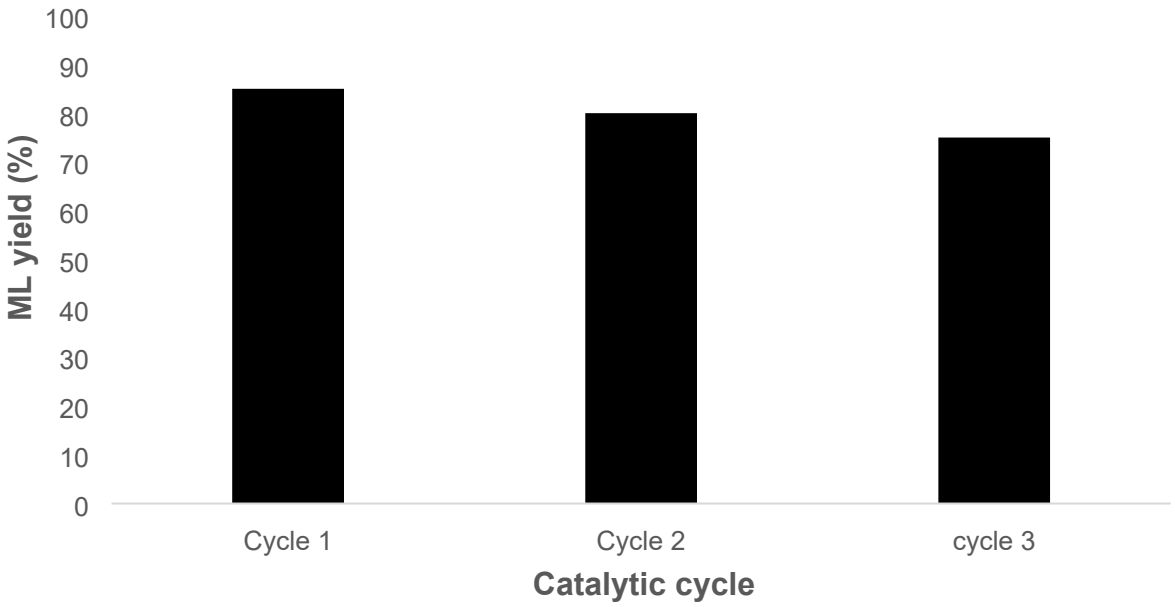


Figure S31 Recyling of Purolite C124-SH after re-hydration between each cycle (magnetic stirring)

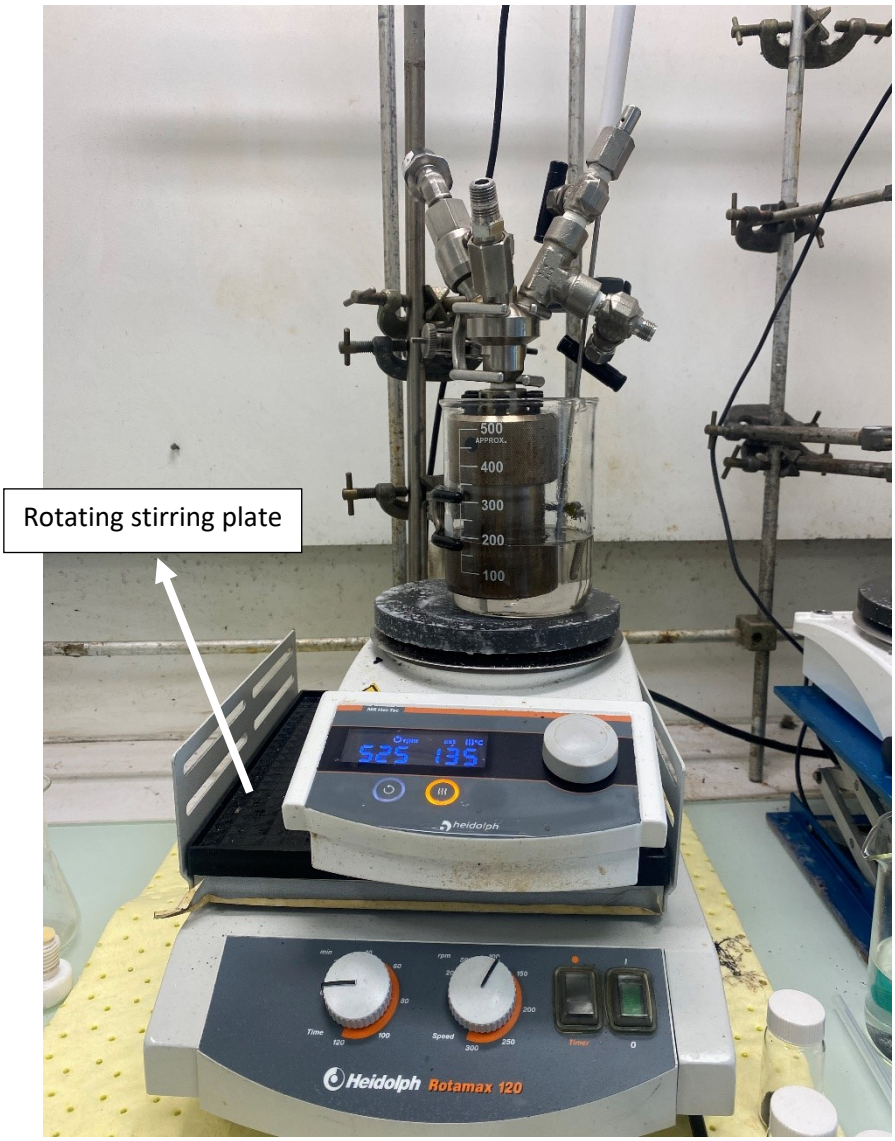
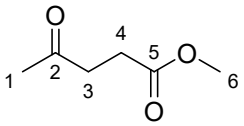


Figure S32. Photo of the orbital stirring

Characterization of the reaction products

Methyl levulinate

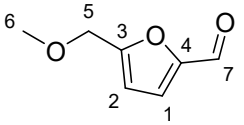


^{1}H NMR (500 MHz, d*6*-Acetone) δ 3.60 (s, 3H), 2.75 (t, 2H), 2.49 (t, 2H), 2.12 (s, 3H).

^{13}C NMR (125 MHz, d*6*-Acetone) δ 206.5, 173.5, 51.7, 38.2, 29.6, 28.2.

UHPLC-HRMS: m/z calculated for $C_6H_{11}O_3$ $[M+H]^+$ 131.0630, found 131.0727.

5-(methoxymethyl)furfural

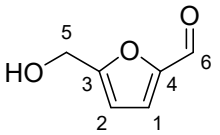


^{1}H NMR (500 MHz, d*6*-Acetone) δ 9.62 (s, 1H), 7.40 (d, *J* = 3.5 Hz, 1H), 6.66 (d, *J* = 3.5 Hz, 1H), 4.48 (s, 2H), 3.34 (s, 3H).

^{13}C NMR (125 MHz, d*6*-Acetone) δ 178.3, 159.1, 153.7, 123.4, 112.2, 66.7, 58.1

UHPLC-HRMS: m/z calculated for $C_7H_9O_3$ $[M+H]^+$ 141.0473, found 141.0546.

5-(hydroxymethyl)furfural

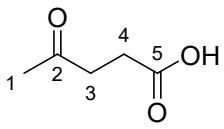


^{1}H NMR (500 MHz, d*6*-Acetone) δ 9.55 (s, 1H), 7.38 (d, *J* = 3.5 Hz, 1H), 6.58 (d, *J* = 3.5 Hz, 1H), 4.73 (s, 1H), 4.64 (s, 2H)

^{13}C NMR (125 MHz, d*6*-Acetone) δ 178.2, 162.8, 153.3, 124.0, 110.2, 57.4.

UHPLC-HRMS : m/z calculated for $C_6H_7O_3$ $[M+H]^+$ 127.0317, found 127.0389.

Levulinic acid



^{1}H NMR (500 MHz, d*6*-Acetone) δ 2.73 (t, 2H), 2.50 (t, 2H), 2.12 (s, 3H).

13C NMR (125 MHz, d*6*-Acetone) δ 206.9, 174.6, 38.1, 29.6, 28.1.

UHPLC-HRMS: m/z calculated for $C_5H_7O_3$ $[M-H]^-$ 115.0473, found 115.0389.