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

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ABSTRACT

The validation of a control strategy for biogas upgrading via light-driven CO_2 consumption by microalgae and H_2S oxidation by oxidizing bacteria using the oxygen photosynthetically generated was performed in a semi-industrial scale (9.6 m^3) photobioreactor. The control system was able to support CO_2 concentrations lower than 2% with O_2 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 CO_2 < 2.4%, CH_4 > 95.5%, O_2 < 1% and no H_2S. Despite the poor robustness of this technology against failures in biogas and liquid supply (CH_4 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 CH_4 content (50–75%) (Surendra et al., 2014). Nevertheless, the presence of contaminants such as CO_2 (30–50%) and H_2S (0.005–2%) hinders the widespread use of this sustainable energy vector (Ryckebosch et al., 2011). In this regard, the removal of CO_2 reduces biogas transportation and compression costs and increases its specific calorific value (Yan et al., 2016). On the other hand, H_2S removal is required since it is a hazardous and corrosive gas that promotes emissions of sulfur oxides (SO_x) 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 CH_4 ≥ 90%, CO_2 ≤ 2–4%, O_2 ≤ 1% and trace levels of H_2S 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 CO_2 removal are widely applied for biogas upgrading (EBA, 2018). However, these technologies often need a previous H_2S/siloxane/H_2O 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 require a two-step process (microaerobic digestion or biofiltration for H_2S removal followed by hydrogenotrophic CO_2 bioconversion into CH_4) and a surplus of electricity from renewable sources (to produce the H_2 required for microbial CO_2 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 CO_2 and H_2S from biogas (Nagarajan et al., 2019). This process is based on the fixation of CO_2 by microalgae in the presence of light and the oxidation of H_2S to S^0/SO_4^{2-} by sulfur-

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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 CO_2 and H_2S uptake occurs, has been carried out under indoors conditions at lab scale (Bahr et al., 2014; Franco-Morgado et al., 2017; Meier et al., 2018; Rodero et al., 2018; Serejo et al., 2015). Nevertheless, the performance of outdoors 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 H_2S and CO_2 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 CO_2 and H_2S 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 indoors conditions with promising results under most conditions tested (biomethane composition of $O_2 < 1\%$ and $CO_2 < 2.5\%$ and $CH_4 > 94\%$) (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 m^3 HRAP with an illuminated surface of 32 m^2 and a depth of 0.3 m, interconnected to a 7 m^3 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 radiance of 24.2 ± 2.0 °C and 25.5 ± 1.3 MJ m^{-2} d^{-1}, respectively) at Chiclana 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 Godos 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 ($CaCO_3$) = 2420 ± 192, chemical oxygen demand (COD) = 793 ± 214, total nitrogen (TN) = 724 ± 118, ammonium ($N\text{-}NH_4^+$) = 579 ± 27, phosphate ($P\text{-}PO_3^{4-}$) = 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 $NaHCO_3$ and Na_2CO_3.

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 CO_2, H_2S 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 m^3 digester located at Chiclana 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% CH_4, 31.5 ± 1.1% CO_2 and 52 ± 57 ppm H_2S. The low content of H_2S in the inlet biogas was mediated by the pretreatment performed to the sewage sludge prior anaerobic digestion. Biogas composition (CO_2, CH_4, O_2 and H_2S) 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 CO_2, O_2 and CH_4 and 1 ppm_v in the case of H_2S. The range of measurement was 0–100 vol% for CO_2 and CH_4, 0–25 vol% for O_2 and 0–10000 ppm_v for H_2S, while the accuracy was ± 1%, ±1%, ±3% and ± 10% of the range for CO_2, CH_4, O_2 and H_2S, 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 O_2 and CO_2 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 CO_2 and O_2 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 O_2 content in biomethane was also selected as controlled variable since a high O_2 desorption in the AC can result in explosive gas mixtures (Di Benedetto et al., 2011). On the contrary, the CH_4 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 H_2S content was not considered either based on the higher H_2S removal efficiencies (REs) associated to the superior H_2S aqueous solubility compared to CO_2.

The control system operated based on the differences between the O_2 and CO_2 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 O_2 content in the upgraded biogas was > 1%, the pump flow rate was decreased due to safety reasons even if the CO_2 content in the upgraded biogas was > 2% (set point value). When the O_2 content in the biomethane was < 1% and CO_2 content > 2%, the control system increased the flow rate of the recycling liquid pump in order to enhance the CO_2 gas–liquid mass transfer. Finally, when the O_2 content in the biomethane was < 1% and CO_2 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 flowrate as a function of the differences between the concentrations of CO_2 and O_2 in the biomethane and the set point values (ΔCO_2 and ΔO_2, respectively).

ΔO_2	ΔCO_2	Power pump variation (%)	Liquid flow rate variation (L h $^{-1}$)
≤0	[(−2)–(−1)]	−6	−45.2
	[(−1)–(−0.5)]	−4	−30.1
	[(−0.5)–0]	−2	−15.1
	[0–0.5]	5	37.6
	[0.5–1]	10	75.3
	[1–5]	15	112.9
	[5–10]	20	150.5
	[10–20]	25	188.2
	>20	30	225.8
[0–0.5]		–5	–37.6
[0.5–1]		–10	–75.3
[1–5]		–15	–112.9
>5		–20	–150.5

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 flowrate (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 flowrate 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 flowrate 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_3^{2-}, the dissociation constants being pka_1 = 6.35 and pka_2 = 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_3^{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_3^{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_2S 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 ppm_v of H_2S) (Sander, 1999). Moreover, since the sulfide dissociation constants are pka_1 = 7.04 and pka_2 = 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 HS^-, thus increasing the H_2S gas–liquid concentration gradient and consequently the mass transfer. In this context, Kang et al. (2020) observed a rapid increase in the aqueous H_2S concentration at pH 10 due to the 100 times higher H_2S equilibrium aqueous concentration in comparison with that at pH 8. On the other hand, the oxidation of HS^- 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^0, $S_2O_3^{2-}$ 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_2S 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

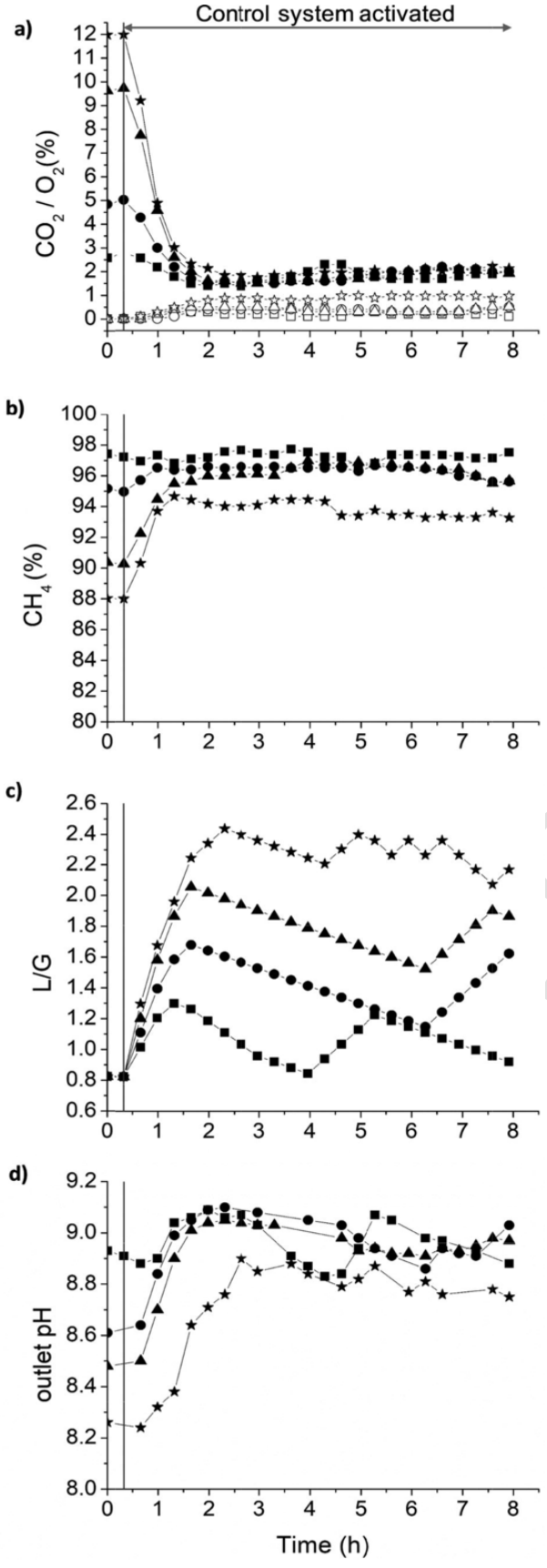

Fig. 1. Time course of a) CO_2 (solid) and O_2 (open) concentrations in the upgraded biogas, b) CH_4 concentration in the upgraded biogas, c) liquid to biogas (L/G) ratio in the absorption column and d) outlet pH of the recycling liquid in the absorption column at a pH of the cultivation broth of 9.50 (square), 9.35 (circle), 9.20 (triangle) and 9.05 (star).

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 CO_2 transferred per recycling liquid volume (Table S1), which allowed to achieve higher CO_2-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 CO_2-REs. This was mediated by the equilibrium shift from CO_2 to HCO_3^- and CO_3^{-2}, which supported higher gas–liquid CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 gradually decreased to 6.0% at the lowest biogas flowrate of 143 L h^{-1} (Fig. 2a). The O_2 and H_2S concentrations in the upgraded biogas were negligible in the absence of control strategy, while CH_4 concentration was correlated to CO_2 removal, with a maximum concentration of 97.6% at 143 L h^{-1} (at the beginning of the assay) and a minimum CH_4 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 (CO_2 content ≤ 2% and CH_4 content ≥ 90%) without control system.

Biomethane quality improved significantly when the control system was active. Indeed, the CO_2 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 H_2S removal was achieved, while low O_2 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 O_2 desorption recorded at higher L/G ratios compared to that reported in section 3.1, where the O_2 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 O_2 gas–liquid mass transfer in this unit. In this context, tur-

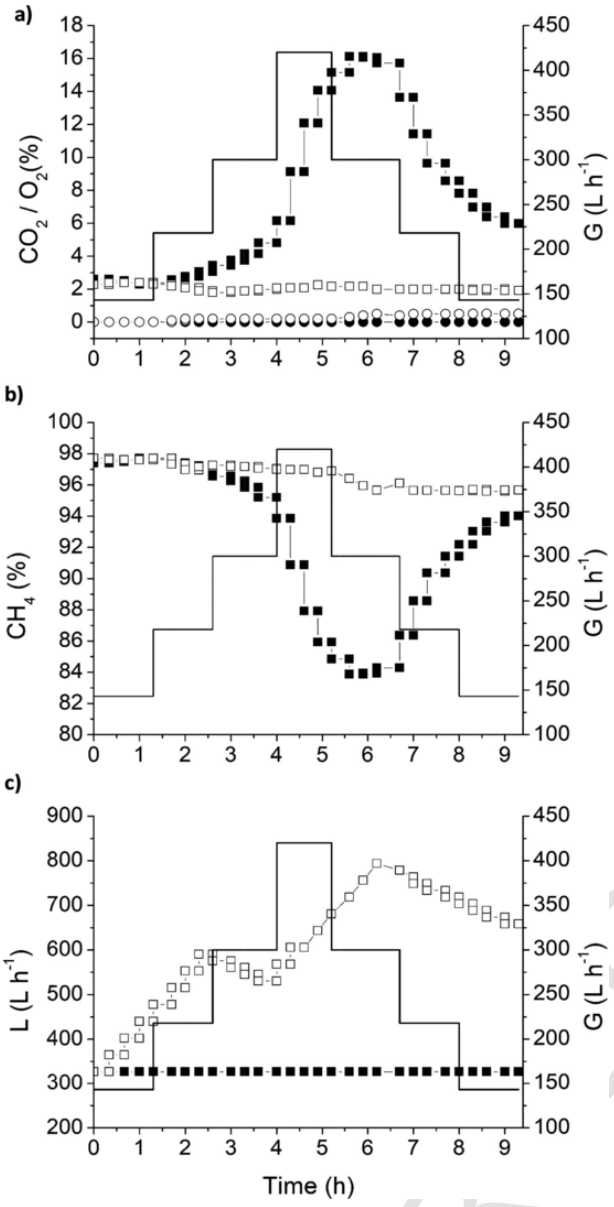

Fig. 2. Time course of a) CO_2 (square) and O_2 (circle) concentrations in the upgraded biogas, b) CH_4 concentration in the upgraded biogas and c) liquid flowrate (L) under controlled (open) and uncontrolled (solid) conditions during the stepwise variation in biogas flowrate (G) (continuous line).

bulence in the AC impacts on the average bubble size, which itself is inversely proportional to both components of the overall mass transfer coefficient (k_la): the specific area (a) and the liquid transport coefficient (k_l) (Bordel et al., 2008). Finally, it should be stressed that the CH_4 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 flowrate 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 CO_2 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 CO_2 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 CH_4 concentration was negatively impacted

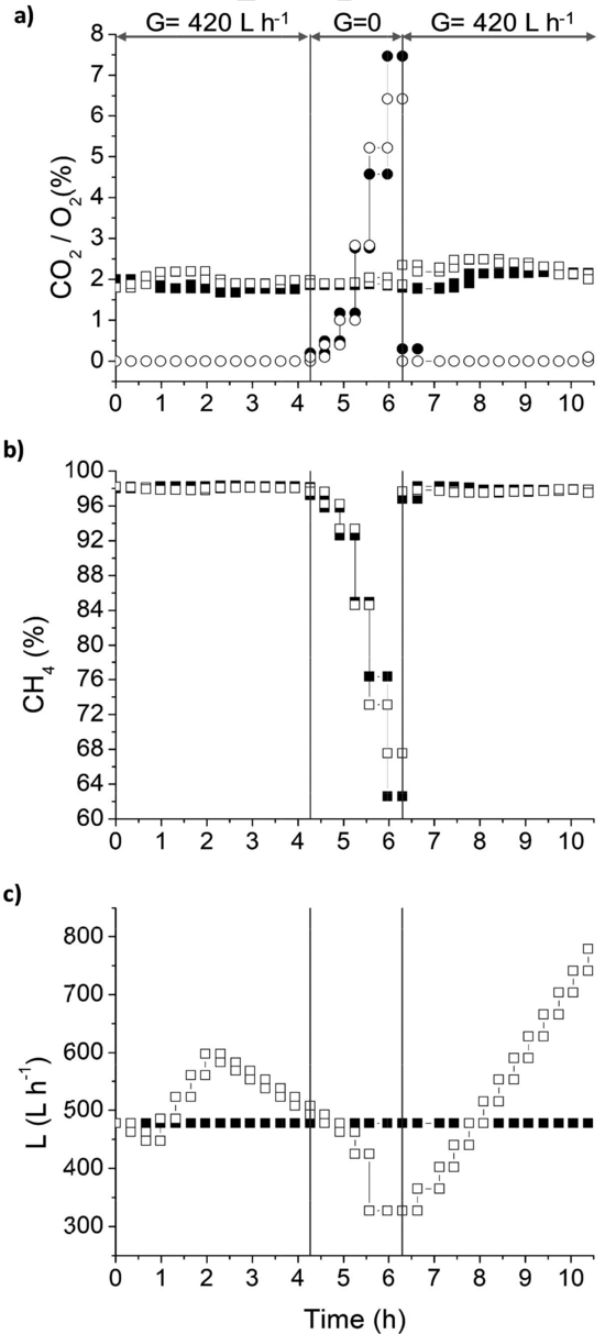

Fig. 3. Time course of a) CO_2 (square) and O_2 (circle) concentrations in the upgraded biogas, b) CH_4 concentration in the upgraded biogas and c) liquid flowrate (L) under controlled (open) and uncontrolled (solid) conditions during a failure in biogas supply (G).

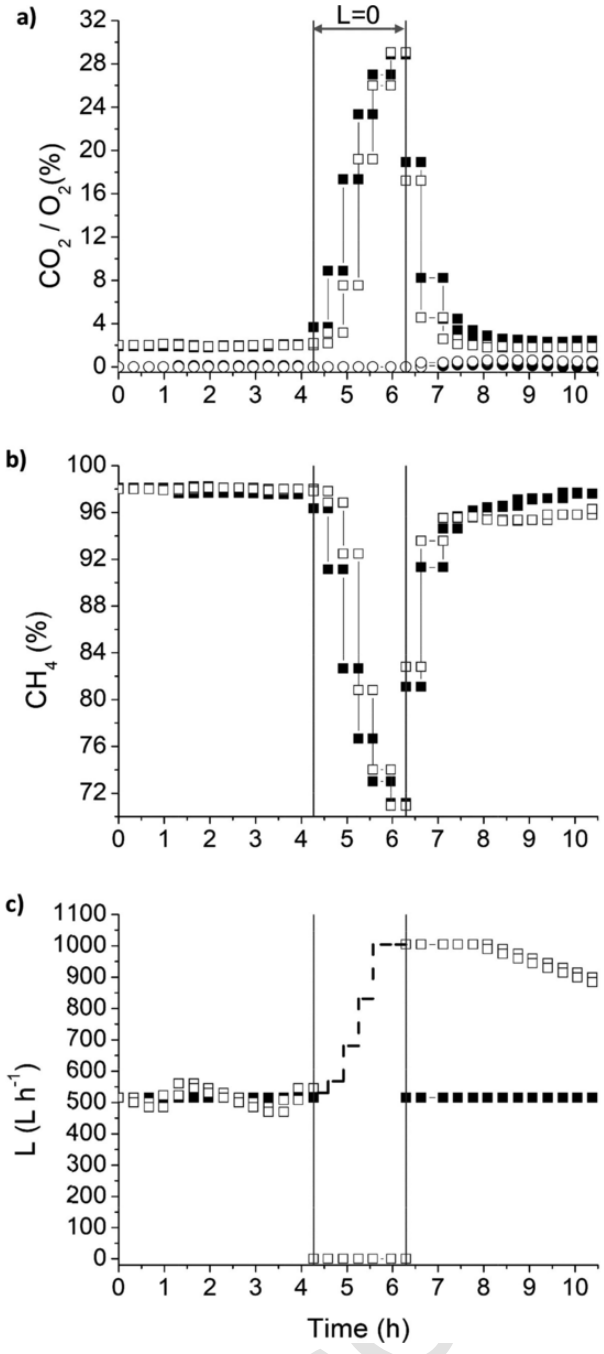

Fig. 4. Time course of a) CO_2 (square) and O_2 (circle) concentrations in the upgraded biogas, b) CH_4 concentration in the upgraded biogas and c) liquid flowrate (L) under controlled (open) and uncontrolled (solid) conditions during a failure in liquid recirculation. The control system unit changes when the liquid pump was off are represented by a dashed line (c).

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_2 concentration up to 7.5% after 2 h (Fig. 3a). When biogas supply was re-started, the O_2 concentration rapidly decreased to 0.3% within 20 min, with an associated increase in CH_4 concentration up to 96.8%, CO_2 concentrations ~1.8% and no H_2S detected (Fig. 3a, b). This rapid increase in CH_4 content was mediated by the high biogas flowrate used during this experiment (420 L h^{-1}), which flushed the air out of the system. However, the CO_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^{-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_2 content in the absence of biogas supply remained constant at ~1.9%, while an increase in the O_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^{-1}) in order to prevent a high O_2 content in the upgraded biogas. In this context, when biogas supply was restarted, CO_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_2 concentration to 2% by the end of the experiment by imposing a liquid flowrate of 779 L h^{-1} (Fig. 3a, c). The CH_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_2S 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_2 content resulting from any variation in the cultivation broth, the system would not be able to recover the initial CO_2 concentration without control.

CO_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_2 concentration in the upgraded biogas rapidly increased up to 28.9% within 2 h, which almost matched the CO_2 concentration of the raw biogas (31.5 ± 1.1%). This poor CO_2-RE was due to the acidification and CO_2 saturation of the liquid present in the biogas AC. However, the CO_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^{-1}). Unfortunately, the system was not able to recover the initial biomethane quality, with CO_2 concentrations of 2.3% after approximately 2.5 h from liquid supply restoration (Fig. 4a). On the other hand, the CH_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_2S concentrations (1 ppm_v) were detected as a result of its low concentration in the raw biogas. Finally, no significant O_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^{-1}) and the CO_2 content remained below 2% (Fig. 4a, c). When the liquid recirculation was stopped, the CO_2 concentration in the upgraded biogas increased up to 29.1%, but no H_2S was detected as under uncontrolled conditions (Fig. 4a). The control system sent control actions of increasing the liquid flowrate (CO_2 measured > CO_2 set point and $O_2 \approx 0$) 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^{-1}). This entailed a decrease in the CO_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_2 content could have been even faster if higher pumping capacity would be available. On the other hand, the O_2 content in the upgraded biogas increased when the liquid pump was turned on as a re-

sult of the high liquid flowrate, but remained always below 1%. Finally, the CH_4 content in the upgraded biogas decreased from 98.0 to 70.9% due to the negligible CO_2-REs in the absence of liquid recirculation. Nevertheless, CH_4 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 O_2 and N_2 desorption from the recycling liquid to the biomethane 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 CO_2 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 (CO_2 < 2% and O_2 < 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

María 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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2020.123207.

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