Prospects of sunlight driven Air-to-Methanol synthesis via CO₂ electrolysis

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Abstract

The race to save planet earth has led to significant advancement in technologies for harvesting renewable energy, carbon capture and conversion. Futures scenarios are being envisioned where CO₂ is captured from air and converted to valuable fuels and chemicals, with methanol (MeOH) being the most coveted product. Here we assess two potential air-to-MeOH pathways that harvest solar power via concentrated photovoltaic (CPV) cells for direct air capture (DAC) of CO₂ and subsequent conversion to MeOH by exploiting CO₂ electrolysis. Specifically, we perform techno-economic and life-cycle analysis on single-step (direct CO₂-to-MeOH electrolysis) and three-step (integration of H₂O electrolysis, CO₂-to-CO electrolysis, and hydrogenation reactor) air-to-MeOH routes. Our results indicate that in current scenario, the envisioned air-to-MeOH routes are not economically and environmentally compelling with high levelized costs of MeOH ~1180–1730 \$/ton_{MeOH} and CO₂ emissions of ~2.29–2.69 ton_{CO₂}/ton_{MeOH}. Using sensitivity analysis, we reveal targets for CPV capital cost (\$290/kW), DAC capital cost (\$375/(ton-CO₂/year)), and electricity emission intensity (<275 kg-CO₂/MWh) which will make the three-step route commercially and environmentally viable as a near-term technology. In contrast, direct CO₂-to-MeOH electrolysis will need drastic performance improvement to be economically competitive, with required current densities >300 mA/cm², energy efficiency >45% and stack stability >2 years. We hope this study will garner the key stakeholders to advance discussions about the cost and potential of this envisioned air-to-fuel technology.

Keywords: MeOH production, economic analysis, greenhouse emission, electrochemical reaction, solar photovoltaic

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1. Introduction

Fossil fuels have traditionally been our preferred energy source as they are cheap to extract, abundant, and have a high calorific value. They are responsible for the tremendous economic growth we have experienced in the last 50 years, but that has come at a cost. The use of fossil fuels has led to an increase in greenhouse gases in the atmosphere.^{1, 2} This has damaged the environment and led to climate change, with the last five years (2015–2019) recorded as the hottest ever on planet earth.³ In order to save our planet, we continue our transition towards renewable energy use and develop technologies for carbon capture, conversion, use, and storage.² A clean and sustainable future can be envisioned as one where all these technologies will be working together for our energy needs and producing valuable fuels and chemicals.

Fortunately, worldwide race on the development of low-cost and sustainable energy technologies has triggered significant progress over the last couple of decades. Solar photovoltaic (PV) power now represents the cheapest and most widely deployed renewable energy source with over 580 GW of cumulative installed capacity worldwide as of 2020.⁴ The levelized cost of electricity (LCOE) from solar PV now competes with fossil fuels and in many geographical locations, it is available at less than 5 cents/kWh.⁵ This has spurred the research, development, and commercialization of electrochemical technologies, including water electrolysis,⁶ and CO₂ electrolysis.⁷ We have witnessed tremendous progress in the field of electrochemical CO₂ reduction to high-value fuels and chemicals such as CO, C₂H₄, HCOOH, which can now be produced at high current densities (>500 mA/cm²) and faradaic efficiencies (>80%).⁷⁻¹¹ In parallel, there has been a significant advancement in the technology for CO₂ capture via the direct air capture (DAC) process. DAC is technically and economically challenging as the concentration of CO₂ in the air is quite low (~400 ppm).¹² Several research groups around the world are developing energy-efficient DAC technology¹³ with a focus on materials and process optimization.¹⁴⁻¹⁶ Carbon Engineering and Climeworks are two of the few companies pursuing DAC technology, with their pilot-scale DAC plant running since 2015 and 2017 respectively, with a capacity to extract ~1–3 ton CO₂/day.^{17, 18} In this regard, an economic study on Carbon Engineering's pilot-plant estimated the cost of CO₂ capture between \$94 and \$232/ton-CO₂.¹⁷ On the other hand, Climeworks reported a capture cost of \$600/ton-CO₂ at its Swiss plant and expected to bring costs down to as low as \$100/ton-CO₂.¹⁹

While these emerging technologies for harvesting solar energy, capturing, and converting CO₂ have received attention, a comprehensive system-level analysis of a process that combines these emerging technologies and provides a glimpse of the future energy landscape is yet to be

reported. In this regard, we present a thorough assessment of a process that captures energy from sunlight and CO₂ from the air to convert it into MeOH in what can be called an “Air-to-MeOH” process. MeOH production is attractive due to its large market size (37 billion USD in 2020), ease of storage, transportation, and its versatility to be converted into olefins or use as a fuel.²⁰⁻²² In order to harvest solar power, we consider harvesting sunlight via concentrated PV (CPV) cells. While silicon-based PV cells dominate the market with ~ 95% share of current production, they are close to reaching their theoretical efficiencies of ~ 29%, leaving only economy of scale as the main driver to reduce the cost of solar electricity in the future.²³ Unlike Si cells, CPV cells based on III-V group elements can theoretically reach over 80% solar cell efficiency.²⁴ CPV cells have reached ~ 47% efficiency and on a modular level, 43.4% efficient CPV modules have been demonstrated.²⁵ Moreover, they can operate at high light concentrations (>1000 suns) largely compensating the higher cost associated with the manufacturing of III-V based cells. Lastly, we use an aqueous solution-based DAC system to provide CO₂, while two different routes for MeOH synthesis are considered based on their relative technology readiness level (TRL). The 1st generation air-to-MeOH pathway integrates a H₂O electrolyzer, CO₂ electrolyzer, and conventional hydrogenation reactor, while the 2nd generation involves direct CO₂ electrolysis process. Our results indicate that the economic feasibility of both the proposed MeOH synthesis routes is significantly influenced by the capital costs of different emerging technologies that is CPV, DAC unit, and electrolyzers. A decrease in capital costs of CPV and DAC could make the 1st generation air-to-MeOH route economically competitive as compared to the current fossil-fuel based MeOH production route. In contrast, the 2nd generation MeOH route will not only require a reduction of capital costs but also require significant improvement in electrolyzer performance i.e. current densities and energy efficiency.

2. Process description

In the proposed pathways, about 1100 metric tons per day (tpd) of MeOH is produced using CO₂ as feedstock, based on the typical capacity of a MeOH plant of 550–5000 tpd.²⁶ The CO₂ feed is received from the DAC unit, while the electric power for the entire plant is generated in a hybrid fashion whereby a CPV solar farm provides electricity during the day and grid electricity is utilized at night. This approach allows for avoiding expensive renewable electricity storage options such as batteries or compressed H₂. We considered two pathways for air-to-MeOH conversion in this study based on their relative TRL (Figure 1). In the first pathway what we can consider as 1st generation, the CO₂-to-CO electrolyzer used is relatively mature with TRL of 6–7 and is commercially available from several companies such as Haldor Topsoe, Siemens, Sunfire,

Avantiun, Opus 12, Dioxide Materials.⁷ Similarly, the H₂O electrolyzer and hydrogenation reactor have a TRL of 7–9 as they are widely available for commercial application.^{27, 28} In the second route, a direct CO₂-to-MeOH electrolyzer (2nd generation) is used which exhibits a TRL of 1–3 given its operation is still in the laboratory-scale.⁷ A schematic of the proposed pathways is shown in Figure 1, with key process parameters presented in **Error! Reference source not found.** and a detailed description is discussed hereafter.

1st generation: Three-step air-to-MeOH pathway

In the 1st generation route, a DAC unit captures and concentrates CO₂ from the air which is fed to the CO₂-to-CO electrolyzer for producing CO via reaction R1.²⁹

The O₂ produced at the anode is directly sent to the compression unit before storage. The CO, H₂O produced at cathode along with the unconverted CO₂ are directed to the gas-liquid separation unit to remove CO₂ and CO from H₂O. The H₂O is recycled to the electrolyzer, while the CO₂ and CO is directed to the hydrogenation reaction for MeOH production via reaction R2 to R4.³⁰

The required H₂ for hydrogenation reactions is supplied by H₂O electrolyzer via reaction R5.⁶

The described process contrasts with the conventional methanol synthesis process where the CO and H₂ for hydrogenation are derived from fossil fuels (mainly from natural gas) via steam reforming. The hydrogenation products are sent for gas-liquid separation to remove the gaseous (unconverted CO₂ and CO) and liquid (i.e., MeOH and water) products. The gaseous products are recycled to the hydrogenation reaction, while the liquid products are sent to the distillation unit for MeOH purification to 99 wt.%.

2nd generation: Single-step air-to-MeOH pathway

The source of CO₂ and electricity is the same as in 1st generation pathway, but the CO₂ is directly fed to a CO₂-to-MeOH electrolyzer, to facilitate the electrochemical reaction (R6).³¹

In the CO₂ electrolyzer, MeOH and H₂ are produced at the cathode, while O₂ produced at the anode is sent to the three-stage compression unit to achieve market specifications (200 bar). The cathode products are sent to the gas-liquid separation unit to separate the gaseous (unconverted CO₂ and H₂) and liquid (electrolyte and MeOH) components. The gaseous components are then directed to the pressure swing adsorption (PSA) unit to remove CO₂ from H₂ which is then recycled back to the CO₂ electrolyzer, while the H₂ is compressed and stored. The electrolyte properties are adapted from literature,³² which considers water as the main component of the electrolyte and we assume that the concentration of MeOH has an insignificant effect on the electrolyzer performance. Therefore, the liquid product of the CO₂ electrolyzer can be continuously recirculated so that a higher concentration (10-60 wt.%) of MeOH is obtained prior to entering the distillation unit. The distillation unit produces high purity MeOH (99 wt.%) and the electrolyte is recycled to the CO₂ electrolyzer.

Figure 1. Schematic illustration of the two air-to-MeOH routes assessed in this study. (Top) Technologically mature 1st generation route comprises three reactors: H₂O electrolyzer, CO₂ electrolyzer and hydrogenation reactor. (Bottom) Futuristic 2nd generation route only requires one reactor for converting CO₂ to MeOH.

An alkaline electrolyzer was selected to facilitate CO₂ electrolysis (1st and 2nd generation). A Proton Exchange Membrane (PEM) electrolyzer was used to facilitate H₂O electrolysis (1st generation) due to its high efficiency, high current density, and high-pressure operation. Aspen Plus is used to model the hydrogenation reactions, gas-liquid separation, compression, and distillation. The capital and operating costs of the Aspen Plus-simulated processes is estimated using Aspen Process Economic Analyzer. Further details regarding the process simulation are provided in the SI. The financial parameters which are constant throughout the analysis are summarized in Table 1. The techno-economic parameters used in base and optimistic scenarios are summarized in Table 2, where the current scenario is represented as the base scenario, and the future scenario is represented as the optimistic scenario.

Table 1. Financial parameters used in this analysis

Parameter	Value	Ref.
MeOH capacity (ton/day)	1100	33
Balance of plant	15% of total equipment cost	34
Project contingency	10% of total project cost	35
Working capital	10% of total project cost including contingency	36
Labor cost (\$/man/hour)	20	37
Land cost (\$/acre)	5,000	38
Income tax	40%	37
Discount rate	10%	37
Depreciation (years)	10	
Salvage value	10%	39
Plant lifetime (years)	20	
Pressure swing adsorption		
TRL	9	40
Capital cost (\$/1000m ³ /h capacity)	1,990,000	32
Electricity consumption (kWh/m ³)	0.25	32
CO ₂ -to-CO electrolyzers		
TRL	6–7	7
Total number of staff	10	39
CO ₂ -to-MeOH electrolyzers		
TRL	1-3	7
Total number of staff	10	39
PEM H ₂ O electrolyzer		
TRL	8	28
Total number of staff	10	39
Concentrated photovoltaic (CPV)		
TRL	6	41
Installation cost	55% of module and tracker cost	42
O&M (\$/kWh)	0.008	42
Total number of staff	10	
Direct air capture		
TRL	5–8	43
O&M, excluding energy (\$/ton CO ₂)	26	17
Electricity requirement (kWh/ton CO ₂)	270	17
Natural gas requirement (GJ/ton CO ₂)	5.25	17

The plant is assumed to be erected in an area with high direct normal irradiance (> 7 kWh/m²/day) with average daylight of 9 hours such as those available in the United States of America^{44, 45} and Saudi Arabia.^{46, 47} In the base scenario, the stack cost of the CO₂ electrolyzer is \$280/kW (\$941/m²) which drops to \$180/kW (\$605/m²) in the optimistic scenario, due to the improvements in performance and economy of scale (Please refer to section 5A of SI).⁴⁸ Based on the literature reports, we assumed CO₂-to-CO electrolyzer is operated at a CO₂ single-pass conversion of 50% for both the base and optimistic scenarios.⁴⁹ The stack cost of the PEM H₂O electrolyzer in the base scenario is \$342/kW (\$12,996/m²)⁴⁸ which decreases to \$143/kW (\$7,722/m²) in the optimistic scenario and are taken from DOE Report 2020.⁴⁸ The stack replacement schedule is shown in Table 2, at a cost of ~15% of the total uninstalled capital cost for PEM electrolyzer⁵⁰ and ~50% of the stack cost for alkaline electrolyzer.⁵⁰ The cost of the CPV module and dual dual-axis tracker in the base scenario is \$920/kW based on current module efficiency of 32% and cumulative installed capacity of ~ 370 MW.⁵¹ In the optimistic scenario the CPV capital cost decreases to \$150/kW, based on a global installed capacity of 189 GW and using a learning rate of 18% (Please refer to section 5B of SI).⁵² The capital cost of DAC is adapted from a pilot-scale unit which costs \$694/ton CO₂ per year.¹⁷ In the optimistic scenario, we assumed a 75% cost reduction due to the increase of cumulative installed capacity by the year 2030.⁵³ A natural gas price of \$6/GJ is selected in the base scenario, dropping to \$4/GJ in the optimistic scenario. A current grid electricity price of \$0.04/kWh is used in the base scenario and considering the rapid drop in the cost of renewable electricity, the electricity price in the optimistic scenario is expected to decrease to \$0.03/kWh.⁵ In this study, the selling price of O₂ and H₂ was also varied according to the market situation as listed in Table 2.

Table 2. Techno-economic parameters used in this analysis

Variable	Base scenario	Optimistic scenario	Ref
CO₂ electrolyzer (to CH₃OH)			
Stack cost (\$/kW)	280	180	48
Balance of plant (BOP)	43% of total capital cost	43% of total capital cost	48
Installation cost	10% of total equipment cost (stack+BOP)	10% of total equipment cost (stack+BOP)	48
Current density (mA/cm ²)	100	300	54
Cell voltage (V)	2.5	2.0	54
CO ₂ conversion (%)	20	50	32
Faradaic efficiency (%)	90	90	54
Replacement (year)	2	7	55
Land factor	1.5	1.5	
Output pressure (bar)	2	2	48

O&M (\$/kWh)	2.5% of the capital cost	2.5% of the capital cost	32
CO₂ electrolyzer (to CO)			
Stack cost (\$/kW)	280	180	48
Balance of plant	43% of total capital cost	43% of total capital cost	48
Installation cost	10% of total equipment cost (stack+BOP)	10% of total equipment cost (stack+BOP)	48
Current density (mA/cm ²)	500	1000	49
Cell voltage (V)	3.0	2.4	49
Faradaic efficiency (%)	90	90	56
CO ₂ conversion (%)	50%	50%	
Replacement (year)	2	7	55
Land factor	1.5	1.5	
Output pressure (bar)	12	30	48
O&M	2.5% of the capital cost	2.5% of the capital cost	32
PEM H₂O electrolyzer			
Stack capital cost (\$/kW)	342	143	57
Balance of Plant (\$/kW)	236	182	57
Installation cost	12% of uninstalled capital cost	10% of total capital	57
Current density (mA/cm ²)	2000	3000	57
Cell voltage (V)	1.9	1.8	57
Stack Replacement (year)	7	10	57
Land factor	1.5	1.5	
Output pressure (bar)	30	70	48, 58
O&M	2.5% of the capital cost	2.5% of the capital cost	59
CPV			
Module and tracker cost (\$/kW)	920	150	60
PV module efficiency (%)	32	45	61
Lifetime (years)	20	20	61
Direct CO₂ capture			
Capital cost (\$/[ton CO ₂ /year])	694	174	17, 53
	6	4	62
Other factors			
Natural gas price (\$/GJ)			5
Grid electricity price (\$/kWh)	0.04	0.03	63
O ₂ selling price (\$/ton)	50	100	64
H ₂ selling price (\$/ton)	1200	1500	

3. Results and discussion

3.1. Economic Analysis

Figure 2a shows the calculated levelized cost of MeOH (LCM). Under the base scenario, the LCM is ~1180 \$/ton and ~1730 \$/ton for 1st and 2nd generation routes, respectively, which is much higher than the current market price of MeOH ranging between 300 to 500 \$/ton.⁶⁵ The low market price of MeOH is due to the mature hydrogenation technology used which converts syngas

(CO and H₂) into MeOH at high temperature (~523.15 K) and high pressure (50–100 bar).⁶⁶ For both air-to-MeOH routes, the operating cost is the dominant (~50%) contributor followed by capital costs (~30%), but these costs are much higher for 2nd generation as compared to the 1st generation leading to higher LCM. This is due to the mature technologies used in 1st generation route, such as the CO₂-to-CO electrolyzer, H₂O electrolyzer, and hydrogenation reactor which operate at much higher current densities and energy efficiencies. On the other hand, in 2nd generation route we used a direct CO₂-to-MeOH electrolyzer, which is still operated on a laboratory scale at moderate current densities and energy efficiency. This results in a larger electrolyzer area, CPV solar farm area, and electricity requirement, thereby resulting in higher capital and operating costs. Another major difference is the contribution of the stack replacement cost in 2nd generation, which is significantly higher than 1st generation, due to the poor stability assumed for catalysts used for direct CO₂-to-MeOH electrolysis. Under the optimistic scenario, the LCM drops drastically for both to ~445 \$/ton and ~470 \$/ton for 1st and 2nd generation routes, respectively. In such a scenario, the LCM of both routes (single-step and three-step) is comparable with the current market price of MeOH. The synergetic effect between the decrease of equipment cost and the increase of catalyst performance results in the decrease of capital and operating costs as shown in Figure 2b and 2c, respectively.

While capital cost of CPV is the dominant contributor to total capital costs, the grid electricity cost is a dominant contributor to annual operating costs. This expected finding can be attributed to the high electricity consumption for MeOH production (1st Gen: 11.4 MWh_e/ton; 2nd Gen: 15.4 kWh_e/ton) which also dictates both the size and cost of the CPV farm. In the optimistic scenario, improvements in catalyst performance reduce the electricity consumption from 11.4 to 10.2 kWh_e/kg-MeOH and 15.4 to 12.0 kWh_e/kg-MeOH for 1st and 2nd generation routes, respectively. The combination of the reduced energy requirement along with a decrease in capital costs, electricity price, and natural gas prices suppress the total capital and operating costs in optimistic scenario. As summarized in Table 2, we forecast significant improvements in the performance of the direct CO₂-to-MeOH electrolyzer versus the more mature CO₂-to-CO and H₂O electrolyzers. This leads to a drastic decrease in capital and operating costs for 2nd generation which results in similar LCM for both routes in the optimistic scenario. We observed that the economic feasibility of air-to-MeOH routes is influenced by multiple economic and technical parameters. In the proceeding section, we carried out a detailed sensitivity analysis to understand the key drivers of air-to-MeOH route.

Figure 2. Breakdown of the (a) levelized cost of methanol (LCM), (b) the capital cost, and (c) the annual operating cost for air-to-MeOH routes in the base and optimistic scenarios. The area between black dashed vertical lines in (a) indicate the current market price range of MeOH. The blue dashed line differentiates 1st generation and 2nd generation air-to-MeOH pathways. The “other” portion in (b) refers to the capital cost associated with land, working capital, contingency, and equipment for separation and compression.

3.2. Sensitivity analysis

A sensitivity analysis was carried out by varying different process parameters, as shown in

Figure 3 and tabulated in Table 3 while keeping the remaining parameters constant at the base scenario. It should be noted that the base scenario used for sensitivity analysis is the same as the optimistic scenario used in Table 2.

Figure 3a and 3b suggest that the LCM is very sensitive to the capital cost of CPV for both routes. As discussed earlier, given the significant energy requirement for the air-to-MeOH process (11.4–15.4 kWh_e/kg MeOH), and the fact that CPV provides power to all the units i.e., DAC, electrolyzer, PSA, and distillation unit makes it important to have capital cost for CPV less than \$292/kW and \$216/kW for 1st generation and 2nd generation pathway, respectively. This huge energy requirement for the air-to-MeOH process is also the reason for the significant influence of electricity prices on the LCM. Similarly, the capital cost of DAC also has a substantial influence on the LCM as CO₂ is the main feedstock for MeOH production. A DAC capital cost of below \$298/(ton-CO₂/year) is needed to lower the LCM to a competitive range (compared with the market price).

An interesting observation for 1st generation pathway (**Error! Reference source not found.a**) is that only the parameters associated with power generation (CPV and grid) and CO₂ capture (DAC) exhibit significant influence on the LCM, while the performance of electrolyzers has minor effect on the LCM. This is due to the maturity of the electrolysis technology used in 1st generation, whereby the different units operate at high performance and a variation within the range taken in this analysis does not affect the LCM. A CPV capital cost of lower than \$291/kW, DAC capital cost less than \$376 (ton-CO₂/year) and a grid electricity price of 3.9 cents/kWh is

required to reduce the LCM below the current market price. In contrast, in the single-step MeOH route of 2nd generation (**Error! Reference source not found.b**), the current density and energy efficiency (EE) also have a significant influence on the LCM. The current density shows a considerable effect, and one would reap the economic benefit when the electrolyzer operates at a current density of $>220 \text{ mA/cm}^2$. An similar finding is reported in the literature,¹² showing the significant effect of current density particularly at low current densities. Regarding EE, the LCM becomes comparable with the market price when the CO₂-to-MeOH electrolyzer operates at EE higher than 47%. From the market aspect, only the O₂ selling price has a moderate influence on the LCM, while the selling price of H₂ and the natural gas price has a minor effect. This can be attributed to the significant amount of O₂ production, while the H₂ production and natural gas consumption are much lower.

Figure 3. The sensitivity analysis of the economic and technical parameters in (a) 1st generation and (b) 2nd generation. In 1st generation, blue and brown colored squares represent the parameters in the H₂O electrolyzer and CO₂ electrolyzer, respectively. The area between the black dashed lines indicates the present market price range of MeOH.

Table 3. The assumed operating and economic parameters for sensitivity analysis

Variable	Worse	Base	Better
Alkaline CO₂ electrolyzer (to CH₃OH)			
Stack capital cost (\$/kW)	280	180	80
Current density (A/cm ²)	0.1	0.3	0.5
Energy efficiency	40%	50%	60%
Replacement (years)	2	7	10
Alkaline CO₂ electrolyzer (to CO)			

Stack capital cost (\$/kW)	280	180	80
Current density (A/cm ²)	0.5	1.0	1.5
Energy efficiency	45%	55%	65%
Replacement (years)	2	7	10
PEM H₂O electrolyzer			
Stack capital cost (\$/kW)	342	143	70
Current density (A/cm ²)	2.0	3.0	4.0
Energy efficiency	65%	70%	75%
Replacement (years)	7	10	20
CPV			
Module and tracker cost (\$/kW)	920	150	100
PV module efficiency (%)	32	39	46
DAC capital cost	694	174	100
Grid electricity price (\$/kWh)	0.04	0.03	0.02
Natural gas price (\$/GJ)	6	4	2
O ₂ Price (\$/ton)	50	100	150
H ₂ selling price (\$/ton)	1200	1500	1800

To get a clear picture about performance targets for 2nd generation route that is via direct CO₂-to-MeOH electrolysis, we carried out a sensitivity analysis by changing parameters which define the performance of an electrolyzer i.e., current density, EE and stability. The EE of an electrolyzer is calculated via the product of the faradaic efficiency (FE) and the applied cell voltage. The applied cell voltage is the sum of the thermodynamic voltage, reaction overpotentials, and cell losses.

Figure 4a illustrates the effect of EE and grid electricity price on the LCM. The adverse effect of low EE on the LCM can be compensated by the low grid electricity price. For example, when EE is ~ 40%, we can afford maximum grid electricity price of ~ 0.025 \$/kWh. However, when the EE increases to 60%, the grid electricity price can be ~ 0.043 \$/kWh. The catalyst stability is also an important factor which effects the operating costs and resulting LCM.

Figure 4b shows the interplay between current density and stability. When operating at high current density of ~ 400 mA/cm², one can even afford to replace the stack on a yearly basis. On the other hand, when operating current density is low (<200 mA/cm²), it will require very stable

(> 5 years) system. The analysis reveals the challenges ahead for direct-CO₂-to-MeOH electrolysis given the fact that till date, demonstrated performance has been low with EE (<20%), current density of <50 mA/cm² and stability of <50 hours.⁵⁴

Figure 4. (a) Effect of CO₂-to-MeOH electrolyzer EE on the LCM. (b) The effect of electrolyzer stability and current density on the LCM. The remaining parameters are kept constant under the base scenario in Table 3.

3.3. Carbon footprint of air-to-methanol pathways

To this end, we conducted a cradle-to-gate life cycle analysis (LCA) on one and three-step air-to-MeOH routes. In this analysis, we focus on the primary energy requirement including natural gas extraction (4 kg-CO₂/GJ⁶⁷) and natural gas combustion (50 kg-CO₂/GJ⁶⁸). We ignored any

emissions associated with construction and decommissioning and water treatment as these contributions are minimal as compared to the operating phase of the plant.⁶⁹ We assumed an emission intensity of electricity from CPV as 19 kg-CO₂/MWh, based on literature reports.⁷⁰ The LCA analysis revealed that the cradle-to-gate CO₂ emissions of proposed route heavily depend on emission intensity of the grid as shown in Figure 5. For example, considering the emission intensity of grid electricity in US (453 kg-CO₂/MWh (Table S.7)), we estimated net CO₂ emissions of ~2.29 kg-CO₂/kg MeOH for 1st generation, which was lower than that of 2nd generation (~2.69 kg-CO₂/kg MeOH). The higher process efficiency of 1st generation (49%) as compared to the one in 2nd generation (43%) resulted in lower CO₂ emissions. These calculated emissions will be two times higher than the conventional MeOH synthesis route using natural gas (0.68 – 1.08 kg CO_{2e}/kg MeOH).⁷¹ The LCA analysis also helps set targets for grid electricity emission intensity, where we observe that an emission intensity of <275 kg-CO₂/MWh and <245 kg-CO₂/MWh is needed for 1st and 2nd generation, for net CO₂ emissions to be within the range of conventional MeOH synthesis route. Based on current projections for the US grid electricity emission intensity,⁷² such a situation would be possible by the year 2050.

The proposed air-to-MeOH routes could also lead to zero or net negative CO₂ emissions if the grid emission is below 97 kg-CO₂/MWh. In this regard, one could consider the example of Iceland where 100% renewable electricity on grid emits only ~8 kg-CO₂/MWh.⁷³ In a such a scenario, net negative CO₂ emissions can be obtained for both 1st generation (–0.54 kg-CO₂/MeOH) and 2nd generation (–0.64 kg-CO₂/MeOH). Beside Iceland, Canada and Sweden with average electricity emission intensities of ~130 kg-CO₂/MWh and ~50 kg-CO₂/MWh, respectively, will also result in net negative CO₂ emissions.⁷⁴ The CO₂ emission intensity when other types of renewable electricity (wind, geothermal, and hydro) substitute CPV electricity is presented in Figure S.8.

Figure 5. The net CO₂ 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.7). The yellow dashed lines indicate the range of CO₂ emission of conventional MeOH synthesis route.⁷¹

4. Conclusion and perspective

We are in a race against time to address the ever-rising CO₂ emissions and resulting climate change. We are under immense pressure to quickly adapt renewable energy sources, develop technologies for energy storage, carbon capture, conversion, and use. A clean and sustainable future can be envisioned as one where all these technologies are working together for our energy needs to produce valuable fuels and chemicals. The importance of MeOH in this context cannot be overstated. Because of its high energy density, ease of storage and transportation, it can potentially act as an excellent energy vector. In this study we have presented a comprehensive TEA and cradle-to-gate LCA of futuristic scenario where different emerging technologies for harvesting renewable energy (concentrated PV), carbon capture (DAC), carbon conversion (CO₂ electrolysis) work hand-in-hand for producing renewable methanol (valuable chemical and energy storage solution) from air with net-negative CO₂ emissions. Based on their TRL, we present two different air-to-MeOH routes: i.e., via integration of H₂O electrolysis, CO₂ electrolysis, hydrogenation reactor and via direct CO₂ electrolysis as near future (1st generation) and long term (2nd generation) possibilities, respectively. Our results indicate that in current scenario, the envisioned air-to-MeOH routes are not compelling with high levelized costs and CO₂ emissions.

At the same time, our analysis also revealed that the three-step route presented in 1st generation could possibly be feasible for renewable MeOH production in near-future when certain

economic conditions fall into place. It will require CPV capital cost of below \$290/kW, DAC capital cost ($< \$380/(\text{ton-CO}_2/\text{year})$), grid electricity price (< 3.9 cents/kWh), and electricity emission intensity ($275 \text{ kg-CO}_2/\text{MWh}$) to get levelized costs and related CO_2 emissions to compete with incumbent MeOH production pathway. While a CPV capital cost of $\sim \$290/\text{kW}$ is certainly challenging, like any technology, it will see its cost dropping down with time once in use and like any breakthrough technology; it can only be brought to life with strong incentives. As an example, the silicon PV industry experienced a massive price drop of more than 80% coming from subsidized industries that could sell products with little to no profit. On the other hand, CPV has suffered from a lack of dedicated supply chain, which has forced every company to develop and produce most of the components (trackers modules, etc.) themselves. Similar cost reductions can be expected with DAC, where a capital cost below $\$380/(\text{ton-CO}_2/\text{year})$ is required to reap economic benefits. These numbers have already been proven on a smaller pilot scale such as the one by Carbon Engineering who estimated the cost of CO_2 capture between $\$94/\text{ton-CO}_2$ and $\$232/\text{ton-CO}_2$.¹⁷ The DAC capital cost is predicted to plummet to $\sim \$174/(\text{ton-CO}_2/\text{year})$ in 2030 as the installed cumulative capacity reach $\sim 4,000 \text{ Mton-CO}_2/\text{year}$.⁵⁴ This capacity would require autonomous and mass production manufacturing process. From the performance point of view, increasing DAC performance is much more challenging as the CO_2 concentration in the atmosphere is small ($\sim 400 \text{ ppm}$). Last but not the least, the CO_2 emissions from the proposed air-to-MeOH routes will decrease as the share of renewable electricity on the grid increases across the world.

On the other hand, direct CO_2 electrolysis route (2nd generation) is an attractive technology but will need drastic improvements in performance to be economically competitive, with required current densities $> 300 \text{ mA}/\text{cm}^2$, EE $> 45\%$ and considerable improvements in catalyst stability (> 2 years). Considering the rapid development of electrochemical technologies, in an optimistic scenario this route would likely be compelling in the future. The emergence of artificial intelligence and machine learning would accelerate the development of catalysts and electrolyzer design. To conclude, the commercialization of air-to-MeOH processes in the near-future will depend on continuous innovation and at the same time needs productive discussions and decisions among the key stakeholders.

Acknowledgement

The author(s) would like to acknowledge the financial support provided by Canada First Excellence Research Fund (CFERF) at University of Calgary for funding this.

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