Supplementary Information (SI)

Greener hydrocarbons: Maximizing efficiency in the electro catalytic upgrading of *n*-caproic acid to renewable fuels

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Experimental procedures

CO_2 detector calibration

The calibration procedure for the CO_2 gas detector was conducted as follows. The detector was first enclosed within a calibration hood to minimize interference from ambient gases. Prior to calibration, the sensor and detector module were powered on and preconditioned for more than 2 h to allow sufficient aging and stabilization. After preconditioning, the detector was reset to factory settings. Subsequently, 99.999% high-purity nitrogen was introduced into the detector at a flow rate of 0.6 mL min^{-1} for 5 min to purge residual air inside the detector. The detector response was monitored until the signal decreased to the baseline level, after which a zero-adjustment command was issued to set the zero point. A certified standard gas containing 15% CO_2 balanced with nitrogen was then introduced at a flow rate of 0.3 mL min^{-1} for 5 min. Once the detector signal stabilized, a calibration command was issued to define the 15% calibration point. After completion of this step, high-purity nitrogen was continuously supplied for an additional 3–5 min to purge any residual high-concentration gas. Next, a standard gas containing 30% CO_2 balanced with nitrogen was introduced at a flow rate of 0.3 mL min^{-1} for 3 min. After the signal reached a stable value, this concentration was defined as the maximum calibration point. Using the three calibration points (0%, 15%, and 30% CO_2), a linear regression was performed to establish the calibration curve. A coefficient of determination (R^2) ≥ 0.999 confirmed a linear response of the CO_2 detector within the calibrated concentration range.

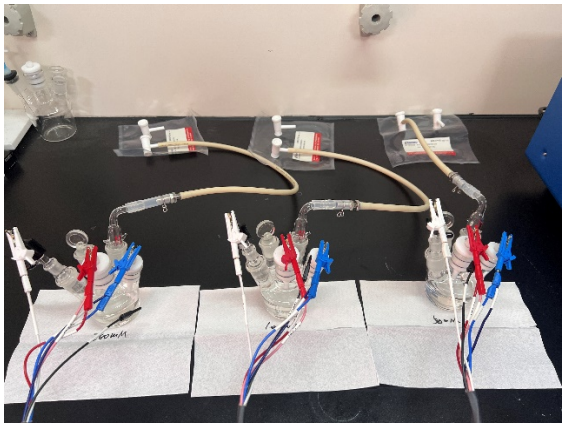

Fig. S1. The gas collection experiment is in progress.

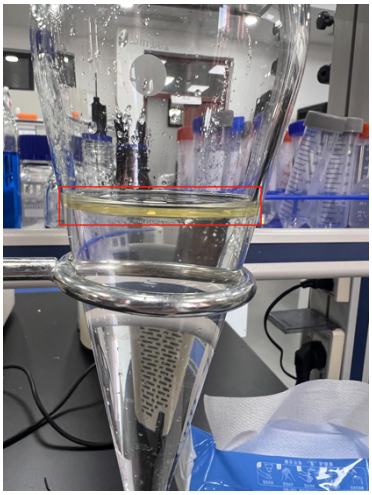

Fig. S2. The phenomenon after the electrolysis is completed and the solution is transferred to a separatory funnel and left to stand for 2 h.

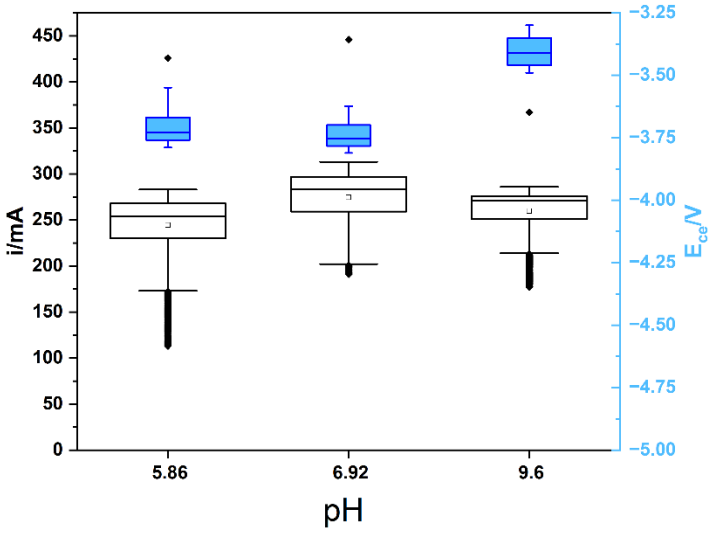

Fig. S3. The current in the circuit and the counter electrode voltage during electrolysis at different pH values.

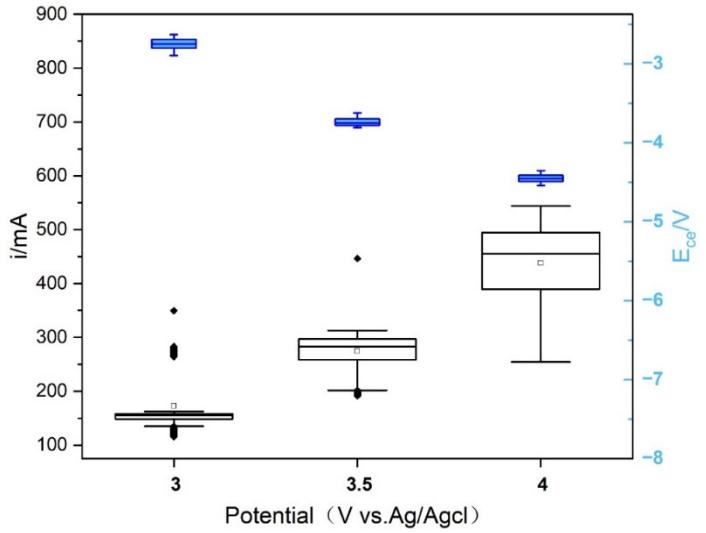

Fig. S4. The current in the circuit and the voltage value of the counter electrode during electrolysis at different voltages.

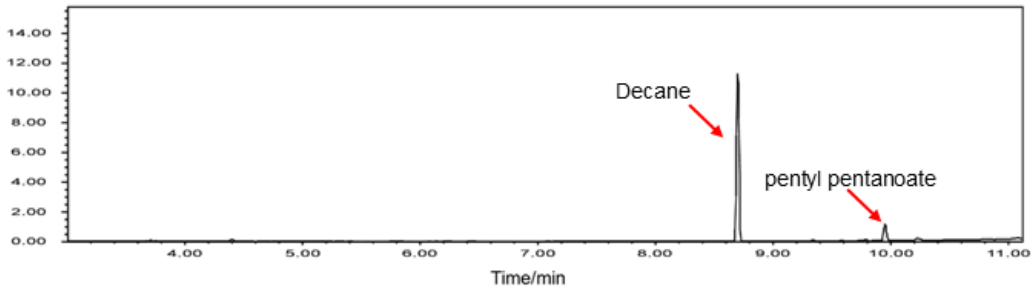

Fig. S5. Chromatogram of components in the organic phase analyzed by GC-MS.

Table S1. When assuming that the coulombic efficiency of the carboxylic acid is 100%, the amount of charge that needs to be transferred over time (Q_t) for the reactions of *n*-caproic acid at different concentrations using eqn (4-6). The FE was set with the range of 0.25 to 1.00.

Concentration (mM)	Q_t(C)			
	0.25 FE	0.50 FE	0.75 FE	1.00 FE
50	120.6	241.2	361.8	482.4
100	241.2	482.5	723.6	964.9
200	482.4	964.9	1447.3	1929.7
300	723.7	1447.3	2171.1	2894.6
400	964.9	1929.7	2894.6	3859.4
500	1206.1	2412.2	3618.3	4824.3
600	1447.3	2894.6	4331.9	5789.1
700	1688.5	3377.0	5065.5	6754.0
800	1929.7	3859.4	5789.1	7718.8
1000	2412.1	4824.3	7236.4	9648.5
1500	3618.2	7236.4	10854.6	14472.8

Table S2. Coulombic efficiency (CE) on different faraday equivalent (FE) and various concentrations of *n*-caproic acid for the Kolbe electrolysis reaction.

Parameters	Concentrations (mM)								
	50	100	200	300	400	500	600	700	800
0.25 FE	61.95%	72.17%	71.70%	81.61%	88.54%	73.92%	84.65%	96.82%	66.70%
0.50 FE	46.74%	52.88%	58.81%	63.43%	63.44%	61.83%	65.46%	64.41%	70.89%
0.75 FE	44.82%	48.87%	50.92%	46.43%	50.75%	44.71%	49.51%	60.55%	58.56%
1.00 FE	41.92%	36.87%	30.21%	45.12%	38.94%	25.62%	35.26%	45.95%	30.83%
Average FE	51.14%	52.70%	52.91%	59.15%	60.42%	50.51%	58.72%	66.93%	56.75%

Table S3. Experimental data of 800 mM *n*-caproic acid at different pH values after 1.00 FE electrolysis (n ≥ 3).

Parameters	pH values		
	5.86	6.92	9.60
Input charge number (cc)		7718.8	
Electrolysis time (s)	36376	28825	27506
Electric energy consumption (Wh)		7.51	
iR (V)	0.65	0.73	0.74
n-Decane production (mg)	2948.76	2905.02	2381.25
The amount of *n*-decane produced per unit of electric energy (g kWh^{-1})	392.64	386.82	317.01
S_{decane} (%)	45.85	45.85	38.31
FEff (%)	51.9	51.2	41.9
CE (%)	69.30	68.20	66.85
Total amount of generated gas (mL)	1646.63	1737.11	1074.35
H_2 (mL, %)	932.8 (56.65%)	1081.52 (62.24%)	746.6 (69.48%)
O_2 (mL, %)	16.50 (1.05%)	15.88 (0.91%)	27.19 (2.53%)
CO_2 (mL, %)	374.98 (22.77%)	272.10 (15.66%)	96.83 (12.97%)