Electronic Supplementary Material (ESI) for Green Chemistry.

Boosting biomass valorisation. Synergistic design of continuous flow reactors and water-tolerant polystyrene acid catalysts for a non-stopping production of esters

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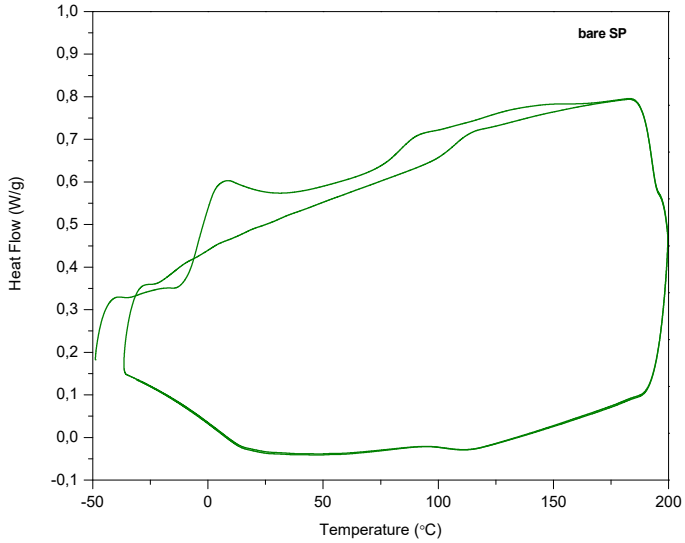

Figure S1. DSC plot for bare SP resin.

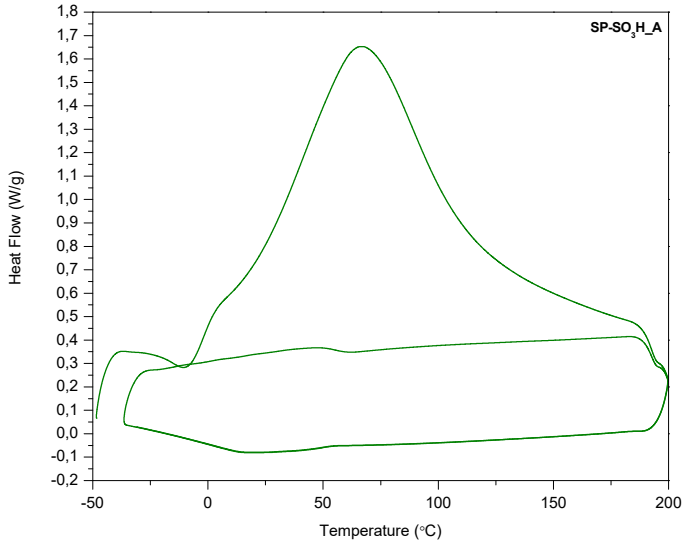

Figure S2. DSC plot for SP-SO_3H_A.

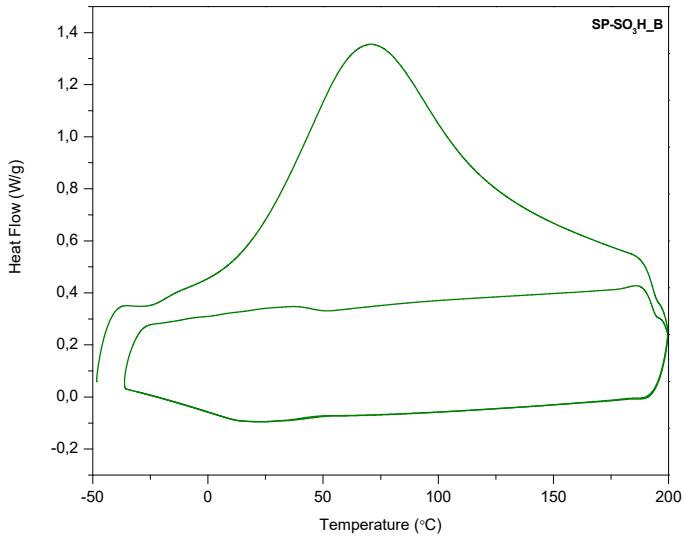

Figure S3. DSC plot for SP-SO_3H_B.

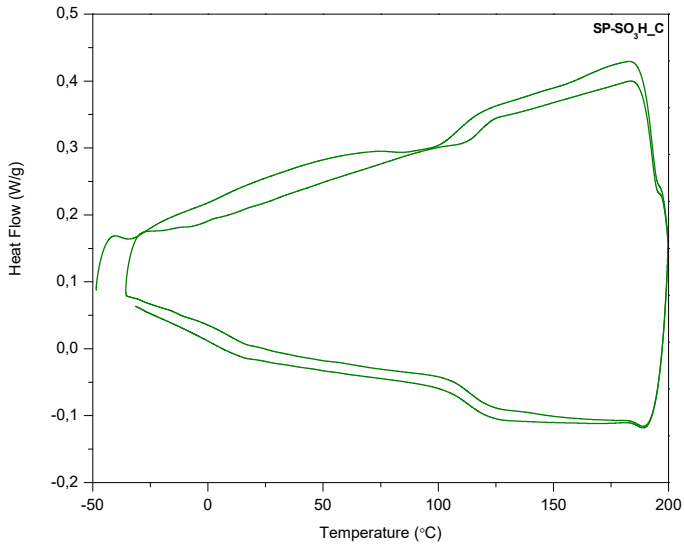

Figure S4. DSC plot for SP-SO_3H_C.

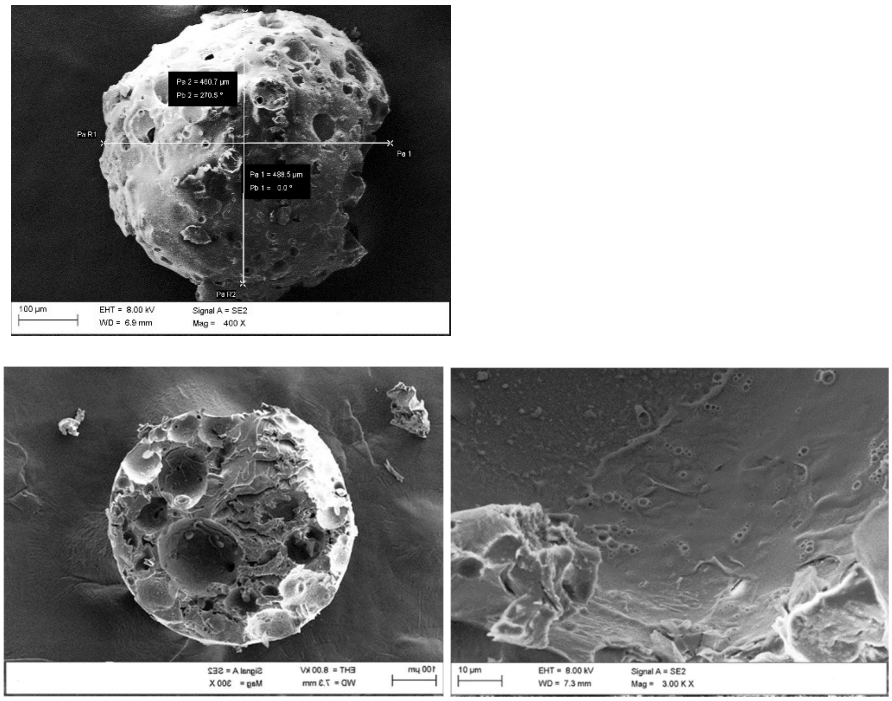

Figure S5. Representative SEM images of external (upper panel) and internal (lower panel) surface of bare SP resin

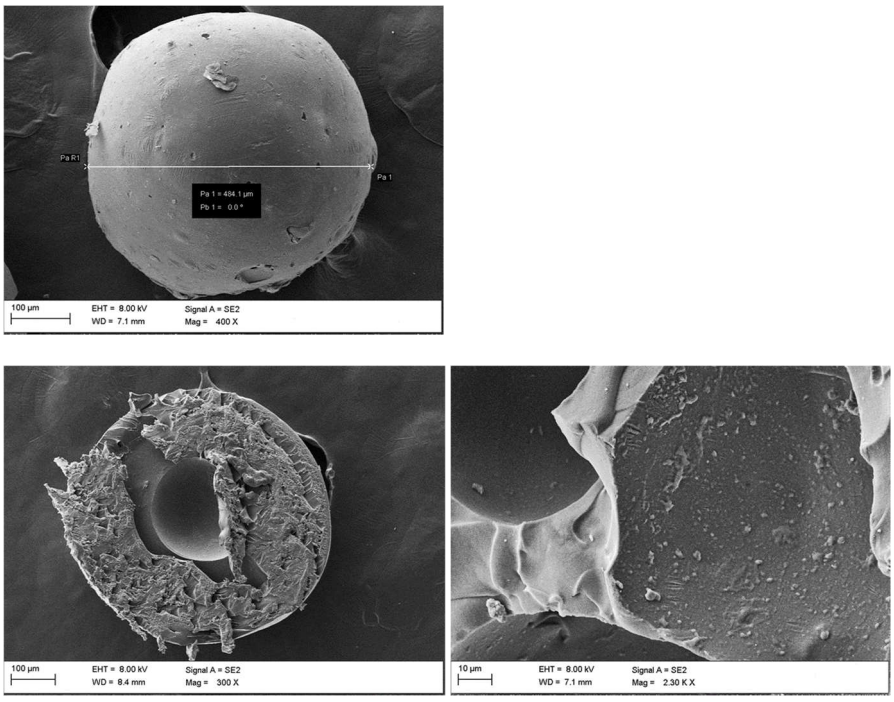

Figure S6. Representative SEM images of external (upper panel) and internal (lower panel) surface of bare SP-SO_3H_B

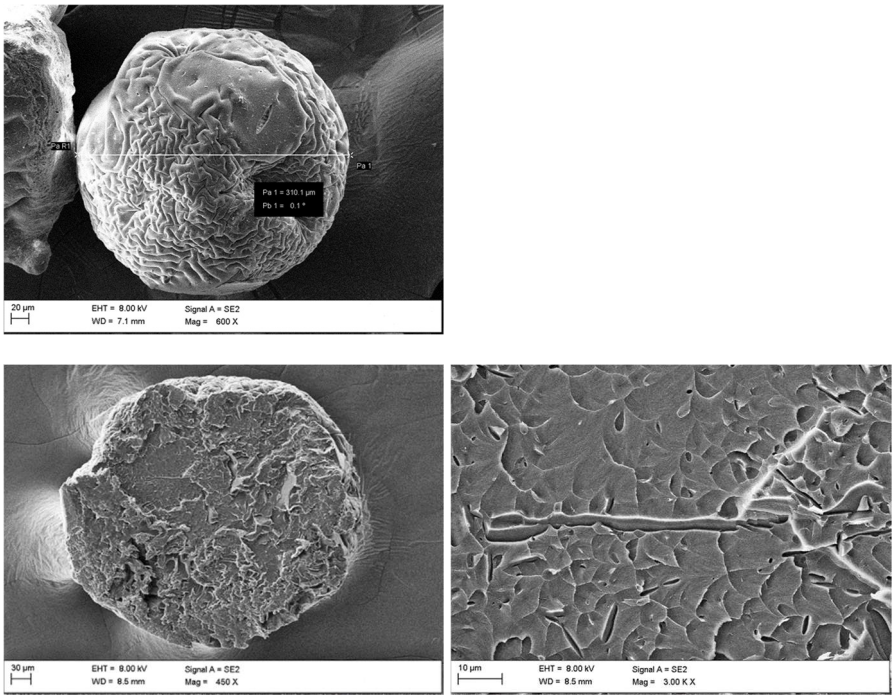

Figure S7. Representative SEM images of external (upper panel) and internal (lower panel) surface of bare SP-SO_3H_C

Table S1. Esterification[1] reaction of LA **5** with 1-pentanol (**6a**) catalyzed by SP-SO_3H_B-C

Entry	Catalyst	t (h)	C (%)[2]
1		1	81
2	SP-SO_3H_B	2	88
3		5	>99
4		1	70
5	SP-SO_3H_C	2	72
6		5	85

[1]Reaction conditions: LA/1-pentanol = 1:10 molar ratio; T=70°C; catalyst amount: 10 mol% (referred to the amount of immobilized -SO_3H moieties). [2] Determined by GLC analysis, by methylating residual LA with diazomethane; remaining material was the unreacted mixture of LA and 1-pentanol.

Table S2. Esterification reaction of LA **5** with 1-pentanol (**6a**) catalyzed by SP-SO_3H_A

Entry	Catalyst (mol%)[1]	LA/ 1-pentanol	T (°C)	t (h)	C (%)[2]
1	4.3	1:5	50	1	63
2	8				78
3	10				76
4	4.3			2	54
5	8				78
6	10				79
7	4.3			5	75
8	8				85
9	10				83
10	4.3		70	1	82
11	8				86
12	10				79
13	4.3			2	86
14	8				93
15	10				80
16	4.3			5	90
17	8				95
18	10				85
19	4.3	1:10	50	1	45
20	8				73
21	10				64
22	4.3			2	46
23	8				73
24	10				72
25	4.3			5	60
26	8				82
27	10				82
28	4.3		70	1	58
29	8				77
30	10				85 90[3]
31	4.3			2	83
32	8				93
33	10				94 94[3]
34	4.3			5	90
35	8				>99
36	10				>99 >99[3]

[1]Referred to the amount of immobilized -SO_3H moieties. [2] Determined by GLC analysis, by methylating residual LA with diazomethane; remaining material was the unreacted mixture of LA and 1-pentanol; [3]Molecular sieves (1:1 wt/wt_{LA}).

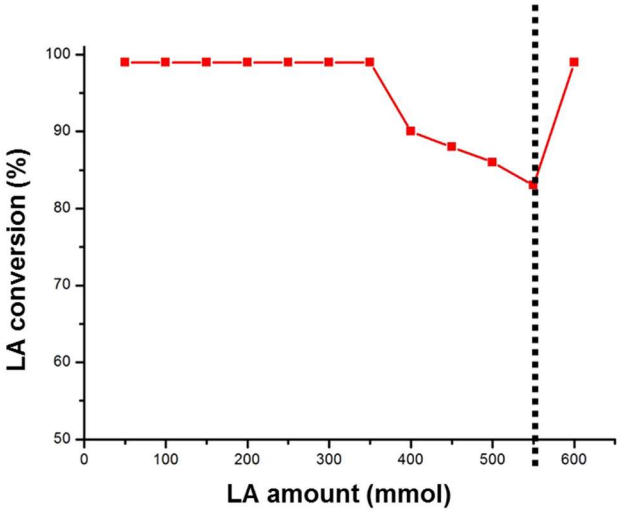

Figure S8. Graphic chart of continuous flow levulinic acid (LA, **5**) feeding (X-axis) and corresponding conversion to **7a** (Y-axis).

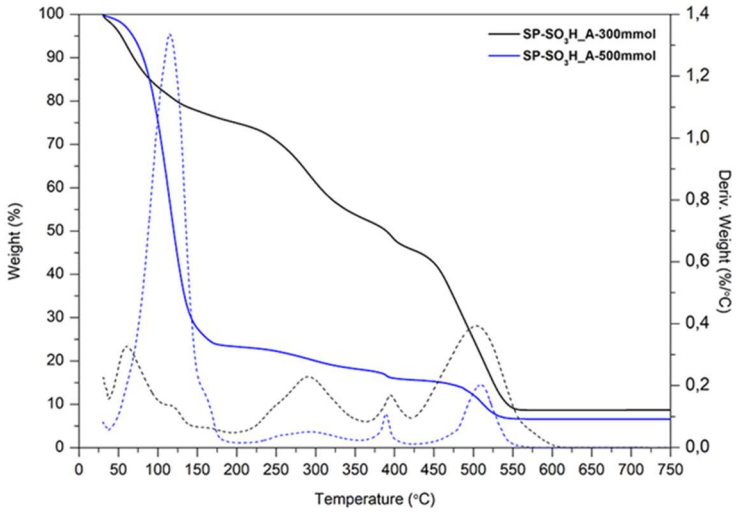

Figure S9. TGA and DTG curves of SP-SO_3H_A samples; Weight loss curves (solid lines) and their respective 1st derivatives (dashed lines) for sample withdrawn at 300 (blue curves) and 500 mmol (black curves) LA conversion.

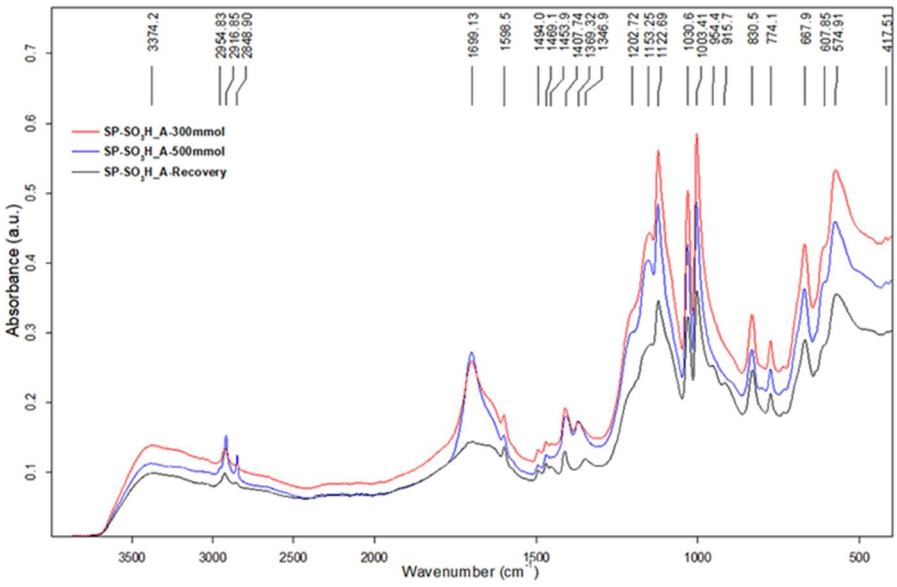

Figure S10. FTIR plots of SP-SO_3H_A samples withdrawn at 300 (red line) and 500 mmol (blue line) LA conversion. FTIR pattern of regenerated SP-SO_3H_A (black line) is also reported for comparison purposes.

E-factor calculation for the esterification reaction of LA (5) with 1-pentanol (6a) under flow conditions.
***E-factor**: [58 g (LA) + 440 g (1-pentanol) - 91 g (pentyl levulinate **7a**) – 380 g (96% recovered excess 1-pentanol)]/91 g (pentyl levulinate **7a**) = 0.29*

E-factor calculation for the esterification reaction of LA (5) with ethanol (6b) under flow conditions.
***E-factor**: [11.6 g (LA) + 46 g (ethanol) - 13.4 g (ethyl levulinate **7b**) – 39.3 g (95% recovered excess ethanol)]/13.4 g (ethyl levulinate **7b**) = 0.36*
The Al_2O_3 scavenger was not considered in the calculation due to its complete regeneration.

E-factor calculation for the esterification reaction of LA (5) with octanol (6e) under flow conditions.
***E-factor**: [11.6 g (LA) + 130 g (1-octanol) - 20.06 g (octyl levulinate **7e**) – 105.3 g (90% recovered excess 1-octanol)]/20.06 g (octyl levulinate **7e**) = 0.81*
The Al_2O_3 scavenger was not considered in the calculation due to its complete regeneration.

E-factor calculation for the esterification reaction of LA (5) with i-propanol (6g) under flow conditions.
***E-factor:** [11.6 g (LA) + 60 g (i-propanol) - 14.22 g (i-propyl levulinate **7g**) – 48.6 g (90% recovered excess i-propanol)]/14.22 g (i-propyl levulinate **7g**) = 0.61*
The Al_2O_3 scavenger was not considered in the calculation due to its complete regeneration.

E-factor calculation for the esterification reaction of LA (5) with sec-butanol (6h) under flow conditions.
***E-factor:** [11.6 g (LA) + 74 g (sec-butanol) - 15.48 g (sec-butyl levulinate **7h**) – 58.6 g (88% recovered excess sec-butanol)]/15.48 g (sec-butyl levulinate **7h**) = 0.74*
The Al_2O_3 scavenger was not considered in the calculation due to its complete regeneration.

E-factor calculation for the esterification reaction of 3-HB (8) with butanol (6d) under flow conditions.
***E-factor:** [10.4 g (3-HBA) + 74 g (1-butanol) - 15.52 g (butyl-3-hydroxybutyrate **9**) – 61.3 g (92% recovered excess 1-butanol)]/15.52 g (butyl-3-hydroxybutyrate **9**) = 0.49*