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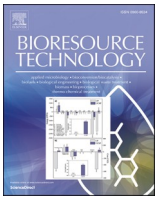

Continuous biomethanation of flue gas-carbon dioxide using bio-integrated carbon capture and utilization

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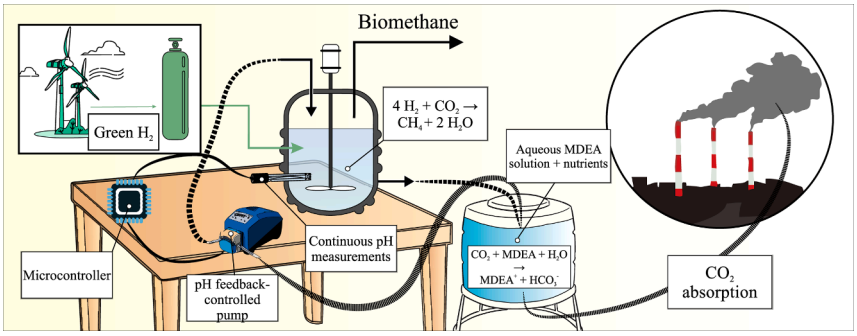
HIGHLIGHTS

- Novel bio-integrated technology for methanation of flue gas-CO_2 was assessed.
- Stable biomethane production was achieved in the continuous BICCU system.
- The amine used was biocompatible and resistant to microbial degradation.
- Methanogens were protected from oxygen by syntrophic microbial associations.
- ~12 % of the H_2 was used to reduce O_2 from the flue gas in this work.

GRAPHICAL ABSTRACT



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ABSTRACT

Biomethanation of carbon dioxide (CO_2) from flue gas is a potential enabler of the green transition, particularly when integrated with the power-to-gas chain. However, challenges arise in achieving synthetic natural gas quality when utilizing CO_2 from diluted carbon sources, and the high costs of CO_2 separation using amine-based solutions make large-scale implementation unfeasible. We propose an innovative continuous biomethanation system that integrates carbon capture and CO_2 stripping through microbial utilization, eliminating expenses with the stripper. Stable continuous biomethane production (83–92 % methane purity) was achieved from flue gas-CO_2 using a biocompatible aqueous n-methyldiethanolamine (MDEA) solution (50 mmol/L) under mesophilic and hydrogen-limiting conditions. MDEA was found to be recalcitrant to biodegradation and could be reused after regeneration. Demonstrating the microbial ability to simultaneously strip and convert the captured CO_2 and regenerate MDEA provides a new pathway for valorization of flue gas CO_2.

1. Introduction

Several countries have pledged to reduce carbon dioxide (CO_2) emissions in the Paris Agreement, in an attempt to limit the average global temperature increase to below 2 °C (Schleussner et al., 2020). A major source of atmospheric CO_2 is flue gases, which constitute of a mix of CO_2, nitrogen (N_2), oxygen (O_2) and a minor fraction of oxidized sulfur and nitrogen oxides (Galbreath and Zygarlicke, 2000; Weber

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et al., 2000). Carbon capture has been shown as a feasible strategy to negate net carbon emissions from flue gas and relies on the CO_2 separation from a flue gas stream for either storage (CCS) (Wilberforce et al., 2021) or utilization (CCU) (Daneshvar et al., 2022). The last refers to the utilization of the CO_2 captured for production of renewable energy or materials, in processes such as methanation. Many of these CCU technologies utilize renewable power for the H_2 based reduction of CO_2 into fuels or chemicals – so called power-to-X (or PtX) technologies.

Methanation offers a promising PtX solution to decrease reliance on natural gas amid geopolitical tensions impacting energy prices (Bohdan et al., 2023). In biological methanation, anaerobic microorganisms produce methane (CH_4) from hydrogen (H_2) and CO_2 (Ripoll et al., 2020). Production of natural gas-graded biomethane from renewable H_2 and CO_2 has been achieved in anaerobic reactors using waste streams with high CO_2 content (Aryal et al., 2021; Jensen et al., 2021; Rachbauer et al., 2016). This process utilizes biological catalysts and operates at low temperature and atmospheric pressure (Angelidaki et al., 2018), and enables production of a renewable e-fuel if biomethane is produced via the power-to-gas process chain, i.e. using green H_2 produced from water electrolysis as source of reducing equivalents (Lefebvre et al., 2016).

Biological methanation has mainly been developed and validated for methanation of biogas from anaerobic digesters (Angelidaki et al., 2018), but could also be used for CO_2 captured and purified from flue gas. Notably, the International Energy Agency reports that flue gas emissions from stationary sources represent a substantial share of anthropogenic CO_2 emissions in Europe, the United States, and China (International Energy Agency, 2020). Consequently, biomethanation of flue gas CO_2 can play an important role in reducing CO_2 emissions, aligning with the goals outlined in the Paris Agreement.

The main bottleneck in biomethanation of flue gas-CO_2, and any other PtX utilization of flue gas, lies on the costs of separating the CO_2 from the flue gas stream (Wang and Song, 2020). Amine scrubbing represents a highly robust technology for this purpose, but it requires high energy input for the stripper reboiler and CO_2 compression (Rochelle, 2009). To overcome the energy penalty, a more energy-efficient solution could be achieved by regenerating CO_2 through biological utilization instead of stripping it with water vapor. This bio-mediated carbon capture and utilization (BICCU) approach previously developed by Sieborg et al. (2024) obtained promising results in batch experiments. However, a continuous bioreactor system for bio-integrated carbon capture and utilization is yet to be designed, developed and studied.

We here propose a completely new system in which an amine is used to capture CO_2 from flue gas and is directly fed into a continuous biomethanation reactor, saving costs related to heat-driven regeneration of the amine and with the work required to compress the CO_2 for subsequent utilization. The new concept behind the proposed process lies in replacing the CO_2 stripping mechanism. Instead of inducing an affinity shift through energy demanding temperature elevation, leading to the release of CO_2 from the amine carriers in the stripper reboiler, the new method induces a concentration shift through consumption of free CO_2 via biomethanation (Reaction 1). In this way, microbial conversion activity is utilized to push the chemical equilibrium of CO_2 and bicarbonate (HCO_3^-) controlled by chemical capture agents like N-methyldiethanolamine (MDEA) (Reaction 2) using Le Chatelier's principle to omit the use of external energy for CO_2 stripping, while at the same time converting the CO_2 to methane.

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad \text{(Reaction 1)}$$

$$MDEAH^+ + HCO_3^- \rightleftharpoons MDEA + H_2O + CO_2 \quad \text{(Reaction 2)}$$

The proposed strategy requires a biocompatible capture agent. Based on previous screenings (Sieborg et al., 2024), the MDEA was chosen as absorbent due to its high CO_2 absorption capacity, compatibility with biological systems, low degradability, and low heat of reaction with CO_2 (Feng et al., 2012; Rinker et al., 1995). We present novel findings from the operation of the first continuous flue gas biomethanation system involving BICCU, where the absorbent is regenerated through CO_2 conversion to CH_4 by hydrogenotrophic methanogens to reduce the process cost of power-to-methane with flue gas as CO_2 source.

2. Materials and methods

2.1. Inoculation and enrichment of hydrogenotrophic methanogens

The continuous stirred reactors (CSTRs) were constructed in glass and had a total working volume of 1.0 L. The CSTRs were equipped with two separate inlets for liquid or gas injection, along with two outlets - one for gas release and the other for liquid recirculation. To ensure thorough mixing, a magnetic stirrer operating at 500 rpm was employed. The concentrations of MDEA were chosen based on the results from previous batch experiments (Sieborg et al., 2024). The reactors were filled with a medium containing phosphate-buffered saline (PBS), yeast extract (25 mg L^{-1}) and either 50 or 100 mmol/L MDEA (reactors R_1 and R_2, respectively). Another reactor was used as control and was not supplied with MDEA (R_C). The bioreactors were inoculated with mesophilic sludge (3205 mg TVS) obtained from a biogas plant (Bånlev Biogas, Trige, Denmark) and were enriched for hydrogenotrophic methanogens through approximately 21 days of incubation before the experiments. During the enrichment, the operation of the reactors was discontinuous regarding the liquid phase, where the liquid was not replaced, but continuous concerning the gas phase. A mixture of H_2 (80 %) and CO_2 (20 %) was diffused into the basal medium at a flow rate of 3.8 N mL min^{-1} (0 °C and 1 atm) using a mass flow controller, and the composition of the outlet gas stream was monitored to assess the biomethane production in the system.

2.2. Operation of the continuous stirred reactors system

The CSTR reactors were fed with rich CO_2-loaded aqueous MDEA (R_1 and R_2) or PBS only (R_C) media, both containing yeast extract (25 mg L^{-1}). To maintain pH control, a feeding pump (EZO-PMP™, Atlas Scientific), a lab-graded pH probe (Atlas Scientific) and a pH reading circuit (EZO™ pH circuit, Atlas Scientific) were linked to an Arduino™ microcontroller. A pH feedback-controlled feeding approach was employed, in which the pump dispensed rich CO_2-loaded solution whenever the pH exceeded the 8.1 threshold. This approach was implemented because the pH increase is linked to the consumption of dissolved inorganic carbon (DIC) species, primarily by hydrogenotrophic methanogens (Ripoll et al., 2020), as shown in Reaction 1, resulting in the regeneration of MDEA (Reaction 2).

The regenerated MDEA was then collected in a tank equipped with diffusors designed to facilitate CO_2 absorption from a diluted stream until saturation (i.e., after no further drop in pH is observed). This process yielded fresh CO_2-loaded MDEA, which could then be reintroduced into the bioreactors using the pH-controlled pump. Gaseous H_2 was diffused in the reaction mixture at a rate of 3.0 N mL min^{-1} L^{-1} (0 °C and 1.013 bar) and the reactor was stirred at 500 rpm. Feeding control by pH was important to provide DIC at the same rate as the CO_2 was consumed, and thus H_2 became the limiting substrate. A detailed overview of the system can be found in Fig. 1.

During phases PI and PII, CO_2 absorption was conducted using clean diluted CO_2 (20 % CO_2 in N_2). This mixture was used to simulate a diluted CO_2 source. In phase PIII, real flue gas was used instead. The flue gas was obtained from a chimney coupled to a 600 kWh combined heat and power gas engine (Jenbacher), fueled by biogas. Prior to combustion, the biogas had been purified to lower its hydrogen sulfide concentration to below 100 ppm. A compressor was used to pump the post-combustion flue gas from the base of the chimney to the flushing tanks where CO_2 absorption occurred.

The composition of the medium was improved in PII with weekly additions of 10 mL L^{-1} modified Wolin's mineral solution (Palabikyan

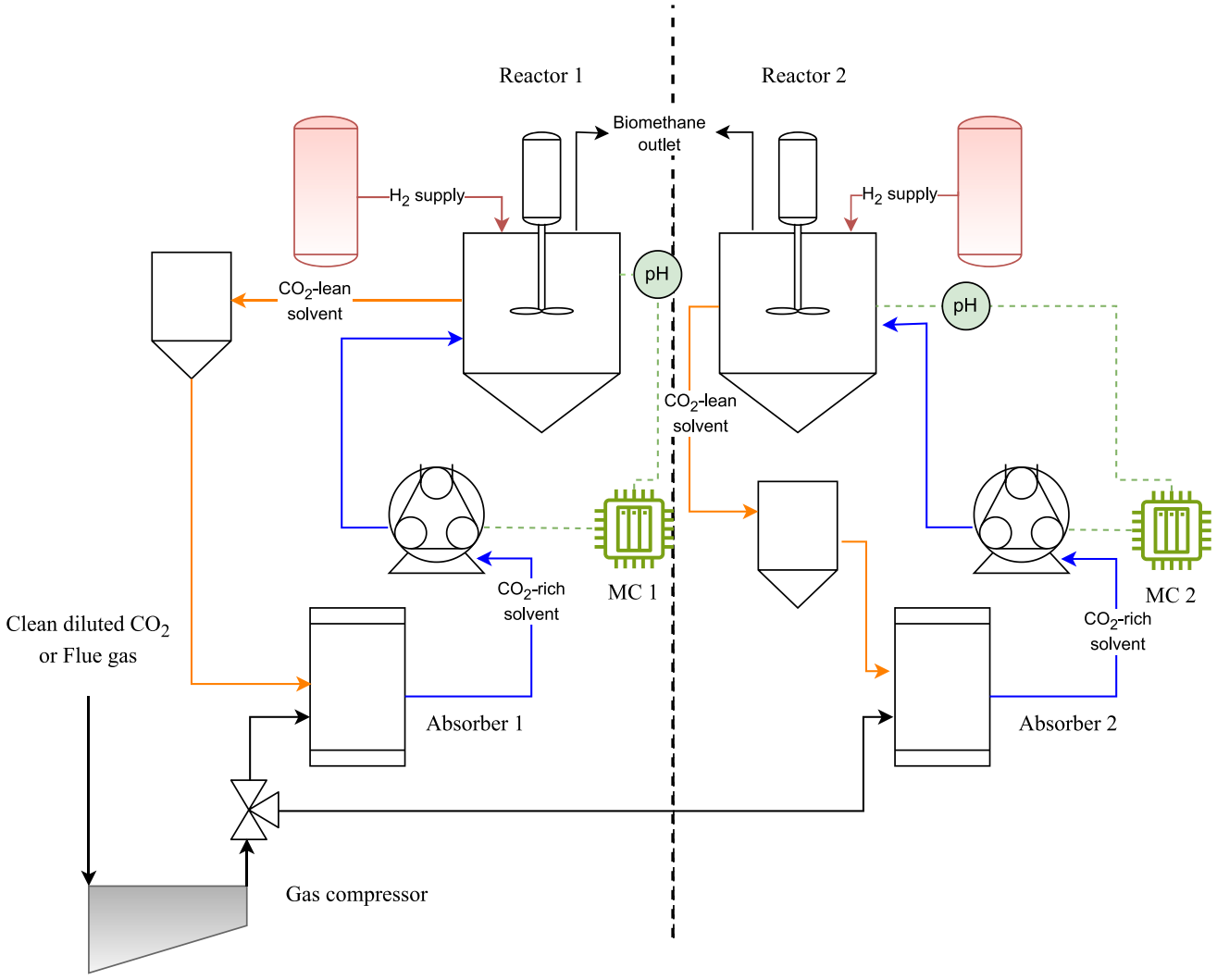


Fig. 1. Detailed diagram of the bio-integrated carbon capture and utilization system used for continuous biomethanation of clean diluted CO_2 (20 % CO_2 in N_2) and post-combustion flue gas-CO_2. The flue gas was composed of N_2, CO_2 (4.0–8.2 %), O_2 (9.93 ± 0.24 %), nitrogen oxides (141 ppm) and carbon monoxides (491 ppm).

et al., 2022) and NH_4Cl (500 mg L^{-1}). These additions were crucial to sustain the microbial growth throughout the rest of the operation (i.e., until the end of PIII).

2.3. Performance evaluation

The response variables used to assess the performance of the continuous bioreactor system were the biomethane fraction (xCH_4, dimensionless) and the volumetric methane production rates (VMPR, in N mL CH_4 L^{-1}). The equations used in the calculations are shown below:

$$xCH_4 = \frac{n_{CH4}}{n_T} \quad (1)$$

$$VMPR = \frac{Q_{gas} \bullet xCH_4 \bullet T_{standard} \bullet P_{local}}{V_R \bullet T_{local} \bullet P_{standard}} \quad (2)$$

in which n_{CH4} and n_T are, respectively, the molar flow ratio of methane and the total molar flow rate; Q_{gas} is the total gas flow rate (N mL), P_{local} and $P_{standard}$ are, respectively, the local and standard atmospheric pressure (1.013 bar); T_{local} and $T_{standard}$ are, respectively, the temperature measured in the flow meter and the standard temperature (K); and V_R is the working volume of the reactor (L).

2.4. Analytical methods

The gas composition (H_2, CO_2, N_2 and CH_4) was analyzed using a Shimadzu GC-2014 with thermal conductivity detector (TCD) and two different columns. A packed column (Restek ShinCarbon ST, Bellafonte, Pennsylvania, USA) was used for H_2 separation with argon as the carrier gas, whereas a Porapak Q column (CS-Chromatographie Service GmbH, Langerwehe, Germany) was used for CO_2, N_2, and CH_4 separation with helium as carrier gas. Volatile fatty acids (VFA) were determined using a gas chromatograph (6890N Agilent Technologies, United States) equipped with a flame ionization detector (FID) and using an HP-INNOWAX (30-m × 0.25-mm × 0.25-μm) capillary column. MDEA was determined in the same 6890N Agilent Technologies GC as described elsewhere (Fürhacker et al., 2003), except that separation was achieved on a ZB-1MS column.

The DIC concentration was measured using a protocol modified from Xie et al. (2018). Briefly, 10 mL of sample were transferred to 60 mL serum bottles containing NaCl (0.1 g) and the flasks were closed with a rubber stopper and aluminum crimp seal. HCl 1 mol/L was added in excess to the samples, and the flasks were incubated for 30 min at 65 °C. GC measurements were carried in the Shimadzu GC-2014 previously described to quantify the formation of CO_2. DIC standards were prepared using $NaHCO_3$.

2.5. CO_2 absorption from flue gas and saturation pH

The saturation pH was used as a monitoring parameter for CO_2 absorption from the diluted CO_2 stream and had a direct influence on the pH control mechanism within the bioreactors. The saturation pH at various MDEA concentrations was calculated based on the assumption that it corresponds to the pH at which bulk gas and liquid phases are in equilibrium, meaning the cessation of gas–liquid mass transfer.

Under equilibrium conditions, there is no concentration gradient between bulk gas and liquid phases, and therefore the driving force from Fick's first law of diffusion is zero (Jensen et al., 2021).

$$J_T = K_L \bullet \left(C_l^* - C_l\right) \tag{3}$$

$$C_l^* - C_l = 0 \tag{4}$$

In Eqs. (8) and (9), J_T is the gas flux from bulk gas to bulk liquid, K_L is the overall mass transfer coefficient, C_l is the concentration of gas dissolved in the liquid phase and C_l^* is the concentration of dissolved gas in equilibrium with bulk gas partial pressure (P_G), given by the Henry's law (Henry, 1803):

$$C_l^* = \frac{P_G}{H_A} \tag{5}$$

in which H_A is the Henry's constant.

Based on the CO_2-bicarbonate buffer system, C_l is the fraction of the DIC that is not ionized under a given pH. Thus, C_l can be related to the DIC concentration using the fraction of ionization (α) derived from the Henderson–Hasselbalch equation (Po and Senozan, 2001):

$$C_l = DIC\,(1-\alpha) \tag{6}$$

$$\alpha = \frac{1}{1+10^{(pK_A-pH)}} \tag{7}$$

in which K_A is the dissociation constant of carbonic acid and $pK_A = -\log K_A$.

Then, substituting Eqs. (5)–(7) in Eq. (4) gives:

$$pH_{sat} = pK_A - \log\left[\frac{1}{\left(1-\frac{\frac{P_G}{H_A}}{DIC}\right)} - 1\right] \tag{8}$$

As DIC and MDEA concentrations are related at a theoretical ratio of 1.0 mol CO_2 mol^{-1} MDEA, Eq. (8) can be rewritten as:

$$pH_{sat} = pK_A - \log\left[\frac{1}{\left(1-\frac{\frac{P_G}{H_A}}{[MDEA]}\right)} - 1\right] \tag{9}$$

in which [MDEA] is the concentration of the capturing agent.

It is noteworthy mentioning that the Henry's constant varies with temperature, therefore affecting the saturation pH.

2.6. DNA sequencing, bioinformatics processing and statistical analysis

Suspended microbial biomass was sampled weekly from R_1 and R_2 and analyzed by DNASense (Aalborg, Denmark). Genomic DNA was extracted using the FastDNA® Spin kit for Soil (MP Biomedicals, USA) according to the manufacturer's protocol. PCR was conducted targeting the archaea/bacteria/eukaryota 16S/18S rRNA gene variable regions 4-8 (abeV48-A). Sequencing libraries were prepared using the SQK-LSK114 kit (Oxford Nanopore Technologies, UK). The DNA library was loaded onto a MinION R10.4.1 flowcell and sequenced using MinKNOW 23.04.6. The sequencing reads were filtered for length (320–2000 bp) and quality (phred score > 15), and downstream processing was conduced using samtools v1.14 (Danecek et al., 2021). Taxonomy was assigned using MiDAS 4.8.1 (Dueholm et al., 2021). Statistical analysis were performed in RStudio IDE running R version 4.3.0 and using the R CRAN package ampvis 2.8 (Albertsen et al., 2015).

3. Results and discussion

3.1. Overview of the biointegrated CCU system

A detailed overview of the BICCU system is presented in Fig. 1. The continuous reactors were operated using a pH feedback mechanism, where MDEA-CO_2 solution was dosed based on the pH levels within the bioreactors. This approach was selected to regulate CO_2 quantities for a given H_2 flow, as it can be challenging to adjust the H_2:CO_2 ratio when these gases are supplied in different states (e.g., gas phase and gas solubilized in a liquid phase). Consequently, H_2 acts as the limiting substrate, with CO_2 supply automatically adapting to H_2 utilization rates. However, it is important to note that the pH of the CO_2-saturated MDEA solution (referred to as saturation pH) is influenced by factors like MDEA concentration, temperature of CO_2 absorption, and CO_2 partial pressure in the diluted CO_2 stream. As a result, pH regulation is impacted by these variables, directly affecting the biomethanation reactor's performance. These limitations are inherent to the pH-controlled feedback mechanism and do not reflect limitations of the BICCU system, as further discussed in section 3.5.

3.2. Biomethane production

Three CSTR reactors were operated in continuous mode over a period of up to 121 days to assess the stability of the proposed configuration for conversion of flue gas-CO_2 to methane under mesophilic conditions. The reactors R_1 and R_2 were operated with MDEA concentrations of 50 and 100 mmol/L, respectively, and R_C corresponded to the control reactor (no MDEA added).

The concentration of CO_2 in the MDEA solution is correlated with pH, such that microbial CO_2 consumption will increase pH values in the reactors. Measurement of pH was therefore tested as a control mechanism in the reactors. The reactors operated with a pH setpoint of 8.1, controlling the addition of CO_2-saturated MDEA-solution. Previous experiments showed that the pH within the reactors and the CO_2 concentration in the headspace are inversely proportional (see Supplementary material). As a consequence, low pH setpoints result in poor CO_2 removal efficiencies and high CO_2 concentrations in the produced methane. On the other hand, values much higher than 8.1 are beyond the range recommended for methanogenesis (Sirohi et al., 2010). The pH setpoint of 8.1 was therefore selected to maximize CO_2 removal efficiency while avoiding inhibition of methanogenesis.

Operation with different quality feed gases were assessed. In phases PI and PII, the solvent was saturated with clean diluted CO_2 (20 % CO_2 in N_2) to investigate whether the proposed reactor configuration was adequate to achieve continuous biomethane production with good quality using a clean diluted CO_2 stream. Fig. 2 shows that reactors R_1 and R_2 produced methane with high-quality standards during the initial days of operation in PI (up to 91 and 84 % CH_4 in R_1 and R_2, respectively). The sudden decrease in methane production in both the reactors observed in the following days demonstrated the necessity of enhancing the medium composition. In phase PII, the composition of the aqueous MDEA medium was improved with the addition of modified Wolin's mineral solution and 0.5 g/L NH_4Cl, which resulted in an immediate recovery of the methane production. The regenerated solvent was re-

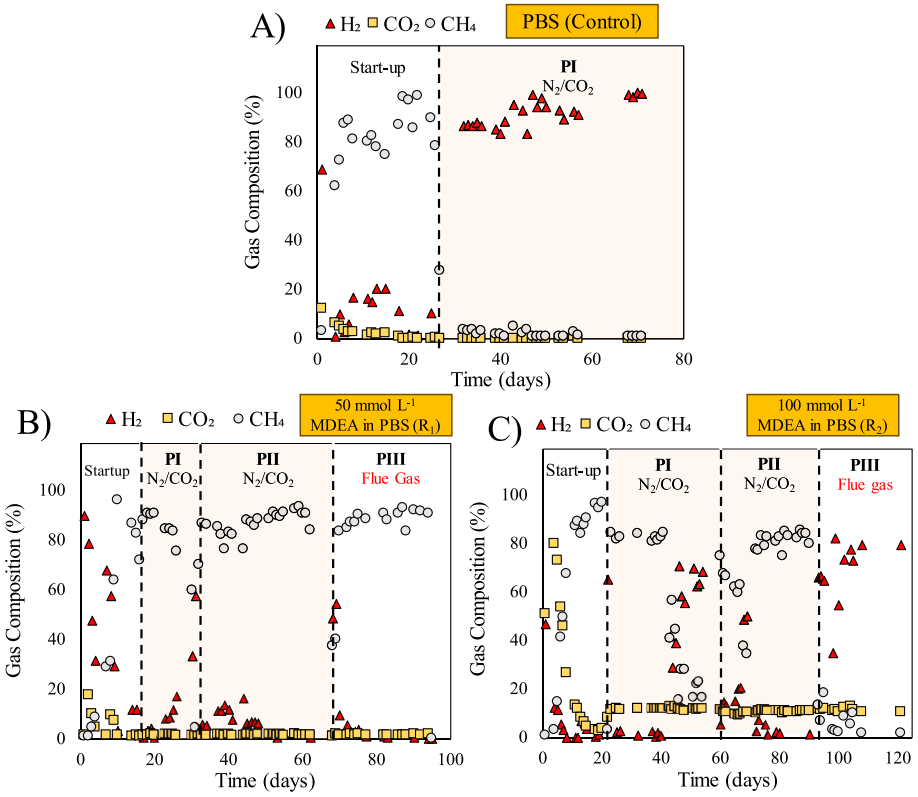


Fig. 2. Composition of the headspace gas as a function of time in the continuous stirred tank reactors (CSTR) fed with CO_2 dissolved in the liquid phase and gaseous H_2. The reactors contained: A) phosphate-buffered saline (PBS) solution; B) 50 mmol/L methyldiethanolamine (MDEA) in PBS; and C) 100 mmol/L MDEA in PBS. CO_2 was absorbed either from a clean diluted stream containing 20 % CO_2 in N_2 (phases PI and PII) or flue gas (Phase PIII). The composition of the medium was improved with the addition of minerals in phase PII and afterwards.

supplied weekly with minerals to ensure that the microbial growth was not limited by nutrients.

It is worth noting that, in biomethanation systems, we aim for a high methane purity, and therefore CO_2 and H_2 are not desired in the produced biomethane. After stabilization in phase PII, no H_2 was observed in the composition of the produced biomethane, in R_1, and the hydrogen content varied from 0 to 6 % in R_2. The reactors stabilized with VMPRs of 542 ± 43 N mL CH_4 L^{-1} d^{-1} and 658 ± 36 N mL CH_4 L^{-1} d^{-1}, respectively, in R_1 and R_2 (Fig. 3). The average VMPR was found to be higher in R_2 compared to R_1 at a 95 % confidence level. Despite the higher CO_2 fractions in the biomethane of R_2 (approximately 11 %) compared to R_1 (<2%), CO_2 did not limit the methane production in R_1 because its feeding rate of CO_2-MDEA was controlled by the utilization rates. Therefore, the slightly lower performance of R_1 was probably due to competing pathways, in which the limiting substrate (H_2) was used to produce metabolites different than methane.

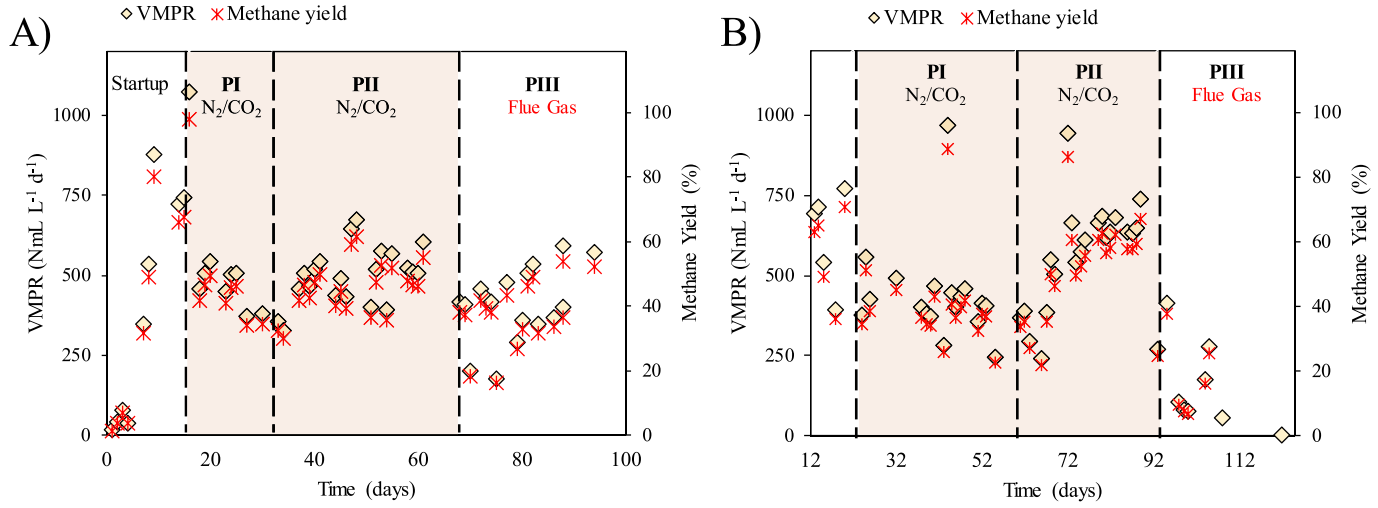


Fig. 3. Volumetric methane production rates (VMPR) and methane yield as a function of time in the continuous stirred tank reactors (CSTR) fed with CO_2 dissolved in the liquid phase and gaseous H_2. The reactors contained: A) 50 mmol/L methyldiethanolamine (MDEA) in phosphate-buffered saline (PBS) solution; and B) 100 mmol/L MDEA in PBS. CO_2 was absorbed either from a clean diluted stream containing 20 % CO_2 in N_2 (phases PI and PII) or flue gas (Phase PIII). The composition of the medium was improved with the addition of minerals in phase PII and afterwards.

In R_C (no MDEA added), we observed a decrease in the methane fraction from approximately 89 % to 78 % after 12 h of phase PI operation, and further to 28 % within 24 h. The methane content was below 3 % during the rest of the experiment. Despite the substantial CO_2 content in the CO_2-saturated phosphate buffer (DIC = 28.9 ± 2.9 mmol/L), the pH in R_C remained below the setpoint, thus unable to activate the CO_2 dosing pump. This limitation stems from the phosphate buffer's pK_A of 7.19, which is insufficient for buffering the system at pH of 8.1 (Liu et al., 2011).

Switching from clean diluted CO_2 to flue gas caused a temporary decrease in the biomethane quality, which dropped to around 50 %, in R_1, for two consecutive days. However, the system experienced a quick recovery, and the methane fraction remained in the range of 83–92 % until the end of the operation. This suggests that the microbial communities acclimated to the impurities contained in the flue gas, such as oxygen (9.93 ± 0.24 %) and trace concentrations of nitrogen oxides and carbon monoxide (Sieborg et al., 2024).

The average VMPR in R_1 was 474 ± 101 N mL CH_4 L^{-1} d^{-1} in phase PIII, which is lower than the 542 ± 43 N mL CH_4 L^{-1} d^{-1} obtained in the operation with clean diluted CO_2. Moreover, the DIC concentrations in R_1 decreased from 71.2 ± 3.4 mmol/L to 53.1 ± 5.2 mmol/L after switching to flue gas as the source of CO_2 (see Supplementary material). The decrease in DIC concentrations was anticipated because of the lower CO_2 partial pressures in the flue gas (4.0–8.2 % CO_2) compared to the clean diluted CO_2 stream. However, this decrease in DIC is not expected to be the cause for decline in biomethane production because H_2 was the limiting substrate, not CO_2.

An inhibiting factor in raw flue gas compared to clean diluted CO_2 is the presence of oxygen, which constituted 9.93 ± 0.24 % O_2 of the flue gas composition. As the H_2 was still fully converted when using flue gas, the presence of oxygen might have increased the demand for hydrogen in pathways other than biomethane production. It is here worth noting that even after extended periods of gas absorption from flue gas, the concentration of dissolved oxygen in the saturated MDEA solution remained below 0.5 mg L^{-1} O_2. This likely occurred due to the presence of facultative aerobes among the microbial communities in suspension (Section 3.6).

In R_2, the methane fraction in the biomethane dropped to 14 % after just one day of operation with flue gas, and it further decreased to less than 2 % in the subsequent days. This resulted in VMPRs falling below 50 N mL CH_4 L^{-1} d^{-1} by the end of the operation. Notably, this decline occurred despite a minor change in the DIC concentration of the saturated MDEA solution, which decreased from 101.2 ± 3.4 mmol/L to 91.1 ± 6.8 mmol/L after switching to flue gas as the source of CO_2 (see Supplementary material). The reduction in biomethane production can be attributed to alterations in the saturation pH of the rich 100 mmol/L MDEA solution, significantly affecting the pH feedback mechanism. The influence of CO_2 partial pressure on saturation pH and its implications for the proposed integrated BICCU system will be discussed in greater detail in Section 3.5.

The VMPRs obtained with 50 mmol/L MDEA and CO_2 captured from flue gas are still lower than those achieved in biomethanation systems used for biogas upgrading, since CO_2 content is considerably higher in biogas (30–50 % of inlet gas) and the CO_2 can be fed directly into the reactors in concentrated gaseous form (Jensen et al., 2021). Nonetheless, the continued production of methane comparable to what is achieved with lab-graded N_2:CO_2 show how the BICCU system is compatible even with flue gases of low CO_2 content with the presence of oxygen, which is considered to be inhibitory to obligate anaerobes like methanogens. Future development of bioreactors for BICCU can improve the reaction rates as has also been observed for reactors employed for biomethanation of biogas.

3.3. Dissolved inorganic carbon loading rate and hydraulic retention time

In contrast to conventional CSTR systems, the HRT is here variable according to the pH-based feed rate of CO_2-saturated MDEA solution. By setting a pH point to trigger the feed pump, the proposed configuration uses the CO_2 utilization efficiency as a fixed parameter, and the HRT therefore fluctuates dependent on pH and subsequent DIC concentrations in the reactor liquid. Fig. 4 shows that the HRT in R_1 (20.2 ± 1.9 h) exceeded that of R_2 (6.9 ± 0.6 h), despite the higher CO_2 concentration in R_2's feed. This discrepancy can be attributed to the average DIC removal efficiencies from influent to effluent of the reactors, which were approximately 3 times higher in R_1 than in R_2 (see Supplementary material). Notably, in ideal CSTR, HRT is proportional to conversion efficiency (Levenspiel, 1999). As both R_1 and R_2 had identical CO_2 utilization rates (both constrained by H_2 supplied at 3.0 N mL min^{-1}), the HRT was automatically adjusted to match the removal efficiencies corresponding to the DIC concentrations in the influent and effluent (pH 8.1) of each reactor.

When absorption was conducted using flue gas as CO_2 source, the HRT decreased to 14.5 ± 5.4 h in R_1. The shorter HRT's result from the lower DIC concentrations achieved in the MDEA solution saturated with flue gas (4.0–8.2 % CO_2) compared to the clean diluted CO_2 (20 % CO_2). When operating with real flue gas there will moreover be other contaminants, like SO_2, which can decrease the CO_2 capture capacity of the capture agents (Liu et al., 2022). As the DIC concentrations decreased, a higher flow rate was required to keep the same DIC loading rate. In R_2, the average HRT decreased to 3.65 ± 1.27 h in phase PIII. This caused a significant drop in the methane production, probably because the HRT was lower than the doubling time of the hydrogenotrophic methanogens, whose minimum doubling times were reported to be around 6 h (Huang et al., 2015). It is relevant to emphasize that the microorganisms were recirculated through the bioreactor together with the amine solution. However, the results suggest that the HRT provided in the last period of operation in R_2 was not sufficient for the microorganisms to perform their metabolic functions. The negative impacts of the shorter HRTs in R_2 can potentially be minimized if the microbial biomass is immobilized in a material support.

3.4. MDEA stability

The stability of the capturing agent is a key feature in post-combustion CO_2 capture technologies. In conventional amine scrubbing systems, the ideal absorbent is stable and does not undergo thermic degradation in the stripper reboiler (Lepaumier et al., 2011, 2009). In the current study, the capturing agent is not exposed to high temperatures, but it is in direct contact with the microorganisms and enzymes involved in CO_2 utilization. The results showed that the concentration of MDEA oscillates around 50 mmol/L, in R_1, and 100 mmol/L, in R_2, during the whole operation (see Supplementary material). The results suggest that MDEA is recalcitrant and is not degraded under anaerobic conditions and mesophilic temperature, or during CO_2 absorption from flue gas when it is exposed to low concentrations of oxygen. Lawal et al. (2005) found that MDEA is susceptible to chemical oxidative degradation at high temperatures (55–120 °C) and pressure (2.5 bar). This highlights the importance of biological methanation of captured CO_2, which is conducted under anoxic conditions, intermediate temperature, and low-pressure conditions. It is important to consider that the same MDEA solution was reused over a period of approximately 120 days, and only a small portion was replaced due to eventual losses of solvent during the operation.

In previous batch experiments conducted by Sieborg et al. (2024), the biocompatibility of MDEA with CO_2-utilizing microorganisms was assessed. The microbial communities demonstrated the ability to strip the CO_2 and regenerate MDEA. However, the long-term stability of MDEA was not investigated at that time. Our current observations indicate that MDEA is not biodegraded, and its concentrations remain stable for at least 120 days. This finding holds significant economic importance, as tertiary amines like MDEA are more costly compared to the typical monoethanolamine used as absorbent in amine scrubbing

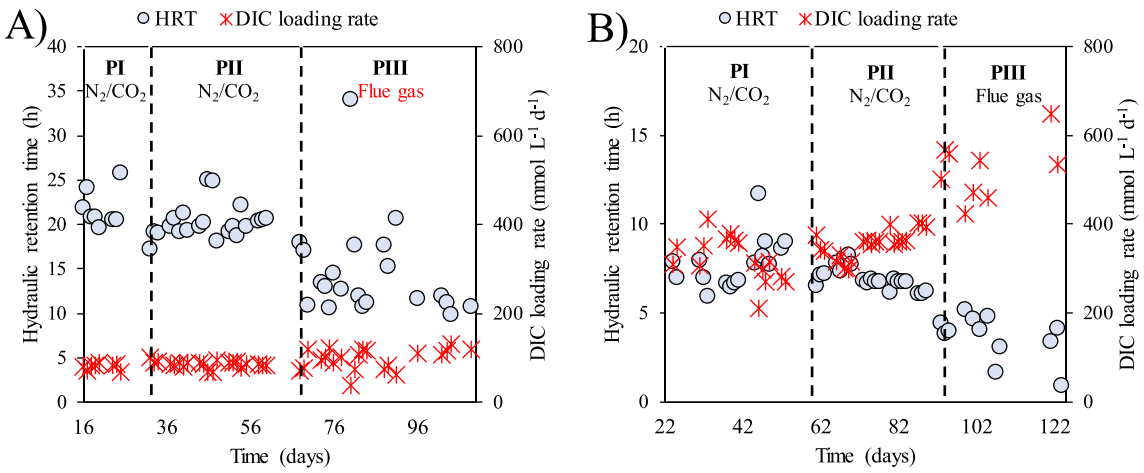


Fig. 4. Hydraulic retention time (HRT) and dissolved inorganic carbon (DIC) loading rate in the continuous stirred tank reactors (CSTR) fed with CO_2 dissolved in the liquid phase and gaseous H_2. The reactors contained: A) 50 mmol/L methyldiethanolamine (MDEA) in phosphate-buffered saline (PBS) solution; and B) 100 mmol/L MDEA in PBS. CO_2 was absorbed either from a clean diluted stream containing 20 % CO_2 in N_2 (phases PI and PII) or flue gas (Phase PIII). The composition of the medium was improved with the addition of minerals in phase PII and afterwards.

processes (Rochelle, 2009). Furthermore, since conventional capture using MDEA employ heating to 120 °C for CO_2 liberation, the low temperatures employed with BICCU could potentially reduce volatility of MDEA and the associated environmental impact of CCU.

3.5. Considerations about the saturation pH in aqueous MDEA solution and perspectives for continuous biomethanation of flue gas-CO_2

The pH of saturation is an important parameter in integrated carbon capture and utilization by microorganisms because: (i) in batch operation, it corresponds to the initial pH of the experiments and most methanogens grow at pH values ranging from 6.0 to 8.0 (Sirohi et al., 2010); and (ii) in continuous reactor systems with pH control, the pH of the rich solvent (i.e. aqueous MDEA saturated with CO_2) plays an important role in the regulation of the pH inside the reactor. Particularly in the reactor configuration proposed in the current study, the pH of the reaction mixture was the parameter used to indicate CO_2 consumption and therefore to control the dosing of the rich amine solution (see Section 2.2). Based on theoretical considerations (Section 2.5), the relationship of saturation pH with temperature, CO_2 partial pressure and MDEA concentration could be formulated.

Fig. 5-A shows the saturation pH in the aqueous amine solution at a given DIC absorption capacity by MDEA and CO_2 partial pressure in the flue gas. As MDEA can capture CO_2 on an equimolar ratio, the DIC and MDEA concentrations will be used interchangeably in this discussion for the sake of simplification (see Supplementary material).

The calculations derived from the Henry's law and Henderson–Hasselbalch equation showed that higher MDEA concentrations give higher saturation pHs with resulting higher DIC concentrations. For instance, 100 mmol/L MDEA solvent absorbing CO_2 from a flue gas with 20 % CO_2 will result in a rich amine solution with pH of 7.49 at 25 °C. Dropping the MDEA concentration to 50 mmol/L will result in a final pH of 7.15 (calculated and measured values diverged in less than 1 %). This phenomenon is related to the increased solubility of CO_2 at higher MDEA concentrations and can be predicted from Eq. (9).

At a fixed MDEA concentration, the saturation pH depends on the temperature and CO_2 partial pressure (Fig. 5-B). Higher temperature of absorption results in higher pH of the saturated MDEA solution. Since CO_2-MDEA is fed into bioreactors in the liquid form, low concentrations of DIC result in higher liquid feed rates and correspondingly shorter HRT's, as demonstrated in the operation of the continuous bioreactors (Section 3.3).

The CO_2 partial pressure is the other key parameter affecting the pH of saturation. The lower the CO_2 concentration in the flue gas, the higher is the saturation pH. For instance, decreasing the CO_2 concentration from 20 to 8 % results in pH shifts in the saturated solvent from 7.15 to 7.59 at 25 °C and 50 mmol/L. Typical CO_2 partial pressures in flue gas are in the range of 3–14 % (Wang and Song, 2020). These concentrations are related to higher saturation pHs, which can reach even higher values at higher temperatures of absorption and higher MDEA concentrations. Any pH setpoint should therefore take into account the different parameters affecting pH of saturation and the resulting reactor operation.

3.6. Dynamics of the microbial communities in the integrated carbon capture and utilization system

The composition of the microbial communities involved in the continuous biomethanation of clean diluted CO_2 and flue gas-CO_2 was investigated using gene amplicon sequencing. Fig. 6-A shows that both the reactors presented similar microbial community structures by the end of the enrichment phase, where both CO_2 and H_2 were supplied in the gas phase and the liquid phase was not replaced. However, when CO_2 was dosed as CO_2-saturated MDEA, R_2 (100 mmol/L MDEA) underwent pronounced shifts in the microbial populations. This was evidenced by the cluster analysis, which showed that samples from R_2 grouped to the right side of the PCA x-axis, whereas R_C (no MDEA added) and R_1 (50 mmol/L) grouped to the left side. Within this last group, R_C retained a similar community composition in its brief operation before CO_2 utilization ceased (Fig. 2). No samples were taken after CO_2 utilization ceased in R_C. R_1 presented gradual shifts in microbial community composition throughout the whole operation.

Methanobacterium was the most abundant genus by the end of the enrichment period, with average relative abundances varying from 37.5 to 60.5 % (Fig. 6). Members of this genus are strictly anaerobic, have optimal growth temperatures at 37–45 °C, and can utilize H_2 as electron donor to reduce CO_2 to CH_4 (Boone, 2015). The predominance of *Methanobacterium* indicates that organisms of this genus are tolerant to the presence of MDEA. *Methanobacterium* further increased in proportion to 58.6 % in R_1, but its average relative abundance decreased to 20.4 % in R_2 during the operation with clean diluted CO_2, in phase PII. The decrease in relative abundance of *Methanobacterium* in R_2 was followed by an increase in *Paracoccus* (4.8 %), *Soehngenia* (10.4 %) and *Acinetobacter* (18.8 %), suggesting that these organisms adapted to the new conditions. Members of genus *Soehngenia* exhibit a fermentative metabolism, producing acetate from H_2 and CO_2 (Parshina et al., 2003). Their rise in R_2 coincides with metabolic shifts towards acetate synthesis

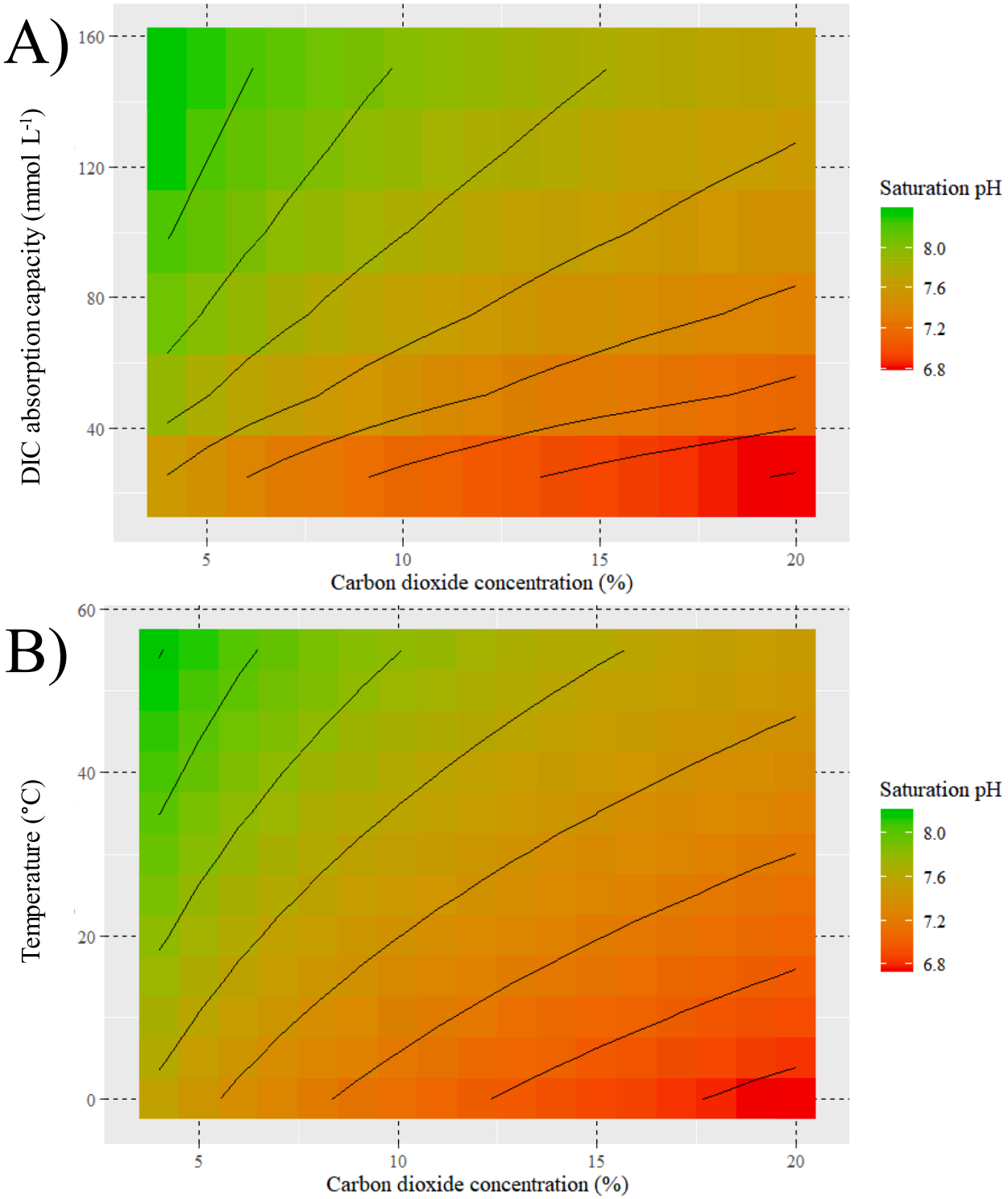
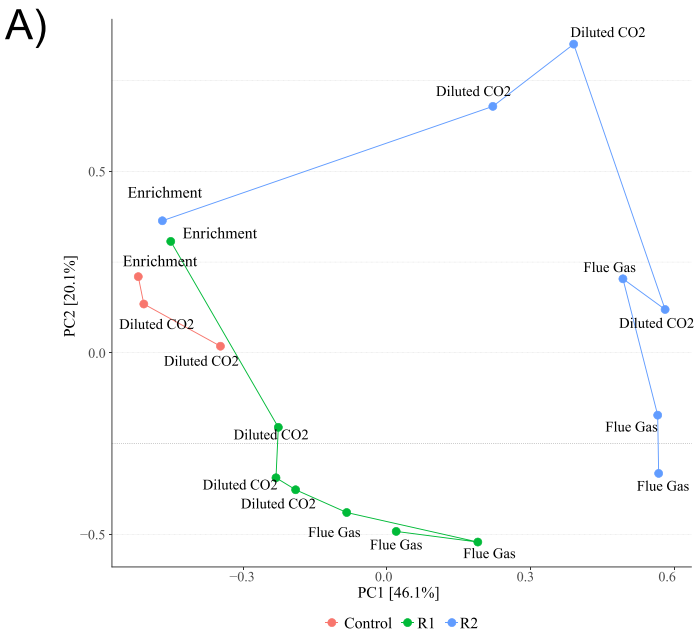


Fig. 5. Ph of aqueous mdea solution saturated with diluted co$_2$. (A) Effects of the dissolved inorganic carbon (DIC) absorption capacity and CO_2 partial pressure at 25 °C; and (B) effects of temperature and CO_2 partial pressure at a fixed DIC absorption capacity (50 mmol/L). DIC and MDEA concentrations are related at a theoretical ratio of 1.0 mol CO_2 mol^{-1} MDEA, or 0.7 mol CO_2 mol^{-1} MDEA, as obtained experimentally.

(see Supplementary material) and a significant reduction in biomethane production during days 61–73. This indicates that *Soehngenia* can outcompete hydrogenotrophic methanogens under higher MDEA concentrations, which was not observed in R_1 or in the control.

Aerobic, microaerophilic and facultative aerobic bacteria such as *Acinetobacter*, *Alcaligenes*, *Pseudomonas,* and *Ochrobactrum* also increased in proportion during phase PII in both the reactors (Akiyama et al., 1992; Baumann, 1968; ElAdawy et al., 2012; Özen and Ussery, 2012). The enrichment of these bacteria could arise during exposure to oxygen in the collecting tanks receiving the CO_2 lean MDEA. Despite this exposure to oxygen in the receiving tanks, we did not observe a reduction in the system's performance associated with the rise in these groups.

After flue gas was used as source of CO_2, both R_1 and R_2 samples shifted towards the lower right side of the PCA plot, indicating that flue



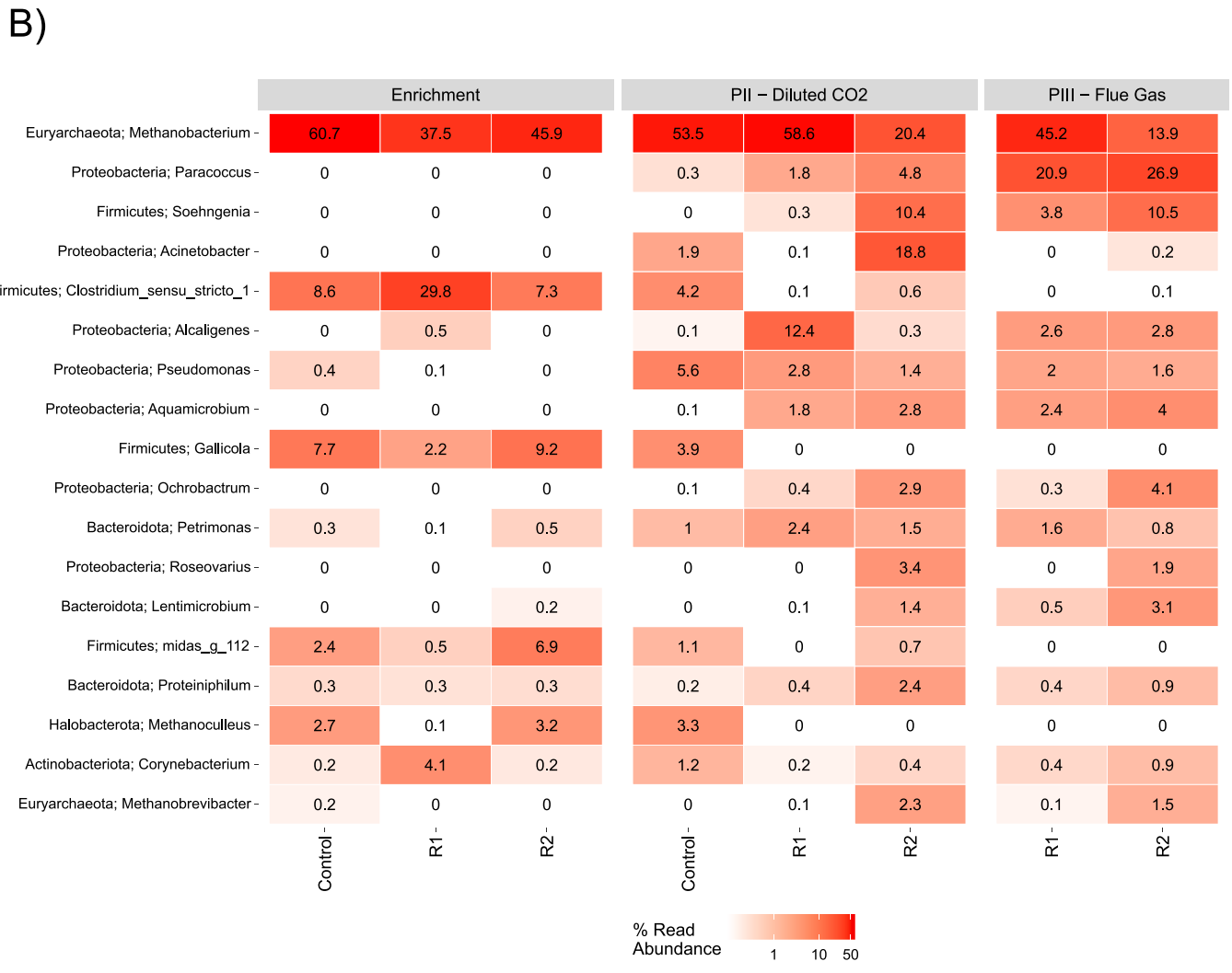


Fig. 6. A) Principal component analysis (PCA) conducted using Bray-Curtis distance and Hellinger transformation for the microbial communities in the continuous stirred tank reactors used for biomethane production from clean diluted CO_2 (PII) or flue gas (PIII). The reactors contained either 50 mmol/L (R_1) or 100 mmol/L (R_2) methyldiethanolamine in phosphate-buffered saline solution. The trajectory between sample points represents the system's operation days starting from the end of the enrichment phase. B) Heatmap of the top 18 operational taxonomic units (OTUs) in R_1 and R_2 during operation with the different feed gases. Known biological function of genus level taxa was retrieved from the MiDAS field guide database.

gas is a relevant source of variation in the dataset. The relative abundance of *Paracoccus* increased from 1.8 to 20.9 %, in R_1, and from 4.8 to 26.9 %, in R_2. Members of this genus can oxidize H_2 with oxygen (Häring and Conrad, 1991), which is consistent with the presence of oxygen in the flue gas. These results further corroborate the reduction of 12 % in the VMPR in R_1 during this period, compared to the operation with clean diluted CO_2, although the same DIC and H_2 loads were applied in both phases (Section 3.2). Therefore, a fraction of the H_2 was utilized in pathways not related to CO_2 utilization, but O_2 reduction instead. The O_2 consumption by *Paracoccus* was important to keep its concentration low (<0.5 mg L^{-1} O_2) even after long periods of gas absorption from flue gas, protecting the methanogenic communities from its inhibitory effects. Although H_2 conversion with O_2 represents a loss of energy, it therefore serves as a mechanism to protect the obligate anaerobes like *Methanobacterium*.

The adaptability of the microbial communities observed in this study is a crucial aspect, making the BICCU system robust and reliable even when exposed to changing conditions. The ability to reduce the cost of flue gas capture and conversion furthermore enables the activation of flue gasses as a resource for production of fuels and chemicals. Renewable natural gas in the form of biomethane, is today mainly supplied from biogas. In Europe, the 2030 target is the production of 1231 PJ renewable biomethane (European Biogas Association, 2022), which could be increased by employing methanation of biogas CO_2. This production, however, only covers a fraction of the European consumption of natural gas corresponding to 13,722PJ in 2022 (Eurostat, 2023). To cover our demand for renewable fuels, there is therefore a dire need for utilizing other CO_2 sources. The proposed BICCU process is potentially suitable for capture and conversion of flue gasses from energy production, fermentation gasses, and flue gasses from chemical industries like cement production, whereas the resulting biomethane could find use in various sectors including energy production, chemical industries, and heavy transportation. The global energy sector alone emitted 36.3 Gt CO_2 in 2021 (International Energy Agency, 2022) and therefore represents a vast and valuable source of CO_2 that can be used as feedstock for production of renewable fuels if cost-efficient carbon capture and utilization can be established. The proposed BICCU process could provide such a route for reducing the energetic economic cost of CCU.

4. Conclusion

Stable biomethanation of flue gas-CO_2 was achieved in the continuous BICCU system using 50 mmol/L MDEA. Shifting to flue gas resulted in a 12 % decrease in the reactor's biomethane production, which was mainly associated with competing pathways related to the oxidation of H_2 in the presence of O_2 from flue gas. Challenges in the operation of the 100 mmol/L reactor arose due to limitations in pH-controlled dosing of CO_2-rich MDEA and lower CO_2 fractions in flue gas. The study demonstrates stable biomethanation of raw flue gas-CO_2 in BICCU systems with continuous bio-mediated regeneration using MDEA as CO_2-capture agent.

CRediT authorship contribution statement

Jean M.S. Oliveira: Methodology, Validation, Formal analysis, Investigation, Data curation, Visualization, Writing – original draft. **Lars D.M. Ottosen:** Writing – review & editing, Funding acquisition. **Michael V.W. Kofoed:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Michael Vedel Wegener Kofoed reports financial support was provided by Apple Inc. Michael VW Kofoed has patent #PCT/EP2023/069435 pending to Aarhus University. Lars DM Ottosen has patent #PCT/EP2023/069435 pending to Aarhus University. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2024.130506.

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