Process development and policy implications for large scale deployment of solar-driven electrolysis-based renewable methanol production

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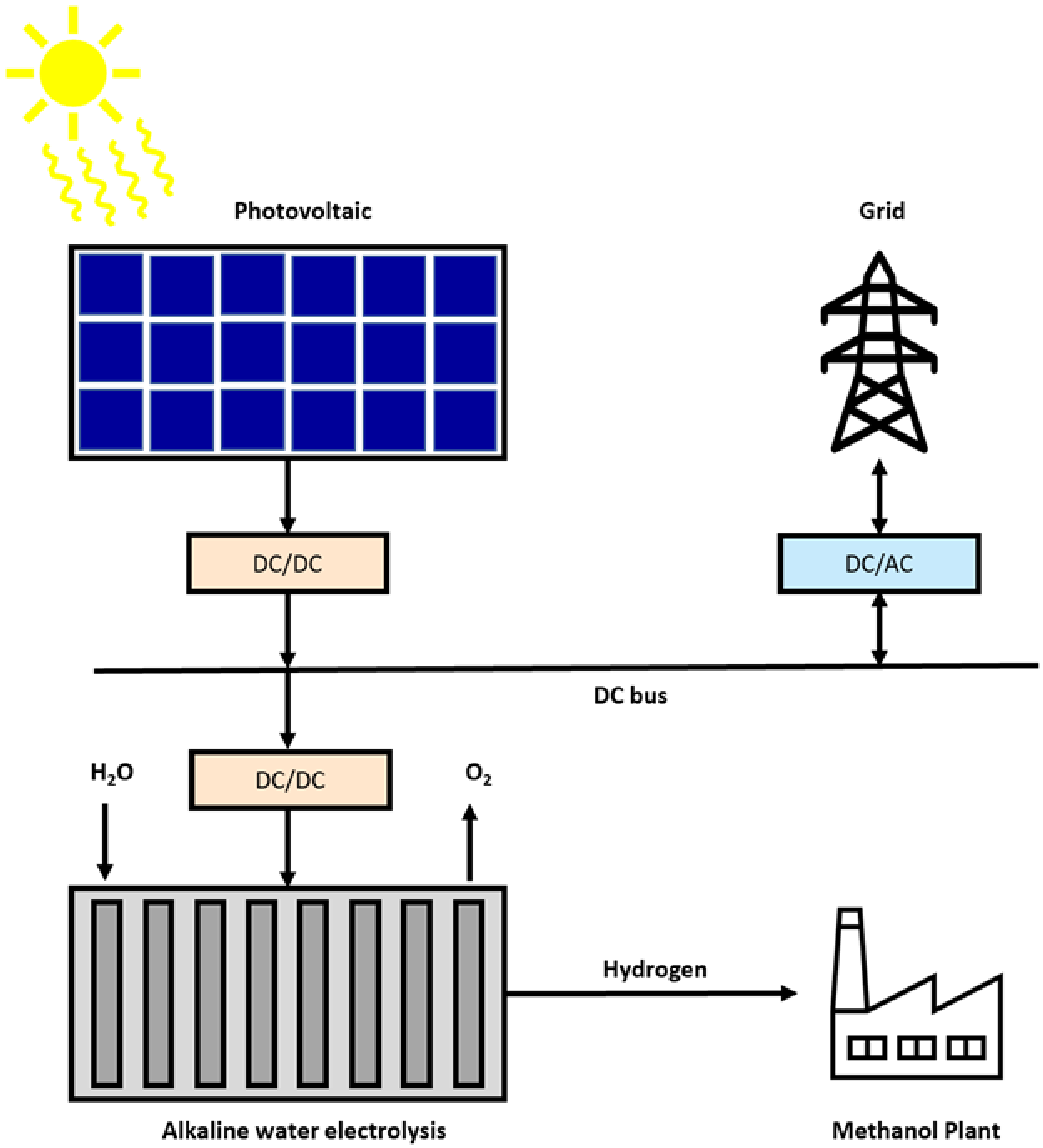

Figure S1 Methodology for determining the minimum production cost of renewable hydrogen produced via solar driven electrolyzer.

Table S1 Average hourly profile of photovoltaic power output (kWh) using large-scale commercial photovoltaic system mounted on leveled ground.

Project	San Pedro de Atacama
Location	San Pedro de Atacama, Provincia de El Loa, Chile
Geographical coordinates	-23.120154°, -67.467041° (-23°07'13", -067°28'01")
Time zone	UTC-04, America/Santiago [CLT]
Elevation	4725 m
Report generated	27 Jul 2022
Generated by	Global Solar Atlas
Map link	https://globalsolaratlas.info/map?s=-23.120154,-67.467041,10&pv=ground,0,26,1500

Average hourly profiles
Total photovoltaic power output [kWh]

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0 - 1	0	0	0	0	0	0	0	0	0	0	0	0
1 - 2	0	0	0	0	0	0	0	0	0	0	0	0
2 - 3	0	0	0	0	0	0	0	0	0	0	0	0
3 - 4	0	0	0	0	0	0	0	0	0	0	0	0
4 - 5	0	0	0	0	0	0	0	0	0	0	0	0
5 - 6	0	0	0	0	0	0	0	0	0	1	3	2
6 - 7	24	12	8	3	1	0	0	1	22	47	46	33
7 - 8	153	136	158	177	140	81	78	147	226	274	266	204
8 - 9	393	385	430	453	429	380	377	430	495	536	522	453
9 - 10	604	607	657	668	638	593	595	650	703	734	715	656
10 - 11	747	760	808	809	777	737	745	800	842	863	839	787
11 - 12	815	843	887	887	853	820	835	886	909	917	899	842
12 - 13	812	842	886	897	875	848	866	907	920	916	900	829
13 - 14	736	781	848	869	846	819	841	886	899	884	847	772
14 - 15	637	679	768	780	756	736	760	802	808	780	747	694
15 - 16	513	556	631	630	609	593	617	658	651	614	591	562
16 - 17	362	398	446	422	402	320	420	451	436	390	376	378
17 - 18	183	205	188	81	14	11	15	85	82	107	120	157
18 - 19	36	35	13	3	0	0	0	2	4	8	13	20
19 - 20	2	1	0	0	0	0	0	0	0	0	0	1
20 - 21	0	0	0	0	0	0	0	0	0	0	0	0
21 - 22	0	0	0	0	0	0	0	0	0	0	0	0
22 - 23	0	0	0	0	0	0	0	0	0	0	0	0
23 - 24	0	0	0	0	0	0	0	0	0	0	0	0

Mathematical model to determine minimum production cost of renewable hydrogen

The power ($P_{t,m}$) produced by the solar plant at time *t* in month *m* is calculated as follows:

$$P_{t,m} = \theta_{t,m} \times C, \ \forall t \in T, \forall m \in M, \tag{1}$$

where $\theta_{t,m}$ is specific power (kWh/kWp) at time *t* in month *m* and *C* is the capacity of the solar plant.

Once renewable power is produced, it can be processed in two ways as follows:

$$P_{t,m} = P1_{t,m} + P2_{t,m}, \ \forall t \in T, \forall m \in M, \tag{2}$$

where $P1_{t,m}$ is the power utilized by electrolyzer at time *t* in month *m*. Whereas $P2_{t,m}$ is the power not utilized by electrolyzer at time *t* in month *m*. The $P2_{t,m}$ is the case when the available power either exceeds the electrolyzer capacity or is below the operating capacity of the electrolyzer.

The $P2_{t,m}$ can be exported to the grid (*G*) as follows:

$$G \leq \sum_{t,m} P2_{t,m}. \tag{3}$$

When solar power is not available, the power exported to the grid (*G*) can be imported ($PI_{t,m}$) at time *t* in month *m* as follows:

$$\sum_{t,m} PI_{t,m} \leq G. \tag{4}$$

The power to the electrolyzer cannot exceed its capacity (δ) and cannot be below the minimum required power (α). To ensure this, logical constraints are modeled as:

$$P1_{t,m} + S_{t,m} \leq \delta, \ \forall t \in T, \forall m \in M, \tag{5}$$

$$P1_{t,m} + S_{t,m} \leq Z_{t,m} \times \zeta, \ \forall t \in T, \forall m \in M, \tag{6}$$

$$P1_{t,m} + S_{t,m} \geq \alpha \times \delta - \zeta \times (1 - Z_{t,m}), \ \forall t \in T, \forall m \in M, \tag{7}$$

where $Z_{t,m}$ represent binary variables to allow power to the electrolyzer at time *t* in month *m* and ζ represents the upper bound for power to the electrolyzer according to the Big-M formulation method.

The hydrogen ($H_{t,m}$) produced by the electrolyzer at time *t* in month *m* is estimated as follows:

$$H_{t,m} = \eta \times (P1_{t,m} + S_{t,m}), \ \forall t \in T, \forall m \in M, \tag{8}$$

where η is the electrolyzer efficiency and $S_{t,m}$ is renewable power imported from the grid at time *t* in month m.

The total annual hydrogen (*TH*) produced is estimated as follows:

$$TH = \sum_{t,m} H_{t,m} \times d_m, \tag{9}$$

where d_m is days in month *m*.

The total annual operating hours of the electrolyzer (*TE*) are estimated as follows:

$$TE = \sum_{t,m} Z_{t,m} \times d_m \quad (10)$$

Finally, economic analysis was performed by formulating a discounted cash flow rate of return analysis model based on CAPEX (capital expenditure) and OPEX (Operating expenditure). The Levelized cost of hydrogen (LCOH) was selected as an economic indicator for evaluating hydrogen cost ($/kg) and defined as follows:

$$LCOH = \frac{NPV\ of\ total\ costs}{NPV\ of\ hydrogen\ production}, \quad (11)$$

where NPV is the net present value. The NPV of total costs is estimated as follows:

$$NPV\ of\ total\ costs = \sum_{n} \frac{CAPEX + OPEX}{(1 + IRR)^n}, \quad (12)$$

where IRR is the internal rate of return. The CAPEX and OPEX are estimated based on the below parameters.

Table S2 Parameters used in optimization to estimate the Levelized cost of hydrogen.

Items	Value
PV CAPEX ($/kWh)	1200
PV OPEX ($/kWh)	14.4
IRR	0.06
Electrolyzer CAPEX ($/kW)	1150
Water (L/kg of H2)	10
Stack replacement (hours)	40000
Stack replacement cost	0.4 of electrolyzer CAPEX
Electrolyzer OPEX ($/kW)	17
Minimum operating capacity of the electrolyzer(kW)	100
Maximum operating capacity of the electrolyzer (kW)	1000

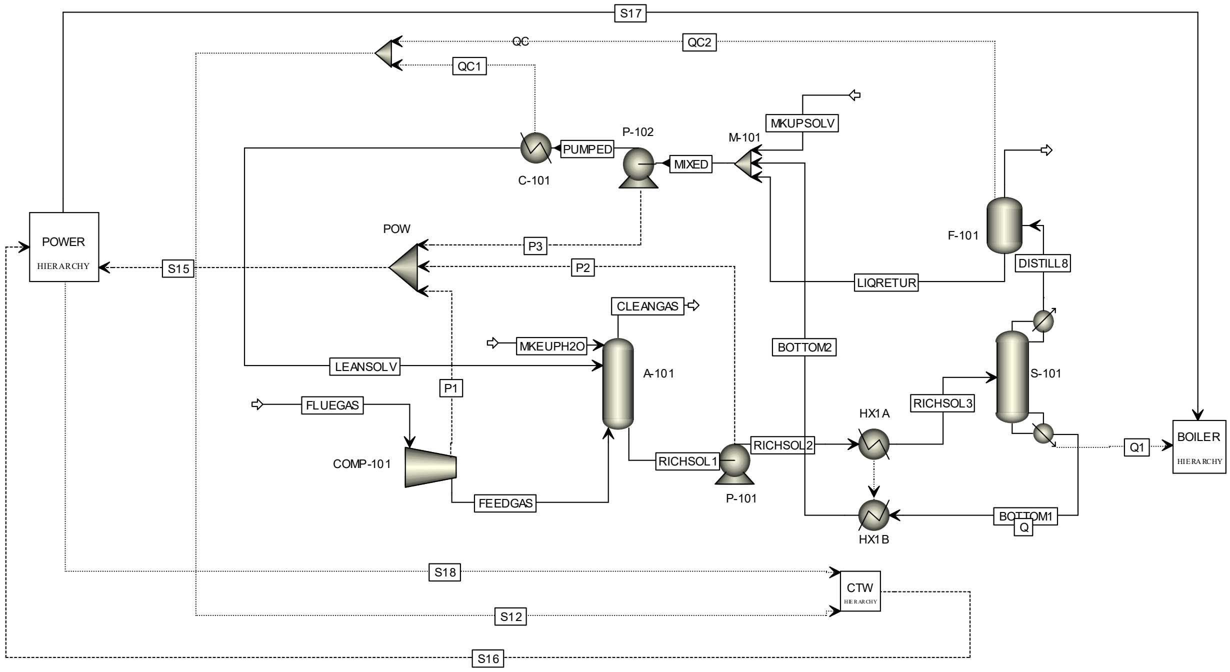

Figure S2 Aspen plus model of carbon dioxide capture plant.

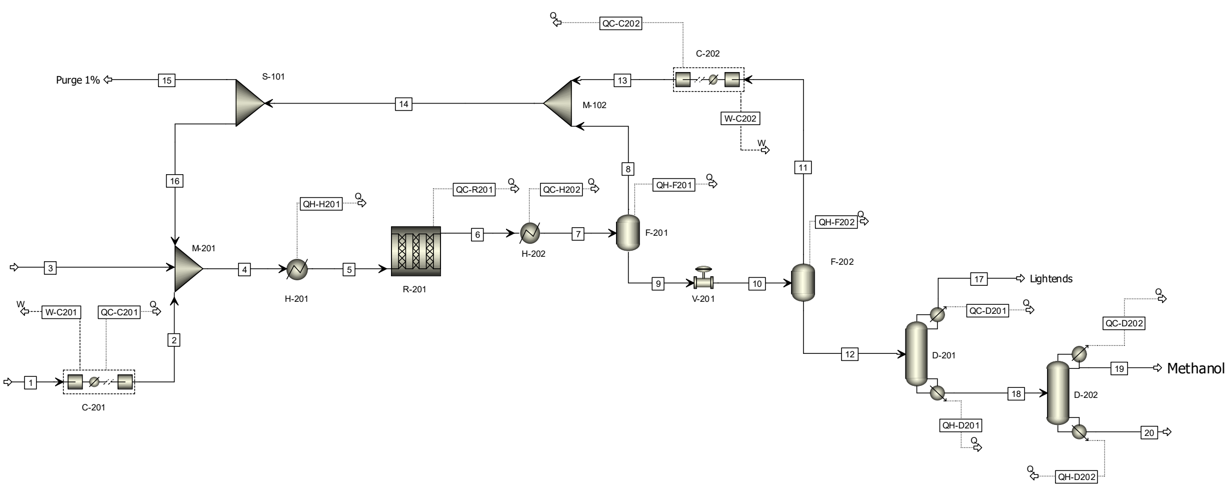

Figure S3 Aspen plus model of base case design.

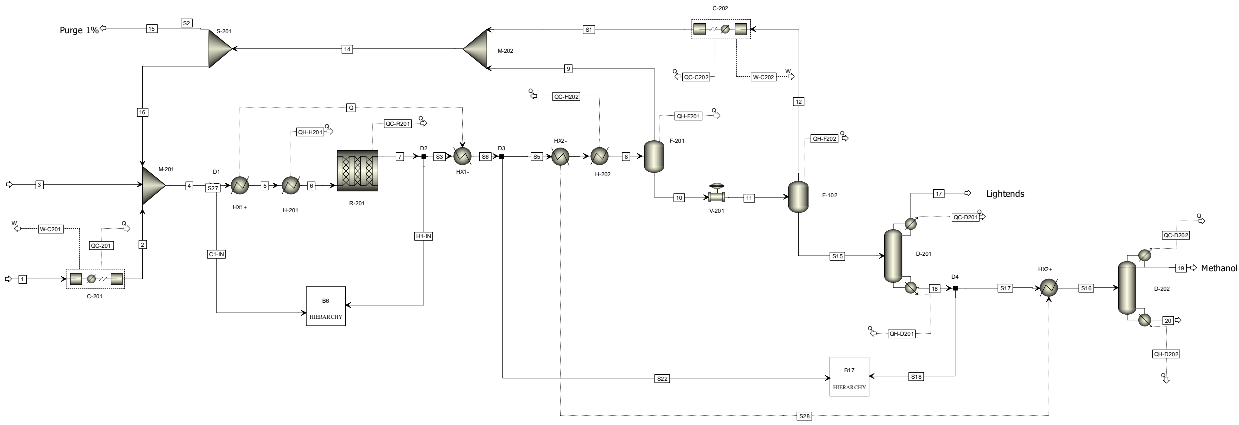

Figure S4 Aspen plus model of integrated design.

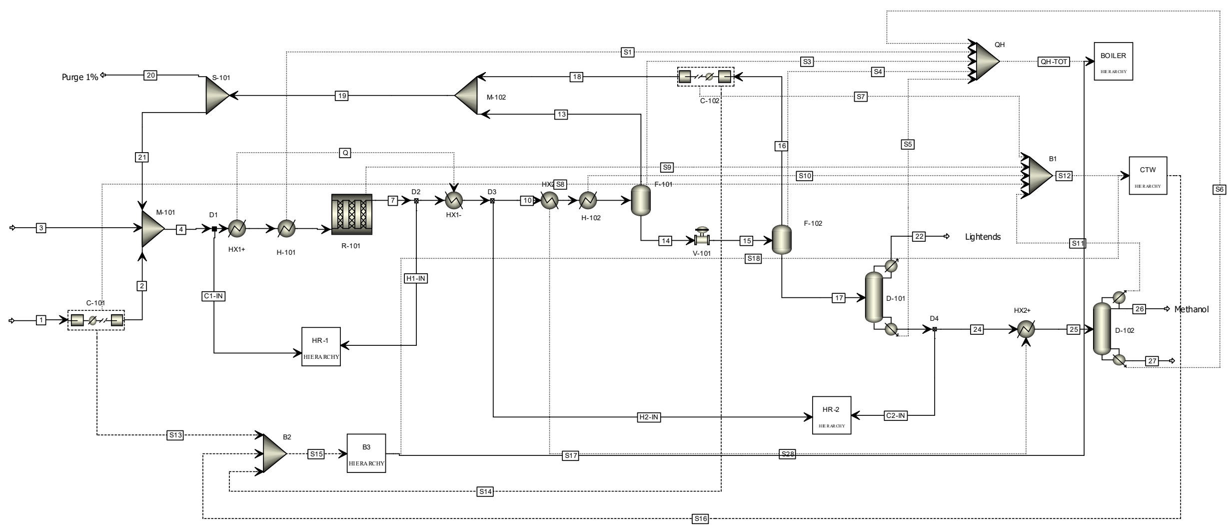

Figure S5 Aspen plus model of 100% renewable design.

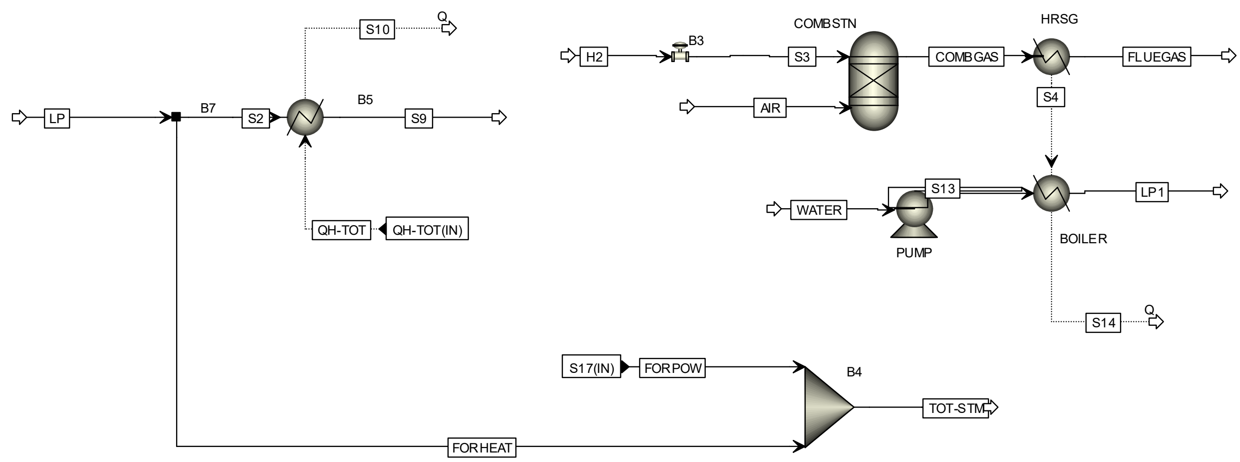

Figure S6 Aspen plus model of boiler design for carbon capture and 100% renewable methanol plants.

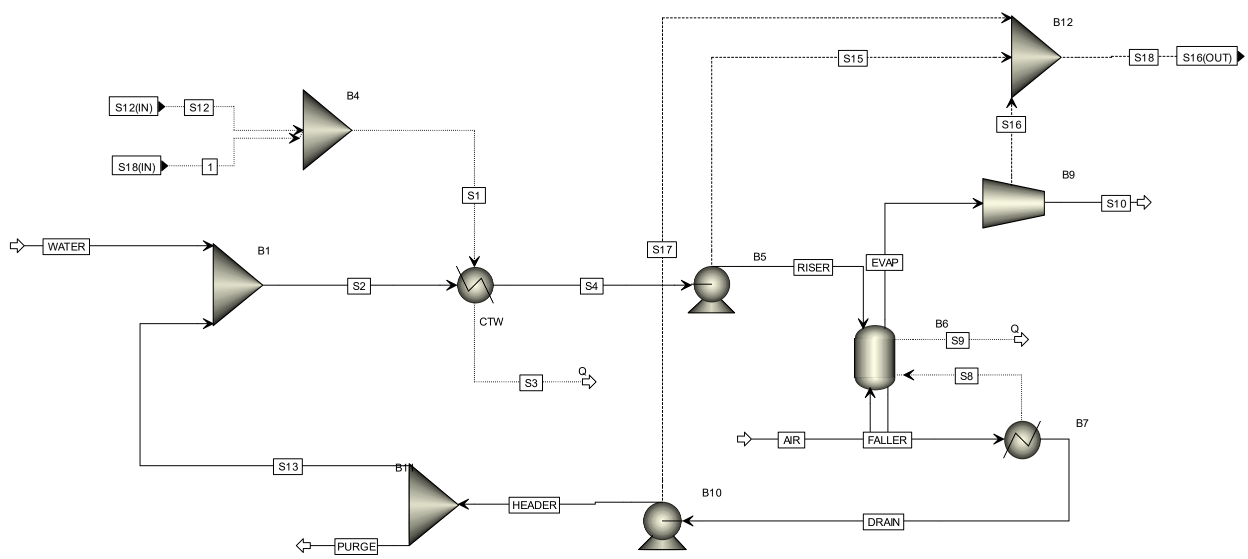

Figure S7 Aspen plus model of cooling tower design for carbon capture and 100% renewable methanol plants.

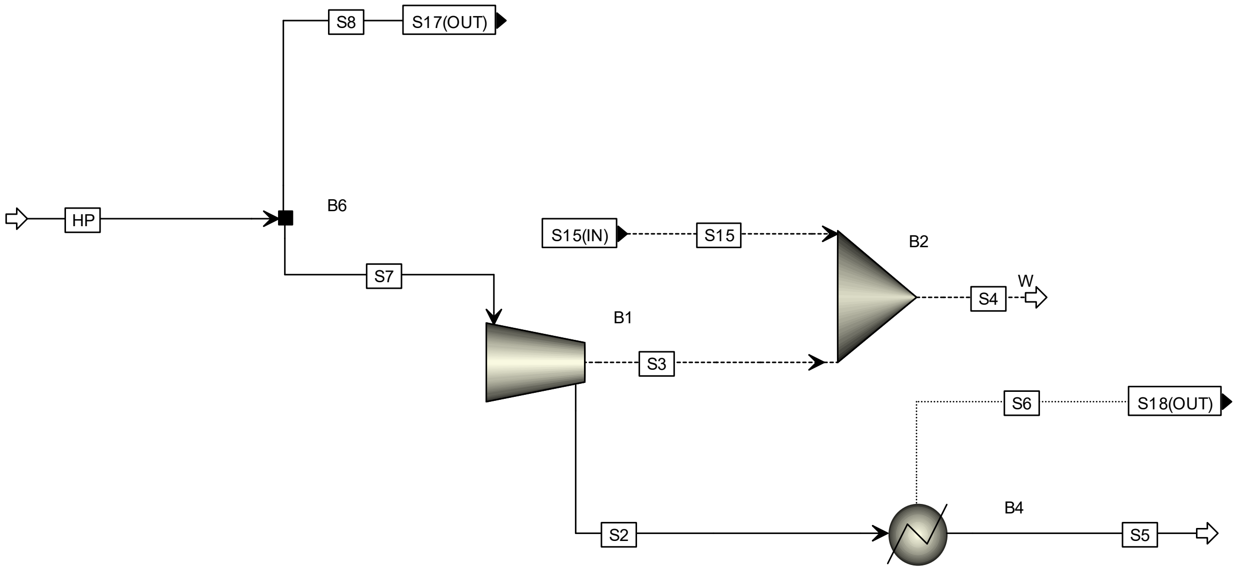

Figure S8 Aspen plus model of power generation for carbon capture and 100% renewable methanol plants.

Table S3 Deterministic price of chemicals and utility.

Chemicals	**Price**
Hydrogen ($/kg)	4 $/kg (Calculated value, see Section 3.1 of MS)
MEA ($/kg)	1.31 $/kg [1]
Heating utility ($/GJ)	4.03 USD/GJ [2]
Electricity ($/GJ)	0.65 USD/GJ [3]
Chilled water	5 USD/GJ [4]
Wastewater	0.041 USD/m^3 [4]

Table S4 Uncertainties chemical prices, utilities, economic indicators, and total capital investment [5,6].

Chemicals	**Price**
Hydrogen ($/kg)	1–6 $/kg
MEA ($/kg)	0.98–1.64 $/kg
IRR	6–14%
TCI	±50%
Utilities	±25%

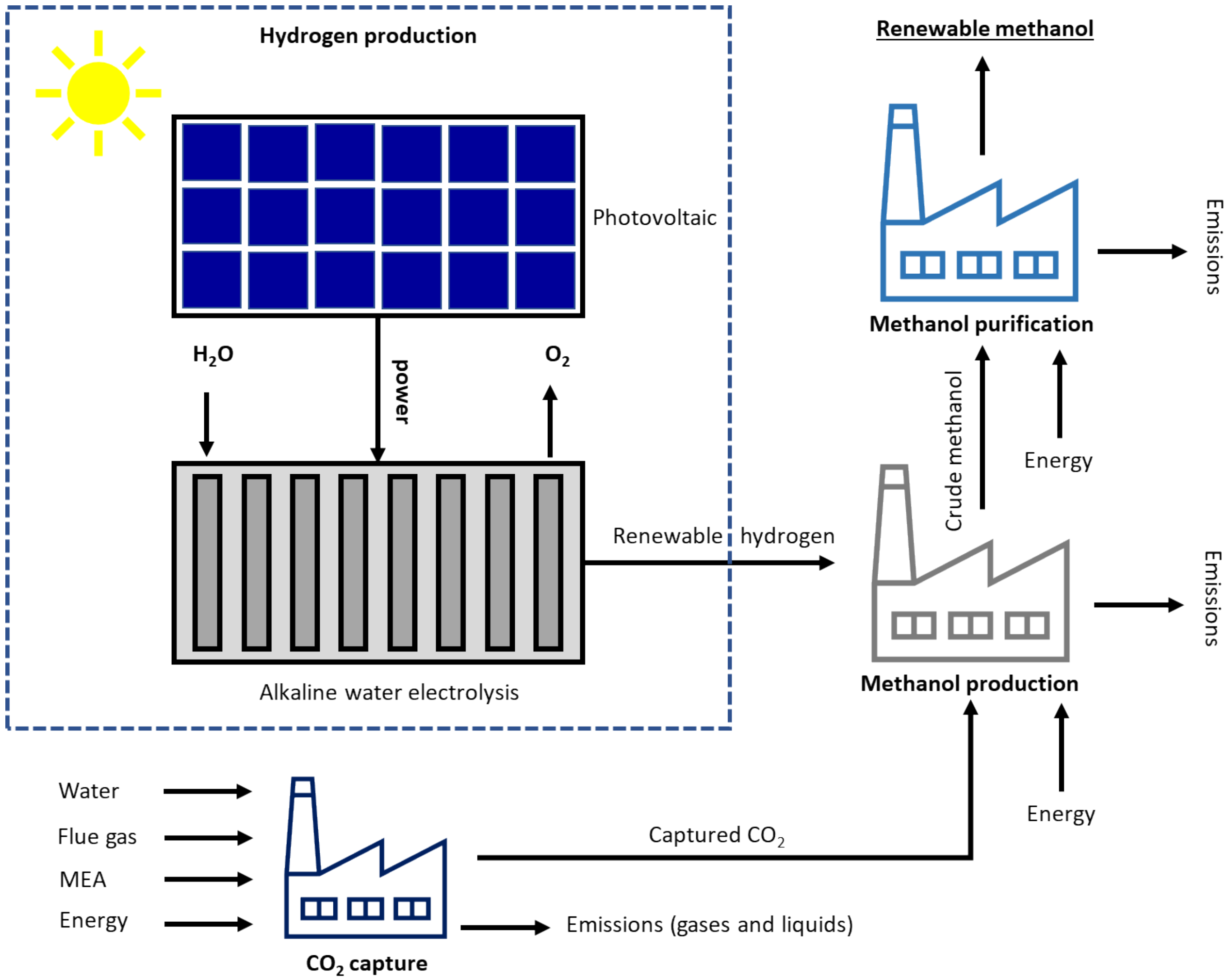

Figure S9 System boundary for gate-to-gate life cycle assessment of methanol production.

Table S5 Material required to produce 1 kg hydrogen from solar-driven electrolysis.

Electrolyzer operation	**Value**
Electricity (kWh/kg H_2)	50.000
Water (kg/kg H_2)	10.000
Nitrogen (g/kg H_2)	0.290
Potassium hydroxide (g/kg H_2)	1.900
Steam (kg/kg H_2)	0.110

Table S6 Inventory data for methanol production. Data is scaled based on one kg methanol.

Item	Fossil-based Methanol	Base design	Integrated design	100% renewable design
Electrolyzer operation				
Renewable electricity	0.00E+00	9.83E+00	9.83E+00	1.28E+01
Water	0.00E+00	1.97E+00	1.97E+00	2.56E+00
Nitrogen	0.00E+00	5.70E-02	5.70E-02	7.43E-02
Potassium hydroxide	0.00E+00	3.73E-03	3.73E-03	4.87E-03
Steam	0.00E+00	2.16E-02	2.16E-02	2.82E-02
CO_2 capture				
Water (kg)	0.00E+00	5.51E-02	5.51E-02	5.51E-02
MEA in flue gas (kg)	0.00E+00	3.05E-05	3.05E-05	3.05E-05
MEA (kg)	0.00E+00	1.33E-04	1.33E-04	1.33E-04
Grid electricity (kWh)	0.00E+00	2.52E-02	2.52E-02	0.00E+00
Heating, LP-steam (kWh)	0.00E+00	5.36E+00	5.36E+00	0.00E+00
Methanol production				
Renewable hydrogen (kg)	0.00E+00	1.97E-01	1.97E-01	2.56E-01
Fossil-derived hydrogen (kg)	1.97E-01	0.00E+00	0.00E+00	0.00E+00
CO_2 (kg)	1.44E+00	1.44E+00	1.44E+00	1.44E+00
Purge (kg)	0.00E+00	0.00E+00	0.00E+00	0.00E+00
CO	3.08E-03	2.87E-03	3.08E-03	3.08E-03
H_2	6.03E-03	5.64E-03	6.03E-03	6.03E-03
Methanol	4.58E-04	4.41E-04	4.58E-04	4.58E-04
CO_2	4.38E-02	4.10E-02	4.38E-02	4.38E-02
H_2O	5.23E-05	5.03E-05	5.23E-05	5.23E-05
Grid electricity (kWh)	1.57E-01	1.65E-01	1.57E-01	0.00E+00
Heating, LP-steam (kWh)	5.07E-02	1.18E+00	5.07E-02	0.00E+00
Methanol purification				
Light gases (kg)				
CO	1.55E-06	1.56E-06	1.55E-06	1.55E-06
H_2	1.56E-06	1.59E-06	1.56E-06	1.56E-06
Methanol	8.06E-10	1.74E-07	8.06E-10	8.06E-10
CO_2	6.85E-03	6.88E-03	6.85E-03	6.85E-03
Wastewater (kg)				
Methanol	5.00E-03	5.03E-03	5.00E-03	5.00E-03
Grid electricity (kWh)	5.45E-03	1.89E-03	5.45E-03	0.00E+00
Heating, LP-steam (kWh)	6.75E-01	9.74E-01	6.75E-01	0.00E+00

Table S7 Ecoinvent 3.6 and ELCD databases selected for life cycle impact assessment of methanol production process.

Processes	Databases
Electricity, high voltage {RoW}| electricity production, solar tower power plant, 20 MW | APOS, U	Ecoinvent 3.6
De-ionised water, reverse osmosis, production mix, at plant, from surface water RER S	ELCD
Nitrogen, via cryogenic air separation, production mix, at plant, gaseous EU-27 S	ELCD
Potassium hydroxide {RER}| production | APOS, S	Ecoinvent 3.6
Water, Tap water {GLO}| market group for | APOS, S	Ecoinvent 3.6
Monoethanolamine {RER}| ethanolamine production | APOS, S	Ecoinvent 3.6
Hydrogen, gaseous {RoW}| hydrogen production, gaseous, petroleum refinery operation | APOS, S	Ecoinvent 3.6
Carbon dioxide, liquid {RoW}| production | APOS, S	Ecoinvent 3.6
Electricity, medium voltage {US}| market group for | APOS, S	Ecoinvent 3.6
Steam, in chemical industry {RoW}| market for steam, in chemical industry | APOS, S	Ecoinvent 3.6

Table S8 Life cycle indicator results of methanol production via different scenarios. Negative sign represents environmental savings while positive represent environmental burden. Environmental savings are obtained by substituting equivalent amount of fossil fuel-based hydrogen and carbon dioxide.

Impact categories	Fossil-based methanol	Base design	Integrated design	100% renewable design
ADP (kg Sb eq.)	1.83E-05	-1.34E-05	-1.35E-05	-1.31E-05
AFFDP (MJ)	4.13E+01	1.54E+00	-4.47E+00	-3.74E+01
GWP100 (kg CO2 eq.)	1.91E+00	1.57E+00	1.10E+00	-9.65E-01
ODP (kg CFC-11 eq.)	4.19E-07	-1.73E-07	-2.08E-07	-4.60E-07
HTP (kg 1,4-DB eq.)	2.37E+00	-1.32E+00	-1.41E+00	-1.77E+00
FWAETP (kg 1,4-DB eq.)	7.18E-01	1.18E-01	5.78E-02	-1.30E-01
MAETP (kg 1,4-DB eq.)	1.72E+03	4.40E+02	1.93E+02	-8.78E+02
TEP (kg 1,4-DB eq.)	2.57E-03	7.03E-04	3.86E-04	-1.03E-03
PCOP (kg C2H4 eq.)	5.25E-04	2.19E-04	1.47E-04	-2.02E-04
AP (kg SO2 eq.)	7.99E-03	3.04E-03	1.50E-03	-5.80E-03
EP (kg PO4 eq.)	1.99E-03	3.97E-04	1.17E-04	-1.29E-03

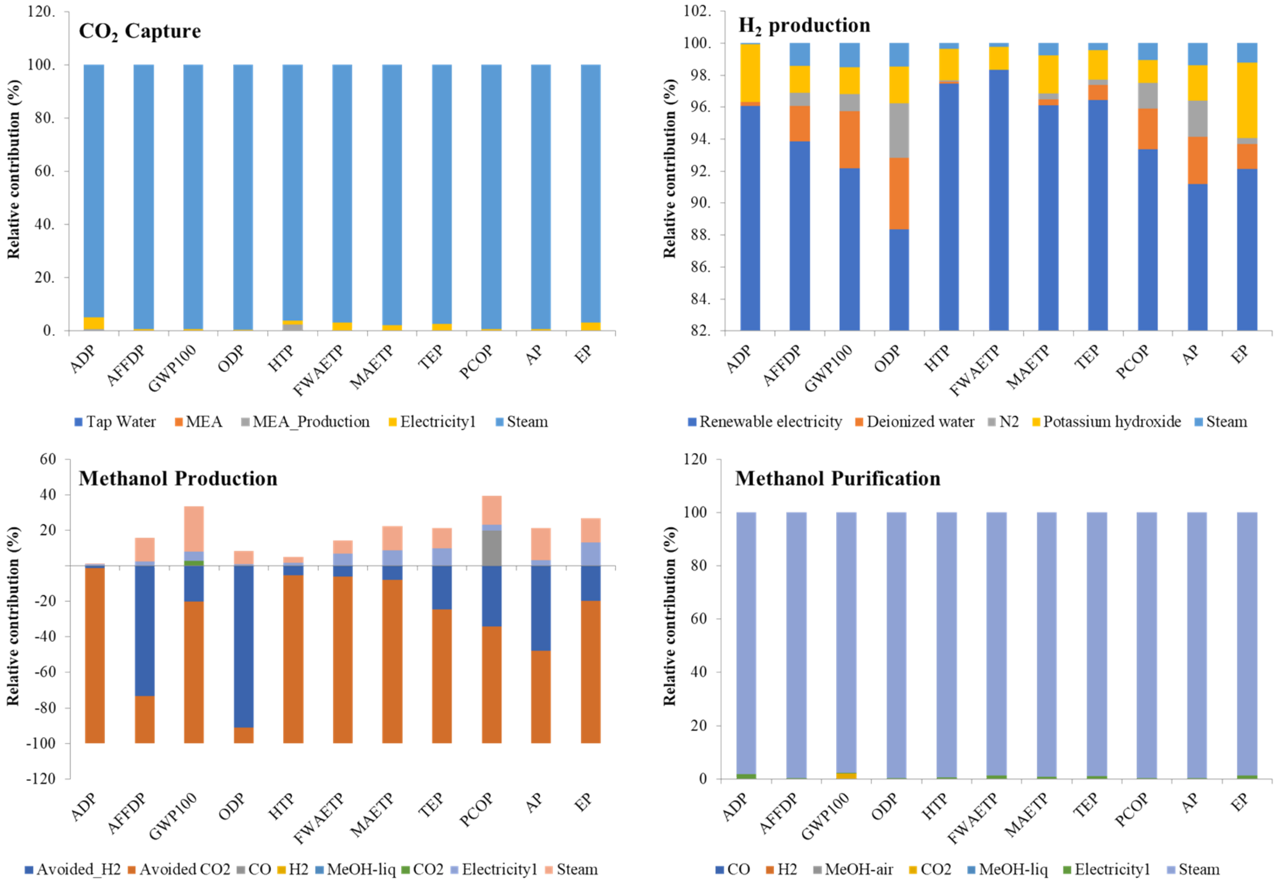

Figure S10 Life cycle profile of a renewable methanol production through base case design. ADP = abiotic depletion potential; AFFDP = fossil fuel depletion potential; GWP100 = global warming potential 100 years; ODP = ozone depletion potential; HTP = human toxicity potential; FWAETP = freshwater aquatic ecotoxicity potential; MAETP = marine aquatic ecotoxicity potential; TEP = terrestrial ecotoxicity potential; PCOP = photo chemical oxidation potential; AP = acidification potential; EP = eutrophication potential.

Table S9 Life cycle indicator results of methanol production via base case design.

Impact categories	CO_2 Capture	H_2 Production	Methanol production	Methanol Purification
ADP (kg Sb eq.)	5.12E-07	3.92E-06	-1.79E-05	8.99E-08
AFFDP (MJ)	2.26E+01	6.32E+00	-3.14E+01	4.08E+00
GWP100 (kg CO2 eq.)	1.79E+00	4.71E-01	-1.02E+00	3.31E-01
ODP (kg CFC-11 eq.)	1.31E-07	3.63E-08	-3.64E-07	2.38E-08
HTP (kg 1,4-DB eq.)	3.72E-01	4.15E-01	-2.17E+00	6.53E-02
FWAETP (kg 1,4-DB eq.)	2.26E-01	4.04E-01	-5.53E-01	4.03E-02
MAETP (kg 1,4-DB eq.)	9.33E+02	4.80E+02	-1.14E+03	1.67E+02
TEP (kg 1,4-DB eq.)	1.20E-03	1.03E-03	-1.73E-03	2.14E-04
PCOP (kg C2H4 eq.)	2.91E-04	1.12E-04	-2.37E-04	5.27E-05
AP (kg SO2 eq.)	5.79E-03	1.69E-03	-5.49E-03	1.05E-03
EP (kg PO4 eq.)	1.06E-03	3.43E-04	-1.20E-03	1.89E-04

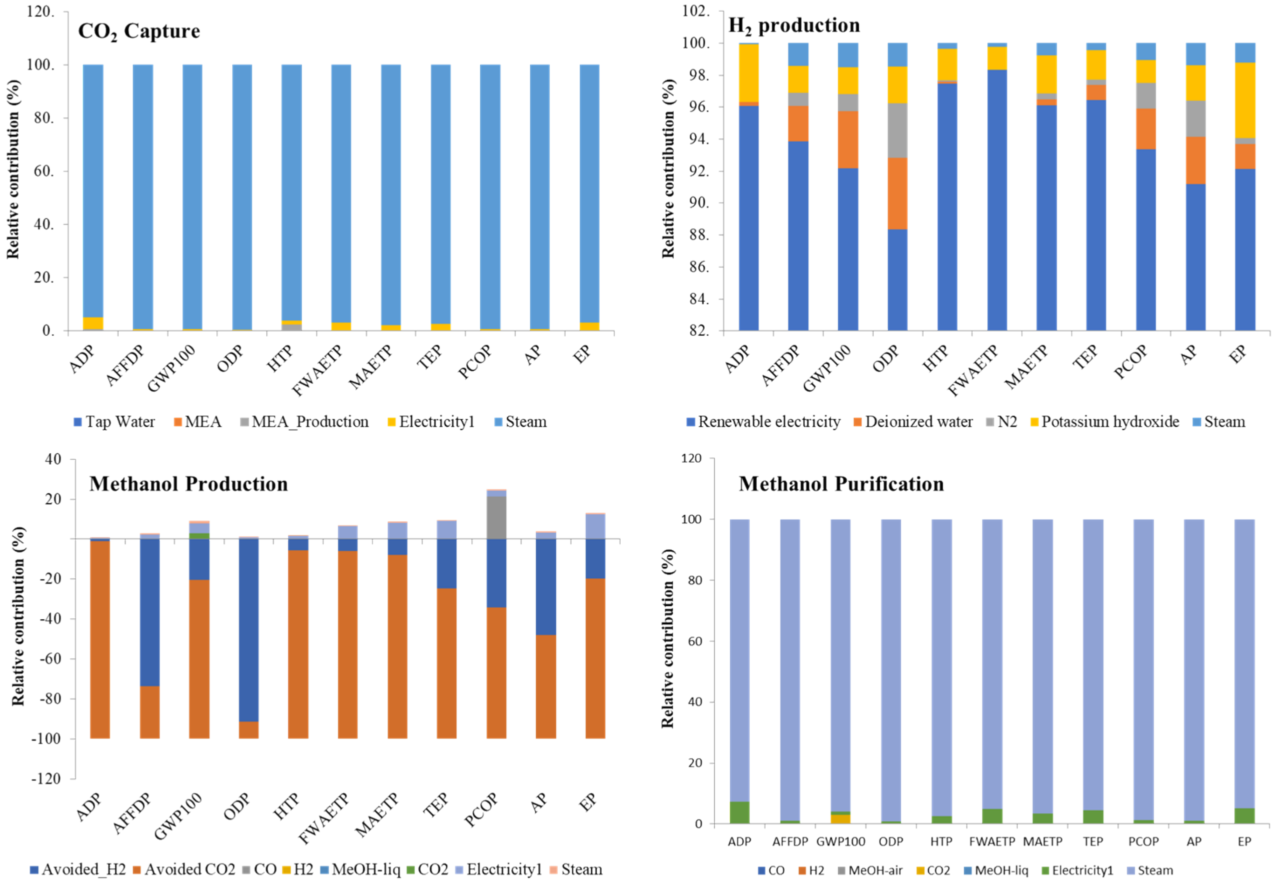

Figure S11 Life cycle profile of a renewable methanol production through integrated design. ADP = abiotic depletion potential; AFFDP = fossil fuel depletion potential; GWP100 = global warming potential 100 years; ODP = ozone depletion potential; HTP = human toxicity potential; FWAETP = freshwater aquatic ecotoxicity potential; MAETP = marine aquatic ecotoxicity potential; TEP = terrestrial ecotoxicity potential; PCOP = photo chemical oxidation potential; AP = acidification potential; EP = eutrophication potential.

Table S10 Life cycle indicator results of methanol production via integrated design.

Impact categories	CO_2 Capture	H_2 Production	Methanol production	Methanol Purification
ADP (kg Sb eq.)	5.12E-07	3.92E-06	-1.80E-05	6.60E-08
AFFDP (MJ)	2.26E+01	6.32E+00	-3.62E+01	2.85E+00
GWP100 (kg CO2 eq.)	1.79E+00	4.71E-01	-1.40E+00	2.33E-01
ODP (kg CFC-11 eq.)	1.31E-07	3.63E-08	-3.92E-07	1.66E-08
HTP (kg 1,4-DB eq.)	3.72E-01	4.15E-01	-2.24E+00	4.62E-02
FWAETP (kg 1,4-DB eq.)	2.26E-01	4.04E-01	-6.02E-01	2.91E-02
MAETP (kg 1,4-DB eq.)	9.33E+02	4.80E+02	-1.34E+03	1.19E+02
TEP (kg 1,4-DB eq.)	1.20E-03	1.03E-03	-1.99E-03	1.53E-04
PCOP (kg C2H4 eq.)	2.91E-04	1.12E-04	-2.93E-04	3.68E-05
AP (kg SO2 eq.)	5.79E-03	1.69E-03	-6.72E-03	7.31E-04
EP (kg PO4 eq.)	1.06E-03	3.43E-04	-1.42E-03	1.36E-04

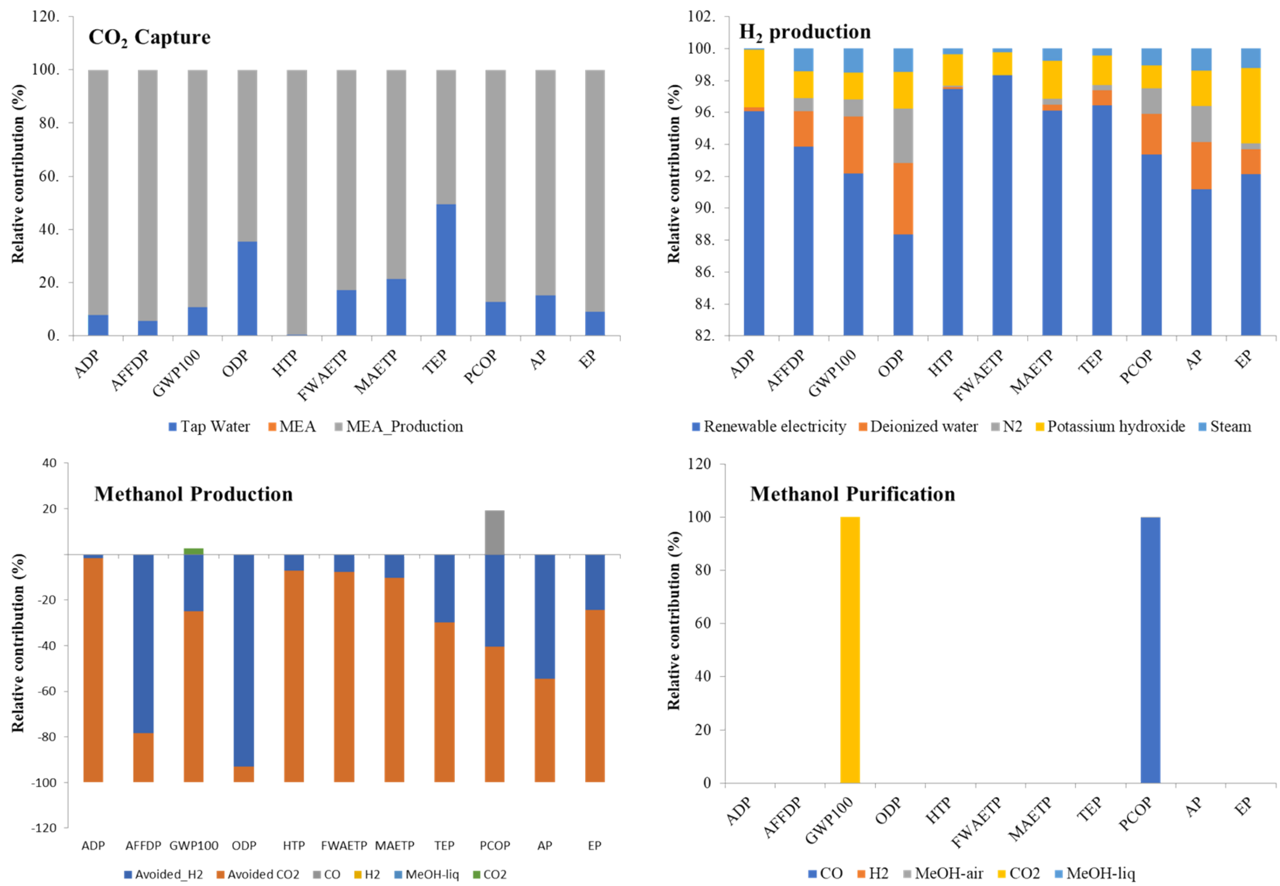

Figure S12 Life cycle profile of a renewable methanol production through 100% renewable design. ADP = abiotic depletion potential; AFFDP = fossil fuel depletion potential; GWP100 = global warming potential 100 years; ODP = ozone depletion potential; HTP = human toxicity potential; FWAETP = freshwater aquatic ecotoxicity potential; MAETP = marine aquatic ecotoxicity potential; TEP = terrestrial ecotoxicity potential; PCOP = photo chemical oxidation potential; AP = acidification potential; EP = eutrophication potential.

Table S11 Life cycle indicator results of methanol production via 100% renewable design.

Impact categories	CO_2 Capture	H_2 Production	Methanol production	Methanol Purification
ADP (kg Sb eq.)	3.69E-09	5.11E-06	-1.82E-05	0.00E+00
AFFDP (MJ)	8.27E-03	8.24E+00	-4.57E+01	0.00E+00
GWP100 (kg CO2 eq.)	3.86E-04	6.14E-01	-1.59E+00	6.85E-03
ODP (kg CFC-11 eq.)	2.87E-11	4.73E-08	-5.07E-07	0.00E+00
HTP (kg 1,4-DB eq.)	8.60E-03	5.41E-01	-2.32E+00	0.00E+00
FWAETP (kg 1,4-DB eq.)	1.62E-04	5.27E-01	-6.57E-01	0.00E+00
MAETP (kg 1,4-DB eq.)	3.13E-01	6.25E+02	-1.50E+03	0.00E+00
TEP (kg 1,4-DB eq.)	7.27E-07	1.34E-03	-2.37E-03	0.00E+00
PCOP (kg C2H4 eq.)	8.04E-08	1.46E-04	-3.48E-04	4.19E-08
AP (kg SO2 eq.)	1.21E-06	2.21E-03	-8.01E-03	0.00E+00
EP (kg PO4 eq.)	9.97E-07	4.47E-04	-1.73E-03	0.00E+00

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