Supporting Information

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Efficient catalytic upgrading of levulinic acid into alkyl levulinates by resin-supported acids and flow reactors

E-factor calculation for batch reaction of LA (0.86 mmol) and 1-pentanol (86 mmol) over PS-pTsOH at 90°C

[1g (LA) + 7.6g (1-pentanol) + 0.25g (Al_2O_3)+ 0.044g (15% of catalyst not recovered) – 1.47g (pentyl levulinate 3) – 6.5 g (96% recovered 1-pentanol)]/1.47g (pentyl levulinate 3)= 0.62

E-factor calculation for batch reaction of LA (0.86 mmol) and 1-pentanol (86 mmol) over Amberlyst-15 at 70°C

[1g (LA) + 7.6g (1-pentanol) + 0.32g (Al_2O_3) + 0.027g (15% of catalyst not recovered) – 1.28g (pentyl levulinate 3) – 6.5 g (96% recovered 1-pentanol)]/1.28g (pentyl levulinate 3)= 0.90

Typical procedure for the preparation of pentyl levulinate 3 over heterogeneous acid catalysts under flow conditions at 90°C.

Flow procedures were performed using a HPLC pump, and PTFE (2 m length, 5 mm ϕ_{int}, 7 mm ϕ_{ext}) or Omnifit Glass Columns (11 cm length, 1 cm ϕ_{int}, 1.4 cm ϕ_{ext}, 4x) as the catalyst column. A pre-mixed mixture of LA **1** and 1-pentanol **2** (1:10 molar ratio) was charged into a tank functioning as a reservoir. Catalysts were mixed and dispersed in 0.5 or 1 mm diameter solid glass beads and charged in the appropriate column. The equipment was connected to the pump by appropriate tubes and valves, and installed into a thermostatic box. The reaction mixture was pumped at the following flow rates: 0.44 mL/min (Aquivion mP98), 0.1 mL/min (A-15), 0.5 ml/min (PS-pTsOH). The flow rates were chosen in order to achieve the highest LA conversion in the shorter time. Reaction was monitored by ^{1}H-NMR, using 4-bromoanisole as internal standard.

E-factor calculation under flow conditions over Amberlyst-15

[7.5g (LA) + 56.8g (1-pentanol) + 2.5g (Al_2O_3) – 11.5g (pentyl levulinate) 3) – 48.9 g (96% recovered 1-pentanol)]/ 11.5 (pentyl levulinate 3) = 0.58

E-factor calculation under flow condition over Aquivion p98

[24.3 (LA) + 184.8 (1-pentanol) – 36.3g (pentyl levulinate 3) –159.6g (96% recovered 1-pentanol)]/36.3g (pentyl levulinate 3) = 0.36

E-factor calculation under flow condition over PS-pTsOH

[32.5(LA) + 246.4 (1-pentanol) + 0.5 g (Al_2O_3) - 52g (pentyl levulinate 3) –210.6g (96% recovered 1-pentanol)] /36.3g (pentyl levulinate 3) = 0.32

Table S1. Esterification reaction[a] of LA with 1-pentanol in batch conditions

entry	catalyst	C (%)[b]
1	-	4
2	Nafion NR50®	60
3	p-TsOH	78

[a]Reaction conditions: 10 mol% catalyst, 1:10 LA/1-pentanol molar ratio, 90°C, 24h. [b] LA conversion to pentyl levulinate **3**, determined by ^{1}H-NMR analysis, using 4-bromoanisole as internal standard; the remaining material was the unreacted mixture of **1** and **2**.

Table S2. Recycling of Aquivion mP98, PS-pTsOH and Amberlyst-15 in esterification reaction[a] of LA with 1-pentanol

Run	catalyst	Yield (%)[b]	Catalyst recover (wt%)
1	Aquivion mP98	72	n.a.
	PS-pTsOH	64	n.a.
	Amberlyst-15	62	n.a.
2	Aquivion mP98	70	98
	PS-pTsOH	58	85
	Amberlyst-15	59	85
3	Aquivion mP98	67	96
	PS-pTsOH	53	85
	Amberlyst-15	58	83
4	Aquivion mP98	68	95
	PS-pTsOH	53	80
	Amberlyst-15	57	45
5	Aquivion mP98	67	96
	PS-pTsOH	53	75
	Amberlyst-15	58	42

[a]Reaction conditions: 10 mol% catalyst, 1:5 LA/1-pentanol molar ratio, 70°C, 24h. [b]Isolated yield of pentyl levulinate **3**.

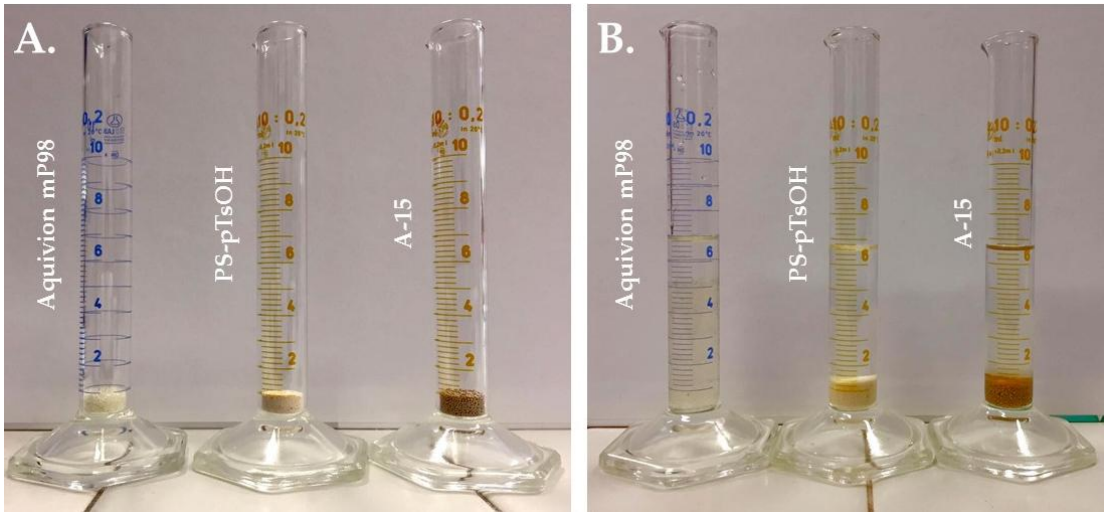

Figure S1. Swelling in 1-pentanol of the three investigated resins.

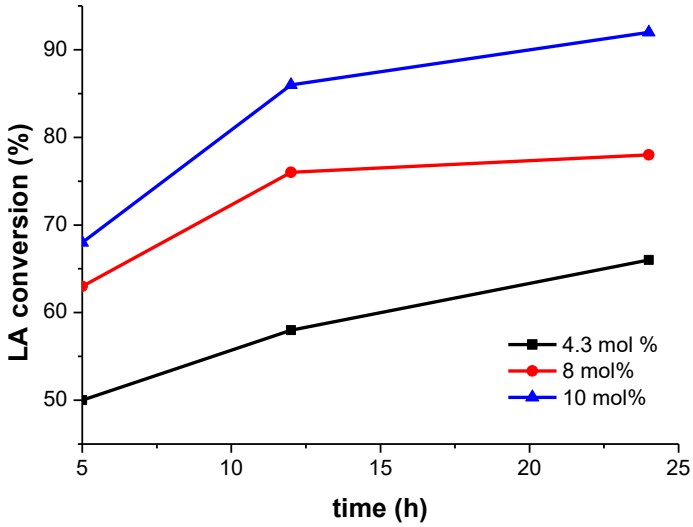

Figure S2. Effect of Aquivion mP98 catalyst loading on conversion of levulinic acid into pentyl levulinate (1:10 LA to pentanol molar ratio, 90°C)

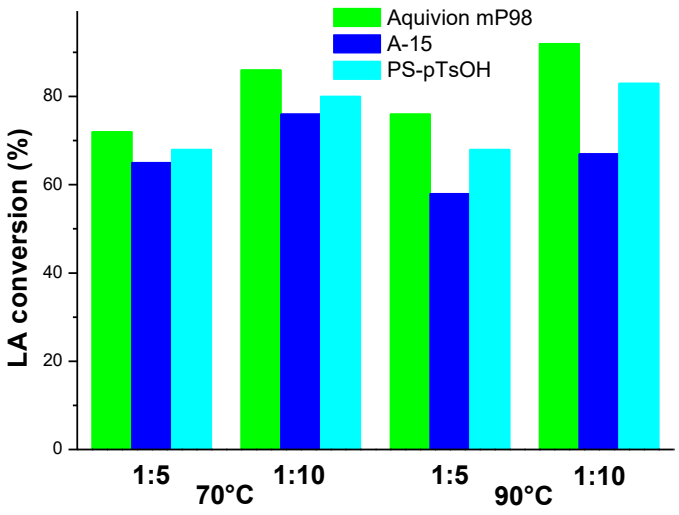

Figure S3. Effect of the mole ratio on conversion of levulinic acid into pentyl levulinate (10 mol% catalyst, 24h)

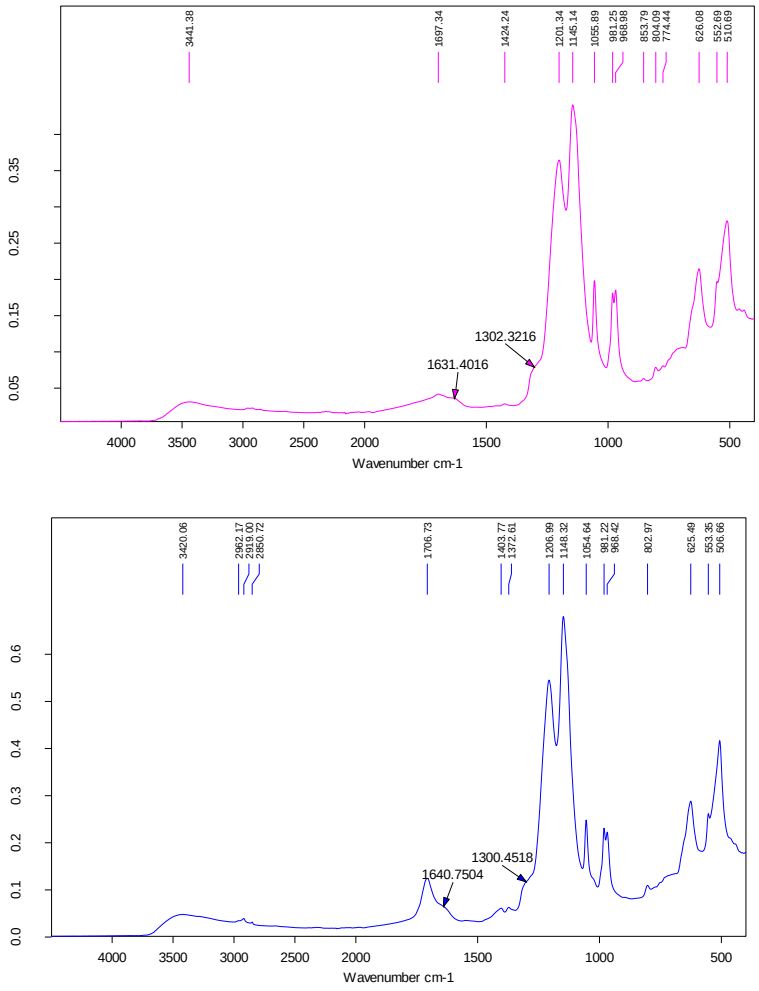

Figure S4. FTIR spectra of Nafion NR50 before use (upper panel) and after esterification reaction of LA with 1-pentanol (lower panel)

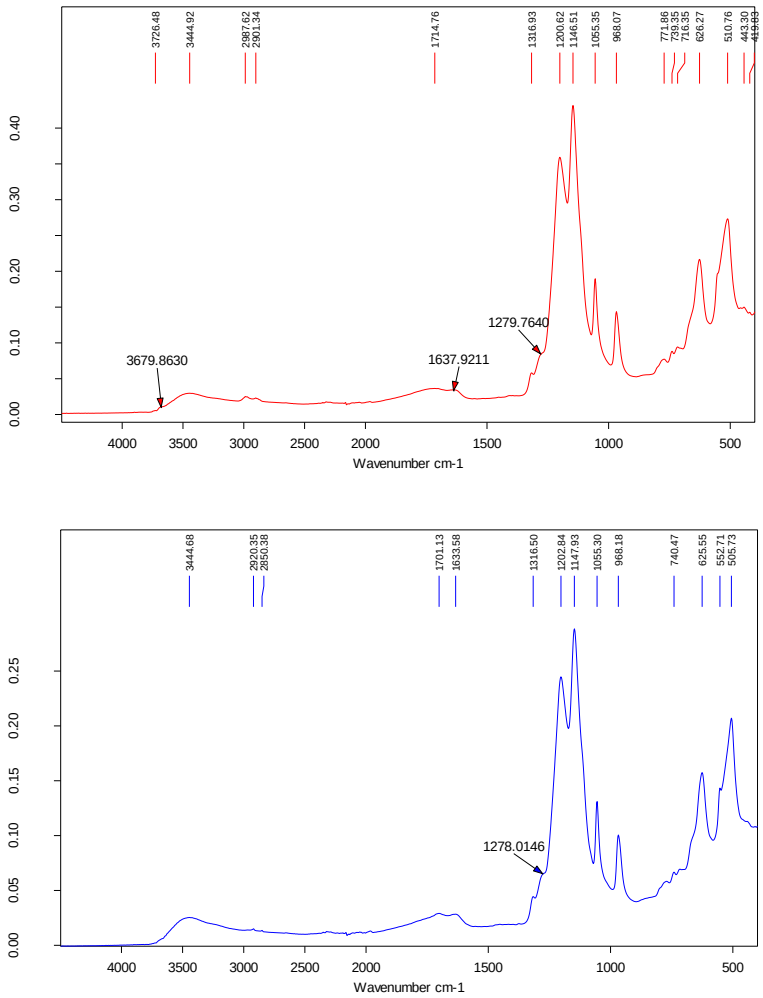

Figure S5. FTIR spectra of Aquivion mP98 before use (upper panel) and after five runs (lower panel).

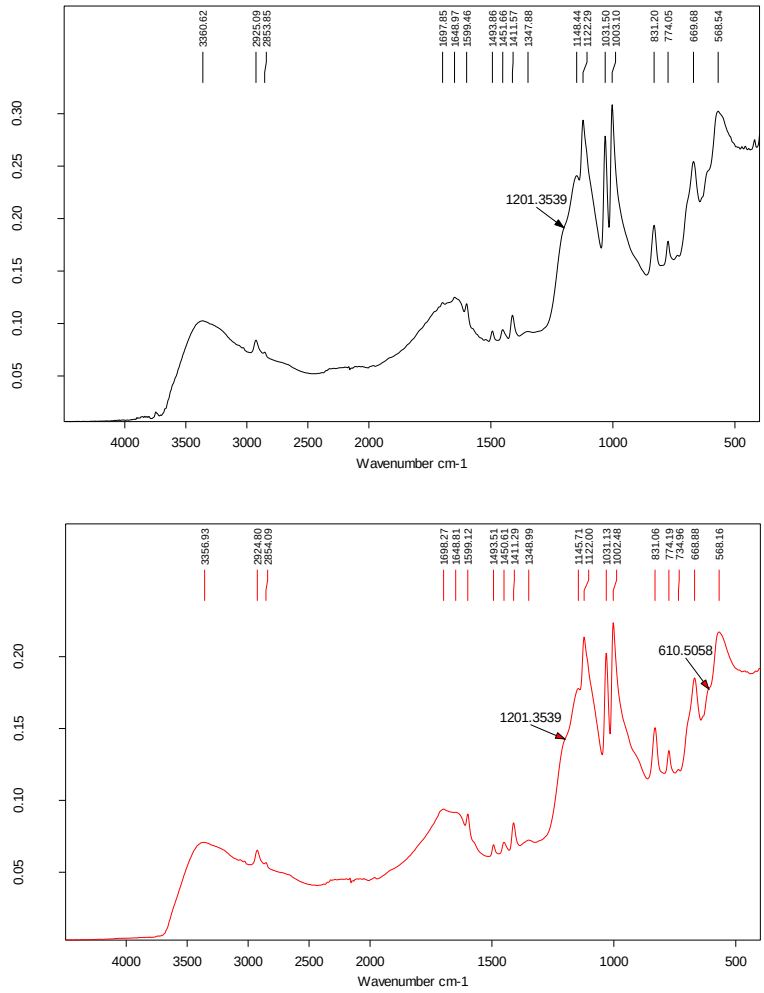

Figure S6. FTIR spectra of PS-pTsOH before use (upper panel) and after five runs (lower panel).

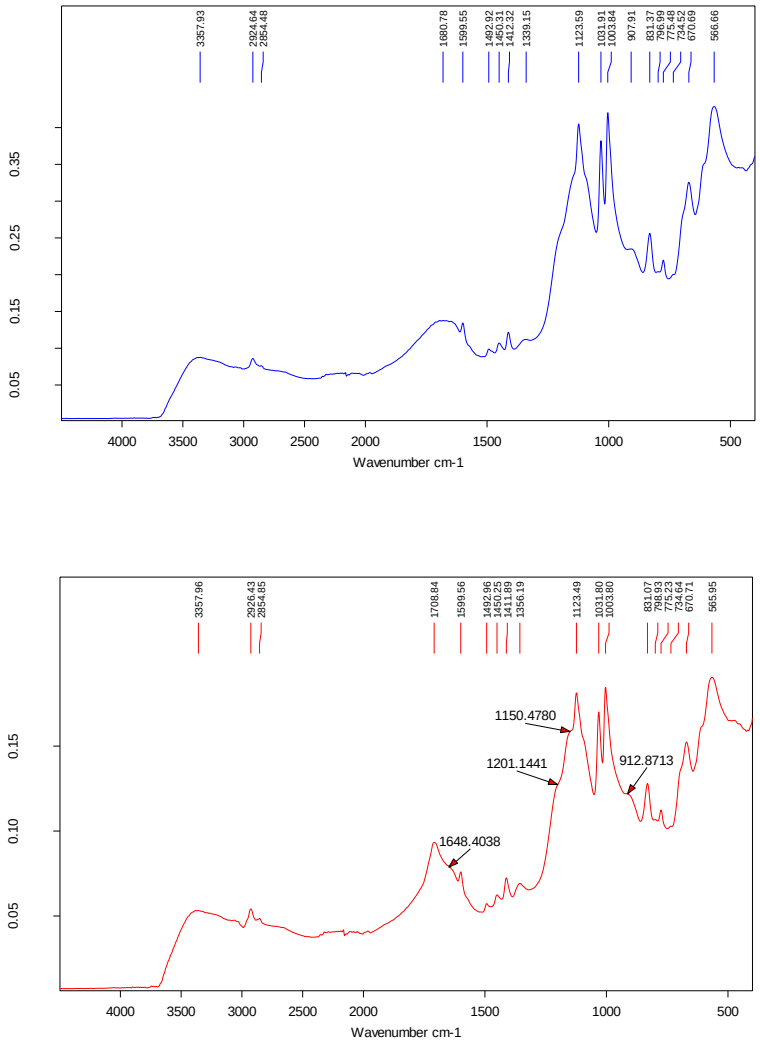

Figure S7. FTIR spectra of Amberlyst 15 before use (upper panel) and after five runs (lower panel).

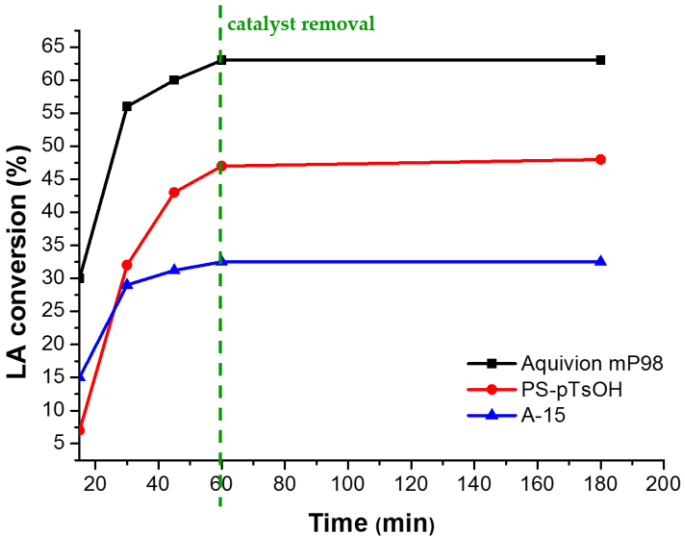

Figure S8. Hot filtration test for the heterogeneous acid catalyzed esterification reaction of LA and 1-pentanol (1:5 molar ratio, 10 mol% catalyst) at 90°C.

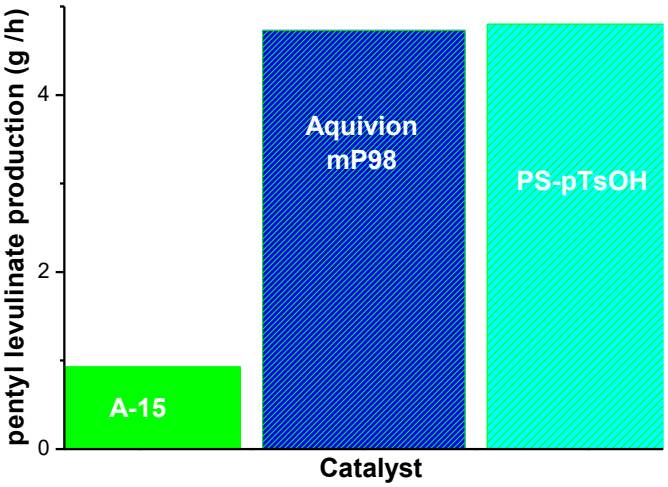

Figure S9. Comparison between the abilities of the investigated catalysts in producing pentyl levulinate **3** under flow conditions.