Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information (SI)

Transition Pathways Towards Net-Zero Emissions Methanol Production

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1. Process parameters

An emerging Direct Air Capture (DAC) technology is being developed by wide spectrum of communities as reflected by several companies that have focused on commercialization of DAC process (Table S.1). Simultaneously, the studies on power-to-methanol routes significantly grow as presented in Table S.2. Few of them are planned for deployment as a pilot-scale power-to-methanol (Table S.3). A Proton Exchange Membrane (PEM) electrolyzer is used to facilitate H_2O electrolysis in 1st generation, while an alkaline electrolyzer is selected to facilitate CO_2 electrolysis in 2nd generation, Aspen Plus is used to model the CO_2 hydrogenation reactions, gas-liquid separation, compression, and distillation (Table S.4). Detail description of simulation is available in Section 3 of the Supplementary Information. In the hydrogenation reactor, the kinetic parameters are adapted from the Haldor Topsøe MK 101 catalysts[1]. Under similar conditions (adiabatic reactor) and feed compositions (H_2 (79.8%), CO (11.4%) and CO_2 (8.8%) at 523.4 K and 30 bar), the model of hydrogenation reaction in this study is in good agreement with the one reported in the literature [2]. The Soave-Redlich-Kwong (SRK) equation of state is selected as a thermodynamic package in the Aspen Plus simulation given it provides high accuracy in the MeOH production process, as reported in the literature [3-6]. To accommodate liquid-liquid separation for MeOH purification, the Non-Random Two-Liquid (NRTL)-RK is selected in the distillation unit. The capital and operating costs of the Aspen Plus-simulated processes is estimated using Aspen Process Economic Analyzer.

Table S.1 List of companies working to commercialize Direct Air Capture technology.

No.	Company	Capturing agent/process	Capacity	Ref.
1	Carbon Engineering	$KOH/CaCO_3$	1 ton per day	7, 8
2	Climeworks	Amine	1000 ton per year	8, 9
3	Global Thermostat	Amine	1000 ton per year	8
4	Infinitree	Ion-exchange	Lab-scale	8
5	Skytree	Benzylamines	Appliance	8

Table S.2 List of literature on techno-economic and life cycle analysis on power to methanol synthesis.

No.	Process	MeOH price ($/ton MeOH)	Remarks	Ref.
1	H_2O electrolysis and CO_2 hydrogenation	670	-Electricity cost = $0.048/kWh -Natural gas cost = 6 US$/GJ -$CO_2$ cost (post-combustion) = 18 US$/ton CO_2 -Life cycle assessment is not reported	10
2	H_2O electrolysis and CO_2 hydrogenation	725	-Electricity cost = $0.048/kWh -$CO_2$ source is post-combustion CO_2 capture -Life cycle assessment is not reported	11
3	H_2O electrolysis and CO_2	970	-Electricity and CO_2 are supplied by wind turbine and direct air capture,	12

	hydrogenation		respectively -Life cycle assessment is not reported	
4	H_2O electrolysis and CO_2 hydrogenation	735 – 1955 (grid) 1155 (onshore wind)	-Electricity (grid) cost: 0.045 – 0.162 $/kWh -Electricity (onshore wind) cost: $0.050/kWh -$CO_2$ is captured from ammonia or biogas process emission -Cradle-to-gate CO_2 emission (net) = – 868 kg-CO_2/ton-MeOH	13
5	H_2O electrolysis and CO_2 hydrogenation	1,105	-Electricity (grid) cost: $0.05/kWh -$CO_2$ cost (post-combustion) = $53/ton CO_2 -Life cycle assessment is not reported	14
6	Direct CO_2-to-methanol electrolysis	1600	-CO_2 cost = $60/ton CO_2 -Electricity cost = $0.04/kWh -Cradle-to-gate CO_2 emission (net) = 512 kg-CO_2/ton-MeOH	15
7	H_2O electrolysis and CO_2 hydrogenation	850	-CO_2 cost = $60/ton CO_2 -Electricity cost = $0.04/kWh -Cradle-to-gate CO_2 emission (net) = 558 kg-CO_2/ton-MeOH	15
8	H_2O electrolysis, CO_2-to-CO electrolysis and CO hydrogenation	1000	-CO_2 cost = $60/ton CO_2 -Electricity cost = $0.04/kWh -Cradle-to-gate CO_2 emission (net) = 470 kg-CO_2/ton-MeOH	15

Table S.3 Pilot-scale power to methanol

No.	Company	Process	Methanol production	Ref.
1	MefCO_2 consortium	H_2O electrolyzer and CO_2 hydrogenation	1 ton per day	16
2	Carbon Recycling International (CRI)	H_2O electrolyzer and CO_2 hydrogenation	4000 ton per year	17
3	Consortium (Engie, Fluxys, Indaver, Inovyn, Oiltanking, Port of Antwerp and the PMV (Flemish Government))	Undisclosed	8000 ton per year (scheduled start in 2022)	18
4	Shunli and Carbon Recycling International	Undisclosed	110,000 ton per year (scheduled start by end of 2021)	19

Table S.4 Summary of the key parameters of air-to-MeOH routes

Description	**1st generation (Two-step air-to-MeOH)**	**2nd generation (Single-step air-to-MeOH)**
Main feeds	CO_2 H_2O	CO_2 H_2O

Preparation		
Equipment	H_2O electrolyzer	Not applicable
Reaction	R1	Not applicable
Aspen Plus	External[1)]	Not applicable
Operating Conditions	See Table 2	Not applicable
Utilities	Electricity	Not applicable
MeOH synthesis		
Equipment	CO_2 hydrogenation	CO_2 electrolyzer
Reaction	R2, R3, R4	R6
Aspen Plus	RPLUG[2)]	External[1)]
Operating Conditions	See Table S.5	See Table 2
Utilities	Natural gas	Electricity
Product purification		
Equipment	Distillation	Distillation
Aspen Plus	RadFrac[4)]	RadFrac[3)]
Utilities	Natural gas Cooling water	Natural gas Cooling water
Energy consumption	~38 GJ/ton MeOH [20]	~60 GJ/ton MeOH [21]

[1)] Please refer to Section 2 for the detail description of external calculation
[2)] Please refer to Section 3 for the kinetic parameters of hydrogenation reaction
[3)] Total condenser
[4)] Partial vapor-liquid condenser

2. Electrochemical reaction

We select the CO_2 electrolysis for methanol production as an example. We specified the production rate of 46,481 kg methanol/hour is produced by the CO_2 electrolysis with the faradaic efficiency of 90%. With the molecular weight of methanol of 32 kg/kmol, the flowrate of methanol production is 403.5 mol/s. The Faraday constants is 96,480 C/s. Based on the reaction of electroreduction of CO_2 into methanol (S.1), we note that the number of required electrons for completing the reaction is 6 electrons.

$$CO_{2(g)} + 6H^+ + 6e^- \leftrightarrow CH_3OH_{(l)} + 3H_2O_{(l)} \quad \text{(S.1)}$$

Thus, the required current (I) can be estimated as follow:

$$I = \frac{(6)(96{,}480 \text{ C/s})(403.5 \text{ mol/s})}{(90\%)} \quad \text{(S.2)}$$

$$I = 259{,}521{,}010 \text{ A} \quad \text{(S.3)}$$

Based the calculated current density in Eq. (S.3), we estimate the mass balance of the electrolyzer.

The required flowrate of CO_2 in the cathode side can be estimated by Eq. (S.4).

$$F_{CO_2} = \frac{(259{,}521{,}010 \text{ A})(90\%)}{(6)(96{,}480 \text{ C/s})} = 403.5 \frac{\text{mol}}{\text{s}} = 63{,}912 \frac{\text{kg}}{\text{h}} \quad \text{(S.4)}$$

Considering the CO_2 conversion of 50%, the CO_2 flowrate entering the electrolyzer is calculated in Eq. (S.5).

$$F_{CO_2 \text{ in}} = \frac{63{,}912 \frac{\text{kg}}{\text{h}}}{50\%} = 127823 \frac{\text{kg}}{\text{h}} \quad \text{(S.5)}$$

Thus, the CO_2 outlet stream of the electrolyzer is calculated as follow:

$$F_{CO_2\, out} = \left(127823 \frac{\text{kg}}{\text{h}}\right)(50\%) = 63{,}912 \frac{\text{kg}}{\text{h}} \quad \text{(S.6)}$$

Please note that the faradaic efficiency of the electrolyzer in 90%. This indicates that 10% of electrons promotes H_2 formation. The flowrate of H_2 is calculated in Eq. (S.7).

$$F_{H_2\, out} = \frac{(259{,}521{,}010 \text{ A})(10\%)}{(6)(96{,}480 \text{ C/s})} = 134 \frac{\text{mol}}{\text{s}} = 968 \frac{\text{kg}}{\text{h}} \quad \text{(S.7)}$$

Besides H_2, H_2O is also produced in the cathode side Eq. (S.8).

$$F_{H_2O\ out} = \frac{(259{,}521{,}010 \text{ A})(90\%)}{(6)(96{,}480 \text{ C/s})} = 403.5 \frac{\text{mol}}{\text{s}} = 26{,}146 \frac{\text{kg}}{\text{h}} \quad \text{(S.8)}$$

The flowrate of H_2O enters the anode side is calculated as follows:

$$F_{H_2O} = \frac{(259{,}521{,}010 \text{ A})(100\%)}{(2)(96{,}480 \text{ C/s})} = 1{,}345 \frac{\text{mol}}{\text{s}} = 87{,}156 \frac{\text{kg}}{\text{h}} \quad \text{(S.9)}$$

The flowrate of O_2 product from the anode side is calculated as follow:

$$F_{O_2} = \frac{(259{,}521{,}010\ \text{A})(100\%)}{(4)(96{,}480\ \text{C/s})} = 672\frac{\text{mol}}{\text{s}} = 77{,}469\frac{\text{kg}}{\text{h}} \tag{S.10}$$

3. Process Simulation

3.1. Hydrogenation reaction

The hydrogenation reactor is simulated in the Aspen Plus as RPlug with the specification as mentioned in Table S.5.

Table S.5 Operating conditions for the hydrogenation reactor

Operating conditions	Values
Temperature (K)	323 – 511
Pressure (bar)	69 (in) – 67 (out)
Length (cm)	1200
Number of tubes	4650
Tube diameter (cm)	4.6
Feed specification	m = (nH_2 – nCO_2)/(nCO + nCO_2) = 2
Conversion	H_2 = 19%; CO = 82%; CO_2 = 48%
Heating fluid temperature (K)	511
Thermal conductivity (W m^{-2} K^{-1})	600 W m^{-2} K^{-1}

The kinetic parameters are taken from Graaf et. al.[1]. The following reactions occur in the hydrogenation reactor:

$$CO + 2H_2 \Leftrightarrow CH_3OH \tag{S.11}$$
$$CO_2 + H_2 \Leftrightarrow CO + H_2O \tag{S.12}$$
$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \tag{S.13}$$

Aspen Plus software has standard form for the rate of reaction equation. Thus, one should rearrange the rate equation in Graaf et. al. [1] to satisfy the Aspen Plus standard. The rearranged rate of reaction equation for reactions Eq. (S.11) to Eq. (S.13) are:

For S.11:

$$r'_{CH_3OH,\,A3} = \frac{k_A K_{CO}\left(f_{CO} f_{H_2}^{3/2} - \dfrac{1}{K_{C1}} \dfrac{f_{CH_3OH}}{f_{H_2}^{1/2}} \right)}{\left(f_{H_2}^{1/2} + \dfrac{K_{H_2O}}{K_{H_2}^{1/2}} f_{H_2O} + K_{CO} c_{CO} f_{H_2}^{1/2} + \dfrac{K_{H_2O}}{K_{H_2}^{1/2}} K_{CO} f_{CO} f_{H_2O} + K_{CO_2} f_{CO_2} f_{H_2}^{1/2} + \dfrac{K_{H_2O}}{K_{H_2}^{1/2}} K_{CO_2} f_{CO_2} f_{H_2O} \right)}$$

For S.12:

$$r'_{CH_3OH,\,B2}=\frac{k_B K_{CO_2}\left(f_{CO_2}f_{H_2}-\dfrac{1}{K_{C2}}f_{H_2O}f_{CO}\right)}{\left(f_{H_2}^{1/2}+\dfrac{K_{H_2O}}{K_{H_2}^{1/2}}f_{H_2O}+K_{CO}f_{CO}f_{H_2}^{1/2}+\dfrac{K_{H_2O}}{K_{H_2}^{1/2}}K_{CO}f_{CO}f_{H_2O}+K_{CO_2}f_{CO_2}f_{H_2}^{1/2}+\dfrac{K_{H_2O}}{K_{H_2}^{1/2}}K_{CO_2}f_{CO_2}f_{H_2O}\right)}$$

For S.13:

$$r'_{CH_3OH,\,C3}=\frac{k_C K_{CO_2}\left(f_{CO_2}f_{H_2}^{3/2}-\dfrac{1}{K_{C3}}\dfrac{f_{CH_3OH}f_{H_2O}}{f_{H_2}^{3/2}}\right)}{\left(f_{H_2}^{1/2}+\dfrac{K_{H_2O}}{K_{H_2}^{1/2}}f_{H_2O}+K_{CO}f_{CO}f_{H_2}^{1/2}+\dfrac{K_{H_2O}}{K_{H_2}^{1/2}}K_{CO}f_{CO}f_{H_2O}+K_{CO_2}f_{CO_2}f_{H_2}^{1/2}+\dfrac{K_{H_2O}}{K_{H_2}^{1/2}}K_{CO_2}f_{CO_2}f_{H_2O}\right)}$$

The values in the following tables is used in the Aspen Plus for determining the kinetic parameter of hydrogenation reaction (RPLUG).

Table S.6 The value of kinetic factor

Reaction	k, kmol/(s kg)	E, kJ/kmol
S.11	4.89×10^{-1}	-113000
S.12	3048426	-152900
S.13	0.00109	-87500

Table S.7 The value of driving force

	Term-1		Term-2	
Reaction	A	B	A	B
S.11	-22.26	5629	29.83	-6204
S.12	-25.68	7421	-30.35	12194
S.13	-25.68	7421	21.74	361

Table S.8 The value of adsorption constant

Term no.	1	2	3	4	5	6
Coefficient A	0	-24.63	-22.26	-46.88	-25.68	-50.31
Coefficient B	0	0	0	0	0	0

The model in this study is in close agreement with the experiment data under the similar operating conditions, as reported elsewhere [2]. In this regard, the gas mixture of H_2 (79.8%), CO (11.4%) and CO_2 (8.8%) was directed various ratio of volumetric flow rate to the catalysts weight ($Ø_v/w$) to the adiabatic fixed bed reactor (Haldor Topsoe MK 101 catalysts) at 523.4 K and 30 bar. The comparison between our model and the literature [2] is presented in Figure S.1.

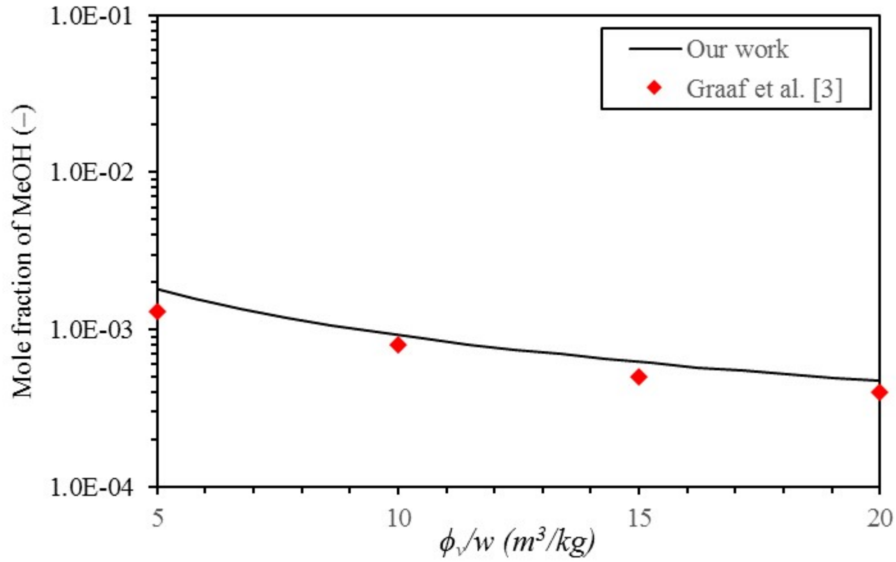


Figure S.1. The mole fraction of methanol in the reactor outlet

3.2. Gas-liquid separation

The mixture of liquid products (MeOH and water) and gas products (CO, CO_2, and H_2) is separated using Flash2 block in Aspen Plus) at 311 K and 67 bars. Under this condition, the gas products are discharged from the top side, while liquid products are dispensed from the bottom side.

3.3. Distillation unit

The liquid products from gas-liquid separation are directed to the distillation unit for product purification. The top and bottom products of distillation unit is MeOH (99 wt.%) and water, respectively. The specification of distillation unit is presented in Table S.9.

Table S.9 The specification of the distillation unit (RadFrac)

Parameters	Value
Condenser	Partial-Vapor-Liquid
Reboiler	Kettle
Valid phases	Vapor-Liquid
Reflux ratio	3.5
Number of stages	26
Feed stage (from top side)	20
Condenser temperature	323.15 K
Condenser pressure	1.01 bar
Property method	NRTL-RK
Free-water phase properties	STEAMNBS

3.4. Compressor

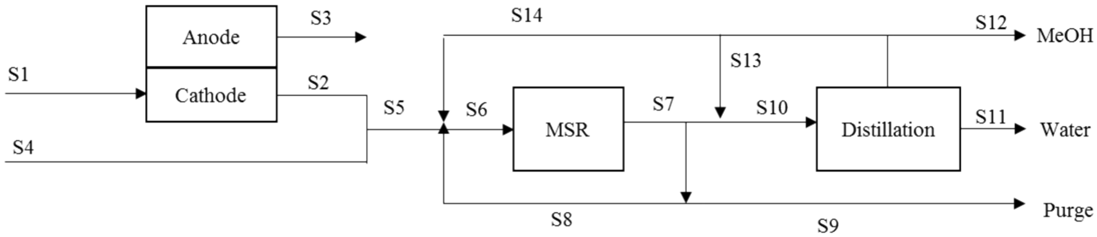
Compressors are important to increase the stream pressure given the hydrogenation reactor operate at elevated pressure. Compressor is simulated using Compr block with the typical specification as listed in Table S.10.

Table S.10 The specification of the compressors (Compr)

Parameters	Value
Type	Polytropic using ASME method
Polytropic efficiency	85%
Mechanical efficiency	99%
Compression ratio	3

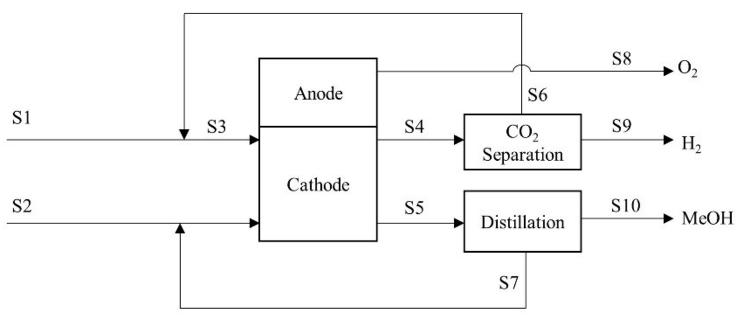
4. Mass balance

The mass balances of the studied air-to-methanol routes are presented in Figure S.2 and Figure S.3.



Stream number	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
Temperature (K)	298	323	323	298	408	323	511	311	311	312	346	323	313	422
Pressure (bar)	1	30	30	1	69	69	67	67	67	2	1	1	2	70
CO (kg/h)	0	0	0	0	0	4,077	4,081	4,076	4	1	0	0	0	1
H_2 (kg/h)	0	8628.8	0	0	8,629	66,568	57,997	57,932	58	7	0	0	0	7
H_2O (kg/h)	77,098	0	0	0	0	487	26,021	487	0	25,533	25,533	0	0	0
CO_2 (kg/h)	0	0	0	62,777	62,777	95,500	33,125	32,510	33	593	0	368	11	213
CH_3OH (kg/h)	0	0	0	0	0	3,283	48,692	3,276	3	45,740	1,341	44,065	328	7
CH_4 (kg/h)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N_2 (kg/h)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
O_2 (kg/h)	0	0	68,469	0	0	0	0	0	0	0	0	0	0	0
Total flows (kg/h)	77,098	8629	68,469	62,777	71,406	169,915	169,915	98,281	98	71,874	26,874	44,433	339	228

Figure S.2 The mass balance of 1[nd] generation (please note that pressure and heat changers may exists between streams)



Stream number	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Temperature (K)	298	298	298	298	298	298	363	323	298	339
Pressure (bar)	1	1	1	1	1	2	1	180	2	1
H_2 (kg/h)	0	0	0	2,179	0	0	0	0	2,179	0
H_2O (kg/h)	0	60,995	0	0	30,988	0	30,988	0	0	0
CO_2 (kg/h)	63,912	0	127,824	63,912	0	63,912	0	0	0	0
CH_3OH (kg/h)	0	0	0	0	46,481	0	11	0	0	46,470
O_2 (kg/h)	0	0	0	0	0	0	0	77,469	0	0
Total flows (kg/h)	63,912	60,995	127,824	66,091	77,469	63,912	30,999	77,469	2,179	46,470

Figure S.3 The mass balance of 2[nd] generation (please note that pressure and heat changers may exists between streams)

5. Economic calculation

The capital cost and operating cost of the Aspen Plus-simulated process such as hydrogenation reactor, distillation, and compression are estimated using Aspen Economic Analyzer. One should note that the capital cost and operating cost covers every single expense in plant construction and operation. In the following texts, we presented the calculation of capital cost and operating cost of electrolyzer, silicon photovoltaic (Si-PV), and direct air capture (DAC).

A. Electrolyzer

In the regard of capital cost of electrolyzer, the CO_2 electrolyzer in 2nd generation is taken as an example. Based on the literature[22], the capital cost of alkaline electrolyzer (1 MW system) is 130 $/kW in the present days, with the reference current density and cell voltage of the given alkaline electrolyzer is 0.3 A/cm^2 and 2.00 V, respectively. The stack cost of the electrolyzer in $/kW is converted into $/m^2 by considering the reference performance of the alkaline electrolyzer under the given scenario (0.2 A/cm^2, 1.68 V[22]). The optimistic scenario is selected as the example.

Stack cost in power (C_w) = $130/kW

Current density (I_d) = 0.2 A/cm^2

Cell voltage (V_c) = 1.68 V

The stack cost in specific area (C_a) is calculated as follow:

$$C_a = \left(130\,\frac{\$}{\text{kW}}\right)\left(\frac{1}{1000}\,\frac{\text{kW}}{\text{W}}\right)\left(0.2\,\frac{\text{A}}{\text{cm}^2}\right)\left(\frac{10^4\,\text{cm}^2}{1\ \ \text{m}^2}\right)$$

$$= 439\,\frac{\$}{\text{m}^2} \qquad \text{(S.14)}$$

Under the optimistic scenario, the current density of CO_2 electrolyzer is predicted to be 300 mA/cm^2. The electrolyzer area (A_e) can be calculated as follow:

$$A_e = \frac{259{,}521{,}010\ \text{A}}{0.3\dfrac{\text{A}}{\text{cm}^2}} = 86{,}507\ \text{m}^2 \qquad \text{(S.15)}$$

The total stack cost (C_{ts}) is estimated as follow:

$$C_{ts} = \left(86{,}507\ \text{m}^2\right)\left(439\,\frac{\$}{\text{m}^2}\right)$$

$$= \$23{,}253{,}083 \qquad \text{(S.16)}$$

The power required by the electrolysis system is calculated based on the as follow:

$$W = 259{,}521{,}010\ A \times 2\ V$$

$$= 519{,}042{,}021\ W \quad (S.17)$$

The balance of plant of the electrolyzer (BOP_e) is 43% of the total stack cost. In this regard, the cost in $/kW is used given the BOPs majorly relates to electrical equipment.

$$BOP_e = (519{,}042{,}021\ W)(1\ kW/1000\ W)(\$60/kW)(43\%)$$

$$= \$31{,}324{,}641 \quad (S.18)$$

The installation cost of the electrolyzer (IC_e) is 10% of the total stack cost.

$$IC_e = (\$54{,}577{,}724)(10\%)$$

$$= \$5{,}457{,}772 \quad (S.19)$$

The total installed cost of CO_2 electrolyzer including BOP (C_{te}):

$$C_{te} = \$23{,}253{,}083 + \$31{,}324{,}641 + \$5{,}457{,}772$$

$$= \$60{,}035{,}496 \quad (S.20)$$

The annual operating and maintenance cost of CO_2 electrolyzer (OM_e) is 2.5% of the total installed cost.

$$OM_e = (\$60{,}035{,}496)(2.5\%)$$

$$= \$1{,}500{,}887/year \quad (S.20)$$

B. Silicon photovoltaic (Si-PV)

The 2nd generation route is selected as the example. The capital cost of silicon photovoltaic (Si-PV) is in the optimistic scenario as listed in Table 2.

Required power = 563,900 kW

Module and tracker cost = $300/kW

Labor, permissting and installation cost = $50/kW

Design, permitting and fee = $50/kW

Total installed Si-PV cost (C_{tpv}) is calculated as follow:

$$C_{tpv} = (300\ \$/kW + 50\ \$/kW + 50\ \$/kW)\ (563{,}900\ kW)$$

$$= \$225{,}560{,}075 \quad (S.21)$$

The annual operation and maintenance cost of Si-PV (OM_{pv}) is calculated as follow:

$$OM_{pv} = \left(10.4\,\frac{\$}{\text{kW}}\right)(563{,}900\ \text{kW})$$

$$= \$5{,}864{,}562 \qquad \text{(S.22)}$$

C. Direct air capture (DAC)

The 2nd generation route is selected as the example. The capital cost of DAC in the optimistic scenario (Table 2) is selected for calculation.

CO_2 production capacity = 506,182 ton-CO_2/year

Capital cost = \$174/(ton-CO_2/year)

The total DAC capital cost (C_{tdac}) is estimated as follow:

$$C_{tdac} = (506{,}182\ \text{ton-}CO_2\text{/year})(\ \$174/(\text{ton-}CO_2\text{/year}))$$

$$= \$88{,}075{,}698 \qquad \text{(S.23)}$$

For the electricity consumption, one should note that the DAC is operated with grid electricity for 18 hours (CPV runs for 6 hours).

Natural gas consumption = 2,044,197 GJ/year

Grid electricity consumption = 78,847,608 kWh/year

Operation and maintenance cost excluding electricity and natural gas = \$26/ton-CO_2

Natural gas price = \$4/GJ

Grid electricity price = 3 cents/kWh

The total operating and maintenance cost of DAC (OM_{dac}) is calculated as follow:

$$OM_{dac} = (\$26/\text{ton-}CO_2)(506{,}182\ \text{ton-}CO_2\text{/year}) + (\$4/\text{GJ})(2{,}044{,}197\ \text{GJ/year})$$

$$+ (3\ \text{cents/kWh})(78{,}847{,}608\ \text{kWh/year})$$

$$= \$13{,}160{,}737\text{/year} + \$8{,}176{,}789\text{/year} + \$2{,}365{,}428\text{/year}$$

$$= \$23{,}702{,}954\text{/year} \qquad \text{(S.24)}$$

6. CO_2 emissions

The emission factor of grid electricity in various countries is shown in Table S.11. Figure S.4 illustrates the projection of CO_2 emission of methanol production from 1st and 2nd generation routes. Under the optimistic scenario, a grid CO_2 emission of less than ~240 and ~200 kg CO_2/MWh are required to be comparable with the CO_2 emission of the conventional route. The breakdown of emission when the non-intermittent renewables are utilized to substitute the electricity is shown in Figure S.5. The emission factor of renewable electricity is summarized in Table S.12.

Table S.11 The average grid emission in various countries

Country	Emission factor (kg-CO_2/MWh)	Reported year	Reference
Saudi Arabia	732	2019	23
India	708	2018	23
China	555	2018	23
Japan	506	2018	23
United States	453	2018	23
Russia	325	2019	23
European Union (EU)	242	2018	24
United states	241	Projection 2050	25
Canada	130	2018	23
European Union (EU)	87	Projection 2040	24
Sweden	50	2019	23
Iceland	8.3	2020	26

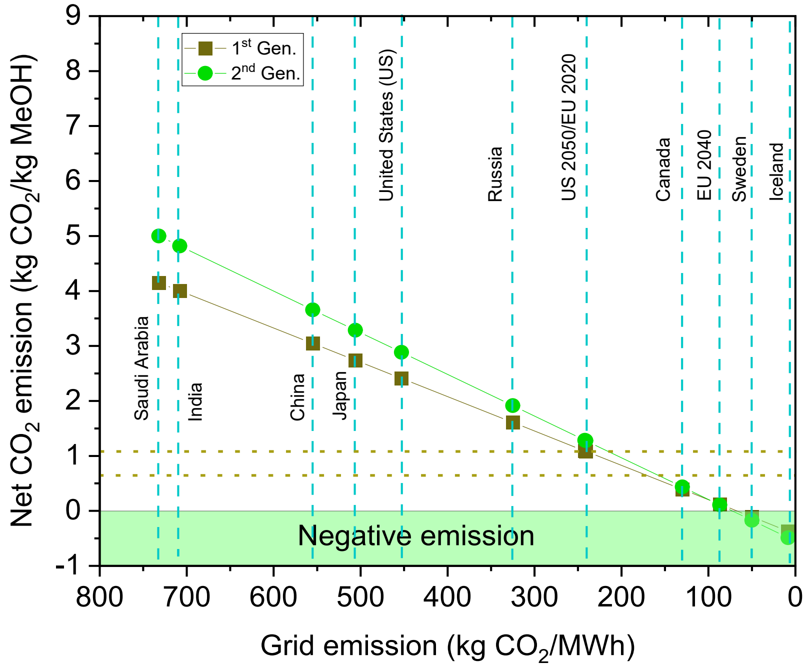
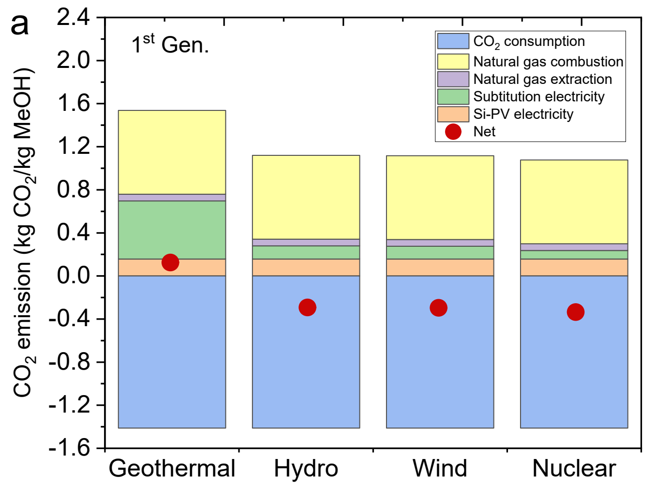


Figure S.4. Net CO_2 emissions from air-to-MeOH production pathways under the optimistic scenario. The blue dashed lines are representative of average electricity emission intensity in various jurisdictions (see Table S.11). The brown dashed lines indicate the range of CO_2 emissions from conventional MeOH synthesis route.[27]



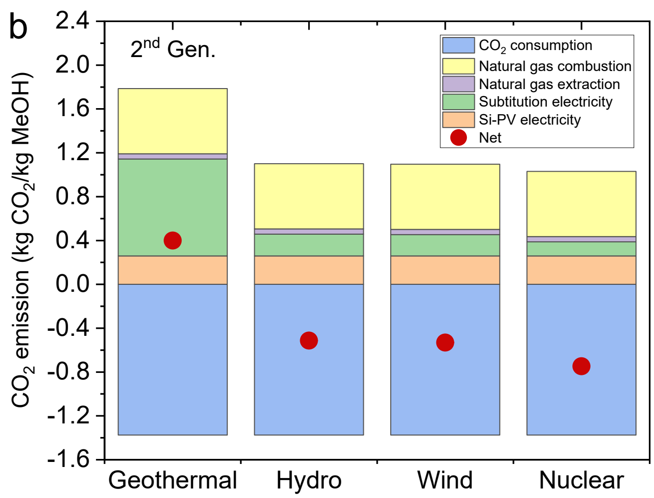


Figure S.5 The breakdown of CO_2 emissions in (a) 1st generation and (b) 2nd generation routes under the base scenario.

Table S.12 The emission factor of renewable electricity

Electricity source	Emission factor (kg-CO_2/MWh)	Reference
Geothermal	82	28
Hydro	19	29
On shore wind	18	30
Nuclear	12	31

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