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Influence of alkalinity and temperature on photosynthetic biogas upgrading efficiency in high rate algal ponds

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ABSTRACT

Algal-bacterial photobioreactors have emerged as a cost-effective platform for biogas upgrading. The influence on biomethane quality of the inorganic carbon concentration (1500, 500 and 100 mg L^{-1}) and temperature (12 and 35 °C) of the cultivation broth was evaluated in a 180 L high rate algal pond (HRAP) interconnected to a 2.5 L absorption column via settled broth recirculation. The highest CO_2 and H_2S removal efficiencies (REs) from biogas were recorded at the highest alkalinity (CO_2-REs of 99.3 ± 0.1 and 97.8 ± 0.8% and H_2S-REs of 96.4 ± 2.9 and 100 ± 0% at 12 and 35 °C, respectively), which resulted in CH_4 concentrations of 98.9 ± 0.2 and 98.2 ± 1.0% at 12 and 35 °C, respectively, in the upgraded biogas. At the lowest alkalinity, the best upgrading performance was observed at 12 °C (CO_2 and H_2S-REs of 41.5 ± 2.0 and 80.3 ± 3.9%, respectively). The low recycling liquid to biogas ratio applied (0.5) resulted in a negligible O_2 stripping regardless of the alkalinity and temperature, which entailed a biomethane O_2 content ranging from 0 to 0.2 ± 0.3%.

1. Introduction

Biogas from the anaerobic digestion of organic matter constitutes a promising renewable energy vector for the production of heat and power in households and industry [1]. Raw biogas is mainly composed of CH_4 (40–75%), CO_2 (25–50%) and other components at lower concentrations such as H_2S (0.005–2%), oxygen (0–1%), nitrogen (0–2%), siloxanes (0–0.02%), ammonia (< 1%) and halogenated hydrocarbons (VOC < 0.6%) [2]. The high content of CO_2 significantly reduces the specific calorific value of biogas, increases its transportation costs and promotes emissions of CO and hydrocarbons during combustion. On the other hand, H_2S is a toxic and malodorous gas that severely reduces the lifespan of the biogas storage structures, pipelines, boilers and internal combustion engines [3]. The removal of these biogas pollutants is mandatory in order to comply with the technical specifications required for biogas injection into natural gas grids (CH_4 > 95%, CO_2 < 2.5–4%, O_2 < 0.001–1% and H_2S + COS < 5 mg/Nm^3) or use as a vehicle fuel [4]. State-of-the-art physical/chemical or biological technologies for CO_2 removal often need a previous H_2S cleaning step, while the few technologies capable of simultaneously removing CO_2 and H_2S from biogas (i.e. water/chemical scrubbing and membrane separation) exhibit a high energy and chemicals consumption, which limits their economic and environmental sustainability for biogas upgrading [5]. In this context, algal-bacterial symbiosis represents a cost-effective and environmentally friendly platform for the simultaneous removal of CO_2 and H_2S from raw biogas in a single step process [6].

Photosynthetic biogas upgrading in algal-bacterial photobioreactors is based on the light-driven CO_2 consumption by microalgae coupled to the oxidation of H_2S to either elemental sulfur or sulfate by sulfur-oxidizing bacteria (i.e. belonging to the Thioalbus genus) using the oxygen photosynthetically produced [3, 7]. The environmental and economic sustainability of the process can be boosted with the integration of wastewater treatment in the photobioreactor devoted to biogas upgrading [8]. In this regard, digestate or domestic wastewater can be used as an inexpensive nutrient source for microalgae and bacteria growth during photosynthetic biogas upgrading, which in turn would reduce the costs associated to nutrients removal [9, 10]. Recent investigations have focused on the optimization of the simultaneous biogas upgrading and digestate treatment in photobioreactors. These studies have identified the optimum photobioreactor configuration [6, 8, 11, 12], the strategies for minimizing oxygen concentration in the biomethane [13, 14] and the influence of light intensity, wavelength and photoperiod regime on the final quality of the upgraded biogas under indoors conditions [15–19]. Unfortunately, most of these previous works did not result in a biomethane composition complying with

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the specifications of most European regulations due to the limited CO_2 mass transfer rates from the raw biogas to the aqueous phase [20]. In this context, a recent study conducted outdoors in a high rate algal pond (HRAP) interconnected to an external absorption column for the simultaneous treatment of biogas and centrate suggested that both alkalinity and temperature in the algal-bacterial broth can play a key role on the final biomethane quality [11]. Indeed, culture broth alkalinity determines the kinetics of both microalgae growth in the HRAP and CO_2/H_2S absorption in the absorption column [21]. Likewise, culture broth temperature directly impacts on the gas/liquid equilibria and biomass growth kinetics [19]. However, despite the relevance of these environmental parameters on the performance of photosynthetic biogas upgrading, no study has evaluated to date the effect of alkalinity and temperature on the final quality of biomethane in algal-bacterial photobioreactors.

This work systematically evaluated the influence of inorganic carbon concentration and temperature in the cultivation broth on biomethane quality in a 180 L HRAP interconnected to a 2.5 L absorption column via external recirculation of the settled cultivation broth under indoor conditions. The tested inorganic carbon concentrations (1500, 500 and 100 mg L^{-1}) are typically encountered in high and medium strength digestates and domestic wastewater, respectively, while the tested temperatures are representative of spring-autumn (12 °C) and summer (35 °C) seasons in temperate climates.

2. Materials and methods

2.1. Biogas and centrate

A synthetic gas mixture composed of CO_2 (29.5%), H_2S (0.5%) and CH_4 (70%), was used in this study as a model biogas (Abello Linde; Spain). Centrate was collected from the anaerobically digested sludge-dehydrating centrifuges at Valladolid wastewater treatment plant (WWTP) and stored at 4 °C prior to use. The average centrate composition was as follows: inorganic carbon (IC) = 459 ± 83 mg L^{-1}, total nitrogen (TN) = 576 ± 77 mg L^{-1} and S-SO_4^{2-} = 4.7 ± 3.4 mg L^{-1}. NH_4Cl was added to the raw centrate to a final TN concentration of 1719 ± 235 mg L^{-1} in order to simulate a high-strength digestate and thus minimize the flow rate of centrate used in the pilot plant.

2.2. Experimental set-up

The experimental set-up was located at the Department of Chemical Engineering and Environmental Technology at Valladolid University (Spain). The set-up consisted of a 180 L HRAP (depth: 15 cm, width: 63 cm, length: 202 cm) with an illuminated surface of 1.2 m^2 divided by a central wall in two water channels. The HRAP was interconnected to a 2.5 L absorption column (Ø: 4.4 cm, height: 165 cm) via external liquid recirculation of the supernatant of the algal-bacterial cultivation broth from a 10 L conical settler coupled to the HRAP (Fig. 1). The remaining algal bacterial biomass collected at the bottom of the settler was continuously recirculated to the HRAP in order to avoid the development of anaerobic conditions in the settler due to an excessive biomass accumulation. The HRAP cultivation broth was continuously agitated by a 6-blade paddlewheel at an internal recirculation velocity of ≈20 cm s^{-1}. A photosynthetic active radiation (PAR) of 1350 ± 660 μmol m^{-2} s^{-1} at the HRAP surface was provided by six high-intensity LED PCBs (Phillips SA, Spain) operated in a 12 h:12 h light/dark regime.

2.3. Operational conditions

Six operational conditions were tested in order to assess the influence of alkalinity and temperature on biomethane quality. The influence of IC concentrations of 1500, 500 and 100 mg L^{-1} was evaluated in stages I–II, III–IV and V–VI, respectively, while a temperature of 35 °C was maintained during stages I, III and V and a temperature of 12 °C during stages II, IV and VI (Table 1). The HRAP was initially filled with an aqueous solution containing a mixture of $NaHCO_3$ and Na_2CO_3 before inoculation to adjust the initial IC concentration to the corresponding concentration set in the operational stage. The IC concentration of the digestate fed to the HRAP during each operational stage was also adjusted accordingly. Thus, IC concentrations of 1500 and 500 mg L^{-1} were obtained by addition of $NaHCO_3$ to the raw centrate, while IC concentrations of 100 mg L^{-1} were achieved via an initial centrate acidification with HCl aqueous solution (37%) to a final pH of 5.5 in order to remove IC by air-aided CO_2 stripping followed by $NaHCO_3$ addition to adjust the IC concentration. The temperature of the HRAP cultivation broth was controlled with an external heat exchanger (Fisherbrand™ Polystat™ Immersion Circulator, Germany). A consortium of microalgae/cyanobacteria (from now on referred to as microalgae) from outdoors HRAPs treating centrate and domestic wastewater at the Department of Chemical Engineering and Environmental Technology at Valladolid University and at the WWTP of Chiclana de la Frontera (Spain), respectively, was used as inoculum in each operational stage.

During the illuminated periods, the HRAP was fed with the modified digestate as a nutrient source at a flow rate of 2 L d^{-1} while synthetic biogas was sparged into the absorption column under co-current flow operation at a flow rate of 4.9 L h^{-1} and a recycling liquid flow rate (L min^{-1}) to biogas flow rate (L min^{-1}) ratio (L/G, dimensionless) of 0.5 [12]. Tap water was continuously supplied in order to compensate water evaporation losses. A biomass productivity of 7.5 g dry matter m^{-2} d^{-1} was set in the six operational stages evaluated by controlling the biomass harvesting rate. The algal-bacterial biomass was harvested by sedimentation after coagulation-flocculation via addition of the polyacrylamide-based flocculant Chemifloc CV-300 (Chemipol S.A) [22]. This operational strategy resulted in a process operation without effluent. Approximately two weeks after the beginning of each stage, the system had already achieved a steady state, which was confirmed by the negligible variation of most parameters during the rest of the stage (variations < 5% of the recorded values).

2.4. Sampling procedure

The ambient and cultivation broth temperatures, the flow rates of digestate, tap water and external liquid recycling, and the dissolved oxygen (DO) concentration in the cultivation broth were monitored three times per week during the illuminated and dark periods. The PAR was measured at the HRAP surface at the beginning of each stage. Gas samples of 100 μL from the raw and upgraded biogas were drawn three times per week in order to monitor the CO_2, H_2S, CH_4, O_2 and N_2 concentrations. The inlet and outlet biogas flow rates at the absorption column were also measured to accurately determine CO_2 and H_2S removals. Liquid samples of 100 mL of digestate and cultivation broth were drawn three times per week and filtered through 0.20 μm nylon filters to monitor pH, dissolved IC, TN and SO_4^{2-}. In addition, liquid samples of 20 mL were also drawn three times per week from the cultivation broth to monitor the TSS concentration. Unfortunately, no analysis of the microbial population structure was conducted in this study.

2.5. Analytical methods

The DO concentration and temperature were monitored with an OXI 330i oximeter (WTW, Germany), while a pH meter Eutech Cyberscan pH 510 (Eutech instruments, The Netherlands) was used for pH determination. The PAR at the HRAP surface was recorded with a LI-250A lightmeter (LI-COR Biosciences, Germany). CO_2, H_2S, O_2, N_2 and CH_4 gas concentrations were analysed using a Varian CP-3800 GC-TCD (Palo Alto, USA) according to Posadas et al. [13]. The dissolved IC and TN concentrations were determined using a Shimadzu TOC-VCSH