Bioresource Technology 225 (2017) 429–437

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Ex-situ biogas upgrading and enhancement in different reactor systems

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HIGHLIGHTS

- Biogas with more than 98% CH_4 was produced in serial upflow and bubble column reactors.
- Increased gas recirculation rate enhanced the biogas upgrading efficiency.
- Biofilm was created on top of the diffuser surface in the bubble column reactor.
- Abundance of novel phylotypes belonging to MBA08 and *Bacteroidales* sp.
- *Methanothermobacter thermautotrophicus* was the most abundant methanogen.

ARTICLE INFO

Article history:
Received 18 October 2016
Received in revised form 28 November 2016
Accepted 30 November 2016
Available online 2 December 2016

Keywords:
Anaerobic digestion
Biogas upgrade
Enhancement
Hydrogenotrophic methanogenesis
Methane

ABSTRACT

Biogas upgrading is envisioned as a key process for clean energy production. The current study evaluates the efficiency of different reactor configurations for *ex-situ* biogas upgrading and enhancement, in which externally provided hydrogen and carbon dioxide were biologically converted to methane by the action of hydrogenotrophic methanogens. The methane content in the output gas of the most efficient configuration was >98%, allowing its exploitation as substitute to natural gas. Additionally, use of digestate from biogas plants as a cost efficient method to provide all the necessary nutrients for microbial growth was successful. High-throughput 16S rRNA sequencing revealed that the microbial community was resided by novel phylotypes belonging to the uncultured order MBA08 and to *Bacteroidales*. Moreover, only hydrogenotrophic methanogens were identified belonging to *Methanothermobacter* and *Methanoculleus* genera. *Methanothermobacter thermautotrophicus* was the predominant methanogen in the biofilm formed on top of the diffuser surface in the bubble column reactor.

1. Introduction

Biogas is produced via a biological process, mediated by different groups of microorganisms, which utilize diverse metabolic pathways to anaerobically digest organic substrates. The composition of biogas is typically 50–70% methane (CH_4), 30–50% carbon dioxide (CO_2) and small amounts of hydrogen sulfide (H_2S) and moisture. The produced biogas is commonly provided to a heat and power unit (CHP) to produce thermal and electrical energy. Nowadays, there is an increasing interest in exploiting biogas as a substitute of natural gas. In order to do so, the calorific value of biogas has to be increased by removing the CO_2, so as to upgrade it to higher fuel standard (Sun et al., 2015b). Therefore, "biogas upgrading" is the process in which the final output gas consists of higher methane concentration compared to raw biogas, mainly due to removal or transformation of carbon dioxide (and supplementary due to removal of other impurities, such as water, hydrogen sulfide and siloxanes). In case that the upgraded biogas is purified to natural gas standards, then the final gas product is called biomethane.

Several commercial or semi-commercial biogas upgrading technologies are available to date. More specifically, according to a recent joint study by IEA Bioenergy Task 40 and 37, on a global level, approximately 280 biogas upgrading plants connected with anaerobic digesters were in operation at the end of 2012 (Thrän et al., 2014). The commercial technologies used for biogas upgrading are mainly absorptive and adsorptive processes, as well as processes based on membrane filtration or cryogenic separation (Wu

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http://dx.doi.org/10.1016/j.biortech.2016.11.124
0960-8524/

et al., 2015; Sun et al., 2016b). Nevertheless, these marketable techniques are facing significant challenges in terms of energy consumption and operating costs (Sun et al., 2015b), which may add a substantial cost to the upgraded gas.

An attractive alternative solution for biogas upgrading is the biological method via hydrogenotrophic methanogenesis. In this concept, CO_2 and H_2 can be biologically converted to methane by the action of autochthonous hydrogenotrophic methanogens without any additional energy input according to Eq. (1).

$$4H_2 + CO_2 \rightarrow CH_4 + H_2O \quad \Delta G^0 = -130.7KJ/mol \tag{1}$$

Following the stoichiometric equation, the addition of H_2 to the system should be four times the CO_2 volume. The H_2 needed in the process has to be generated by an external source. A sustainable technology for H_2 production relies to water electrolysis utilising the excess energy from wind mills (Turner et al., 2008). Indeed, it has been reported that especially in northern EU countries, such as Denmark, more than 26% of the electricity from wind is a temporary surplus (Sovacool, 2013). Therefore, the excess or surplus electricity produced from wind mills during the peak periods must be consumed or exported, otherwise this energy will be lost or will cause grid instability (Georgilakis, 2008; Carton and Olabi, 2010). Nowadays, water electrolysis using renewable energy sources (RES), such as wind or solar power, is considered the only environmentally friendly technology in large scale application to obtain H_2 for bioconversion of CO_2 to CH_4 (Muñoz et al., 2015). It is well known that the utilization of H_2 as renewable energy carrier presents major challenges not yet solved, which are associated with its low density that requires high storage volume infrastructure (Jürgensen et al., 2014), while the direct exploitation of H_2 as transport fuel is still under development (Muñoz et al., 2015). In contrary, the integration of different energy sources (i.e. wind or solar energy and biomass) and the supply of power to remote from the centralized grid rural areas are becoming more attractive in the energy policy design. In this context, the biological biogas upgrading via hydrogenotrophic methanogenesis opens new avenues in the power to gas (P2G) technology due to the more efficient exploitation of RES. Another important advantage is that the externally provided CO_2 is not removed or precipitated but transformed into CH_4, enhancing the final energy value of the output "windgas" (i.e. use wind-mill surplus energy to produce methane) or "solargas" (i.e. use solar surplus energy from solar panels to produce methane). The biological biogas upgrading process can be defined in three different concepts; (a) *in-situ* biogas upgrade technology, in which H_2 is delivered inside the liquid phase of a biogas reactor and subsequently the H_2 is coupled with the endogenous CO_2 contained in the reactor resulting in generation of CH_4, (b) *ex-situ* biogas upgrade technology, in which CO_2 from external sources (e.g. biogas, syngas etc) and H_2 are injected inside the liquid phase of a reactor containing (pure or enriched) hydrogenotrophic cultures, resulting in their conversion to CH_4, and (c) hybrid biogas upgrade technology, in which *in-situ* and *ex-situ* biogas upgrading are implemented together forming an integrated system. In the hybrid technology, usually initially *in-situ* technology captures a part of the CO_2, upgrading the biogas to higher grade e.g. 80–90% CH4, followed by *ex-situ* process, where the enriched biogas is polished to a CH4 content >98%. The advantage of the hybrid technology is that it addresses the problem of pH enhancement during the *in-situ*, while a considerably smaller separate reactor is needed for the *ex-situ*.

Previous research on biological biogas upgrading and enhancement has experimentally proven that the biomethanation efficiency can be equal or higher than 95% (Luo and Angelidaki, 2013; Díaz et al., 2015). Additionally, this process has been demonstrated to be fast as methane formation was commenced even from the first day of reactor operation (Lee et al., 2012). However, technical challenges related to increased pH due to consumption of bicarbonate caused in some cases slight inhibition of methanogenic process (Luo et al., 2012). Moreover, another study found that the low gas-liquid mass transfer rate of H_2 limits its availability for methanogens and therefore the gas recirculation flow rate and the reactor design are key factors for a successful biogas upgrading process (Bassani et al., 2016). As it can be understood these challenges have to be addressed in order to consolidate the concept in the market, to create a robust technology and maximize the efficiency of the system.

The aim of the present study was to evaluate and compare different reactor configurations (i.e. serial upflow, continuously stirred tank and bubble column reactors) regarding their conversion efficiencies and quality of effluent gas product during *ex-situ* biogas upgrading. Furthermore, the produced gas was recirculated inside the reactors at two rates in order to determine whether this strategy could improve the gas-liquid mass transfer rate of H_2, and thus, benefit the upgrading process. An additional aim of the current study was to test the applicability of digested manure as culture media, which is directly available at no cost from biogas plants. To the best of our knowledge, all the research studies on *ex-situ* biogas upgrading in the literature have been performed using synthetic media as a source of nutrients (Lee et al., 2012; Luo and Angelidaki, 2012; Díaz et al., 2015). Finally, besides the reactor configuration, the microbial composition is a fundamental driving force in determining the quality of the produced biogas. In order to have a clear understanding of the microbial dynamicity and its role in the hydrogenotrophic methanogenesis, a high-throughput sequencing of 16S rRNA gene amplicons was performed in samples obtained from all the examined reactors.

2. Materials and methods

2.1. Continuously fed biogas upgrading reactors

The experiment was performed using three different reactor configurations; a) two upflow reactors in series denoted as R1 + R2, b) a Continuous Stirred Tank Reactor (CSTR) denoted as R3 and c) a bubble column reactor denoted as R4. The selection the serial and bubble column reactor was based on the concept to improve the gas-liquid mass transfer rate by increasing the contact area and time between the injected gasses and the liquid. The working volume for each upflow reactors in series was 1.4 L. The corresponding volume for the bubble column and the CSTR was 1.2 L. A schematic representation of the reactor configurations is given in Fig. 1. A gas mixture of 23:15:62 (%) corresponding to CH_4:CO_2:H_2 was injected in the reactors R1, R3, and R4 through two stainless steel diffusers (2 μm pore size) per reactor. The gas mixture was stored inside gas tight aluminium bags and was provided to the diffusers using peristaltic pumps. The bags were filled with fresh gas mixture every other day. R2 was fed with the effluent gas of R1. The gas feed flow rate was 3 L/L-reactor ·day. In order to evaluate the gas-liquid mass transfer, two different gas recirculation rates were applied; 4 L/h during the days 0–18 (Period I) or 12 L/h during the days 19–51 (Period II). Additionally, the CSTR was equipped with a magnetic stirrer at a mixing speed of 300 rpm to maintain the homogeneity of the liquid. The operating temperature of the reactors was set to 52 ± 1 °C in accordance with a previous study, which demonstrated that the thermophilic conditions lead to higher biomethanation and CO_2 conversion efficiency compared to mesophilic conditions (Bassani et al., 2015). On a daily basis, 80 mL of digested slurry, which was serving as nutrient source, was provided to the reactors using peristaltic pumps. During the first days of the experiment, foam was generated inside the