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

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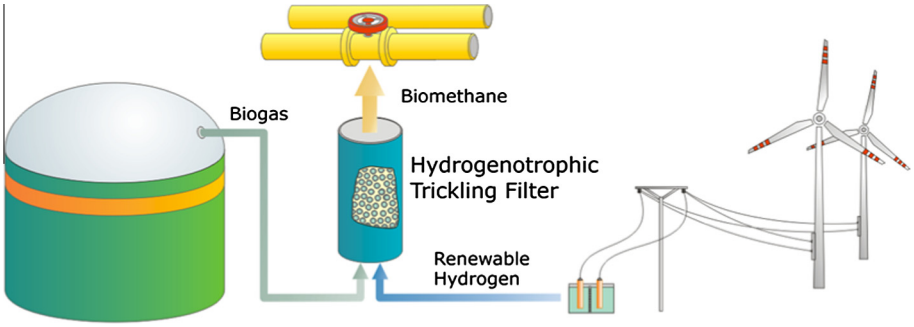
HIGHLIGHTS

- 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,

USA). During the accurate measuring campaign, higher precision was required for control and measurement of inlet flows of H_2 and biogas. Therefore, gas meters were replaced by electronic mass flow controllers (MFC 8111 for H_2 and MFC 8110 for air; correction factor of 0.8, Bürkert, Germany).

2.2. Source of H_2 and biogas

Biogas was provided by a 0.5 m^3 pilot-scale biogas plant that was directly connected to the trickle-bed reactor. Daily, 2.4 kg substrate (0.05 kg every 30 min) consisting of a pre-fermented mixture of pig feed and refined sugar (sucrose) with a chemical oxygen demand (COD) in the range of 197×10^{-3}–240×10^{-3} kg/kg were fed. The corresponding organic loading rate was 1.4 kg/m^3 × day. For the pre-fermentation, 24 kg freshly prepared feed were mixed with 1 L fully fermented feeding material to reduce the pH in the feed and such prevent methane formation in the storage vessel. The pre-fermented substrate had a pH of 3.2, ammonium-nitrogen (NH_4—N) and Total Kjeldahl Nitrogen (TKN) content in the range of 0.11×10^{-3}–0.19×10^{-3} kg/kg and 1.39×10^{-3}–1.49×10^{-3} kg/kg, respectively. Volatile fatty acids (VFA), alcohols and residual saccharides were determined to be between 59.16 and 63.47 kg/m^3, 92.18 and 95.37 kg/m^3, 25.75 and 40.40 kg/m^3, respectively.

Temperature in the fermenter was kept at 37 °C and pH ranged from 7.4 to 7.7. Total Kjeldahl Nitrogen and NH_4—N ranged from 2.77×10^{-3} to 3.12×10^{-3} kg/kg and 1.25×10^{-3} to 1.65×10^{-3} kg/kg, respectively, during time of operation.

A schematic overview of the overall experimental set-up including anaerobic digester and trickle-bed reactor for subsequent biogas upgrading is presented in Fig. 1.

It should be noted that the anaerobic reactor served as a mere tool to provide real biogas. Only a portion of the biogas produced (depending on the operational conditions of the trickle-bed reactor, 5.5–15%) was delivered to the biomethanation step. The dry composition of the biogas was as follows: 36–42% CO_2, 58–64% CH_4, H_2S <50 ppm, other components <0.2%.

H_2 was delivered from a gas bottle (quality 5.0, Messer Austria, Austria) through a stainless steel pipe.

2.3. Analytical methods

For monitoring of the biogas reactor, the amount of feed added, temperature, pH and gas pressure were documented daily. The pH in the trickle-bed reactor (measured in the recirculation vessel) and gas flow rates (after the implementation of gas flow controllers) were recorded electronically every 30 s. Additionally, gas flows were cross-checked manually by soap film flowmeters (1×10^{-6} m^3, Agilent Technologies, USA) several times a day. In both reactors NH_4—N content and TKN were measured once a month, and VFA concentrations were determined weekly.

For substrate characterization of pre-fermented feed for the anaerobic digester, chemical oxygen demand (COD), NH_4—N, TKN and VFA were analyzed.

2.3.1. Gas composition

Gas qualities of inlet and outlet gas were measured at least daily (with the exception of weekends) during the experimental phase. Samples were withdrawn using a 250 µL (2.5×10^{-7} m^3) gas-tight syringe (Hamilton, CH) and analyzed by GC (HP 7890A, Agilent Technologies, USA) equipped with two detection pathways. In both paths, a first capillary column (Agilent 19095P-Q03, 15 m) served for preliminary separation of H_2 and air compounds (N_2 and O_2) from methane and CO_2. These two groups of components were analyzed by applying different subsequent columns: methane and CO_2 were separated in a capillary column (Agilent 19095P-Q04, 30 m) while air compounds and H_2 were separated in a molecular sieve column (Agilent 19095-MS6, 30 m). Air compounds and H_2 were then detected by PDD (250 °C), while methane and CO_2 (after conversion to methane with H_2 by a nickel catalyst) were detected by FID (280 °C).

Gas samples were injected manually. The injector temperature was 105 °C and the split ratio 1:25. Separation was carried out at 30 °C oven temperature. At the end of each run (480 s), the oven temperature was raised to 105 °C for 600 s to free the system of water potentially introduced with the gas sample. The GC method was calibrated using external standard gas mixtures (Linde, Germany).

Gas amounts given are calculated as Norm cubic meters (m^3_n) (0 °C, 101.325 kPa) following the recommendations of DIN 1343.

2.3.2. Free volatile fatty acids

Volatile fatty acids in the biogas plant as well as in the recirculation liquid of the trickle-bed reactor were monitored weekly. Concentrations of acetic acid, propionic acid, *iso*-butyric acid, butyric acid, valeric and *iso*-valeric acid were determined by HPLC analyses (Agilent 1100 Series HPLC System with G1362A refractive index detector, Agilent Technologies, USA). Separation was done on

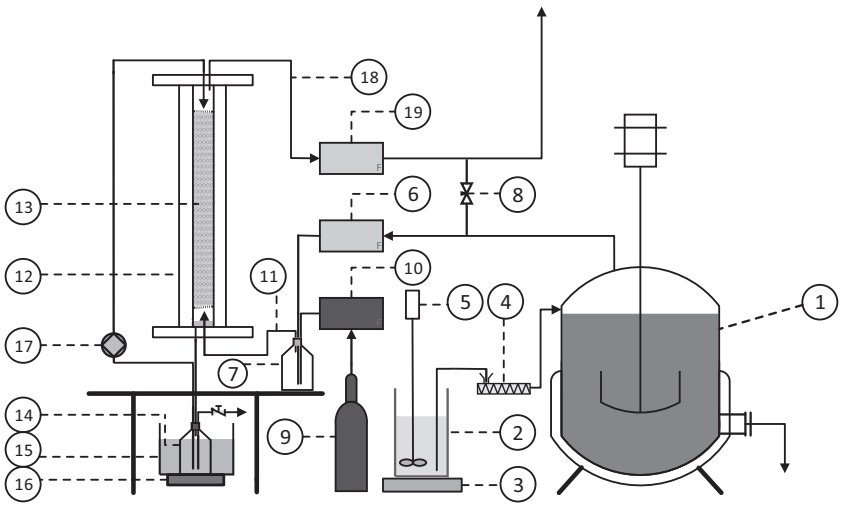

Fig. 1. Schematic overview of the experimental set-up. ① biogas plant, ② substrate tank, ③ digital scale, ④ spiral pump, ⑤ propeller stirrer, ⑥ mass flow controller (biogas), ⑦ gas mixing chamber, ⑧ needle valve (pressure regulation), ⑨ hydrogen bottle, ⑩ mass flow controller (H_2), ⑪ sample port inlet gas, ⑫ trickle-bed reactor, ⑬ carrier material, ⑭ nutrient broth, ⑮ temperature controlled water bath, ⑯ magnetic stirrer, ⑰ peristaltic pump, ⑱ sample port outlet gas, and ⑲ flow meter outlet gas.

a IC Sep ICE-Coregel 87H3 column (Transgenomic, USA) with a mobile phase of 50 mol/m^3 H_2SO_4 at a flow rate of 1.5×10^{-7} m^3/s. Column oven and detector temperature were 65 °C and 55 °C, respectively. Samples were prepared by Carrez precipitation and centrifugation to eliminate interfering compounds following the protocol given in DIN 38 414-19. For calibration, mixed standards were prepared from pure substances (p.a. grade) at concentration levels of 10, 40, 100, 500 and 1000 ppm.

2.3.3. Chemical oxygen demand, Total Kjeldahl Nitrogen and ammonium nitrogen

Determination of COD, TKN and NH_4—N to characterize substrate and effluent of the anaerobic digestion plant was done according to standard analytical procedures (German standard methods for the examination of water, wastewater and sludge).

Chemical oxygen demand was analyzed according to DIN 38414 (S9), NH_4—N was determined by vapor distillation and subsequent titration of ammonia (DIN 38406 (E5), Distillation Unit K-350, Büchi Labortechnik, Switzerland). For TKN determination samples were previously digested with sulfuric acid (VDLUFA EN 13342, Digest Automat K-438, Büchi Labortechnik, Switzerland).

3. Results and discussion

3.1. Inoculation and start-up of trickle-bed reactor

The trickle-bed reactor was inoculated with a mixed anaerobic consortium from the 0.5 m^3 anaerobic digester. Prior to inoculation the system was flushed with nitrogen to establish anaerobic conditions for the subsequent immobilization procedure. Anaerobic sludge was diluted with mineral media 1:5 and recirculated at a rate of 4.17×10^{-6} m^3/s for three days to immobilize the microbes in the packed bed. After that, the mix of biogas and H_2 was supplied and the sprinkling of mineral media from the top of the trickle-bed reactor was started. Inlet gas flow (biogas and H_2) was set to 1.0×10^{-6} m^3/s with an intended stoichiometric H_2:CO_2 ratio of 4:1 using flow meters. During the start-up phase, operation conditions were not fully optimized with regard to inlet gas mix or retention time. Initially, volatile fatty acids (mainly acetate) accumulated in the trickle-bed reactor (Fig. 2), presumably due to incomplete biofilm formation or the more favorable conditions for homoacetogenic bacteria. Moreover, pH shifts in the media led to either increased solubility (at rising pH) or degassing of CO_2 (at decreasing pH) in the liquid phase and hence, altered the gas composition at the inlet. However, with time (~from day 60 on) and more experience of process handling (e.g., more accurate adjustment of inlet gas mix ratio, combined with occasional substitution of part of the recirculation liquid by fresh media) the observed fatty acid accumulation was overcome and pH stabilized in the range of 6.8–7.0.

In the following 3 months (day 60–150) the trickle-bed reactor was operated with ambivalent results. The performance of the reactor in terms of biogas upgrading was acceptable. Conversion rates in the range of 75–96% CH_4 (with only few outliers due to process disturbances) were observed at an average H_2 load of 5.0 $m^3_n/m^3_{reactor\ vol.} \times d$. Therefore it can be presumed that biofilm formation of methanogenic archaea and adaptation to the process conditions was largely completed although a slight tendency to higher methane production rates towards the end of this period might be perceived.

However, difficulties linked to accurate control and measurement of gas flows were experienced.

It should be underlined that it is much more challenging to operate a system combination incorporating a real biogas reactor compared to synthetic biogas supply from bottled gas. The lower feed-gas pressure in the range of less than 3000 Pa (<30 mbar) makes accurate control of the gas flow extremely tricky. Any small change in pressure loss within the trickling filter caused quite significant variations. Such problems are largely avoided if highly pressurized bottled gas is applied. Due to this inaccuracy, certain inconsistencies occurred when mass balances for ingoing and outgoing gas flows were calculated. Therefore, this period of investigation was devoted to improvement of system control rather than parameter studies. In order to more precisely adjust gas flow rates and thus achieve stable conversion, the instrumental effort on flow regulation and monitoring had to be increased. On this account, needle valves for gas flow adjustment were replaced by electronic mass flow controllers with automatic data recording.

3.2. Experimental phase – parameter optimization

Once all changes of the system configuration were implemented, the experimental phase started. Inlet gas flow rate and H_2/CO_2 ratio were precisely adjusted (and double checked by soap

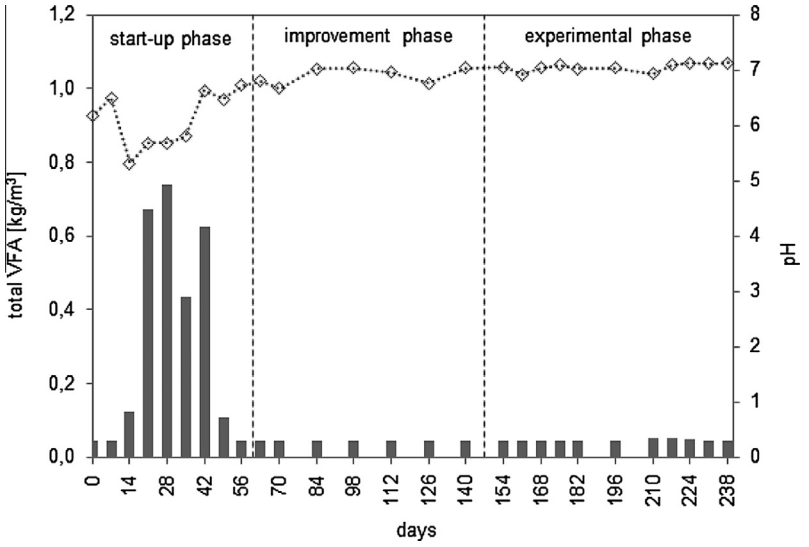

Fig. 2. Development of total VFA concentration (gray bars) and pH value (diamond shape with dotted line) in recirculation liquid of trickle-bed reactor throughout the entire operational period.

film flow meters) to allow evaluation of optimal H_2/CO_2 ratio and minimal retention time. An overview of all parameter settings and corresponding operational periods is provided in Table 1.

3.2.1. Evaluation of optimal H_2/CO_2 ratio

The first set of trials aimed at working out the optimal H_2/CO_2 ratio to achieve highest CO_2 conversion in combination with maximum methane concentration in the outlet gas. For this purpose, the H_2/CO_2 ratio of the inlet gas was gradually reduced from 6.7 to 3.7. The gas retention time was maintained in the range of 2.5–3.5 h which provided sufficient time for microbial conversion of CO_2 and H_2 as known from previous experience. Fig. 3 gives an overview of the methane concentration as well as residual CO_2 achieved in the outlet gas. The empirically determined optimum ratio for maximum methane content is between 3.67 and 4.15. This is in line with the stoichiometric ratio of 4 according to Eq. (1). As expected, at higher H_2/CO_2 ratio complete conversion of CO_2 occurred but residual H_2 was found in the outlet gas. On the other hand, at ratios lower than the stoichiometric ratio, residual concentrations of CO_2 (up to 3.9%) were detected at the outlet of the reactor (Fig. 3).

These results are in line with findings reported in other studies on hydrogenotrophic methanation. Lee et al. [28] reported on the effect of H_2/CO_2 ratios in the range of 1–8. Up to a ratio of 4, methane production followed the stoichiometry and even exceeded the theoretical maximum at a ratio of 5. According to their explanation, this was due to residual carbonate remaining in the system from feeding insufficient H_2 at lower ratios. At higher ratios, methane production started to decrease significantly. Burkhardt et al. [26] also state an optimum H_2/CO_2 ratio of 4. Data obtained in the current study suggest a H_2 demand slightly below 4 which indicates that a small portion of the CO_2 was consumed by the microorganisms for biomass build-up.

3.2.2. H_2 loading rate/necessary minimum retention time

The second set of experiments addressed the maximum H_2 loading rate or minimum retention time within the reactor. Here, the H_2/CO_2 ratio was kept constant at the stoichiometric ratio of around 4 (3.7–4.1) and the volumetric H_2 loading rate was gradually increased. With increasing H_2 load, retention time was reduced from initially 3 h to 1.3 h at maximum H_2 loading.

According to Monod kinetics in combination with mass transfer limitations, highest methane production rates are achieved when a surplus of the gaseous substrates, H_2 and CO_2 is provided. Consequently, high volumetric methane production is typically linked to lower final methane concentrations in the produced gas [11]. While aiming at highest reactor performance in terms of conversion rates the envisaged gas quality is therefore the main criterion limiting the maximum gas throughput.

In contrast to other biological gas treatment systems (e.g., a biofilter for removal of organic substances from exhaust gas), here the gas volume passing through the reactor is not constant. Due to H_2 consumption during CO_2 conversion, gas volume within the trickle-bed reactor gradually decreases. Consequently, the gas flow

Table 1
Parameter settings for evaluation of optimal H_2/CO_2 ratio (no. 1–5) and minimum retention time (no. 6–11).

Parameter setting no.	LR_{H2} min – max (mean) ($m^3_n/m^3_{reactor\ vol.} \times d$)	LR_{biogas} ($m^3_n/m^3_{reactor\ vol.} \times d$)	Average RT of total flow at inlet (h)	H_2/CO_2 ratio (m^3_n/m^3_n)	Operational duration (h)
1	4.98–7.47 (5.44)	3.17	2.9	6.6–6.7	264
2	4.98–7.63 (6.07)	3.47	2.6	5.9–6.2	336
3	4.98	2.37	3.3	4.4–4.9	72
4	4.98–6.25 (5.80)	2.19	3	3.9–4.2	96
5	4.98–5.73 (5.48)	1.98	3.2	3.7–3.9	72
6	4.98–5.21 (5.02)	2.90	3.0	3.7–3.9	216
7	5.75	3.32	2.6	4.1	72
8	6.50	3.74	2.3	4.0	24
9	7.47–7.63 (7.50)	4.44	2.0	3.8–4.1	144
10	9.64–10.17 (9.83)	6.17	1.5	3.7–4.1	144
11	10.68–11.16 (10.95)	6.88	1.3	3.8–4.0	144

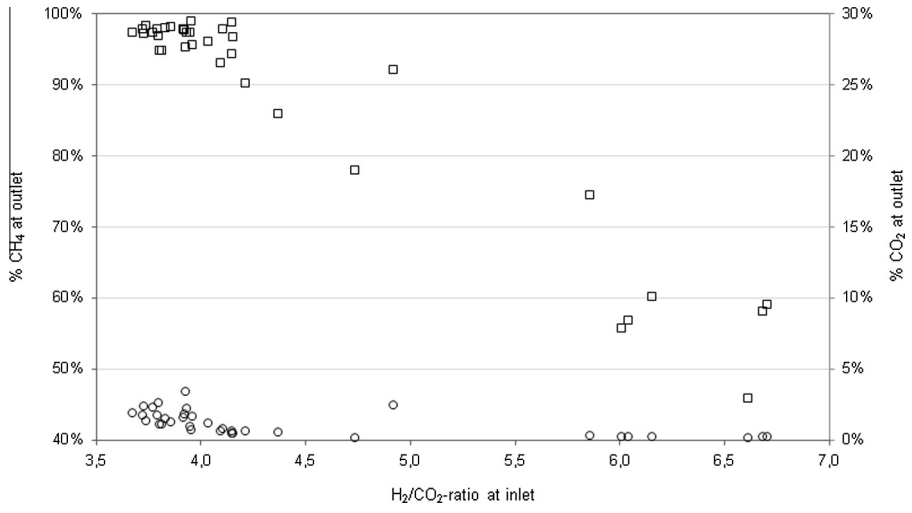

Fig. 3. Influence of H_2/CO_2 inlet ratio on final methane concentration (open squares) and residual CO_2 at the reactor outlet (open circles) at H_2 loading rates of 5.02–7.50 $m^3_n/m^3_{reactor\ vol.} \times d$.

rate changes from bottom to top. The absolute retention time in the reactor is therefore dependent on the conversion rate itself. It should also be noted that no adverse effects of side components – other than CO_2 and H_2 – in biogas (and also H_2 enriched synthetic waste gas and combustion gas) were reported for methanation by a pure culture of *Methanothermobacter marburgensis* in a CSTR and hence can be considered as inert gas flow [14]. Retention times provided here refer to total volumetric loading at the gas inlet versus packed volume of the reactor.

Methane production and CO_2 conversion were evaluated at H_2 loading rates of LR_{H2} = 5.02–10.95 $m^3_n/m^3_{reactor\ vol.} \times d$. Each setting of parameters was evaluated for a period of at least 24 h and at least two complete data sets (gas composition and flow at in and outlet) were analyzed. After a parameter change the system was allowed to stabilize for a minimum of 48 h before new data were collected.

As shown in Fig. 4, complete CO_2 conversion (>96% CO_2 conversion, >97% CH_4) was achieved up to a loading rate of 6.5 $m^3_n\ H_2/m^3_{reactor\ vol.} \times d$, corresponding to a retention time of 2.3 h. At a load of 7.5 $m^3_n\ H_2/m^3$ a slight decline in final methane concentration occurred, however, with still excellent quality of the offgas (95.4% CH_4). With further increase of H_2 loading (i.e. decrease of retention time) conversion rates gradually declined. These findings might be compared to data provided by Burkhardt et al. [26] who conducted experiments with a very similar set up: a 6.1×10^{-2} m^3 trickle-bed reactor filled with packing material with a specific surface 305 m^2/m^3 operated at similar temperature (35 °C), however, fed with a pure H_2/CO_2 mixture. Methane qualities of approximately 95% were achieved at H_2 loading rates of 4.83 $m^3_n/m^3_{reactor\ vol.} \times d$. Even higher H_2 loading rates up to 6.0 $m^3_n/m^3_{reactor\ vol.} \times$ d were tested but methane concentration at these conditions are not provided. Preliminary test were also conducted with biogas (methane concentration 77%) as substrate. At a H_2 loading rate of 0.51 $m^3_n/m^3_{reactor\ vol.} \times$ d methane enrichment up to a methane concentration of 96% was observed.

Alitalo et al. [27] report on biocatalytic methanation of H_2 and CO_2 in a serial two-reactor system with a total volume of 4.0×10^{-3} m^3 and liquid recirculation. Much higher H_2 loads of up to 25.2 $m^3/m^3_{reactor\ vol.} \times d$ were applied. Stable and efficient conversion was achieved at H_2 loading rates of 7.2 $m^3/(m^3_{reactor\ vol.} \times d)$ (calculated from data provided) with methane concentrations of around 95% in the outlet gas. With a maximal methane productivity of 6.35 $m^3/m^3_{reactor\ vol.} \times d$ the maximum productivity observed was 5 times higher compared to Burkhardt et al. [26] and 2.5 times higher compared to the results reported here. However, in contrast to Burkhardt et al. [26] and the current experiments where high flow plastic carriers were applied, Alitalo et al. [27] used a filling material exhibiting an extremely high surface area (vermiculite shales and granular perlite). The total operation time of the system was 47 days and it still needs to be demonstrated that such extremely dense packing material allows long operation without clogging.

Lee et al. [28] report on biological conversion of CO_2 to CH_4 in an up-flow anaerobic fixed bed reactor (7.8×10^{-3} m^3 working volume). At a stoichiometric H_2/CO_2 ratio of 4 complete CO_2 conversion (100%) was achieved at mixed gas retention times of above 3.8 h but decreased to 71% when retention time was reduced to 2 h. In the current study, at the same retention time (2 h, corresponding to LR_{H2} = 7.50 $m^3_n/m^3_{reactor\ vol.} \times d$) excellent CO_2 conversion of 97.2% was still observed.

3.2.3. Volumetric methane productivity/upgrading capacity

Muñoz et al. [11] carried out a comprehensive review on the current physical/chemical and biological technologies for biogas upgrading. They summarize data from thirteen studies on chemoautotrophic CO_2 conversion to CH_4 out of which six were operated in the mesophilic range. In liquid phase (continuously stirred tank reactors) maximum volumetric methane productions reported were in the range of 2.4–4.1 $m^3\ CH_4/m^3_{reactor\ vol.} \times d$, packed beds reached values of 1.17–1.34 $m^3\ CH_4/m^3_{reactor\ vol.} \times d$. One study operating a hollow fiber biofilm membrane bioreactor even provided a methane production of 4.6 $m^3\ CH_4/m^3_{reactor\ vol.} \times d$. It is worth mentioning that under thermophilic conditions significantly higher methane production rates of up to 144 $m^3/m^3_{reactor\ vol.} \times d$ are claimed for continuously operated reactor systems. Rittmann et al. [25] also reported on such high methane production rates for thermophilic archaea in their literature survey on biomethanation rates. The following summary of volumetric methane productivities for different reactor types is provided: 285–689 $m^3\ CH_4/m^3_{reactor\ vol.} \times d$ for CSTR systems, 123–144 $m^3\ CH_4/m^3_{reactor\ vol.} \times d$ for fixed bed reactors and 78 $m^3\ CH_4/m^3_{reactor\ vol.} \times d$ for a hollow fiber set-up.

Certain caution is necessary when comparing the cited values to the results achieved in the current study. It is obvious that in mass transfer limited systems reactor performance is highly dependent on the intensity of gas–liquid contact and to a lower extent on microbial activity. For example, vigorously stirred CSTRs easily outperform other process configurations, however, with the draw-

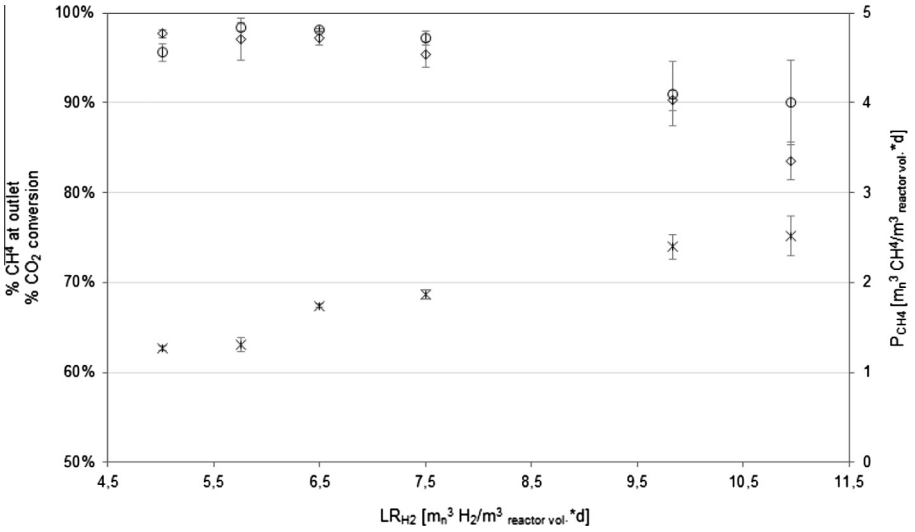

Fig. 4. Influence of increased H_2 loading rate LR_{H2} on methane production rate P_{CH4} (cross), final CH_4 concentration at gas outlet of trickle-bed reactor (open diamond) and CO_2 conversion (open circle). Error bars are given as standard deviation from mean values.

back of much higher energy demand. Moreover, most experiments were conducted with pure H_2/CO_2 mixtures while real biogas already contains high amounts of methane. Reduced partial pressures of the convertible gasses that influence their gas–liquid mass transfer have an adverse impact on process performance and efficiency [14].

The above-cited reviews do not include the studies of Burkhardt et al. [26] and Alitalo et al. [27], which were published later on and are more comparable to the investigated system set-up. The highest methane productivities achieved there are 1.49 $m^3_n/m^3_{reactor\ vol.} \times d$ and 6.35 $m^3/m^3_{reactor\ vol.} \times d$, respectively. In comparison, the experiments presented here exhibited a maximum methane productivity of 2.52 $m^3_n\ CH_4/m^3_{reactor\ vol.} \times d$. In terms of biogas throughput (CO_2 content ~40%) the maximum upgrading capacity achieved was 6.9 m^3_n biogas per m^3 reactor volume per day. However and as already shown, at maximum upgrading capacity the final methane content decreased to 84%. If higher methane concentrations (>96%) are required the biogas upgrading capacity is considerably lower: 3.7 m^3_n biogas/$m^3_{reactor\ vol.} \times d$. One other study reports on continuous biomethanation of test gas (H_2, CH_4 and CO_2 with the ratio 60:25:15) in an external reactor configuration using a hydrogenotrophic enrichment culture. Luo and Angelidaki [19] used an external stirred tank reactor and state a 95% methane content at a gas loading rate of 2.4 $m^3/m^3_{reactor\ vol.} \times d$. Even at fourfold loading rate and at optimized conditions, they achieved around 90% methane concentration.

3.2.4. Compliance of achieved gas quality with biomethane standards

Table 2 lists an overview of European national standards regarding the quality of biomethane for grid injection or as vehicle fuel.

In the current study gas composition was addressed only in terms of CH_4, CO_2 and H_2. At optimum conditions it was possible to achieve CH_4 concentrations of 98% and residual H_2 was less than 0.1%. This gas quality complies even with the tightest standards without the need for any additional CO_2 removal step. If less rigid standards, as e.g., established in the Netherlands, have to be fulfilled (>80%) loading rates can be almost doubled (10.95 versus 6.5 $m^3_n/m^3_{reactor\ vol.} \times d$). This makes the process even more attractive with respect to the required reactor volume for biogas upgrading. However, grid injection is not only linked to CH_4 content but also the Wobbe index. It is obvious that in a practical application additional techniques might be necessary with respect to removal of water vapor and unwanted gases such as H_2S or NH_3.

3.2.5. Considerations for practical process implementation

All in all maintenance of the system (after solving the technical problems) was quite simple and included only (i) flushing of trickle-bed to remove surplus biomass and (ii) change of liquid media. Even pH regulation was not necessary. Despite the long-term recirculation of the same media, no adverse effects on reactor performance, e.g., caused by trace contaminants in the biogas, were observed. Such it was demonstrated that long term operation under "real life" conditions does not elicit unforeseen problems. It is also worth noting that depletion of the nitrogen source was not observed and that ammonia levels measured in the liquid phase were relatively constant. It is presumed that sufficient ammonia was delivered with the impurities contained in biogas.

Start-up was also relatively easy and, despite the initial acidification, no major problems were encountered. Our experience suggests that, under optimized conditions, the start-up period is not more than 2–4 months until full conversion capacity is achieved. Once stable operation conditions were achieved the system turned out to be quite robust. After short-term shut downs (e.g., due to technical modifications) as well as after changes in H_2 loading rate full performance was re-established within 24 h.

In this context another advantage of the trickle-bed configuration should be emphasized. Trickle-bed reactors allow plug flow operation [34], i.e. that along with microbial conversion, a H_2 gradient occurs from into outlet. This allows high substrate conversion due to high H_2 partial pressure in the inlet zone to be combined with high final methane concentrations in a single reactor. Consequently, and in combination with the already underlined low power input and the advantages of plug flow operation, the design in form of a trickle-bed reactor is considered a straight forward approach.

According to general design criteria the typical reactor size of 500 kW_{el} biogas plant (substrate: 20% manure, 80% energy crops) is 3800 m^3 yielding around 1,900,000 m^3_n biogas/year [35], resulting in an average biogas production of around 1.37 m^3_n biogas per m^3 reactor volume and day. Employing the results obtained, a preliminary estimation of the necessary size of the trickle-bed reactor might be made. In case of an aspired methane content of 80%, the necessary volume is approximately 20% of the anaerobic digester volume. For a methane concentration >96% it is around 37% of the digester volume. The calculated sizes of the upgrading reactor system still seem to be high. However, with a view on to the discussion above there is much room for performance improvement, e.g., with respect to size of carrier material or operation temperature.

4. Conclusions

The current study provides concise data on upgrading capacity and corresponding gas quality obtained from a long term operated trickle-bed reactor system supplied with biogas produced on site. Our results show that long-term operation of an external trickle-bed bioreactor for methanation of biogas (produced on site) by an adapted microbial consortium is a feasible option for biogas upgrading. During the operational period of 240 days no adverse

Table 2
National quality standards for biomethane grid injection or for utilization as vehicle fuel. Extract from information collected by IEA Bioenergy, Task 37 [1].

Compound	Unit	France	Germany	Sweden	Switzerland		Austria	The Netherlands
		L gas H gas[a]	L gas H gas[a]		Lim. Inj.	Unlim. Inj.		
Wobbe index	MJ/m^3_n	42.48–46.8 48.24–56.52	37.8–46.8 46.1–56.5	–	–	–	47.7–56.5	43.46–44.41
Methane content	Vol-%	–	–	95–99	>50	>96	–	>80
Carbon dioxide	Vol-%	<2	<6	–	<6		⩽2[b]	–
Hydrogen	Vol-%	<6	⩽5	–	<5		⩽4[b]	<12
Relative humidity	ρ	–	–	–	<60%		–	–
Sulfur	mg/m^3_n	<100[c]	<75[d]	<30	<23	<30	⩽5	<45

[a] Injection of low (L) and high (H) quality gas.
[b] Mole percentage.
[c] Maximum permitted.
[d] Average content.

effects on reactor performance (e.g., caused by trace contaminants in the biogas) were observed. It was demonstrated that long-term operation under "real life" conditions does not elicit unforeseen problems. Although other reactor designs might provide higher volumetric methane productivities, the presented set-up enables simple and robust on-site biogas upgrading with excellent gas quality and very little effort for maintenance.

As shown, the gas quality obtained complies with strictest direct grid injection criteria. In combination with the H_2 generation from excess solar or wind energy, the investigated approach is an interesting concept to integrate biogas plants in a wider network for reliable renewable energy.

Author contributions

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Glossary

COD: chemical oxygen demand
FID: flame ionization detector
GC: gas chromatography
HPLC: high pressure liquid chromatography
NH_4—N: ammonium nitrogen
PDD: pulsed discharge ionization detector
TKN: Total Kjeldahl Nitrogen
VFA: volatile fatty acids