

Bio-integrated carbon capture and utilization: at the interface between capture chemistry and archaeal CO₂ reduction

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Carbon capture and utilization (CCU) covers an array of technologies for valorizing carbon dioxide (CO₂). To date, most mature CCU technology conducted with capture agents operates against the CO₂ gradient to desorb CO₂ from capture agents, exhibiting high energy penalties and thermal degradation due to the requirement for thermal swings. This Perspective presents a concept of Bio-Integrated Carbon Capture and Utilization (BICCU), which utilizes methanogens for integrated release and conversion of CO₂ captured with capture agents. BICCU hereby substitutes the energy-intensive desorption with microbial conversion of captured CO₂ by the methanogenic CO₂-reduction pathway, utilizing green hydrogen to generate non-fossil methane.

The global emissions of anthropogenic greenhouse gases have risen immensely during the past decades, with energy consumption from fossil fuel combustion being the main driver for around two-thirds of the total greenhouse gas emissions¹. In 2022, the annual global greenhouse gas emissions from energy-related fossil fuel combustion and industrial processes reached 41.3 Gt_{CO₂-eq}, where carbon dioxide (CO₂) emissions accounted for 89% of the total emissions (36.8 Gt_{CO₂})². However, the United Nations Climate Change Conference (COP28) declared the ‘beginning of the end’ of the fossil fuel era by the end of 2023³. The adoption of a renewable-based energy infrastructure has accelerated in the last decade with renewable electricity generation constituting 7858 TWh in 2021⁴. The transformation of the energy system towards heavy electrification has been envisioned as a significant factor in achieving carbon neutrality by 2050⁵. However, the hard-to-abate sector, including heavy transport and industrial processes, relies heavily on chemical energy carriers with a high volumetric energy density and remains difficult to electrify and decarbonize⁶. Here, Power to X (PtX) provides a potential solution that enables the conversion of electricity to chemical energy carriers, and combining it with Carbon Capture and Utilization (CCU) represents a

critical technology to supply carbon-based energy carriers (e-fuels) for reaching the 2050 net zero emission target.

Various post-combustion carbon capture technologies are currently available, with chemical scrubbing being the most mature technology relying on solvent-based absorption and desorption conducted on the scale of megaton CO₂ captured annually^{7,8}. Conventional CCU with amine scrubbing consists of multiple steps, including CO₂ capture by solvent absorption, CO₂ release by heat desorption, CO₂ dehydration and compression for storage and transport, and long-term storage or utilization in various downstream chemical and biological processes. Despite the many point sources of flue gas and a high potential for capturing CO₂, conventional carbon capture with chemical scrubbing is attenuated by high energy penalties due to the dilute CO₂ concentrations in flue gas, constituting up to 30% of the typical power plant output⁹. In conventional CO₂ desorption from capture agents, the energy equivalent to the heat of absorption is added in a reboiler unit at the desorption column to induce the desorption and release of CO₂. The typical thermal reboiler duty for the CO₂ desorption column is 3.5–4.0 GJ t⁻¹ CO₂^{10–12}. Substantial research is therefore directed toward reducing the reboiler duty by modifying the

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capture agents and using blends that comprise capture agents with additives. Activators enhance the absorption and desorption kinetics and chemicals minimize the oxidative and thermal degradative behaviors¹³. The reboiler duty can furthermore be reduced by optimizing the desorption process parameters, such as adjusting operating pressures in the desorption unit and regulating reboiler temperatures¹⁴. Hence, multiple pilot-scale studies have demonstrated routes for reducing the reboiler duty of the desorption unit to a range of 1.9–3.6 GJ t⁻¹CO₂^{15–17}.

In the future fossil-free society based on a circular economy, the captured CO₂ is considered a valuable commodity that must be utilized to produce chemicals and fuels, which currently are fossil-based. However, carbon utilization preceded by carbon capture is limited by additional expenses for storing and transporting CO₂, which requires dehydration to avoid corrosion and compression (−0.4 GJ t⁻¹CO₂)¹⁸. Thus, a group of new concepts based on integrated carbon capture and utilization (ICCU) is currently being developed, where captured CO₂ is directly synthesized into valuable compounds simultaneously with the desorption from the capture agents. Hereby, the energy expenses for CO₂ purification by desorption, transportation, dehydration, and compression are eliminated, improving the competitiveness of the capture process. The current ICCU processes include thermocatalysis¹⁹, electrochemical catalysis²⁰, photoelectrocatalysis²¹, and biofixation with microalgae and cyanobacteria²². Nevertheless, several drawbacks have challenged the ICCU technologies. Thermocatalytic ICCU processes entail high temperatures and pressure to convert the CO₂. Although isothermal operation can mitigate the energy penalty from the desorption, substantial efforts are required to identify a potentially stable and efficient CO₂ sorbent capable of synergistically matching the reaction with the catalyst²³. Furthermore, electrochemical catalysis offers the prospects of being conducted at milder temperatures, but this approach necessitates the utilization of expensive catalysts due to the chemical inertness of CO₂²⁴. Accordingly, additional gas conditioning of the raw flue gas will be essential to avoid poisoning the catalysts.

In contrast to chemical catalysts, biocatalysts such as methanogens can handle various contaminants such as hydrogen sulfide (H₂S) and sulfur dioxide (SO₂)²⁵, which otherwise would deactivate the chemical catalysts used in both ICCU and CCU processes²⁶. Methanogens belong to the domain Archaea and can be divided into three different physiological categories based on their substrate: hydrogenotrophic methanogens, methylotrophic methanogens, and acetoclastic methanogens²⁷. The former is a key component in biological methanation, a robust Power to X (PtX) technology, where CO₂ is reduced to methane (CH₄) using renewable H₂ from water electrolysis. Species important for the biomethanation process include *Methanobacterium*, *Methanobrevibacter*, and *Methanoculleus*, which all have been reported to be enriched during biogas upgrading, whereas the relative abundance of acetoclastic methanogens (species within the *Methanosarcinaceae* family) is usually experienced to decrease during biomethanation^{28,29}. A common denominator for these microorganisms is their anaerobic trait, which renders them inhibited by oxygen (O₂). Biomethanation has currently exclusively been utilized with feedstocks of biogas CO₂^{25,30,31} and syngas CO₂^{32,33} and has not been suited for direct conversion of flue gas CO₂ due to the flue gas composition containing O₂, which is detrimental to the obligate anaerobic methanogens. Furthermore, the CO₂ is diluted with N₂, which creates a dilute CH₄ stream of <20% without any potential downstream application. The development of a technology that enables the biological utilization of flue gas CO₂ would thus increase the potential of CO₂ feedstock substantially, as biogenic CO₂ from biogas only constituted 0.024 GtCO₂ by 2020 in Europe³⁴, which is a mere fraction (−1%) of the 2.5 GtCO₂ emitted in Europe³⁵. Targeting CH₄ creates a versatile energy vector that indirectly electrifies the hard-to-abate sector while utilizing the already established natural gas grid infrastructures in the TWh

magnitude⁶. However, the CH₄ must comply with the standards of the distribution and storage grids, which are defined by the specific pipeline networks in the range 70–98% CH₄ in the EU³⁶.

This Perspective unfolds a concept for ICCU with simultaneous desorption and conversion of CO₂ to CH₄ based entirely on a microbiological driving force that enables biomethanation to be applied to dilute flue gases. Using methanogens for ICCU will ultimately alleviate the energy penalties and thermal degradation of the capture agent related to conventional carbon capture while reducing the number of process units required for CCU. This CO₂ transformation route of bio-integrated carbon capture and utilization (BICCU) is currently demonstrated at a low Technology Readiness Level (TRL), but the concept, challenges, and prospects are presented here.

Bio-integrated carbon capture and utilization

The BICCU process captures the CO₂ in an absorption column similar to the conventional CCU process but eliminates the demand for utilizing heat as a driving force for CO₂ desorption. Instead, the proposed BICCU process relies on the biochemistry of anaerobic respiration of hydrogen- (H₂) and CO₂-consuming microorganisms—in this case, hydrogenotrophic methanogens. The microorganisms' inherent enzymatic activity catalyzes the simultaneous desorption and conversion of CO₂ into CH₄ at ambient pressure and either mesophilic (20–45 °C) or thermophilic temperatures (45–60 °C). The result is a technology that makes CCU work with the CO₂ gradient instead of against it by utilizing methanogens to maintain the gradient. The reducing equivalent for desorbing the CO₂ from the capture agent and converting it into CH₄ is H₂ produced from water electrolysis with renewable electricity, thereby classifying it as a PtX technology. The biological desorption of CO₂ regenerates the capture agents for recycling back to the absorption column for further carbon capture. Initial studies have benchmarked the performance and robustness of methanogenic microorganisms for the BICCU process by capturing raw flue gas from a biogas engine and converting it into CH₄^{37,38}. Several unit operations associated with CO₂ desorption, conditioning, storage, and transport can be eliminated when applying simultaneous biological desorption and conversion. The resulting energy savings for the BICCU system with a capture unit, bioreactor unit, and electrolyzer unit will be −3.6 GJ t⁻¹CO₂ corresponding to a 17–29% energy saving compared to the conventional CCU technology depending on whether the upstream energy balance for H₂ production is included in the energy balance³⁸ (Fig. 1).

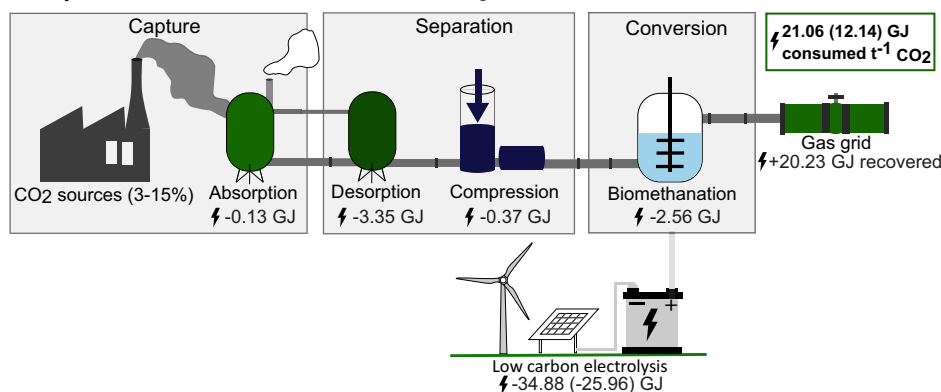
The energy efficiency of the H₂ production in water electrolysis (4.5–7.0 kWh m⁻³H₂)³⁹ contributes substantially to the overall process energy loss (−52% assuming 4.75 kWh m⁻³H₂) due to energy losses from the power supply heat losses in the rectifier, stack heat losses, energy consumption for auxiliaries for the balance of plant, and cooling requirements³⁸. However, providing electrons in the form of H₂ will be essential for reducing the captured CO₂ regardless of the PtX technology applied. It is expected that the performance metrics of electrolysis will be improved by the rapid electrolysis maturation initiatives, such as the US Hydrogen Earthshot⁴⁰, hereby supporting further development and maturation of PtX technologies like BICCU.

Absorption and desorption

The CO₂ point sources targeted for carbon capture, such as flue gas from burners and boilers, are diluted, since they are operated with atmospheric air containing excess oxygen to ensure clean burning, reduced soot and CO emission. The resulting CO₂ concentration is therefore in general 3–15% for combustion processes depending on the fuel type^{41–43}. Other sources of CO₂ relevant to the BICCU process could be industrial sources like non-combustion processes, such as cement plants, which emit 0.6 t CO₂ t⁻¹ cement produced⁴⁴.

Due to the dilute nature of flue gases, the CO₂ must be separated from the exhaust or industrial gasses by capturing it in an absorption

A) Conventional Carbon Capture and Utilization



B) Bio-Integrated Carbon Capture and Utilization

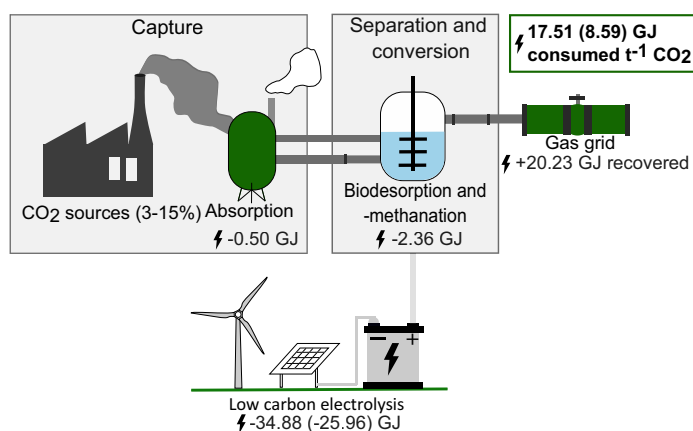


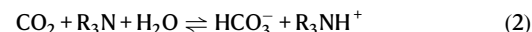
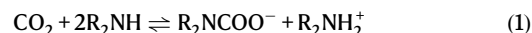
Fig. 1 | Process diagrams of conventional CCU and BICCU. A Conventional CCU. **B** BICCU. The conventional CCU process captures CO₂ by absorbing it in capture agents and utilizes thermal energy for CO₂ desorption. This process is followed by downstream compression and dehydration for storage and transport of the CO₂ to a CO₂ utilization unit of methanation for producing grid injectable CH₄. In contrast, the BICCU process captures CO₂ by absorbing the CO₂ in a capture agent followed

by combined microbial-mediated desorption and utilization by using renewable produced H₂ to convert the CO₂ directly into grid-injectable CH₄. The energy balances for both systems are presented, with values expressed as GJ t⁻¹ CO₂ captured. Heat integration for the biomethanation process has not been considered. The numbers in parenthesis represent a scenario where electrolysis has no energy loss. All numbers are sourced from ref. 38.

column containing a solvent that selectively interacts with the CO₂ by chemical absorption. The CO₂ absorption from flue gas could, in principle, be achieved with the intrinsic physical CO₂ absorption with water, where weak molecular forces of Van der Waals or electrostatic interactions absorb the CO₂. However, according to Henry's law, the thermodynamic equilibrium between CO₂ in the gas and aqueous phase will exhibit an absorption capacity that is linearly correlated with the partial pressure of CO₂⁴⁵, which would require a CO₂ concentration of >59.3% CO₂ to be cost-effective⁴⁶. Instead, chemical absorption with a capture agent that selectively interacts with the CO₂ can considerably enhance the CO₂ absorption kinetics and capacity. These capture agents possess a strong affinity for reacting with CO₂ to form chemical intermediate compounds that reversibly capture the CO₂.

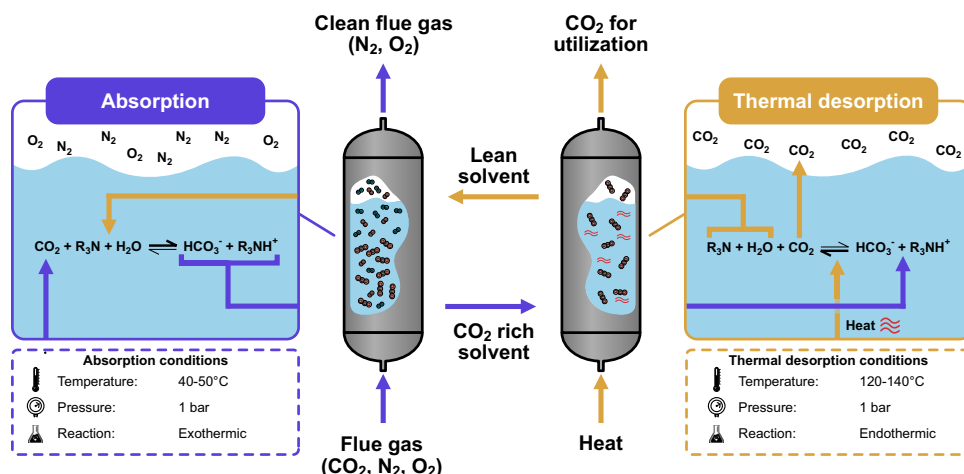
The most widely employed capture agents for chemical absorption are amines, which can react with CO₂ in an acid-base reaction by two different reaction pathways. Non-sterically hindered primary and secondary amines react with CO₂ in a two-step mechanism, where CO₂ is initially converted into a zwitterion intermediate, which becomes deprotonated by an additional amine and thus proceeds to form a stable carbamate limiting the stoichiometric CO₂ loading to 0.5 mol_{CO₂} mol_{amine}⁻¹ (Eq. 1). In contrast, the mechanism of CO₂ capture by tertiary amines relies on the amines base-catalytic effect, which hydrates CO₂ to produce bicarbonate (HCO₃⁻) in a stoichiometric CO₂

loading of 1 mol_{CO₂} mol_{amine}⁻¹ (Eq. 2).



The CO₂ absorption with amines is an exothermic process, and adding heat to the system reverses the reaction and pushes the equilibrium toward the release and desorption of CO₂ by disrupting the chemical interactions between the capture agent and the CO₂⁴⁷ (Fig. 2A). For primary and secondary amines, the capture agents interact with the CO₂ through covalent bonds, whereas tertiary amines elicit a shift in the chemical equilibrium to CO_{2(aq)}/HCO₃⁻(aq)⁴⁸. The energy required for the release of aqueous or covalently bound CO₂ is equal to the heat released by the exothermic CO₂ absorption in the absorption unit. However, the heating requirement for the desorption of CO₂ (reboiler duty) in conventional carbon capture is not limited to the heat of reaction for desorption, since the capture agent is in an aqueous solution that must be heated up to effectively reverse the CO₂ binding. The heating requirement for stripping the CO₂ from the aqueous solution can thus be designated to the sum of three principal components⁴⁹ (q_{reb} in Eq. 3). The heating requirement for 1) the heat of reaction required to reverse the equilibrium and release the CO₂ from

A) Conventional Carbon Capture



B) Bio-Integrated Carbon Capture and Utilization

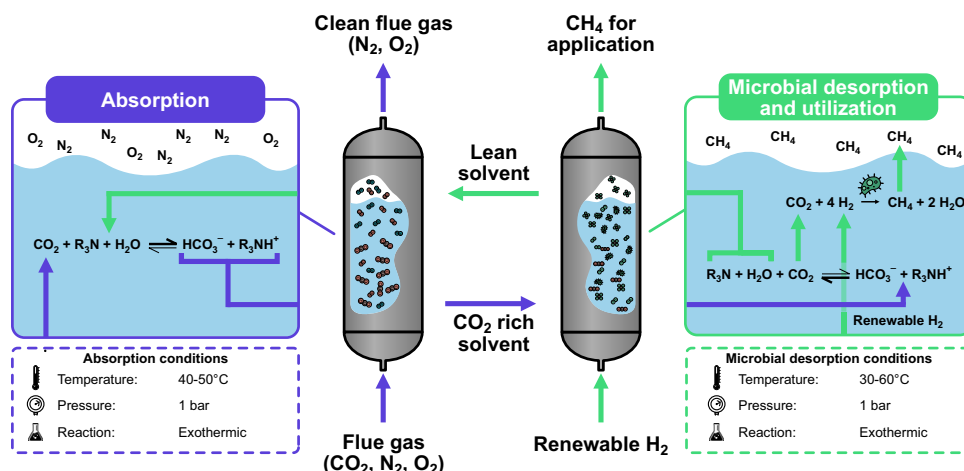


Fig. 2 | A schematic of the desorption process in conventional thermal-based carbon capture and the microbial-mediated BICCU process. A In the conventional carbon capture using a tertiary amine, the CO_2 is absorbed in the absorption unit and transported to the desorption unit, where heat pushes the equilibrium toward CO_2 , thereby regenerating the amines. The liberated CO_2 is sent for

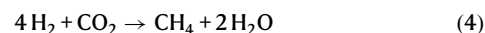
downstream compression, while the regenerated amines can be recirculated to the absorption column. **B** In the BICCU process, the CO_2 is also captured by amines in the absorption unit and transported to the desorption unit, where microorganisms pull the equilibrium toward CO_2 by continuously converting it to CH_4 while regenerating the amines.

the capture agents by disrupting the chemical interactions between the capture agent and CO_2 (q_{abs}), but also 2) the sensible heat, which corresponds to the heat required for increasing the temperature of the CO_2 rich aqueous amine solution to the required regeneration temperature (q_{sens}), and 3) the latent heat of vaporization of the water in the aqueous amine (q_{vap}). Here, the heat of vaporization constitutes a significant energy sink in the conventional carbon capture and in the case of the primary amine, monoethanolamine (MEA) constitutes ~80% of the reboiler duty energy distribution⁵⁰.

$$q_{\text{reb}} = q_{\text{sens}} + q_{\text{vap}} + q_{\text{abs}} \quad (3)$$

Thus, the capture agent's high affinity toward CO_2 consequently entails a high energy requirement to push the equilibrium toward liberating the CO_2 to create a purified CO_2 stream. Furthermore, energy must be invested for downstream storage and subsequent

conversion of the purified CO_2 , which challenges the economics of CCU. In contrast, the BICCU process presents an alternative solution to eliminating the reboiler duty, where the CO_2 in the carbonate equilibrium is utilized as a reactant for conversion into CH_4 by using reducing equivalents of H_2 to disrupt the chemical interactions between CO_2 and the capture agent by the biomethanation reaction (Eq. 4).



The inherent metabolic activity of the hydrogenotrophic methanogens can convert the dissolved CO_2 into CH_4 . Due to Le Chatelier's principle, the bicarbonate equilibrium is shifted to the reactant side, hence desorbing more CO_2 from the capture agent. Facilitating the CO_2 desorption with a bio-mediated conversion mechanism enables the regeneration of the capture agents, which can be circulated back to the absorption column (Fig. 2B).

Table 1 | Selection criteria for the CO₂ capture agents in conventional solvent-based carbon capture and BICCU

General design parameters for CO ₂ capture agents	Conventional carbon capture (Heat-mediated desorption)	BICCU (Bio-mediated desorption)
<ul style="list-style-type: none"> - Fast CO₂ absorption kinetics - High net-CO₂ capacity - Low enthalpy of reaction 	<ul style="list-style-type: none"> - High T_{\max} for thermal degradation - Low amine volatility - Low aerosol formation - Low nitrosamine formation - Low latent heat of vaporization - Low sensible heat requirements 	<ul style="list-style-type: none"> - Bioavailable CO₂ binding - Low cellular toxicity - Biologically stable to avoid microbial decomposition

Transforming the conventional carbon capture with amines based on thermal desorption to a microbial-mediated desorption process in the BICCU process will reduce the energy requirements significantly since the desorption occurs at lower temperatures of <60 °C, where the sensible heat (q_{sens}) and heat of vaporization (q_{vap}) will become negligible. Low-temperature desorption has been researched for many years and can be achieved through utilizing e.g., biphasic thermomorphic amines⁵¹. However, although these low-temperature desorption processes for the liberation of CO₂, including BICCU, reduce q_{vap} and q_{sens} , energy is still needed for the endothermic desorption of CO₂ (q_{abs}). Therefore, BICCU has the additional advantage that the required energy for the endothermic desorption of CO₂ can be supplied via the exothermic biomethanation process. The majority of the energy introduced to the bioreactor as H₂ is conserved by the methanogens in the form of CH₄ (~79%) whereas the remaining ~21% of the energy, corresponding to $\Delta H_{298\text{K}} = -165 \text{ kJ mol}^{-1} \text{ CO}_2$ ⁵², is either converted to heat due to the exothermic nature of the methanogens or will become available for the production of biomolecules through assimilatory processes. Studies have shown that in contrast to the aerobic metabolism of C6 sugars, hydrogenotrophic methanogens are entropy-driven and mainly produce heat over biomolecules⁵³—a phenomenon also observed in pilot-scale biomethanation reactors supplied with gaseous CO₂ and H₂⁵². The thermophilic conditions at ~50 °C required for the bioreactor thus couple remarkably well with the temperature conditions of 50 °C in the absorption unit due to the exothermic CO₂ absorption. The advantage of combining capture chemistry and biology through BICCU is, therefore, not only to reduce the energy cost for CO₂ liberation, but also to provide a potential energetic integration of chemical CO₂ scrubbing with exothermic bioreactors.

The development of aqueous solutions of amines as an absorption medium for conventional carbon capture has been ongoing since the process development in 1930⁵⁴, emphasizing various capture agent characteristics that render the capture process economically feasible and environmentally friendly. Substantial research efforts in reducing capital expenses have involved increasing the CO₂ absorption kinetics and net-CO₂ capacities of the capture agent, which reduces the size requirement of the absorption unit⁵⁵. Simultaneously, efforts in reducing the operating expenses (OPEX) have been approached by reducing the enthalpy of the reaction and increasing the concentration of aqueous amines to minimize the energy lost for reversing the equilibrium to desorb CO₂ and for heating and vaporizing water⁵⁶, and solvent losses through oxidative and thermal degradation⁵⁷. A knowledge spillover can thus be exploited for the maturation of the BICCU technology by utilizing the comprehensive research effort within conventional carbon capture with amine scrubbing. However, combining capture agents and microbial catalysts also requires novel developments within microbiology and capture chemistry.

In general, the carbamate formation involving covalent interactions between the primary/secondary amines and CO₂ entails high absorption rate kinetics, but with correspondingly high enthalpies of reaction required for CO₂ desorption. Tertiary amines are, in contrast, associated with lower enthalpies of reaction and higher CO₂ absorption capacities but are limited by slow absorption kinetics⁵⁸. Much attention has been given to addressing this trade-off between capture

rate and energy demand through the development of novel capture agents and blends⁵⁹, which will also dictate the efficiency of the BICCU process and become essential design criteria for capture agent selection, as listed in Table 1.

In conventional carbon capture, the high temperatures applied in the desorption unit necessitate critical considerations of the thermal stability (T_{\max}) of the capture agent. The thermal stability is directly related to the capture agent's resistance to thermal degradation⁶⁰, amine volatility, and aerosol formation⁶¹. The BICCU concept eliminates the desorption unit and the associated high temperatures and could potentially reduce the environmental and health concerns of conventional carbon capture and the OPEX associated with replacing the degraded amines. Another significant environmental concern with conventional carbon capture is the formation and accumulation of carcinogenic nitrosamines from accelerated thermal and oxidative amine degradation at high temperatures in the desorption unit, and amines reacting with NO_x impurities from the flue gas in the absorption unit⁶². However, the high temperatures in the desorption unit have also been found to partly mitigate nitrosamine accumulation by further decomposing the nitrosamines thermally⁶³. The multiple pathways to nitrosamine formation and degradation thus require further research to evaluate the fate of nitrosamines in BICCU.

When designing and developing capture agents for the BICCU process, thermal stability is no longer an essential design criterion (Table 1). Instead, the bio-mediated desorption requires capture agents that are non-inhibitory to the microorganisms, recalcitrant to microbial degradation, and employ weak CO₂ bonding, such as bicarbonate formation with tertiary amines, to enable the bio-mediated CO₂ stripping for capture agent regeneration. However, to design and develop suitable candidates of capture agents for the BICCU process, a further understanding of the microbial driving force for desorbing the CO₂ is required.

Microbial CO₂ desorption mechanism from a tertiary amine

To advance the development of the BICCU process, it is essential to understand the underlying mechanisms that drive CO₂ desorption by hydrogenotrophic methanogens. The mechanism of simultaneous microbial desorption and conversion is thus theoretically explained and exemplified by applying the tertiary amine MDEA as a capture agent. During absorption, MDEA base-catalyzes the hydration of CO₂, forming HCO₃⁻, which is in equilibrium with small amounts of soluble CO₂ (i.e., the carbonate equilibrium, Eq. 2). The hydrogenotrophic methanogens convert the soluble CO₂ intracellularly by the CO₂-reduction pathway, where they utilize inherent enzymes encoded by their genome to convert CO₂ to CH₄ with H₂ as the electron source (Fig. 3).

The CO₂-reduction pathway is well-described in literature^{64,65}, but is here summarized due to its importance in the BICCU process. Once the captured CO₂ enters the cellular cytoplasm, it undergoes a series of step-wise reductions by cytoplasmic electron carriers, which receive electrons from H₂ supplied from water electrolysis using renewable power. The C1-intermediates are transported in the cell by the coenzymes, resulting in the formation of CH₄ by the reduction of methyl-CoM by methyl-CoM-reductase. The resulting heterodisulfide

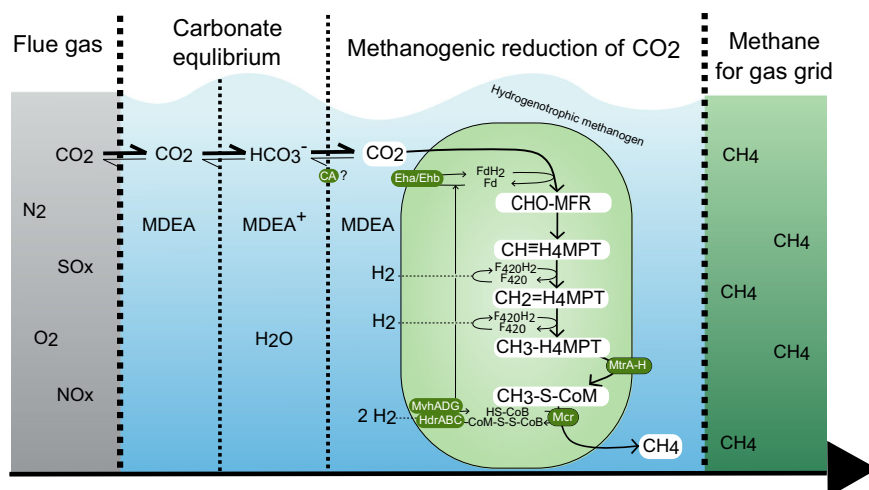


Fig. 3 | Proposed mechanism of methanogenic desorption and CO₂ conversion. The mechanism is exemplified by MDEA as the capture agent and a hydrogenotrophic methanogen without cytochromes. The microbial conversion of the CO₂ keeps the partial pressure low, which shifts the equilibria to the right and pulls the CO₂ from MDEA. A simplified version of the CO₂-reduction pathway shows the

stepwise C1 reduction to CH₄, with the C1-intermediates being highlighted by white boxes. The CH₄ separates naturally into the gas phase and can be used for gas grid injection. MDEA is not metabolized by microorganisms and can thus be recycled to the absorption column.

compound (CoM-S-S-CoB) is recycled by a cytosolic hydrogenase-hetero-disulfide reductase complex (MvhADG-HdrABC). This exergonic reaction is thermodynamically coupled with the endergonic reduction of ferredoxin, which facilitates the first step in the CO₂-reduction pathway, making the CO₂-reduction pathway a cyclic process. An electrochemical gradient is maintained across the cell membrane throughout the process by enzymes such as MtrA-H and the Eha and Ehb complexes, resulting in ATP synthesis and energy conservation (Not shown in Fig. 3). The partial pressure of CO₂ is thus kept low by the microbial CO₂ consumption and shifts the carbonate equilibrium according to Le Chatelier's principle, which enables the BICCU technology to work with the CO₂ gradient instead of against it as in conventional amine-based carbon capture.

The shift in carbonate equilibrium in the BICCU process may be further mediated biologically by cellular carbonic anhydrases (CAs), which catalyze the interconversion of CO₂ and HCO₃⁻. Although their physiological role in methanogens is yet to be confirmed, CAs have been speculated to facilitate CO₂ transfer across the cell membrane and concentrate the CO₂ intracellularly to ensure sufficient levels for subsequent enzymatic conversion⁶⁶. Additionally, cytoplasmic CA could concentrate the inorganic carbon in the form of HCO₃⁻, which is a substrate for the CO₂ fixation enzymes in the anabolic methanogenic metabolism⁶⁷. The hydrogenotrophic methanogen *Methanococcus maripaludis* has been reported to secrete extracellular CA, thus making it likely that other hydrogenotrophic methanogens may share this trait⁶⁸. The presence of extracellular CAs could potentially accelerate the rates of CO₂ conversion in the BICCU process, as they together with MDEA control the bidirectional shift in the carbonate equilibrium. Extracellular CAs would be recycled along with the microorganisms to the absorption column, where they could aid in capturing CO₂ from flue gas, if stable at the alkaline pH⁶⁹. However, further research is needed to clarify the individual impacts of MDEA and CAs on the carbonate equilibrium and to further characterize the importance of methanogenic CAs in terms of CO₂ acquisition.

The rate of methanogenic substrate conversion can be described with Michaelis-Menten kinetics, with research so far mostly focusing on determining the kinetic parameters for H₂ uptake⁷⁰. However, the CO₂ uptake is more of interest for the BICCU process, as it influences the lower limit for microbial CO₂ desorption and the maximum CO₂ conversion rate. One study reported the microbe-specific Michaelis-Menten constant (K_m) for *Methanobacterium congolense* to be 2.5 mM for

CO₂ conversion⁷¹. This suggests that the maximum CO₂ conversion rate would be achieved at 5 mM CO₂ and above. However, it was confirmed from initial studies on BICCU with a mixed microbial culture that the CO₂ conversion rates will decrease with MDEA concentrations from 30 mM and below, suggesting a variation across methanogenic strains to metabolize the captured CO₂ and that the CO₂ concentration is indeed a limiting factor^{37,38}. The potential for BICCU will, therefore, potentially depend on both the microbial species and the capture agent employed, as the CO₂-loading and the ability to convert it are two crucial elements for the process.

Rate and stability of the biological process

The biological conversion of CO₂ and H₂ to methane (i.e., biomethanation) is a widely researched process that can be operated under various conditions and reactor configurations, utilizing the robustness of mixed anaerobic microbial cultures for conversion of CO₂ and upgrading of biogas^{30,31,72}. Implementations at industrial scale include the 2.5 MW ex-situ biomethanation plant by Hitachi Zosen Inova Schrack GmbH in Switzerland⁷³ and the 1 MW facility by Electrochaea GmbH in Denmark⁷⁴. The latter demonstrated a CH₄ production capacity of 800 L_{CH4} L_{reactor}⁻¹ d⁻¹, emphasizing that biomethanation is both scalable and can achieve high conversion rates⁷⁴. Additionally, the biomethanation concept relies on renewable, regenerative, and eco-friendly microorganisms as biocatalysts, which enables long-term continuous operation as demonstrated for up to 1200 days with highly concentrated CO₂ sources such as biogas⁷². However, the application is currently limited to streams with a high CO₂ concentration and without O₂ unless the BICCU technology is applied, and continuous operation of bioreactors with diluted CO₂ as the substrate has thus only been demonstrated for up to 80 consecutive days³⁷. The same continuous BICCU reactor experienced an enrichment of the genus *Paracoccus* when exposed to an O₂-rich capture agent, indicating a potential biological O₂ scavenging mechanism by utilizing electrons from H₂. The use of complex cultures could thus be a way to alleviate O₂-stress and maintain the anaerobic conditions necessary for biomethanation.

The H₂ gas-liquid mass transfer rate is often the limiting factor in biomethanation processes, as H₂ is poorly soluble in aqueous solutions, with a Henry coefficient of 0.00078 mol kg⁻¹ bar⁻¹ at 25 °C⁴⁵. Different gas-liquid contactor technologies have been developed to enhance the gas-liquid mass transfer of H₂ to the active methanogenic

microorganisms, including gas diffusers for the creation of small gas bubbles⁷⁵, gas-phase bioreactors³¹, and membrane bioreactors⁷⁶. Alternatively to exogenous H₂ addition, future developments in bio-electrochemical systems, where H₂ is produced in situ⁷⁷, could present a platform for BICCU.

Besides ensuring sufficient amounts of dissolved H₂, it is also crucial to minimize inhibition of the hydrogenotrophic methanogens by compounds detrimental to their metabolism. Such compounds include hydrogen sulfide and carbon monoxide in conventional bi-methanation processes, where methanogenic communities have been reported to be adaptable to syngas^{32,33,78}, and to be able to coexist with sulfur oxidizers⁷⁹. In addition to these toxic compounds, inhibitors relevant to the BICCU process include SO_x and NO_x from the industrial flue gasses. NO₂ has been reported to dissolve as NO₂⁻ and NO₃⁻ in a 0.1 M MDEA solution⁸⁰, with especially NO₂⁻ showcasing toxicity towards methanogens, with the extent depending on the methanogenic species⁸¹. However, synergistic relationships between microorganisms in complex cultures may alleviate the accumulation of these contaminants by e.g., simultaneous denitrification and methanogenesis, which have been reported in anaerobic biofilm reactors⁸². Accordingly, a lab-scale BICCU CSTR reactor managed to operate for 25 days on flue gas containing 141 ppm NO_x with a complex mixed culture³⁷. Long-term operation is, however, needed to investigate whether NO_x accumulates to inhibitory levels or whether microbial synergies are relevant in this context. SO₂ is captured by tertiary amines as sulfite, which inhibits methanogenesis due to the inactivation of methylcoenzyme M reductase^{83,84}. However, the enzyme sulfite reductase and its homologs have also been reported across methanogens, making them able to tolerate small SO₃⁻² amounts⁸⁵. The current BICCU studies were conducted on flue gas with SO_x compounds but it remains unexplored whether the presence of SO_x is a problem for long-term operation. Besides SO_x and NO_x, the toxicity of the capture agent is also of high importance, as initial studies reported microbial inhibition when using MDEA concentrations above 70 mM³⁸. The exact inhibitory mechanism is still to be reported, but methanogens can be inhibited by structural analogs of coenzyme M, the compound involved in the final step in methane formation, as well as by medium or long-chain fatty acids through disruption of the cell membrane⁸⁶. Minimizing microbial inhibition is critical since the BICCU process should operate with the highest possible concentration of capture agent as it increases the CO₂-loading in the process and hence the rate and capacity. Increasing the capture agent concentration can only be accomplished within the range compatible with biological activity. In engineered systems using the continuous addition of a CO₂-rich capture agent, a high CO₂ load can be maintained by adjusting the capture agent volume and the recirculation rate. However, lowering the hydraulic retention time of the CO₂-rich liquid in the combined biomethanation-desorption reactor through an increased recirculation rate will risk washing out the microbes. Research has demonstrated maximum doubling rates of ~1.6 h with an 80:20 mixture of H₂:CO₂ for *Methanothermobacter thermoautotrophicus*⁸⁷, which is a potential biocatalyst candidate often cultivated for biomethanation⁸⁸. This will limit the potential CO₂ load to 16.8 L L⁻¹ d⁻¹ for a 50 mM MDEA solution, which previously had been used for BICCU³⁷. However, the capture agent may introduce less favorable conditions that reduce the growth rate of the methanogens, and a potential solution to mitigate the washout risk would thus be to decouple the hydraulic retention time and the microbial biomass retention time, e.g., by retaining the microorganisms in a biofilm or biostructures on a solid support. This would furthermore prevent biomass O₂ exposure in the absorption column and reduce O₂-inhibition. Accordingly, ongoing state-of-the-art research and development within conventional biomethanation already point toward trickle bed reactors, a three-phase reactor bioreactor type with a fixed solid bed of carrier materials for biofilm immobilization, as a suitable reactor

candidate³¹. Utilizing a bioreactor with a primary phase of gas, where the microbial biocatalysts are immobilized in a self-produced matrix of biofilm induces several advantages such as 1) reducing the liquid film layer that creates H₂ gas-liquid mass transfer resistance, 2) detaching the microbial retention time from the hydraulic liquid retention time, and 3) enabling a controllable gas retention time due to plug flow approaching gas flow conditions without requiring high auxiliary power consumptions for agitation and gas sparging⁸⁹. Naturally, these bioreactor types that allow the microbial biocatalyst to be retained in the bioreactor serve as a promising platform for BICCU.

Besides exposure to toxic compounds, methanogens can also be inhibited by an unfavorable pH, as most hydrogenotrophic methanogens grow optimally within the pH range 6.8–8.5⁹⁰. Due to the alkaline properties of most amine-based capture agents, the solvent pH will be reduced when enriched with acidic CO₂, whereas the microbial CO₂ conversion will increase the pH. A complete microbial conversion of the captured CO₂ is desirable for the efficiency of the process but might not be achievable due to the pH reaching inhibitory high levels prior to full depletion. On the other hand, a high pH is favorable for CO₂ capture as most amines are deprotonated above pH 10–11 and are more efficient at capturing the acidic CO₂ in this configuration. It is therefore a trade-off between obtaining process conditions that fit both the physiological optimums of the microbial community and the CO₂ absorption efficiency in the absorption column. The fluctuating pH will furthermore constitute a selection pressure in a mixed methanogenic community, as observed in a continuous lab-scale BICCU reactor. The relative abundance of the genus *Methanobacterium* increased during reactor operation, indicating tolerance to higher pH levels imposed by the CO₂-depleted MDEA, making this genus especially interesting for the BICCU process³⁷.

Outlook

The maturity of a technology can be assessed by its TRL, with 9 being the highest and describing a system proved in its operational environment and 1 being the lowest with only fundamental principles having been observed and reported⁹¹. To date, the BICCU technology has only been reported in lab-scale proof-of-concept experiments, to a TRL of 2. However, a strong point of the concept is that it combines elements of mature technologies—amine-based carbon capture, and biological methanation. Both have a TRL of 7–9—which can accelerate the maturation and enhance the technology scale-up potential. Accumulated knowledge from the last century can thus be a stepping stone for developing BICCU technology, which relies on capture agent properties such as fast absorption kinetics, high CO₂ capacities, and low heat of reactions.

The application of BICCU can be expanded to other CO₂-consuming microorganisms than methanogens. It has already been shown that CO₂ assimilation for biomass production by microalgae growth can be promoted when supplied with a capture agent (i.e., polyethylene glycol 200)⁹². However, microalgae require light for their photosynthesis, resulting in complex photoreactors with a large footprint. Another naturally occurring bioprocess with CO₂ as a reactant is homoacetogenesis, where homoacetogens such as *Clostridium* and *Acetobacterium* produce acetic acid from CO₂ and H₂ by the Wood-Ljungdahl pathway. Acetic acid is a platform molecule that can be converted into single-cell protein (i.e., power-to-protein⁹³) or used as a building block for acetyl-CoA-derived chemicals⁹⁴. The global demand for acetic acid reached 14 million tons in 2019, with the majority being produced by methanol carbonylation⁹⁵, making new sustainable production routes necessary. However, acetic acid is non-volatile and would be contaminated with the capture agent in the aqueous phase, unlike CH₄, which naturally separates into the gas phase. Furthermore, the shift in equilibrium shown in Eq. 2 results in H₂O formation, which would dilute the soluble product, rendering the downstream processing difficult when targeting liquid-based products. Acetic acid

production by BICCU is therefore restricted and requires future optimization to avoid costly downstream separation of the capture agent and acetate. The microbial CO₂ conversion might not be restricted to the natural autotrophic pathways, as an artificial CO₂-fixation pathway was recently designed, constructed, and demonstrated in *E. coli*, yielding acetyl CoA as the final product⁹⁶. A combination of artificial microbial pathways and BICCU would facilitate the production of a wide range of molecules to valorize the captured CO₂ under mild conditions. However, whether this heavily engineered strain is competitive with the established biological process chains for CO₂ conversion remains to be seen.

The BICCU technology concept holds the potential to become a viable and sustainable system that exploits the CCU and PtX approach envisioned for future energy systems. The combined bio-mediated desorption and conversion of the CO₂ eliminates the desorption unit, downstream CO₂ processing for storage and transport, and consecutive processing for utilization, resulting in a simplified process and energy savings in the range of 17–29%³⁸. Furthermore, the reduction of the temperature from 120–140 °C in the thermal desorption to 30–60 °C in the bioreactor would potentially impede the thermal and oxidative degradation of the amine, thus improving the environmental impact of the process. However, regardless of the concept's potential, the development and integration of this biomethanation-derived technology face a critical challenge when full capture and utilization of industrial CO₂ flue gas streams are targeted. The efficiency of the amine scrubbing is limited to the CO₂ loading capacity in the liquid capture agent, which is regulated by the capture agent concentration. Therefore, considerable biological and technical optimization is still necessary to achieve an industrially relevant technology. Critical elements of future research include (1) identifying absorbents with higher methanogenic biocompatibility at elevated capture agent concentrations and (2) identifying the right microorganisms capable of stripping the CO₂ from the capture agents. Furthermore, developing a combined CCU and PtX technology concept relies on expanding the PtX infrastructure to supply H₂ from renewable sources to ensure that the CO₂ emissions for the overall process are kept at a minimum. As low-emission H₂ production projects are increasing globally⁹⁷, it seems plausible to rely on renewable H₂ as a reducing equivalent for neutralizing and utilizing the CO₂ emissions from flue gasses.

In conclusion, BICCU is a promising technology concept for negating energy penalties in CO₂ capture, as the thermal desorption unit is replaced by a bioreactor that serves as a multifunctional reactor for the simultaneous release and conversion of the captured CO₂ to CH₄ by hydrogenotrophic methanogens. To further advance the technology, future research should be directed toward identifying biocompatible capture agents and robust microorganisms as many traditional capture agents have inhibitory effects on the microbiome.

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Author contributions

M.V.W.K. conceptualized the concept. M.V.W.K., M.U.S. and A.K.H.N. conceived the project. M.V.W.K., A.K.H.N. M.U.S. initiated the paper and developed the outline. A.K.H.N. and M.U.S. wrote the first draft. L.D.M.O., K.D. and M.V.W.K. contributed during the preparation of the manuscript. M.V.W.K. supervised the project. All authors approved the submission.

Competing interests

M.V.W.K., M.U.S. and L.D.M.O. have a patent, PCT/EP2023/069435, to Aarhus University. The patent presents a method to capture CO₂ from diluted CO₂ sources with a CO₂ capture agent mixed with the methanogenic biocatalyst for integrated and conversion of CO₂ to CH₄. M.V.W.K., A.K.H.N. and L.D.M.O. have a patent pending, EP23218999, to

Aarhus University. The patent presents a method to separate the CO₂-converting microorganisms and the CO₂-loaded capture agent. No other authors have competing interests.

Additional information

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