Influence of the seasonal variation of environmental conditions on biogas upgrading in an outdoors pilot scale high rate algal pond

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ABSTRACT

The influence of the daily and seasonal variations of environmental conditions on the quality of the upgraded biogas was evaluated in an outdoors pilot scale high rate algal pond (HRAP) interconnected to an external absorption column (AC) via a conical settler. The high alkalinity in the cultivation broth resulted in a constant biomethane composition during the day regardless of the monitored month, while the high algal-bacterial activity during spring and summer boosted a superior biomethane quality. CO_2 concentrations in the upgraded biogas ranged from 0.1% in May to 11.6% in December, while a complete H_2S removal was always achieved regardless of the month. A limited N_2 and O_2 stripping from the scrubbing cultivation broth was recorded in the upgraded biogas at a recycling liquid/biogas ratio in the AC of 1. Finally, CH_4 concentration in the upgraded biogas ranged from 85.6% in December to 99.6% in August.

Keywords: Algal-bacterial photobioreactor; Biogas upgrading; Biomethane; Outdoors operation; Yearly evaluation.

1. Introduction

Biogas from the anaerobic digestion of wastewaters and organic waste constitutes a renewable source of energy to generate electricity or heat (Muñoz et al., 2015). However, the use of biogas as a substitute of natural gas or fuel in transportation requires an effective purification to levels set by national regulations. For instance, biogas injection into natural gas grids typically requires concentrations of $CH_4 \geq 95\%$, $CO_2 \leq 2\%$, $O_2 \leq 0.3\%$ and trace levels of H_2S (Muñoz et al., 2015; Toledo-Cervantes et al., 2017).

Algal-bacterial processes have emerged as a platform technology capable of simultaneously removing CO_2 and H_2S in a single stage, and constitute a cost-effective and environmentally friendly alternative to conventional biogas upgrading technologies (Bahr et al., 2014; Muñoz et al., 2015). Biogas upgrading in algal-bacterial photobioreactors is based on the oxidation of H_2S to SO_4^{2-} by sulfur oxidizing bacteria promoted by the high dissolved oxygen (DO) concentrations in the scrubbing cultivation broth, and on the photosynthetic fixation of the absorbed CO_2 by microalgae. The economic and environmental sustainability of this biotechnology can be boosted via digestate supplementation as a nutrient and water source, which will support an effective recovery of nutrients in the form of algal-bacterial biomass (Posadas et al., 2017; Toledo-Cervantes et al., 2016).

Biogas upgrading coupled to digestate treatment has been typically evaluated indoors in high rate algal ponds (HRAPs) interconnected to biogas absorption columns (AC) under artificial illumination (Alcántara et al., 2015; Bahr et al., 2014; Meier et al., 2015;

Posadas et al., 2016, 2015; Serejo et al., 2015; Toledo-cervantes et al., 2017; Toledo-Cervantes et al., 2017, 2016). The optimization of this process has reached promising results in terms of biomethane quality (CH_4 concentrations of 96.2±0.7 %), nutrient removal (total nitrogen (TN)-removal efficiencies (REs) of 98.0±1.0 % and P-PO_4^{-3}-REs of 100±0.5 %) and biomass productivities (15.0 g m^{-2} d^{-1}) (Toledo-Cervantes et al., 2017). Comparable results were also obtained by Posadas et al. (2017) in a similar biogas upgrading photobioreactor configuration operated outdoors during summer in Spain, when solar irradiation, temperature and the number of sun hours were most favorable to support algal-bacterial activity. In this context, a systematic year-round evaluation of the influence of the daily and seasonal variations of environmental conditions on biogas upgrading and nutrient recovery from digestate is needed to validate this technology under outdoor conditions.

This study investigated for the first time the year-round performance of biogas upgrading in an outdoors pilot HRAP interconnected to an external AC by monthly monitoring the daily variations of biogas quality and cultivation broth parameters under continental climate conditions.

2. Materials and methods

2.1. Biogas and centrate

A synthetic biogas mixture composed of CO_2 (29.5%), H_2S (0.5%) and CH_4 (70%) was used as a raw biogas in the present study (Abello Linde; Spain). Centrate was monthly obtained from the centrifuges dehydrating the anaerobically digested mixed sludge of Valladolid wastewater treatment plant (WWTP) and stored at 4 ºC. The composition of centrate varied along the experimental period as a result of the seasonal operational variations of the WWTP: total organic carbon (TOC) = 16-523 mg L^{-1}, inorganic carbon (IC) = 450-600 mg L^{-1}, TN = 374-718 mg L^{-1}, P-PO_4^{3-} = 26-135 mg L^{-1} and SO_4^{2-} = 0-38 mg L^{-1}. The IC concentration in the centrate was adjusted to 1999 ± 26 mg L^{-1} via addition of $NaHCO_3$ and Na_2CO_3 in order to maintain the required high alkalinity and pHs (≥9) in the cultivation broth to support an effective CO_2 and H_2S absorption in the AC (Posadas et al., 2017).

2.2. Experimental set-up

The experimental set-up, constructed according to Posadas et al. (2017), was located outdoors at the Department of Chemical Engineering and Environmental Technology of Valladolid University (41.39º N, 4.44º W). The pilot plant consisted of a 180 L HRAP with an illuminated area of 1.20 m^2 (width = 82 cm; length = 170 cm; depth = 15 cm) and two water channels divided by a central wall and baffles in each side of the curvature. The internal recirculation velocity of the cultivation broth in the HRAP was ≈ 20 cm s^{-1}, which was supported by the continuous rotation of a 6-blade paddlewheel. The HRAP was interconnected to an external 2.5 L bubble AC (height = 165 cm; internal diameter = 4.4 cm) provided with a metallic biogas diffuser of 2 µm pore size located at the bottom of the column. The HRAP and the AC were interconnected via an external liquid recirculation of the algal-bacterial cultivation broth from an 8 L conical settler (Fig. 1). The efficiency of the settler in terms of biomass removal was almost complete.

<Figure 1>

2.3. Operational conditions and sampling procedures

Process operation was carried out from November the 1st 2016 to October the 30st 2017. The HRAP was inoculated to an initial concentration of 210 mg TSS L^{-1} with a microalgae inoculum composed of *Leptolyngbya lagerheimii (54%), Chlorella vulgaris (28%), Parachlorella kessleri (9%), Tetrademus obliquus (5%) and Chlorella minutissima (2%)* from an indoor HRAP treating biogas and centrate at the Department of Chemical Engineering and Environmental Technology of Valladolid University (Spain). Five different operational stages (namely I, II, III, IV and V) were defined as a function of the temperature, photosynthetic active radiation (PAR), number of sun hours and biomass productivity imposed (Table 1). The synthetic biogas was sparged into the AC under co-current flow operation at 74.9 L d^{-1} under a recycling liquid to biogas ratio (L/G) of 1.0 according to Posadas et al. (2017), which resulted in gas and liquid retention time of 48 min and. The liquid velocity accounted for 2 m h^{-1}. The HRAP was fed with IC-supplemented centrate as a nutrient source at a flow rate of 3.5 L d^{-1}, which entailed a hydraulic retention time of 50 d. Tap water was supplied in order to compensate water evaporation losses and allow process operation without effluent (Table 1).

<Table 1>

The pH, temperature and DO concentration in the cultivation broth of the HRAP, AC and settler, along with PAR, were monitored every thirty minutes during the daytime of one day every month where the environmental conditions were representative of the conditions in the entire month. Gas samples of 100 µL from the upgraded biogas were drawn every hour to monitor the gas concentrations of CH_4, CO_2, H_2S, O_2 and N_2. Liquid samples of 100 mL from the cultivation broth of the HRAP, AC and settler were drawn every two hours to monitor the concentrations of dissolved TOC, IC, TN.

2.4. Analytical procedures

PAR was measured using a LI-250A light meter (LI-COR Biosciences, Germany), while pH was determined with an Eutech Cyberscan pH 510 (Eutech instruments, The Netherlands). Temperature and DO were measured using an OXI 330i oximeter (WTW, Germany). Gas concentrations of CH_4, CO_2, H_2S, O_2 and N_2 were determined using a Varian CP-3800 GC-TCD according to Posadas et al. (2015) (Palo Alto, USA). Dissolved TOC, IC and TN concentrations were measured using a Shimadzu TOC-VCSH analyzer (Japan) coupled with a TNM-1 chemiluminescence module.

3. Results and discussion

3.1. Biogas Upgrading

<Figure 2>

3.1.1 CO_2 biomethane concentration

Negligible variations in CO_2 concentration in the biomethane were recorded throughout the daytime regardless of the operational month likely due to the high alkalinity of the cultivation broth (Fig. 2; Fig. S6). These results were in agreement with Posadas et al. (2017), who observed a constant CO_2 concentration in the upgraded biogas during the daytime in a similar set-up operated with a high ionic strength cultivation broth (IC concentration ≈2660±48 mg L^{-1}). This study also suggested that the influence of the cultivation broth temperature on CO_2 absorption (Henry's law constant ranged from H_{CO2}≈1.27 at 8.3 ºC in November to H_{CO2}≈0.59 at 40.3 ºC in July) was lower than that of the IC concentration (Sander, 2015). Hence, the biomethane CO_2 concentration in stage I ranged from 1.4% in January to 11.6% in December. This concentration varied from 0.1% in March to 3.9% in May during stage II, and from 0.6% in June to 2.2% in July in stage III. CO_2 concentrations in stage IV and V ranged from 0.4% to 1.8% and from 0.8% to 1.2%, respectively (Fig. 2). Thus, the concentration of CO_2 in the biomethane produced in the algal-bacterial photobioreactor complied during most of the year with European regulations, which require CO_2 concentrations ≤2% prior injection into natural gas grids or use as a vehicle fuel (Muñoz et al., 2015). The high CO_2 REs here obtained (estimated from ≈60.7% in December to 99.7% in May) were promoted by the optimum L/G ratio reported by Posadas et al. (2017) and the high pHs/alkalinity of the cultivation broth in the AC, which enhanced CO_2 absorption (Lebrero et al., 2016; Posadas et al., 2015; Toledo-Cervantes et al., 2016). These results were in accordance with Rodero et al. (2017), who reported an increase in the CO_2-RE from 30.8% to 99.3% when alkalinity increased from 102±7 mg IC L^{-1} to 1581±135 mg IC L^{-1} at 35.0ºC in a similar photobioreactor configuration under indoor conditions.

This year-round evaluation of the performance of the algal-bacterial photobioreactor confirmed the key role of biotic mechanisms on this biogas upgrading technology (Fig. 2). Hence, despite the low temperatures of the cultivation broth during winter increased CO_2 aqueous solubility, the lower pHs of the cultivation broth supported by the low photosynthetic activity (from 8.1 to 9.0) resulted in higher CO_2 concentrations in the upgraded biogas. The higher photosynthetic activity mediated by the favorable environmental conditions prevailing during spring and summer, along with the accumulation of IC in the cultivation broth from 1785 mg L^{-1} to 4599 mg L^{-1} from stage II to V, increased the pH from 8.8 to 9.8, which resulted in biomethane CO_2 concentrations complying with most international regulations. In this context, although a 60% decrease in CO_2 solubility is expected when the cultivation broth temperature increases from 10 to 40°C, the high CO_2 concentration gradient supported by the high alkalinity/pH of the cultivation broth during stages II - V compensated this decrease in CO_2 solubility.

3.1.2 H_2S biomethane concentration

H_2S was completely removed in the system regardless of the environmental parameters and alkalinity. This higher elimination compared to the removal of CO_2 was attributed to the higher H_2S aqueous solubility (Henry´s law constant ranging from H_{H2S} ≈3.58 at 8.3 ºC to H_{H2S} ≈1.80 at 40.3 ºC) (Sander, 2015). The high pHs also promoted the complete removal of this acidic gas in the AC (Bahr et al., 2014). These results were in accordance to Posadas et al. (2017), who reported a complete removal of H_2S during the simultaneous treatment of centrate and biogas in a similar outdoors experimental set-up, and to Toledo-Cervantes et al. (2016) who also observed a complete depletion of H_2S during the optimization of photosynthetic biogas upgrading under laboratory conditions. In brief, the H_2S concentration in the biomethane herein obtained complied with most European regulations for biomethane injection into natural gas grids or use as a vehicle fuel, which requires H_2S levels ≤ 5 mg m^{-3} (Muñoz et al., 2015).

3.1.3 N_2 and O_2 concentrations in the biomethane

Despite no clear trend in the evolution of biomethane N_2 concentration along the daytime was recorded, the highest O_2 concentrations in the upgraded biogas were recorded around midday, concomitantly with the highest DO concentrations in the cultivation broth (Fig. S3; Fig. S8). Biomethane N_2 and O_2 concentrations during stage I ranged from 0.0% in November to 5.5% and 1.8%, respectively, in January. During stage II, N_2 and O_2 concentrations varied from 1.2% (April) and 0.3% (March), respectively, to 5.9% (March) and 2.4% (May), respectively. In stage III, these concentrations ranged from 0.1% and 0.0% (July), respectively, to 3.3% (June) and 1.5% (July), respectively. During stage IV, N_2 and O_2 concentrations fluctuated from 0.0% (August) to 5.2% and 1.9% (September), respectively. Finally, N_2 and O_2 concentrations during stage V ranged from 1.9% and 0.4%, respectively, to 3.2% and 1.2%, respectively (Fig. S8). Overall, the highest N_2 and O_2 concentrations in the upgraded biogas were recorded during stages I and II (and during September in stage III) likely due to the lower ambient temperatures, which increased the solubility of these gases in the HRAP and their further desorption in the AC.

The previous optimization of the L/G ratio in the AC entailed a low N_2 and O_2 desorption (Posadas et al., 2017). Thus, the O_2 concentrations here recorded in the biomethane were in accordance to Posadas et al. (2017) and Serejo et al. (2015), who reported values ranging from 0% to 2% and from 0% to 4%, respectively, in a similar experimental set-up (under outdoors and laboratory conditions, respectively) at a L/G of 0.5. The O_2 concentration in the upgraded biogas only complied with international regulations during the periods of low PAR (≤1%), which requires a further optimization.

3.1.4 CH_4 biomethane concentration

Negligible variations in the CH_4 concentration of the upgraded biogas were recorded throughout the daytime regardless of the operational month (Fig. 2). Hence, CH_4 concentration in the biomethane in stage I ranged from 85.6% in December to 94.8% in January. During stage II, CH_4 concentration varied from 90.4% in March to 97.2% in May, and from 94.5% to 99.0% in stage III (July). Finally, the range of CH_4 concentrations in stage IV and V were 93.0%-99.6% and 94.5%-96.0%, respectively (Fig. 2). Therefore, the CH_4 concentration in the biomethane here produced during stages II-V complied with most European regulation for injection into natural gas grids or use as a vehicle fuel (Muñoz et al., 2015). The higher CH_4 concentrations from stage II onwards were mainly due to the higher CO_2 removals and lower N_2 and O_2 desorptions recorded (Fig. 2). These concentrations were in accordance to Posadas et al. (2017) and Toledo-Cervantes et al. (2017), who reported CH_4 concentrations of 92.0% and 96.2%, respectively, in the upgraded biogas using the same photobioreactor configuration. Finally, negligible CH_4 losses by absorption in the AC were measured regardless of the operational month as a result of the low CH_4 aqueous solubility (Henry´s law constant of CH_4 ranged from H_{CH4} ≈0.044 at 8.3 ºC to H_{CH4} ≈0.028 at 40.3ºC) (Sander, 2015). Finally, it should be noted that the CH_4 content in the upgraded biogas remained constant during the night period as a result of the high buffer capacity and pH of the cultivation broth.

4. Conclusions

This work constitutes the first year-round evaluation of biogas upgrading in a pilot scale outdoors HRAP. The high alkalinity and pHs in the cultivation broth were identified as key parameters to maintain a constant biomethane composition during the daytime. Environmental conditions significantly influenced the quality of biomethane. CO_2, H_2S and CH_4 concentrations in the upgraded biogas complied with most international regulations for biomethane injection into natural gas grids or use as a vehicle fuel. This study confirmed the year-round feasibility of outdoors algal-bacterial processes for the simultaneous removal of CO_2 and H_2S from biogas coupled to nutrient removal from digestates.

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FIGURE CAPTIONS

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

Figure 2. Time course of the concentration of CO_2 (■) and CH_4 (▲) in the upgraded biogas during one diurnal cycle under steady state as a function of the operational months.

Figure 1
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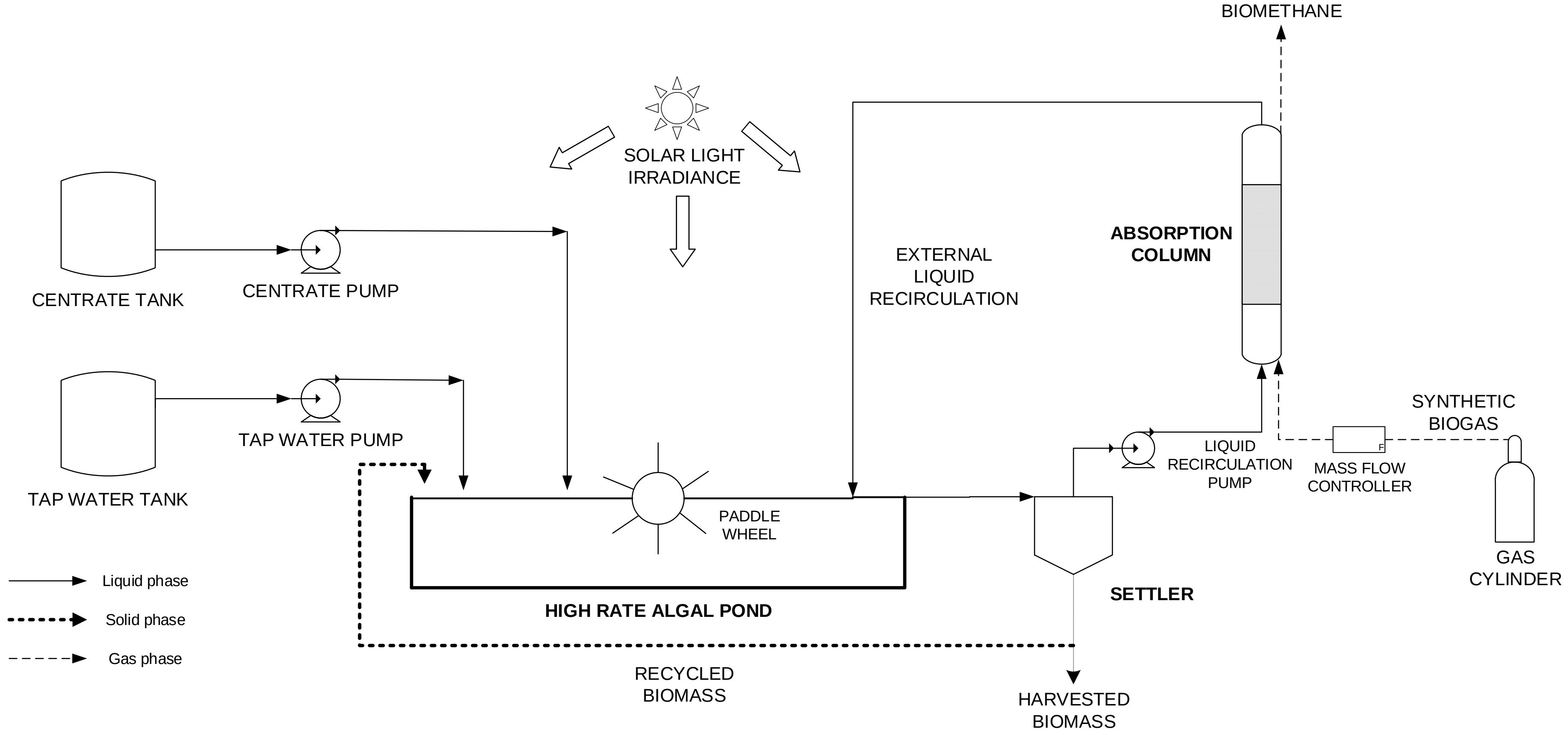

Figure 2
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Figure 2. Time course of the concentration of CO_2 (■) and CH_4 (▲) in the upgraded biogas during one diurnal cycle under steady state as a function of the operational months.

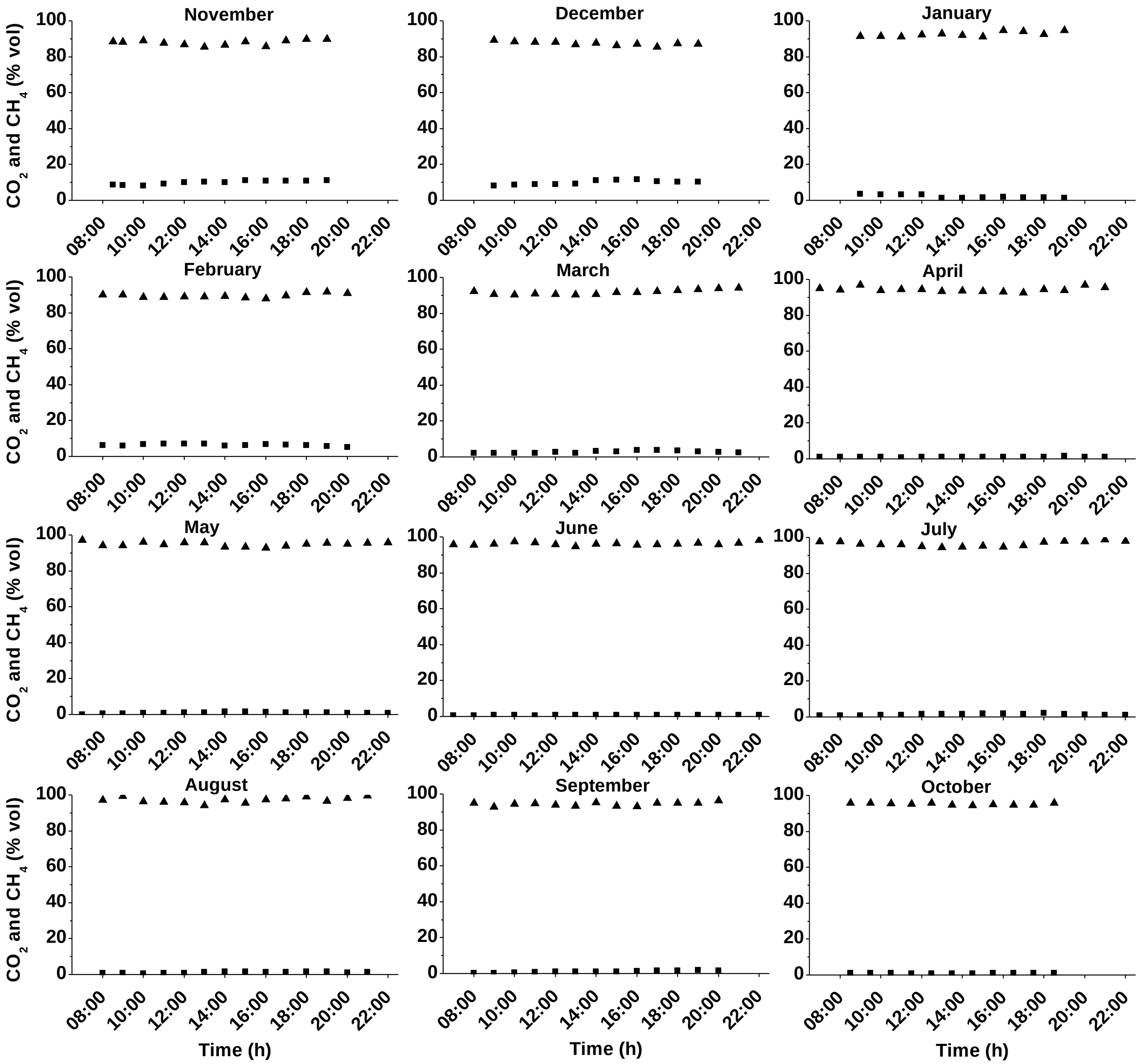

Table 1

Table 1. Environmental and operational parameters during the five operational stages.

		Parameter			
Stage	**Month**	**Average ambient temperature** (ºC)	**Average photosynthetic active radiation** (µmol m-2 s-1)	**Nº of sun hours** (h)	**Biomass Productivity** (g m^{-2} d^{-1})
I	November 30, 2016	4.4 ± 1.6	170 ± 33	10 ± 1	0.0
	December 28, 2016	7.5 ± 4.9	349 ± 119	10 ± 1	
	January 31, 2017	10.2 ± 3.9	339 ± 174	10 ± 1	
	February 28, 2017	14.1 ± 6.6	921 ± 237	12 ± 1	
II	March 29, 2017	14.2 ± 6.2	1213 ± 191	13 ± 1	7.5
	April 26, 2017	8.6 ± 1.5	301 ± 138	14 ± 1	
	May 31, 2017	23.1 ± 5.8	1399 ± 183	15 ± 1	
III	June 28, 2017	20.3 ± 2.7	297 ± 105	15 ± 1	15.0
	July 27, 2017	28.5 ± 6.5	1411 ± 155	15 ± 1	
IV	August 25, 2017	26.0 ± 6.3	1070 ± 199	13 ± 1	22.5
	September 27, 2017	20.7 ± 7.2	1009 ± 237	12 ± 1	
V	October 26, 2017	18.4 ± 7.0	113 ± 83	10 ± 1	15.0