Influence of liquid-to-biogas ratio and alkalinity on the biogas upgrading performance in a demo scale algal-bacterial photobioreactor

David Marín[1, 2, 3], Antonio Ortíz[4], Rubén Díez-Montero[4], Enrica Uggetti[4], Joan García[4], Raquel Lebrero[1, 2], Raúl Muñoz[1, 2, *]

[1] Department of Chemical Engineering and Environmental Technology, School of Industrial Engineering, University of Valladolid, Dr. Mergelina, s/n, 47011, Valladolid, Spain.

[2] Institute of Sustainable Processes, University of Valladolid, Dr. Mergelina, s/n, 47011, Valladolid, Spain.

[3] Universidad Pedagógica Nacional Francisco Morazán, Boulevard Centroamérica, Tegucigalpa, Honduras.

[4] GEMMA – Group of Environmental Engineering and Microbiology, Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya – BarcelonaTech, c/ Jordi Girona 1-3, Barcelona E-08034, Spain.

[*] Corresponding author: mutora@iq.uva.es

ABSTRACT

The influence of the liquid-to-biogas ratio (L/G) and alkalinity on methane quality was evaluated in a 11.7 m^3 outdoors horizontal semi-closed tubular photobioreactor interconnected to a 45-L absorption column (AC). CO_2 concentrations in the upgraded methane ranged from <0.1 to 9.6% at L/G of 2.0 and 0.5, respectively, with maximum CH_4 concentrations of 89.7% at a L/G of 1.0. Moreover, an enhanced CO_2 removal (mediating a decrease in CO_2 concentration from 9.6 to 1.2%) and therefore higher CH_4 contents (increasing from 88.0 to 93.2%) were observed when increasing the alkalinity of the AC cultivation broth from 42±1 mg L^{-1} to 996±42 mg L^{-1}. H_2S was completely removed regardless of the L/G or the alkalinity in AC. The continuous operation of the photobioreactor with optimized operating parameters resulted in contents of CO_2 (<0.1%-

1.4%), H_2S (<0.7 mg m^{-3}) and CH_4 (94.1%-98.8%) complying with international regulations for methane injection into natural gas grids.

Keywords: Algal-bacterial photobioreactor, Alkalinity, Biogas upgrading, Liquid/Gas ratio, Outdoors conditions.

1. Introduction

The anaerobic digestion (AD) of organic solid waste and sludge from wastewater treatment generates a biogas that represents a potential renewable energy source capable of generating electricity and reduce the dependence on fossil fuels (Muñoz et al., 2015). Biogas can be purified and injected into natural gas grids or used as a vehicle fuel, or desulphurised and used for the generation of domestic heat or steam and electricity in industry (Andriani et al., 2014; Muñoz et al., 2015). In this regard, a growing contribution of biogas to the EU energy sector has been observed within the past years, with an increase in the numbers of biogas producing plants by a factor of 3 (from 6,772 in 2009 to 17,439 by the end of 2016) (European Biogas Association, 2017). The upgrading of biogas prior injection into natural gas grids or use as a vehicle fuel is required due to the large number and high concentrations of impurities in raw biogas: CO_2 (15-60%), H_2S (0.005-2%), O_2 (0-1%), N_2 (0-2%), CO (<0.6%), NH_3 (<1%), siloxanes (0-0.2%) and volatile organic compounds (<0.6%) (Ryckebosch et al., 2011). In this context, most international regulations establish that a methane composition of $CH_4 \geq 95\%$, $CO_2 \leq$ 2-4%, $O_2 \leq 1\%$ and negligible amounts of H_2S is mandatory for its injection into natural gas grids, while a lower CH_4 content is required when methane is used as a vehicle fuel (Muñoz et al., 2015). The removal of biogas contaminants like H_2S reduces the corrosion in pipelines, engines and biogas storage structures, while the reduction in CO_2 contributes to increase the calorific value of methane and reduces its transportation costs (Posadas et al., 2015).

Nowadays, several biological technologies are available to remove CO_2 and H_2S from biogas. For instance, chemoautotrophic biogas upgrading is used for the removal of CO_2, while biofiltration or in situ micro-aerobic AD are applied for H_2S removal (Farooq et al., 2018; Marín et al., 2018a; Muñoz et al., 2015). The removal of only one biogas contaminant at a time represents the main disadvantage associated to these biological technologies, resulting in the need of implementing two-stage biological upgrading processes. Likewise, several physical-chemical technologies are commercially available to remove CO_2 and H_2S from biogas. Membrane separation, pressure swing adsorption or chemical/water/organic scrubbing are applied for CO_2 removal, while *in-situ* chemical precipitation or adsorption onto activated carbon or metal ions provide satisfactory levels of H_2S removal (Marín et al., 2018a; Muñoz et al., 2015; Toledo-cervantes et al., 2017). Two sequential stages are also necessary for a complete biogas upgrading, which entails an increase in investment and operational costs. In this context, algal-bacterial photobioreactors can be engineered as an environmentally friendly and cost-effective technology due to their capacity to simultaneously remove CO_2 and H_2S in a single stage process (Bahr et al., 2014).

Algal-bacterial processes have emerged as a cost-competitive technology capable of removing CO_2 and H_2S from biogas in a single stage at low environmental impacts (Bahr et al., 2014; Muñoz et al., 2015). Biogas upgrading in algal-bacterial photobioreactors is based on the simultaneous photosynthetic fixation of CO_2 by microalgae and the oxidation of H_2S to SO_4^{2-} by sulfur oxidizing bacteria promoted by the high dissolved oxygen (DO) concentration present in the cultivation broth as a result of photosynthesis (Posadas et al., 2017, 2015; Toledo-Cervantes et al., 2016). Photosynthetic biogas upgrading has been recently evaluated indoors in high rate algal ponds (HRAPs) interconnected to a biogas absorption column (AC) under artificial illumination. Bahr et al. (2014) demonstrated for the first time the capability of microalgal-bacterial processes for the simultaneous removal of CO_2 and H_2S from biogas. Serejo et al. (2015) studied the influence of the liquid/biogas (L/G) ratio on the composition of the upgraded biogas. Posadas et al. (2016) optimized the biogas upgrading process in a HRAP using centrate as a source of nutrients under laboratory conditions, while Rodero et al. (2018) evaluated the influence of alkalinity and temperature on the photosynthetic biogas upgrading efficiency in an indoor HRAP. In addition, Posadas et al. (2017) evaluated the simultaneous biogas upgrading and centrate treatment in a HRAP operated under outdoors conditions during summer, while Marín et al. (2018a,b) investigated the influence of the yearly variations of environmental conditions on the biogas upgrading performance. Nevertheless, and despite the satisfactory results obtained so far, new photobioreactor configurations should be tested in order to overcome design constraints associated to algal ponds such as their high footprint. In this sense, semi-closed or closed tubular photobioreactors have been proposed as a promising alternative to reduce land requirement, while offering higher photosynthetic efficiencies, enhanced biomass productivities and a superior CO_2 mass transfer (Toledo-Cervantes et al., 2018).

This study investigated for the first time the biogas upgrading potential of an outdoors pilot-scale hybrid (semi-closed) horizontal tubular photobioreactor (PBR) interconnected to an external AC. The influence of the L/G ratio and the alkalinity of the cultivation medium in the AC on the quality of the upgraded biogas was assessed and optimized. In addition, the PBR-AC was operated continuously under optimized process parameters.

2. Materials and methods

2.1 Biogas

The biogas used in this experiment was obtained from the anaerobic digestion of microalgal biomass in a pilot anaerobic digester located at the Agròpolis experimental campus of the Universitat Politécnica de Catalunya-BarcelonaTech (Catalunya, Spain) (García et al., 2018; Uggetti et al., 2018). The average biogas composition was CO_2 (13.7 ± 1.0%), H_2S (0.1 ± 0.05%) and CH_4 (86.2 ± 1.0%).

2.2 Experimental set-up

The experimental set-up was built outdoors at the Agròpolis experimental campus of the Universitat Politécnica de Catalunya-BarcelonaTech (41.29ºN, 2.04ºE). The horizontal hybrid (semi-closed) tubular photobioreactor (PBR) consisted of 2 lateral open tanks made of polypropylene (width=1 m; length=5 m; depth=0.6 m) interconnected by 16 low density transparent polyethylene tubes (length=47 m; diameter=125 mm). The total working volume of the PBR was 11.7 m^3. The cultivation broth was continuously circulated in each tank by a 6-blade paddlewheel with a rotational speed of 9-12 rpm, which resulted in a velocity of the cultivation broth inside the tubes of 0.20-0.25 m s^{-1}. This recirculation rate ensured a homogeneous distribution and mixing of the cultivation broth and a turbulent flow inside the tubes, avoiding biomass settling. The different height level between the two open tanks caused a gravity flow through 8 tubes from the deep side of one tank to the shallow side of the opposite one (Uggetti et al., 2018). The open tanks supported the release of the DO accumulated along the closed tubes and also provided a cooling effect via water evaporation, thus preventing the occurrence of the extremely high temperatures that would be reached in completely closed tubular PBRs. The PBR was interconnected to a separate 45 L bubble AC (internal diameter=12 cm; height=4 m) made of PVC and provided with a ring of seven metallic biogas diffusers of 2 µm pore size located at the bottom of the column. (Fig. 1).

<Figure 1>

2.3 Operational conditions and experimental procedure

The PBR was inoculated at an initial concentration of 220 mg volatile suspended solids (VSS) L^{-1} with a microalgal consortium composed of *Chlorella vulgaris*, *Stigeoclonium tenue, Nitzschia closterium and Navicula amphora,* obtained from an outdoors HRAP located at the facilities of the Environmental Engineering and Microbiology Research Group (GEMMA) the Universitat Politécnica de Catalunya-BarcelonaTech (Gutiérrez et al., 2016). The PBR was operated as the third of a set of 3 identical PBRs interconnected in series and treating 2.3 m^3 d^{-1} of agricultural wastewater with the following composition: total organic carbon (TOC) = 131 ± 80 mg L^{-1}, inorganic carbon (IC) = 36 ± 10 mg L^{-1}, total nitrogen (TN) = 15 ± 7 mg L^{-1} and total phosphorus (TP) = 0.9 ± 1.0 mg L^{-1}. Three experimental series were conducted as described below:

2.3.1 Influence of the liquid-to-biogas ratio in the absorption column on the quality of the upgraded biogas

L/G ratios ranging from 0.5 to 5.0 were tested in order to optimize the quality of the upgraded biogas. Biogas was sparged into the AC at 100 L d^{-1}, while the cultivation broth from the PBR was supplied in co-current mode at different flow rates in order to provide

L/G ratios of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0. The duration of each L/G ratio condition was at least four times the hydraulic retention time (HRT) of the liquid in the AC (Table 1). The ambient and cultivation broth temperatures, the pH, dissolved TOC, IC, TN, N-NH_4^+ and TP concentrations in the cultivation broth of the PBR, and the composition of the raw and upgraded biogas were analyzed in triplicate at the end of each operational condition.

<Table 1>

2.3.2 Influence of the alkalinity in the cultivation broth on the quality of the upgraded biogas

In order to assess the impact of different alkalinities of the cultivation broth in the AC on the upgrading efficiency, a carbonate solution ($NaHCO_3$ and Na_2CO_3) with a concentration of 16,000 mg L^{-1} of IC was injected at the bottom of the AC in co-current mode (Fig. 1, dashed line). Biogas flowrate and L/G ratio were fixed at 100 L d^{-1} and 0.5, respectively. Carbonate solution flowrates of 0, 1, 2, 3 and 5 L d^{-1} (corresponding to an IC concentration in the cultivation broth of the AC of 42 ± 1; 311 ± 6; 634 ± 48; 996 ± 42 and 1,557 ± 26 mg L^{-1}, respectively) were tested in order to optimize the quality of the upgraded biogas. Each carbonate solution flowrate was maintained for at least four times the HRT of the liquid in the AC. The ambient and PBR cultivation broth temperatures, the pH, dissolved TOC, IC, TN, N-NH_4^+ and TP concentrations in the cultivation broth of the PBR, and the composition of the raw and the upgraded biogas were analyzed in triplicate at the end of each operational condition.

2.3.3 Continuous photosynthetic biogas upgrading operation

Biogas upgrading performance of the demo scale PBR was evaluated throughout 42 days under continuous operation. The optimum operating parameters previously identified were selected: biogas flowrate of 100 L d^{-1}, L/G ratio of 0.5 and the supplementation of 2.0 L d^{-1} of carbonate solution to the AC. The ambient and cultivation broth temperatures, the pH, dissolved TOC, IC, TN, N-NH_4^+ and TP concentrations in the cultivation broth of the PBR, and the composition of the raw and the upgraded biogas were analyzed in duplicate once per week.

2.4 Analytical procedures

The concentration of CH_4, CO_2, N_2 and O_2 in biogas and methane were determined using a gas chromatograph (GC) equipped with a thermal conductivity detector (Trace GC Thermo Finnigan with Hayesep packed column). Injector, detector and oven temperatures were maintained at 150, 250 and 35 ºC, respectively, with helium as a carrier gas. The concentration of H_2S in the raw biogas was determined using Gastec colorimetric tubes, while its concentration in the upgraded methane was analyzed by a Dräger X-am 5000 electrochemical sensor (lower detection limit of 0.5 ppm_v). Temperature and pH were measured *in-situ* by a pH-meter with temperature sensor (Mettler Toledo, USA). Dissolved TOC, IC and TN concentrations were determined using a C/N analyzer (21005, Analytikjena, Germany). The analysis of TP concentration was performed according to the Ascorbic Acid Method of Standard Methods (APHA, 2005), while N-NH_4^+ concentration was measured by a colorimetric method according to Solorzano (1969). The determination of the concentration of total suspended solids (TSS) and VSS in the PBR was performed according to Standard Methods (APHA, 2005), and the temperature of the cultivation broth was periodically monitored with a temperature sensor (Campbell Scientific Inc., USA).

3. Results and discussion

3.1 Influence of the liquid-to-biogas ratio in the absorption column on the quality of the upgraded biogas

The composition of the methane produced in the PBR-AC varied depending on the L/G ratio tested (Fig. 2). At a L/G ratio of 2.0, CO_2 was not detected in the upgraded methane, thus achieving minimum concentrations < 0.1% according to the GC detection limit. On the contrary, a maximum concentration of 9.6 ± 0.1% was recorded at a L/G ratio of 0.5 (Fig. 2). These results were in accordance with Posadas et al. (2017), who recorded the highest concentration of CO_2 in methane at the lowest L/G ratio (≈12.0% at a L/G ratio of 0.5). L/G ratios > 2.0 supported a significant decrease in the CO_2 concentration of the upgraded biogas, which ranged from <0.1 to 1.4% (corresponding to removal efficiencies (REs) between 90.4 and >99.9%). On the other hand, H_2S was not detected in the upgraded methane regardless of the tested L/G ratio, its complete removal being attributed to the high aqueous solubility of this biogas contaminant. An efficient removal of H_2S from raw biogas in algal-bacterial PBRs with a negligible impact of the L/G ratio has been consistently reported both in outdoors (Posadas et al. 2017) and indoors HRAPs (Serejo et al. 2015).

Unfortunately, the concentrations of N_2 and O_2 recorded in the upgraded biogas increased from 3.4% at a L/G ratio of 0.5 to 11.9% at a L/G ratio of 5.0 (Fig. 2), which clearly indicated that the stripping of these gases from the recirculating cultivation broth was promoted at higher liquid flowrates (Sovechles and Waters, 2015). These results were in accordance with Toledo-Cervantes et al. (2016), who reported N_2/O_2 concentrations between 2.5 and 37.0% at L/G ratios ranging from 0 to 40 in a closed tubular photobioreactor. Likewise, Posadas et al. (2017) also reported an increase in N_2 and O_2 concentration in the upgraded biogas from 1.4 to 18.3% when the L/G ratio increased from 0.5 to 5, respectively. Similarly, Rodero et al., 2019 found N_2/O_2 concentrations ranging from 6.6 and 11.4% at L/G ratios ranging from 1.2 to 3.5 in an outdoors HRAP.

Finally, a maximum concentration of CH_4 of 89.7% in the upgraded biogas was recorded at a L/G ratio = 1 (Fig. 2). Interestingly, although further increases in the L/G ratio resulted in lower CO_2 concentrations, they also mediated a higher desorption of N_2 and O_2, which negatively impacted the final concentration of CH_4 in the upgraded biogas.

<Figure 2>

3.2 Influence of the alkalinity in the cultivation broth on the quality of the upgraded biogas

The supplementation of a carbonate solution to the absorption column resulted in an improved quality of the final methane. In this context, average concentrations of CO_2 of 9.6 ± 0.2; 2.6 ± 0.2; 1.3 ± 0.0; 1.2 ± 0.0 and 1.1 ± 0.2% were recorded at IC concentrations in the AC cultivation broth of 42 ± 1; 311 ± 6; 634 ± 48; 996 ± 42 and 1,557 ± 26 mg L^{-1}, respectively (Fig. 3). The increase in CO_2-REs resulting from the addition of alkalinity (from 24.0 ± 0.2% at 42 ± 1 mg IC L^{-1} to 91.9 ± 0.2% at 1,557 ± 26 mg IC L^{-1}) was associated to the concomitant increase of pH in the cultivation broth of the AC (from 6.5 ± 0.1 at 42 ± 1 mg IC L^{-1} up to 9.3 ± 0.0 at 1,557 ± 26 mg IC L^{-1}). The beneficial effect of alkalinity on CO_2 removal performance has been previously reported in literature. For instance, Rodero et al. (2018) reported CO_2-REs of 97.8 ± 0.8, 50.6 ± 3.0 and 41.5 ± 2.0% during the operation of an indoors HRAP interconnected to an AC using a feeding nutrient solution with an average IC concentration of 1,500 mg L^{-1}, 500 mg L^{-1} and 100 mg L^{-1}, respectively. On the other hand, the higher solubility of H_2S compared to that of CO_2 also mediated complete removals of this biogas contaminant regardless of the alkalinity of the AC cultivation broth. These results were in accordance with Franco-Morgado et al. (2017), who reported values of H_2S-REs of 99.5 ± 0.5% throughout the operation of an indoors HRAP interconnected to an AC using a highly carbonated medium at a pH of 9.5. Likewise, Rodero et al. (2018) observed H_2S-REs of 100.0 ± 0.0, 94.7 ± 1.9 and 80.3 ± 3.9% using a feeding nutrient solution with an average IC concentration of 1,500 mg L^{-1}, 500 mg L^{-1} and 100 mg L^{-1}, respectively.

The N_2 and O_2 concentration in the upgraded biogas increased from 2.4% at an IC concentration of 42 ± 1 mg L^{-1} to 6.1% at 1,557 ± 26 mg IC L^{-1} (Fig. 3). This increase was attributed to the enhanced N_2 and O_2 stripped out from the recycling cultivation broth mediated by the increase in medium salinity (which ultimately decreased the solubility of these gases).

Finally, the lowest concentration of CH_4 in the upgraded biogas (88.0%) was recorded at an IC concentration of 42 ± 1 mg L^{-1}, increasing up to a maximum concentration of 93.2% at 634 ± 48 mg L^{-1} (Fig. 3). Interestingly, higher carbonate supplementation rates did not result in an additional increase in the CH_4 content. The increased CH_4 concentration at higher alkalinity loads was attributed to the limited desorption of N_2 and O_2 when operating at the optimum L/G ratio and the high absorption efficiency of CO_2 and H_2S due to the acidic nature of these gases. Similar results were obtained by Rodero et al. (2018), who reported CH_4 contents of 98.9 ± 0.2, 80.9 ± 0.8 and 75.9 ± 0.7% at average

IC feed concentrations of 1,500, 500 and 100 mg L^{-1}, respectively. Therefore, the results herein obtained confirmed the key role of alkalinity on the methane quality.

<Figure 3>

3.3 Continuous photosynthetic biogas upgrading operation

The optimum operating parameters (i.e. L/G ratio of 0.5 and supplementation of a 16,000 mg IC L^{-1} solution to the AC at a flowrate of 2.0 L d^{-1}) identified in sections 3.1 and 3.2 were selected to test the performance of the PBR during the continuous upgrading of raw biogas coupled with the treatment of the mixed wastewater.

3.3.1 Biogas upgrading

The composition of the methane obtained exhibited a rather constant value along the 42 days of operation (Fig. 4). CO_2 concentrations ranged between <0.1% and 1.4%, corresponding to REs >91.0% (Fig. 4). The previous optimization of key operating parameters such as the L/G ratio and the alkalinity in the cultivation broth of the AC supported these consistent CO_2 removals. Similarly, Marín et al. (2018a) reported values of CO_2 concentration in the upgraded biogas ranging from 0.7 to 1.9% throughout the operation of an outdoors HRAP interconnected to an external AC. It is important to highlight that the CO_2 concentrations here obtained fulfilled most international regulations for methane, which require CO_2 concentrations ≤ 2-4% to be acceptable for injection into natural gas grids (Muñoz et al., 2015). Moreover, no H_2S was detected in the methane during the whole experimental period regardless of the environmental conditions, which agreed with the results previously observed during the optimization assays. Therefore, the resulting methane also complied with the maximum H_2S levels enforced by international regulations for methane injection into natural gas grids (< 5 mg m^{-3}) (Muñoz et al., 2015).

The N_2 and O_2 concentration in the upgraded biogas ranged from 0.9 to 5.9% throughout the entire operating period (Fig. 4), similar concentrations to those recorded by Marín et al. (2018a), who reported N_2 and O_2 contents in the upgraded biogas between 0.5 and 6.3% during the operation of an outdoors HRAP interconnected to an AC. Likewise, Posadas et al. (2017) also recorded similar N_2 and O_2 concentrations of 1.4-6.1% in the upgraded biogas. Unfortunately, these concentrations exceeded most of the time the maximum quality requirements demanded for methane injection into natural gas grids of ≤ 1% (please note that the GC-TCD method did not allow to quantify separately O_2 and N_2). O_2 is a hazardous biomethane contaminant based on its associated explosion risks, while the presence of N_2 typically lowers the content of the biomethane. Therefore, a further optimization of the technology in order to avoid an active stripping of N_2 and O_2 from the cultivation broth into the upgraded methane is still necessary.

Finally, high CH_4 concentrations in the upgraded biogas ranging from 94.1 to 98.9% were recorded during this continuous assay (Fig. 4), likely due to the high CO_2-REs, the complete elimination of H_2S and the limited N_2 and O_2 desorption obtained under these operating conditions. In this regard, the quality of the upgraded methane was similar or even higher in terms of CH_4 content than that reported in previous studies. Indeed, Posadas et al. (2017) obtained CH_4 concentrations in the upgraded biogas of 87.0 - 93.0%, while Marín et al. (2018a) achieved values up to 97.8% in a similar outdoors experimental set-up (HRAP-AC) with a L/G ratio of 1.0 and IC concentrations in the cultivation broth of ~ 2,600 mg IC L^{-1}. Finally, it should be highlighted that process performance here recorded in this demo-scale PBR was superior to that recently recorded by Rodero et al. (2019) in an outdoors 10 m^3 HRAP interconnected to an AC, where CH_4 concentrations did not exceed 91% in the upgraded biogas. In this context, a minimum CH_4 concentrations of ≥ 95% must be typically ensured prior injection of the methane into natural gas grids in most international methane regulations (Muñoz et al., 2015).

<Figure 4>

3.3.2 Wastewater Treatment

Wastewater treatment performance in the PBR during biogas upgrading was evaluated in terms of dissolved TOC, IC and TN removal (Fig. 5). Dissolved TOC concentrations in the influent and effluent varied throughout the process with values ranging from 69.9 to 277.3 mg L^{-1} in the influent and from 90.4 to 217.0 mg L^{-1} in the effluent (Fig. 5). The low TOC-REs recorded were attributed to the low biodegradability of the mixture of agricultural and domestic wastewater used as influent to the PBR. Moreover, the significant water evaporation rates from the cultivation broth in the open tanks and the lysis of the microalgae generated during photosynthetic CO_2 fixation likely contributed to increase the TOC concentration in the effluent in comparison to that of the influent, thus resulting in the negative TOC-REs observed. On the other hand, the dissolved IC concentration in the influent varied from 21.6 to 46.3 3 mg L^{-1} and from 29.8 to 91.8 mg L^{-1} in the effluent (Fig. 5). Although no correlation between the IC concentration in the effluent of the PBR and the addition of the carbonate solution in the AC was found due to the high dilution effect associated to the large volume and short hydraulic retention time of the PBR, the high values of pH in the PBR ranging between 7.9 and 8.9 might have promoted the increase in the IC concentration of the effluent supported by biogas absorption. Finally, no effective TN removal was observed during the entire experimental period, with dissolved TN concentrations in the influent (ranging from 9.1 to 25.0 mg L^{-1}) comparable to those recorded in the effluent (ranging from 11.1 to 25.9 mg L^{-1}) (Fig. 5).

<Figure 5>

4. Conclusions

This work constitutes, to the best of our knowledge, the first validation of photosynthetic biogas upgrading in a pilot-scale semi-closed PBR interconnected to an AC under outdoors conditions. Both the L/G ratio and the alkalinity in the AC were identified as key parameters influencing the quality of the final methane, with optimum values of 0.5 and 634 ± 48 mg L^{-1}, respectively. The implementation of the optimum operating parameters during continuous operation resulted in a methane with CO_2 concentrations of <0.1%-1.4%, H_2S<0.5ppm_v and CH_4 contents of 94.1-98.9%, which complied with most international regulations for methane injection into natural gas grids.

E-supplementary data of this work can be found in online version of the paper.

Acknowledgements

This work was supported by the project INCOVER. The project has received funding from the European Union’s Horizon 2020 research and innovation programme under the grant agreement No. 689242. The financial support the Regional Government of Castilla y León and the FEDER programme (UIC 71 and CLU-2017-09) is also gratefully acknowledged. E. Uggetti and R. Díez-Montero would like to thank the Spanish Ministry of Science, Innovation and Universities for their research grants (IJCI-2014-21594 and FJCI-2016-30997, respectively).

REFERENCES

(1) Andriani, D., Wresta, A., Atmaja, T.D., Saepudin, A., 2014. A Review on Optimization Production and Upgrading Biogas Through CO2 Removal Using Various Techniques. Appl. Biochem. Biotechnol. 172, 1909–1928. doi:10.1007/s12010-013-0652-x

(2) APHA, 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed. Public Health Association, Washington DC.

(3) Bahr, M., Díaz, I., Dominguez, A., González Sánchez, A., Muñoz, R., 2014. Microalgal-biotechnology as a platform for an integral biogas upgrading and nutrient removal from anaerobic effluents. Environ. Sci. Technol. 48, 573–581. doi:10.1021/es403596m

(4) European Biogas Association, 2017. EBA Statistical Report 2017 [WWW Document]. URL http://european-biogas.eu/2017/12/14/eba-statistical-report-2017-published-soon/ (accessed 11.13.18).

(5) Farooq, M., Almustapha, M.N., Imran, M., Saeed, M.A., Andresen, J.M., 2018. In-situ regeneration of activated carbon with electric potential swing desorption (EPSD) for the H2S removal from biogas. Bioresour. Technol. 249, 125–131. doi:10.1016/j.biortech.2017.09.198

(6) Franco-Morgado, M., Alcántara, C., Noyola, A., Muñoz, R., González-Sánchez, A., 2017. A study of photosynthetic biogas upgrading based on a high rate algal pond under alkaline conditions: Influence of the illumination regime. Sci. Total Environ. 592, 419–425. doi:10.1016/j.scitotenv.2017.03.077

(7) García, J., Ortiz, A., Álvarez, E., Belohlav, V., García-Galán, M.J., Díez-Montero, R., Álvarez, J.A., Uggetti, E., 2018. Nutrient removal from agricultural run-off in demonstrative full scale tubular photobioreactors for microalgae growth. Ecol. Eng. 120, 513–521. doi:10.1016/j.ecoleng.2018.07.002

(8) Gutiérrez, R., Ferrer, I., González-Molina, A., Salvadó, H., García, J., Uggetti, E., 2016. Microalgae recycling improves biomass recovery from wastewater treatment high rate algal ponds. Water Res. 106, 539–549. doi:10.1016/j.watres.2016.10.039

(9) Marín, D., Posadas, E., Cano, P., Pérez, V., Blanco, S., Lebrero, R., 2018a. Seasonal variation of biogas upgrading coupled with digestate treatment in an outdoors pilot scale algal-bacterial photobioreactor. Bioresour. Technol. 263, 58–66. doi:10.1016/j.biortech.2018.04.117

(10) Marín, D., Posadas, E., Cano, P., Pérez, V., Lebrero, R., Muñoz, R., 2018b. Influence of the seasonal variation of environmental conditions on biogas upgrading in an outdoors pilot scale high rate algal pond. Bioresour. Technol. 255, 354–358. doi:10.1016/j.biortech.2018.01.136

(11) Muñoz, R., Meier, L., Diaz, I., Jeison, D., 2015. A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. Rev. Environ. Sci. Biotechnol. 14, 727–759. doi:10.1007/s11157-015-9379-1

(12) Posadas, E., Marín, D., Blanco, S., Lebrero, R., Muñoz, R., 2017. Simultaneous biogas upgrading and centrate treatment in an outdoors pilot scale high rate algal pond. Bioresour. Technol. 232, 133–141. doi:10.1016/j.biortech.2017.01.071

(13) Posadas, E., Serejo, M.L., Blanco, S., Pérez, R., García-Encina, P.A., Muñoz, R., 2015. Minimization of biomethane oxygen concentration during biogas upgrading in algal-bacterial photobioreactors. Algal Res. 12, 221–229. doi:10.1016/j.algal.2015.09.002

(14) Posadas, E., Szpak, D., Lombó, F., Domínguez, A., Díaz, I., Blanco, S., García-Encina, P.A., Muñoz, R., 2016. Feasibility study of biogas upgrading coupled with nutrient removal from anaerobic effluents using microalgae-based processes. J. Appl. Phycol. 28, 2147–2157. doi:10.1007/s10811-015-0758-3

(15) Rodero, M. del R., Lebrero, R., Serrano, E., Lara, E., Arbib, Z., García-Encina, P.A., Muñoz, R., 2019. Technology validation of photosynthetic biogas upgrading in a semi-industrial scale algal-bacterial photobioreactor. Bioresour. Technol. 279, 43–49. doi:10.1016/j.biortech.2019.01.110

(16) Rodero, M. del R., Posadas, E., Toledo-Cervantes, A., Lebrero, R., Muñoz, R., 2018. Influence of alkalinity and temperature on photosynthetic biogas upgrading efficiency in high rate algal ponds. Algal Res. 33, 284–290. doi:10.1016/j.algal.2018.06.001

(17) Ryckebosch, E., Drouillon, M., Vervaeren, H., 2011. Techniques for transformation of biogas to biomethane. Biomass and Bioenergy 35, 1633–1645. doi:10.1016/j.biombioe.2011.02.033

(18) Serejo, M.L., Posadas, E., Boncz, M.A., Blanco, S., García-Encina, P., Muñoz, R., 2015. Influence of biogas flow rate on biomass composition during the optimization of biogas upgrading in microalgal-bacterial processes. Environ. Sci. Technol. 49, 3228–3236. doi:10.1021/es5056116

(19) Solorzano, L., 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnol. Oceanogr. 799–801. doi:10.4319/lo.1969.14.5.0799

(20) Sovechles, J.M., Waters, K.E., 2015. Effect of ionic strength on bubble coalescence in inorganic salt and seawater solutions. AICHE 61, 2489–2496. doi:doi.org/10.1002/aic.14851

(21) Toledo-cervantes, A., Estrada, J.M., Lebrero, R., Muñoz, R., 2017. A comparative analysis of biogas upgrading technologies : Photosynthetic vs physical / chemical processes. Algal Res. 25, 237–243. doi:10.1016/j.algal.2017.05.006

(22) Toledo-Cervantes, A., Morales, T., González, Á., Muñoz, R., Lebrero, R., 2018. Long-term photosynthetic CO2 removal from biogas and flue-gas: Exploring the potential of closed photobioreactors for high-value biomass production. Sci. Total Environ. 640–641, 1272–1278. doi:10.1016/j.scitotenv.2018.05.270

(23) Toledo-Cervantes, A., Serejo, M.L., Blanco, S., Pérez, R., Lebrero, R., Muñoz, R., 2016. Photosynthetic biogas upgrading to bio-methane: Boosting nutrient recovery via biomass productivity control. Algal Res. 17, 46–52. doi:10.1016/j.algal.2016.04.017

(24) Uggetti, E., García, J., Álvarez, J.A., García-Galán, M.J., 2018. Start-up of a microalgae-based treatment system within the biorefinery concept: From wastewater to bioproducts. Water Sci. Technol. 78, 114–124. doi:10.2166/wst.2018.195

FIGURE CAPTIONS

Figure 1. Schematic diagram of the experimental set-up used for the continuous photosynthetic upgrading of biogas.

Figure 2. Concentration of CO_2 (■), $N_2 + O_2$ (◆) and CH_4 (○) in the upgraded biogas at different L/G ratios.

Figure 3. Concentration of CO_2 (■), $N_2 + O_2$ (◆) and CH_4 (○) in the upgraded biogas at different IC concentration in the cultivation broth of the AC.

Figure 4. Time course of the concentration of CO_2 (■), $N_2 + O_2$ (◆) and CH_4 (○) in the upgraded biogas during continuous process operation.

Figure 5. Time course of the influent (solid symbols) and effluent (empty symbols) concentrations of total organic carbon (squares), inorganic carbon (diamonds) and total nitrogen (circles) throughout the continuous operation of the PBR.

Figure 1. Schematic diagram of the experimental set-up used for the continuous photosynthetic upgrading of biogas.

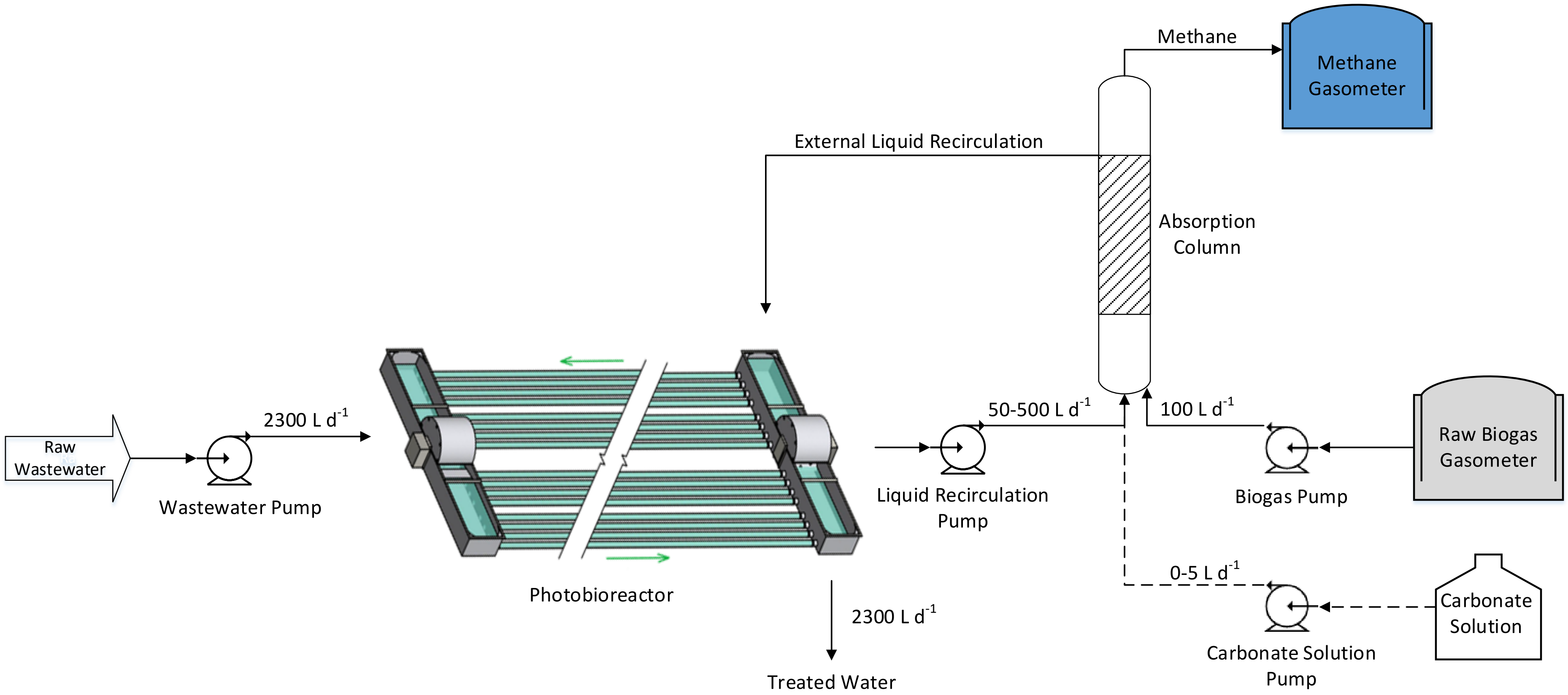


Figure 2. Concentration of CO_2 (■), N_2 + O_2 (◆) and CH_4 (○) in the upgraded biogas at different L/G ratios.

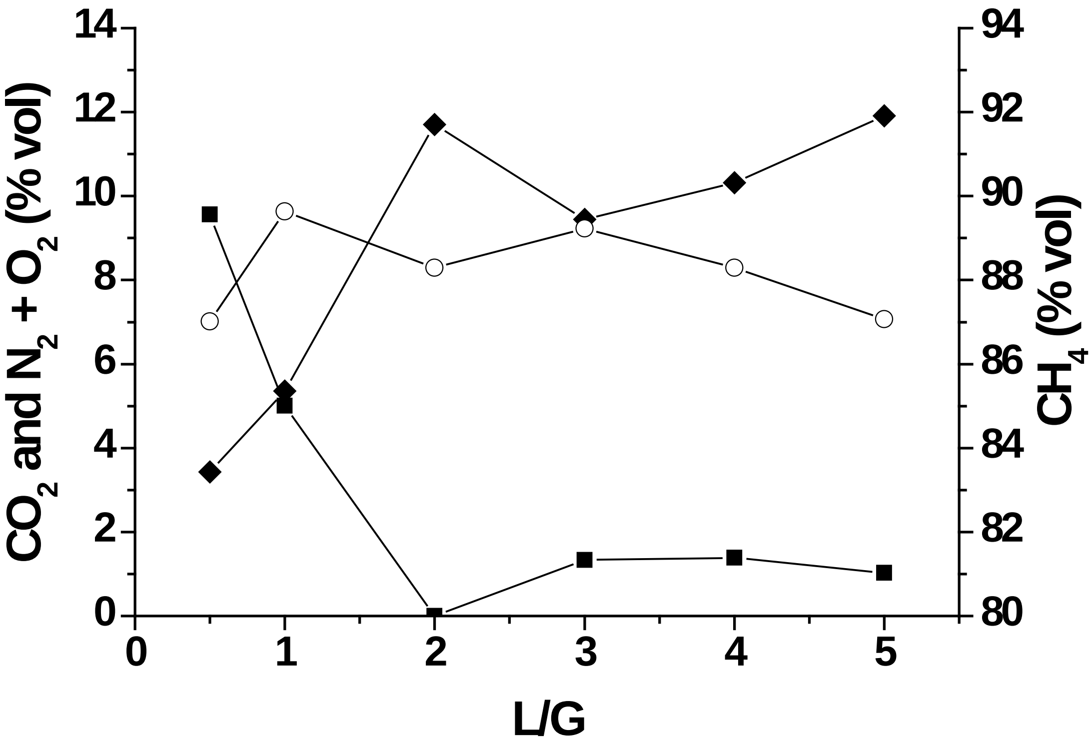


Figure 3. Concentration of CO_2 (■), $N_2 + O_2$ (◆) and CH_4 (○) in the upgraded biogas at different IC concentration in the cultivation broth of the AC.

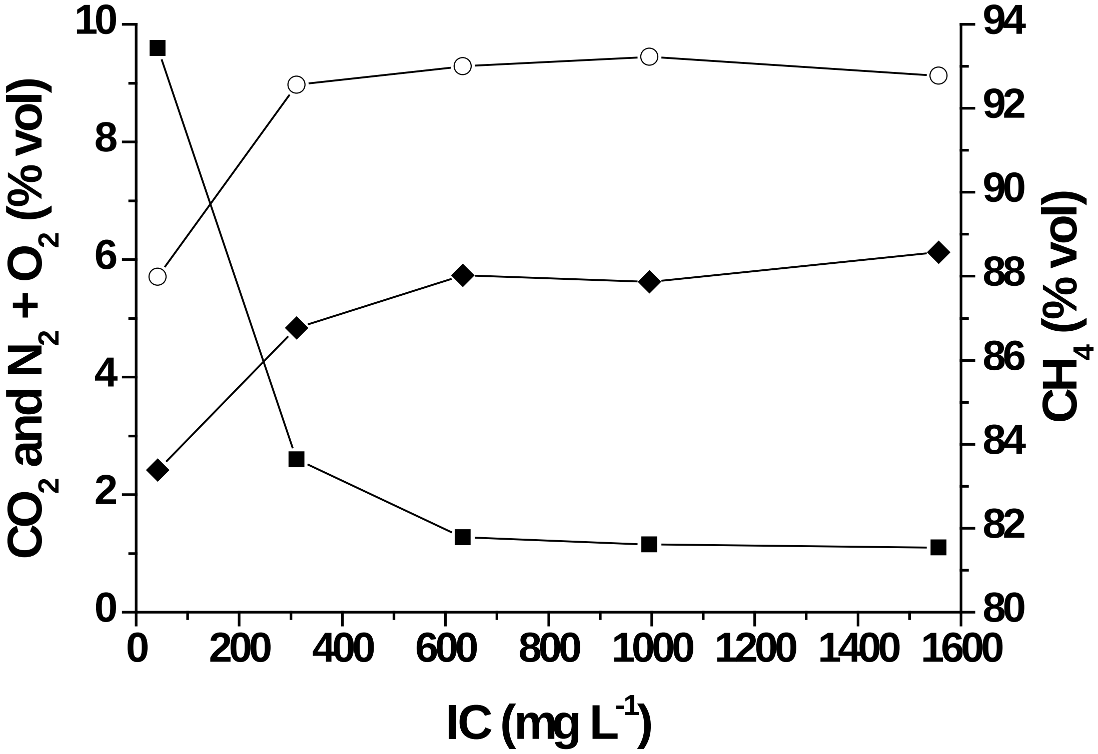


Figure 4. Time course of the concentration of CO_2 (■), N_2 + O_2 (◆) and CH_4 (○) in the upgraded biogas during continuous process operation.

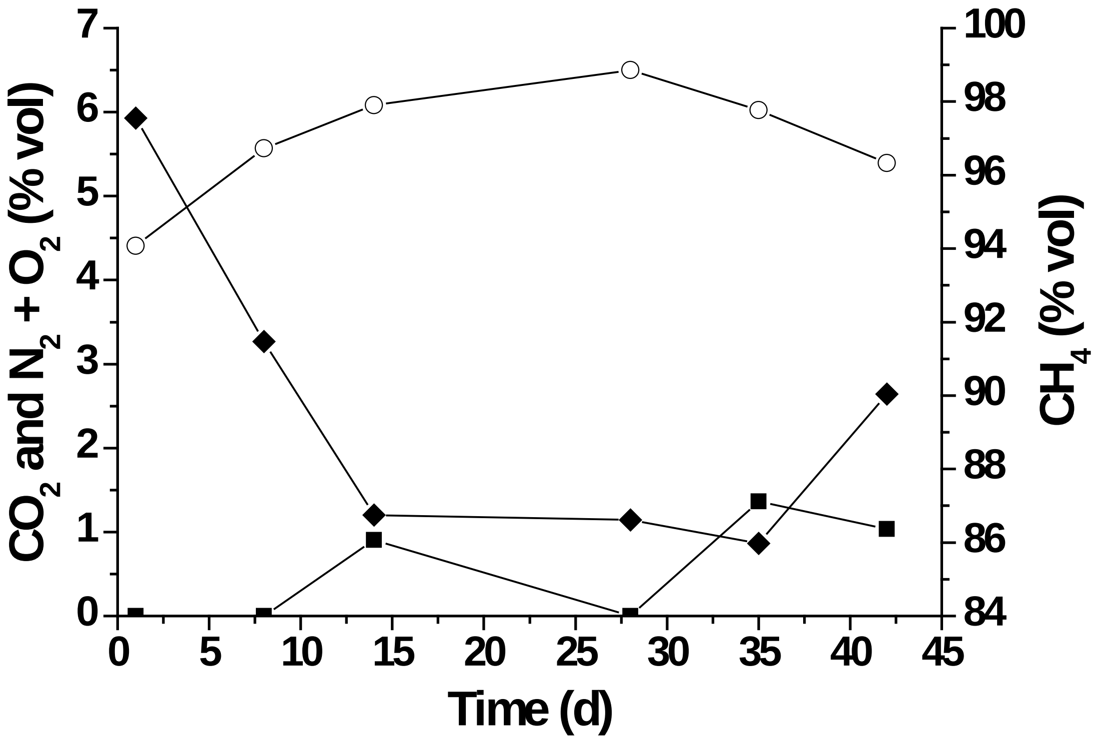


Figure 5. Time course of the influent (solid symbols) and effluent (empty symbols) concentration of total organic carbon (squares), inorganic carbon (diamonds) and total nitrogen (circles) throughout the continuous operation of the PBR

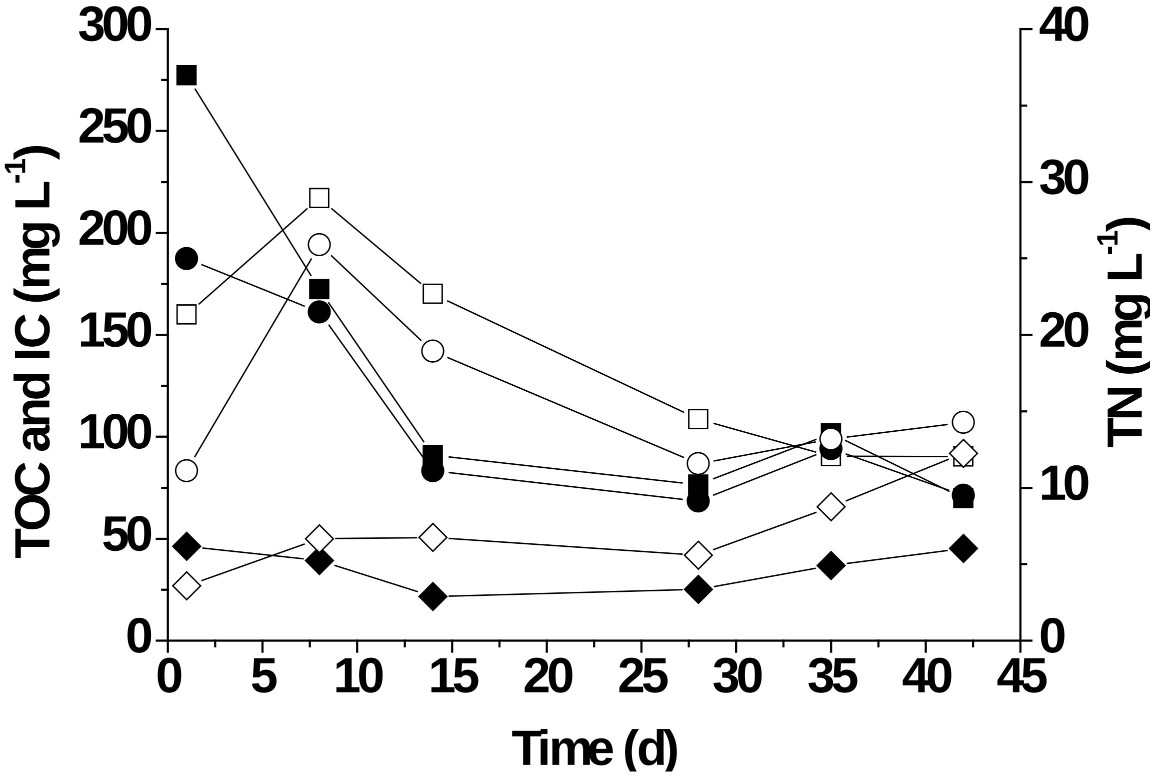


Table 1. Operational parameters during the evaluation of the influence of the L/G ratio in the AC.

L/G ratio	**Liquid flowrate ($L\ d^{-1}$)**	**Biogas flowrate ($L\ d^{-1}$)**	**Biogas HRT (h)**
0.5	50	100	10.8
1.0	100	100	5.4
2.0	200	100	2.7
3.0	300	100	1.8
4.0	400	100	1.4
5.0	500	100	1.1

Influence of liquid-to-biogas ratio and alkalinity on the biogas upgrading performance in a demo scale algal-bacterial photobioreactor

David Marín[1, 2, 3], Antonio Ortíz[4], Rubén Díez-Montero[4], Enrica Uggetti[4], Joan García[4], Raquel Lebrero[1, 2], Raúl Muñoz[1, 2, *]

[1] Department of Chemical Engineering and Environmental Technology, School of Industrial Engineering, University of Valladolid, Dr. Mergelina, s/n, 47011, Valladolid, Spain.

[2] Institute of Sustainable Processes, University of Valladolid, Dr. Mergelina, s/n, 47011, Valladolid, Spain.

[3] Universidad Pedagógica Nacional Francisco Morazán, Boulevard Centroamérica, Tegucigalpa, Honduras.

[4] GEMMA – Group of Environmental Engineering and Microbiology, Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya – BarcelonaTech, c/ Jordi Girona 1-3, Barcelona E-08034, Spain.

[*] Corresponding author: mutora@iq.uva.es

1. Influence of alkalinity on the quality of the upgraded biogas

Figure S1. Influence of the IC concentration in the cultivation broth of the AC on the pH of the cultivation broth in the (○) PBR and (■) AC.

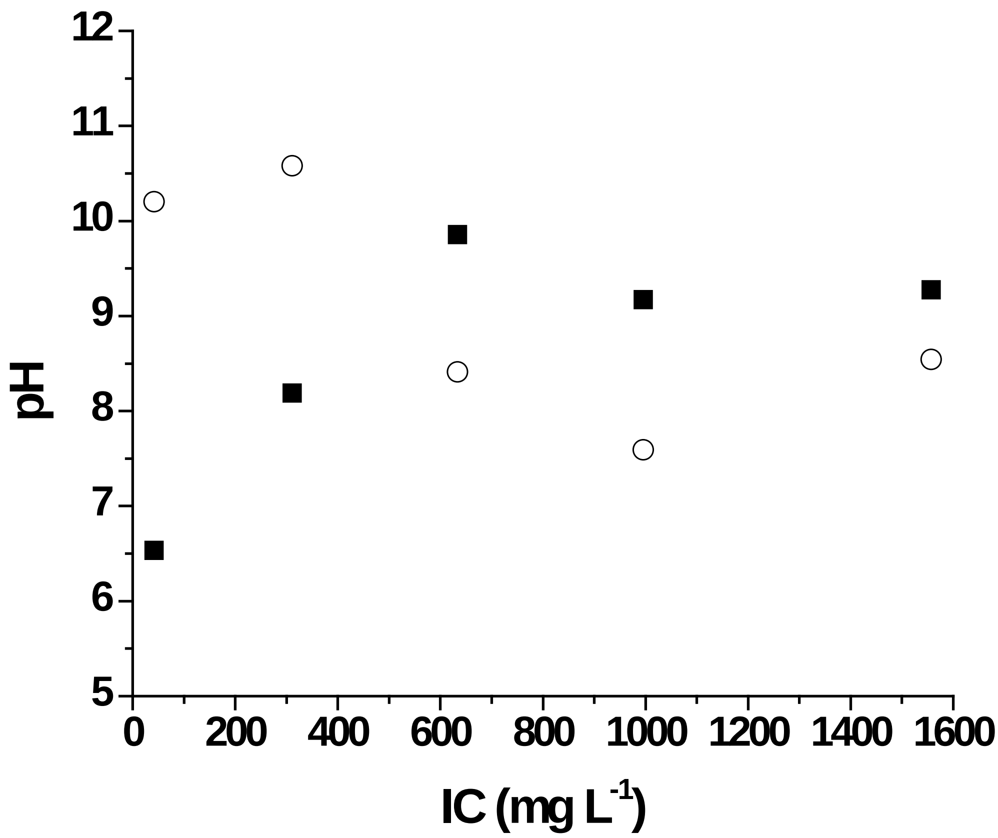
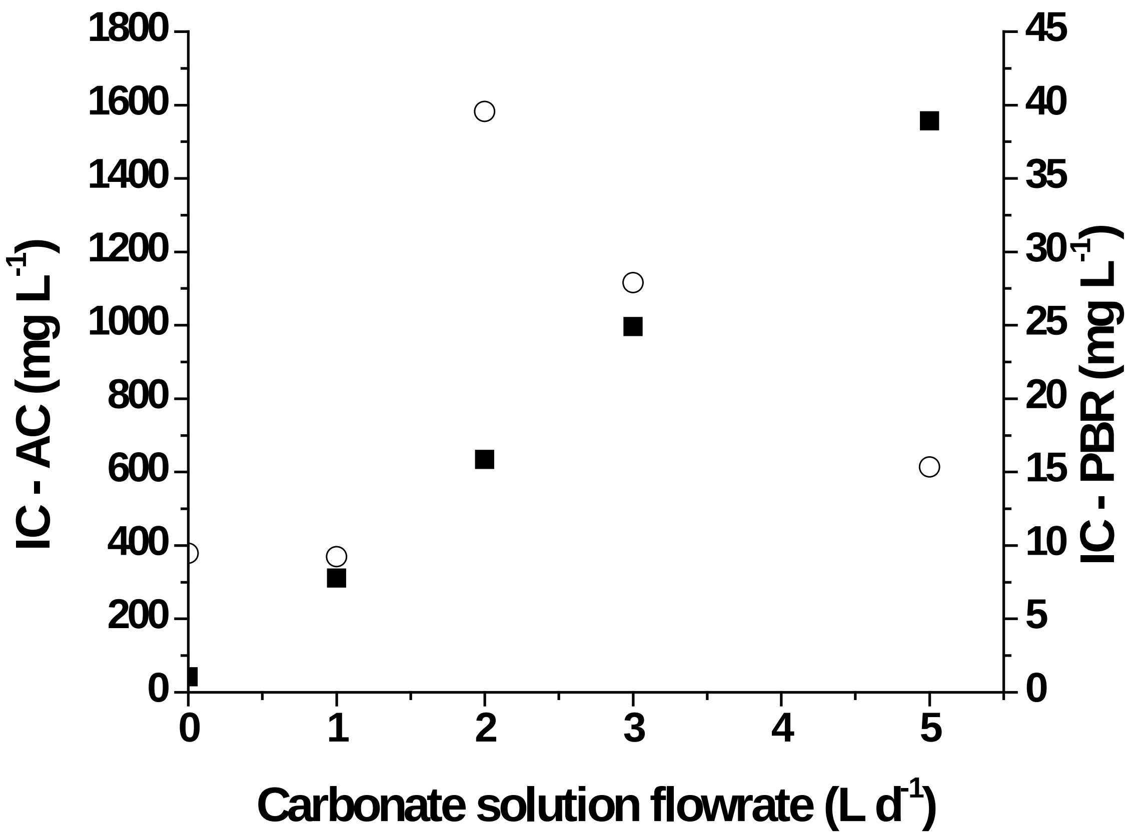
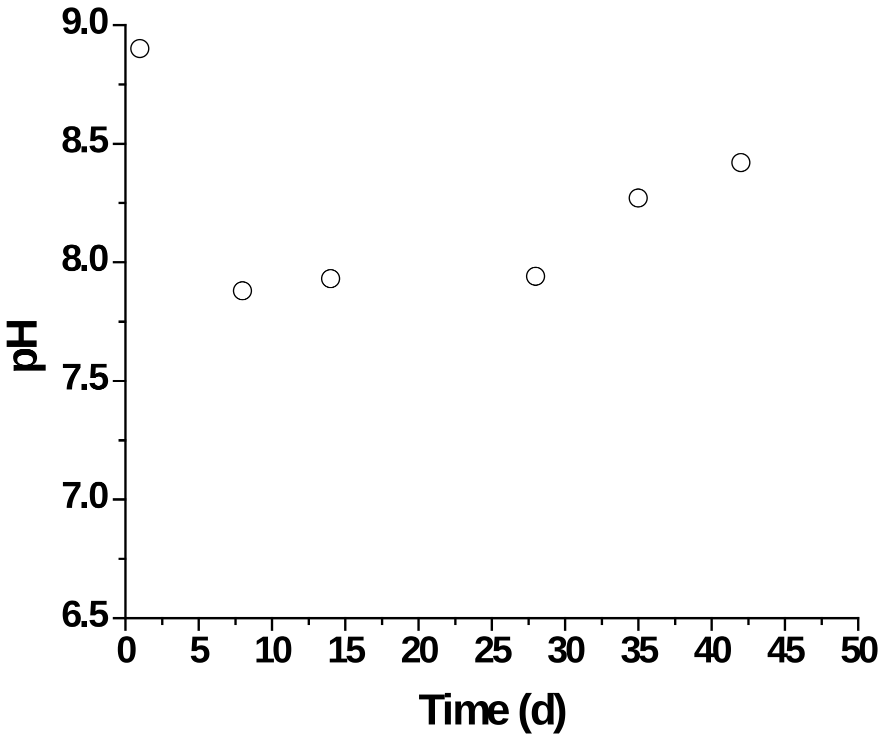


Figure S2. Influence of the carbonate solution flowrate on the IC concentration in the cultivation broth of the (○) PBR and (■) AC.



2. Continuous Operation

Figure S3. Time course of the pH in the cultivation broth of the PBR during the continuous biogas upgrading assay.



3. Temperature and biomass concentration

Table S**1.** Temperature and biomass concentration in the PBR during the evaluation of the influence of the L/G ratio on the quality of the upgraded biogas.

L/G ratio	Temperature in the AC (ºC)	Temperature in the PBR (ºC)	TSS (g L^{-1})
0.5	29.9	27.4	0.11
1.0	30.3	28.0	0.15
2.0	33.4	37.2	0.20
3.0	33.5	36.9	0.45
4.0	32.3	35.0	0.37
5.0	32.4	22.1	0.27

Table S2. Temperature and biomass concentration in the PBR during the evaluation of the influence of the alkalinity of the cultivation broth in AC on the quality of the upgraded biogas.

IC Concentration (mg L^{-1})	Temperature in the AC (ºC)	Temperature in the PBR (ºC)	TSS (g L^{-1})
42	31.7	28.4	0.40
311	32.5	27.4	0.43
634	31.3	29.4	0.49
996	35.0	32.8	0.19
1557	31.3	30.1	0.25

Table S3. Temperature and biomass concentration in the PBR during the continuous photosynthetic biogas upgrading experiment.

Day	Temperature in the AC (ºC)	Temperature in the PBR (ºC)	TSS (g L-1)
1	32.4	26.1	0.98
8	31.6	21.2	1.27
14	33.4	21.0	0.77
28	31.3	19.2	0.68
35	30.5	16.1	1.27
42	31.2	18.2	0.98