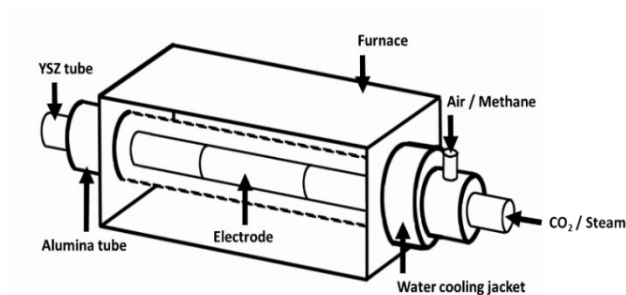


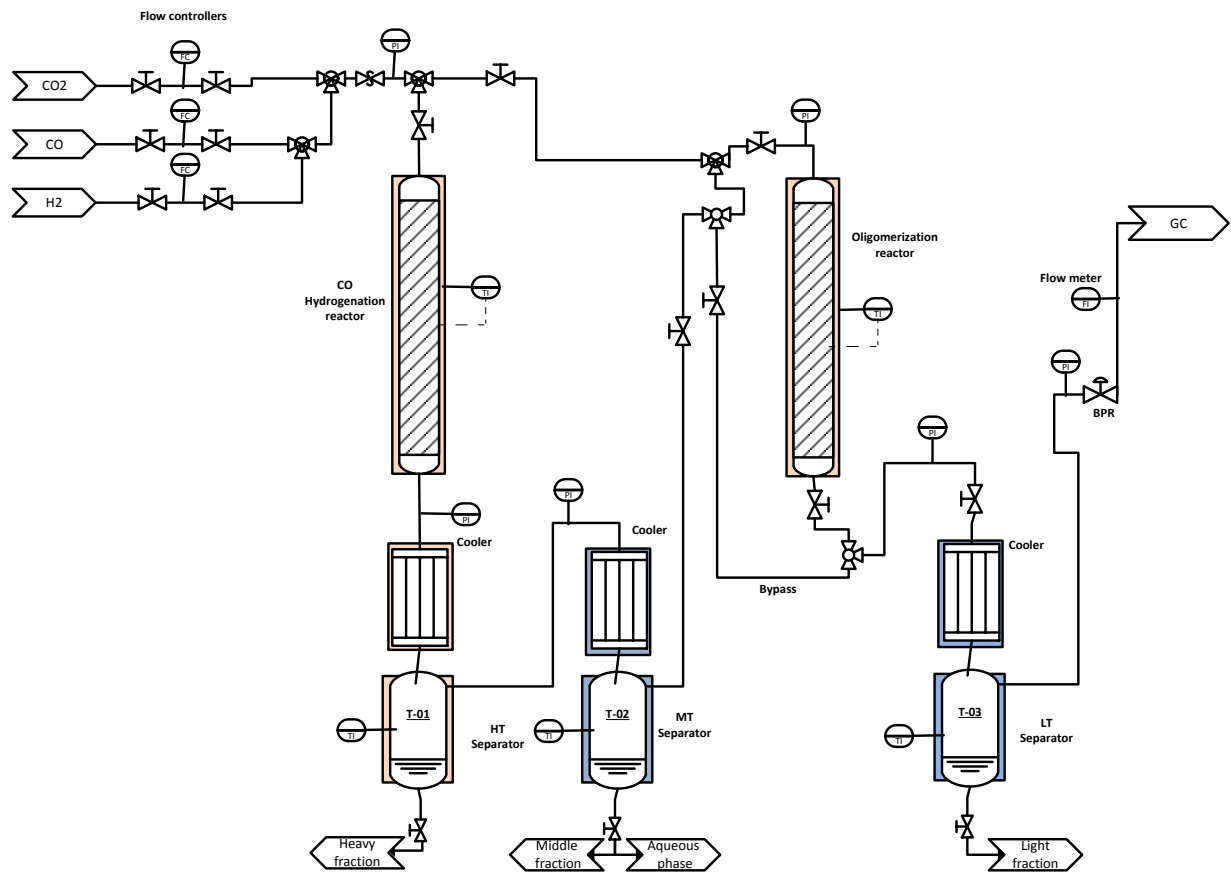
Supplementary Information:

Techno-Economic Analysis of a Sustainable Process for Converting CO₂ and H₂O to Feedstock for Fuels and Chemicals

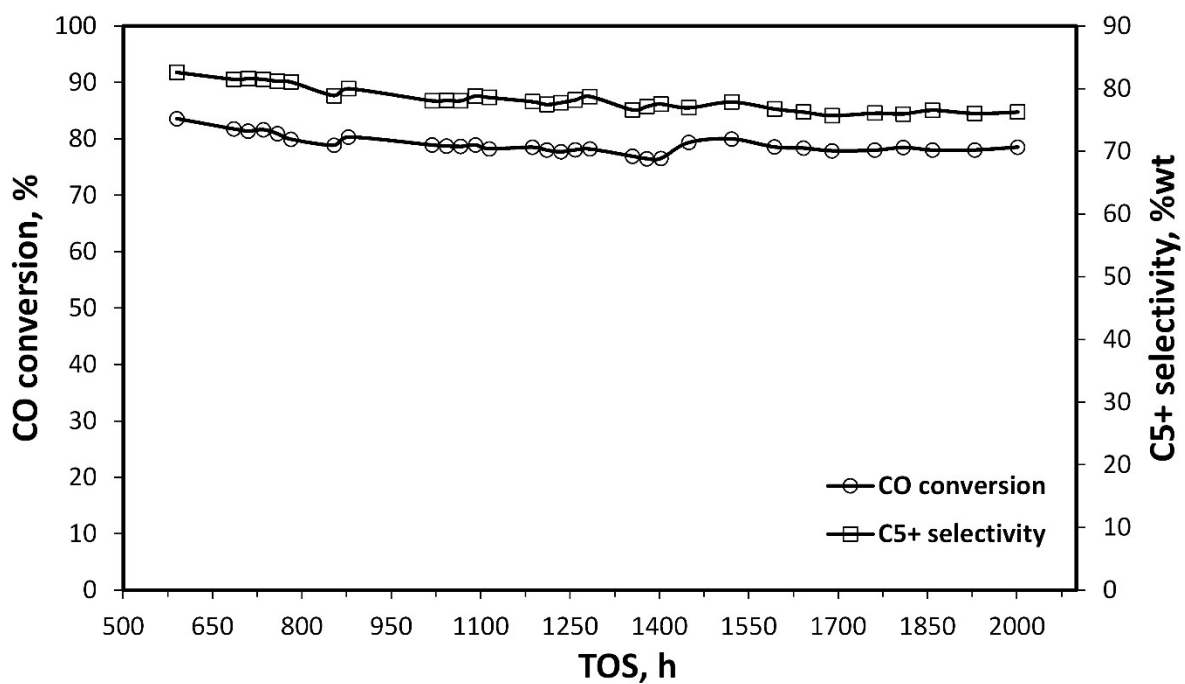
Ani Kulkarni*, Tomy Hos, Miron V. Landau, Daniel Fini, Sarbjit
Giddey and Moti Herskowitz*



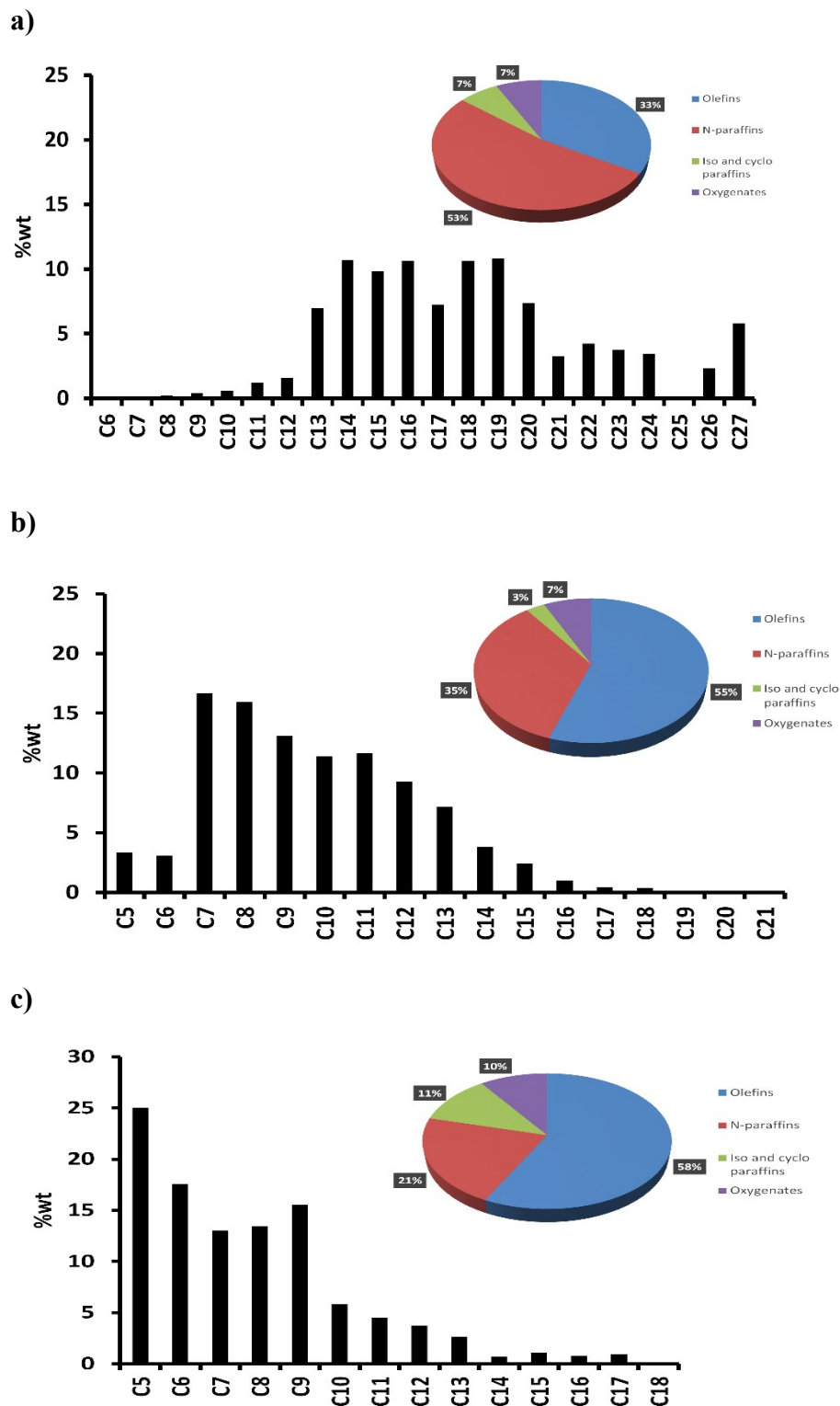
Supplementary Figure 1. Schematic of test setup used for measurement of solid oxide electrolysis cell



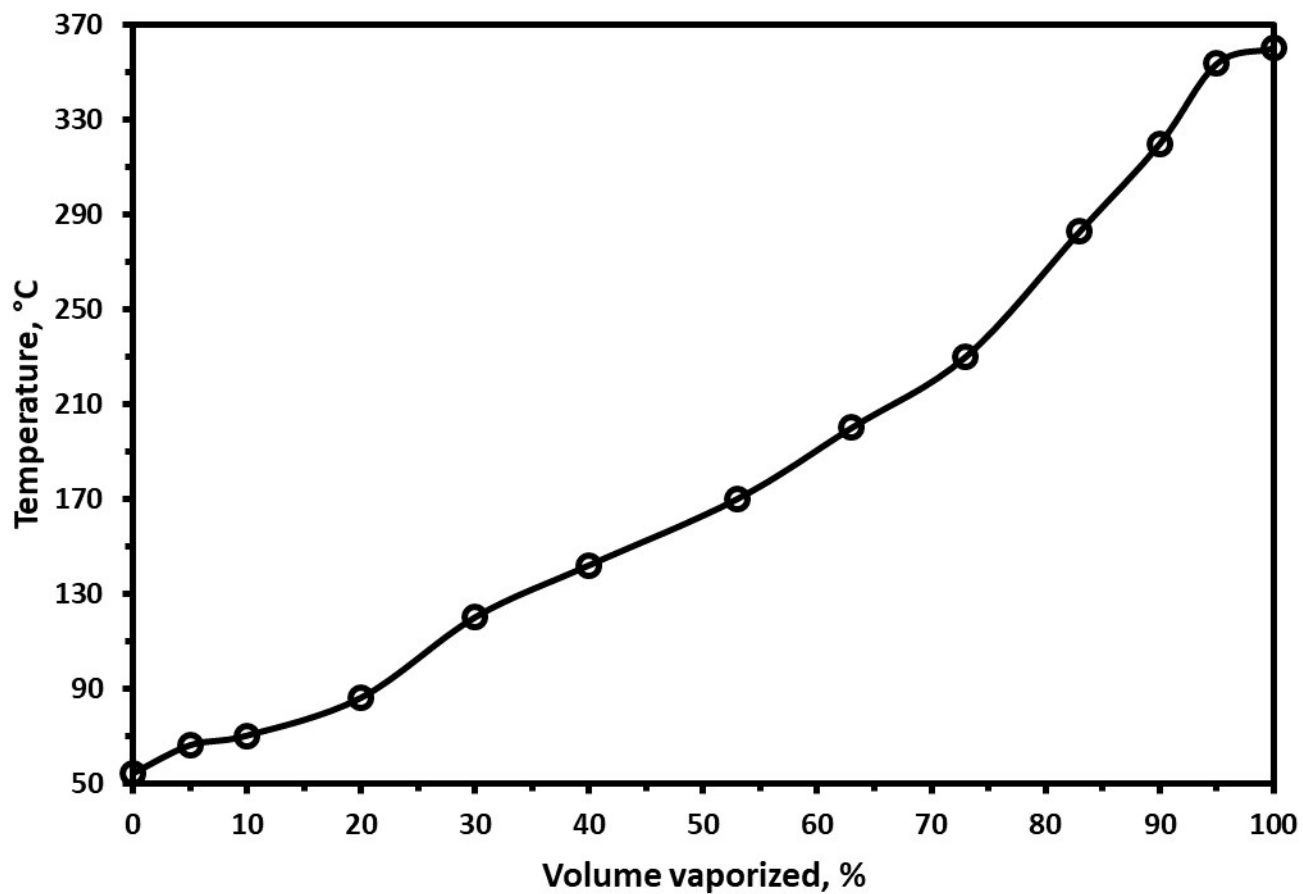
Supplementary Figure 2. Schematic drawing of CO conversion experimental rig



Supplementary Figure 3. 2,000h life test in mini-pilot unit at 50 bar, $WHSV_{CO}=1.1 \text{ g CO h}^{-1} \text{ gcat}^{-1}$, molar H_2/CO of 0.7 and CO_2 content of 6 v/v%.



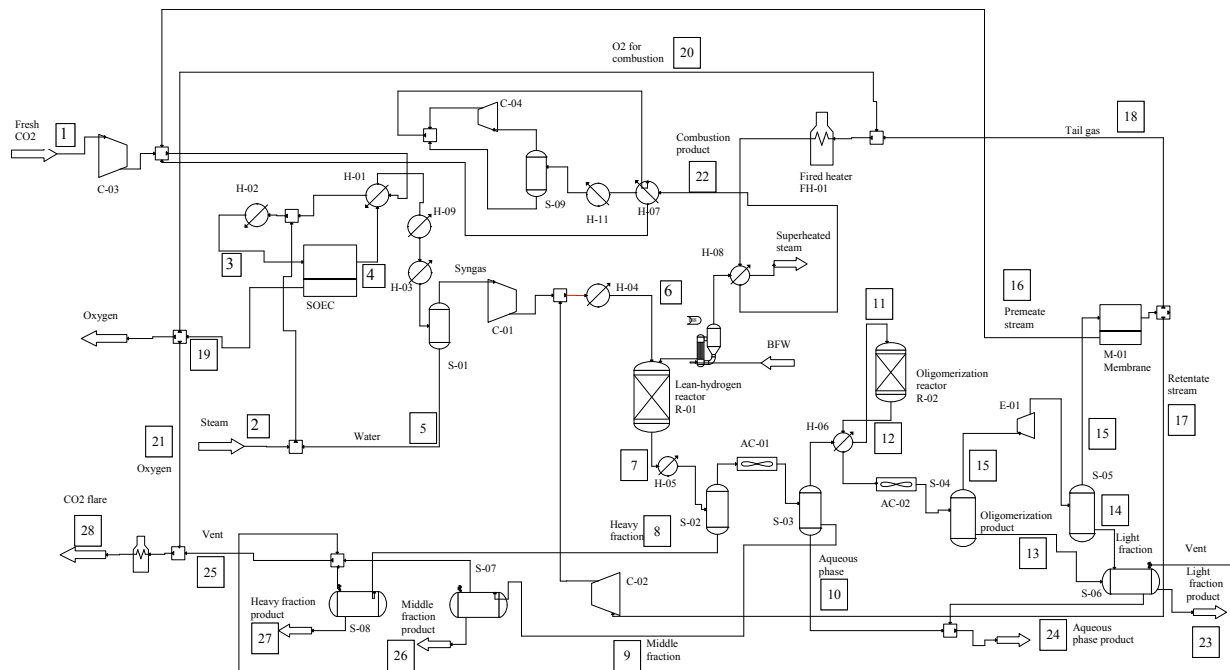
Supplementary Figure 4. Carbon number distribution and composition after 2,000h on stream in mini-pilot unit. a) Effluent from high-temperature separator (25%wt of total product). b) low-temperature separator (55%wt of total product). c) low-temperature separator after oligomerization (20%wt of total product).



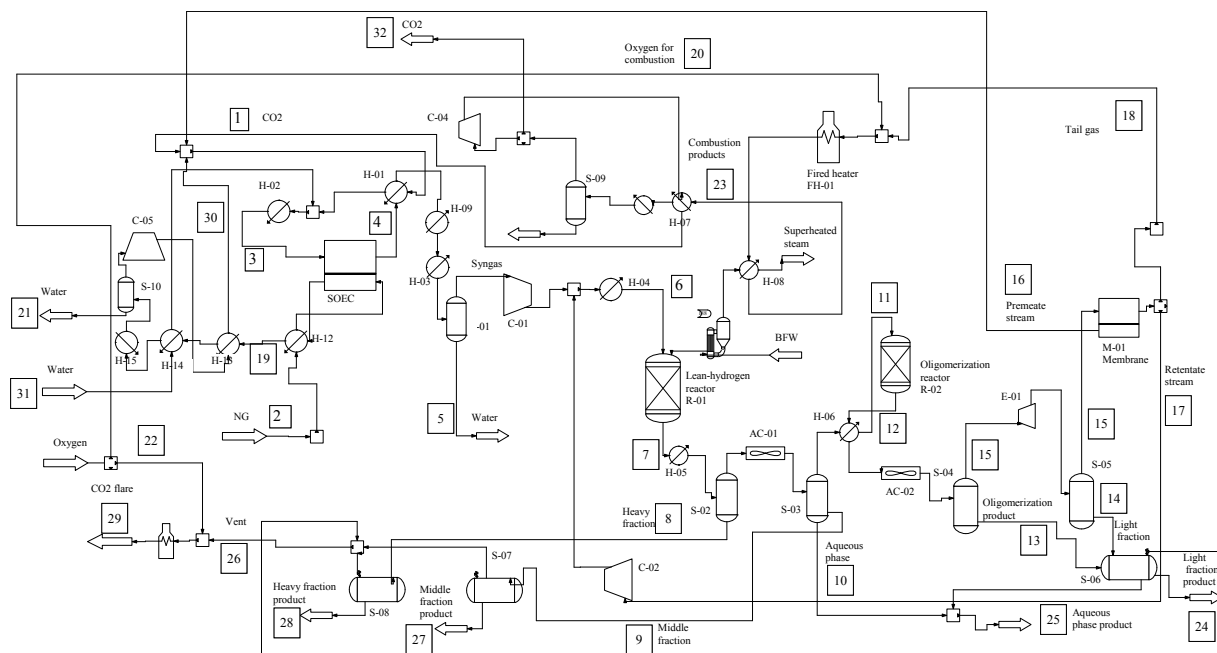
Supplementary Figure 5. Distillation curve of organic liquid product obtained by using the ASTM D86 method.

Supplementary Table 1. Input parameters for the process simulation

Parameter	Value
SOEC Operating conditions	800°C and 9 Bar
Lean hydrogen operating conditions	270-275°C, 60Bar and WHSV _{CO} =1 gCO h ⁻¹ gcat ⁻¹
Oligomerization operating conditions	230-255°C, 59Bar and WHSV=0.8 h ⁻¹
SOEC Performance	X _{CO₂} , X _{H₂O} =0.81
Lean hydrogen reactor Performance	X _{CO} =0.80, X _{H₂} =0.73, S _{C₅₊} =78%.
Oligomerization reactor Performance	X _{olefins} =0.78, S _{C₅₊} =88%.
Methane assisted SOEC Performance	X _{CH₄} =0.89, S _{partial combustion} =58%.
Condensation conditions of light product fraction	5°C, 20Bar
Ratio of recycle syngas stream (Q_{syngas recycle}/Q_{Tail gas})	1.5
SOEC powered by RE productivity	64.0Wh/mol syngas
Methane-assisted SOEC productivity	10.7Wh/mol syngas
Lean Hydrogen productivity	0.17kg liquid product/kg CO



Supplementary Figure 6. Process flow sheet of the integrated process powered by RE



Supplementary Figure 7. Process flow sheet of the integrated process powered by NG

Supplementary Table 2. Detailed mass balance for integrated process powered by RE

Stream no.	1	2	3	4	5	6	7	8	9	10
Stream name	Fresh CO ₂	Fresh Water	SOEC Inlet	SOEC Outlet	Water condens.	Lean-hydrogen Inlet	Lean-hydrogen outlet	Heavy fraction product	Middle fraction product	First aqueous phase
Temperature, °C	40	40	800	800	40	270	275	200	55	55
Pressure, Bar	1.1	1.1	9.0	8.7	8.5	60	59.7	59.5	59.4	59.4
Mass Flow rate, kg/h										
CO			760	13,903		15,272	3,053	1	4	
CO ₂	8,757		25,494	4,844		7,237	16,312	11	109	
H ₂			103	710		771	206	0		
H ₂ O		4,175	6,702	1,273	1,088	186	543	0		390
CH ₄			58	58		369	582	0	2	
C ₂ H ₆						176	302	0	3	
C ₂ H ₄						33	201	0	2	
C ₃ H ₈						124	203	0	6	
C ₃ H ₆						15	268	0	5	
C ₄ H ₁₀						106	211	1	11	
C ₄ H ₈						17	219	1	10	
Oxygenates						6	197			41
C ₅₊ (Org. liquid)						90	2,106	528	1,065	
O ₂										
Total	8,757	4,175	33,117	20,788	1,088	24,402	24,402	542	1,217	431

Stream no.	11	12	13	14	15	16	17	18	19	20
Stream name	Oligomer. inlet	Oligomer. outlet	Oligomer. product	Oligomer. light product	Membrane feed	Permeate side	Retentate side	Tail gas	Oxygen	Oxygen for Tail gas combustion
Temperature, °C	235	260	97	5	35	35	35	35	800	800
Pressure, Bar	59.3	59.1	59.0	20.0	19.5	9.2	19.3	19.3	1.0	1.0
Mass Flow rate, kg/h										
CO	3,047	3,047	5	2	3,040	760	1,368	912		
CO ₂	16,191	16,191	121	112	15,958	11,968	2,394	1,596		
H ₂	205	205	0		205	103	62	40		
H ₂ O	152	152	99	51	2	2	0	0		
CH ₄	580	580	2	1	577	58	312	208		
C ₂ H ₆	299	299	3	3	293		176	117		
C ₂ H ₄	200	55	0	0	54		33	22		
C ₃ H ₈	197	229	7	8	214		124	90		
C ₃ H ₆	262	26	1	1	24		15	10		
C ₄ H ₁₀	199	223	14	27	182		106	76		
C ₄ H ₈	209	35	2	5	28		17	11		
Oxygenates	158	158	43	107	9		6	3		
C ₅₊ (Org. liquid)	513	1,012	594	268	150		90	60		
O ₂									12,328	3,063
Total	22,212	22,212	891	585	20,736	12,891	4,703	3,145	12,328	3,063

Stream no.	21	22	23	24	25	26	27	28
Stream name	Oxygen for purge	Combustion product	Light fraction product	Aqueous phase	Vent	Middle fraction product	Heavy fraction product	CO2 flare
Temperature, °C	800	294	30	25	25	25	60	30
Pressure, Bar	1.0	1.0	2.0	2.0	1.0	2.0	1.0	1.0
Mass Flow rate, kg/h								
CO					12			
CO ₂		4,769			353			503
H ₂								
H ₂ O		1,439		540				73
CH ₄					5			
C ₂ H ₆					9			
C ₂ H ₄					2			
C ₃ H ₈					21			
C ₃ H ₆					7			
C ₄ H ₁₀			41			11	1	
C ₄ H ₈			7			10	1	
Oxygenates				191		0	0	
C ₅₊ (Org. liquid)			862			1,065	528	
O ₂	168					0	0	
Total	168	6,208	910	731	409	1,086	530	576

Supplementary Table 3. Detailed mass balance for integrated process powered by NG

Stream no.	1	2	3	4	5	6	7	8	9	10
Stream name	Recycled CO ₂	Fresh Methane	SOEC Inlet	Cathode side Outlet	Water condens.	Lean-hydrogen Inlet	Lean-hydrogen outlet	Heavy fraction product	Middle fraction product	First aqueous phase
Temperature, °C	150	40	800	800	40	270	275	200	55	55
Pressure, Bar	9.0	9.0	9.0	8.7	8.5	60	59.7	59.5	59.4	59.4
Mass Flow rate, kg/h										
CO			3,903	13,900		15,267	3,049	1	6	
CO ₂	5,015		19,390	3,684		5,858	14,829	11	166	
H ₂			539	701		753	173			
H ₂ O			1,793	341	320	21	459			401
CH ₄		3,375	544	544		1,418	1,633	1	7	
C ₂ H ₆						177	304		5	
C ₂ H ₄						33	203		3	
C ₃ H ₈						108	189		7	
C ₃ H ₆						15	270		10	
C ₄ H ₁₀						96	201	1	17	
C ₄ H ₈						17	222	1	19	
Oxygenates						5	201			89
C ₅₊ (Org. liquid)						66	2,101	579	1,166	
O ₂										
Total	5,015	3,375	26,169	19,170	320	23,834	23,834	594	1,406	490

Stream no.	11	12	13	14	15	16	17	18	19	20	21
Stream name	Oligomer. inlet	Oligomer. outlet	Oligomer. product	Oligomer. light product	Membrane feed	Permeate side	Retentate side	Tail gas	Anode side outlet	Oxygen for Tail gas combustion	Water
Temperature, °C	235	260	97	5	35	35	35	35	800	25	40
Pressure, Bar	59.3	59.1	59.0	20.0	19.5	9.2	19.3	19.3	5.0	1.0	5.0
Mass Flow rate, kg/h											
CO	3,041	3,041	3	2	3,036	759	1,366	911	3,144		
CO ₂	14,652	14,652	74	83	14,495	10,871	2,174	1,450	3,517		13
H ₂	173	170			170	87	52	31	453		
H ₂ O	58	58	4	51	3	2		1	2,879		2,854
CH ₄	1,625	1,625	3	2	1,620	162	875	583	382		
C ₂ H ₆	299	299	2	3	294		177	117			
C ₂ H ₄	201	56			56		33	23			
C ₃ H ₈	182	202	4	7	191		108	83			
C ₃ H ₆	260	26		1	25		15	10			
C ₄ H ₁₀	183	206	12	28	166		96	70			
C ₄ H ₈	202	34	1	4	29		17	12			
Oxygenates	112	112	13	89	10		5	5			
C ₅₊ (Org. liquid)	356	863	446	307	110		66	44			
O ₂										4,395	
Total	21,344	21,344	562	577	20,205	11,881	4,984	3,340	10,375	4,395	2,867

Stream no.	22	23	24	25	26	27	28	29	30	31	32
Stream name	Oxygen for vent stream	Combustion product	Light fraction product	Aqueous phase	Vent	Middle fraction product	Heavy fraction product	CO ₂ flare	Anode recycle stream	Water feed SOEC	CO ₂ Purge
Temperature, °C	25	294	30	25	25	25	60	30	800	25	30
Pressure, Bar	1.0	1.0	2.0	2.0	1.0	2.0	1.0	1.0	9.0	1.0	1.0
Mass Flow rate, kg/h											
CO					12				3,144		
CO ₂		5,569			334			516	3,504		554
H ₂									453		
H ₂ O		2,166		456				95	26	1,767	
CH ₄					13				382		
C ₂ H ₆					10						
C ₂ H ₄					3						
C ₃ H ₈					18						
C ₃ H ₆					11						
C ₄ H ₁₀			40			17	1				
C ₄ H ₈			5			19	1				
Oxygenates				191			0				
C ₅₊ (Org. liquid)			753			1,166	579				
O ₂	210		0								
Total	210	7,735	798	647	401	1,202	581	611	7,509	1,767	554

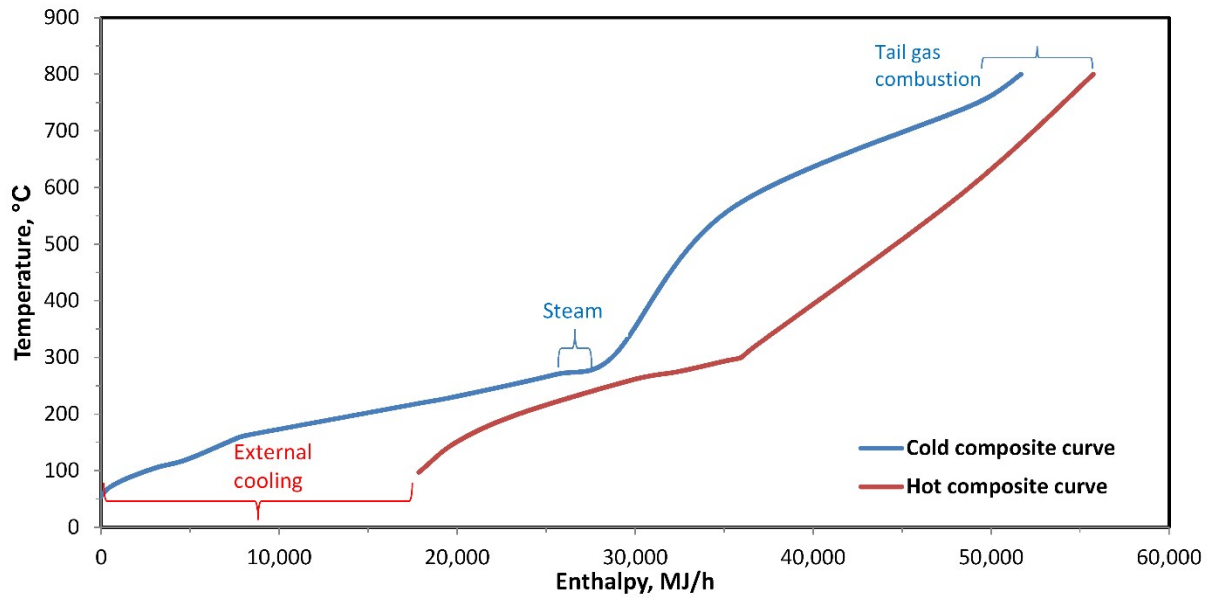
Supplementary Table 4. Energy balance for the established heat exchanger network

Heat exchanger	Stream number	Type	T _{in} , C	T _{out} , C	Heat load, MJ/h
H-01	4	Hot	800	320	16,822
	1+16+22	Cold	86	750	
H-02 ^a	3	Cold	492	800	14,800
H-03 ^b	4	Hot	150	40	6,200
H-04	6	Cold	164	270	4,086
	Steam	Hot	300	260	
H-05	7	Hot	275	200	2,677
	BFW	Cold	159	217	
H-06	11	Cold	55	230	5,233
	12	Hot	260	97	
H-07	22	Cold	70	120	1,560
	22	Hot	294	80	
H-08	Steam	Cold	270	300	2,395
	22	Hot	588	294	
H-09	4	Hot	320	150	5,261
	BFW	Cold	105	270	
H-10 ^a	BFW	Cold	217	270	2,538
H-11 ^b	22	Hot	80	40	3,345
AC-01 ^c	11	Hot	200	55	6,506
AC-02 ^c	12	Hot	97	55	1,672

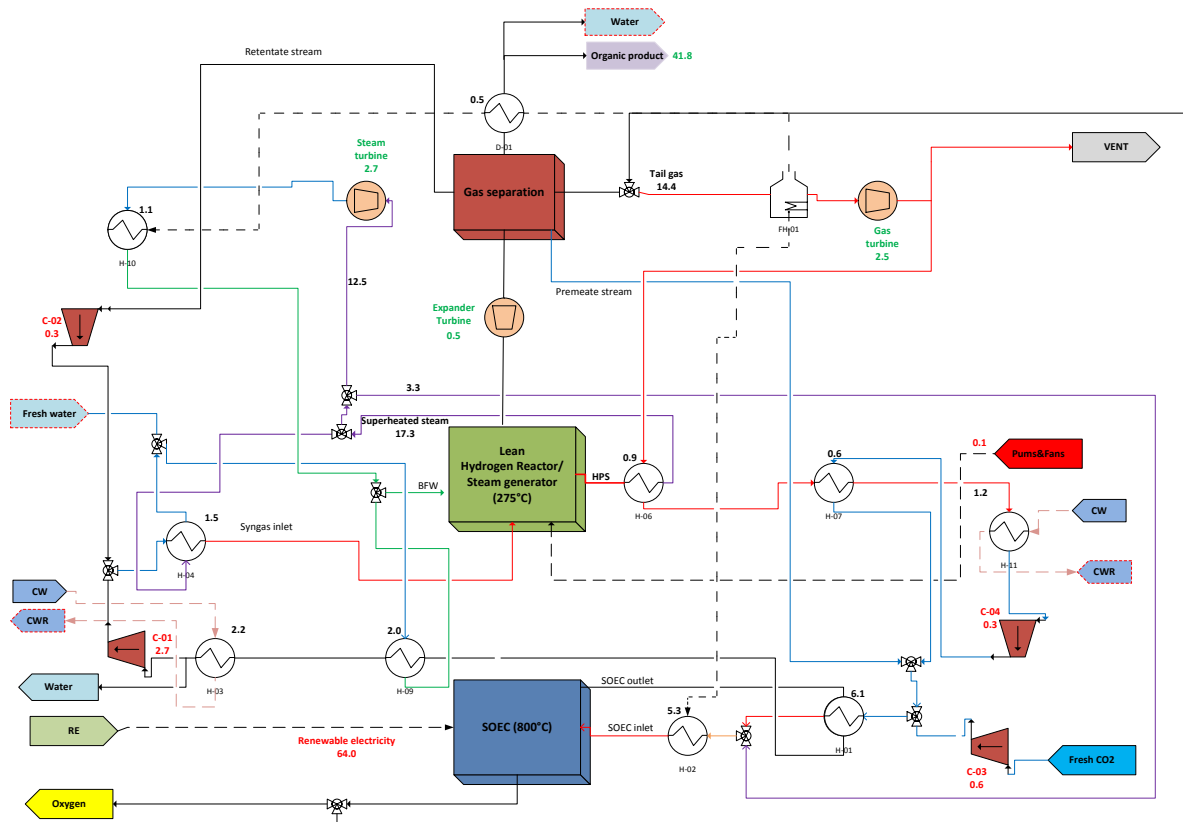
^aHeating by tail gas combustion.

^bCooling by cold water.

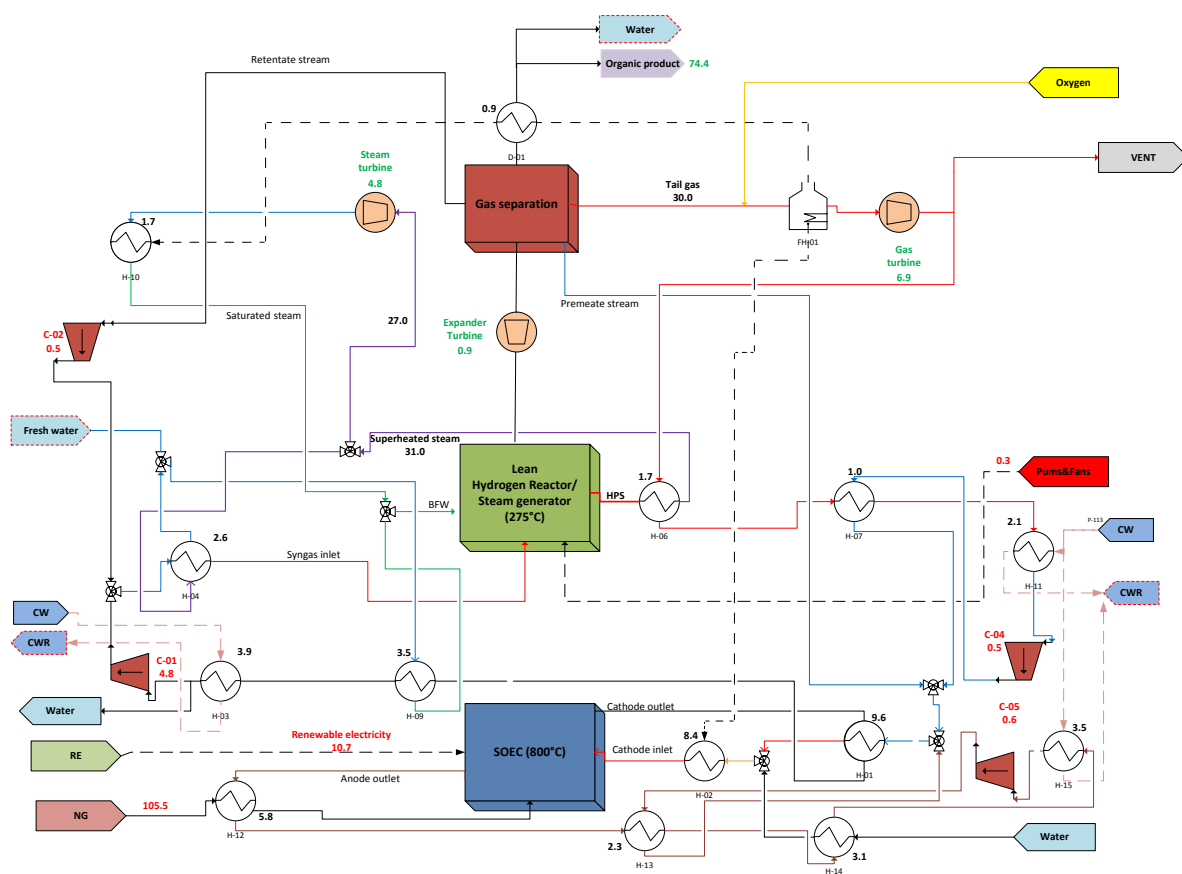
^cCooling by air cooler.



Supplementary Figure 8. Composite curve of the integrated process. A minimum pinch point of 10°C was defined for heat exchangers network.



Supplementary Figure 9. Energy flow diagram of overall process powered by RE. The numbers indicate the energy content or power requirement of each stream in W-h per mol syngas produced in the SOEC.



Supplementary Figure 10. Energy flow diagram for Methane-assisted SOEC process. The numbers indicate the energy content or power requirement of each stream in W-h per mol syngas produced in the cathode side.

Tag No	Description	Size	Purchase cost, \$M	Ref.
R-01	Lean hydrogen reactor	No. of tubes:1,830, D=0.038m, H=12m	3.00	Manufacturer
C-01	Backpressure steam turbine compressor	$M_{\text{steam}}=5.8\text{kg/sec}$, $P=2.1\text{MW}$	1.60	Manufacturer
C-02	Lean hydrogen Recycle compressor	$P=0.2\text{MW}$	0.51	
C-03&E-01	CO ₂ Turbo expander-compressor	$P=0.4\text{MW}$	1.25	Manufacturer
C-04	Tail gas Recycle compressor	$P=0.2\text{MW}$	0.51	
R-02	Oligomerization reactor	$V=25\text{m}^3$	0.13	[1]
H-01	Heat exchanger	$A=300\text{m}^2$	0.15	
H-02	Heat exchanger	$A=110\text{m}^2$	0.06	
H-03	Heat exchanger	$A=130\text{m}^2$	0.07	
H-04	Heat exchanger	$A=75\text{m}^2$	0.07	
H-05	Heat exchanger	$A=180\text{m}^2$	0.16	
H-06	Heat exchanger	$A=300\text{m}^2$	0.30	
H-07	Heat exchanger	$A=30\text{m}^2$	0.03	
H-08	Heat exchanger	$A=95\text{m}^2$	0.09	
H-09	Heat exchanger	$A=300\text{m}^2$	0.30	
H-10	Heat exchanger	$A=15\text{m}^2$	0.01	
H-11	Heat exchanger	$A=100\text{m}^2$	0.06	
A-01	Air cooler	$A=11\text{m}^2$	0.02	
A-02	Air cooler	$A=6\text{m}^2$	0.01	
S-01	Gas liquid separator	$V=3.5\text{m}^3$	0.07	
S-02	Gas liquid separator	$V=1.5\text{m}^3$	0.09	
S-03	Gas liquid-liquid separator	$V=2.0\text{m}^3$	0.12	
S-04	Gas liquid separator	$V=0.7\text{m}^3$	0.06	
S-05	Gas liquid separator	$V=1.5\text{m}^3$	0.06	
S-06	Gas liquid-liquid separator	$V=1.8\text{m}^3$	0.06	
S-07	Gas liquid separator	$V=1.0\text{m}^3$	0.04	
S-08	Gas liquid separator	$V=0.5\text{m}^3$	0.03	
S-09	Gas liquid separator	$V=0.7\text{m}^3$	0.03	
C-01	Cooling tower&Pumps	$Q=0.088\text{m}^3/\text{sec}$	0.12	[1]
P-01/02/03/04	Single-stage centrifugal pumps	$Q=0.002\text{m}^3/\text{sec}$	0.03	[1]
M-01	Polymeric membrane	$A=300\text{m}^2$	0.15	[3-4]
G-01	Gas Turbine	$P=2.0\text{MW}$	1.50	[5-6]

D-01	Distillation unit	D=0.4m, H=5m, Q=0.42MW	0.10	
	Total		10.79	

Supplementary Table 5. Summary of purchase cost for main equipment units^a

^a Cost data derived from CHAMCAD costing tool if not stated otherwise

Supplementary Table 6. Summary of additional main equipment units for MPE^a

Tag No	Description	Size	Purchase cost, \$M	Ref.
C-05	Anode Recycle compressor	P=0.3MW	0.72	
H-12	Heat exchanger	A=120m ²	0.07	
H-13	Heat exchanger	A=50m ²	0.04	
H-14	Heat exchanger	A=85m ²	0.06	
H-15	Heat exchanger	A=100m ²	0.06	
S-10	Gas liquid separator	V=0.9m ³	0.04	
H-01	Gas Turbine extension	P=3.0MW	0.60	[5-6]
C-01	Cooling tower extension	Q=0.123m ³ /sec	0.02	[1]
P-05/06	Single-stage centrifugal pumps	Q=0.001m ³ /sec	0.01	[1]
	Total		1.62	

^a Equipment costs were obtained from CHEMCAD if not stated otherwise.

Supplementary Table 7. Cost of utilities and materials

Utility/Material	Cost, \$/ton	Units	SOEC powered by RE		Methane-assisted SOEC		Ref.
			Quantity, ton/year	Cost M\$/year	Quantity, ton/year	Cost M\$/year	
Cooling water	0.03	\$/ton	2,500,000	0.08	3,540,000	0.11	[1]
Process water	0.5	\$/ton	33,400	0.02	-	-	[1]
CO ₂ capture	22	\$/ton	70,056	1.54	-	-	[7-8]
Oxygen	24	\$/ton	-72,784	-1.75	36,832	0.88	[9]
Waste water treatment	2	\$/ton	4,320	0.01	4,320	0.01	[1]
Fe catalyst	30,000 ^a	\$/ton	15 ^b	0.45	15	0.45	
ZSM-5 catalyst	30,000 ^a	\$/ton	15 ^b	0.45	15	0.45	
Natural gas ^c	195	\$/ton			27,000	5.27	[10]

^a Own assumption.

^b Catalyst replacement every one year was assumed based on the exp. results.

^c The cost was translated from 3.9\$/MMBTU.

Supplementary Table 8. Annual operational expenses for production of 500bpd¹⁻²

Fixed expenses	SOEC powered by RE, \$M	Methane- assisted SOEC, \$M
Maintenance ^a	2.87	3.21
Operating labour ^b	0.90	0.90
Laboratory costs ^c	0.23	0.23
Supervision ^d	0.23	0.23
Plant overheads ^e	0.45	0.45
Capital charges ^f	1.72	1.92
Local taxes ^g	1.15	1.28
Insurance ^h	1.15	1.28
Total fixed expenses	8.69	9.49
Variable expenses		
Raw materials ⁱ	1.56	0.88
Catalysts	0.90	0.90
Miscellaneous operating materials ^j	0.29	0.32
Utilities	0.08	0.11
Oxygen credit	-1.75	-
Total variable expenses	1.08	2.22
Indirect cost^k	1.47	1.76
Energy expenses	19.20	6.15
Annual production expenses	30.44	19.61

^a 5% of fixed capital. Includes: cost of maintenance labor and the materials needed for the maintenance; ^b 3 operators/shift*5 shifts*60,000\$; ^c 25% of Operating labor; ^d 25% of operating labor; ^e 50% of operating labor. Includes: general management, general clerical staff and safety; ^f 3% of fixed capital. Interest payments due on any debt or loans used to finance the project; ^g 2% of fixed capital; ^h 2% of fixed capital; ⁱCost of CO₂ capture and process water; ^j 10% of

maintenance expenses. Includes: safety clothing, accessories; ^k 15% of fixed and variable costs. Includes: Sales expense, overheads and Contingency.

Supplementary Table 9. Assumptions for economic model

Parameter	Value
Economic plant life	30 years
Discount rate	10%
Construction time	2 years
1 st year	66% of fixed capital
2 nd year	34% of fixed capital+ Working capital+ 30% of fixed costs
3 rd year	85% of design basis production rate
Fixed expenses growth rate	0.5%/year
Productivity degradation rate	0 %/year
Plant operation time	8,000h/year

Supplementary Table 10. Utilities requirements for different Carbon recycle ratios

Utility/Material	Units	Carbon recycle ratios		
		0	0.5	0.95
Cooling water	ton/year	2,127,500	2,327,500	2,500,000
Process water	ton/year	50,100	40,080	33,400
CO2 capture	ton/year	210,040	140,440	70,056
Oxygen	ton/year	-64,152	-68,152	-72,784
Waste water treatment	ton/year	3,542	3,974	4,320
Fe catalyst	ton/year	13	14	15
ZSM-5 catalyst	ton/year	13	14	15

Supplementary Table 11. Economic parameters for different Carbon recycle ratios

Carbon recycle ratio	0	0.5	0.95
Plant installed cost, \$M	40.5	43.39	44.59
SOEC installed cost, \$M	12.82	12.82	12.82
Total capital investment (TCI), \$M	55.98	59.02	60.28
Annual expenses	\$M		
Maintenance	2.67	2.81	2.87
Operating labour	0.9	0.9	0.9
Laboratory costs	0.23	0.23	0.23
Supervision	0.23	0.23	0.23
Plant overheads	0.45	0.45	0.45
Capital charges	1.6	1.69	1.72
Local taxes	1.07	1.12	1.15
Insurance	1.07	1.12	1.15
Total fixed expenses	8.22	8.55	8.69
Variable expenses			
Raw materials	4.65	3.11	1.56
Catalysts	0.81	0.84	0.9
Miscellaneous operating materials	0.27	0.28	0.29
Utilities	0.07	0.08	0.08
Oxygen credit	-1.54	-1.64	-1.75
Total variable expenses	4.26	2.67	1.08
Indirect cost	1.87	1.68	1.47
Energy expenses	18.3	18.7	19.2
Annual production expenses	32.65	31.6	30.44
LCOP, \$/liter of liquid product	1.62	1.43	1.29

Supplementary Table 12. Economic parameters for different plant capacities.

Plant scale, bpd	200	500	1,500	5,000
Total capital investment (TCI), \$M	34.79	60.28	116.55	239.88
Annual expenses	\$M			
Maintenance	1.66	2.87	5.55	11.43
Operating labour	0.90	0.90	1.20	1.50
Laboratory costs	0.23	0.23	0.30	0.38
Supervision	0.23	0.23	0.30	0.38
Plant overheads	0.45	0.45	0.60	0.75
Capital charges	0.99	1.72	3.33	6.86
Local taxes	0.66	1.15	2.22	4.57
Insurance	0.66	1.15	2.22	4.57
Total fixed expenses	5.78	8.69	15.72	30.43
Variable expenses				
Raw materials	0.62	1.56	4.67	15.58
Catalysts	0.36	0.90	2.70	9.00
Miscellaneous operating materials	0.17	0.29	0.56	1.14
Utilities	0.03	0.08	0.25	0.84
Oxygen credit	-0.70	-1.75	-5.24	-17.47
Total variable expenses	0.48	1.08	2.94	9.09
Indirect cost	0.94	1.47	2.80	5.93
Energy expenses	7.68	19.20	57.60	192.00
Annual production expenses	14.88	30.44	79.06	237.45
LCOP, \$/liter of liquid product	1.64	1.29	1.06	0.91

Supplementary Table 13. Economic and technical input parameters for battery storage¹¹⁻¹²

Investment, \$/kW	Variable cost, \$/MWh	Fixed cost, \$/kW	Lifetime, years	Efficiency, %	LCOE, \$/MWh
160	2.1	7.2\$/kW	15	95	140

Supplementary Table 14. Capex and Opex for plant operated by RE with large scale battery storage

Assumed availability factor	0.3
Total capital investment, \$M	331.9
Annual production expenses, \$M/year	53.86
LCOP, \$/liter of liquid product	2.78

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