Development of a control strategy to cope with biogas flowrate variations during photosynthetic biogas upgrading

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ABSTRACT

The design and evaluation of a control system for a photosynthetic biogas upgrading unit was successfully carried out in this study. This control system ensured a specific biomethane quality under any disturbance in the biogas flowrate. The recycling liquid flowrate, and indirectly the liquid to biogas (L/G) ratio, was selected as the manipulated variable in order to maintain the CO_2 and O_2 content of biomethane, and therefore comply with the requirements for its use as natural gas substitute (≤2.5% and ≤1.0%, respectively). The control system was able to maintain the biomethane CO_2 content below the set point value under a stepwise increase in the biogas flowrate from 60 to 150 ml min^{-1}, together with negligible H_2S concentrations and an O_2 stripping from the recycling liquid to the biomethane lower than 1%, thus obtaining a consistent biomethane quality over time. On the contrary, the biomethane CO_2 content increased up to 13.2% under this stepwise increase in the biogas flowrate without control system. Successful results were also obtained when the control system was challenged with stepwise surges in the biogas flowrate between 60 and 120 ml min^{-1} under different temperatures (15 and 35°C) and

inorganic carbon concentrations (1500, 500 and 100 mg L^{-1}) when the recycling liquid entering the absorption column presented a pH=10. However, the high liquid flowrates required at a cultivation broth pH of 8.5 as a result of the low CO_2 mass transfer led to an excessive O_2 desorption to the biomethane, resulting in biomethane O_2 contents >1%.

Keywords: Algal-bacterial processes; biogas upgrading; biomethane; photobioreactor; process control.

1. Introduction

Biogas is a byproduct obtained from the anaerobic digestion of organic waste and wastewater. It is typically composed of CH_4 (40-75%), CO_2 (30-50%), H_2S (0.005-2%) and other pollutants at trace level concentrations, such as oxygen, nitrogen, ammonia, siloxanes and volatile organic compounds [1]. The high CH_4 content has encouraged the use of biogas as a bioenergy vector for the production of heat and power, and even as a substitute of natural gas. However, the presence of other components apart from CH_4 hinders its direct injection into the natural gas grids or its use as a vehicle fuel. For instance, CO_2 results in higher greenhouse gas emission during biogas combustion, increases biogas transportation costs and reduces its specific calorific value. Similarly, H_2S reduction is highly recommended due to its corrosive, malodorous and pernicious nature [2]. In this context, biogas upgrading prior use as a vehicle fuel or its injection into natural gas grids is a compulsory step which must ensure concentrations of $CH_4 \geq 90\%$, $CO_2 \leq 2\text{-}4\%$, $O_2 \leq 1\%$ and trace levels of H_2S according to most international regulations [3,4].

Physical/chemical technologies for CO_2 removal often need a preliminary H_2S abatement stage and exhibit high energy and chemical requirements that jeopardize the economic

viability of biomethane as a renewable substitute of natural gas. On the other hand, biological technologies such as biofiltration or *in situ* microaerobic digestion for H_2S removal coupled to hydrogenotrophic biogas upgrading for CO_2 removal always involve a two-stage process [5]. In this regard, photosynthetic biogas upgrading through algal-bacterial processes represents a cost-effective and environmentally sustainable alternative for the simultaneous CO_2 and H_2S removal [6]. During photosynthetic biogas upgrading, microalgae use solar light energy to capture the CO_2 present in biogas, while H_2S is oxidized to S^0/SO_4^{2-} by sulfur-oxidizing bacteria using the oxygen photosynthetically produced [7]. In addition, the nutrients required to support microalgal and bacterial growth in this technology can be obtained from wastewaters from different sources, which contributes to enhance its environmental sustainability [8]. Photosynthetic biogas upgrading is typically implemented in two interconnected units consisting of a bubble absorption column (AC) that removes the unwanted pollutants from the biogas and a high rate algal pond (HRAP) where the biological processes above described occur.

Several works have evaluated the performance of photosynthetic biogas upgrading coupled to wastewater treatment under indoor conditions at a constant biogas flowrate [9–14]. However, the performance of anaerobic digestion is affected by multiple variables such as temperature, mixing regime, or feedstock composition and load, whose fluctuations could lead to changes in the daily biogas production and composition. These changes impact on the subsequent upgrading process and can compromise the quality of the biomethane produced [15–18]. Moreover, a recent study in an outdoors HRAP interconnected to an AC showed that the photosynthetic biogas upgrading performance is influenced by the environmental conditions prevailing throughout the year. Therefore, variations in the temperature, pH or alkalinity of the cultivation broth (i.e. associated to

rain or evaporation) ultimately impact on the CO_2 and H_2S mass transfer in the AC and consequently on the biomethane quality [19]. Thus, the development of a control system for the photosynthetic biogas upgrading process is necessary in order to make the process more robust towards environmental or operational fluctuations, and to ensure a biomethane complying with most regulations for its use as a natural gas substitute.

In this context, the liquid to gas ratio (L/G) has been identified as an important operating parameter in gas-liquid mass transfer units [20,21]. An increase in the gas flow rate reduces the mass transfer between the two phases, which is attributed to both the lower gas residence time and bubble coalescence. Conversely, an increase in the liquid flow rate entails a higher gas absorption in the liquid phase due to the higher the contact area, but an enhanced stripping of compounds from the liquid to the gas phase [22]. For instance, Serejo et al. [23] observed an increase in CO_2 removal efficiency at increasing L/G ratios up to 15; while a complete H_2S removal was achieved regardless of the tested L/G ratio due to the higher H_2S aqueous solubility. Nevertheless, an increase in the L/G ratio in the biogas absorption column also resulted in a higher O_2 concentration in the upgraded biogas, due to an enhanced desorption of the dissolved oxygen from the microalgae cultivation broth [24]. In this regard, the L/G ratio in the AC is a key operational parameter that must be optimized during photosynthetic biogas upgrading in order to guarantee consistent CO_2 and O_2 concentration in the biomethane.

This study aimed at designing and evaluating the performance of a control system for biogas upgrading in a HRAP interconnected to an AC to cope with fluctuations in biogas production over time. The process response against variations in biogas flowrate under

different environmental conditions (alkalinity, pH and temperature) was assessed with and without control system.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up was composed of an indoor 180 L HRAP interconnected to a 2.5 L AC via external liquid recirculation of the supernatant from a 10 L settler (Fig.1). The HRAP was continuously fed at 3 L d^{-1} with a mineral synthetic medium (pH 10) that simulated the composition of a high strength digestate from the anaerobic digestion process. The mineral medium had the following composition (g L^{-1}): 7.60 $NaHCO_3$, 3.70 Na_2CO_3, 0.58 K_2HPO_4, 1.91 NH_4Cl, 0.10 $MgSO_4 \cdot 7H_2O$, 0.02 $CaCl_2 \cdot 2H_2O$, 0.005 $FeSO_4 \cdot 7H_2O$ and 5 mL of a trace element solution prepared according to the *Spirulina* mineral salt medium recommended by the SAG Culture Collection [25]. The HRAP was continuously illuminated at ~1350 μmol m^{-2} s^{-1} and agitated at an internal recirculation velocity of ~20 cm s^{-1}. Synthetic biogas composed of 70% CH_4, 29.5% CO_2 and 0.5% H_2S (which is a typical composition of biogas obtained from the anaerobic digestion of sewage sludge or agro-industrial bio-waste [5,26]) was sparged co-currently with the recycling liquid into the AC via a metallic gas diffuser of 2 μm pore size located at the bottom of the AC.

<Fig.1>

The biogas flow rate variations were conducted using a mass flow controller (Aalborg, USA) connected to a synthetic biogas cylinder (Fig.1). The recycling liquid flow rate in the AC was pumped using a variable flow peristaltic pump DINKO D-25Vplus (Spain). The system was operated under steady state at an initial L/G ratio of 0.5 based on previous studies and at a constant liquid flow rate of 30 ml min^{-1} [27]. The upgraded biogas was accumulated in a Tedlar bag prior measuring its composition (CH_4, CO_2, H_2S and O_2

content) in an online gas analyzer INCA 4001 (UNION Instruments GmbH, Germany). The control unit was composed of a field-programmable gate array (FPGA) «myRio 1900» via an interface developed in LabVIEW 2014 (National Instruments). The pH of the cultivation medium was determined using a pH meter Eutech Cyberscan pH 510 (Eutech instruments, The Netherlands).

2.2. Control system design

A rule-based control method aiming at maintaining a biomethane quality over time under biogas flow rate fluctuations was developed. The control rules were designed based on previous observations. This type of control was selected because of the constraints imposed by the analyzer (with a sampling time of 1-2 hours), which prevented the use of standard control methods such as PID. Moreover, a rule-based control allowed taking advantage of the practical experience accumulated by the research team in the operation of this type of plants. In addition, the system was non-linear and time-varying, which would require the use of some type of gain-scheduling with the associated problems of tuning under different operating conditions. The CO_2 content in the upgraded biogas was chosen as one of the controlled variables since H_2S removal efficiency (RE) is typically higher than CO_2-RE due to the ~3 times higher H_2S Henry's Law constant (C_L/C_G), while CH_4 losses in the absorption column are negligible due to its low aqueous solubility [28]. Additionally, the O_2 content in the upgraded biogas resulting from the desorption of dissolved O_2 in the AC was the other controlled variable taken into account since a high concentration of O_2 in biomethane can result in explosive mixtures [29]. O_2 and CO_2 concentrations in the biomethane were fixed at a set point of 1% and 2.5%, respectively, in order to comply with most international regulations. The manipulated variable was the recycling liquid flow rate, which determines the L/G ratio in the AC (Fig.2).

<Fig. 2>

Fig. 3 shows the rules of the control system where $\Delta CO_2 = [CO_2]_{measured} - [CO_2]_{sp}$, $\Delta O_2 = [O_2]_{measured} - [O_2]_{sp}$; the value "measured " being the one obtained from the gas analyser and the set point (sp) the value fixed based on the target values of most international regulations. When the O_2 content in the biomethane was higher than 1% (set point value) (rule 1), the flow rate of the liquid pump was decreased even if the CO_2 content in the upgraded biogas was higher than the set point CO_2 concentration due to safety reasons. When O_2 content in the biomethane was < 1% and CO_2 content > 2.5%, the control system increased the flow rate of the recycling liquid pump in order to enhance CO_2 absorption (rule 2). In the case of rule 3, when CO_2 and O_2 concentration in the upgraded biogas complied with the set-point, the flow rate of the recycling liquid pump was decreased in order to save energy. In this context, the amount of change in the recycling liquid flow rate was variable depending on the values of the variables involved (O_2 and CO_2 concentration in the upgraded biogas) as shown in Fig.3.

<Fig. 3>

2.3. Step response of the control system interconnected to a HRAP

The proposed control system was evaluated under different perturbations in the biogas flow rate in order to test its effectiveness and robustness. First, a 4 h step increase from G = 60 to 150 ml min^{-1} and back to 60 ml min^{-1} was carried out to test the response of the system under biogas flow rate surges. Secondly, a similar step with a higher duration was implemented in order to ensure that the control system was able to maintain the steady state. Finally, the biogas flow rate was stepwise increased by 10 ml min^{-1} every 2 hours from 60 to 120 ml min^{-1} in the first 12 h and decreased to 60 ml min^{-1} within the next 12 h. This simulated real fluctuations in a biogas production process. The composition of the

upgraded biogas accumulated in the Tedlar bag was measured every two hours prior actuation of the control system, except in the case of the biogas flowrate of 150 ml min^{-1} where measurements were conducted every hour. These sampling times were selected based on the sampling volume requirements by the biogas analyzer and the low value of the biogas flows used in this laboratory scale set-up. All the experiments consisted of two similar consecutive biogas flowrate cycles under controlled and uncontrolled (without any change in the recycling liquid flowrate) conditions, in order to evaluate the effectiveness and significance of the control system. The values of the changes implemented in the liquid flowrate depending on the CO_2 and O_2 concentrations are summarized in Table S1 (Supplementary data).

2.4. Validation of the control system at varying biogas flowrates under different environmental conditions

Process response to the stepwise variations in biogas flowrate (stepwise variations from 60 to 120 ml min^{-1} for 12 h and from 120 to 60 ml min^{-1} for the next 12 h) was validated under controlled and uncontrolled conditions at different temperatures (15 and 35°C), pH (10 and 8.5) and inorganic carbon (IC) concentrations (1500, 500 and 100 mg L^{-1}) in the recycling liquid. The experiments were carried out in duplicate. For this purpose, a similar mineral medium, with different concentrations of $NaHCO_3$ and Na_2CO_3 to achieve the desired IC concentration and pH, was used as recycling liquid in the absorption column. The temperature of the recycling liquid before entering the absorption column was adjusted using an external heat exchanger (Fisherbrand™ Polystat™ Immersion Circulator, Germany) and the temperature in the absorption column was maintained using an external coil connected to a heat exchanger (Huber CC1-E Immersion-Thermostat Control, Germany). A different set of variations in the recycling liquid

flowrate (power pump changes) were used during these experiments due to the necessity of changing the pipe of the peristaltic liquid pump for the highest flowrate requested during some of these assays (Table S2 Supplementary data).

3. Results and discussion

3.1. Step response of the control system

<Fig.4>

Figure 4 shows the response of CO_2 and H_2S concentration in the upgraded biogas and pH in the recirculating broth at the outlet of the absorption column under controlled and uncontrolled conditions during a 4 hours biogas flowrate step increase from 60 to 150 ml min^{-1}, and back to 60 ml min^{-1}, along with the liquid flow rate during the control period. The performance of the experimental system was significantly affected when biogas flow rate was increased from 60 to 150 ml min^{-1} for 4-h. Hence, CO_2 concentration in the upgraded biogas increased from 1.5 to 10.7%, which corresponded to a CO_2-RE decrease from 95 to 64%, concomitantly with the 4-h step increase in the biogas flowrate when the control system was not running (Fig. 4a). Similarly, an increase in the H_2S content from zero to 400 ppm_v in the upgraded biogas (which corresponded to a H_2S-RE decrease from 100 to 92%) was observed as a result of the surge in biogas flow rate (Fig. 4b). This deterioration of the system performance was recorded in spite of the high alkalinity of the cultivation broth (~2500-3000 mg IC L^{-1}), which was associated to an IC accumulation mediated by water evaporation and the high strength medium used as nutrient source in the HRAP. The increase in the biogas flowrate (×2.5) at a constant liquid flowrate resulted in a decrease in the L/G ratio from 0.5 to 0.2, which likely mediated CO_2 and H_2S saturation of the recycling cultivation broth with the subsequent decrease in the pH along the AC. In this context, the pH decreased from a value of 10 at the bottom of the

AC to 9.6 and 8.4 at the top of the AC at biogas flowrates of 60 and 150 ml min^{-1}, respectively (Fig. 4c). This drop in the pH along the AC resulted in a lower CO_2 and H_2S gas-liquid mass transfer due to the decrease in the concentration gradient of these acidic gases in the liquid phase. The O_2 content in the upgraded biogas remained almost constant at ~0.2%, as a result of the constant liquid flowrate and the low L/G ratios. Likewise, Toledo-Cervantes et al. [14] reported O_2 concentrations in the biomethane below 0.1% in a similar indoor system at L/G ratios ranging from 0.3 and 0.5.

When the control system was initiated, CO_2 content of the upgraded biogas increased up to 5.4% (~2 times less than that without control) during the first surge in biogas flowrate to 150 ml min^{-1}, and remained under the set point value during the duration of the second flowrate step (Fig. 4a). The lower CO_2 content recorded in the upgraded biogas during the latter step could be explained by the higher liquid flowrate (L) imposed by the control system prior to the second surge in biogas flowrate. The H_2S content of the upgraded biogas during this experiment was negligible regardless of the biogas flowrate, due to its high solubility in water and the effectiveness of the proposed control system (Fig. 4b). The higher CO_2 and H_2S-REs achieved when the control system was active could be attributed to the lower acidification of the cultivation broth between the bottom and the top of the AC as a result of the lower amount of CO_2 and H_2S transferred per volume of recycling liquid when the liquid flow rate in the AC was actively controlled. Moreover, the O_2 content in the upgraded biogas remained under the set point value along the entire period. Overall, the maximum L/G ratio recorded was 1.3 at a liquid flowrate of 77 ml min^{-1} (Fig. 4c), which ensured a good biomethane quality (CH_4 content >95%) during most of the experiment.

When the step increase in biogas flowrate was maintained for 12 h in order to confirm the ability of the system to maintain a steady state over time, the CO_2 content in the upgraded

biogas increased up to 13.2% when the control system was not active (Fig. 5a). The lower CO_2 content in the upgraded biogas observed during the 4-h step test confirmed that the system was not able to reach steady state at a biogas flowrate of 150 ml min^{-1}. In this context, only ~4-5 h after the step increase in the biogas flowrate, the CO_2 content in the upgraded biogas remained almost constant. On the contrary, the maximum H_2S content obtained in this experiment was 230 ppm_v lower than during the 4-h step test (Fig. 5b). The increase in H_2S removal during this experiment could be attributed to a higher dissolved oxygen (DO) concentration in the cultivation broth and/or bacteria activity during these days, which ultimately enhanced H_2S oxidation. Unfortunately, data of DO or pH in the cultivation broth of the HRAP was not continuously recorded and this hypothesis could not be fully confirmed.

<Fig. 5>

The control system showed a similar performance regardless of the duration of the biogas flowrate step increase: a maximum CO_2 content of 4.9% in the upgraded biogas (~2.7 times lower than that without control) was achieved in both step increases from 60 to 150 ml min^{-1} (Fig. 5a), which correlated with the similar L/G ratios recorded when increasing the biogas flowrate. In addition, the H_2S content in the upgraded biogas reached 120 ppm_v with the increase in the biogas flowrate, obtaining a nearly complete removal afterwards (H_2S-RE >99%) (Fig. 5b). Likewise, the O_2 concentration remained under the set point value during both experiments with and without control system. Moreover, identical maximum liquid flowrate values (77 ml min^{-1}) and consequently L/G ratios (1.3) were obtained in both step increase experiments (Fig. 5c). The lower CH_4 concentration recorded during the step increase was 93.4% and approximately three hours after the step (the control system had acted 3 times), a suitable biomethane quality (CH_4 content >95%) was achieved. The results revealed that the implementation of a control system in a large-

scale biogas upgrading unit would entail a faster and even more accurate process response as a result of the shorter time between measurements.

The biogas flowrate was also stepwise increased by 10 ml min^{-1} every 2 h from 60 to 120 ml min^{-1}. Without the control system, the CO_2 concentration in the upgraded biogas increased up to 7.8%, already exceeding the CO_2 set point (2.5%) at a biogas flowrate of 90 ml min^{-1} (corresponding to L/G ratios < 0.33) (Fig. 6a). These results were in accordance with Toledo-Cervantes et al. [14], who recorded CO_2-REs of 70.3 and 97.3% at L/G ratios of 0.3 and 0.5, respectively, operating under co-current mode under a similar high pH and alkalinity of the cultivation broth than those tested in this study. When the biogas flowrate stepwise decreased from 150 to 60 ml min^{-1}, the CO_2-RE slowly increased due to the previous acidification of the cultivation broth, and the system was not able to recover the initial biomethane quality (CO_2 content ≤ 2.5%) even at the lowest biogas flowrate of 60 ml min^{-1}. In addition, the H_2S content in the upgraded biogas increased up to 280 ppm_v (Fig. 6b), while the O_2 remained lower than the set point value (1%) as in the previous experiments.

<Fig. 6>

The maximum CO_2 concentration in the upgraded biogas when the control system was active was 3.1% (~2.5 times lower than that without control). A value lower than the set point was obtained after two control actions (Fig. 6a). The lowest CO_2-RE recorded was 89.5%, compared to the lowest value of 73.6% observed without control. In accordance with the results obtained without control, the CO_2 content in the upgraded biogas exceeded the set point value when the L/G ratio was lower than 0.38. Furthermore, the H_2S content in the biomethane was negligible regardless the biogas flowrate, which confirmed the robustness of the control system for H_2S removal using the CO_2 content in upgraded biogas as controlled variable. O_2 content in the biomethane remained below 1%

with a maximum liquid flowrate and L/G ratio of 77 ml min^{-1} and 1.1, respectively (Fig. 6c). Finally, CH_4 concentration in the upgraded biogas was >94 % during the complete experimentation period, thus demonstrating the effectiveness of the control system even if the biogas flowrate variations occurred as sequential steps of lower magnitude.

Overall, the control strategy implemented in the experimental set-up consisting of a HRAP interconnected with an AC was able to maintain the operational variables below the set-points under multiple biogas flowrate surges, thus providing the required biomethane quality during most of the experimental period. However, the response of the system when operating under different environmental conditions (mediated by seasonal changes) could be different. Therefore, a further validation of the control system was carried out by assessing the upgrading performance at different alkalinities, pHs and temperature values.

3.2. Validation of the control system under different environmental conditions

3.2.1. Alkalinity

The alkalinity of the cultivation broth has been previously identified as a key parameter on CO_2 and H_2S removal in photosynthetic biogas upgrading. A high alkalinity medium results in a high buffer capacity and; consequently, in improved CO_2 and H_2S mass transfer rates as a result of the low decrease in the pH along the absorption column [13]. In this context, high strength digestates or agroindustrial wastewaters (i.e. piggery wastewaters) could be used to achieve an effective photosynthetic biogas upgrading since they usually contain high inorganic carbon concentrations (~1500 mg L^{-1}) [30,31]. For instance, Marin et al. [24] supplemented a carbonate solution to the AC in order to increase the alkalinity of the recycling liquid, and improved the CO_2 and H_2S-REs when the photobioreactor was fed with an agricultural wastewater with a low IC concentration

(36 mg L^{-1}). However, carbonate dilution might occur due to rainfall or no carbonate addition in outdoor systems. Then, the use of medium strength digestates (~500 mg IC L^{-1}) or domestic wastewaters (~100 mg IC L^{-1}), which are typically found in wastewater treatment plants, is the most common operating alternative. Under these scenarios, a decrease in the upgrading process efficiency could occur, the validation of the control system under different alkalinity conditions being necessary [19].

The stepwise increase in biogas flowrate from 60 to 120 ml min^{-1} without control system resulted in maximum CO_2 contents in the upgraded biogas of 13.4, 18.0 and 19.6%, while H_2S concentration reached 552, 1440 and 2033 ppm_v at a pH of 10 and IC concentrations of 1500, 500 and 100 mg L^{-1}, respectively (Fig. S1 – Supplementary Material). The highest CO_2 and H_2S removals were obtained at the highest alkalinity content (1500 mg IC L^{-1}), while the CO_2 content in the upgraded biogas at lower alkalinities was higher than the set point value even at the lowest biogas flowrate. The system performance was significantly improved when the control system was turned on. Immediately after the increase in biogas flowrate to 70 ml min^{-1}, the CO_2 content in the upgraded biogas exceeded the set point except for the experiment at 1500 mg IC L^{-1}. In the assays at IC concentrations of 500 and 100 mg L^{-1}, the control system increased the recycling liquid flowrate to 50 and 57 ml min^{-1}, respectively, based on the values of the previously stablished rules (Table S1). As a consequence, the highest CO_2 concentrations recorded in the upgraded biogas were 3.7, 4.2 and 5.1% at IC concentrations of 1500, 500 and 100 mg L^{-1}, respectively. These results demonstrated that when the control system was active, the influence of the alkalinity on the upgrading performance was significantly reduced (Fig. 7a). Similarly, the maximum H_2S content in the upgraded biogas was 12, 184 and 331 ppm_v at 1500, 500 and 100 mg IC L^{-1}, respectively (Fig. 7b). On the other hand, no significant O_2 concentration was measured in the upgraded biogas (<1%) even at 100 mg

IC L^{-1}. Maximum liquid flowrates of 57, 99 and 99 ml min^{-1}, corresponding to maximum L/G ratios of 0.5, 1.1 and 1.1, were recorded at 1500, 500 and 100 mg IC L^{-1}, respectively. It is important to notice that, although similar maximum liquid flowrates were set at 500 and 100 mg IC L^{-1}, the highest flowrate was maintained during longer periods of time at the lowest alkalinity (Fig. 7c). These results agreed with Bahr et al. [6], who recorded an O_2 content in the biomethane below 1% at a L/G 1.2 regardless of the pH.

<Fig. 7>

3.2.2. pH

pH also exerts a high influence on CO_2 and H_2S removal in the absorption process due to the significant improvement of the solubility of these gases at high pH values. Under optimal conditions of alkalinity in the cultivation broth, typically encountered in high strength digestates (pH>9, 1500 mg IC L^{-1}), a high pH value (up to 11) is expected in the cultivation broth of a photosynthetic biogas upgrading unit as a result of the pH increase mediated by CO_2 uptake during microalgal photosynthesis [30,32,33]. Nevertheless, a continuous, long-term exposition to high biogas flowrates could lead to the acidification of the cultivation broth even at this high alkalinity. In this sense, the performance of the control system was assessed under high alkalinity at two different pH values (10 and 8.5). In spite of the high alkalinity of the recycling liquid, CO_2 content in the upgraded biogas under uncontrolled conditions increased up to 21.9% at pH 8.5, corresponding to CO_2-RE of 25.8%, while the maximum CO_2 concentration recorded at a pH 10 was 13.4% (Fig. S2). Indeed, the minimum CO_2 concentration recorded under these conditions and pH 8.5 was 16% (greater than the highest CO_2 value during the experiment at pH 10). In the case of H_2S, the highest concentration recorded was 941 ppm_v at pH 8.5 versus 12 ppm_v at pH 10 (Fig. S2). These results highlight the key role of the operational pH in the absorption process of these acidic gases, and were in agreement with Bahr et al. [6], who

recorded CO_2 removals lower than 20% at pH 7 and almost a complete CO_2 removal at pH 10 regardless of the liquid flowrate.

As a result of the lower CO_2-REs at pH 8.5 and, consequently, the high difference between the CO_2 measured and CO_2 set point when the control system was turned on, the increase in the flowrate of the recycling liquid pump was higher compared to other assays, reaching 204 and 211 ml min^{-1} during the first and second biogas surges, respectively (Fig. 8d). Therefore, at L/G ratios > 1.5, the O_2 content in the upgraded biogas increased over the O_2 set point value (1%). Hence, the recycling liquid flowrate was reduced by the control system during the next step, regardless of the CO_2 concentration in the upgraded biogas due to the priority of the established rules. As a result, the CO_2 content during these assays did not comply with the established set point value since the O_2 content increased when increasing the liquid flowrate (Fig. 8c). These results were in accordance with Marin et al. [24], who recorded an increase in the content of N_2+O_2 in the upgraded biogas from ~5 to ~12% at increasing the L/G ratio from 1 to 2. Nevertheless, the control system mediated a decrease in the CO_2 content to 4.4% (CO_2-RE of 85%), which was 3.5 times lower than the lowest value recorded without the control system (Fig. 8a). Moreover, the maximum H_2S concentration in the upgraded biogas under these conditions was 238 ppm_v, H_2S being completely removed during most of the time (Fig. 8b).

<Fig. 8>

3.2.3. Different temperature conditions

Temperature is an important environmental variable, which has to be taken into account specially when operating outdoor systems. This variable has a significant influence on gas solubility (decreasing with the increase in the temperature), the ionic equilibria, and consequently, the pH [34]. Moreover, temperature affects microalgae and bacteria

growth, the optimal temperature for microalgae activity being between 15 and 35ºC, depending on the strain [35]. Therefore, the control system was evaluated under two representative temperatures typically found during autumn-spring and summer in mild climates.

Under uncontrolled conditions, the CO_2 and H_2S concentrations in the upgraded biogas reached values of 11.4 and 11.7% and 393 and 305 ppm_v at 15 and 35ºC, respectively (Fig. S3). The similarity between the values recorded at both temperatures was attributed to the high alkalinity of the cultivation broth. These results were in agreement with Rodero et al. [13], who demonstrated the negligible influence of the temperature at high alkalinity of the cultivation broth, while at low alkalinity, lower temperatures enhanced CO_2-REs. Similarly, when the control system was turned on, the highest CO_2 content in the upgraded biogas was 4.7 and 4.4% at 15 and 35ºC, respectively, while almost a complete H_2S removal was obtained regardless of the liquid flowrate and temperature (Fig. 9a, b). Finally, similar liquid flowrates were needed during the experiments (highest liquid flowrate of 64 ml min^{-1} at 35ºC vs. 57 ml min^{-1} at 15ºC), resulting in low O_2 concentrations <1% consistent with the low L/G ratios (<0.6) (Fig. 9c).

<Fig.9>

Conclusions

The recycling liquid flowrate was identified as a key operational variable in the control of the CO_2 and O_2 content in the upgraded biogas during photosynthetic biogas upgrading. The control system developed was capable of guaranteeing a CO_2 content lower than 2.5% during most of the experimental period regardless of the temperature and the alkalinity of the cultivation broth. Moreover, the O_2 remained lower than 1% and negligible concentrations of H_2S were recorded, obtaining a CH_4 concentration in the

upgraded biogas >94%. On the contrary, the target biomethane quality was not achieved at a pH 8.5 due to the concomitant increase of both the O_2 and CO_2 concentrations in the upgraded biogas requiring opposite control strategies, confirming that pH was a critical operating parameter in these systems. In summary, the control system was effective under most tested laboratory conditions assuring an optimal liquid flowrate over time at low investment costs, although further optimization and validation under outdoor conditions and demo scale is still required.

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Appendix A. Supplementary data

References

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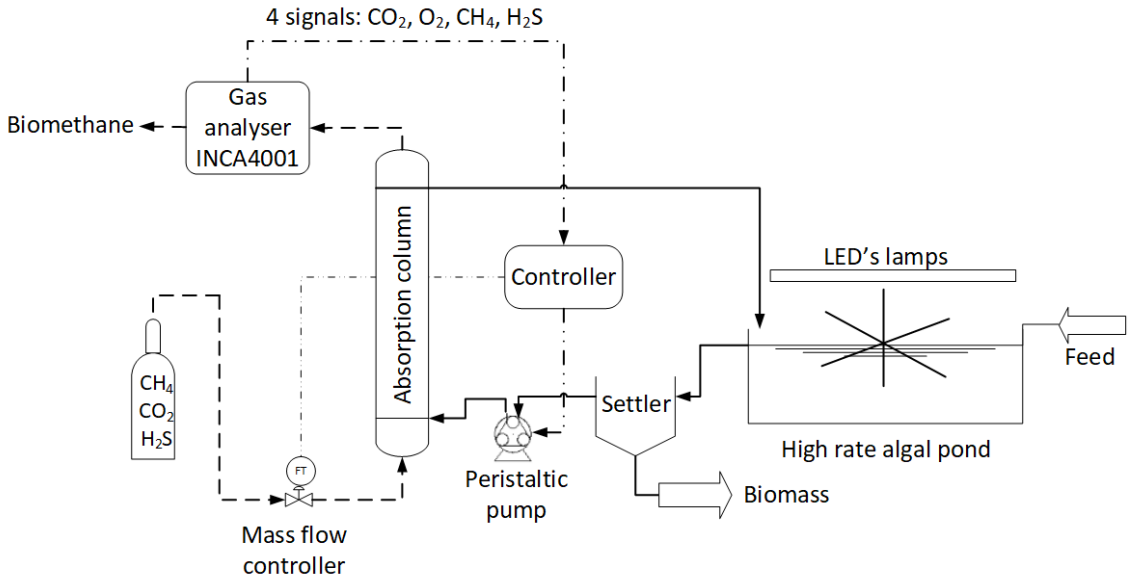


Fig. 1. Experimental set-up and control layout for photosynthetic biogas upgrading

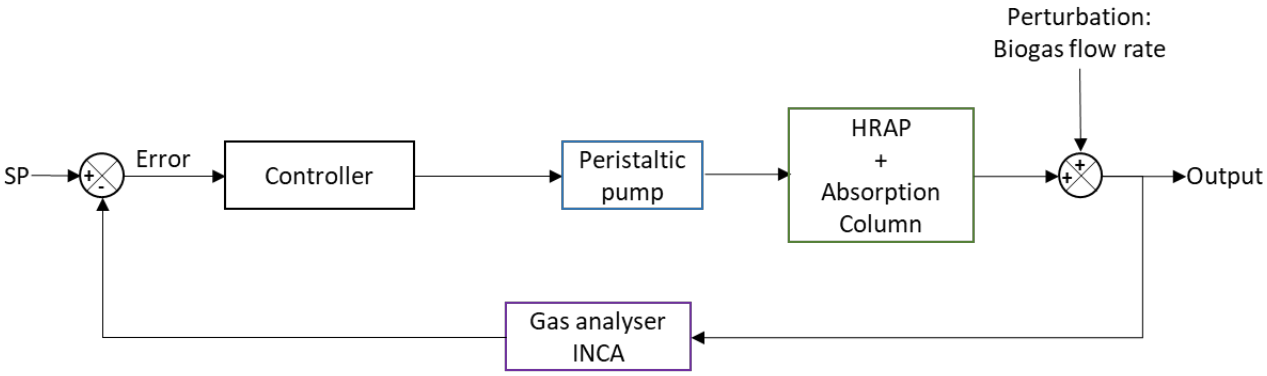
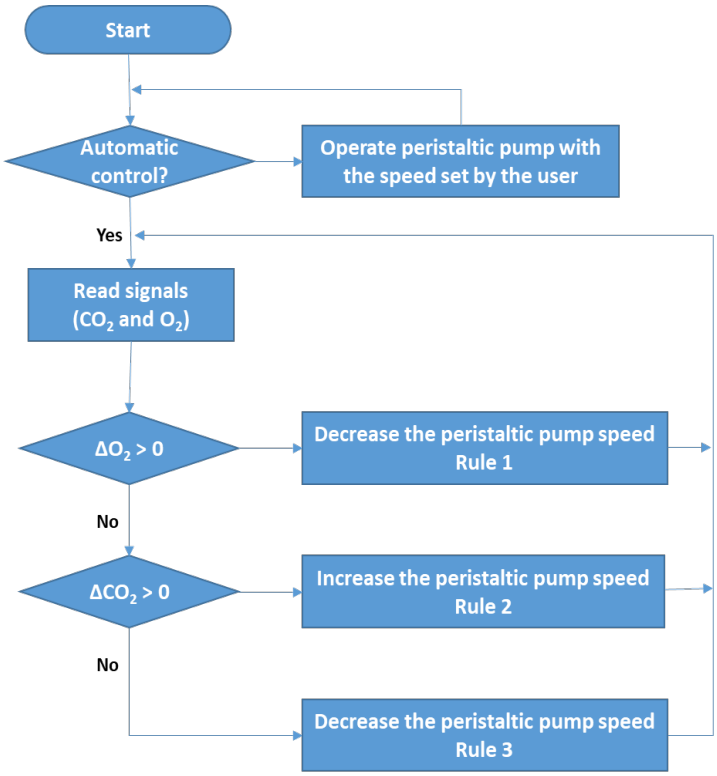


Fig. 2. Block diagram of the control system



Rule1:

ΔO2 > 5 → pump speed decrease 30%
ΔO2 ϵ [1 … 5] → pump speed decrease 25%
ΔO2 ϵ [0.5 … 1] → pump speed decrease 20%
ΔO2 ϵ [0 … 0.5] → pump speed decrease 15%

Rule2:

ΔCO2 > 10 → pump speed increase 40%
ΔCO2 ϵ [5 … 10] → pump speed increase 30%
ΔCO2 ϵ [1 … 5] → pump speed increase 25%
ΔCO2 ϵ [0.5 … 1] → pump speed increase 20%
ΔCO2 ϵ [0 … 0.5] → pump speed increase 15%

Rule3:

ΔCO2 ϵ [-0.5 … 0] → pump speed decrease 2.5%
ΔCO2 ϵ [-1 … -0.5] → pump speed decrease 5%
ΔCO2 ϵ [-2.5 … -1] → pump speed decrease 7.5%

Fig. 3. Flow diagram of the ruled-based control system and rule values

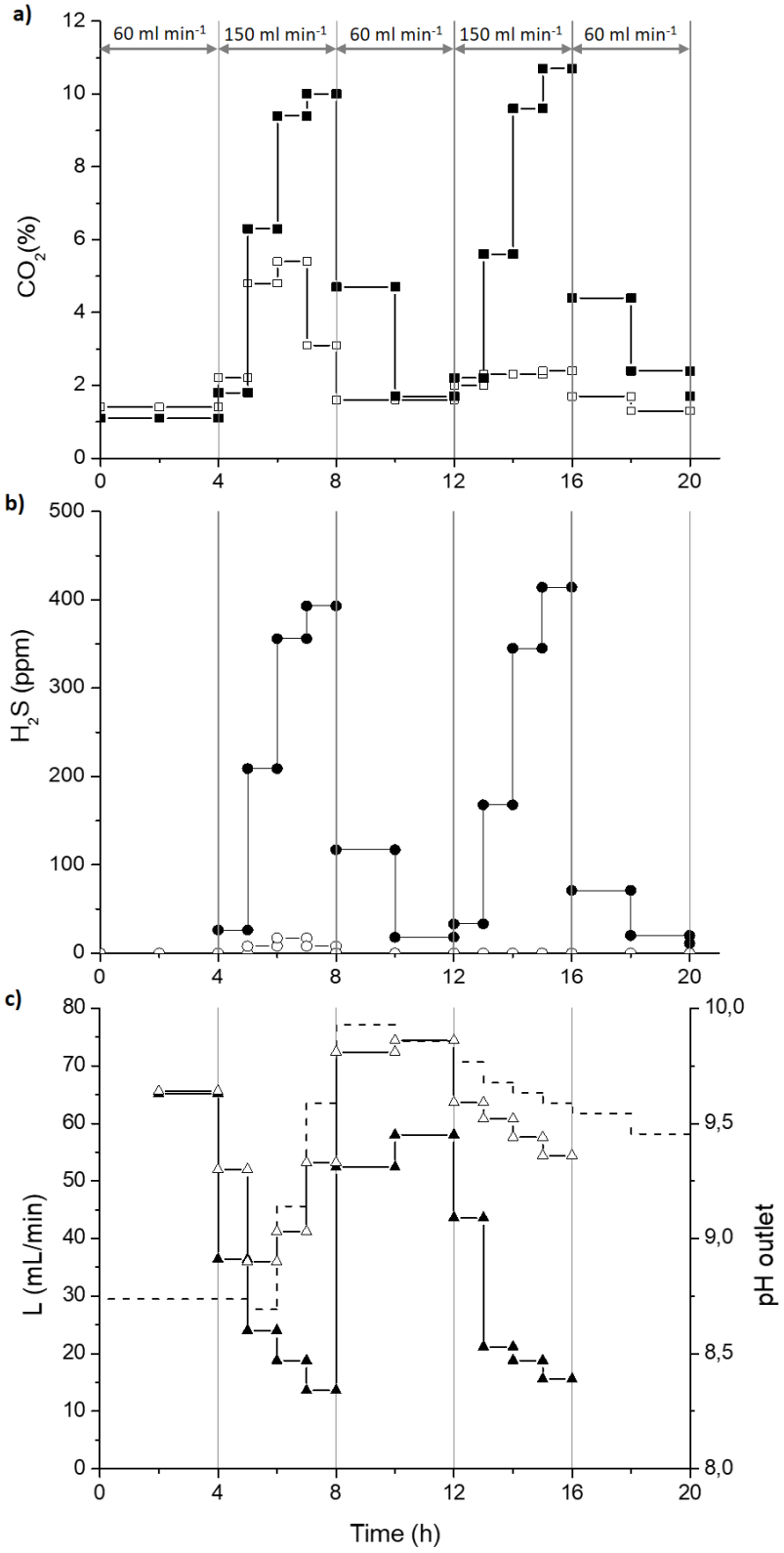


Fig.4. Time course of a) CO_2 content, b) H_2S content of the upgraded biogas and c) liquid flow rate (dashed line) and pH at the outlet of the absorption column under controlled (open) and uncontrolled (solid) conditions during the 4-h biogas flowrate step increase experiment.

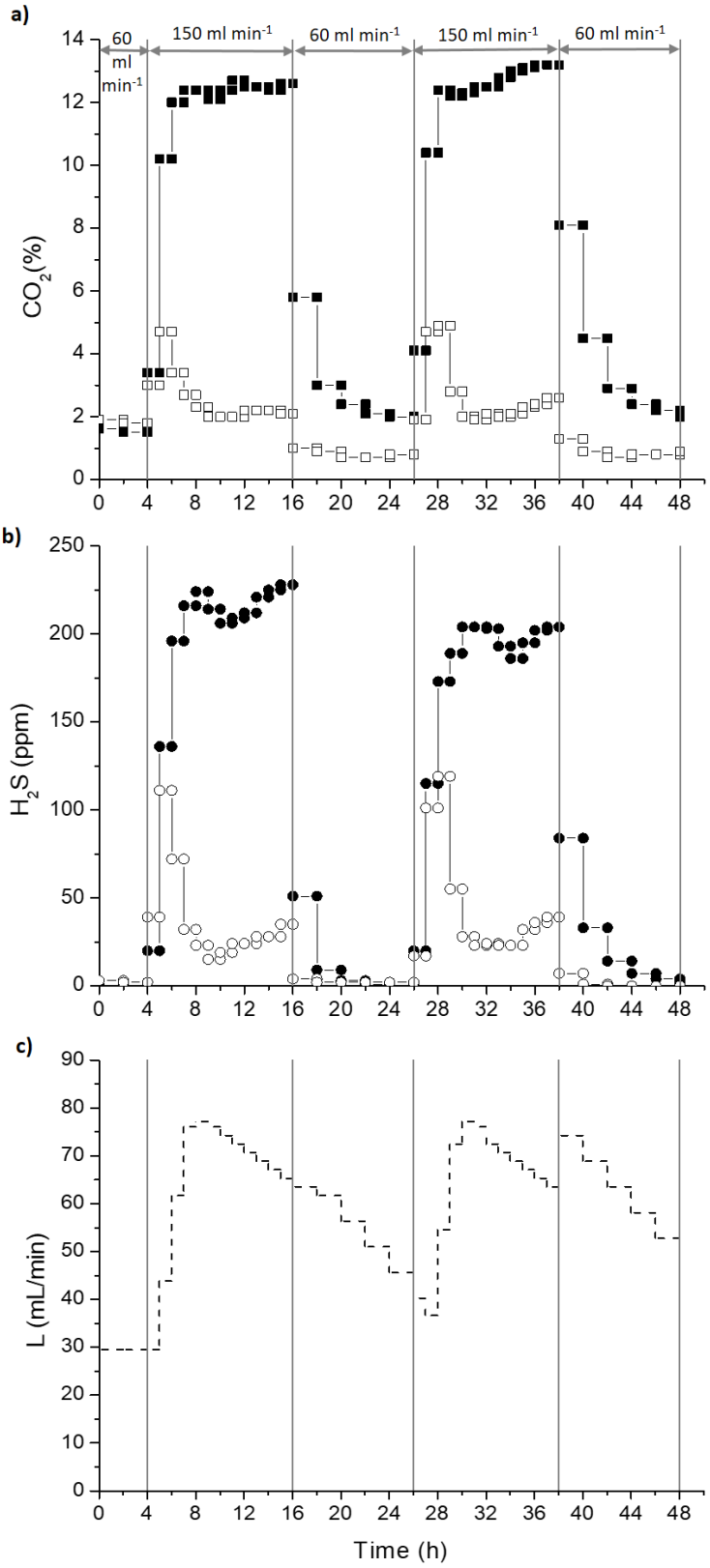


Fig.5. Time course of a) CO_2, b) H_2S content of the upgraded biogas under controlled (open) and uncontrolled (solid) conditions and c) liquid flowrate during the 12-h biogas flowrate increase step experiment.

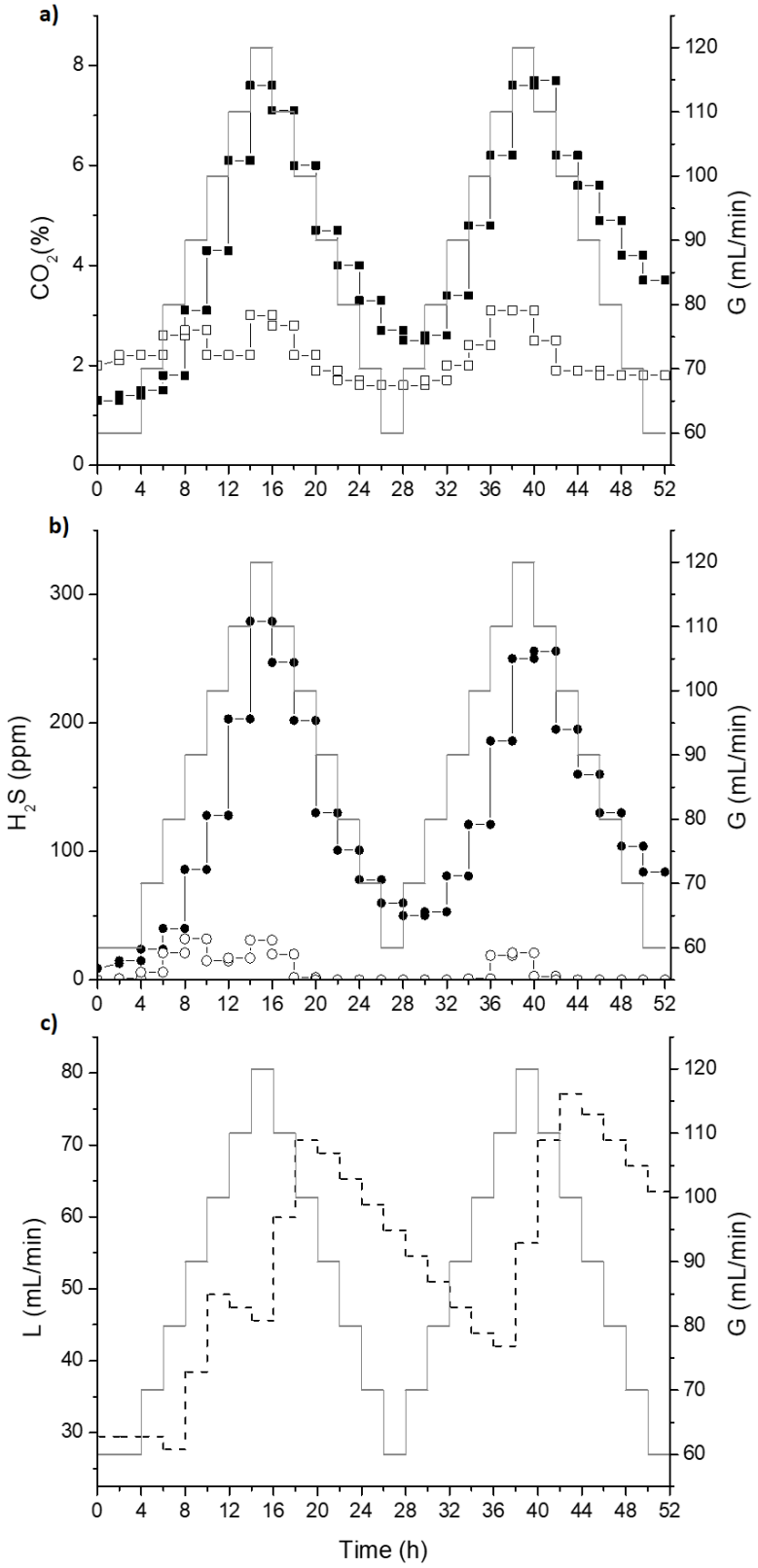


Fig.6. Time course of a) CO_2, b) H_2S content of the upgraded biogas under controlled (open) and uncontrolled (solid) conditions and c) liquid flow rate (dashed line) during the stepwise biogas flowrate increase (continuous line) by 10 ml min^{-1} from 60 to 120 ml min^{-1}

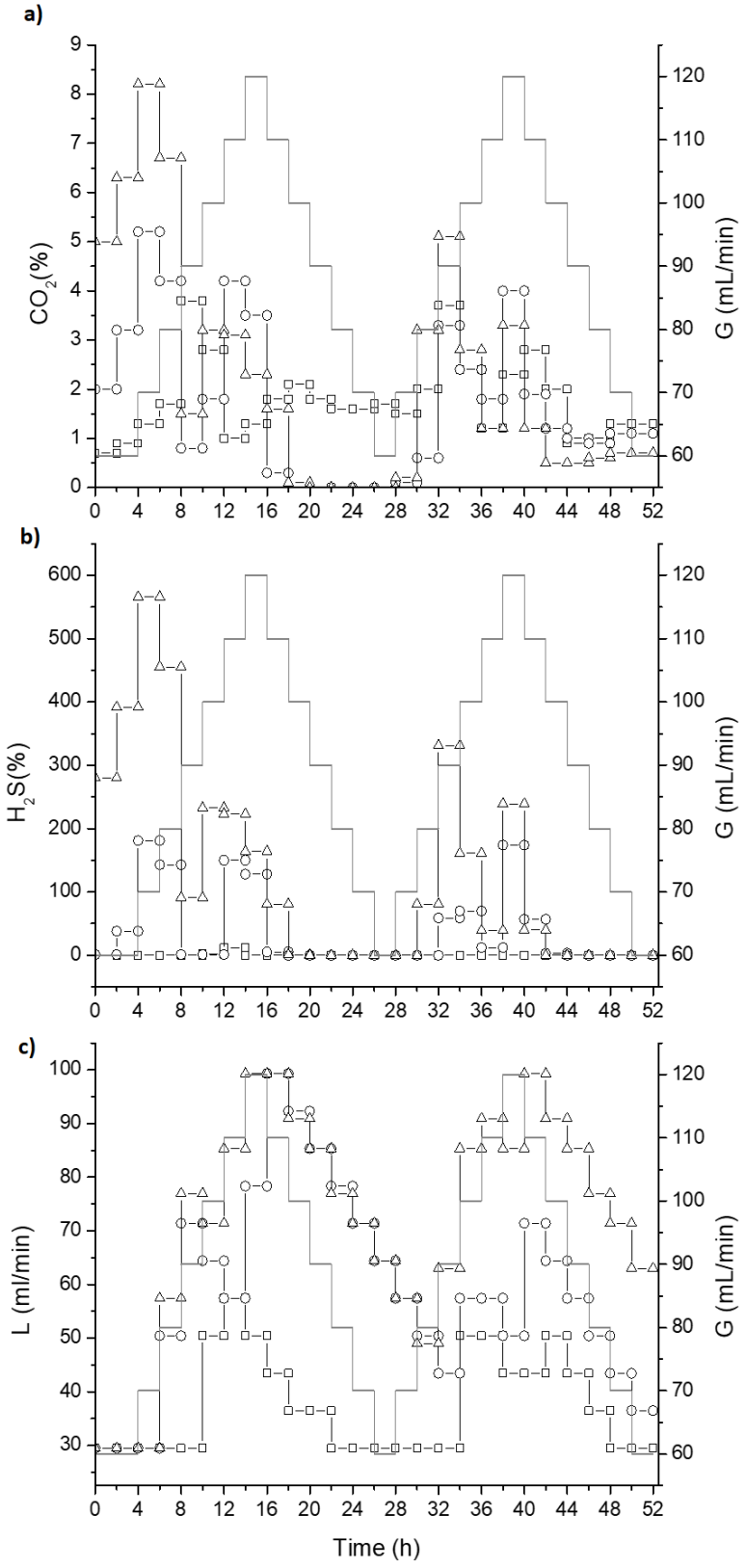


Fig.7. Time course of a) CO_2, b) H_2S content in the upgraded biogas and c) liquid flow rate under controlled conditions at IC concentration of 1500 (square), 500 (circle) and 100 mg L^{-1} (triangle).

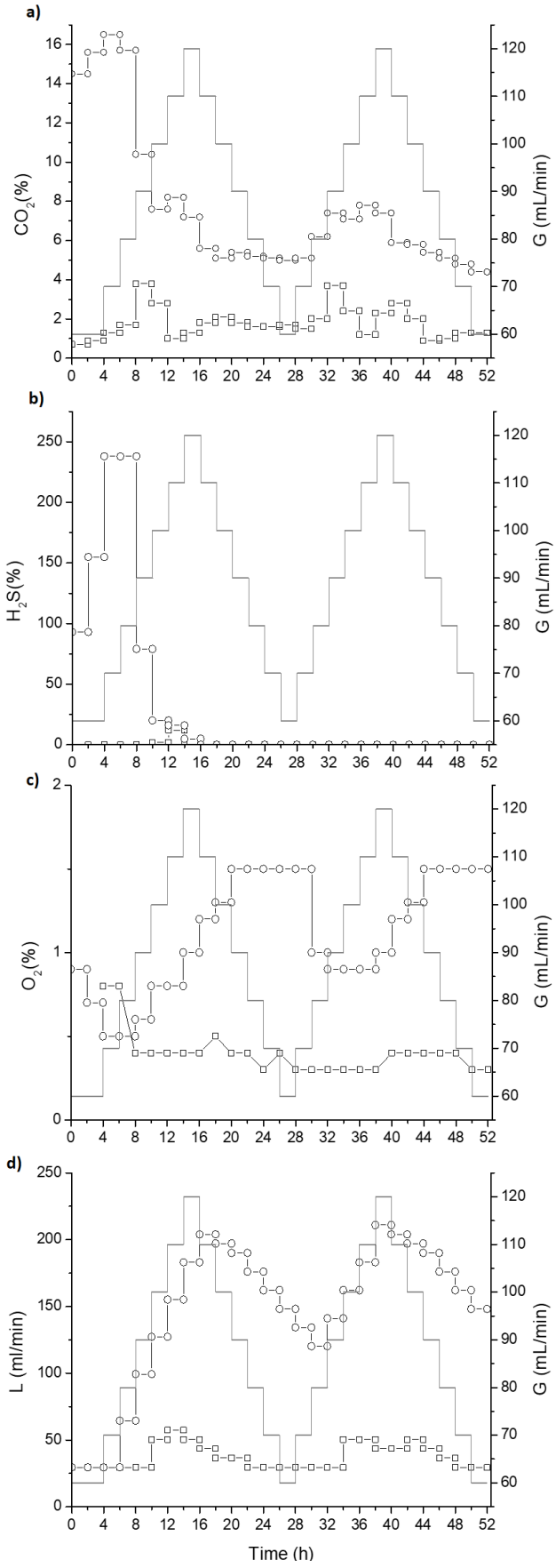


Fig.8. Time course of a) CO_2, b) H_2S c) O_2 content in the upgraded biogas and d) liquid flow rate under controlled conditions at pH 10 (square) and 8.5 (circle).

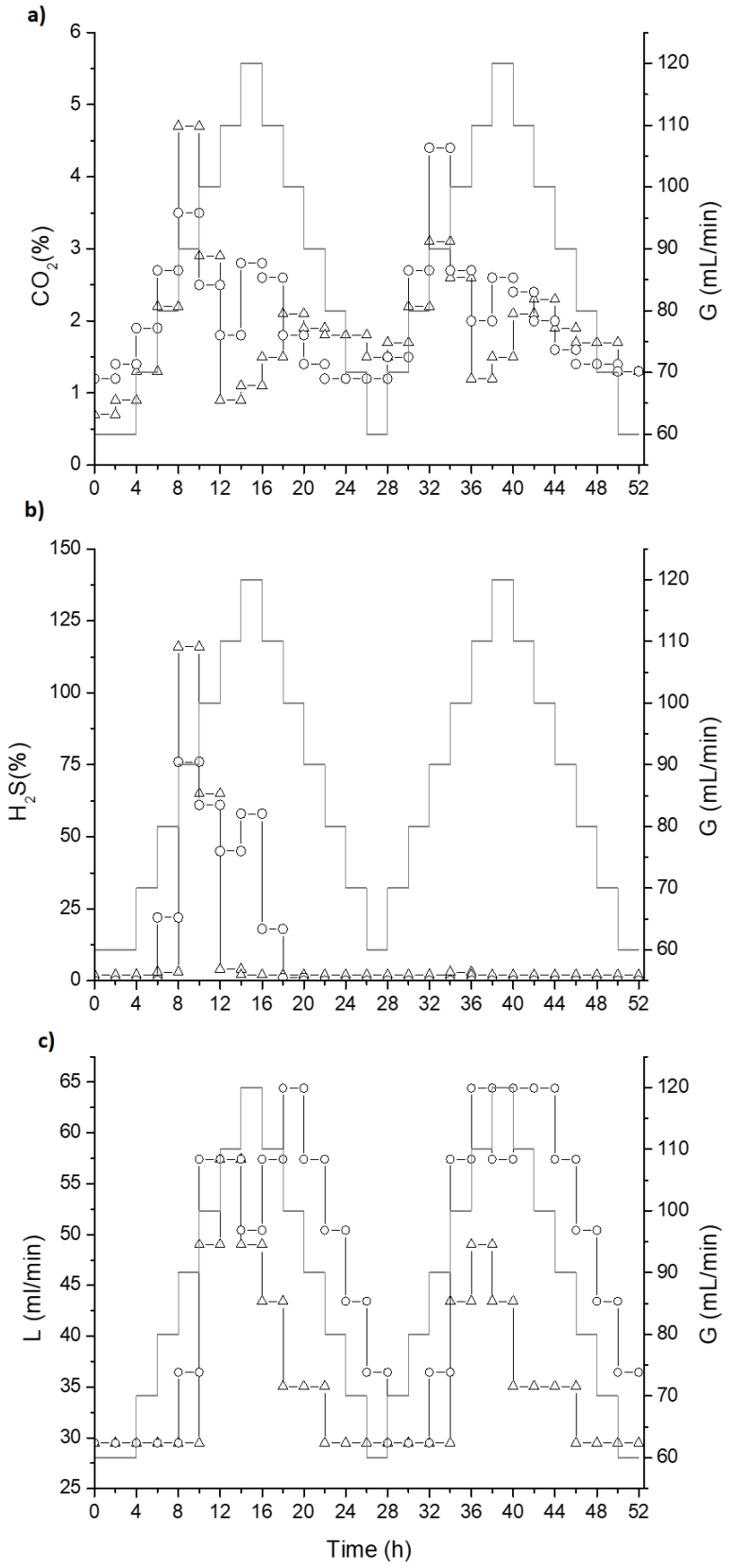


Fig.9. Time course of a) CO_2, b) H_2S content in the upgraded biogas and c) liquid flow rate under controlled conditions at 35 (circle) and 15 ºC (triangle).