Performance evaluation of a control strategy for photosynthetic biogas upgrading in a semi-industrial scale photobioreactor

María del Rosario Rodero a,b, Andrea Carvajal a,c, Zouhayr Arbib d, Enrique Lara d, César de Prada b, Raquel Lebrero a,b, Raúl Muñoz a,b,c

a Department of Chemical Engineering and Environmental Technology, University of Valladolid, Dr. Mergelina s/n., Valladolid 47011, Spain
b Institute of Sustainable Processes, University of Valladolid, 47011 Valladolid, Spain
c Departamento de Ingeniería Química y Ambiental, Universidad Técnica Federico Santa María, Av. España, 1680 Valparaíso, Chile
d FCC Servicios Ciudadanos, Av. del Camino de Santiago, 40, edificio 3, 4ª planta, 28050 Madrid, Spain

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A B S T R A C T

The validation of a control strategy for biogas upgrading via light-driven CO₂ consumption by microalgae and H₂S oxidation by oxidizing bacteria using the oxygen photosynthetically generated was performed in a semi-industrial scale (9.6 m³) photobioreactor. The control system was able to support CO₂ concentrations lower than 2% with O₂ contents ≤ 1% regardless of the pH in the cultivation broth (ranging from 9.05 to 9.50). Moreover, the control system was efficient to cope with variations in biogas flowrate from 143 to 420 L h⁻¹, resulting in a biomethane composition of CO₂ < 2.4%, CH₄ > 95.5%, O₂ < 1% and no H₂S. Despite the poor robustness of this technology against failures in biogas and liquid supply (CH₄ concentration of 67.5 and 70.9% after 2 h of biogas or liquid stoppage, respectively), the control system was capable of restoring biomethane quality in less than 2 h when biogas or liquid supply was resumed.

1. Introduction

Biogas from the anaerobic digestion of the organic matter present in solid waste, wastewater or energy crops constitutes a valuable source of renewable energy. This green gas can be used for heat and/or power generation due to its high CH₄ content (50–75%) (Surendra et al., 2014). Nevertheless, the presence of contaminants such as CO₂ (30–50%) and H₂S (0.005–2%) hinders the widespread use of this sustainable energy vector (Ryckebosch et al., 2011). In this regard, the removal of CO₂ reduces biogas transportation and compression costs and increases its specific calorific value (Yan et al., 2016). On the other hand, H₂S removal is required since it is a hazardous and corrosive gas that promotes emissions of sulfur oxides (SOₓ) during combustion (Brito et al., 2017). In this context, biogas upgrading is a mandatory step to enable its use as vehicle fuel or its injection into natural gas grids, which requires concentrations in biogas of CH₄ ≥ 90%, CO₂ ≤ 2–4%, O₂ ≤ 1% and trace levels of H₂S according to most international regulations (Muñoz et al., 2015). The recast Renewable Energy Directive (RED II) sets an overall EU target to achieve at least a 32% consumption of energy from renewable sources by 2030, which includes an annual increase of 1.3% in the share of renewable energy in the heating sector and the use of a minimum of 14% renewable energy in the transport sector by 2030 (Directive (EU) (2018)/2001, 2018). Therefore, biomethane has become increasingly attractive in Europe during the past years, where the number of biogas upgrading plants has increased from 187 to 540 in the 2011–2017 period, with a biomethane production up to 19352 GWh in 2017 (EBA, 2018). However, a cost-competitiveness and sustainable biogas upgrading technology is still necessary to boost the use of this promising energy source.

Nowadays, physicochemical methods such as water/organic/chemical scrubbing, pressure swing absorption and membrane separation for CO₂ removal are widely applied for biogas upgrading (EBA, 2018). However, these technologies often need a previous H₂S/siloxane/H₂O abatement step and exhibit a high energy and chemical demand that jeopardize the environmental and economic feasibility of biomethane (Awe et al., 2017). On the other hand, biological biogas upgrading requires a two-step process (microaerobic digestion or biofiltration for H₂S removal followed by hydrogenotrophic CO₂ bioconversion into CH₄) and a surplus of electricity from renewable sources (to produce the H₂ required for microbial CO₂ reduction) (Angelidaki et al., 2018; Muñoz et al., 2015). In this context, photosynthetic biogas upgrading is an attractive alternative for the concomitant and cost-competitive removal of CO₂ and H₂S from biogas (Nagarajan et al., 2019). This process is based on the fixation of CO₂ by microalgae in the presence of light and the oxidation of H₂S to S²⁻/SO₄²⁻ by sulfur-
oxidizing bacteria using the oxygen produced by microalgal photosynthesis (Sun et al., 2016). Moreover, digestate from anaerobic digestion, a nutrient-rich effluent from the process, can be used as N and P source to support microalgal/bacterial growth, which improves the environmental and economic sustainability of this green technology (Ouyang et al., 2015).

The optimization of photosynthetic biogas upgrading coupled with nutrient recovery from digestates, which is commonly implemented in a bubble biogas scrubbing column (AC) interconnected via culture broth recirculation to a photobioreactor where the absorbed CO₂ and H₂S uptake occurs, has been carried out under indoor conditions at lab scale (Bahar et al., 2014; Franco-Morgado et al., 2017; Meier et al., 2018; Rodero et al., 2018; Serejo et al., 2015). Nevertheless, the performance of outdoo systems is governed by the daily and seasonal variations in environmental conditions, the pH in the cultivation broth being a critical parameter that impacts on both H₂S and CO₂ gas–liquid mass transfer in the AC (Bose et al., 2019; Posadas et al., 2017). In addition, the efficiency of the upgrading process could be affected by variations in the daily production and composition of biogas, process shutdowns or technical failures in equipment. In this regard, del Rodero et al. (2019) designed a control system to cope with possible disturbances during photosynthetic biogas upgrading based on the optimization of the liquid to biogas ratio (L/G), which is a key factor determining the CO₂ and H₂S absorption in the AC (Meier et al., 2019). The control system was systematically evaluated in a 180 L high rate algal pond (HRAP) interconnected to an AC under indoor conditions with promising results under most conditions tested (biomethane composition of O₂ < 1% and CO₂ < 2.5% and CH₄ > 94%) (Rodero et al., 2019). However, the validation of any control strategy at a demo scale under outdoors conditions is a requirement prior full-scale implementation of this technology.

This study constitutes, to the best of our knowledge, the first evaluation under outdoors conditions and semi-industrial scale of the performance of a control system devoted to maintain or restore biomethane quality under environmental variations (different pH of the cultivation broth, daily biogas production fluctuations) or operational failures during photosynthetic biogas upgrading.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up was composed of a 9.6 m³ HRAP with an illuminated surface of 32 m² and a depth of 0.3 m, interconnected to a 7 m³ conical settler prior to a 150 L biogas AC via an external recirculation of the cultivation broth. The system was operated outdoors during summer conditions (average ambient temperature and light radiation of 24.2 ± 2°C and 25.5 ± 1.3 MJ m⁻² d⁻¹, respectively) at Chilacana de la Frontera WWTP (36.42’N, 6.15’W) (Spain). The HRAP consisted of two water channels divided by a central wall made of concrete blocks and two flow rectifiers in each loop to avoid dead zones, backflow and eddies (de Gódos et al., 2016). The HRAP was continuously agitated at an internal liquid recirculation velocity of ≈30 cm s⁻¹ by a 6-blade paddlewheel. The average composition of the real centrate, fed at a flow rate of 160 L d⁻¹, was (mg L⁻¹): alkalinity (CaCO₃) = 2420 ± 192, chemical oxygen demand (COD) = 793 ± 214, total nitrogen (TN) = 724 ± 118, ammonium (NH₄⁺) = 579 ± 27, phosphate (PO₄³⁻) = 60 ± 17 and volatile suspended solids (VSS) = 320 ± 248. The inorganic carbon (IC) concentration of the HRAP cultivation broth was adjusted to 1907 ± 109 mg L⁻¹ by addition of NaHCO₃ and Na₂CO₃.

The algal-bacterial biomass was harvested from the bottom of the settler at a rate providing a fixed biomass productivity of 30 g m⁻² d⁻¹. The algal-bacterial biomass was continuously produced (from CO₂, H₂S and nutrient fixation) and harvested, with a fraction being recirculated. This process, and the stability of the algal-bacterial biomass, was confirmed during a recent one-year round evaluation of the technology conducted by the authors (Marín et al., 2018).

Biogas, obtained from the anaerobic digestion of sewage sludge in a 20 m³ digester located at Chilacana de la Frontera WWTP, was sparged into the AC using a polypropylene fine bubble diffuser (ECOTEC, Spain) under countercurrent flow configuration with the clarified cultivation broth (pumped from the top of the settler). Raw biogas composition was 70.5 ± 1.7% CH₄, 31.5 ± 1.1% CO₂ and 52 ± 57 ppm H₂S. The low content of H₂S in the inlet biogas was mediated by the pretreatment performed to the sewage sludge prior anaerobic digestion. Biogas composition (CO₂, CH₄, O₂ and H₂S) was measured using an online gas analyzer INCA 4001 (UNION Instruments GmbH, Germany). The resolution of the sensors of the biogas analyzer was 0.1 vol% for CO₂, O₂ and CH₄ and 1 ppm, in the case of H₂S. The range of measurement was 0–100 vol% for CO₂ and CH₄, 0.25–200 vol% for O₂ and 0–10000 ppm, for H₂S, while the accuracy was ± 1%, ± 1%, ± 3% and ± 10% of the range for CO₂, CH₄, O₂ and H₂S, respectively. The control module was composed of a Programmable Logic Controller (PLC) “S7-315” via an interface developed using the software Human Machine Interface (HMI) Scada “WinCC Flexible 2008 SP4” (Siemens). The pH of the recycling liquid was measured using a Crison pH 4603 probe coupled to a Crison Multimeter 44 display (Barcelona, Spain). The concentration of dissolved IC in the cultivation broth was determined by means of a Shimadzu TOC-VCSH analyzer (Japan) equipped with a TNM-1 chemiluminescence module.

2.2. Control system strategy

A rule-based control system was implemented in order to maintain a biomethane quality over time according to the results reported by del Rodero et al. (2019) during the evaluation of the control system under lab scale indoors conditions. The controlled variables were the O₂ and CO₂ concentration in the biomethane, while the manipulated variable was the recycling liquid flow rate, which consequently modified the L/G ratio in the AC. A set point value of 2% and 1% were set for CO₂ and O₂ concentrations, respectively, in order to comply with the target values for biomethane use as natural gas substitute in most international legislations (including the recent European Standard UNE-EN 16723). The O₂ content in biomethane was also selected as controlled variable since a high O₂ desorption in the AC can result in explosive gas mixtures (Di Benedetto et al., 2011). On the contrary, the CH₄ content in the upgraded biogas was not chosen as controlled variable since negligible losses are typically accounted as a result of its low aqueous solubility, while H₂S content was not considered either based on the higher H₂S removal efficiencies (REs) associated to the superior H₂S aqueous solubility compared to CO₂.

The control system operated based on the differences between the O₂ and CO₂ concentration measured in the upgraded biogas and the set point values fixed, the changes implemented in the recycling liquid flowrate being summarized in Table 1. When the O₂ content in the upgraded biogas was > 1%, the pump flow rate was decreased due to safety reasons even if the CO₂ content in the upgraded biogas was > 2% (set point value). When the O₂ content in the biomethane was < 1% and CO₂ content > 2%, the control system increased the flow rate of the recycling liquid pump in order to enhance the CO₂ gas–liquid mass transfer. Finally, when the O₂ content in the biomethane was < 1% and CO₂ content < 2%, thus complying with the standard values, the flow rate of the recycling liquid pump was also decreased in order to save energy.
Table 1
Variations in the recycling liquid flow rate as a function of the differences between the concentrations of CO$_2$ and O$_2$ in the biogas and the set point values ($\Delta$CO$_2$ and $\Delta$O$_2$, respectively).

<table>
<thead>
<tr>
<th>$\Delta$O$_2$</th>
<th>$\Delta$CO$_2$</th>
<th>Power pump variation (%)</th>
<th>Liquid flow rate variation (L h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\leq 0$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[(−2)−(−1)]$</td>
<td>−6</td>
<td>−45.2</td>
<td></td>
</tr>
<tr>
<td>$[(−1)−(−0.5)]$</td>
<td>−4</td>
<td>−30.1</td>
<td></td>
</tr>
<tr>
<td>$[(−0.5)−0]$</td>
<td>−2</td>
<td>−15.1</td>
<td></td>
</tr>
<tr>
<td>$[0−0.5]$</td>
<td>5</td>
<td>37.6</td>
<td></td>
</tr>
<tr>
<td>$[0.5−1]$</td>
<td>10</td>
<td>75.3</td>
<td></td>
</tr>
<tr>
<td>$[1−5]$</td>
<td>15</td>
<td>112.9</td>
<td></td>
</tr>
<tr>
<td>$[5−10]$</td>
<td>20</td>
<td>150.5</td>
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<tr>
<td>$&gt;20$</td>
<td>30</td>
<td>225.8</td>
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<tr>
<td>$[0−0.5]$</td>
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<td>−37.6</td>
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<td>$[0.5−1]$</td>
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<td>$&gt;5$</td>
<td>−20</td>
<td>−150.5</td>
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</table>

2.3. Validation of the control strategy

The performance of the proposed control strategy was evaluated under different pH values in the cultivation broth (9.05, 9.20, 9.35, 9.50) for 8 h when the system operated under steady state. The initial L/G ratio was 0.8 (corresponding to the lowest L/G ratio that could be reached in the demo experimental set-up).

Process response to the stepwise variations in biogas flow rate (every 1 h and 20 min) from 143 L h$^{-1}$ to 218, 300 and 420, and back to 143 L h$^{-1}$, was tested under controlled and uncontrolled conditions. The inlet pH of the cultivation broth in the AC was 9.20 and the initial liquid flow rate was maintained at 327 L h$^{-1}$ (minimum value) during the uncontrolled conditions.

Finally, the robustness of the technology towards operational failures in biogas supply and in the liquid recirculation was assessed. After process monitoring for 4 h under steady state, the biogas compressor or the recycling liquid pump were turned off for 2 h, and subsequently switched on again followed by process monitoring for the next 4 h under controlled and uncontrolled conditions. During the robustness test, the inlet pH of the cultivation broth in the AC was 9.35, the biogas flow rate was set at 420 L h$^{-1}$ and the initial L/G was fixed based on the minimum L/G ratio able to provide a satisfactory biomethane quality (CO$_2$ content ≤ 2%) under these operational conditions (L/G ≈ 1.1–1.2).

In all experiments, the composition of the upgraded biogas was measured every 20 min prior actuation of the control system.

3. Results and discussion

3.1. Evaluation of process performance under different pH in the cultivation broth

The effect of the pH of the cultivation broth on the performance of photosynthetic biogas upgrading was evaluated. The upgraded biogas composition, L/G ratios and recycling liquid pH at the outlet of the AC under uncontrolled (initial values) and controlled conditions at different pHs of the cultivation broth (9.5, 9.35, 9.2 and 9.05) are shown in Fig. 1. In this regard, a slight drop in the pH of the cultivation broth (−0.15) caused a remarkable decrease in the CO$_2$ gas–liquid mass transfer in the AC under uncontrolled conditions despite the high alkalinity of the cultivation broth (1907 ± 109 mg IC L$^{-1}$). The CO$_2$ concentration in the upgraded biogas increased from 2.7 ± 0.1 to 4.9 ± 0.1, 9.7 ± 0.1 and 12.0 ± 0.0%, which corresponded to CO$_2$-REs of 93.4, 87.7, 77.9 and 68.5%, at a pH of 9.50, 9.35, 9.20 and 9.05, respectively, exceeding the CO$_2$ set point value (2%) at a L/G ratio of 0.8 (Fig. 1a). These results agreed with those reported in a pilot scale HRAP by Bahr et al. (2014), who obtained CO$_2$-REs < 50% at a pH of 9 and a L/G ratio of 0.4 and CO$_2$-REs > 90% at a pH of 10. Likewise, del Rodero et al. (2019) recorded CO$_2$ concentrations in the upgraded biogas < 2% and 16% at a pH of 10 and 8.5, respectively, under similar conditions (L/G ratio of 0.5 and 1500 mg IC L$^{-1}$ in the cultivation broth). In this context, dissolved inorganic carbon in water is a mixture of CO$_2$ (aq), HCO$_3^−$ and CO$_2^{2−}$, the dissociation constants being $pK_a2 = 6.35$ and $pK_a3 = 10.3$ at 25 °C (Lee and Pirt, 1984). In our particular study, the dissolved inorganic carbon in the liquid phase was composed of HCO$_3^−$ (main species) and CO$_2^{2−}$ in the range of pH tested (9.05–9.50). In this specific range, a slight increase in pH of 0.15 shifted the equilibrium towards more CO$_2^{2−}$-formation, thus increasing the CO$_2$ gas–liquid concentration gradient, and consequently higher CO$_2$ removals were achieved.

On the other hand, a complete H$_2$S removal was achieved regardless of the pH of the cultivation broth as a result of its higher aqueous solubility compared to CO$_2$ (according to Henry’s dimensionless constant) and low concentration in the inlet biogas (52 ± 57 ppmv of H$_2$S) (Sander, 1999). Moreover, since the sulfide dissociation constants are $pK_a1 = 7.04$ and $pK_a2 = 11.95$ at 18 °C (Smet et al., 1998), the predominant species in the liquid phase in the range of pH studied (9.05–9.50) was H$_2$S$^−$, thus increasing the H$_2$S gas–liquid concentration gradient and consequently the mass transfer. In this context, Kang et al. (2020) observed a rapid increase in the aqueous H$_2$S concentration at pH 10 due to the 100 times higher H$_2$S equilibrium aqueous concentration in comparison with that at pH 8. On the other hand, the oxidation of H$_2$S in the liquid phase can be chemical (supported by the high dissolved oxygen in the cultivation broth) and/or biological (by sulfur-oxidizing bacteria, i.e. Thioalbus genus) (Meier et al., 2018; Toledo-Cervantes et al., 2016). In this regard, although sulfur oxidation can result in different products (S$_2^−$, S$_2$O$_3^{2−}$ and SO$_4^{2−}$), SO$_4^{2−}$ is typically the major end-product due to the high dissolved oxygen (up to 21.6 mg O$_2$ L$^{-1}$) and pH in the cultivation broth of algal-bacterial photobioreactors (Kang et al., 2020; Meier et al., 2018).

Consequently, the CH$_4$ concentration in the upgraded biogas accounted for 97.3 ± 0.1, 95.1 ± 0.1, 90.3 ± 0.1 and 88.0 ± 0.0% at a pH of 9.50, 9.35, 9.20 and 9.05, respectively, under uncontrolled conditions, while O$_2$ concentration in the upgraded biogas was always negligible due to the low initial L/G ratio (0.8) (Fig. 1). In this regard, Toledo-Cervantes et al. (2017) recorded a slightly higher O$_2$ desorption in the upgraded biogas (O$_2$ content < 0.8%) under counter-current operation at a L/G ratio of 0.8 (similar conditions to this study), while the O$_2$ content was almost zero under co-current operation.

When the control system was initiated, the CO$_2$ concentration decreased to values lower than the set point (2%) after 1 h at the highest pH (9.50) and 2 h at the lowest (9.05), and remained stable afterwards (Fig. 1a). No H$_2$S concentration was detected in the upgraded biogas regardless of the pH. Interestingly, the O$_2$ concentrations in the biomethane were higher when the control was active compared to those without control as a result of the higher L/G ratios in the AC. However, these concentrations remained below the set point (O$_2$ concentration = 1%) in most of the experiments except at a pH of 9.05, where a maximum O$_2$ concentration of 1% was achieved (Fig. 1b). Maximum L/G ratios of 1.3, 1.7, 2.1 and 2.4, which corresponded to liquid flowrates of 515, 681, 816 and 967 L h$^{-1}$, were recorded at a pH...
of 9.50, 9.35, 9.20 and 9.05, respectively (Fig. 1c). In fact, a lower decrease in the pH along the AC was obtained when the control system was active (0.2 ± 0.1 vs 0.7 ± 0.1) due to process operation at higher L/G ratios (Fig. 1d). This lower decrease in the pH at higher L/G ratios was associated to the lower mass of CO₂ transferred per recycling liquid volume (Table S1), which allowed to achieve higher CO₂-REs (Posadas et al., 2017). In this context, the limited acidification of the liquid along the AC due to the higher L/G ratios when the system was controlled resulted in higher CO₂-REs. This was mediated by the equilibrium shift from CO₂ to HCO₃⁻ and CO₃²⁻, which supported higher gas–liquid CO₂ concentration gradients.

3.2. Process response to stepwise variations in biogas flowrate

The daily production of biogas might vary as a result of changes in the feedstock mass flowrate or composition and temperature in the anaerobic digester, which directly impacts on the upgrading process (Kim and Lee, 2016; Theuerl et al., 2019). Fig. 2 shows the upgraded biogas composition and liquid flowrate in the AC under controlled and uncontrolled conditions during the stepwise variations in biogas flowrate from 143 L h⁻¹ to 218, 300 and 420, and back to 143 L h⁻¹.

The CO₂ concentration in the upgraded biogas increased from 2.5 to 14.1%, when the biogas flowrate was stepwise increased from 143 to 218, 300 and 420 L h⁻¹ under uncontrolled conditions (at a constant liquid flowrate of 327 L h⁻¹), which corresponded to a decrease in the L/G ratio from 2.3 to 0.8. These results were in accordance with Marín et al. (2019), who reported a decrease in the CO₂ content from 9.6% to negligible values when increasing the L/G ratio from 0.5 to 2.0. Subsequently, when the biogas flowrate was stepwise decreased from 420 to 300 L h⁻¹, the CO₂ concentration slightly increased up to 16.1% as a result of the previous acidification of the liquid remaining in the AC. Then, the concentration of CO₂ gradually decreased to 6.0% at the lowest biogas flowrate of 143 L h⁻¹ (Fig. 2a). The O₂ and H₂S concentrations in the upgraded biogas were negligible in the absence of control strategy, while CH₄ concentration was correlated to CO₂ removal, with a maximum concentration of 97.6% at 143 L h⁻¹ (at the beginning of the assay) and a minimum CH₄ concentration in the upgraded biogas of 83.9% at 300 L h⁻¹ (after the decrease from 420 L h⁻¹) (Fig. 2b). Overall, the system was not able to achieve a biomethane quality complying with most international standards (CO₂ content ≤ 2% and CH₄ content ≥ 90%) without control system.

Biomethane quality improved significantly when the control system was active. Indeed, the CO₂ concentration recorded in the upgraded biogas reached a maximum of 2.4% (~6.7 times lower than that without control) and remained almost constant at ~2% regardless the stepwise variations in biogas flowrate from 143 L h⁻¹ to 218, 300 and 420, and back to 143 L h⁻¹ (Fig. 2a). A complete H₂S removal was achieved, while low O₂ concentrations in the biomethane (~0.5%) were recorded even at the maximum L/G ratio of 4.9 (corresponding to a liquid flowrate of 703 L h⁻¹) (Fig. 2c). These high L/G ratios occurred during the stepwise decrease in the biogas flowrate, since the liquid flowrates imposed by the control system were still high due to the culture broth acidification caused by the previous biogas flowrates. In this context, the lower O₂ desorption recorded at higher L/G ratios compared to that reported in section 3.1, where the O₂ concentration in the biomethane was 1% at a pH of 9.05 and a L/G ratio of 2.3, could be attributed to the higher liquid flowrate reached in the previous section (967 L h⁻¹) and the lower biogas flowrate (143 or 218 L h⁻¹) in the present experiment, which supported a lower turbulence in the AC and a lower O₂ gas–liquid mass transfer in this unit. In this context, tur-

Fig. 1. Time course of a) CO₂ (solid) and O₂ (open) concentrations in the upgraded biogas, b) CH₄ concentration in the upgraded biogas, c) liquid to biogas (L/G) ratio in the absorption column and d) outlet pH of the recycling liquid in the absorption column at a pH of the cultivation broth of 9.50 (square), 9.35 (circle), 9.20 (triangle) and 9.05 (star).
bulence in the AC impacts on the average bubble size, which itself is inversely proportional to both components of the overall mass transfer coefficient (ka): the specific area (a) and the liquid transport coefficient (k_l) (Bordel et al., 2008). Finally, it should be stressed that the CH₄ concentration in the upgraded biogas was > 95.5% during the complete experimental period under controlled conditions (Fig. 2b). In brief, the control strategy implemented was effective to cope with variations in the biogas flow rate over time.

3.3. Robustness under operational failures in biogas supply and in the liquid recirculation

Operational failures typically occur in biogas upgrading plants at full scale, which impacts on biomethane quality during the failure and/or afterwards when the system is restored. This requires the evaluation of the control system performance under the most relevant equipment failures in photosynthetic biogas upgrading (stoppage of biogas supply or liquid recirculation). The upgraded biogas composition and liquid flowrate in the AC under controlled and uncontrolled conditions during a 2 h failure in biogas supply or liquid recirculation are shown in Figs. 3 and 4, respectively.

Under uncontrolled conditions at a L/G ratio of 1.1, the CO₂ concentration in the upgraded biogas accounted for 1.8 ± 0.1% during the initial hours of the experiment assessing the robustness of the technology against a failure in biogas supply. The concentration of CO₂ remained constant at 1.9% for the next 2 h without biogas supply (Fig. 3a), which could be attributed to the biomethane accumulated in an open to atmosphere gasometer located immediately after the biogas analyzer. Interestingly, the CH₄ concentration was negatively impacted

Fig. 2. Time course of a) CO₂ (square) and O₂ (circle) concentrations in the upgraded biogas, b) CH₄ concentration in the upgraded biogas and c) liquid flow rate (L) under controlled (open) and uncontrolled (solid) conditions during the stepwise variation in biogas flow rate (G) (continuous line).

Fig. 3. Time course of a) CO₂ (square) and O₂ (circle) concentrations in the upgraded biogas, b) CH₄ concentration in the upgraded biogas and c) liquid flow rate (L) under controlled (open) and uncontrolled (solid) conditions during a failure in biogas supply (G).
by the biogas compressor failure, decreasing from 98.1 to 62.6% after 2 h without biogas supply (Fig. 3b). This decrease can be explained by the entrance of air in the system, which was confirmed by the increase in O\textsubscript{2} concentration up to 7.5% after 2 h (Fig. 3a). When biogas supply was re-started, the O\textsubscript{2} concentration rapidly decreased to 0.3% within 20 min, with an associated increase in CH\textsubscript{4} concentration up to 96.8%, CO\textsubscript{2} concentrations ~1.8% and no H\textsubscript{2}S detected (Fig. 3a, b). This rapid increase in CH\textsubscript{4} content was mediated by the high biogas flowrate used during this experiment (420 L h\textsuperscript{-1}), which flushed the air out of the system. However, the CO\textsubscript{2} concentration slightly increased to ~2.2% following 1.5 h from the restoration of biogas supply (due to a slight decrease in the pH of the cultivation broth) and remained constant afterwards.

When the control system was initiated, the liquid flowrate fluctuated between 448 and 598 L h\textsuperscript{-1} during the first hours of experiment in order to maintain biomethane quality under optimal conditions in terms of energy consumption (Fig. 3a, c). The CO\textsubscript{2} content in the absence of biogas supply remained constant at ~1.9%, while an increase in the O\textsubscript{2} concentration from 0 to 6.4% was recorded as a result of air entrance, similar to that observed without control system (Fig. 3a). Thus, the control system decreased the liquid flowrate down to the minimum value (327 L h\textsuperscript{-1}) in order to prevent a high O\textsubscript{2} content in the upgraded biogas. In this context, when biogas supply was restarted, CO\textsubscript{2} concentration in the upgraded biogas increased up to 2.5% as a result of the low liquid flowrate. Nevertheless, the system was able to decrease the CO\textsubscript{2} concentration to 2% by the end of the experiment by imposing a liquid flowrate of 779 L h\textsuperscript{-1} (Fig. 3a, c). The CH\textsubscript{4} concentration in the biomethane decreased from 98.0 to 67.5% in the absence of biogas supply, increasing to 97.7% within only 20 min after the resumption of biogas supply (Fig. 3b). No H\textsubscript{2}S was detected in the upgraded biogas along the experiment under controlled conditions. Overall, similar results were obtained under controlled and uncontrolled conditions, the system without control being even more effective when biogas supply was restarted. However, in case of an eventual increase in the CO\textsubscript{2} content resulting from any variation in the cultivation broth, the system would not be able to recover the initial CO\textsubscript{2} concentration without control.

CO\textsubscript{2} content in the upgraded biogas remained constant at 1.9 ± 0.1% during the first hours under uncontrolled conditions at a L/G of 1.2 in the experiment assessing the robustness of the technology against a shutdown in the liquid supply to the AC. When the recirculating liquid pump was turned off, CO\textsubscript{2} concentration in the upgraded biogas rapidly increased up to 28.9% within 2 h, which almost matched the CO\textsubscript{2} concentration of the raw biogas (31.5 ± 1.1%). This poor CO\textsubscript{2}-RE was due to the acidification and CO\textsubscript{2} saturation of the liquid present in the biogas AC. However, the CO\textsubscript{2} concentration in the upgraded biogas rapidly decreased when the liquid pump was turned on since the liquid retention time in the AC was only 17.5 min under the working liquid flowrate (515 L h\textsuperscript{-1}). Unfortunately, the system was not able to recover the initial biomethane quality, with CO\textsubscript{2} concentrations of 2.3% after approximately 2.5 h from liquid supply restoration (Fig. 4a). On the other hand, the CH\textsubscript{4} content in the upgraded biogas decreased from 97.9 to 71.1% and increased up to 97.7% when the liquid pump was restarted (Fig. 4b). Despite the acidification of the scrubbing solution during the period without liquid renewal in the AC, negligible H\textsubscript{2}S concentrations (1 ppm) were detected as a result of its low concentration in the raw biogas. Finally, no significant O\textsubscript{2} concentrations (<0.2%) were recorded in the upgraded biogas along this experiment.

When the control system was active, minor variations in the liquid flowrate were recorded (470–560 L h\textsuperscript{-1}) and the CO\textsubscript{2} content remained below 2% (Fig. 4a, c). When the liquid recirculation was stopped, the CO\textsubscript{2} concentration in the upgraded biogas increased up to 29.1%, but no H\textsubscript{2}S was detected as under uncontrolled conditions (Fig. 4a). The control system sent control actions of increasing the liquid flowrate (CO\textsubscript{2} measured > CO\textsubscript{2} set point and O\textsubscript{2} ≤ 0) during the period with no liquid supply since it was not able to detect the liquid pump failure. Therefore, when the liquid pump was switched on, the liquid flowrate imposed by the control system corresponded to the maximum pump flowrate (~1000 L h\textsuperscript{-1}). This entailed a decrease in the CO\textsubscript{2} content of the upgraded biogas faster than under uncontrolled conditions due to the higher L/G ratio (2.4 vs 1.2) (Fig. 4c). However, the decrease in the CO\textsubscript{2} content could have been even faster if higher pumping capacity would be available. On the other hand, the O\textsubscript{2} content in the upgraded biogas increased when the liquid pump was turned on as a re-
surfactant of the high liquid flowrate, but remained always below 1%. Finally, the CH₄ content in the upgraded biogas decreased from 98.0 to 79.9% due to the negligible CO₂-REs in the absence of liquid recirculation. Nevertheless, CH₄ content rapidly increased up to 95.8% when the liquid supply was restored although this value was lower compared to process operation without control system. This decrease was mediated by the higher O₂ and N₂ desorption from the recycling liquid to the bio-methane as a result of the higher recycling liquid flowrate. Overall, the control system was able to provide a satisfactory biomethane quality in the event of a liquid supply stoppage, while in the absence of control system the CO₂ concentration remained > 2% after liquid supply restoration.

4. Conclusions

The control system based on changes in the recycling liquid flowrate was able to meet the target biomethane quality (CO₂ < 2% and O₂ < 1%) regardless of the pH and biogas flowrate. Despite the poor robustness of this technology against failures in biogas and liquid supply was confirmed, the control system restored the biomethane quality satisfactorily after the event of a stoppage in biogas supply and liquid recirculation. This control strategy validated in an outdoors semi-industrial scale photobioreactor would overcome the negative effects of environmental variations or operational failures on photosynthetic biogas upgrading performance, ensuring a consistent biomethane quality.

CRediT authorship contribution statement

Maria del Rosario Rodero: Investigation, Methodology, Data curation, Writing - original draft. Andrea Carvajal: Conceptualization, Methodology, Data curation. Zouhayr Arbib: Project administration, Resources. Enrique Lara: Project administration, Resources. César de Prada: Methodology, Software. Raquel Lebrero: Conceptualization, Funding acquisition, Supervision, Writing - review & editing. Raúl Muñoz: Conceptualization, Funding acquisition, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


