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Biological biogas upgrading capacity of a hydrogenotrophic community in a trickle-bed reactor

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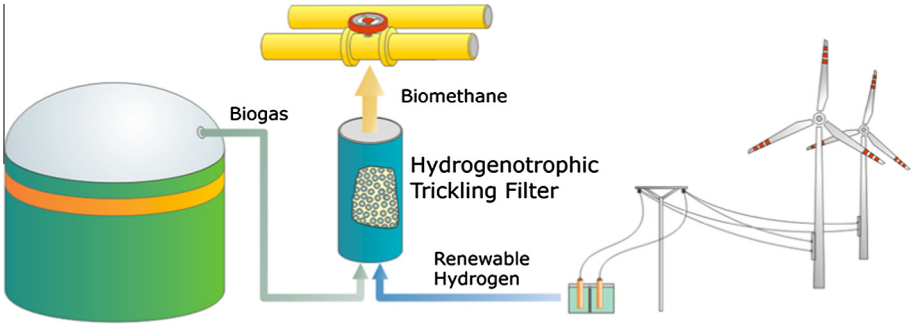
HIGHLIGHTS

- Data on long term operation of a system supplied with real biogas are presented.
- Ex-situ biological methanation is feasible for biogas upgrading.
- Gas quality obtained complies with strictest direct grid injection criteria.
- Biomethane can act as flexible storage for renewable surplus electricity.

GRAPHICAL ABSTRACT



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ABSTRACT

The current study reports on biological biogas upgrading by means of hydrogen addition to obtain biomethane. A mesophilic (37 °C) 0.058 m^3 trickle-bed reactor with an immobilized hydrogenotrophic enrichment culture was operated for a period of 8 months using a substrate mix of molecular hydrogen (H_2) and biogas (36–42% CO_2). Complete CO_2 conversion (> 96%) was achieved up to a H_2 loading rate of 6.5 m^3_n $H_2/m^3_{reactor\ vol.} \times d$, corresponding to 2.3 h gas retention time. The optimum H_2/CO_2 ratio was determined to be between 3.67 and 4.15. CH_4 concentrations above 96% were achieved with less than 0.1% residual H_2. This gas quality complies even with tightest standards for grid injection without the need for additional CO_2 removal. If less rigid standards must be fulfilled H_2 loading rates can be almost doubled (10.95 versus 6.5 m^3_n $H_2/m^3_{reactor\ vol.} \times d$) making the process even more attractive. At this H_2 loading the achieved methane productivity was 2.52 m^3_n $CH_4/m^3_{reactor\ vol.} \times d$. In terms of biogas this corresponds to an upgrading capacity of 6.9 m^3_n biogas/$m^3_{reactor\ vol.} \times d$. The conducted experiments demonstrate that biological methanation in an external reactor is well feasible for biogas upgrading under the prerequisite that an adequate H_2 source is available.

1. Introduction

Renewable energies such as biomass, wind and solar power will significantly contribute to the future energy mix. However, specifically wind and solar energy pose the problem of limited buffer capacity to cover peak renewable energy production. Moreover, the transition to clean energy requires new concepts for their integration into existing infrastructure and distribution networks.

The current study describes the biological upgrading of biogas by means of molecular hydrogen (H_2) injection. The investigated approach incorporates two concepts intensively discussed in the renewable energy sector. The first concept is upgrading of biogas, i.e. the removal of CO_2 and trace gases to yield pure methane [1–3]. The background is the relatively low efficiency of on-site biogas conversion into electric energy. Upgrading and injection

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into the natural gas grid does not only allow the use of available infrastructure to deliver energy to the place of demand but also makes beneficial use of the storage capacity of the gas grid [4–6].

The second concept involved is power-to-gas. The idea behind power-to-gas is to use renewable electricity to produce H_2 with the option to subsequently convert it, together with CO_2, into methane [7]. Hydrogen and methane from renewable electricity can be used in mobility, industrial processes, heat supply and electricity generation applications. When compared to methane, hydrogen has distinct disadvantages like its low volumetric energy density and a lack of infrastructure for storage and utilization [8]. In contrast, conversion to methane allows storage in the gas grid and use in a variety of consumption areas. Power-to-gas provides efficient means to store electric energy in order to compensate the fluctuations in electricity generation from wind and solar energy. It facilitates sustained storage of electricity produced in renewable manner which cannot be immediately delivered to the electric grid in times of excessive energy generation [9,10].

Current biogas upgrading technologies are based on the removal of CO_2 from biogas. A number of technical options – such as pressurized water scrubbing, chemical absorption, pressure swing adsorption and membrane separation – are established at full scale [1,2,11]. However, instead of energy intensive removal of CO_2 from the biogas stream, biological biogas upgrading applies special microorganisms to convert CO_2 together with H_2 (preferably produced from solar or wind energy) into methane. These microorganisms, termed CO_2-type hydrogenotrophs, belong to the domain Archaea. They are part of the microbial consortium present in any biogas plant and closely interact with syntrophic bacteria that convert organic acids and alcohols into acetate, CO_2 and H_2. CO_2-type hydrogenotrophs utilize the previously produced H_2 via anaerobic respiration, using the following reaction [12,13]:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (1)$$

The same transformation may be achieved by a catalytic chemical reaction (Sabatier process). However, as also stressed by other researchers, biological methanation has several advantages, among them that it takes place at more moderate temperatures than the chemical process and that it has a higher resistance to gas contaminations, such as H_2S, organic acids and NH_4 [11,14–16].

It has been attempted to directly inject H_2 into the biogas reactor to increase the share of methane in the produced biogas [17–19]. However, this approach has several drawbacks. Efficient biogas production depends on close interplay of syntrophic bacteria with methanogenesis for H_2 removal. Due to thermodynamic constraints, conversion of organic acids into H_2 occurs only at very low H_2 concentrations (or low H_2 partial pressure). Injection of H_2 into the anaerobic reactor might therefore inhibit syntrophic bacteria and lead to reduced substrate conversion rates. Martin et al. [20] reported on an increase in pH due to direct hydrogen addition in the digester which subsequently led to inhibition of methanogenesis. In addition, in-situ approaches typically result in low volumetric CH_4 production rates and hence, low CH_4 content [21]. To avoid these problems, a two-step approach was applied in the current study involving a separate biological process where CO_2 conversion takes place.

Biological methanation of CO_2 with H_2 by pure cultures is a well-studied process [22–25]. The concept of H_2 addition for biocatalytic methanation of CO_2 was also proven for adapted hydrogenotrophic communities. Different reactor types, including stirred tank, bubble column, packed bed and hollow fiber membrane bioreactors, were evaluated in lab scale under mesophilic and thermophilic conditions [26–30]. In their review on prerequisites for successful bioprocess development of biological methanation Rittmann et al. [25] discuss the suitability of these various bioreactor designs. As outlined, the gas/liquid mass transfer in particular of H_2 is known to be a bottleneck in biomethanation [31] and therefore the most important criteria when choosing the bioreactor type. Moreover, the required volumetric power input plays a vitally important role for the overall efficiency. A trickle-bed reactor with an immobilized biofilm, as used in the present investigations, provides a large contact area between microorganisms and gas as well as liquid phase. Another advantage of this reactor type is that no additional mechanical power input is needed.

There are a significant number of studies on biological methanation but most of them focus on fundamental aspects and apply synthetic gas mixtures. Only a few of them investigate the use of real biogas [14,20,22]. To prove the claimed advantages, detailed information on operation under realistic conditions is still missing with respect to the further practical development of H_2 utilization for biogas upgrading. To fill this gap, the present study reports on the set-up and long-term operation of a technical plant comprising an anaerobic digester and a subsequent trickle-bed column for biomethanation by an adapted microbial consortium. Detailed results obtained during a measuring campaign are presented.

2. Material and methods

2.1. Trickle-bed reactor

The trickle-bed reactor consisted of a glass column with a height of 1.5 m and an inner diameter of 0.08 m. The ends were sealed in a gas-tight manner with two heavy plastic caps bearing the gas inlet and outlet as well as a drip-funnel (0.03 m Ø) sprinkling device on top and a bottom drain for liquid circulation. Polypropylene packing rings (Hiflow rings type 15-7, RVT Process Equipment, Germany) served as the carrier material for the biofilm, offering a high specific surface of 313 m^2/m^3 at a void fraction of 91%. The reactor had a packed volume of 0.00578 m^3. Carrier material was selected according to pre-existing experience from biogas purification (adsorption and microbial oxidation of H_2S) [32]. The carrier material was also recommended by the manufacturer as highly suitable for gas–liquid reactors and exhibits a similar specific surface area as used by other researchers for biotrickling filters [33]. A temperature-control hose was wrapped around the glass cylinder to maintain the trickling filter at 37 ± 2 °C. Mineral media was recirculated via a peristaltic pump at a rate of 4.17×10^{-6} m^3/s out of a 2.0×10^{-3} m^3 reservoir placed in a water bath. Slight pulsations of the flow (caused by the working mode of the peristaltic pump) supported homogenous distribution of the recirculated media via the drip funnel. The appropriate flow rate was developed in initial tests, where the aim was to obtain homogenous wetting of the bed without flooding. The liquid recirculation rate remained unchanged throughout the experiment. The only exceptions were occasional short-term flushes of the trickle bed to remove excess biomass during the start-up phase.

Composition of the media was as follows (kg/m^3): 408.0×10^{-3} KH_2PO_4, 426.0×10^{-3} Na_2HPO_4, 110.0×10^{-3} $CaCl_2 \times 2\ H_2O$, 100.0×10^{-3} $MgCl_2 \times 6\ H_2O$, 300.0×10^{-3} NH_4Cl, 300.0×10^{-3} NaCl, 1.0×10^{-3} conc. HCl, 0.05×10^{-3} H_3BO_3, 0.07×10^{-3} $ZnCl_2$, 0.05×10^{-3} $CuCl_2 \times 2\ H_2O$, 2.0×10^{-3} $MnCl_2 \times 4\ H_2O$, 0.1×10^{-3} $(NH_4)_6Mo_7O_{24} \times 4\ H_2O$, 0.09×10^{-3} $AlCl_3 \times 6\ H_2O$, 1.0×10^{-3} $CoCl_2 \times 6\ H_2O$, 0.3×10^{-3} $NiCl_2 \times 6\ H_2O$, 1.0×10^{-3} EDTA (Disodium salt), 2.0×10^{-3} $FeCl_2 \times 4\ H_2O$, 0.126×10^{-3} Na_2SeO_3, 360.3×10^{-3} $Na_2S \times 9\ H_2O$.

The mixture of biogas and H_2 was supplied continuously at the bottom of the reactor below the carrier material. Biogas quantity, as well as gas inflow and outflow were monitored by drum-type gas meters (MGC-1 V3, Ritter Apparatebau GmbH, Germany) during the start-up phase. Flow rates of inlet gas mix were manually adjusted by flow tube meters with needle valves (Aalborg,