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Overcoming the energy–water nexus in dry regions – water-positive production of green hydrogen carriers and base chemicals: the DryHy project – technical aspects†

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The application of Direct Air Capture (DAC) for extracting CO₂ from the atmosphere has a great potential to reduce net CO₂ emissions and help achieve climate goals. Besides storing the separated CO₂, it can be used as a carbon feedstock for producing CO₂-neutral e-fuels, marking a critical research focus area. Despite advancements in various DAC technologies and processes, their large-scale implementation remains limited, among other reasons, because of the large amounts of energy required to power such processes. This article explores the utilization of DAC for water-conscious production of methanol in sunny regions, using cost-efficient photovoltaic power. The selected approach is presented, which involves a process on demonstrator scale with amine-based DAC for CO₂ and water separation from air, high-temperature electrolysis using solid oxide electrolysis cells (SOEC) for syngas production, and subsequent methanol synthesis. We also discuss alternative methods, potential locations, and implementation strategies, highlighting the advantages but also the challenges of producing green methanol in sunny regions outside Germany.

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1 Introduction

The anthropogenic climate change is one of the grand challenges of this century. Due to the vast emissions of greenhouse gases such as CO₂, the average surface temperature has risen by 1.09 °C compared to the pre-industrial (1850–1900) age and is expected to exceed 2 °C by 2100 if emissions continue unabated.¹ In order to mitigate climate change a carbon neutral economy has to be achieved by preventing CO₂ emissions and employing negative emission technologies (NET) for processes that cannot be made CO₂ neutral.^{2,3} There are two key

approaches for this transformation: a fuel shift from fossil energy carriers to renewable production of electricity and the development of circular CO₂-technologies, often termed as power-to-X.⁴

For Germany, studies show that it will be challenging to satisfy the energy demand with domestic renewable power production.^{5–7} Consequently, energy imports will play an important role in achieving climate neutrality, as these studies assume that domestic renewable power generation will be complemented by green energy imports, especially in periods of low energy output from wind and solar. Additionally, renewable power can be harvested more efficiently in other regions. For example, Fig. 1 shows the average photovoltaic potential around the globe. As anticipated, regions around the subtropics exhibit significantly higher solar potential compared to northern countries. This includes most of Africa, especially the north and the south, Australia, Mexico, the USA, Chile as well as Arabia. This geographic advantage is crucial for the efficient and cost-effective supply of renewable power.

However, most of these regions contain a vast amount of dry land with low infrastructure and low energy demand, e.g., wide parts of Africa, Arabia or Australia. Therefore, there is a dire need for energy carrier technologies to transfer the energy from its point of generation to the demand side. Energy transfer *via*

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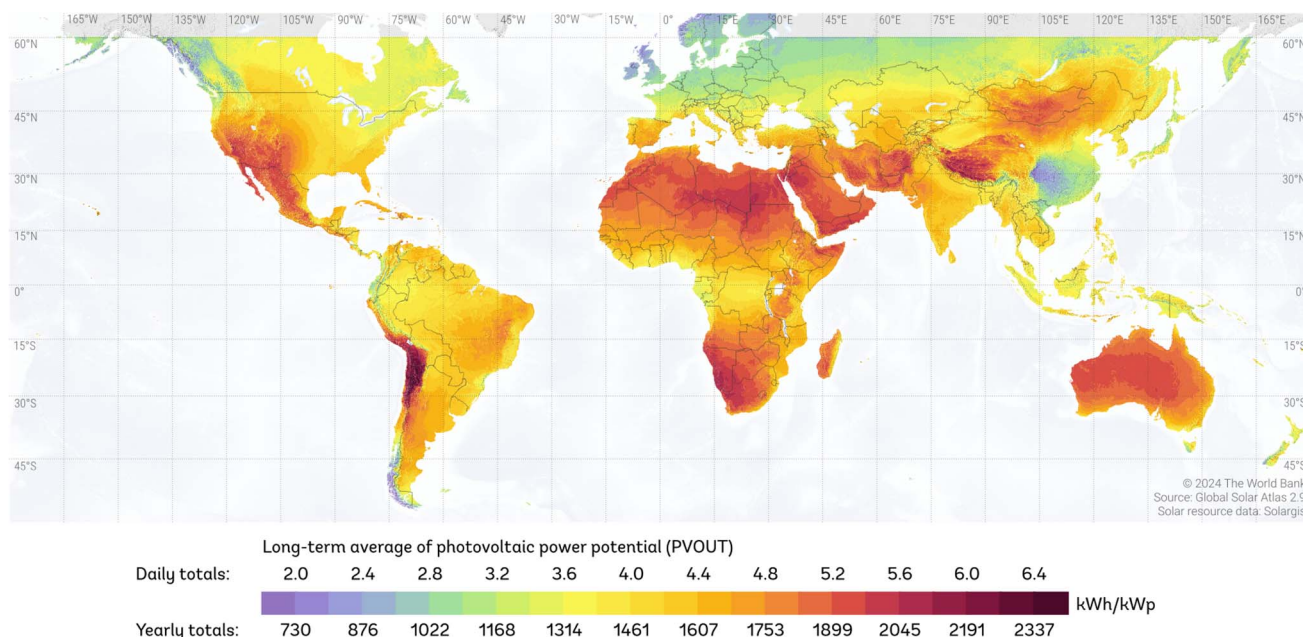


Fig. 1 The average photovoltaic power potential around the globe. Figure adapted from "Solar resource map" © 2021 Solargis licensed under CC BY-SA 4.0 (<https://solargis.com>).

high-voltage transmission lines is often not an option, as the suitable infrastructure at the generation side might be missing and transport over extremely large distances (*e.g.*, continents) is not viable.⁸ Therefore, alternative energy carriers are necessary such as hydrogen and its derivatives.^{2,9,10} Here the energy is stored in chemical bonds and transportation of the chemical compounds can be facilitated by pipelines, tank vessels and fuel trucks. Additionally, producing hydrogen or its derivatives from renewable power has the added benefit that these compounds can be used as commodity chemicals as well and thereby defossilize the chemical industry.

Among the potential candidates, methanol appears to be very promising: firstly, methanol is a liquid with reasonable volumetric energy density making transportation, *e.g.*, in a tank vessel, more feasible compared to hydrogen and secondly, allows for easy handling and storage.^{11–13} Moreover, as of today, the market size of methanol is already large with more than 100 Mt y^{−1} (ref. 13 and 14) owing to its use in fuel blending or use in the chemical industry, *e.g.*, in the methanol-to-olefin process for the synthesis of polymers. Lastly, the synthesis of methanol from syngas is well established, which eliminates the need to develop entirely new synthesis routes.¹⁵

Nonetheless, there are multiple challenges for the synthesis of cost-efficient, green methanol. First and foremost, cost-efficient renewable power generation is needed, as many studies on the production of e-fuels show that the production costs are mainly dependent on the costs of the primary energy source.^{17–19} Additionally, to produce methanol, a CO₂-negative carbon feedstock is required, *e.g.*, biomass or CO₂ from direct air capture (DAC), and a hydrogen source, typically water. However, as illustrated in Fig. 2, the aridity index is particular low in subtropical regions,¹⁶ which coincide with areas

identified as having a high photovoltaic power potential in Fig. 1. This indicates an inverse correlation between high solar irradiation and the availability of water, with regions experiencing very high solar irradiation typically being arid.²⁰ Thus, in order to avoid competing with drinking water, it is necessary to generate green methanol water-neutral or even water-positive.

The water-positive generation of green methanol is the main focus of the DryHy project. DryHy employs amine-based DAC technologies, which belong to the most advanced and most energy efficient DAC processes that are currently available.²¹ In addition, amine-based DAC does not only separate CO₂, but also separates water, which is typically an undesired byproduct in DAC processes. However, DryHy employs an innovative approach whereby the water produced as a byproduct of the DAC is utilized for electrolysis, in contrast to the depletion of local water sources, which is a consequence of common synthesis approaches for e-fuels. The DAC device for CO₂ and H₂O separation from air is combined with a downstream solid oxide electrolyzer cell (SOEC) for syngas production and a methanol reactor.

This approach will be implemented on a demonstrator scale with the objective of bridging the gap between small-scale research and industrial application, thereby facilitating the transition of the technology to a more mature market position. With this, the DryHy project aims to provide technologies for achieving the climate goals, while increasing the energy security through diversification and lowering costs by methanol production in regions with cheap renewable power generation. Additionally, the project aims at establishing new partnerships and opening up new market options. In the following, the approach, synergies and challenges of the DryHy process are discussed from a technical perspective.



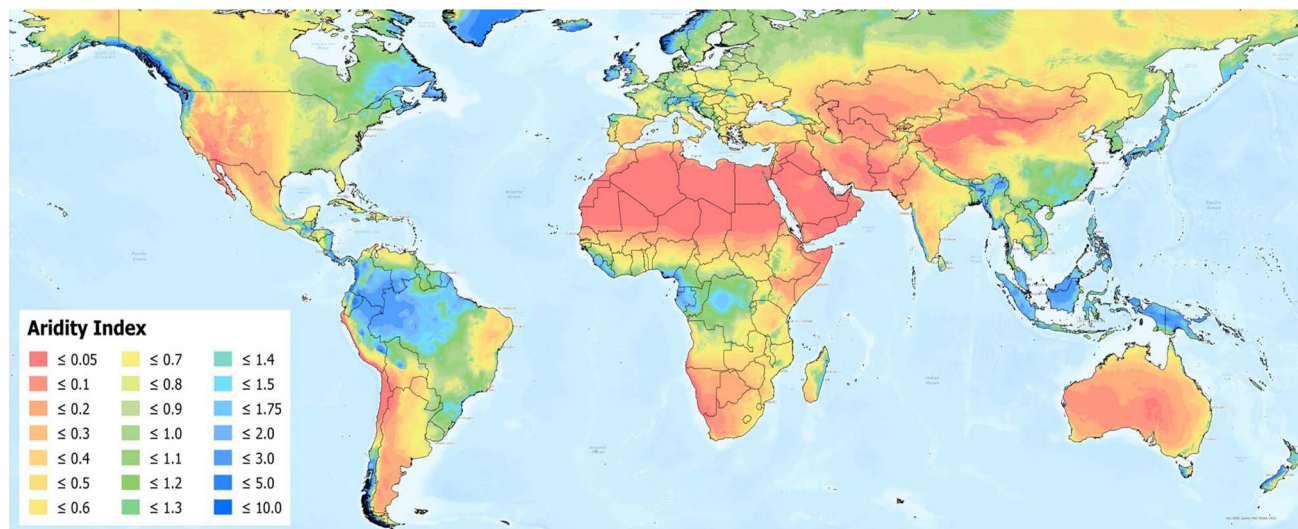


Fig. 2 The aridity index around the globe. The aridity index is defined as the mean annual precipitation in relation to the mean annual reference evapotranspiration.¹⁶ Figure adapted from Zomer *et al.*¹⁶ licensed under CC BY-SA 4.0.

2 The DryHy approach

The conceptual design of the DryHy process is presented in a process flow diagram in Fig. 3. The designed process comprises three sub-processes. First, the DAC process extracts both water and CO₂ from ambient air and separates them. Any surplus water captured is purified for use as drinking water. The captured water and carbon dioxide are then directed to a co-electrolysis process, where syngas is produced *via* high-temperature electrolysis using solid oxide electrolysis cells (SOEC). In the final sub-process, the produced syngas is converted into methanol.

Solar energy powers the entire process. Depending on economic considerations, the plant will either operate only during daylight hours, with a hot stand-by phase during the night, or continuously over the 24 hour cycle using a suitable photovoltaic energy storage such as batteries. Additionally, there is potential for heat integration due to the exothermic reactions occurring in the methanol production sub-process.

3 Direct air capture

The term DAC encompasses a range of technologies that facilitate the capture of CO₂ from the atmosphere and subsequent enrichment. To achieve this at the low concentration of 400 ppm CO₂ in air, processes are required that selectively bind CO₂. Typically, the strong interaction of carbon dioxide, a Lewis acid, with a corresponding Lewis base is exploited. For example, amines in amine-based DAC or an aqueous hydroxide solution in calcium looping can be suitable bases to bind CO₂. To release CO₂ and regenerate the base, heat is usually used.

Numerous technologies for direct air capture have been developed.^{22–24} Of these, however, amine-based chemisorption of carbon dioxide and calcium looping are the most advanced and technologically mature.^{21,23,25,26} Since the DryHy process

focuses on the demonstration level, only these two technologies, which are available beyond the laboratory scale, are discussed in detail in this article.

As depicted in Fig. 4a, calcium looping consists of two cycles, a sodium-based cycle and a calcium-based cycle. In the sodium cycle, CO₂ is captured by contacting air with an aqueous solution of sodium hydroxide, which dissolves the CO₂ as sodium carbonate. Subsequently, the carbonate solution is mixed with calcium hydroxide, precipitating the carbonate as calcium carbonate and regenerating the sodium hydroxide. In the calcium cycle, the precipitate is dried and calcined at temperatures exceeding 700 °C to form gaseous CO₂ and solid calcium oxide.²⁵ Finally, the calcium oxide is regenerated to calcium hydroxide by the addition of water.

While calcium looping can capture CO₂ very selectively with high purity and reasonable energy consumption (6–10 GJ t^{−1}),²¹ there are some drawbacks. Firstly, a calciner unit requires high temperatures, which are usually provided by burning fuels inside the reactor. In order to achieve carbon neutrality and pure CO₂ as product, a carbon neutral fuel is needed and pure oxygen not to dilute the CO₂ with nitrogen from air.²⁵ Secondly, contacting large amounts of air with an aqueous sodium hydroxide solution results in a significant amount of water evaporation and thus, a high water consumption. For example, Carbon Engineering specified the water consumption of their technology to 4.7 tons per ton of CO₂.²⁷ In particular, when considering the context of water-conscious CO₂ capture in arid regions, this technology is not an appropriate solution.

Amine-based DAC utilizes chemisorption of CO₂ on porous, amine-functionalized adsorbents.²⁸ CO₂, a Lewis acid, interacts strongly with the amine groups, which act as Lewis base, forming a carbamate in dry conditions.²⁵ In the presence of water, the water itself can adsorb on the amine groups as well due to their polar nature. However, unlike most adsorbents, where a competitive adsorption between water and CO₂ is observed, amine-based adsorbents feature a cooperative effect.^{29,30} In the



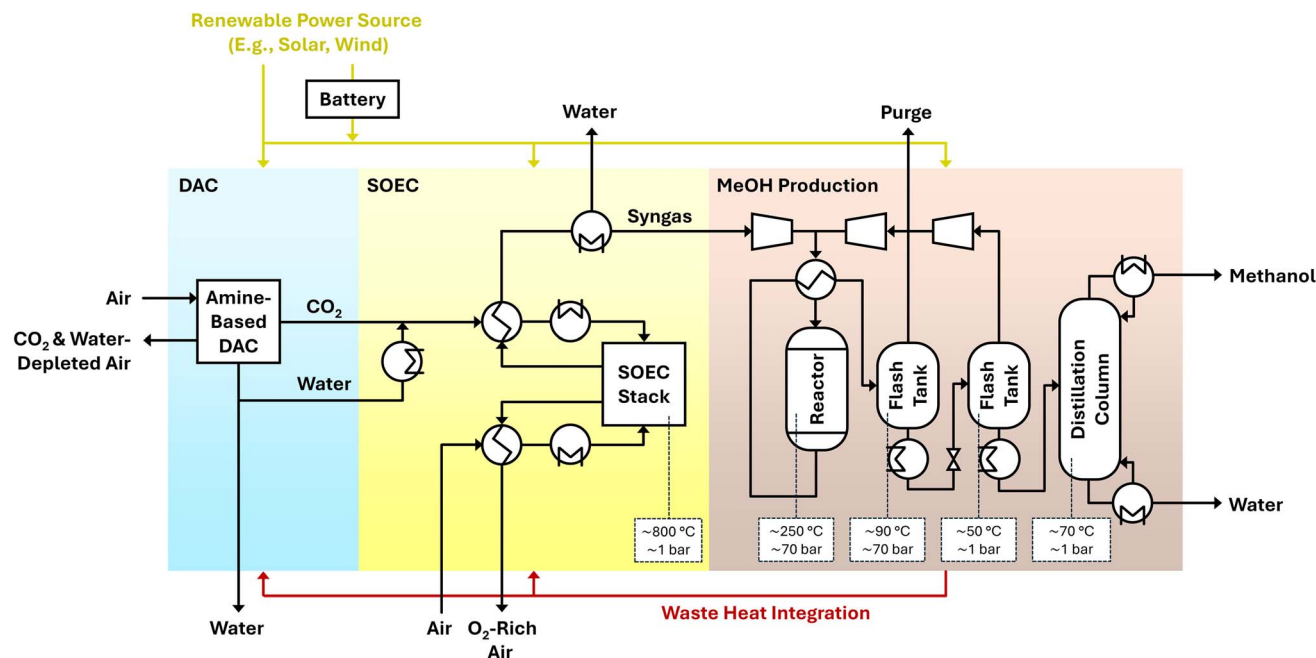


Fig. 3 Simplified process flow diagram of the overall process. Black arrows show material flows while yellow and red arrows show energy flows (electricity and heat respectively). Fluid moving equipment and storage units (final and intermittent) are omitted. Only some heat exchangers are included. Different process alternatives will be compared during the DryHy project. The demonstration unit tested during the project will produce approximately 6 kg of methanol per hour.

presence of water, the CO_2 forms a bicarbonate with water at the amine group leading to an enhanced CO_2 capacity.²⁵

For the separation process usually a temperature-vacuum-swing adsorption (TVSA) approach is used (Fig. 4b):²¹ at ambient conditions, air is streaming through a packed bed of the solid amine adsorbent. Once the adsorbent is saturated, CO_2 is released shifting the equilibrium by increasing the temperature (usually 80–130 °C)²¹ and applying vacuum. After the bed is cooled down again, the cycle can start again.

In comparison to calcium looping, the TVSA process uses much lower temperatures for regeneration, making the integration of waste heat possible. However, the TVSA process is a discontinuous process. Thus, to achieve near-continuous production, typically multiple packed bed shifted in cycle time are used. In addition, alternatives to TVSA processes are being developed that move the adsorbent itself through zones of adsorption and regeneration leading to a continuous production of CO_2 .³¹

Usually the separation of water from air besides CO_2 is regarded as disadvantageous, as the desorption of additional water increases the energy demand during regeneration. However, at the current state it is not possible to capture only CO_2 without capturing water in amine-based DAC. In addition, the energy consumption of amine-based DAC is usually estimated to be about 4.8–8.3 GJ t^{-1} ,^{21,32,33} which is comparable to the estimated energy consumption of calcium looping. Accordingly, there is no discernible advantage in terms of energy efficiency when employing calcium looping instead of the water-positive amine-based DAC. In the context of the DryHy project, the water, which is obtained as byproduct from the

amine-based DAC, is essential in order to provide water for the production of methanol. The amount of water depends on adsorbent and process design as well as weather conditions. Fasihi *et al.* reported a mass ratio of 0.8 : 1 to 2 : 1 for water to CO_2 of the Climeworks DAC technology.³² However, data in this regard is scarce and further research especially in regard to temperature and relative humidity dependence is needed, as the amount of water separated will likely differ in northern Europe from a placement in an arid region in northern Africa as well as vary over time as the weather conditions change.

Usually a CO_2 purity of about 90% up to more than 99.9% can be achieved with this technology.³² Besides water, other contaminants include mostly N_2 and O_2 from air. In addition, ammonia might be present in traces as well from the decomposition of the adsorbent, which, due to its high solubility in water, will be mostly present in the aqueous phase. Reports of trace impurities such as NO_x , SO_x or H_2S in the product gas are scarce. SO_x has been reported to adsorb irreversibly on the amines leading to blocking of the adsorption site and degradation of the adsorbent.^{25,34} Nonetheless, it will be important to keep track of the traces of sulfur components in the product gas, as these can cause severe degradation of the SOEC.

4 Solid oxide electrolyser cells

In DryHy the conversion of water and carbon dioxide to syngas is achieved using Solid Oxide Electrolyzer Cells (SOEC).^{35–38} Solid oxide electrolysis is a high-temperature technology that uses a solid oxide ceramic material as the electrolyte and can be used to split water, carbon dioxide, or a mixture of both into hydrogen,



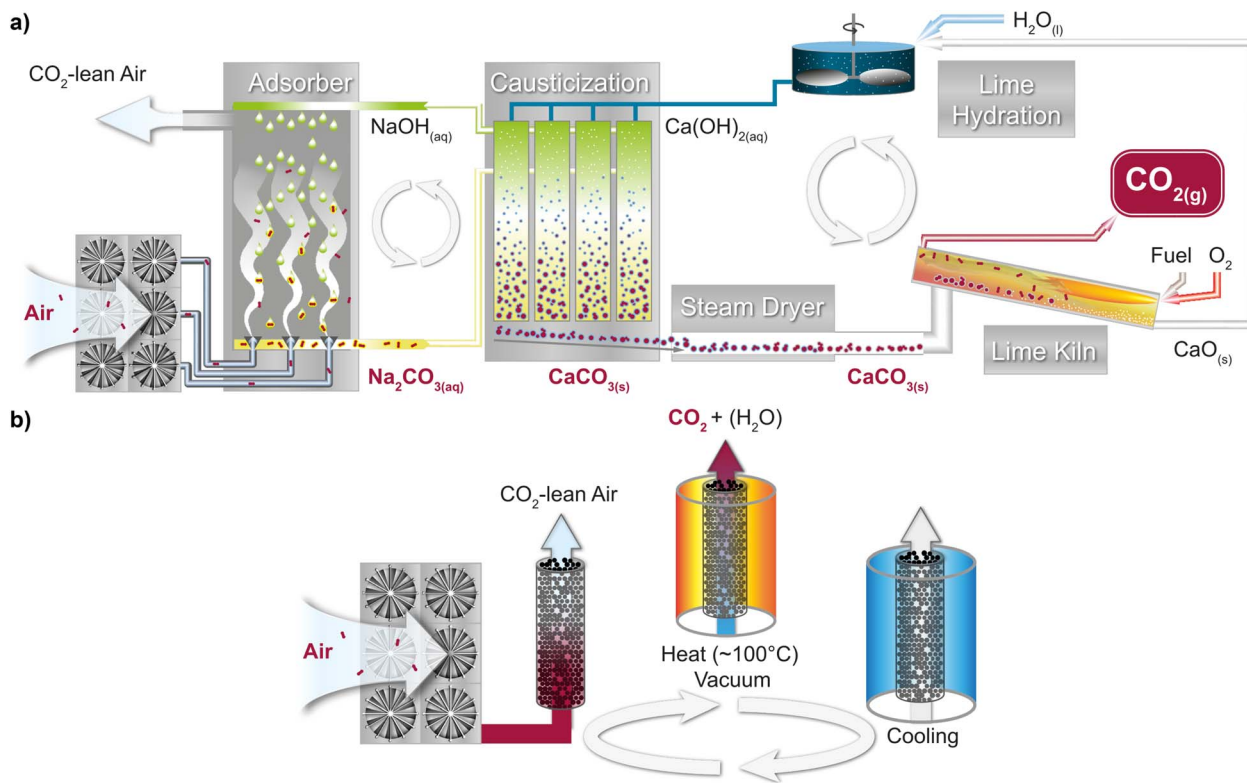
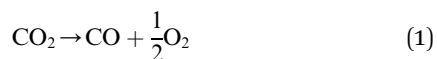


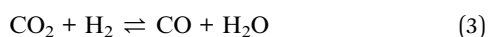
Fig. 4 Schematic representation of DAC technologies. (a) Calcium looping, featuring the chemical reaction between atmospheric CO_2 and aqueous sodium hydroxide to form sodium carbonate, followed by the calcium cycle, where calcium hydroxide regenerates NaOH via causticization and calcination steps. (b) Amine-based DAC, including the capture of atmospheric CO_2 in a packed bed of solid amine sorbent, followed by regeneration at elevated temperature and cool-down.

carbon monoxide, and oxygen. SOEC is a promising technology for renewable power generation integration, enabling efficient hydrogen production, carbon recycling, and the synthesis of syngas for sustainable fuel and chemical production.³⁹

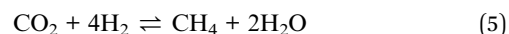
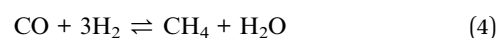
The SOEC technology enables the direct conversion of water and CO_2 into syngas (a mixture of hydrogen and carbon monoxide) at high temperatures (usually 600–850 °C) and atmospheric pressure.^{39,40} The main electrochemical reactions that take place inside the SOEC when it operates in co-electrolysis mode are given below:



Further, the reverse water-gas shift reaction takes place and is often considered to reach equilibrium rapidly at operation conditions.



Depending on the operation temperature, methanation might occur to some extent inside the SOEC. Both methanation reactions presented are exothermic and favored by lower temperatures and higher pressures.



In DryHy, the SOEC sub-process comprises an evaporator for the production of steam, two heat exchangers and two heating plates, the SOEC stack, as well as a condenser for water condensation and separation from the stack outlet stream (Fig. 3).

Over the last half-century, electrolysis technologies have rapidly developed. Some of the most important ones are: alkaline electrolysis, proton exchange membrane (PEM) electrolysis and solid oxide electrolysis (SOE).^{35,38,41,42} While all three technologies are mainly developed for hydrogen production, solid oxide electrolysis can be effectively used for syngas production.

The SOEC distinguishes itself from other electrolysis technologies for two main reasons. Firstly, the high temperature facilitates faster kinetics and higher ionic conductivity, resulting in a decrease of the ohmic resistance of the solid oxide electrolyte and other cell components. The superior kinetics of SOEC technology are evident when comparing the area-specific resistance (ASR) of various electrolysis methods, with SOEC exhibiting lower resistances compared to alkaline and proton exchange membrane (PEM) electrolysis systems.³⁹ Lower resistance leads to reduced voltage losses and less electrical power consumption. Finally, due to the higher operation temperatures, it requires less electrical work and can make use of more



heat instead, this way a higher percentage of the total energy demand can be provided through heat. This is best exemplified by thermodynamics as shown below.

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

In the above equation, ΔG is the change in Gibbs free energy and equals the electrical work that must be added to the system, while $T\Delta S$ (the product of temperature times the entropy change, which is positive for electrolysis mode) equals the heat that needs to be added to the system. For the same ΔH (the enthalpy change does not change significantly as temperature increases^{43,44}), the electrical work that must be added to the system decreases with increasing temperature. At the same time, the heat that must be added to the system increases.⁴⁰ Overall, the SOEC achieves the conversion of CO₂ and water in a single system with high energy efficiency and the flexibility to vary between heat and electrical supply to a certain degree. The high energy efficiency of solid oxide electrolysis cell systems has already been demonstrated experimentally in small-scale systems for hydrogen production^{45,46} and generally accepted to be higher than this of other electrolysis technologies.⁴⁷ Within the DryHy project, energy efficiencies for syngas production will also be assessed using a demonstration system.

It is worth noting that producing a syngas mixture is not the only option for producing methanol and other green hydrogen carriers. Synthesis routes from a mixture of H₂ and CO₂ are also possible and circumvent the need for CO₂ reduction to CO *via* SOEC.^{48,49} Techno-economic analyses done by Zhang *et al.* show the syngas pathway to be a feasible approach for methanol production,^{50,51} and, showed it to produce methanol at a lower price than the alternative that starts from a mixture of H₂ and CO₂.⁴⁹ Several techno-economic analyses have been conducted in the past years on the power-to-methanol topic,^{52–54} a comprehensive techno-economic analysis, incorporating the specific features of the DryHy process, will also be conducted during the project to benchmark its performance against alternative approaches.⁵⁵

The SOEC technology also has certain challenges. The degradation of solid oxide electrolysis cells poses a significant challenge to their long-term stability and performance. The rate of degradation depends on a number of factors including the selected material, fabrication methods, and operation conditions. The operation mode and conditions that impact the long-term stability of a SOEC comprise the operation temperature, current density, as well as the composition and purity of the feed gas.^{43,56,57}

In the relevant literature a wide range of degradation rates have been reported for solid oxide cells. This is to be expected, since degradation rates depend on operating mode and conditions, feed composition and stack/system design. Some studies report degradation rates of 3.96%/1000 h,⁵⁷ while others report significantly lower degradation rates of 0.6%/1000 h (ref. 58) or even 0.33%/1000 h (ref. 39) (percentages correspond to cell voltage change).⁵⁸ Therefore, it is important to point out that even though SOEC offers faster kinetics and higher energy efficiency, the (often) faster degradation of the cells⁴⁷ means

that they might eventually be outperformed by other electrolysis methods. To the best of our knowledge, there's no techno-economic study comparing electrolysis technologies taking into account cell degradation.

One potential cause of degradation is the redox cycling of nickel (Ni) in the Ni/yttria-stabilized zirconia (YSZ) electrode. This occurs when the reducing atmosphere, typically maintained by recirculation of hydrogen or syngas, is interrupted. In such cases, Ni oxidizes to NiO, leading to a volumetric expansion. This volumetric expansion generates mechanical stress within the electrode, causing cracks, delamination, and severe structural damage. Redox cycling results in irreversible degradation by compromising electron conduction pathways and reducing the electrochemical surface area, further weakening the electrode–electrolyte interface.^{59,60} It is therefore essential to implement the necessary mechanisms and safety measures to maintain a reductive atmosphere, even in the event of an unforeseen shutdown.

Further, nickel migration and agglomeration within the Ni/YSZ cermet contribute to long-term degradation. Ni particles coarsen and migrate under high temperatures and current densities, leading to a reduction in active sites for electrochemical reactions. This depletion of Ni from localized areas impairs the overall efficiency of the cell, as fewer catalytic sites remain for the electrochemical processes to occur.^{59,60}

Another reason for degeneration is the formation and deposition of solid carbon in downstream system components and within the SOEC fuel electrode itself. The deposition of solid carbon, including the formation of carbon nanotubes, within the fuel electrode of the SOEC can block active sites, disrupt electron pathways, and cause additional structural stress. Carbon deposition in downstream components can also lead to blockages of, *e.g.*, heat exchangers, negatively affecting system performance and durability through increased pressure losses, reduced heat transfer surface as well as metal dusting. Preventing carbon formation is essential, particularly in high-carbon-content environments or when operating with syngas, but it is manageable by careful selection of operation conditions.^{61–63}

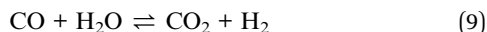
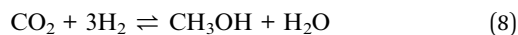
Finally, SOEC degradation is accelerated by impurities such as silicon, chromium, and sulfur, which may originate from system components or feed gases. These impurities can poison the active catalyst sites, and accelerate material breakdown, impacting both the electrode and electrolyte.^{60,64} Mitigating degeneration is crucial for developing more durable SOECs. Current research focuses on optimizing material composition, improving electrode stability, reducing the impact of redox cycling and carbon deposition, and optimizing operating parameters.^{59,60}

5 Methanol production

The production of methanol from syngas is a well-established and thoroughly studied process.^{15,65–68} The most commonly used process variant comprises a high-pressure tubular flow reactor, two flash tanks, and a distillation column for downstream processing. The reactor is packed with a catalyst composed of CuO/ZnO/Al₂O₃ and operates under conditions of



240–270 °C and 50–100 bar.⁶⁹ Within the reactor, the following reactions occur:



The methanol process presents some potential for heat integration. The reactions inside the methanol reactor are overall exothermic, producing heat that can be used upstream either for the DAC or the steam generation. Note that the second reaction (*cf.* eqn (8)) produces water as a by-product. The flash tanks separate the gaseous components such as carbon monoxide and hydrogen to be recycled, while the distillation column purifies methanol by separating it from water.

The composition of the syngas plays an important role in the efficiency and topology of the methanol production process. For example, when CO₂ is present in the syngas, water will be produced which will need to be separated *via* an energy-intensive distillation process, leading to lower overall process efficiencies. In addition, the formed water in CO₂-rich methanol synthesis can inhibit the reaction kinetics due to water adsorption known as reversible effect.^{70–72} Long-term stability may be crucially affected by the formed water in CO₂-based methanol synthesis leading to sintering of the catalyst which causes a frequent replacement of catalyst regarded as drawback in terms of economic performance.^{65,70,71,73} Furthermore, higher CO₂ content will lead to lower methanol single pass conversion. Thus, limiting the amount of carbon dioxide in the produced syngas might be beneficial.

Alternatively, the carbon dioxide can be separated at the start of the methanol process with absorption and recycled upstream to avoid distillation downstream. But the presence of high CO and low CO₂ contents in syngas leads to elevated formation of by-products like higher alcohols.^{74,75} All these alternatives must be studied and optimized to ensure that an optimal process design is found for the DryHy concept.

6 Process implementation

The combination of these three technologies has great potential, but for their implementation in the DryHy process, several challenges must be investigated and overcome. Primarily, the impact of impurities from DAC on the SOEC needs rigorous experimental examination, with particular focus on the influence of sulfuric components (SO_x), as these can cause degradation.⁵⁶ However, unless placed in the vicinity of an emitting source (*e.g.*, industry or volcano) the concentration of sulfuric components is expected to be negligible small. For example, the SO₂ concentration is typically far below 1 ppm.⁷⁶ Additionally, data indicates that sulfuric components such as SO₂ are irreversibly adsorbed in the DAC.³⁴ Nonetheless, this should be closely monitored as data in this regard is still scarce.

As mentioned above, other typical components include nitrogen and oxygen from air as well as small amounts of ammonia from possible degradation of the adsorbent. The

ammonia does not present an issue, especially in small traces, as it thermally decomposes to nitrogen and hydrogen in the temperature range used in the SOEC.⁷⁷

Any oxygen in form of O₂ present in the CO₂ can react with the produced hydrogen to water and thus, lower the efficiency of the SOEC. However, as oxygen is typically only present in low concentrations (well below 2%), the efficiency loss is limited. Additionally, this side reactions produces heat and, therefore, lowers the heating demand of the SOEC. Consequently, it has to be seen, if and to what extent oxygen actually impacts the efficiency.

As an inert gas, nitrogen does not impact the SOEC significantly, but will be relevant in the methanol reactor. For efficient syngas usage, any syngas that did not react in the methanol reactor in the first pass is recycled to be used again. Consequently, any nitrogen contamination will accumulate in the loop and, therefore, increase the amount of gas that needs to be purged. To avoid emitting poisonous gas, the offgas will be burnt, oxidizing H₂ and CO to H₂O and CO₂, respectively. Since the CO₂ stems from the DAC, the overall process is still CO₂-negative, but the purge will slightly lower the efficiency. Other significant emissions are not expected from the DryHy process.

Since the DAC is not only removing CO₂ but also water from the air, the impact of DAC on the water content in the local atmosphere has to be monitored. Especially, a potential impact on the rain building mechanisms has to be studied. As this will strongly depend on the size of the DAC plant, a simulation approach is a suitable way to investigate this correlation for various plant sizes.

Furthermore, the formation of carbon post-SOEC presents a considerable challenge. Fig. 5 delineates the conditions under which carbon formation can occur spontaneously at the outlet of an isothermal SOEC for various carbon-to-hydrogen ratios. The Boudouard equilibrium, methane reforming and methane

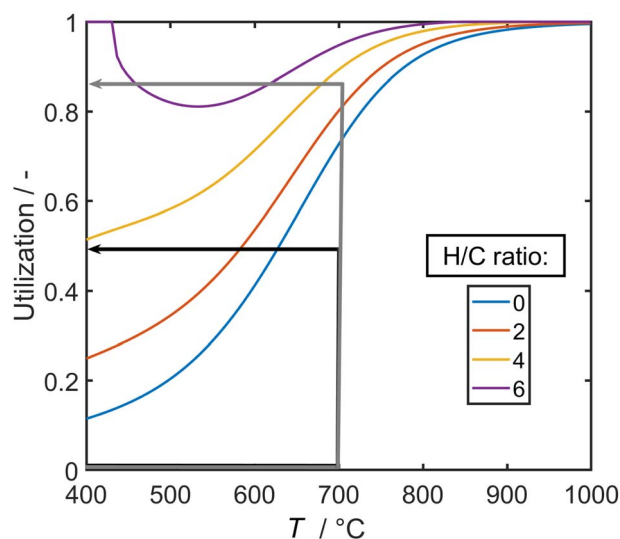
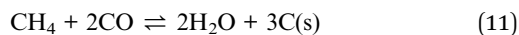


Fig. 5 Carbon formation limit as a function of temperature and utilization of CO₂ and water as well as the H/C ratio. Carbon formation is thermodynamically favored when operating in conditions above the corresponding curve. The methodology for the calculations is given in the ESI.†



decomposition that lead to the formation of solid carbon are shown below.



Carbon formation can be avoided either by staying in the “thermodynamic-safe region” (below the respective carbon formation boundary) or by operating in a region, where carbon formation is spontaneous, but suppressed by a rapid cool-down to overcome the kinetics of the carbon-forming reactions. These two scenarios are depicted for a feed with a hydrogen-to-carbon atom ratio of 4 : 1 (the required ratio for methanol production). In the first scenario (shown with a gray arrow in Fig. 5), high utilization rates are achieved (roughly 85%) and rapid cooling is applied to overcome the kinetics of carbon formation. Alternatively, the second scenario (shown with a black arrow on Fig. 5) maintains low utilization rates (roughly 50%) to remain within the “thermodynamic-safe region” and definitively avoids carbon formation.

The operation mode of the SOEC has implications on the process layout as well. For operation in the thermodynamic safe region, a significant amount of CO_2 and water is left in the product gas, which has to be separated before feeding it to the methanol reactor. Otherwise, a significant amount of water would be produced together with methanol, which would require energy-intense separation. Additionally, a higher hydrogen-to-carbon ratio of 6 : 1 would be necessary for the reaction of CO_2 to methanol, while also shifting the equilibrium more towards the educts.⁶⁵ Consequently, a low conversion to methanol per pass would be the result if CO_2 is present in significant amounts. To avoid this, any CO_2 leaving the SOEC could be separated, *e.g.*, by amine washing, while most of the water can be condensed. Subsequently, both, CO_2 and water, can be recycled to the SOEC. However, the separation of water and CO_2 will add to the energy requirements of the process.

The alternative, applying a high utilization and preventing carbon formation by rapid cool-down, can be carried out (*e.g.*, by spraying the hot syngas with water or mixing it with steam and later on separating the water with condensation) without the necessity for additional carbon dioxide separation processes, as the CO_2 content in the syngas is low. But in turn, a device with rapid cooling ability is required, and fast cooldown of the produced syngas likely means that little to no heat can be recovered by the hot syngas stream. For the process layout, it will be essential to thoroughly analyze, which of these two approaches is overall more energy efficient and offers more benefits.

Further, the dynamic power supply necessitates study. It is imperative to develop effective ramp-up and ramp-down strategies, as well as to establish a hot stand-by operation mode to manage the entire power cycle efficiently.

For future developments, it is also important to consider the scalability of the DryHy process and its technologies. The scale-

up of DAC systems is one of the major research focuses of this technology with companies such as Climeworks or Carbon Engineering pushing the limits of the current DAC plant size. For amine-based solid sorbent DAC, a modular approach is possible and often deployed.²¹ In a modular design, the DAC system is partitioned into modules of the same size, which enable mass production of the same unit and bringing down production costs.²¹ Nonetheless, at the current state, DAC is an expensive technology and capital and operational costs need to come down in the future to make DAC-based process approaches economically more viable.

Similarly, issues with scaling up the SOEC technology must also be considered. A recent review by Jolaoso *et al.*⁷⁸ found four main obstacles in scaling up the SOEC technology. Namely, making the SOEC stacks larger and more robust, overcoming the degradation issues, the integration of renewable power sources, and assessing how competitive they are with their competitors, namely alkaline and PEM electrolysis. The DryHy project presents a great opportunity for addressing these challenges.

Since methanol synthesis, especially from syngas being rich in CO , is an industrially proven technology already operated in large units, scaling the process is not seen as a problem.⁷⁹ Moreover, even adaptations of the reactor to the DryHy context are not expected to cause hindering issues because of the use of fixed-bed technology which is known as unproblematic in up-scaling.⁷³

Finally, the economic and social dimensions of implementing the DryHy strategy must also be addressed to ensure its viability. Techno-economic analysis should optimize the capital and operational costs and provide deep insights into the cost structures as well as the sensitivity of the process towards efficiency losses. Material intensities and criticalities should be carefully analyzed as well, including the emissions from materials produced (cradle-to-grave life cycle analysis). Additionally, it is relevant to evaluate the effectiveness of the DryHy process chain in comparison to alternative power-to-X routes, especially in the context of application in arid regions. A comprehensive examination of the economic implications can be found in another source.⁵⁵

Similarly, establishing cooperations, and building public acceptance in regions suitable for the DryHy process will be crucial for transferring the process into application as well. Therefore, the technology transfer has to be investigated by fostering the exchange with local stakeholders, establishing collaborations and adapting the DryHy concept to locally accepted business models. For this purpose, it is important to make sure that the technical expertise is available at the desired location. Overall, comprehensive studies and strategic planning are essential to overcome these multifaceted challenges and achieve effective implementation.

7 Conclusions

Combining DAC with SOEC and renewable power sources offers a promising solution for producing climate-neutral methanol and other green hydrogen carriers. Amine-based DAC can provide CO_2 as well as water, which can be directly and efficiently converted into syngas utilizing the SOEC. Subsequently,



the generation of methanol (or fuels) from syngas is a straightforward process.

Harvesting solar energy and producing methanol in sun-rich regions, such as Africa, is especially beneficial for the DryHy process. While the high photovoltaic power potential reduces costs, the separation of water from air by the DAC conserves water resources, which are usually scarce in dry regions. In the future, this approach can foster economic growth and stability, benefiting both local and global markets. Moreover, the transport and utilization of green methanol can leverage existing infrastructure, making it economically viable and sustainable.

Challenges remain in implementing these technologies. The effect of impurities in the CO₂ and water mixture from the DAC on the SOEC and methanol reactor needs to be studied closely. Nitrogen and oxygen can potentially lower the efficiency of the process, whereas trace impurities such as sulfuric components can lead to degradation of the SOEC. Additionally, not much data is available on the effect of temperature and humidity on the water-to-CO₂ ratio supplied by the DAC and its impact on the DryHy process chain. Finally, the system needs to be designed to adapt to fluctuating energy supplies. Thus, future research should focus on optimizing dynamic behavior and developing storage technologies for energy and intermediate products as well.

In summary, DAC combined with renewable power generation and SOEC offers a sustainable method for green methanol production, supporting climate goals and economic benefits. Continued research and pilot projects are essential to overcome challenges and fully realize this technology's potential.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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