Electronic Supplementary Information

Temperature effect on the steric and polar Taft substituent parameter values

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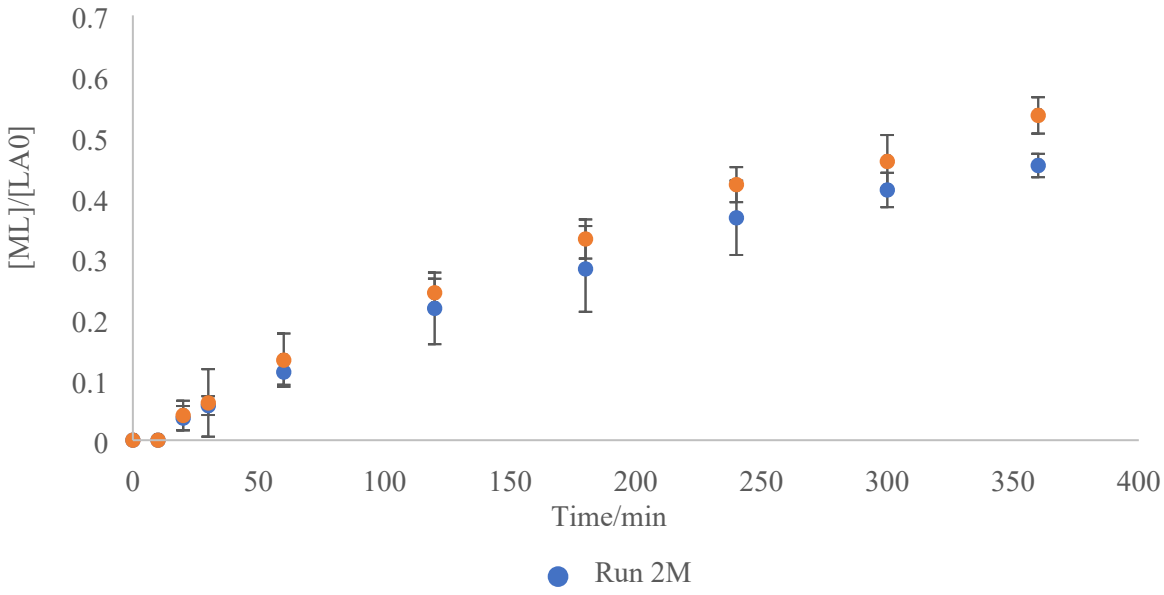
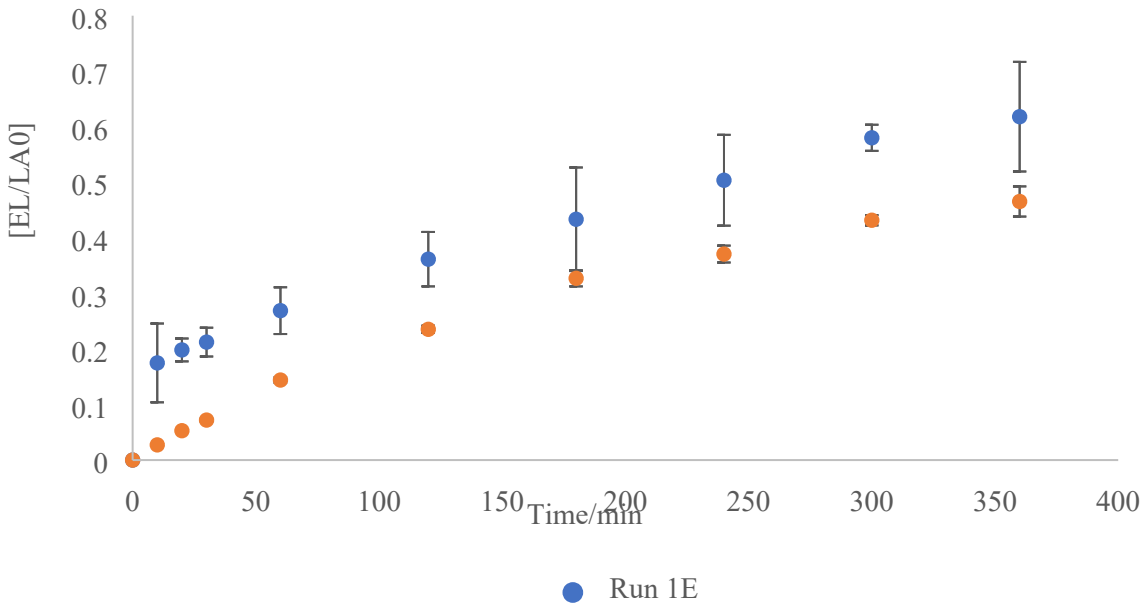


Figure S1. Repeatability of LA esterification with methanol by comparing Run 2M and Run 3M



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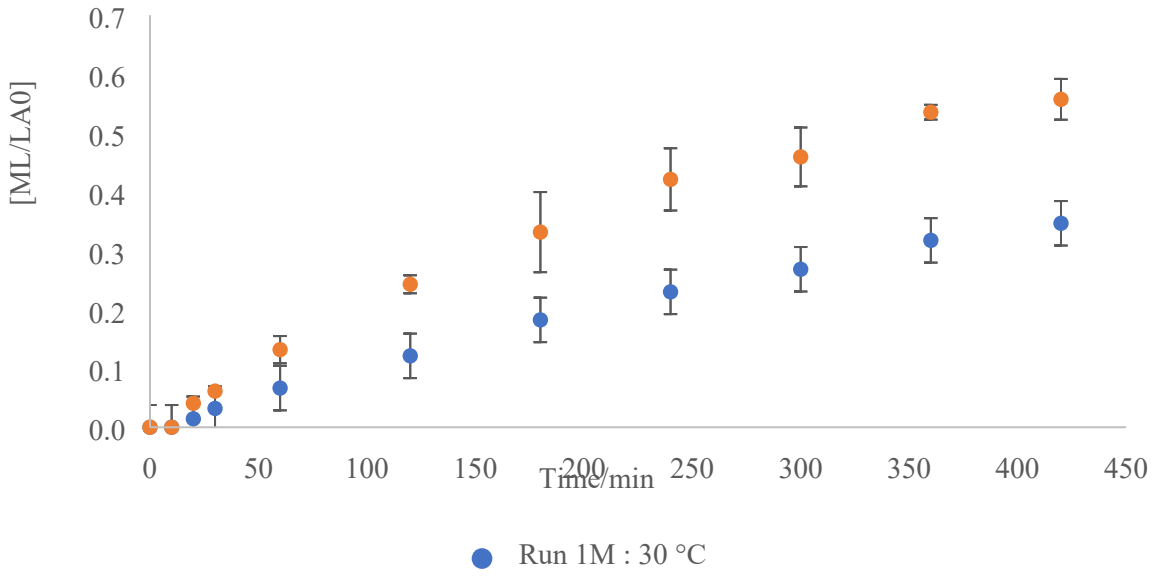

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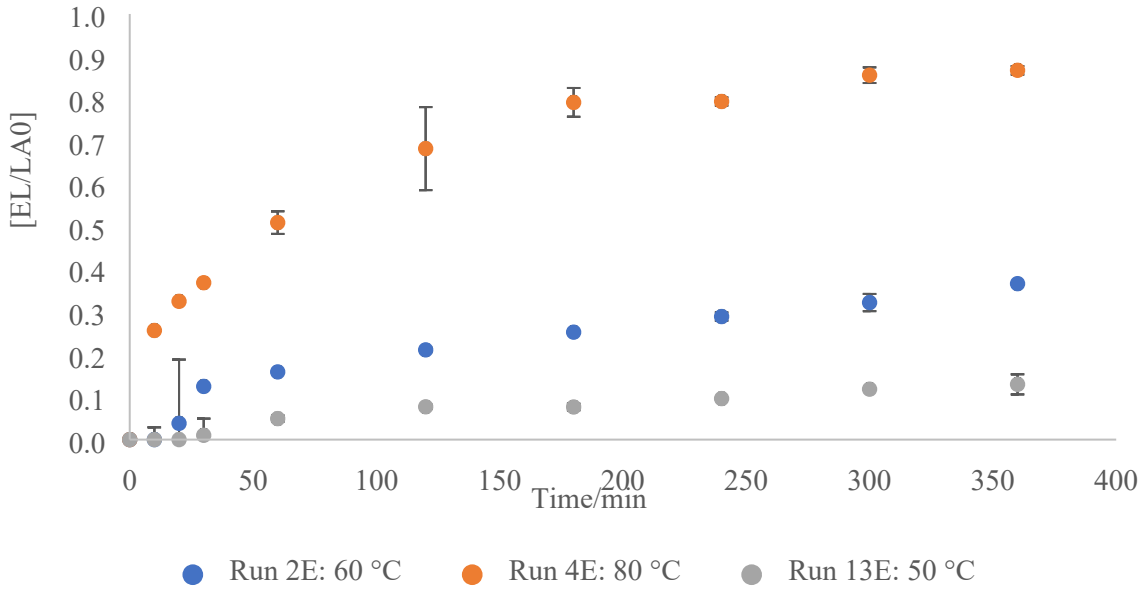

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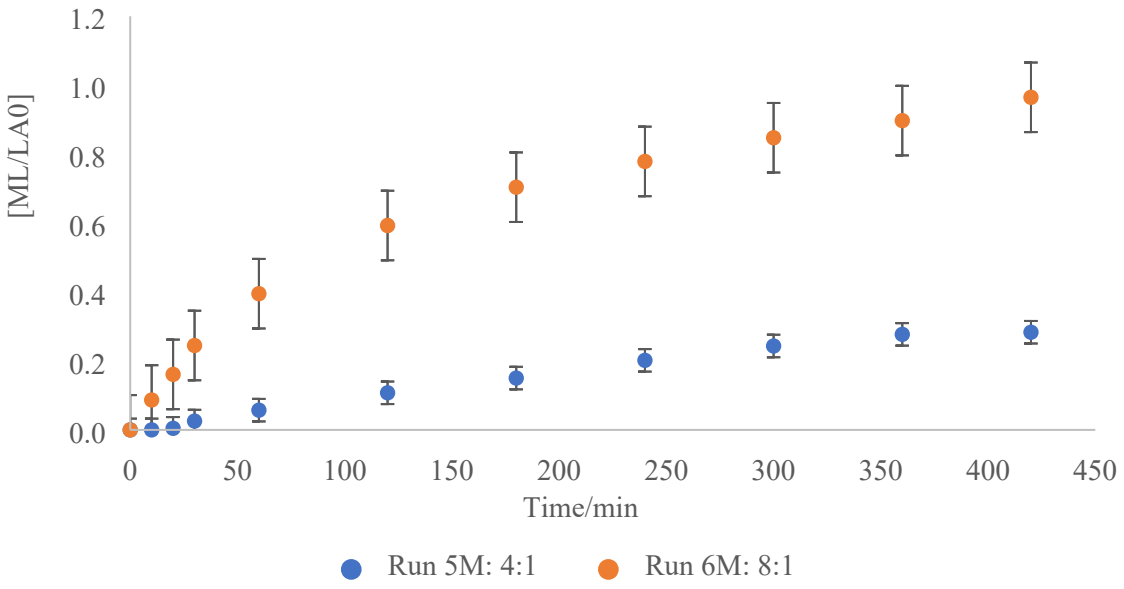

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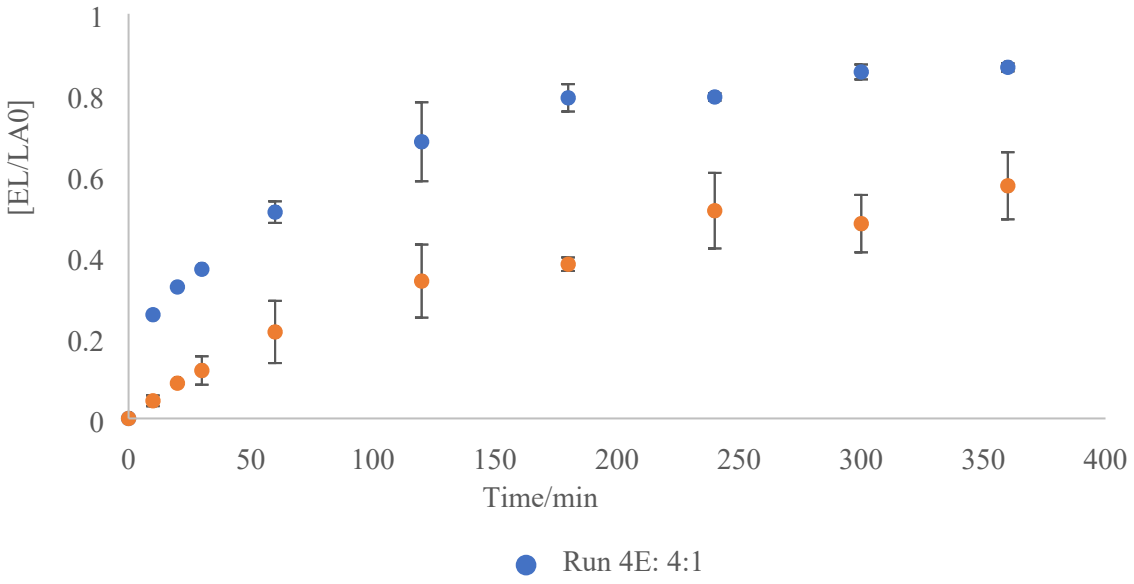

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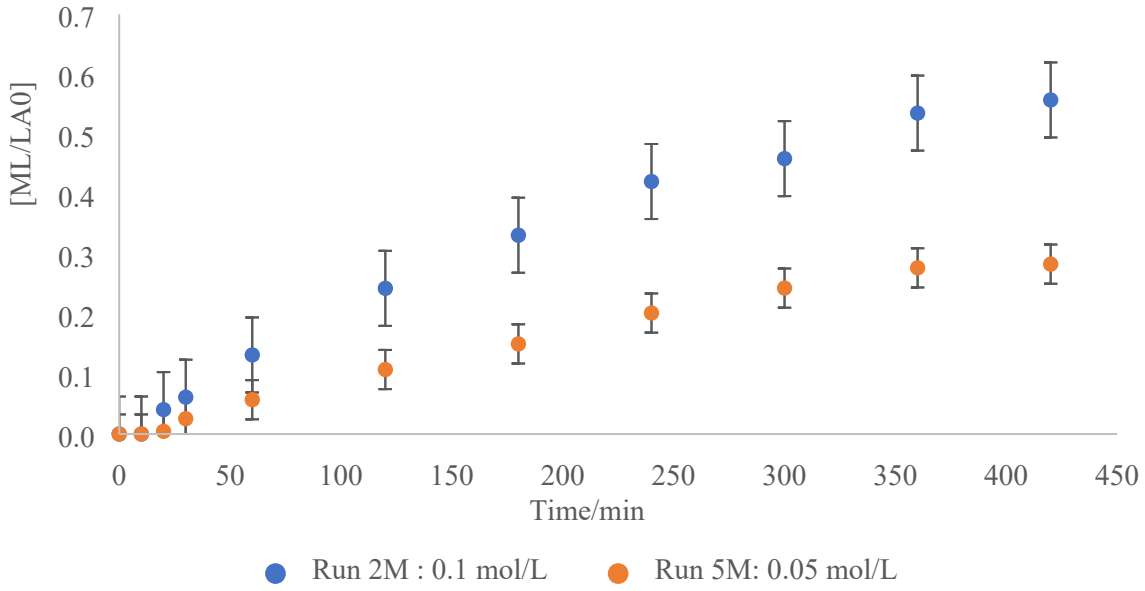

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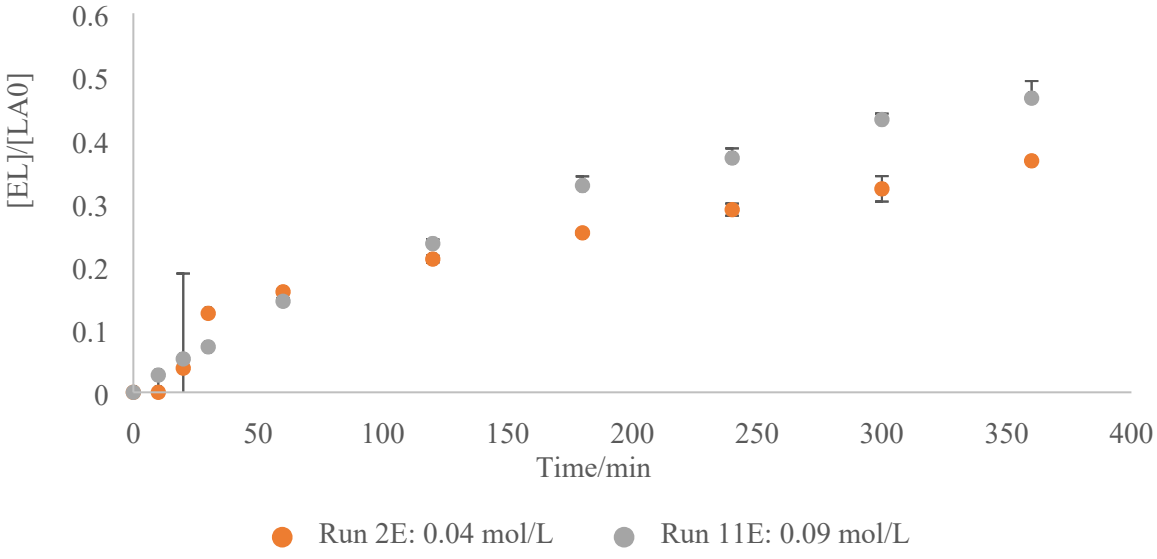

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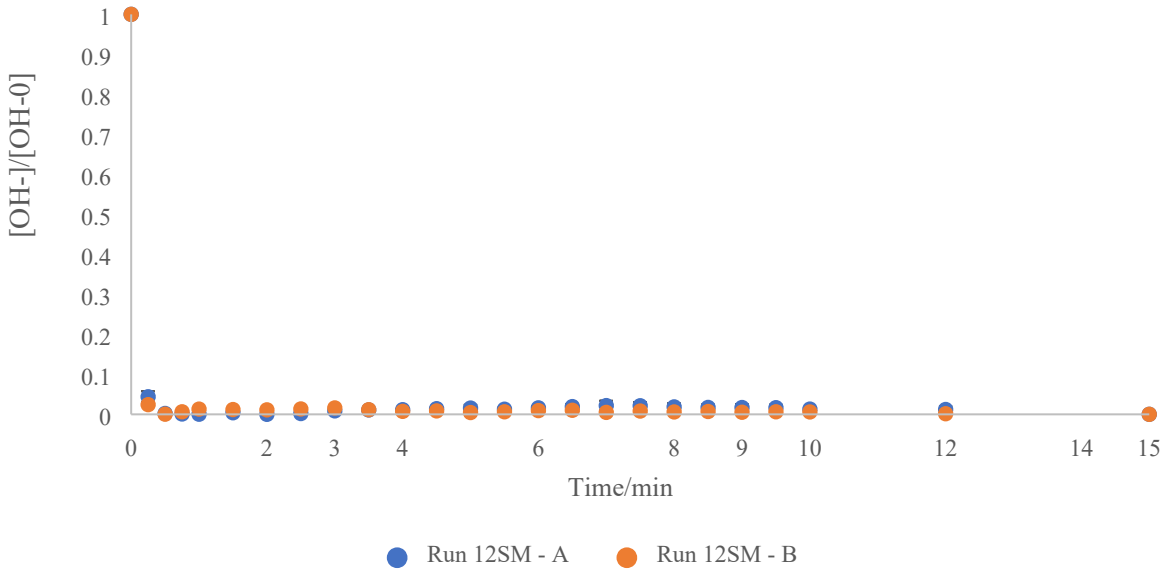

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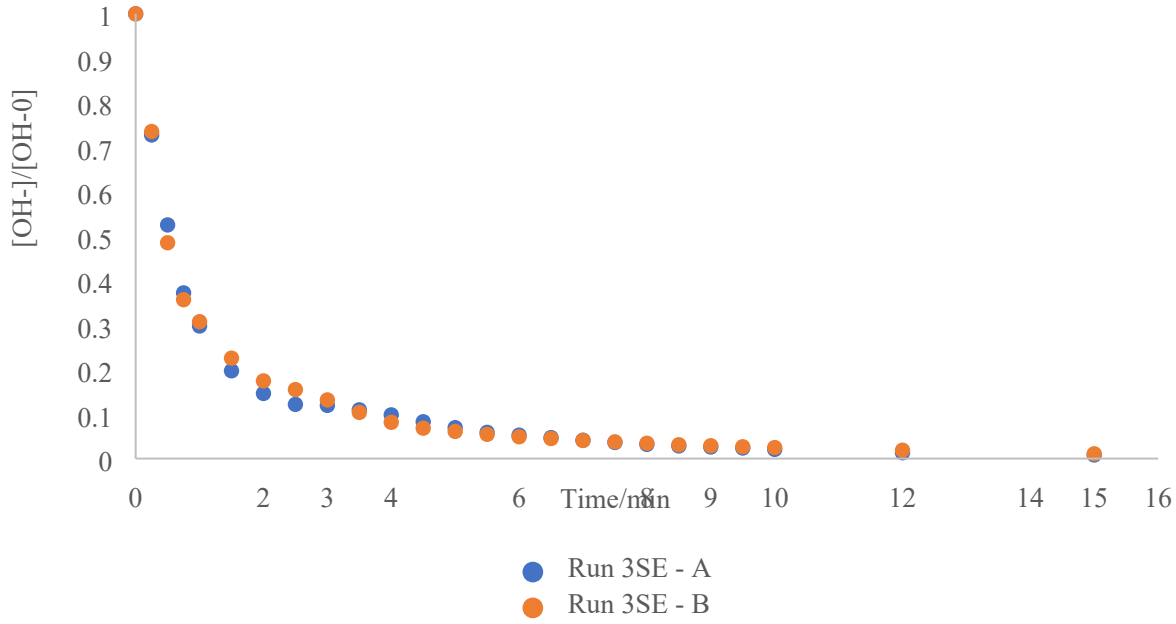

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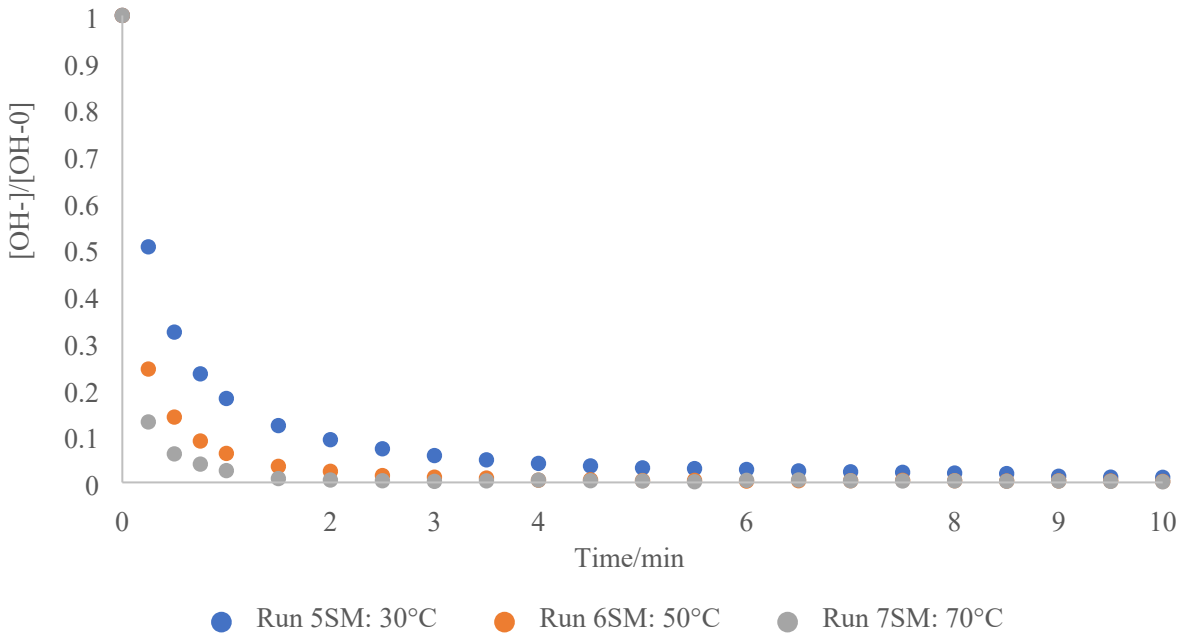

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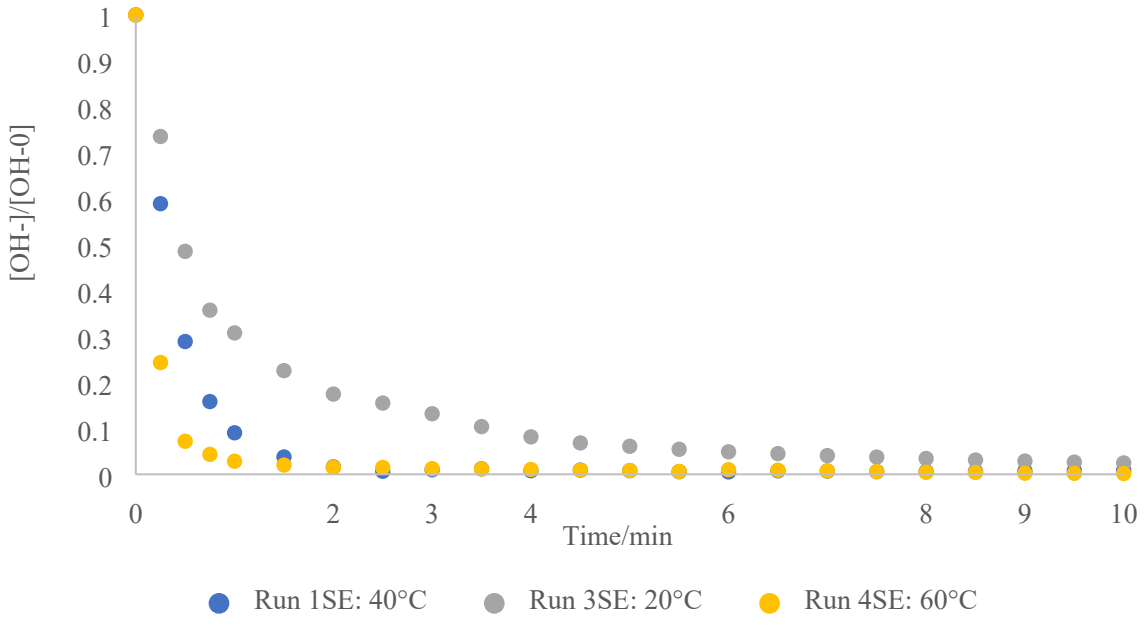

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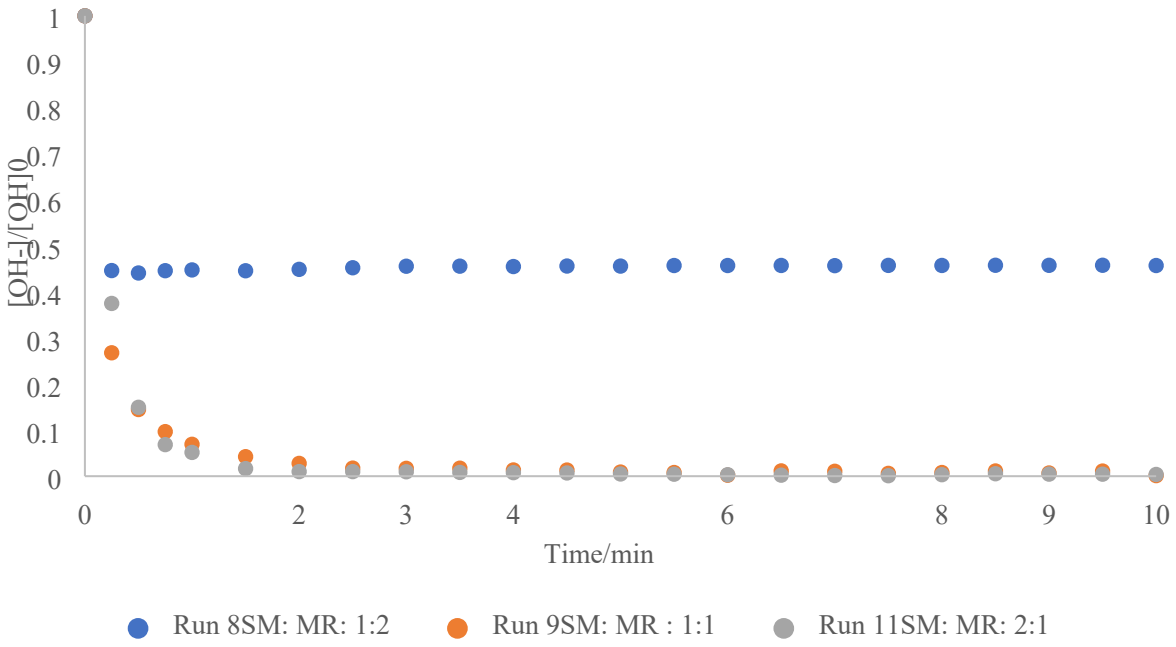

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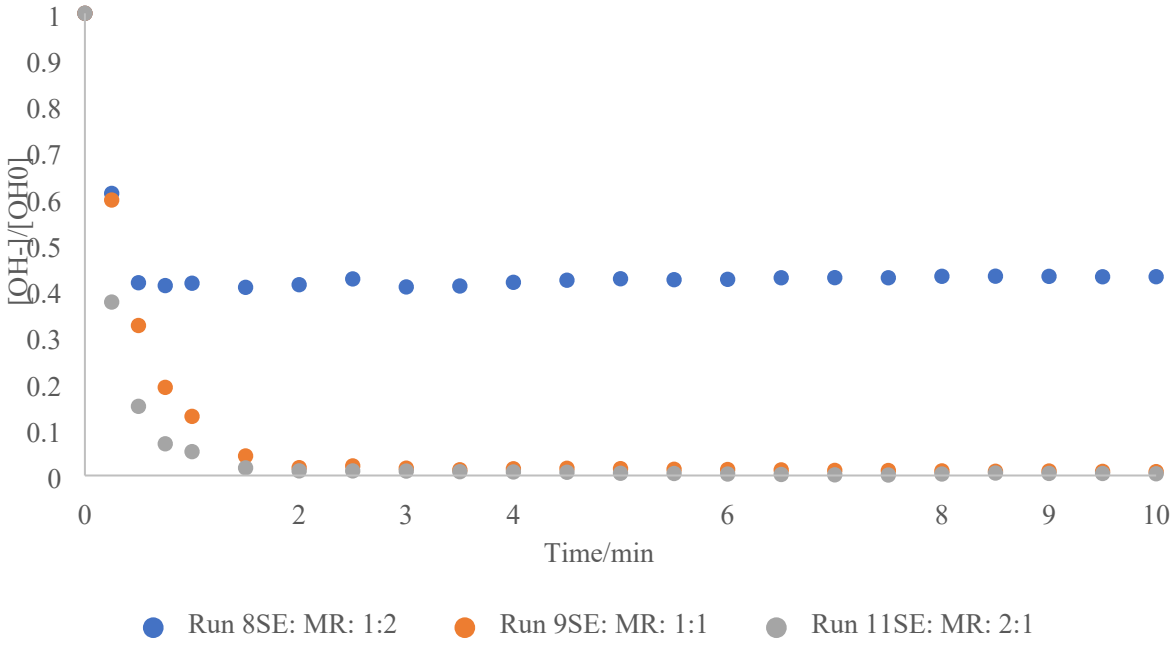


Figure S14: Effect of molar ratio on the kinetics of EL saponification by comparing Runs 8SE, 9SE and 11SE

2. Modeling Section

Material balances for the esterification system are

$$\frac{d[LA]}{dt} = -\,r^{W}_{esterification}$$

$$\frac{d[ROH]}{dt} = -\,r^{W}_{esterification}$$

$$\frac{d[RL]}{dt} = r^{W}_{esterification}$$

$$\frac{d[W]}{dt} = r^{W}_{esterification}$$

Material balances for the saponification system are

$$\frac{d[RL]}{dt} = -\,r^{W}_{saponification}$$

$$\frac{d[NaOH]}{dt} = -\,r^{W}_{saponification}$$

$$\frac{d[LA^{-}]}{dt} = r^{W}_{saponification}$$

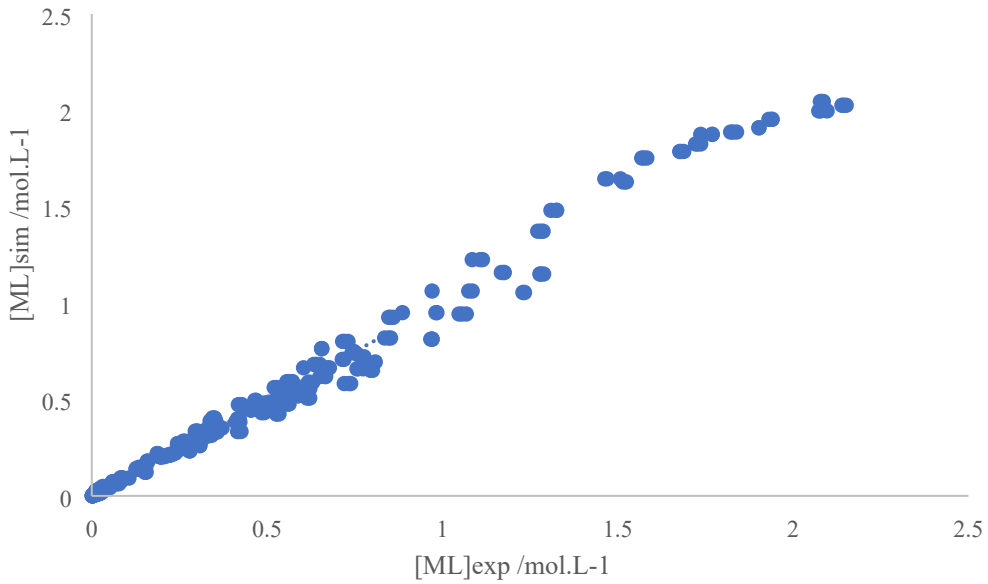
$$\frac{d[ROH]}{dt} = r^{W}_{saponification}$$

Table S1. Dissociation constant values for sulfuric and levulinic acids in water solvent

	Value	Unit
K_I (first dissociation of H_2SO_4)	Infinity	-
K_{II} (second dissociation of H_2SO_4)	$\frac{0.011}{55.5}$	-
K_{III} (dissociation of LA)	$\frac{2.57 \cdot 10^{-5}}{55.5}$	-

	$ln\left(k_c^W(T_{ref})\right)$	$\frac{E_a^W}{R \cdot T_{ref}}$	$ln\left(K_c^W(T_{ref})\right)$	$\frac{\Delta H_r^W}{R \cdot T_{ref}}$
$ln\left(k_c^W(T_{ref})\right)$	1			
$\frac{E_a^W}{R \cdot T_{ref}}$	-0.521	1		
$ln\left(K_c^W(T_{ref})\right)$	-0.757	0.457	1	
$\frac{\Delta H_r^W}{R \cdot T_{ref}}$	0.449	-0.751	-0.51	1

Table S2. Normalized covariance matrix of the estimated constants for ML synthesis



	$ln\left(k_c^W(T_{ref})\right)$	$\frac{E_a^W}{R \cdot T_{ref}}$	$ln\left(K_c^W(T_{ref})\right)$	$\frac{\Delta H_r^W}{R \cdot T_{ref}}$
$ln\left(k_c^W(T_{ref})\right)$	1			
$\frac{E_a^W}{R \cdot T_{ref}}$	-0.506	1		
$ln\left(K_c^W(T_{ref})\right)$	-0.707	0.367	1	
$\frac{\Delta H_r^W}{R \cdot T_{ref}}$	0.401	-0.776	-0.278	1

Figure S15. Parity plot for the synthesis of ML.

Table S3. Normalized covariance matrix of the estimated constants for EL synthesis

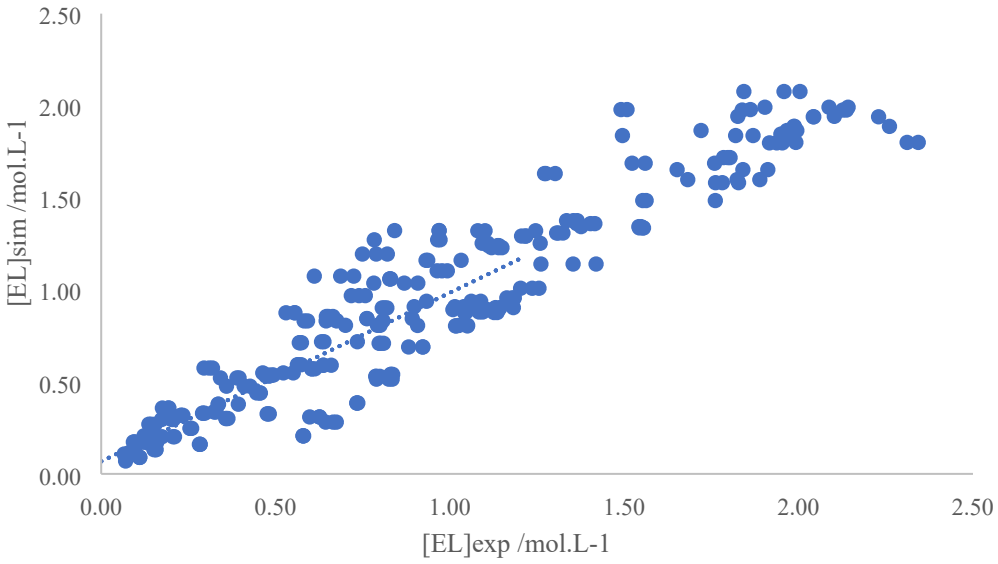


Figure S16. Parity plot for the synthesis of EL

Table S4. Normalized covariance matrix of the estimated constants for ML saponification

	$ln\left(k_c^W(T_{ref})\right)$	$\frac{E_a^W}{R \cdot T_{ref}}$
$ln\left(k_c^W(T_{ref})\right)$	1	
$\frac{E_a^W}{R \cdot T_{ref}}$	0.795	1

Table S5. Normalized covariance matrix of the estimated constants for EL saponification

	$ln\left(k_c^W(T_{ref})\right)$	$\frac{E_a^W}{R \cdot T_{ref}}$
$ln\left(k_c^W(T_{ref})\right)$	1	
$\frac{E_a^W}{R \cdot T_{ref}}$	0.633	1

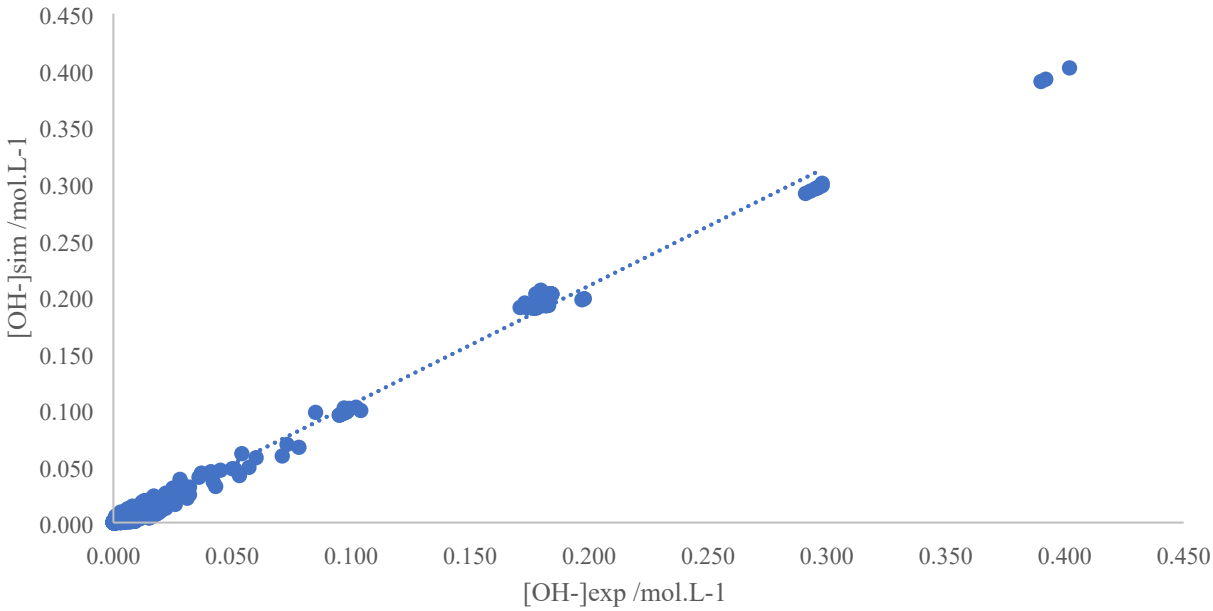


Figure S17. Parity plot for the ML saponification.

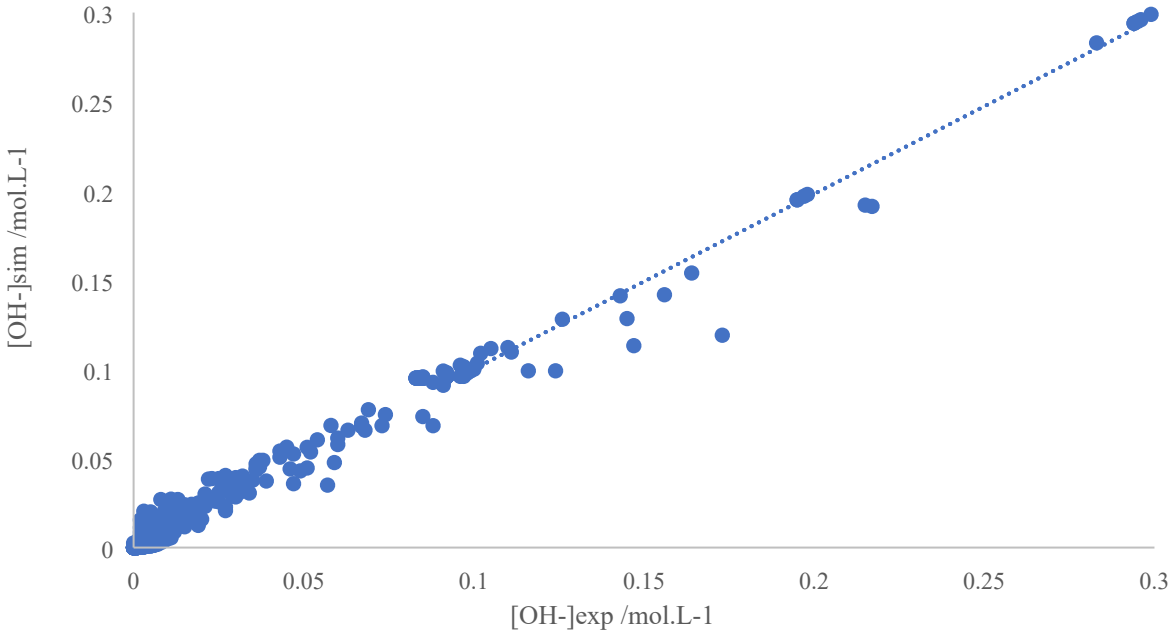


Figure S18. Parity plot for EL saponification.

Table S6. Taft polar (σ*) and steric (Es) substituent values for MeOH and EtOH with temperature.

Temperature/°C	Es	σ*
20	-0.05682	-0.20347
25	-0.06937	-0.19695
30	-0.0815	-0.19064
35	-0.09323	-0.18454
40	-0.1046	-0.17863
45	-0.1156	-0.17291
50	-0.12627	-0.16737