Supplementary Information

Highly Selective, Energy-Free, and Environmentally Friendly One-Pot Production of Linear α-Olefin from Biomass-Derived Organic Acid in a Dual-Bed Catalyst System

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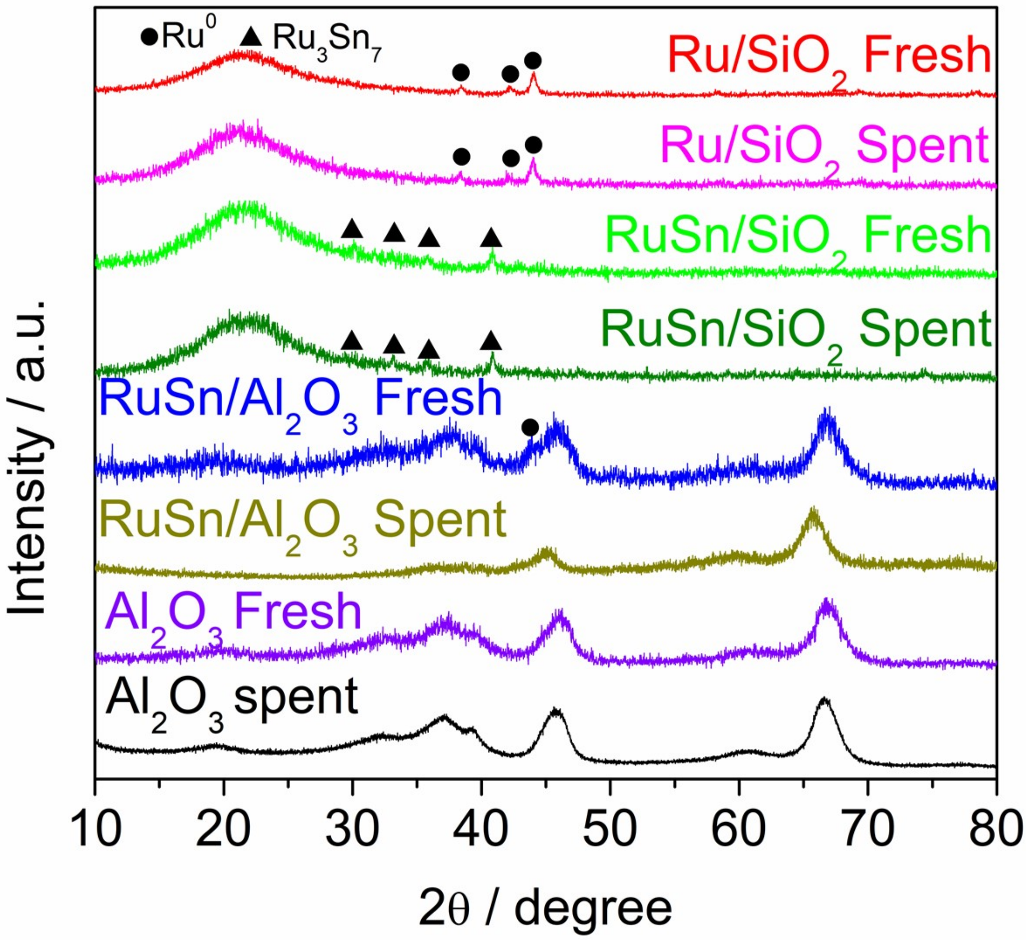


Fig. S1. PXRD patterns of Ru/SiO_2, $RuSn/SiO_2$, $RuSn/Al_2O_3$ and Al_2O_3 catalysts.

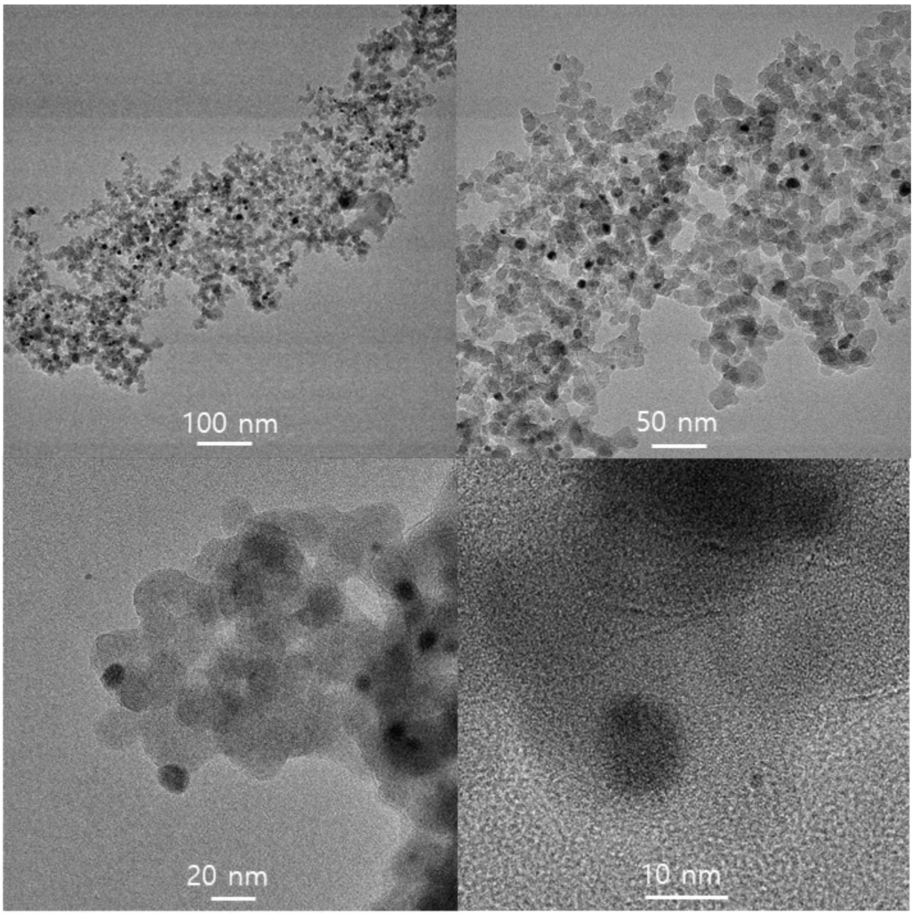


Fig. S2. Structural images of RuSn/SiO_2 catalyst.

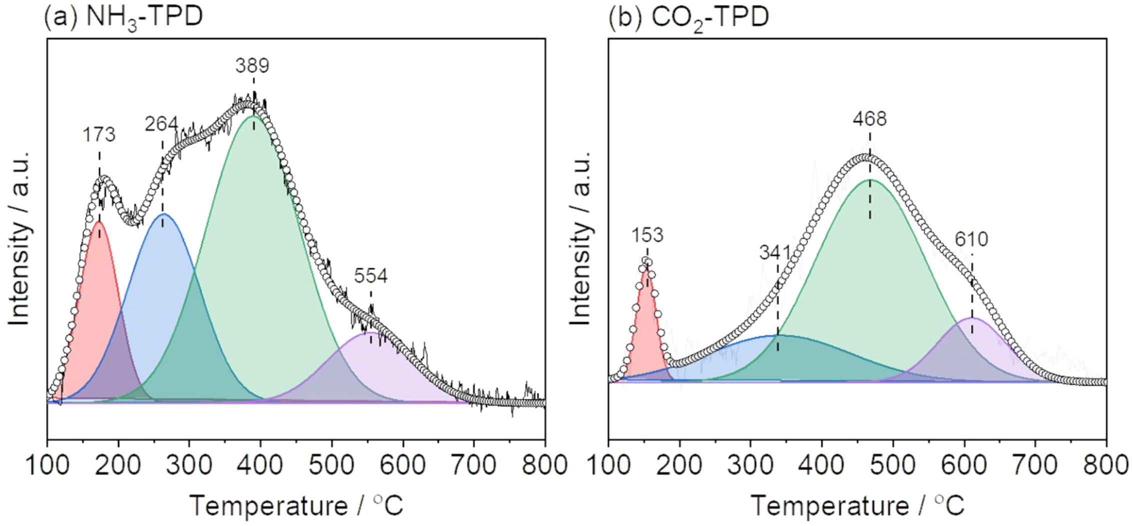


Fig. S3. (a) NH_3 and (b) CO_2 desorption profile of Al_2O_3 sample with respect to temperature.

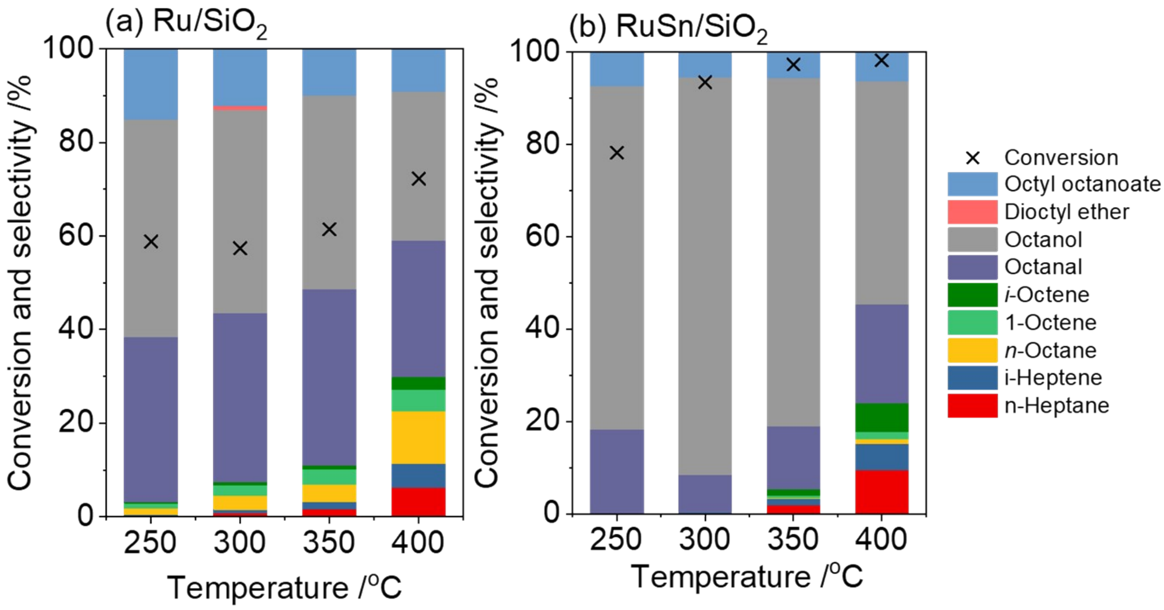


Fig. S4. Octanoic acid conversion and product selectivity over (a) Ru/SiO_2 and (b) $RuSn/SiO_2$ catalysts as a function of temperature. The reaction was conducted at 20 atm of pressure, H_2/feed molar ratio of 70.8, and WHSV of 4 h^{-1}.

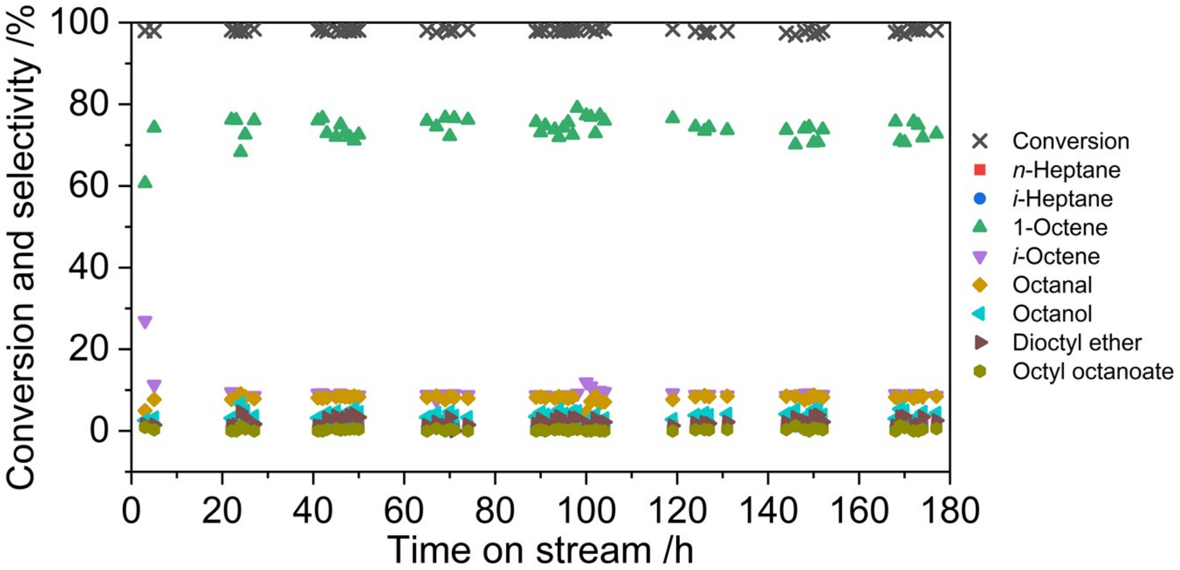


Fig. S5. Long term activity test of dual bed catalysts containing $RuSn/SiO_2$ and γ-Al_2O_3 for the HDO of octanoic acid. The reaction was performed at 20 atm, 350 °C, WHSV of 1.5 h^{-1}, H_2/feed molar ratio of 70.8, 1 gr $RuSn/SiO_2$, and 0.5 gr γ-Al_2O_3 loading.

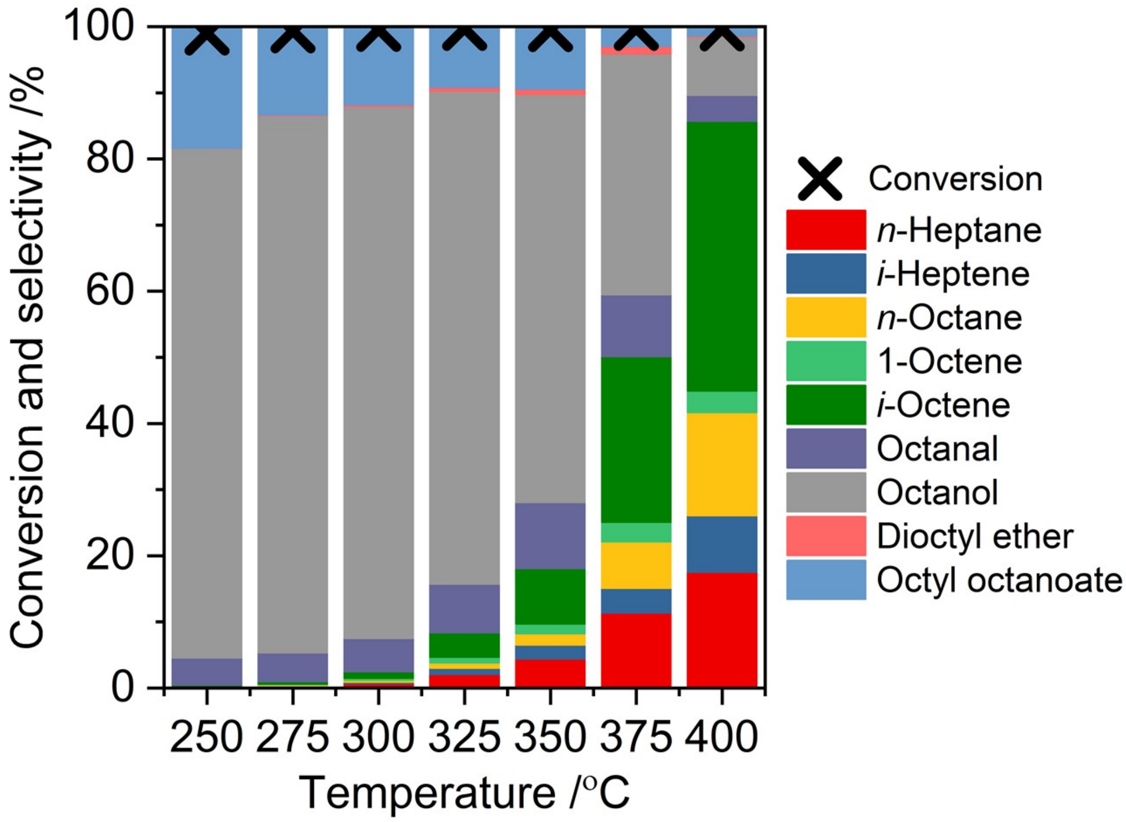


Fig. S6. Hydrogenation of octanoic acid over $RuSn/SiO_2$ at different temperatures. Reaction conditions: H_2/feed = 70.8, WHSV = 1 h^{-1}, and pressure = 20 atm.

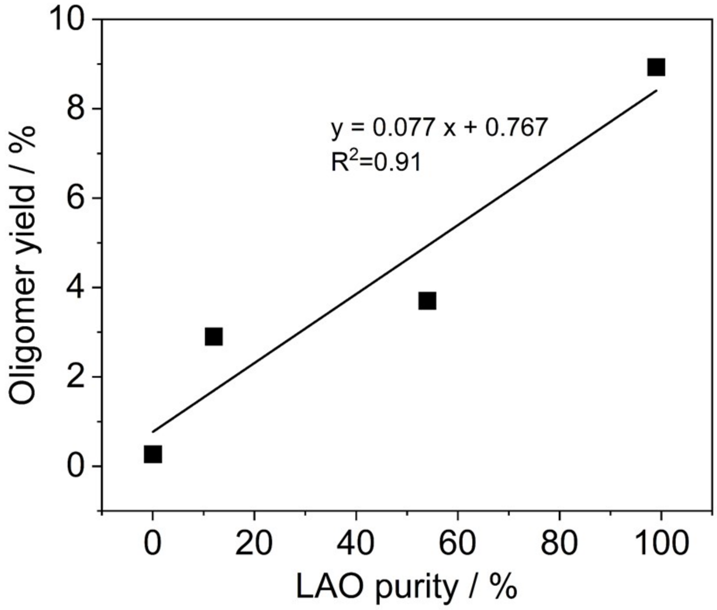


Fig. S7. Correlation between LAO purity and oligomer yield as obtained from Huber et al.[1]

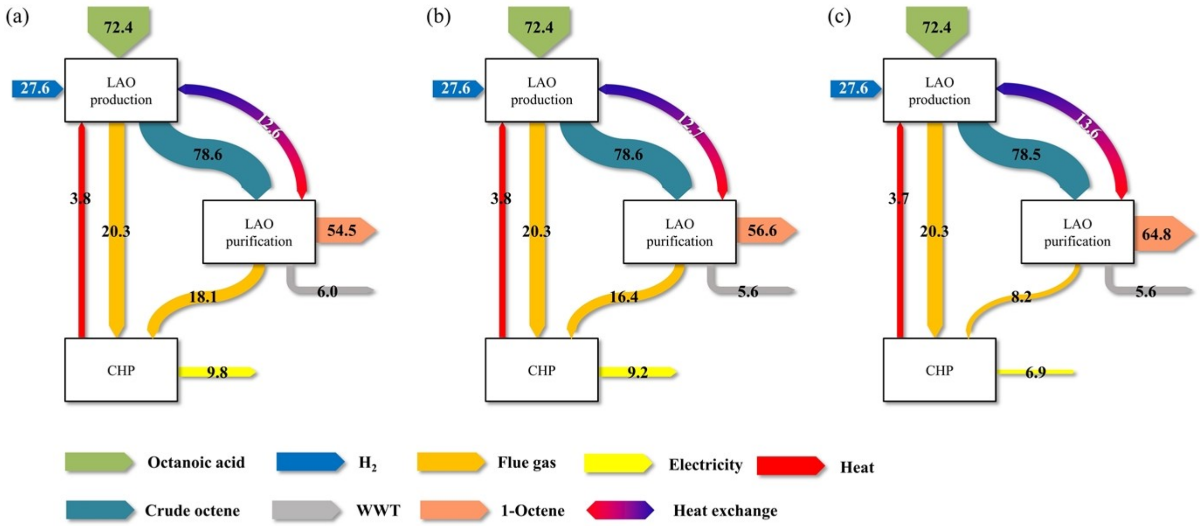
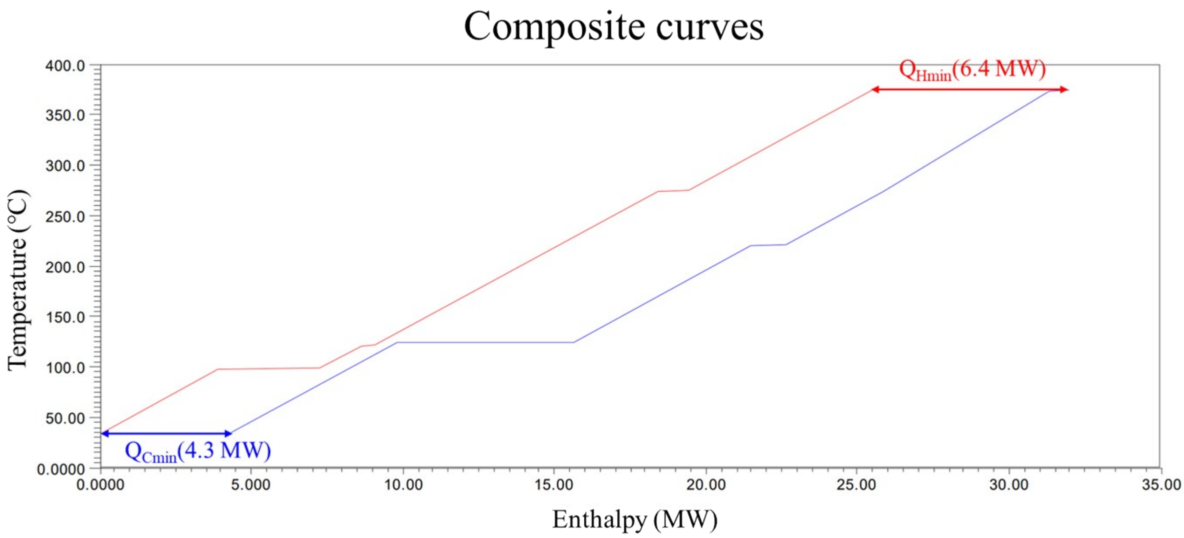


Fig. S8. Energy flow diagram of the integrated catalytic conversion process for (a) case 1, (b) case 3, and (c) case 4 using 100 units of bio-based octanoic acid and hydrogen energy contents.



Block		Inlet T (°C)	Outlet T (°C)	Enthalpy (MW)	units
H-1	↗	35.6	275.0	14.68	9.41
Bed1	↙	275.5	275.0	0.93	0.60
H-2	↗	275.0	375.0	5.49	3.52
Bed2	↗	374.5	375.0	0.60	0.39
C-1	↙	375.0	35.0	20.91	13.40
D-1, bottom	↗	125.0	125.5	5.77	3.70
D-1, top	↙	99.5	99.0	3.31	2.12
D-2, bottom	↗	221.4	221.9	1.07	0.69
D-2, top	↙	122.5	122.0	0.37	0.23

Utility stream		Inlet T (°C)	Outlet T (°C)	Cp [kJ/kg/°C)]
LP(50p)	↙	185.5	184.5	1994.3
HP (616p)	↙	386.0	385.0	1686.9
CW	↗	25.0	35.0	4.2

Fig. S9. Composite curves for Case 2 obtained using Aspen Energy Analyzer. The total minimum hot and cold utility requirements were 6.4 and 4.3 MW respectively.

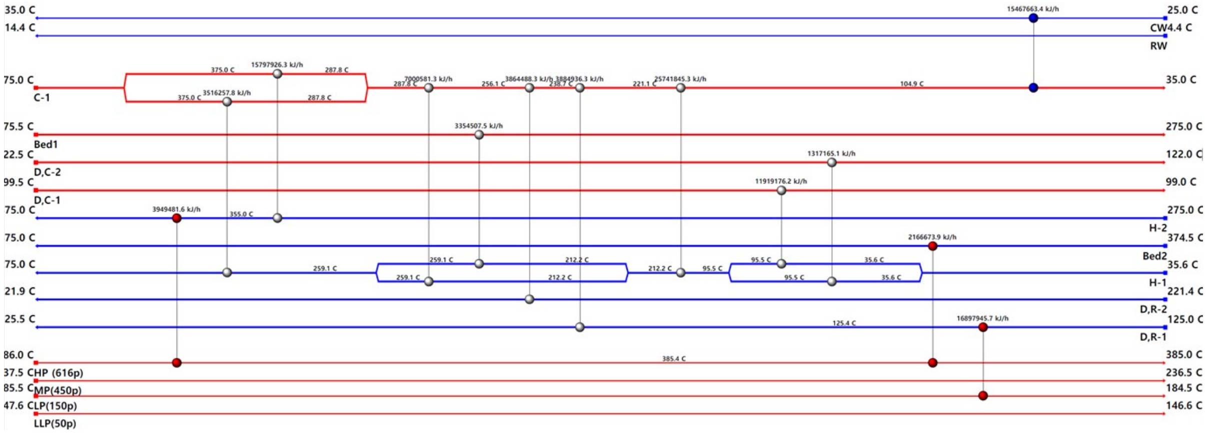


Fig. S10. The designed heat exchanger network for the integrated process (Case 2), obtained using ASPEN Energy Analyzer (minimum temperature difference (ΔT_{min}) is 10K; the estimated total minimum area requirement (A_{min}) is 20,020 m^2

Alpha Olefin Productivity Calculation

The productivity of α-olefin (1-octene) was calculated using following equation:

$$Productivity\ of\ \alpha - olefin \left[\frac{mmol_{\alpha - olefin}}{g_{cat}.h}\right] = \frac{n_{\alpha - olefin}}{m_{cat}}$$

where $n_{\alpha\text{-olefin}}$ is the amount of α-olefin formed in mmol/h and m_{cat} is the mass of catalyst in g. The comparison of productivity between our result and the result from other literatures is shown in Table S1.

Table S1. Activity comparison of dehydration catalysts in the literatures.

Catalyst	Feed	T/°C	P/atm	WHSV[a]/h^{-1}	Alcohol Conversion/%	α-Olefin Selectivity/%	Productivity/$mmol_{\alpha\text{-olefin}} \cdot g_{cat}^{-1}.h^{-1}$	I
γ-Al_2O_3	Octanoic acid	350	30	3.3	89.6	62.6	10.08	t s
15% Cs/SiO_2	1-octanol	350	4.1	0.5	11	46	0.192	2
15% Cs/SiO_2[b]	1-octanol[c]	350	4.1	0.01	32	100	0.022	2
Nano-Al_2O_3+ThO_2	1-octanol	300	0	N.A[d]	99.8	90	3.83	3
Nano-Al_2O_3+Nb_2O_5	Stearic alcohol	300	0	N.A[d]	100	80	4.39	4

[a]based on octanol conversion.
[b]after 30h of reaction.
[c]mixed feed of alcohols (1-octanol, 1-decanol, and 1-dodecanol).
[d]batch reaction. Reaction time = 6 h.

Table S2. Detailed stream data of the integrated LAOs production process using bio-based octanoic acid (For Case 1)

Stream	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**H_2**	**OA**	**PURGE**
Temperature [℃]	26.2	35.5	275.0	350.0	35.0	35.0	98.7	129.5	121.9	221.0	35.0	35.0	34.1	25.0	25.0	35.0
Pressure [atm]	20.3	20.3	20.3	20.3	20.3	20.3	1.0	1.0	1.0	1.0	20.3	20.3	20.3	20.3	1.0	20.3
Mass flow [t/d]	282.5	579.6	579.6	579.6	579.6	288.3	78.2	210.1	150.9	59.3	291.3	270.9	297.1	26.2	282.5	282.5
Octanoic acid	282.5	282.5	282.5	11.6	11.6	11.6	-	11.6	-	11.6	-	-	-	-	282.5	282.5
H_2	-	279.6	279.6	272.5	272.5	-	-	-	-	-	272.5	253.4	279.6	26.2		-
Heptane	-	0.7	0.7	1.2	1.2	0.4	0.4	-	-	-	0.8	0.7	0.7	-	-	-
i-Heptene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Octane	-	0.5	0.5	1.3	1.3	0.7	0.7	-	-	-	0.5	0.5	0.5	-	-	-
Octanal	-	1.1	1.1	14.9	14.9	13.7	13.7	-	-	-	1.2	1.1	1.1	-	-	-
Octanol	-	-	-	20.9	20.9	20.9	4.3	16.6	-	16.6	-	-	-	-	-	-
Octyl octanoate	-	-	-	14.9	14.9	14.9	-	14.9	-	14.9	-	-	-	-	-	-
1-Octene	-	4.9	4.9	136.9	136.9	131.7	0.3	131.4	**131.3**	0.1	5.3	4.9	4.9	-	-	-
Trans-3-octene	-	0.0	-	0.7	0.7	0.7	-	0.7	0.7	-	-	-	-	-	-	-
Trans-2-octene	-	0.4	0.4	10.8	10.8	10.4	-	10.4	10.4	-	0.4	0.4	0.4	-	-	-
i-Octene	-	0.3	0.3	8.8	8.8	8.4	-	8.4	8.4	-	0.3	0.3	0.3	-	-	-
DOE	-	-	-	16.0	16.0	16.0	-	16.0	-	16.0	-	-	-	-	-	-
H_2O	-	4.6	4.6	63.8	63.8	58.8	58.8	0.1	0.1	-	5.0	4.6	4.6	-	-	-
CO_2	-	2.1	2.1	2.3	2.3	-	-	-	-	-	2.3	2.1	2.1	-	-	-
O_2	-	2.8	2.8	3.1	3.1	-	-	-	-	-	3.1	2.8	2.8	-	-	-

Table S3. Detailed stream data of the integrated LAOs production process using bio-based octanoic acid (For Case 2)

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	H_2	OA	PURGE
Temperature [°C]	26.2	35.6	275.0	375.0	35.0	35.0	99.0	125.5	122.0	221.9	35.0	35.0	34.1	25.0	26.2	35.0
Pressure [atm]	20.3	20.3	20.3	20.3	20.3	20.3	1.0	1.0	1.0	1.0	20.3	20.3	20.3	20.3	20.3	20.3
Mass flow [t/d]	282.5	582.0	582.0	582.0	582.0	288.2	78.8	209.4	180.8	28.6	293.7	273.2	299.5	26.3	282.5	282.5
Octanoic acid	282.5	282.5	282.5	13.3	13.3	13.3	-	13.3	-	13.3	-	-	-	-	282.5	282.5
H_2	-	279.6	279.6	272.4	272.4	-	-	-	-	-	272.4	253.3	279.6	26.3		-
Heptane	-	0.6	0.6	1.0	1.0	0.3	0.3	-	-	-	0.7	0.6	0.6	-	-	-
i-Heptene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Octane	-	0.7	0.7	1.8	1.8	1.1	1.1	-	-	-	0.7	0.7	0.7	-	-	-
Octanal	-	1.1	1.1	14.8	14.8	13.6	13.6	-	-	-	1.2	1.1	1.1	-	-	-
Octanol	-	0.0	0.0	7.2	7.2	7.2	0.9	6.3	-	6.3	-	-	-	-	-	-
Octyl octanoate	-	0.0	0.0	5.2	5.2	5.2	-	5.2	-	5.2	-	-	-	-	-	-
1-Octene	-	5.8	5.8	158.3	158.3	152.1	0.3	151.8	**151.6**	0.2	6.3	5.8	5.8	-	-	-
Trans-3-octene	-	0.1	0.1	1.7	1.7	1.7	-	1.7	1.7	-	0.1	0.1	0.1	-	-	-
Trans-2-octene	-	0.5	0.5	15.6	15.6	15.1	-	15.1	15.0	0.0	0.6	0.5	0.5	-	-	-
i-Octene	-	0.4	0.4	13.0	13.0	12.5	-	12.5	12.5	0.0	0.5	0.4	0.4	-	-	-
DOE	-	-	-	3.5	3.5	3.5	-	3.5	0.0	3.5	-	-	-	-	-	-
H_2O	-	4.4	4.4	67.3	67.3	62.5	62.4	0.1	0.1	-	4.8	4.4	4.4	-	-	-
CO_2	-	1.9	1.9	2.1	2.1	-	-	-	-	-	2.0	1.9	1.9	-	-	-
O_2	-	4.2	4.2	4.6	4.6	-	-	-	-	-	4.6	4.2	4.2	-	-	-

Table S4. Detailed stream data of the integrated LAOs production process using bio-based octanoic acid (For Case 3)

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	H_2	OA	PURGE
Temperature [℃]	26.2	35.5	275.0	350.0	35.0	35.0	98.8	128.8	121.9	221.5	35.0	35.0	34.1	25.0	25.0	35.0
Pressure [atm]	20.3	20.3	20.3	20.3	20.3	20.3	1.0	1.0	1.0	1.0	20.3	20.3	20.3	20.3	1.0	20.3
Mass flow [t/d]	282.5	580.4	580.4	580.4	580.4	288.2	77.4	210.8	156.8	54.1	292.2	271.7	297.9	26.2	282.5	20.5
Octanoic acid	282.5	282.5	282.5	12.8	12.8	12.8	-	12.8	-	12.8	-	-	-	-	282.5	-
H_2	-	279.6	279.6	272.5	272.5	0.0	-	-	-	-	272.5	253.4	279.6	26.2	-	19.1
Heptane	-	0.8	0.8	1.3	1.3	0.4	0.4	-	-	-	0.9	0.8	0.8	-	-	0.1
i-Heptene	-	0.3	0.3	0.4	0.4	0.1	0.1	-	-	-	0.3	0.3	0.3	-	-	-
Octane	-	0.4	0.4	1.0	1.0	0.6	0.6	-	-	-	0.4	0.4	0.4	-	-	-
Octanal	-	1.1	1.1	14.4	14.4	13.2	13.2	-	-	-	1.1	1.1	1.1	-	-	0.1
Octanol	-	-	-	17.9	17.9	17.9	3.4	14.5	-	14.5	-	-	-	-	-	-
Octyl octanoate	-	-	-	13.3	13.3	13.3	-	13.3	-	13.3	-	-	-	-	-	-
1-Octene	-	5.2	5.2	142.1	142.1	136.5	0.3	136.3	**136.1**	0.1	5.5	5.2	5.2	-	-	0.4
Trans-3-octene	-	-	-	0.6	0.6	0.6	-	0.6	0.6	-	-	-	-	-	-	-
Trans-2-octene	-	0.4	0.4	11.4	11.4	11.0	-	11.0	11.0	-	0.4	0.4	0.4	-	-	-
i-Octene	-	0.3	0.3	9.4	9.4	9.1	-	9.1	9.0	-	0.3	0.3	0.3	-	-	-
DOE	-	-	-	13.3	13.3	13.3	-	13.3	-	13.3	-	-	-	-	-	-
H_2O	-	4.6	4.6	64.3	64.3	59.4	59.4	0.1	0.1	-	4.9	4.6	4.6	-	-	0.3
CO_2	-	3.1	3.1	3.4	3.4	-	-	-	-	-	3.3	3.1	3.1	-	-	0.2
O_2	-	2.2	2.2	2.4	2.4	-	-	-	-	-	2.4	2.2	2.2	-	-	0.2

Table S5. Detailed stream data of the integrated LAOs production process using bio-based octanoic acid (For Case 4)

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	H_2	OA	PURGE
Temperature [℃]	26.2	35.6	275.0	375.0	35.0	35.0	98.9	125.6	122.3	225.8	35.0	35.0	34.1	25.0	25.0	35.0
Pressure [atm]	20.3	20.3	20.3	20.3	20.3	20.3	1.0	1.0	1.0	1.0	20.3	20.3	20.3	20.3	1.0	20.3
Mass flow [t/d]	282.5	587.2	587.2	587.2	587.2	287.8	79.9	207.9	179.5	28.4	299.4	278.5	304.7	26.2	282.5	21.0
Octanoic acid	282.5	282.5	282.5	12.2	12.2	12.2	-	12.2	-	12.2	-	-	-	-	282.5	0.0
H_2	-	279.6	279.6	272.4	272.4	-	-	-	-	-	272.4	253.4	279.6	26.2	-	19.1
Heptane	-	0.7	0.7	1.1	1.1	0.4	0.4	-	-	-	0.7	0.7	0.7	-	-	0.1
i-Heptene	-	0.4	0.4	0.5	0.5	0.1	0.1	-	-	-	0.4	0.4	0.4	-	-	0.0
Octane	-	1.2	1.2	3.3	3.3	2.0	2.0	-	-	-	1.3	1.2	1.2	-	-	0.1
Octanal	-	1.2	1.2	15.5	15.5	14.2	14.2	-	-	0.0	1.3	1.2	1.2	-	-	0.1
Octanol	-	-	-	5.6	5.6	5.5	0.7	4.8	-	4.8	-	-	-	-	-	-
Octyl octanoate	-	-	-	8.3	8.3	8.3	-	8.3	-	8.3	-	-	-	-	-	-
1-Octene	-	5.2	5.2	142.4	142.4	136.8	0.3	136.5	**136.4**	0.1	5.6	5.2	5.2	-	-	0.4
Trans-3-octene	-	0.2	0.2	4.4	4.4	4.3	-	4.2	4.2	-	0.2	0.2	0.2	-	-	0.0
Trans-2-octene	-	0.8	0.8	22.1	22.1	21.3	-	21.3	21.2	0.1	0.8	0.8	0.8	-	-	0.1
i-Octene	-	0.6	0.6	18.4	18.4	17.7	-	17.7	17.6	0.1	0.7	0.6	0.6	-	-	0.0
DOE	-	-	-	2.8	2.8	2.8	-	2.8	-	2.8	-	-	-	-	-	-
H_2O	-	4.4	4.4	67.0	67.0	62.2	62.1	0.1	0.1	0.0	4.8	4.4	4.4	-	-	0.3
CO_2	-	2.9	2.9	3.2	3.2	-	-	-	-	-	3.1	2.9	2.9	-	-	0.2
O_2	-	7.5	7.5	8.1	8.1	-	-	-	-	-	8.1	7.5	7.5	-	-	0.6

Table S6. Energy analysis

Case	Heat Exchanger Network (HEN)				Energy efficiency (%)
	Before		After		
	Heating/MW	Cooling/MW	Heating/MW	Cooling/MW	
Case 1	31.3	28.9	7.2	4.8	64.2
Case 2	33.8	31.3	7.9	5.3	72.0
Case 3	31.4	29.0	7.3	4.9	65.8
Case 4	33.8	31.2	7.9	5.3	71.6

Table S7. Input and output balance for the LAO production processes.

Material/utility		Case			
		Case 1	Case 2	Case 3	Case 4
Input	Octanoic acid [a]/kg	2.15	1.86	2.08	2.07
	H_2[b]/kg	0.20	0.17	0.19	0.19
Output	Electricity/kW [c]	2.79	1.68	2.54	1.88
	1-Octene/kg [purity/%]	1 [87%]	1 [84%]	1 [87%]	1 [76%]

[a] The environmental impact was calculated based on the experimental data in previous study.[5]
[b] Hydrogen, liquid (RoW) | hydrogen cracking, APME | APOS, U
[c] Electricity, high voltage (KR) | heat and power co-generation, natural gas, combined cycle power plant, 400MW electrical | APOS, U

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