

A green chemistry approach to catalytic synthesis of ethyl levulinate

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Supporting information

Table S1 Binodal points data for the pseudo-ternary mixtures containing DES (either ChCl:OxAc or ChCl:pTSA), EL, and LA or EtOH, at 313.15 or 333.15 K, in mass fraction.¹

DES	313.15 K						333.15 K					
	W _{DES}	W _{EL}	W _{LA}	W _{DES}	W _{EL}	W _{EtOH}	W _{DES}	W _{EL}	W _{LA}	W _{DES}	W _{EL}	W _{EtOH}
ChCl:OxAc	0.545	0.213	0.241	0.142	0.656	0.202	0.334	0.354	0.311	0.152	0.659	0.189
	0.648	0.154	0.198	0.237	0.576	0.187	0.267	0.422	0.312	0.207	0.585	0.208
	0.701	0.135	0.164	0.361	0.445	0.193	0.255	0.441	0.304	0.325	0.502	0.173
	0.792	0.098	0.110	0.433	0.393	0.173	0.207	0.472	0.321	0.399	0.434	0.167
	0.104	0.564	0.332	0.525	0.329	0.147	0.066	0.637	0.297	0.521	0.329	0.149
	0.191	0.483	0.325	0.659	0.218	0.123	0.107	0.583	0.310	0.625	0.249	0.126
	0.056	0.615	0.329	0.741	0.166	0.093	0.424	0.304	0.272	0.660	0.231	0.109
	0.273	0.368	0.360	0.758	0.155	0.088	0.493	0.261	0.246	0.710	0.192	0.098
	0.302	0.339	0.359				0.600	0.199	0.201			
	0.364	0.282	0.354				0.674	0.164	0.162			
	0.448	0.239	0.313				0.710	0.141	0.149			
							0.752	0.093	0.154			
ChCl:pTSA	0.445	0.506	0.049	0.546	0.438	0.016	0.544	0.428	0.028	0.545	0.445	0.010
	0.284	0.642	0.074	0.368	0.594	0.038	0.377	0.593	0.030	0.374	0.610	0.016
	0.209	0.710	0.081	0.278	0.671	0.051	0.298	0.672	0.030	0.290	0.688	0.022
	0.165	0.748	0.087	0.228	0.714	0.058	0.247	0.724	0.029	0.232	0.740	0.029

¹ Standard uncertainties, u, are u (T) = 0.03 K, u (w) = 0.004

Table S2 Optimisation of the operational conditions for the esterification of LA to EL under conventional heating and stirring method.¹

Entry	Catalyst	Catalyst loading [wt%]	EtOH:LA molar ratio	T [K]	t [h]	LA conversion ² [%]	EL Yield ² [%]
1	-	-	5	343.15	180	9.78	4.47
2	ChCl	5	5	343.15	180	9.45	4.64
3	OxAc	5	5	343.15	180	12.70	10.31
4		5	5	343.15	180	17.44	12.81
5		10	5	343.15	180	24.11	21.49
6		20	5	343.15	180	34.90	31.89
7		35	5	343.15	180	42.01	39.21
8		50	5	343.15	180	43.57	40.20
9		110	5	343.15	180	55.80	55.80
10		185	5	343.15	180	72.15	70.29
11		5	5	313.15	180	8.54	0.88
12		5	5	323.15	180	12.44	2.38
13		5	5	333.15	180	17.29	9.25
14	ChCl:OxAc	5	5	353.15	180	19.53	15.88
15		5	5	363.15	180	22.45	19.10
16		5	5	343.15	10	8.05	1.97
17		5	5	343.15	60	15.92	10.22
18		5	5	343.15	120	20.78	13.75
19		5	5	343.15	300	24.23	83.76
20		5	1	343.15	180	27.37	25.89
21		5	2	343.15	180	22.52	17.70
22		5	3	343.15	180	21.88	16.93
23		5	4	343.15	180	22.33	18.00
24		5	6	343.15	180	22.99	16.92

¹ Standard uncertainties, u, are u (T) = 0.03 K, u (conv./yield) = 0.02%

² GC-FID analysis

Table S3 The esterification of LA to EL using alternative energy sources and 5 wt% of either ChCl:OxAc or ChCl:pTSA, with EtOH to LA molar ratio of 5.¹

Entry	Energy input	Catalyst	T [K]	t [min]	LA conversion ² [%]	EL Yield ² [%]
1	Conventional	ChCl:OxAc	343.15	10	8.05	1.97
2			343.15	60	15.92	10.22
3			343.15	120	20.78	13.75
4			343.15	180	17.44	12.81
5	Ultrasound	pTSA	343.15	180	100.00	98.13
6		ChCl:OxAc	343.15	10	17.99	8.37
7			343.15	60	19.28	10.77
8			343.15	180	20.63	14.89
9		ChCl:pTSA	343.15	10	68.12	61.29
10			343.15	60	73.09	66.17
11			343.15	180	100.00	95.13
12	Mechanical force	ChCl:OxAc	301.15	2	33.60	5.77
13			301.15	5	15.56	6.89
14			301.15	10	17.54	8.87
15		ChCl:pTSA	301.15	2	55.00	50.15
16			301.15	5	63.65	54.34
17			301.15	10	70.14	61.38
18	Microwave	ChCl:OxAc	343.15	2	35.22	6.63
19			343.15	10	15.10	7.00
20			343.15	60	17.28	10.81
21			393.15	10	18.55	10.14
22			413.15	10	58.13	56.57
23		ChCl:pTSA	343.15	2	66.34	54.68
24			343.15	10	61.53	61.53
25			343.15	60	73.40	66.81
26			393.15	10	73.88	72.00
27			413.15	10	76.32	76.32

¹ Standard uncertainties, u, are u (T) = 0.03 K, u (conv./yield) = 0.02%

² GC-FID analysis