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Pathways to Industrial-Scale Fuel Out of Thin Air from CO_2 Electrolysis

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Summary

The use of CO_2, water and renewable electricity as direct feedstocks for the synthesis of chemicals and fuels is a seemingly-appealing means of transitioning away from a reliance on fossil fuels. Electrochemical CO_2 reduction in particular has been championed as a technology aiding in the energy transition. Despite continuous technical improvements, however, the consideration of CO_2 electrolyzers within a chemical process remains largely unaddressed. Given the need to capture CO_2 prior to electrochemical conversion, up convert most CO_2 reduction products, and operate on renewable electricity, it is essential that we start thinking about CO_2 electrolyzers as part of a larger system, rather than as an independent technology. In other words, what is the endgame for CO_2 electrolyzers? To initiate these discussions within the CO_2 reduction community, we considered the use of CO_2 electrolyzers as one technology in the 'air-to-barrel' production of 10,000 tons methanol/day. Looking at the role of the CO_2 electrolyzers in the process, we highlight the distribution of energy resources required, the potential for process integration and the importance of increasing current densities even further. A key conclusion finds that a 6 order-of-magnitude gap exists between current catalyst areas and industry-sized applications, emphasizing the need to begin research on scaling CO_2 catalysts and electrolyzers immediately if they are to contribute to the upcoming energy transition.

Keywords: CO_2 Electrolyzers; Scaling novel energy technologies; Renewable Energy; Methanol Synthesis;

Electricity generation from solar irradiation and wind offers a globally-abundant energy source which can be used in combination with nuclear energy and carbon capture and sequestration to reduce global greenhouse gas emissions and transition away from fossil fuels as a primary energy source.[1] As the fraction of renewables in the energy mix increases, large scale energy storage technologies become increasingly important and will need to be deployed to cope with peak demand and intermittency on both daily and seasonal time scales.[2,3] The most efficient route, however, is always to use renewable electricity directly. Nevertheless, in case excess electricity cannot be used immediately, an increasingly utilized route is to store electrical power in batteries due to the >90% round-trip energy efficiency of charging and discharging.[4,5] Large-scale battery systems can also be deployed anywhere and are well suited to balance diurnal variations of renewable electricity generation. However, conventional battery technology at the scale of > 100MWh[6] only has the capacity to provide continuous power for a few hours before depletion. One means of storing abundant renewable energy on seasonal time scales is to use dense energy carriers.[7,8] This route can store energy directly or indirectly in the form of chemical bonds, such as methane, ethanol, ethylene, ammonia and methanol,[9–12] and has resulted in a renewed focus on technologies such as electrochemical CO_2 reduction to provide these chemicals synthetically. In addition, certain applications such as air traffic and heavy-duty transport directly rely on hydrocarbon molecules as fuels and may be hard pressed to find alternatives with the necessary energy density/weight/volume requirements. Therefore, there is a critical necessity to maintain a large volume of hydrocarbon chemicals and fuels in the foreseeable future, while the challenge is to change to a more sustainable material and energy feedstock for their production.

The chemicals and fuels created using fluctuating solar-driven renewable energy sources (e.g. electricity from photovoltaics or wind turbines) are commonly referred to as solar fuels. The reagents for solar fuels in the future should be naturally occurring and abundant (H_2O, N_2, CO_2), and originally in (thermodynamic) equilibrium with our environment. A well-known example is the production of hydrogen using renewable energy sources, which can for instance be produced through the electrolysis of water[13] or via direct photo-electrochemical water splitting.[14–16] For any solar fuel to make a substantial contribution to our future energy system, the scale-up and integration potential of a particular processing route is crucial. Only when deployed at scales significant compared to the size of the global energy system (~TW), will a technology have a notable impact on the energy transition. At present, however, the creation of high energy density chemicals and fuels using renewable electricity remains both technically and economically out of reach as compared to current fossil-fuel routes. The majority of demonstrations using renewable electricity for power-to-fuels has been hydrogen production via water electrolysis (green hydrogen), where a large number of plants <100 kW have been examined.[17] The largest planned hydrogen plants operating on intermittent renewable electricity as of 2019 are on the <10 MW scale (see REFHYNE, Germany; HyBalance, Denmark; H2Future, Austria).

The number of academic studies and commentaries on carbon-based solar fuels, almost all inspired by the problem of large-scale solar energy storage, has grown significantly in recent years as indicated by the large number of recent reviews.[18,19] One of these routes uses electrochemical reduction of CO_2, also known as CO_2 electrolysis, as the primary conversion technology. Due to the relative maturity of the field, however, most studies in CO_2 electrolysis focus on solving problems that play out on nano-, micro- or mesoscopic scales, i.e. the development of new catalysts, supports and membranes.[20–23] However, with the final application and global scales in mind, it is important to start considering scales from meters to many kilometers in the analyses, which includes the capture/delivery of reactants, and relevant conditions needed for a usable final product.[24,25] These analyses are imperative for determining at what point CO_2 reduction catalysts, supports and membranes have been sufficiently developed in the lab, and are ready to be developed further into commercial technologies which requires a different research methodology. Additional research efforts can then be shifted towards the broader technological application and the complicated process of complete system design, integration and optimization,[25–27] while defining new operating conditions for ongoing fundamental studies. Finally, a back-of-the-envelope determination of the physical scales of sub-processes that will be required to run an oft-discussed solar fuels plant using CO_2 electrolyzers is extremely valuable to put into perspective what is required of researchers, governments and industry for this technology to contribute to the energy transition within a reasonable timeframe.

In this perspective, we provide a high-level analysis of a process which uses CO_2 electrolyzers to convert atmospheric CO_2 into solar fuels using renewable electricity. The goal of this work is to clearly elucidate the physical scales and energy requirements of CO_2 electrolyzers within an industrial-scale plant. By doing so we hope to provide a physical and tangible end goal for current CO_2 electrolyzer research that motivates further applied directions. To perform this analysis we first propose and describe a technical pathway from atmospheric CO_2 to a final product, and determine the approximate renewable energy input and efficiency of each step in the process, taking note of integration opportunities between technologies. From these energy inputs, we take practical operating conditions into account (e.g. wind speed, current densities, location) to determine the minimum physical scales of CO_2 capture units, renewable energy inputs and CO_2 electrolyzer catalyst areas required to replace today's industrial scale mega-plants with a renewable solar fuel alternative. From this analysis we lastly provide perspectives on the practicalities of small vs large plants and a centralized vs decentralized approach for the production of energy-dense fuels using CO_2 electrolyzers from comparatively dilute renewable energy resources.

For simplicity, our analysis considers that electricity is generated by solar PV modules and CO_2 for the system is provided via direct air capture (DAC). Methanol is chosen as a final product due to its high energy density (22.7 MJ/kg; 18 MJ/L HHV), its versatility to be converted into a variety of products (e.g. gasoline, kerosene) and its ability to be made from CO and H_2, two small molecules which can be produced electrochemical from CO_2 and H_2O. A scale of 10,000 tons of methanol/day, the size of a large industrial chemical plant (see Shell's ~16,500 ton/day equivalent Pearl Gas-to-Liquid),[28] is chosen to exemplify the scale of renewable electricity, air capture units and electrochemical equipment that will be required if future solar fuels are produced on the order of today's existing mega-plants. While many chemical routes exist to produce fuels and intermediates from CO_2 (e.g. reverse water-gas shift, direct CO_2 to methanol heterogeneous catalysis[27,29,30], solid-oxide CO_2 electrolysis[31]), we have chosen to highlight one specific combination of technologies as a tool for indicating the typical footprint, compatibility and energy balance of an integrated capture and conversion system.

Solar-driven synthesis routes for methanol using CO_2 electrolyzers

Commercial methanol (MeOH) synthesis is a two-step process in which the energy and molecules in a fossil fuel (i.e. methane) are converted to methanol.[32,33] The first step of the process uses steam-methane reforming to convert CH_4 into a mixture of H_2, CO and a few percent of CO_2. This synthesis gas is subsequently converted to methanol in the second step that operates at elevated temperatures (≈250 °C) and pressures (≈50-100 bar). While methanol synthesis cannot be directly created electrochemically from CO_2 with high selectivities or current densities at this point in time,[34–37] CO_2 and water electrolyzers have the capacity to replace the steam methane reforming step of current methanol synthesis by producing CO and H_2 from CO_2 and H_2O. In essence the energy, carbon and hydrogen content of CH_4 are replaced by solar energy, CO_2 and H_2O.

For a purely solar-driven methanol synthesis process, which doesn’t rely on industrial inputs (e.g. CO_2 from cement, steel plants, etc.), these CO_2 and H_2O molecules will need to come from feedstocks initially in equilibrium with the environment. A suitable feedstock is water (from the environment) and CO_2 from air at 400 ppm. For the CO_2 electrolyzer to operate, this dilute CO_2 from the atmosphere first needs to be concentrated. For the direct air capture of CO_2 we have used potassium hydroxide (KOH) as a capture solvent, where ambient CO_2 is converted into carbonate upon contact. Here the KOH and CO_2 are then recovered using an electrically-driven bipolar membrane electrodialysis step.[38] The KOH is then recirculated to the capture unit while CO_2 remains in an aqueous electrolyte and is pressurized to 50 bar in a $KHCO_3$ electrolyte, before being fed to the CO_2 electrolyzer.

The overall reaction for solar-to-methanol synthesis is then described by the stoichiometric reaction in Eq. 1 and shown in the Supporting Information (SI):

$$CO_2(from\ air\ at\ 400\ ppm) + 2H_2O(l) \rightarrow CH_3OH(l) + 1.5O_2(g)\ ;\ (\Delta G_0 \approx 23.1 \frac{GJ}{ton\ MeOH}) \qquad (1)$$

In this equation the entropic contribution of separating CO_2 from an ideal mixture is also included as 20 kJ/mol CO_2 (0.64 GJ/ton MeOH).

With these boundaries in mind, an electrified methanol synthesis route driven by solar energy can then be envisaged by combining 5 individual, yet integrated sub-processes: (1) conversion of sunlight to electricity via photovoltaic modules, (2) an atmospheric CO_2 capture system using aqueous KOH as a capture agent, (3) bipolar membrane electrodialysis coupled with water-splitting for regeneration of the capture solvent, (4) electrochemical conversion of CO_2 and water to synthesis gas (CO + H_2), and finally (5) a standard methanol synthesis step. An overall proposed reaction scheme of the process is presented in Fig. 1.

With these envisioned sub-processes we can now fully expand the overall reaction described in Eq. 1 to include the electrochemical formation of syngas via a CO_2 capture and concentration step using bipolar membrane electrodialysis (Eq. 2), the formation of CO via a CO_2 electrolyzer (Eq. 3), the formation of H_2 via a H_2O electrolyzer (Eq. 4), and the synthesis of methanol (Eq. 5):

$$CO_2(400ppm) \rightarrow CO_2(aq) \tag{2}$$

$$CO_2(aq) \rightarrow CO(g) + 0.5O_2(g) \tag{3}$$

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \tag{4}$$

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l) \tag{5}$$

The proposed scheme in Fig. 1 for methanol synthesis was chosen as integration possibilities exist between the CO_2 capture, regeneration and conversion processes. In addition, the BPMED regeneration reaction can be driven electrically rather than using heat regeneration. As discussed later, the need for CO_2 electrolyzers to operate using CO_2 in the gas or liquid phase, as well as the heat resources available in the process, can further influence the technology utilized in the CO_2 capture step.

While a reaction scheme and the specific technologies are proposed here in order to create a realistic air-to-barrel scenario, many possible alternate processes exist, and it might take some time before a final, preferred combination of technologies is realized. Nevertheless, the above exercise allows us to proceed with an analysis of the energy requirements and physical scales for each sub-process in a 10,000 ton/day plant.

Energy efficiency and distribution of a solar-driven methanol synthesis process

To gain an understanding of the energy requirements, efficiency and scale of such a proposed air-to-barrel system, and the requirements of CO_2 electrolyzers versus other sub-processes, we can take information known about each individual technology and combine them together to assess the entire system.

The initial sub-process in the solar methanol synthesis route (Fig. 1) is the CO_2 capture reactor. Hollow fiber gas-liquid membrane contactors[39] are well suited for the CO_2 capture step as these systems provide excellent contact between the aqueous capture solvent and the wind blowing through the reactor. Here aqueous potassium hydroxide (KOH) is chosen as a capture medium given its integration with downstream CO_2 conversion. Upon interaction with hydroxide, CO_2 is fully converted to dissolved potassium carbonate, capturing CO_2 within a salt solution. For regeneration in the next sub-process the capture solution in then pressurized to 50 bar using a pump. The capture process itself is estimated to require 13 kJ/mol CO_2.[40] From the capture unit, the CO_2 is regenerated electrochemically in a bipolar membrane electrodialysis (BPMED) step.[38] Here, KOH can be regenerated and recycled back to the capture step while a separate stream now containing dissolved CO_2 in a pressurized water stream can be fed to the electrocatalytic system. This BPMED step requires a practical power input of approximately 215 kJ/mole CO_2 (see SI for details).[41] The advantage of running electrodialysis at high pressures is that the CO_2 produced essentially remains dissolved in water, which makes it an excellent feedstock for the subsequent CO_2 electrolysis operation, avoiding the typical gas regeneration step that would otherwise require ~100 kJ/mol CO_2. In addition, the CO_2 in the pressurized aqueous stream can further be converted to pressurized CO, which is necessary for methanol synthesis which operates at 50 bar. Avoiding compression of both CO and H_2 during production saves on the order of ~80 kJ/mol CO_2 converted (see Fig.2 and SI). Therefore, process integration with up and downstream systems, and the direct need for a high-pressure feedstock for methanol synthesis can already give practical and minimum operating conditions for pressurized CO_2 electrolysis which deviate from most ambient pressure academic studies.[20,42,43]

The electrochemical reduction of CO_2 (Eq. 3) then follows the electrodialysis step, producing CO as a product, as well as O_2 as a by-product of the anode reaction. As the solubility of CO in water is much less than that of CO_2, this unit will produce pressurized gaseous CO which is separated by phase, collected and sent to the methanol synthesis step. Pressurized CO_2 reduction not only helps to increase current density but increased pressure aids the reaction in achieving near-unity selectivity.[44] The solubility of CO_2 in 1 M $KHCO_3$ is 1.05 M at 25 ºC and 50 bar, which ensures that CO_2 will remain dissolved at the chosen concentrations for the electrolysis process. In a parallel process, H_2 is produced via water electrolysis (Eq. 4), again under a pressure of 50 bar. Due to the stoichiometry required for methanol synthesis, two H_2 molecules will be required for every CO molecule.

While water electrolyzers are more technically established than CO_2 electrolyzers, both units are targeting overall energy efficiencies of roughly 70%.[13,45–47] Recent work by the Kenis group using glycerol oxidation for the anodic reaction for example has also recently shown higher CO electrolyzer energetic efficiencies by removing the energy-intensive water oxidation step.[48] Using an assumed 70% efficiency for both electrolyzers, the energy required for water and CO_2 electrolysis is then 816 kJ/mol CO_2 and 404 kJ/mol CO_2, respectively (see SI for calculation). The overall energy efficiency of syngas production (CO + $2H_2$) from CO_2 (400 ppm) and H_2O under ambient conditions (Eq. 6) is then shown to be ~60% following from the combined performance of CO production (Eq. 2-3) and H_2 production (Eq. 4) (see Supplementary Information):

$$CO_2(from\ air\ at\ 400\ ppm) + 2H_2O(l) \rightarrow CO(g) + 2H_2(g) + 1.5O_2(g) \qquad (6)$$

At this point in the process, both CO and H_2 have been produced at pressure from their initially ambient environmental conditions. The synthesis gas with a 1:2 CO to H_2 ratio can now be converted in the standard methanol synthesis process described above using a standard Cu/ZnO-based catalyst. The efficiency of this individual sub-process is about 83%, which is determined by the exothermicity of the methanol synthesis from synthesis gas.

With the energy requirements of all sub-processes defined, the overall efficiency of the methanol synthesis plant can now be determined. The overall efficiency can be defined as the higher heating value (HHV) of the methanol (22.7 GJ/ton MeOH) produced, normalized by the required input of electrical energy. The main electricity consuming steps in the process are related to the capture of CO_2 through BPMED, and the separate electrochemical steps for producing H_2 and CO. To get an idea of the efficiency of the total plant, we will only take these main steps into account and neglect consumption of electricity by pumps and other equipment which are in general negligible compared to these more intensive processes.

The efficiency of methanol production E is now given by:

$$E = HHV(methanol) / \{ E_{H2O\ electrolyzer} + E_{CO2\ electrolyzer} + E_{BPMED} + E_{Capture} \} \qquad (7)$$

Here, from the assumed efficiency of both water electrolysis (HHV H_2 produced / required power input) and CO_2 electrolysis (HHV CO produced / power input) the energy requirements are 816 kJ/mol CO_2 and 404 kJ/mol CO_2, respectively. Furthermore, the BPMED capture unit and air contactor requirements are approximated as 215 kJ/mol CO_2 and 13 kJ/mol CO_2 as described above, respectively. Here, for context, all values are relative to mol of CO_2 converted, and consequently, mol of methanol created. The total energy requirement is then 1448 kJ/mol CO_2 converted (see Fig. 2) and as a result, the overall energy efficiency of methanol production is around 50%.

Due to the energy lost during the process, attention also needs to be paid to heat management. As water and CO_2 electrolysis have the largest contributions to the processes' energy requirements, and the current density in electrolyzers is typically larger than in BPMED, a significant amount of heat will be produced in the electrolysis step. For electrolyzer energy efficiencies of 70% there will then be 366 kJ/mol CO_2 of heat generated during electrolysis. A typical individual water electrolysis unit of 1.2 MW (300 Nm^3/hr electrolyzer from Nel) then gives 360 kW of heat per electrolyzer at ~80 °C in an alkaline electrolyzer configuration.[49] As water electrolyzers have been already scaled to industrial size, proper heat management to maintain the equipment has been developed for individual systems and for Nel's >50 MW combined systems. In addition to the heat produced in the exothermic methanol synthesis (~250 °C), and its higher operational temperature, opportunities may be available for using mid- to high-temperature waste heat for heat utilization in other processes.

Relative scale of each sub-process

In the design of new energy technologies, it is important to determine early on in research if the proposed solution has the capacity to be scaled to the physical sizes needed to accomplish its envisioned end goal. Similarly, estimating and comprehending the eventual size of a technology can help streamline designs towards commercialization by removing untenable options. Here we approximate important physical sizes of the air-to-barrel methanol synthesis using CO_2 electrolyzers from the energy analysis in the previous sections and practical operating conditions for each technology. Specifically, we estimate the required area of fans to capture CO_2 from the air, the minimum area of photovoltaics required to power the synthesis process, and the geometric area of catalytic material required to operate a CO_2 electrolyzer for a 10,000 tons/day plant.

First, it is necessary to estimate the typical size of the CO_2 capture plant, symbolized by an array of fans in Fig. 1. It is first assumed that when using an alkaline KOH capture sorbent, 50% of CO_2 (η_{Cap}) entering the fan structure can be captured[50] and transformed into methanol from the initial CO_2 concentration of 400 ppm in the air. A 10,000 ton/day methanol plant would then require 27,500 tons of CO_2 to pass through the fans each day to capture the 13,750 tons of CO_2 required for the plant, assuming no losses in other parts of the process. Using an air density of 1.184 kg/m^3 which contains 0.608 g CO_2/kg air, this means that approximately 38.2 km^3 of air/day must pass through the capture area ($V_{air,req} = \frac{1}{\rho_{air}} \frac{m_{air}}{m_{CO_2,air}} \frac{m_{CO_2,req}}{\eta_{cap}}$). The outlet of the capture unit would then contain 200 ppm of CO_2 with these assumptions.

The frontal surface area, A, required can then be found as a function of the wind velocity across the face. Taking an average assumed wind speed of 2 m/s in Eq. 8, the expected cross-sectional area of fans required to capture the required CO_2 from the air is then on the order of 0.22 km^2. Higher wind speeds than this are possible (the average onshore wind speeds in the Netherlands are >6 m/s)[51], which would reduce the capture area required. This process, however, assumes continuous operation and does not take air speed slowdown due to the structure and process into account. Therefore the necessary capture area can be defined as,

$$A_{capture} = \frac{Volume\ of\ air\ required\ per\ day}{v_{wind}} [m^2] \tag{8}$$

where v_{wind} is the velocity of the wind and the surface area A is expressed in m^2.

Note that with the proposed capture system and parameters, the CO_2 captured per year per unit of capture area is ~22.7 tons CO_2/m^2/year (at 13,750 tons CO_2/day and a 0.22 km^2 capture area). This value is similar to that reported by Climework's amine-based capture plant in Zurich (900 tons CO_2/year over ~40 m^2 frontal area = 22.5 tons CO_2/m^2/year).[52]

To power the electrochemical systems in this methanol plant, it will also be necessary to have a large renewable energy source. From the above estimation of 1435 kJ/mol CO_2 converted, a 10,000 tons/day methanol plant will then require a continuous electrical power source of 5.19 GW. To get an idea of the dimensions of the solar farm required to power such a solar methanol plant, we assume that the process is driven by photovoltaic panels. As an example, here we approximate the photovoltaic installation size that would be needed to provide the total amount of energy to run the plant, independent of storage needs between the intermittent energy sources and the continuous downstream methanol synthesis.

From the National Renewable Energy Laboratory's (NREL's) PVWatts® solar calculator tool, the average annual solar irradiation in Amsterdam, for example, would be 3.67 kWh/m^2/day using a 2-axis tracking solar array. Assuming a solar panel efficiency of 20%, this equates to an average energy output of 30.6 W/m^2 of solar panels over the year. This implies that for a global-scale plant, producing 10,000 tons MeOH/day, the minimum area of PV panels will need to be around 170.2 km^2 (see SI for further details). Reports from NREL, however, show that an additional amount of indirect land-use is required, meaning that only about 70% of a solar park's land will be capturing solar energy.[53] Taking this additional consideration into account, a land area of 243.1

km^2 is needed to meet the minimum energy requirements for the methanol plant. A comparison between the surface areas required for CO_2 capture and power supply reveals that for all practical purposes, the area of the photovoltaic panels will be at least two orders of magnitude larger than the effective area of the CO_2 capture unit.

A separate order of scale calculation that provides perspective on future industrial electrochemical processes is the approximate catalyst area that will be needed in CO_2 electrolyzers. Most current research takes places on the scale of 1 cm^2, or 0.0001 m^2 while several papers in literature have used various systems to reach CO_2 to CO current densities in the realm of 0.4 A/cm^2, with varying Faradaic efficiencies.[44,54–56] For this currently accessibly reaction rate of 0.4 A/cm^2, and assuming 100% Faradaic efficiencies for CO production, the active catalyst area required for an industrial plant capable of converting 13,750 tons CO_2/day is approximately 175,000 m^2, or 0.175 km^2. The only means of measurably reducing this value is by decreasing the overall plant size, or further increasing the CO_2 reduction current density, as shown in Fig. 3. For electrolyzers converting CO_2 to CO for methanol synthesis, the catalyst area needed is then inversely proportional to the achievable current densities and directly proportional to the size of the plant.

Observing Fig. 3 we can then see that from a capital cost and electrolyzer size perspective, we are motivated to achieve even higher current densities than have been reported in literature to date. At 2.5 A/cm^2 for example, the 0.175 km^2 catalyst area shrinks to 0.028 km^2 for a 10,000 tons/day plant. To be able to reach these current densities however an abundance of CO_2 needs to be able to reach the catalyst's surface, while ensuring that H_2 evolution does not disproportionately increase at higher operating voltages. High pressures and gas-diffusion layer/membrane electrode assemblies have been shown to greatly enhance reaction rates, but are almost an order or magnitude away from demonstrating reaction rates of 2.5 A/cm^2. Combining gas-diffusion electrodes with pressurization is one interesting route to try to increase reaction rates further, but only a few examples exist in literature.[54,56] An additional barrier to realizing higher reaction rates in a commercial system is also the desire to reach high single-pass conversion efficiencies for CO_2. Converting a large fraction of the inputted CO_2 then maximizes the value of CO_2, while minimizing separation and recycling costs. Achieving high CO_2 utilizations however inherently implies that the partial pressure of CO_2 will decrease throughout the device, proportionally decreasing the limiting current density for CO_2 reduction. Finally, increasing current density will require increases in the system cell voltage, which increases the energy requirements of the CO_2 electrolyzers and the area of PV panels needed. Independent of the exact current density assumed, Fig. 3 highlights that the required catalyst area for CO_2 electrolyzers is resoundingly large and demonstrates that substantial reactor engineering lies between the current field of research and future applications. For this reason alone, research into scaling of CO_2 electrolyzers and the most stable operating conditions is of utmost importance if this technology is to meaningfully be used in the upcoming energy transition.

To put the magnitude of these calculated air capture, solar PV, and catalyst areas in perspective, we can compare these values against some of the largest existing or planned similar plants and installations (Fig. 4). Here we can see that the solar PV area needed for the 10,000 tons/day air-to-barrel plant is on a similar order of magnitude to the solar land area of the Pavagada Solar Park.[57] The minimum area of CO_2 capture units, however, is 3 orders of magnitude larger than the largest Climeworks plant installed in Zurich.[58] Finally, and with the largest disparity, the largest CO_2 reduction catalyst areas to date[23,59] are only <0.04 m^2 versus the estimated 0.175 km^2 catalyst areas estimated for these plants. While this difference itself is phenomenal, we can also see that such a methanol plant also requires substantially larger catalyst areas for the CO_2 electrolyzer than even the largest water electrolyzer (Nel, Norsk Hydro),[49,60] chlori-alkali plant (Dow-Mitsui)[61] and Proton-Exchange-Membrane (PEM) electrolyzer units,[62] which are predicted as 37,500 m^2, 13,500 m^2 and 167 m^2, respectively (see SI for details). In light of this current gap between the needed catalyst size and existing technology, tough discussions need to take place regarding whether some of the proposed technological configurations or materials for electrochemical CO_2 reduction in literature are capable of scaling to the sizes needed to impact global capacities. Furthermore, this result highlights the need for additional efforts to be placed on developing scaled-up and scaled-out CO_2 electrolyzer systems in parallel to developing better catalysts.

Finally, a common theme here for several of the integrated components is the continuous discussion around planar areas of materials and systems, rather than volumes. This differs from thermally-driven processes which have traditionally scaled closer to the volume of components and subsequently benefitted from economies of scale, leading to extremely large plants. In the analysis presented here, we see that the need for renewably-driven processes to scale by increasing cross-sectional area (e.g. solar panels, capture areas, electrolyzer catalysts) may force us to change the current way in which we produce chemicals, which is via mega plants. Since economies of scale are comparatively less beneficial for electrically-driven chemical processes, and the proposed areas needed for a 10,000 tons/day plant are extremely large, decentralized or smaller installations may then be more desired practically and economically. Further discussions are then needed to determine what level of centralization vs. decentralization will be optimal for future energy systems, and subsequently the production of dense-energy carriers from dilute renewable resources. Additional considerations are resource availability, geography, and political factors, which can motivate or demotivate large-scale plants or local generation and usage. In either case, the total area of installations needed to impact current production routes is linearly correlated by the total amount of CO_2 that we will need to convert, which should add further perspective to the urgency to scale current technology routes.

Future Outlook and Summary

One of the drivers of performing the above analysis is to determine how an air-to-barrel approach to CO_2 conversion can provide a broad-brush assessment of some practical operating conditions and constraints for individual steps in the process. This is particularly true for CO_2 electrolyzers which have not yet been examined in an integrated system, despite the motivations of their future role in the energy transition. While the above described case is for one specific set of technologies, it does already tell us that the technology required to capture CO_2 must be able to integrate with CO_2 conversion, and that if the CO_2 conversion process does not make a ‘final’ product, then the CO_2 conversion must also be able to integrate with further downstream processing. A more detailed process and system analyses in the future will help to identify further opportunities and constraints for solar fuels production using CO_2 electrolyzers as a conversion technology, which can then allow for proper comparisons against competing technologies (reverse water-gas shift, direct CO_2 to methanol heterogeneous catalysis[27,29,30], solid-oxide CO_2 electrolysis[31]).

In our case, the constraints of methanol synthesis, and conditions necessary for BPMED both require that CO_2 electrolysis be performed at higher pressures than are regularly reported in literature. Interestingly, removing CO_2 as a gas from the recovered capture solvent by depressurizing or regeneration, for instance, requires additional energy compared to using the saturated solution directly (Fig. 2). Therefore, such a case study can provide new boundary conditions necessary for industrial CO_2 electroreduction, and consolidate both fundamental and practical research to operate in realistic conditions.

As technology improves there will be further opportunities to expand and exchange different components to optimize system efficiencies further, however the required inlet and outlet conditions remain relatively fixed. One example of this is the possibility for CO_2 electroreduction in a gas-diffusion system instead of a pressurized aqueous system.[63,64] While gaseous CO_2 would have to be removed from the BPMED at a specific energy cost, which may justify or motivate using amine-based direct air capture over alkaline capture, the overall gains in efficiency made in the CO_2 reduction reaction may outweigh any additional energy requirements within the capture stage. Unless the gas-diffusion system were pressurized, however, substantial energy would then be required to compress CO and H_2 for the synthesis step, which could remove any gains in overall efficiency. Further, replacing the BPMED step with a thermally driven release of CO_2 from a capture solvent using waste heat, may allow for the direct use of gas-diffusion layer configurations for CO_2 reduction while reducing the renewable electrical energy requirements of the overall unit.

It is our hope that the process intensification and integration described in the example air-to-barrel case will aid the CO_2 electroreduction community in assessing relevant operating conditions that will be needed to scale the technology to a practical level. Considering these operating conditions and constraints can provide a new playground to understand fundamental reaction phenomena and optimize catalyst/electrolyte/reactor systems, while providing motivation to accelerate the technology towards its end goal. By envisioning the future energy and size requirements of CO_2 electrolyzers within a solar fuels process, and comparing that to progress in the research field today, we can then start to assess when and how electrochemical CO_2 reduction will play a measurable role in the upcoming energy transition.

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Author Contributions

All authors contributed to the conceptualization of the work. T.B. and W.A.S. acted as primary writers of the original manuscript while all authors reviewed and edited the manuscript. W.A.S. was responsible for manuscript correspondence and overall supervision of the manuscript.

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Figure Titles and Legends

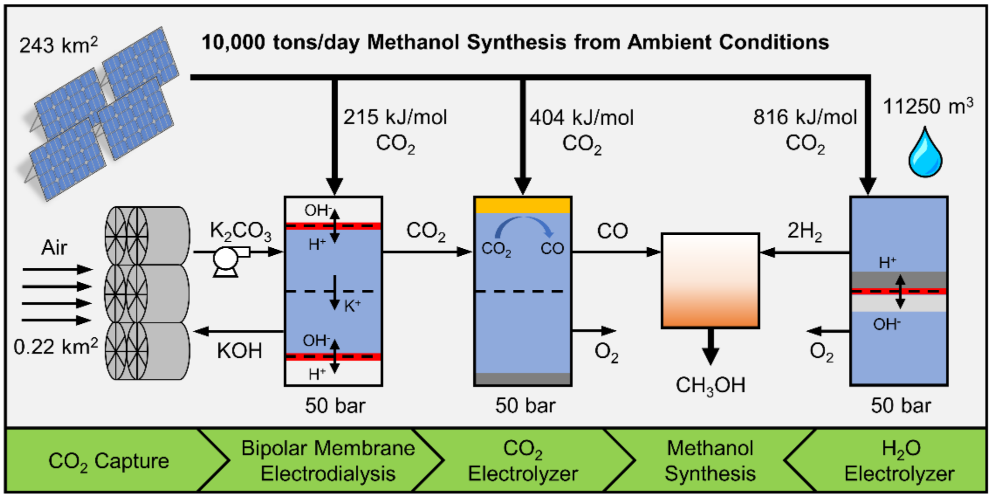

Figure 1: Air-to-barrel methanol synthesis from ambient environmental inputs.

A proposed scheme for methanol synthesis using ambient solar energy, CO_2 and water. The order of magnitude area of a solar photovoltaic park and the frontal area of a CO_2 capture unit, as well as water volume inputs, are illustrated for a 10,000 tons/day methanol plant. The energy requirements for each primary component are presented in kJ mol^{-1} CO_2 converted and include the Bipolar Membrane Electrodialysis (BPMED) step, CO_2 electrolyzers and H_2O electrolyzers.

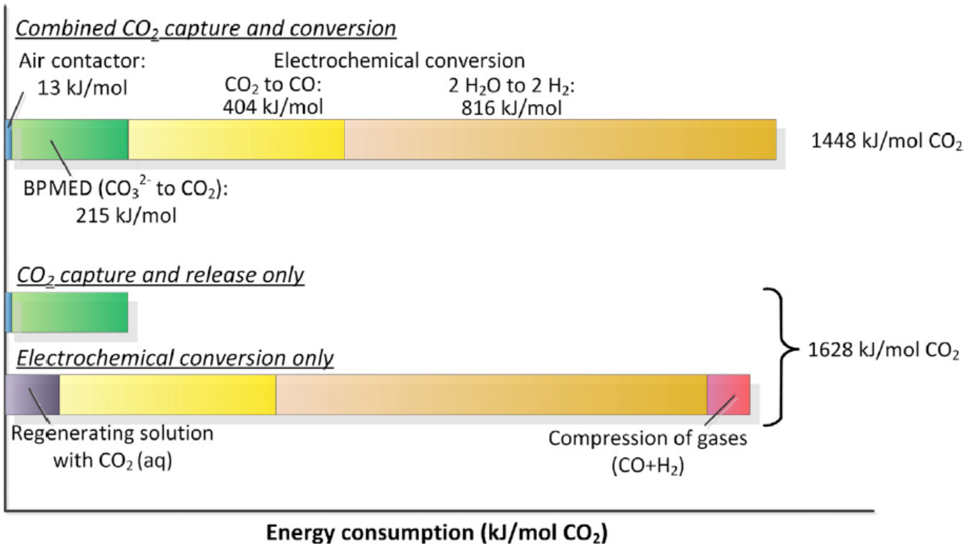

Figure 2: Process energy requirements

Breakdown of energy contributions for the processes of direct air capture, electrochemical regeneration with BPMED and electrochemical production of CO and H_2 from CO_2 and H_2O. Values for energy consumption are estimated to be 13 kJ/mol for direct air capture[40] and 215 kJ/mol for the BPMED.[41] Also shown are the comparative energy requirements for a process releasing CO_2 from a capture solvent and needing to pressurize CO and H_2 prior to methanol synthesis.

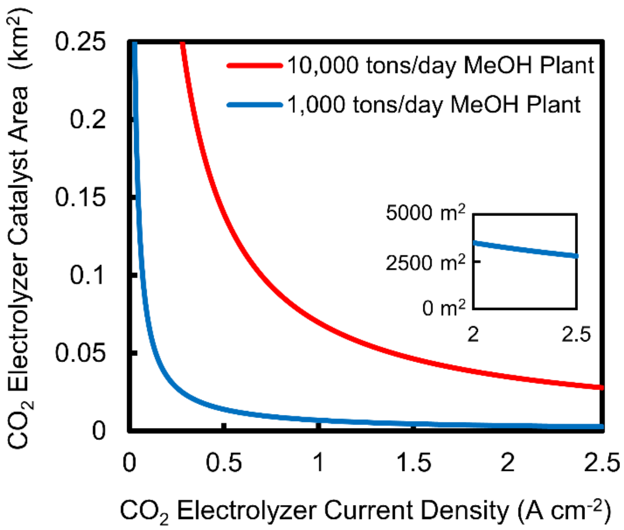

Figure 3: CO_2 Electrolyzer Catalyst Areas

The impact of current density and methanol plant size on the required catalyst area for a commercial CO_2 electrolyzer. The comparative areas for a 10,000 tons/day and 1,000 tons/day air-to-barrel methanol plant are shown. All areas are determined on a geometric basis and a CO Faradaic Efficiency of 100% is assumed.

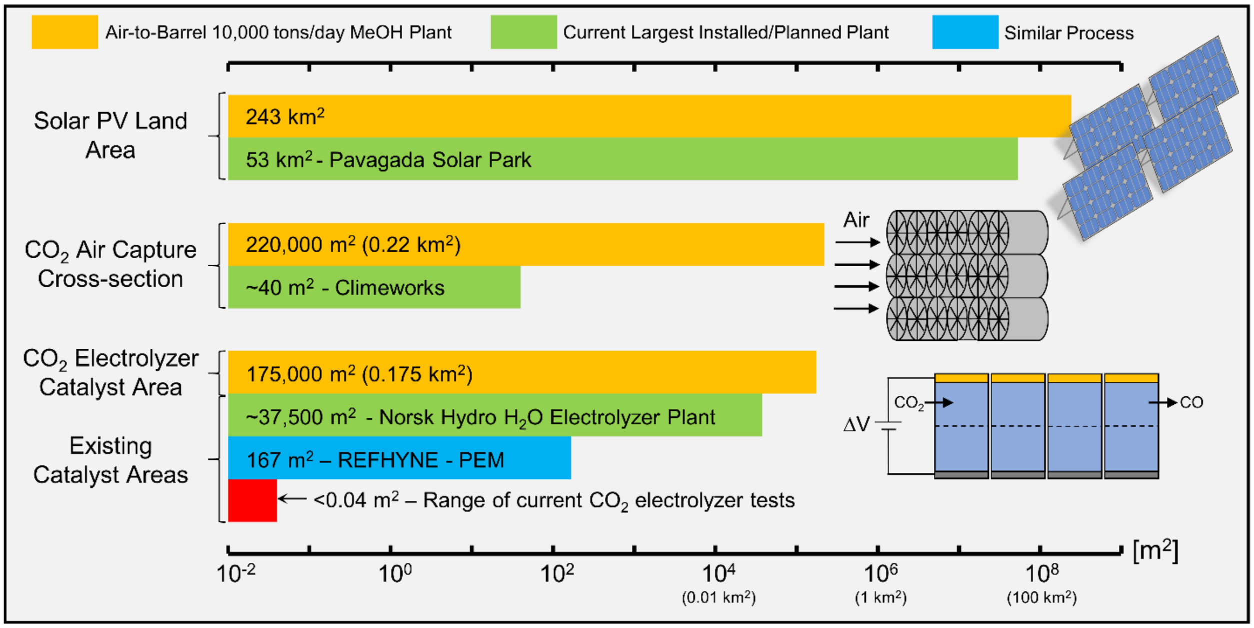

Figure 4: Critical scales of each sub-process

Important solar photovoltaic, direct air capture and CO_2 electrolyzer catalyst areas (in orange) needed to build a 10,000 tons/day air-to-barrel methanol plant using ambient molecules as an input. The CO_2 electrolyzer areas assume currently achievable current densities of 0.4 A cm^{-2} for CO at 100% Faradaic Efficiency. These areas are compared to the world's largest or largest planned installations for each respective technology to provide context to the orders of magnitudes needed for centralized solar fuel production. The range of current reported CO_2 electrolyzers is also reported.