

1 **Influence of the diffuser type and liquid-to-biogas ratio on biogas**
2 **upgrading performance in an outdoor pilot scale high rate algal pond**

3 David Marín^{1, 2, 3}, Alessandro A. Carmona-Martínez^{1, 2}, Raquel Lebrero^{1, 2}, Raúl
4 Muñoz*^{1, 2}

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

7 ²Institute of Sustainable Processes, Dr. Mergelina, s/n, 47011, Valladolid, Spain.

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

9

10 * Corresponding author: mutora@iq.uva.es

11

12 **ABSTRACT**

13 Four different types of biogas diffusers (metallic of 2 μm , porous stone, and two ceramic
14 membranes of 0.2 and 0.4 μm) were evaluated to improve the quality of biomethane in
15 an outdoor pilot scale photobioreactor interconnected to an external biogas absorption
16 unit. Each type of diffuser was tested independently using three different liquid to biogas
17 (L/G) ratios (0.5, 1 and 2). No significant difference was recorded in the CH₄
18 concentrations of biomethane (i.e. > 93.0%) working with the different types of diffusers
19 at L/G ratios > 1. Only the metallic biogas diffuser supported CH₄ concentrations higher
20 than 94.0% at a L/G ratio of 0.5. The increase in L/G ratio induced the stripping of the
21 dissolved N₂ and O₂ into the biogas, which compensated the decrease in CO₂
22 concentration mediated by the higher pH value of the scrubbing solution. The ANOVA
23 of the results here obtained confirmed that both the type of biogas diffuser and the L/G
24 ratio significantly determined the quality of the upgraded biogas.

25

26 **Keywords:**

27 Algal-bacterial photobioreactor; Biogas upgrading; Diffusers; Liquid/gas ratio; Outdoor
28 cultivation.

29

30 **1. Introduction**

31 Nowadays, the biogas generated as a byproduct from the anaerobic treatment of organic
32 waste and wastewater might represent an environmental problem if it is not energetically
33 valorized. Biogas must be partially purified prior use as a renewable energy vector
34 capable of reducing the dependence on fossil fuels in order to produce electricity and heat
35 for industrial and domestic applications [1,2]. A stricter biogas purification must be
36 implemented in order to fulfil with international regulations for its injection into natural
37 gas grids or use as vehicle fuel. Typical compositions in biomethane standards are: CH₄
38 $\geq 90-95\%$, CO₂ $\leq 2-4\%$, O₂ $\leq 1\%$ and negligible amounts of H₂S [2,3].

39

40 Algal-bacterial processes have emerged as an environmentally friendly and cost-
41 competitive alternative to conventional physicochemical processes capable of
42 simultaneously removing CO₂ and H₂S in a single stage process [2,4–6]. In algal-
43 bacterial cultures, sulfur oxidizing bacteria oxidize the H₂S contained in biogas into SO₄²⁻
44 using the high dissolved oxygen (DO) concentrations present in the cultivation broth as a
45 result of photosynthetic activity, while CO₂ is photosynthetically fixed by microalgae
46 using solar energy [7,8]. Microalgae-based biogas upgrading processes have been
47 optimized under indoor conditions in photobioreactors interconnected to external biogas
48 scrubbing units under artificial illumination and using metallic diffusers to sparge the
49 biogas into the absorption column [8–11]. Similarly, photosynthetic biogas upgrading has
50 been validated under outdoor conditions in different photobioreactor configurations.
51 Posadas et al. [12] evaluated the simultaneous upgrading of biogas and wastewater

52 treatment in a 180 L algal pond using a metallic diffuser and liquid to biogas (L/G) ratios
53 of 0.5, 1.0, 2.0 and 5.0. Marín et al. [13,14] evaluated the influence of the seasonal
54 variations of environmental conditions on biogas upgrading performance in a 180 L
55 photobioreactor fed with carbonate supplemented centrate, using a metallic diffuser and
56 L/G ratio of 1.0. Similarly, Rodero et al. [15] investigated the influence of biogas flow
57 rate and L/G ratios on biomethane quality in a 9.6 m³ algal pond using a polymeric
58 membrane diffuser. In addition, Marín et al. [16] assessed the influence of the L/G ratio
59 and alkalinity in the cultivation broth on the quality of the upgraded biogas in a 11.7 m³
60 horizontal hybrid tubular photobioreactor using metallic diffusers. Table 1 summarizes
61 the different types of photobioreactor configuration and biogas diffusers tested, along
62 with the recorded CH₄ concentration in the upgraded biogas. Despite the promising
63 results obtained so far, the effect of the type of diffuser used for biogas sparging in the
64 absorption column on the biomethane quality has not been systematically assessed. The
65 type of diffuser will directly impact on the mass transfer, and therefore on the removal of
66 the target pollutants in the biogas scrubbing unit, thus constituting a key element of
67 process optimization.

68 <Table 1>

69 In this sense, the influence of four different types of biogas diffusers with different pore
70 sizes (namely metallic of 2 µm, porous stone, ceramic membrane of 0.2 and 0.4 µm) at
71 three L/G ratios on biogas upgrading performance was herein investigated in an outdoor
72 pilot scale photobioreactor interconnected to an external biogas absorption unit.

73

74 **2. Materials and methods**

75 **2.1 Biogas and synthetic digestate**

76 A synthetic biogas mixture composed of CO₂ (29.5%), H₂S (0.5%) and CH₄ (70%) was
77 used as a raw biogas in the present study (Abello Linde; Spain). The synthetic digestate
78 (SWW) used consisted of (per liter of distilled water): 6.00 g NaHCO₃, 3.00 g Na₂CO₃,
79 0.94 g K₂HPO₄, 1.91 g NH₄Cl, 0.02 g CaCl₂·2H₂O, 0.005 g FeSO₂·7H₂O, 0.10 g
80 MgSO₄·7H₂O and 5 ml of a micronutrient solution (composed of 0.10 g ZnSO₄·7H₂O,
81 0.10 g MnCl₂·4H₂O, 0.20 g H₃BO₃, 0.02 g Co(NO₃)₂·6H₂O, 0.02 g Na₂MoO₄·2H₂O,
82 0.0005 g CuSO₄·5H₂O, 0.70 g FeSO₄·7H₂O and 1.02 g EDTA·2Na·2H₂O per liter of
83 distilled water). The resulting composition of the SWW was: total organic carbon 51 ± 8
84 mg L⁻¹, inorganic carbon 1211 ± 51 mg L⁻¹ and total nitrogen 528 ± 33 mg L⁻¹. The
85 composition of the SWW, characterized by a high nutrient concentration and high
86 alkalinity, was selected according to Toledo-Cervantes et al., [8] and Wilkie et al., [17].

87

88 **2.2. Experimental set-up**

89 The experimental plant used for this experimentation was located outdoor at the Institute
90 of Sustainable Processes of Valladolid University (Spain). The experimental set-up was
91 integrated by a 180-L open photobioreactor divided in two water channels and with one
92 baffle at each side of the photobioreactor. The open photobioreactor has an illuminated
93 surface of 1.20 m² (length of 170 cm; depth of 15 cm; width of 82 cm). The cultivation
94 broth inside the photobioreactor was recirculated with a velocity of 20 cm s⁻¹ by a 6-blade
95 paddlewheel. A biogas scrubbing column of 2.5 L (height: 165 cm; internal diameter: 4.4
96 cm) operating at atmospheric pressure was interconnected to the photobioreactor through
97 a conical settler of 8 L. (Fig. 1). The implementation of a biogas scrubbing bubble column,
98 and consequently the need for diffusers to sparge biogas, was selected due to the fact that
99 the high concentrations of biomass present in the recirculating liquid will entail a severe

100 clogging and malfunctioning in other types of biogas scrubbing technologies such as
101 spray towers or packed absorption columns.

102 <Figure 1>

103

104 **2.3. Operational conditions and sampling procedures**

105 Process operation was carried out from September the 4th to October the 8th 2019. The
106 photobioreactor was inoculated with a culture previously grown in an outdoors
107 photobioreactor at an initial concentration of 450 mg total suspended solids L⁻¹. The
108 microalgal inoculum was composed of *Mychonastes homosphaera*, *Pseudanabaena sp.*
109 *and Scenedesmus sp.* with a share (based on the number of cells) of 82, 17 and 1%,
110 respectively. The photobioreactor was fed with SWW as a nutrient source at a flow rate
111 of 3.5 L d⁻¹. Four different types of biogas diffusers with different pore sizes were
112 successively installed at the bottom of the scrubbing unit in order to analyze their
113 influence on biogas upgrading performance: a cylindrical metallic diffuser with a pore
114 size of 2 µm (height: 2.3 cm; diameter: 1.7 cm), a rectangular porous stone with a
115 heterogeneous pore size distribution (length: 3.0 cm; height: 1.5 cm; width: 1.5 cm), a
116 cylindrical ceramic membrane with a pore size of 0.2 µm (height: 20.0 cm; diameter: 1.0
117 cm) and a cylindrical ceramic membrane with a pore size of 0.4 µm (height: 20.0 cm;
118 diameter: 1.0 cm). Three different L/G ratios were tested under process operation with
119 each diffuser. In this sense, the biogas was sparged into the scrubbing unit, through the
120 different types of diffusers at 72 L d⁻¹. The liquid recirculation from the settler to the
121 absorption unit was operated under co-current flow at rates of 36, 72 and 144 L d⁻¹
122 (corresponding to hydraulic retention times, HRT, in the column of 100, 50 and 25 min,
123 respectively), resulting in L/G ratios of 0.5, 1.0 and 2.0, respectively. The different
124 combinations of diffusers and L/G ratios were tested sequentially for each type of

125 diffuser, starting with the lowest L/G ratio of 0.5 and ending with the highest L/G ratio
126 of 2.0. The pH in the photobioreactor remained constant during all experimentation period
127 at an average value of 9.1 ± 0.1 . Tap water was supplied in order to compensate water
128 evaporation losses in the open photobioreactor and allow process operation without
129 effluent. Gas samples of 100 μL of the upgraded biogas were drawn every two hours to
130 monitor the gas concentrations of CO_2 , H_2S , N_2 , O_2 and CH_4 . The pH in the
131 photobioreactor and in the scrubbing unit was also monitored every two hours. The
132 photosynthetic active radiation (PAR), DO concentration, and ambient and
133 photobioreactor temperatures were daily monitored in each test (Table A1).

134

135 **2.4. Analytical procedures**

136 Gas concentrations of CO_2 , H_2S , N_2 , O_2 and CH_4 in the raw and upgraded biogas were
137 determined using a Varian CP-3800 GC-TCD according to Posadas et al. (2015) (Palo
138 Alto, USA). pH was determined with an Eutech Cyberscan pH 510 (Eutech instruments,
139 The Netherlands). PAR, DO concentrations, and ambient and photobioreactor
140 temperature were measured according to Marín et al., [13].

141

142 **2.5. Statistical analysis**

143 The results here presented were provided as the average values along with their standard
144 deviation from five replicate measurements for each test run. An analysis of variance
145 (ANOVA) was performed to determine the influence of the biogas diffusers on the quality
146 of the upgraded biogas.

147

148 **3. Results**

149 **3.1 Metallic diffuser**

150 CO₂ concentration in the upgraded biogas reached values of 3.4, 3.4 and 1.3% and
151 removal efficiencies (REs) of 88.9, 88.8 and 95.7% at L/G ratios of 0.5, 1.0 and 2.0,
152 respectively (Fig. 2a). The pH in the scrubbing unit decreased by 4.5, 4.4 and 2.9%, at
153 L/G ratios of 0.5, 1.0 and 2.0, respectively (Table 2). H₂S from raw biogas was
154 completely removed regardless of the L/G ratio. On the other hand, N₂ concentrations
155 reached values of 1.5, 1.9 and 3.0%, while O₂ concentrations in the upgraded biogas
156 reached values of 0.2, 0.1 and 0.5% at L/G ratios of 0.5, 1.0 and 2.0, respectively (Fig.
157 2a). Finally, CH₄ concentrations in the upgraded biogas of 94.9, 94.6 and 95.2% were
158 recorded at L/G ratios of 0.5, 1.0 and 2.0, respectively (Fig. 2a).

159 <Table 2>

160 <Figure 2>

161 **3.2 Porous stone diffuser**

162 CO₂ concentration in the biomethane accounted for 11.1, 3.8 and 1.2%, which
163 corresponded to CO₂-REs of 63.4, 87.3 and 95.9% at L/G ratios of 0.5, 1.0 and 2.0,
164 respectively (Fig. 2b). The reduction in the pH of the recirculating culture medium in the
165 absorption unit at L/G ratios of 0.5, 1.0 and 2.0 were 10.0, 5.4 and 4.4%, respectively
166 (Table 2). H₂S from the raw biogas was completely removed regardless of the L/G ratio.
167 N₂ concentration reached values of 0.4, 1.1 and 3.0%, while O₂ concentrations accounted
168 for 0.1, 0.2 and 1.0% at L/G ratios of 0.5, 1.0 and 2.0, respectively. Finally, the CH₄
169 concentrations observed at a L/G ratio of 0.5, 1 and 2 were 88.4, 94.8 and 94.7%,
170 respectively (Fig. 2b).

171

172 **3.3 Ceramic Membrane**

173 The CO₂ concentrations achieved when using the ceramic membrane diffuser of 0.2 µm
174 at L/G ratios of 0.5, 1.0 and 2.0 were 12.3, 3.9 and 1.4%, respectively, and 11.8, 1.2 and

175 1.1% when using the ceramic membrane of 0.4 μm , respectively. Therefore, the CO_2 -
176 REs corresponded to 59.5, 87.1 and 95.3% (ceramic membrane of 0.2 μm), and 61.0, 95.9
177 and 96.3% (ceramic membrane of 0.4 μm) (Fig. 2c; 2d). The decrease in pH in the
178 cultivation medium in the experiment conducted with the ceramic membrane of 0.2 μm
179 was higher than that with a pore size of 0.4 μm at L/G ratios of 0.5 and 1.0, and negligible
180 in both membranes at a L/G ratio of 2 (Table 2). H_2S from raw biogas was completely
181 removed in both ceramic membranes regardless of the L/G ratio. On the other hand, N_2
182 concentration in the experiments with the ceramic membrane of 0.2 μm reached values
183 of 0.9, 2.4 and 4.2%, respectively, and 1.5, 2.5 and 3.9% in the ceramic membrane of 0.4
184 μm at L/G ratios of 0.5, 1.0 and 2.0. O_2 concentration in the upgraded biogas reached
185 values of 0.2, 0.7 and 0.7% when using the ceramic membrane of 0.2 μm at L/G ratios of
186 0.5, 1 and 2, and 0.7, 0.3 and 0.5% with the ceramic membrane of 0.4 μm , respectively,
187 (Fig. 2c; 2d). Finally, CH_4 concentrations in the upgraded biogas using the ceramic
188 membrane of 0.2 μm were 86.7, 93.0 and 93.6%, respectively, and 86.0, 96.0 and 94.5%
189 with ceramic membrane of 0.4 at L/G of 0.5, 1 and 2, respectively (Fig. 2c; 2d).

190

191 **4. Discussion**

192 The diffuser that provided the most efficient upgrading of biogas at a L/G of 0.5 was the
193 2 μm metallic diffuser, which was the only one that fulfilled with most international
194 regulations required for biogas injection into natural gas grids or use as a vehicle fuel:
195 $\text{CH}_4 \geq 90\text{-}95\%$, $\text{CO}_2 \leq 2\text{-}4\%$, $\text{O}_2 \leq 1\%$ and negligible amounts of H_2S [2,18,19]. When
196 a L/G ratio of 1.0 was used, the four diffusers exhibited a similar upgrading performance
197 in terms of CH_4 concentration, reaching values up to 96.0%. This increase in CH_4
198 concentrations was promoted by the increase in pH in the absorption unit, which
199 supported a higher CO_2 -REs due to the enhanced gradient of CO_2 concentration between

200 the biogas and liquid phase. Similarly, the four diffusers provided comparable CH₄
201 concentrations (up to 95.2%) at a L/G of 2. However, this increase in the cultivation
202 medium pumped into the biogas scrubbing unit resulted in increased in N₂ and O₂
203 concentrations regardless of the type of diffuser tested. This can be explained by the
204 superior dissolved gas stripping at higher liquid flowrates, which negatively impacted on
205 the final concentration of CH₄ in the upgraded biogas [20]. The biogas quality at a L/G
206 ratios of 1 and 2 fulfilled with the current European biomethane standard regardless of
207 the diffuser configuration [2,18,19]

208

209 Overall, the results herein obtained confirmed that the metallic diffuser was the best
210 system to purify biogas at the L/G ratios typically implemented in photosynthetic biogas
211 upgrading processes in open photobioreactors. These results were in accordance to Marín
212 et al. [16], who reported higher CH₄ concentrations at decreasing L/G ratios. Indeed, the
213 CH₄ content in biomethane decreased from 89% at L/G of 1 to 87% at L/G of 5 in an
214 outdoor horizontal hybrid tubular photobioreactor constructed with metallic diffusers for
215 biogas upgrading.

216

217 Finally, an ANOVA test was carried out to elucidate the influence of the type of diffusers
218 and the L/G ratio on the quality of the upgraded biogas. The F critical value (value that
219 will define if the means for each component are significantly different) was 3.2 for the
220 three different L/G ratios tested in this work. The F values (ratio between the mean square
221 of the component and the mean square of the error) for CH₄, CO₂, N₂ and O₂ were 206.7,
222 274.5, 28.9 and 36.3, respectively, at the L/G ratio of 0.5 (Table 3a). On the other hand,
223 the F values at L/G ratio of 1.0 were 18.5, 152.6, 53.3 and 21.4 for the above mentioned
224 gases, respectively (Table 3b). Finally, the F values at L/G ratio of 2.0 were 16.7, 3.4,

225 19.2 and 4.0 for CH₄, CO₂, N₂ and O₂, respectively (Table 3c). The F values were greater
226 than the F critical value of 3.2 regardless of the biomethane component, which confirmed
227 that the quality of biomethane varied significantly with the type of diffuser and the L/G
228 ratio implemented in the photosynthetic biogas upgrading process.

229 <Table 3>

230 Unfortunately, the concentration of methane in the cultivation broth returned to the algal
231 pond has not been measured in this particular study. However, no methane slippage into
232 the photobioreactor was expected due to the low aqueous solubility of methane (according
233 to its Henry's Law constant, $H_{CH_4} \approx 0.03$ at 25 °C) compared to other contaminants (i.e.
234 CO₂ and H₂S, $H_{CO_2} \approx 0.83$ and $H_{H_2S} \approx 2.45$ at 25 °C). In addition, it was hypothesized
235 that the inherent presence of bacteria (e.g. methanotrophs) would eventually oxidize any
236 CH₄ transferred to the cultivation broth.

237

238 **5. Conclusions**

239 This study demonstrated the statistically significant influence of the type of biogas
240 diffuser and the L/G ratio in the scrubbing unit on the quality of biomethane in an outdoor
241 pilot scale photobioreactor. L/G ratios > 1.0 supported a significant decrease in CO₂
242 concentration in the upgraded biogas along with a superior stripping of O₂ and N₂ from
243 the scrubbing solution regardless of the type of diffuser used. The 2 μm metallic diffuser
244 provided the highest CH₄ concentration in the upgraded biogas regardless of the L/G ratio
245 (94.6-95.2%), which complied with most international regulations for biomethane
246 injection into natural gas grids.

247

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253

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- 336

337 **FIGURE CAPTIONS**

338 **Figure 1.** Schematic diagram of the outdoor experimental pilot plant used for the
339 photosynthetic purification of biogas.

340 **Figure 2.** Concentration of CH₄, CO₂, N₂ and O₂ in the upgraded biogas using (a)
341 metallic 2 μm, (b) porous stone, (c) ceramic membrane 0.2 μm and (d) ceramic membrane
342 0.4 μm diffusers.

Figure 1. Schematic diagram of the outdoor experimental pilot plant used for the photosynthetic purification of biogas.

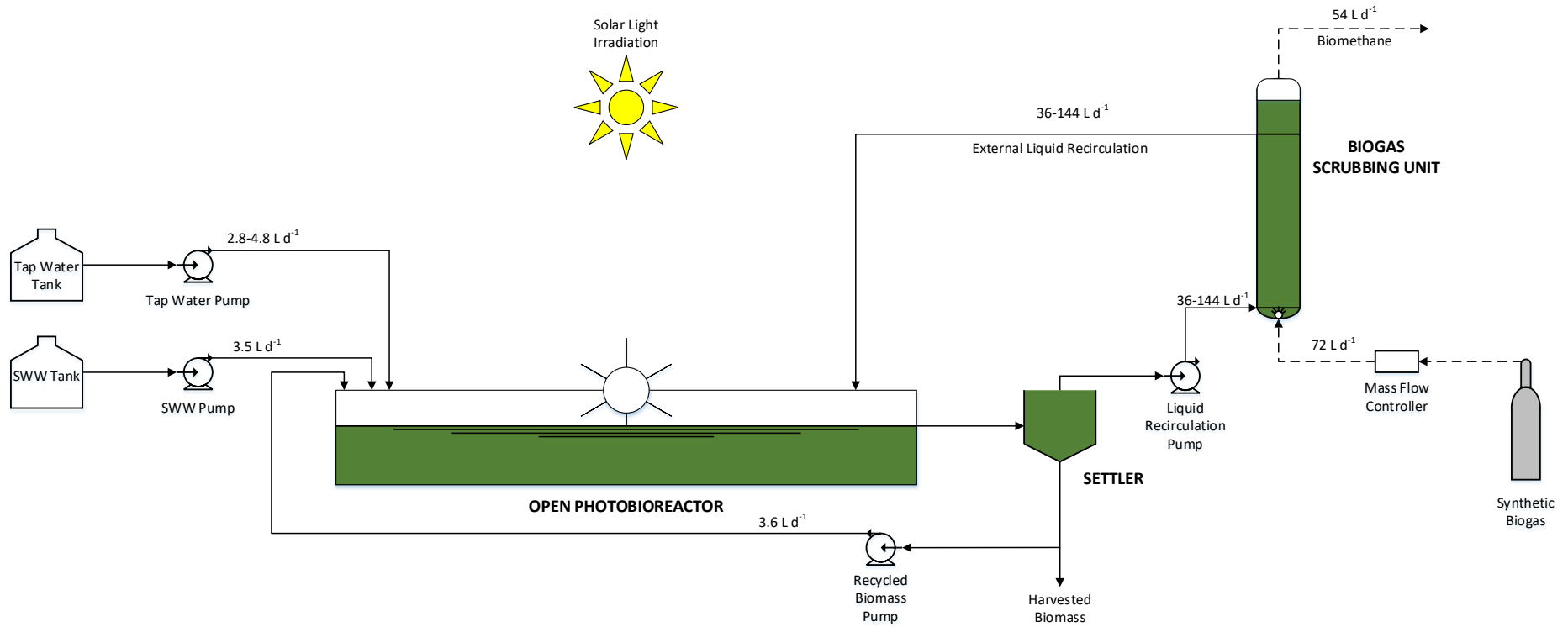


Figure 2. Concentration of CH₄, CO₂, N₂ and O₂ in the upgraded biogas using (a) metallic 2 μm, (b) porous stone, (c) ceramic membrane 0.2 μm and (d) ceramic membrane 0.4 μm diffusers.

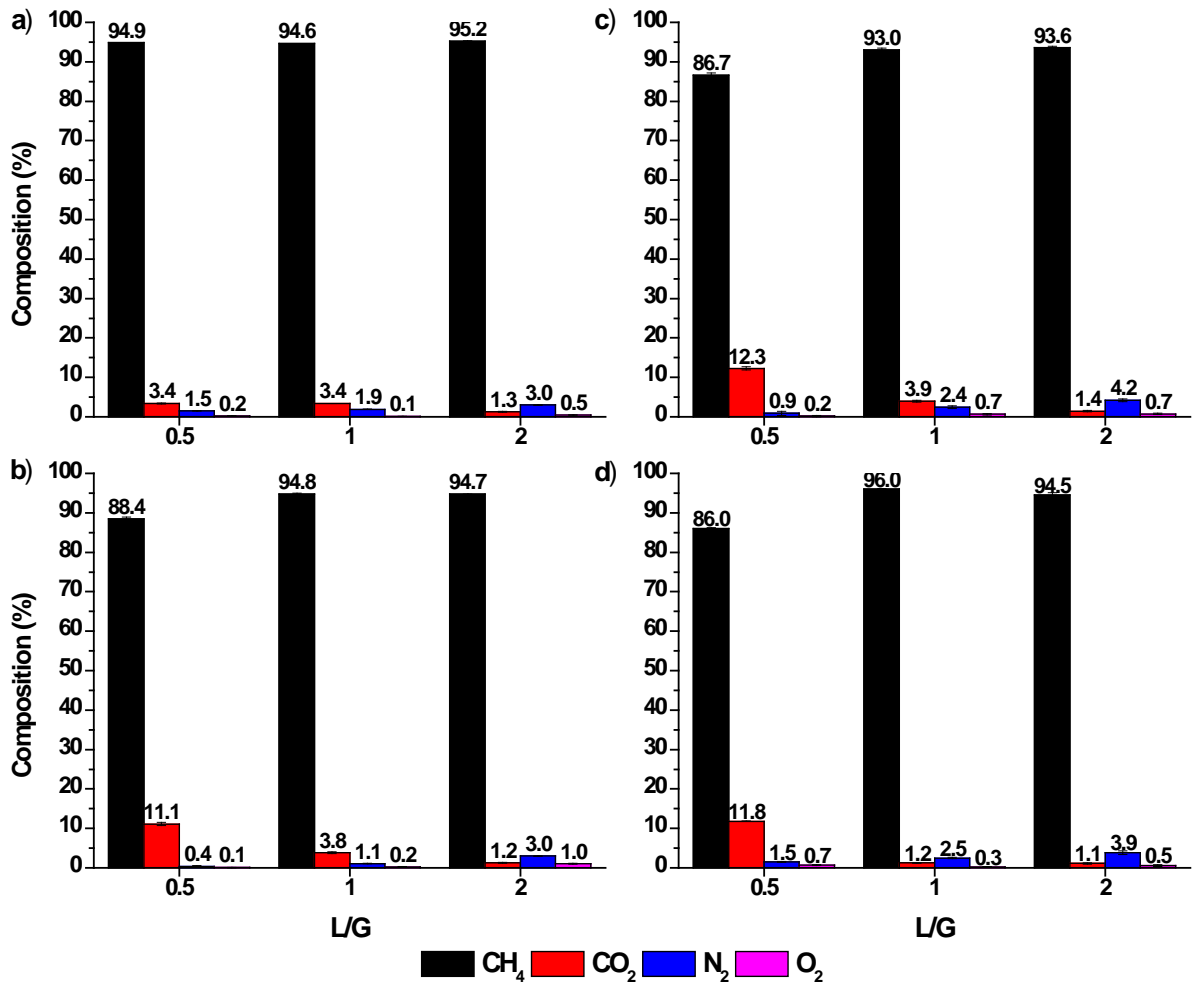


Table 1. CH₄ concentration in the upgraded biogas using different photobioreactor configurations with different types of diffuser.

Reference	Photobioreactor configuration	L/G ratios tested	Type of Diffuser	CH₄ concentration (%)
Toledo-Cervantes et al. (2016)	Indoor 180 L HRAP	1; 5; 10 and 20	Metallic 2 μm	95; 88; 68 and 68
Toledo-Cervantes et al. (2017)	Indoor 180 L HRAP	0.3; 0.5; 0.8 and 1	Metallic 2 μm	95; 98; 98 and 96
Rodero et al. (2018)	Indoor 180 L HRAP	1	Metallic 2 μm	98
Posadas et al. (2017)	Outdoor 180 L HRAP	0.5; 1; 2 and 5	Metallic 2 μm	86; 90; 92 and 80
Marín et al. (2018a)	Outdoor 180 L HRAP	1	Metallic 2 μm	85 – 98
Rodero et al. (2019b)	Outdoor 9.6 m ³ HRAP	1.2; 2.1 and 3.5	Polymeric membrane	85; 89 and 90
Marin et al (2019)	Outdoor 11.7 m ³ horizontal hybrid tubular photobioreactor	0.5; 1; 2; 3; 4 and 5	Metallic 2 μm	87; 90; 88; 89; 88 and 87

Table 2. pH values and decrease (as percentage) in the of the cultivation broth in the biogas scrubbing unit using the different types of diffusers.

Type of diffuser	L/G								
	0.5			1			2		
	Bottom	Top	Decrease (%)	Bottom	Top	Decrease (%)	Bottom	Top	Decrease (%)
Metallic	8.95	8.55	4.5 %	9.10	8.70	4.4 %	9.20	8.93	2.9 %
Porous Stone	9.09	8.18	10.0 %	9.13	8.64	5.4 %	9.14	8.74	4.4 %
Ceramic Membrane 0.2 μm	9.08	8.03	11.6 %	9.11	8.29	9.0 %	9.03	8.66	4.1 %
Ceramic Membrane 0.4 μm	9.02	8.68	3.8 %	9.05	8.75	3.3 %	9.15	8.78	4.0 %

Table 3. Analysis of variance of biogas at L/G ratios of (a) 0.5, (b) 1 and (c) 2.

a)

	Sum of squares	Degrees of freedom	Mean square	F	F critical
CH ₄	224.0	3.0	74.7	206.7	3.2
Error	5.8	16.0	0.4		
CO ₂	242.9	3.0	81.0	274.5	3.2
Error	4.7	16.0	0.3		
N ₂	4.9	3.0	1.6	28.9	3.2
Error	0.9	16.0	0.1		
O ₂	1.0	3.0	0.3	36.3	3.2
Error	0.1	16.0	0.0		

b)

	Sum of squares	Degrees of freedom	Mean square	F	F critical
CH ₄	10.8	3.0	3.6	18.5	3.2
Error	3.1	16.0	0.2		
CO ₂	23.1	3.0	7.7	152.6	3.2
Error	0.8	16.0	0.1		
N ₂	6.0	3.0	2.0	53.3	3.2
Error	0.6	16.0	0.0		
O ₂	0.7	3.0	0.2	21.4	3.2
Error	0.2	16.0	0.0		

c)

	Sum of squares	Degrees of freedom	Mean square	F	F critical
CH ₄	6.6	3.0	2.2	16.7	3.2
Error	2.1	16.0	0.1		
CO ₂	0.3	3.0	0.1	3.4	3.2
Error	0.5	16.0	0.0		
N ₂	5.7	3.0	1.9	19.2	3.2
Error	1.6	16.0	0.1		
O ₂	0.4	3.0	0.1	4.0	3.2
Error	0.6	16.0	0.0		

Supplementary Material

Influence of the diffuser type and liquid-to-biogas ratio on biogas

upgrading performance in an outdoor pilot scale high rate algal pond

David Marín^{1, 2, 3}, Alessandro A. Carmona-Martínez^{1, 2}, Raquel Lebrero^{1, 2}, Raúl Muñoz*^{1,2}

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

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

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

* Corresponding author: mutora@iq.uva.es

Table A1. Environmental parameters during each test.

Parameter	Diffuser and L/G											
	Metallic			Porous Stone			Ceramic Membrane 0.2 μm			Ceramic Membrane 0.4 μm		
	0.5	1	2	0.5	1	2	0.5	1	2	0.5	1	2
Ambient Temperature (°C)	10.0	13.0	13.0	14.0	15.0	11.0	13.0	13.0	12.0	14.0	11.0	10.0
Photobioreactor Temperature (°C)	11.2	12.1	11.6	14.9	15.1	10.7	12.3	11.4	14.1	13.7	11.1	12.3
PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	69	54	58	84	88	126	73	67	27	65	396	83
DO (mg O ₂ L ⁻¹)	3.1	4.2	3.9	6.4	6.8	6.8	7.3	6.4	3.7	6.6	7.2	4.9

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