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Influence of operating pressure on the biological hydrogen methanation in trickle-bed reactors

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ABSTRACT

In order to investigate the influence of pressures up to 9 bar absolute on the productivity of trickle-bed reactors for biological methanation of hydrogen and carbon dioxide, experiments were carried out in a continuously operated experimental plant with three identical reactors. The pressure increase promises a longer residence time and improved mass transfer of H_2 due to higher gas partial pressures. The study covers effects of different pressures on important parameters like gas hourly space velocity, methane formation rate, conversion rates and product gas quality. The methane content of 64.13 ± 3.81 vol-% at 1.5 bar could be increased up to 86.51 ± 0.49 vol-% by raising the pressure to 9 bar. Methane formation rates of up to 4.28 ± 0.26 $m^3\,m^{-3}\,d^{-1}$ were achieved. Thus, pressure increase could significantly improve reactor performance.

1. Introduction

Power-to-gas technology allows the conversion of electrical energy to synthetic natural gas (SNG) via electrolytic hydrogen production and its subsequent conversion together with carbon dioxide to methane and water (Clegg and Mancarella, 2015). This process is beneficial in many ways. Firstly, a significant quantity of electrical energy, produced by fluctuating renewable energy sources including wind and solar power, is able to be managed and stored (Leonzio, 2017). Another advantage is the high specific energy density of SNG (1.200 kWh m^{-3} at 200 bar). A longer storage period from minutes to months is also possible because of the existing high storage capacities in the gas grid (Kirchbacher et al., 2017). Thus, the well established gas grid can be used as a powerfull energy storage and transportation system for electric energy.

The production of SNG with the power-to-gas technology is a two-step process. First, electrical energy is transformed into oxygen (O_2) and hydrogen (H_2) by electrolysis of water. In the second step, H_2 is converted with an external CO or CO_2 source to methane (CH_4) via methanation (Götz et al., 2016). The methanation reaction can take place either in catalytic or biological reactors. Catalytic processes usually operate at temperatures between 200 and 550 °C, pressures of up to 100 bar and have a very high methane formation rate (MFR), which describes the specific methane yield, calculated as a function of the reactor volume. In order to achieve the same output, significantly larger reactor volumes are necessary for a biological reactor (Barbarossa and Vanga, 1992; Bartholomew, 2001). A typical value for evaluating the performance of a reactor is the gas hourly space velocity (GHSV). It refers to the incoming gases and according to Götz et al. (2016) the efficiency at the same MFR of biological reactors with GHSV of up to 300 h^{-1} is significantly lower than that of catalytic ones with GHSVs up to 5000 h^{-1}.

On the other hand, the catalytic processes has some disadvantages compared to the biological pathway. For example, nickel catalysts which are commonly used in the thermochemical power-to-gas technology, demand high purity standards of the feed gases (Barbarossa and Vanga, 1992; Bartholomew, 2001). Sulphur and sulphur-containing components are known catalyst poisons for the nickel catalysts used in catalytic methanation (Bartholomew, 2001; Götz et al., 2016). For many applications, the feed gas must be cleaned before injection into the methanation reactor (sulphur content ≪ 1 ppm) (Götz et al., 2016). In contrast, the biological methanation process appears to be very robust, meaning that it will not be affected by impurities of the feed gases or infections with foreign organisms (Götz et al., 2016; Liew et al., 2016; Seifert et al., 2013). Even minor disruptive components such as sulphur and oxygen were found to have no effect on the biological methanation (Bartholomew, 2001; Götz et al., 2016). Seifert et al. (2013) investigated the conversion of real gases (synthesis gas, biogas and flue gas) by *methanothermobacter marburgensis*. Methane formation

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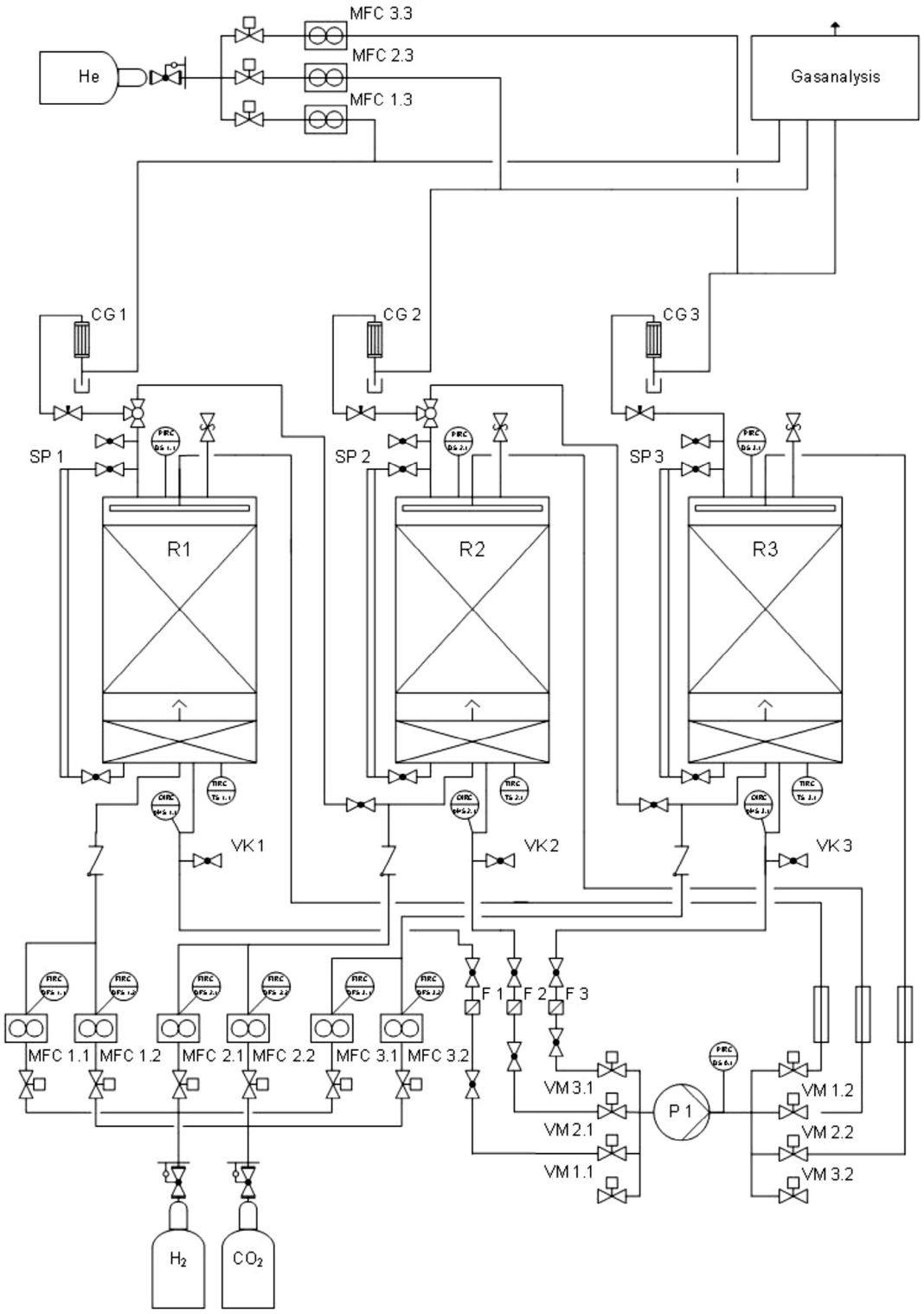

Fig. 1. Piping and instrument diagram of the test facility with the three trickle-bed reactors (R1–R3), the injection of the educt gases CO_2 and H_2 (MFC 1.1–MFC 3.2), the circulation unit of the nutrient solution (P 1, VM 1.1–VM 3.2), the gas analysis and the gas quantity measurement (MFC 1.3–MFC 3.3) with He as the tracer-gas.

was not affected by the presence of sulfur components or short chain hydrocarbons. Furthermore, some of these components can be partly removed by biological methanation (Bartholomew, 2001; Götz et al., 2016). For example, Strevett et al. (1995) investigated the reaction behavior of hydrogen-sulfite (H_2S) containing biogas and showed that even H_2S was also degraded.

Biological methanation is not only more robust against impurities than the catalytic reaction; it is also more flexible in relation to load changes. Immediate load changes from 100% to 0% were achieved as well as re-start after standstill times of up to 23 days. In contrast, a minimum load is often required for catalytic processes (Götz et al., 2016).

Besides these advantages, the biological methanation has the disadvantage, that large reactors are required due to the low volume related productivity (Götz et al., 2016). The literature indicates a limitation of the MFR due to slow transition of the feed-gases into the

liquid phase containing the microorganisms. Especially H_2 is limiting this essential mass transfer due its nearly 23 times lower solubility compared to CO_2 in water or similar liquids (Barik et al., 1988; Guiot and Cimpoia, 2012; Klasson et al., 1990; Wise et al., 1978). Therefore, the enhancement of the gas-liquid mass transfer is the key parameter to improve the volumetric productivity of the biological hydrogen methanation (BHM) (Seifert et al., 2014). Consequently, the biggest technical design challenge of a BHM reactor is to increase the microbial availability of the gaseous substrates H_2 and CO_2.

In continuously stirred tank reactors, mechanical agitation and stirring are the most common methods used to enhance the transfer of gases and other substances. However, the required amount of electrical energy is expensive (Alitalo et al., 2015). The achievable retention times of the gas in these reactors are remarkably short. After injecting the source gases into such reactors, gas bubbles are formed immediately, which rise to the surface within seconds. Due to the low surface area of these bubbles, the mass transfer and the metabolic rates are severely reduced (Burkhardt and Busch, 2013). Process optimization should therefore improve the gas-liquid mass transport and, at the same time, enable high concentrations of microorganisms (Klasson et al., 1992, 1991; Vega et al., 1990).

Burkhardt et al. (2015) used a trickle-bed reactor for biological methanation, where microorganisms are immobilized in a biofilm on the surface of a packed bed and sprinkled by a process liquid (Alitalo et al., 2015). Using gaseous substrates, trickle-bed reactors have significantly higher phase contact surfaces compared to fixed-bed reactors like anaerobic filters. In this way, mass transport is improved which increases the final productivity of the whole system (Burkhardt et al., 2015). Another advantage of this reactor type is, that nearly no additional mechanical power input is needed and the pressure drop is relatively low (Rachbauer et al., 2016). Trickle bed reactors also enable high conversion rates in biological methanation, thus leading to methane concentrations in the product gas of more than 98% even at higher hydrogen loading rates compared to other biological methanation systems (Burkhardt et al., 2015).

In principle, the mass transfer from the gaseous to the liquid phase can also be enhanced by elevating the operating pressure of the reactor (Klasson et al., 1992, 1991; Vega et al., 1990). High pressure is not expected to influence methanation. Chen et al. (2014) and Merkle et al. (2017) investigated the two-stage anaerobic digestion process in a continuous experimental plant with operating pressures of up to 9 and 50 bar, respectively. Lindeboom et al. (2011) and Merkle et al. (2017) examined the influence of operating pressures up to 100 bar on the biological conversion efficiency in batch systems. Even at these high pressures, no biological process disturbances is reported.

The aim of this study is to investigate the influence of high operating pressures on the productivity of trickle-bed reactors used for biological power-to-gas technology. For this purpose, a continuously operated and completely automated test facility was developed and built up at the University of Hohenheim. In test series, the influence of the operating pressure on gas quality, methane formation rate and retention time was explored.

2. Methods

2.1. Experimental setup

The experimental-plant was realized with three identical trickle-bed reactors, which can be operated up to a pressure of 10 bar absolute. A single reactor consisted of a 1 m long stainless steel pipe with an inner diameter of 0.15 m and a volume of 22.5 L. The structure of the plant is shown as a piping and instrumentation diagram in Fig. 1.

The reaction space of each reactor was equipped with a fixed bed and a trickle-bed to immobilize the microorganisms. The trickle-bed was in the gas-filled compartment of the reactor and had a volume of 13 L and a hight of 0.74 m. The 1.5 L fixed-bed conduced the microorganisms in the sump of the reactor in the liquid phase as a settling area. The idea of this additional fixed-bed beneath the trickle-bed was to ensure that the gaseous reactants dissolved in the circulated process liquid were converted rapidly and almost completely, too. The packing elements used in this experiment are HX09 and are from Christian Stöhr GmbH & Co. KG, Germany. They are made of HDPE recyclat, and have a diameter of 9 mm, a length of 7 mm and a surface area of 861 $m^2\,m^{-3}$. Thus, a surface of 11.193 m^2 and 1.296 m^2 is available in the trickle-bed and the fixed-bed of each lab-scale reactor, respectively.

The reactors were sealed with blank flanges, to which the reactor-peripherals as well as the sensors were attached. The operating pressure of each reactor was measured using the 261AS absolute pressure transmitter from ABB Ltd., Switzerland. Due to the use of highly volatile and corrosive hydrogen, the pressure sensors were equipped with gold-coated membranes. Temperature and pH-value were recorded using Easytemp TMR31 compact thermometers and Memosens CPS16D combined pH/redox electrodes from Endress + Hauser Messtechnik GmbH + Co.KG., Germany. Since the pH/redox combined electrodes must be removed for periodic calibration, they were installed in the reactor-periphery near VK 1, VK 2 and VK 3 in Fig. 1.

In addition to CO_2 and H_2, the methanogenetic microorganisms need a wide variety of nutrients to achieve high metabolic rates (Vintiloiu et al., 2013). These nutrients were presented with the process liquid, which was gained from the hydrolysate produced with the first stage (hydrolysis-acidification step) of a two-stage biogas process operated with maize silage (Merkle et al., 2017). It contained the necessary nutrients and trace elements that the microorganisms needed. Remaining organic acids and alcohols in the process liquid had been converted quite fast in the reactor and are not responsible for the high quantity of methane produced. Nevertheless, the gas and methane yield resulting from the degradation of the acids and alcohols was calculated and the product-gas is adjusted accordingly to Lemmer and Krümpel (2017).

In order to improve the mass transfer of the gases, the nutrient solution for the microorganisms was sprinkled over the fixed bed in countercurrent with the gases. As the solution passed through the fixed bed, the nutrients were absorbed by the attached microorganisms and accumulated in the reaction chamber in the sump. The sighting tubes SP 1, SP 2 and SP 3 (Fig. 1) outside the reactor were used to control the filling level inside the reaction chamber. Liquid filters (F 1, F 2, F 3) with a pore size of 25 µm protected the central gear pump P 1 against particles. Because a central pump (P 1) was used for circulation in all three reactors, it was possible to switch between various closed circuits by using magnetic valves VM 1.1–VM 3.2 (Bürkert Type 6240 – Servo-assisted 2/2 way piston valve). The circuits were changed every 60 s, resulting in an overall “trickling time” of 20 min per hour and reactor, which corresponds with a recirculation flow of 50 $L\,h^{-1}$ to a liquid quantity of 16.7 $L\,h^{-1}$.

Water is a by-product of the methanation of hydrogen and carbon dioxide and dilutes the nutrient solution. For this reason, half of the nutrient solution was removed and replaced with a fresh one before starting a new run.

For a constant and adjustable temperature level, the reactors were installed in individual heated water baths, which were insulated with 40 mm PU foam mats. In order to ensure a constant temperature distribution, they were heated parallel with a quad distributing adapter and an SE-26 Heating Circulator from Julabo GmbH.

The process gases were provided from gas bottles, which were obtained from the Westfalen AG. H_2 and CO_2 were used in quality 3.0. With mass flow controller (MFC) MFC 1.1–MFC 3.2 of the type 8742 from Bürkert GmbH & Co. KG, the gases could be injected into the reactors at volumes from 1.2 to 60 $L\,h^{-1}$ (H_2) and 0.3 to 15 $L\,h^{-1}$ (CO_2). The product gases were released from the reactors by a mechanical pressure control valve. Subsequently, the product gases flowed through the gas coolers CG 1, CG 2 and CG 3 for condensate removal.

2.2. Experimental procedure

Prior to the start of the experimental procedure, the reactors were filled with already overgrown packing elements taken from a working methane reactor of a two-stage anaerobic fermentation system described by Merkle et al. (2017). After a start-up period and preliminary testing phase of six months, a steady state was reached.

An increase in the operating pressure promises to improve the mass transfer and increase the availability of the reactant gases. Therefore, various pressure stages were tested at 9, 5 and 1.5 bar absolute. The pressure levels were set parallel in each reactor. For a clear representation, the results of the reactors were calculated as an arithmetic average.

The flow rates of the mass flow controllers were adjusted to a H_2/CO_2 ratio of 4, resulting in a volume flow rate of 10 L h^{-1} (H_2) and 2.5 L h^{-1} (CO_2). The operating temperature was set at 40 °C. The flow rates were adjusted at a high level in order to avoid a complete conversion of the feed gases. This was done to emphasize the differences of the investigated pressure levels.

The examined pressure levels were tested simultaneously in the three reactors. Each pressure level was kept stable for a period of 380–388 h each. During the tests, the pH values, temperature, pressure and redox potential as well as the amount of educt gases were recorded. The product gas quality was measured every 30 min by a gas chromatograph 3000l-GC from Inficon GmbH, Germany.

During the experimental phases, the process liquid was sampled directly at VK 1, VK 2 and VK 3 (Fig. 1) approximately every 80 h in order to measure the content of volatile fatty acids, the chemical oxygen demand, conductivity and salinity as well as the ammonium concentration from the untreated sample.

2.3. Analytical

According to Krümpel et al. (2016) the quality of the product-gases was analyzed by an Inficon 3000l-GC with two columns. H_2, N_2, O_2 and CH_4 were analyzed by Channel A, and the carrier gas was Argon. Channel B, with the carrier gas Helium, was used for the analysis of CO_2 and H_2S. Both channels were connected to an individual TCD-sensor. Injector temperature and sample inlet for both channels were set to 60 °C. To purge the line from the sample point to the GC, the internal pump operated for 45 s at approximately 15–30 ml/min.

To determine the amount of gas produced, a defined amount of Helium tracer gas (quality 5.0) was added by mass flow controllers 8742 from Bürkert GmbH & Co. KG MFC 1.3–MFC 3.3 (Fig. 1) to the gas stream after the reactor and the gas cooler. In the subsequent analysis by gas chromatography, the gas composition was determined. Since the proportions of the gases and the amount of tracer gas are known, the total amount of produced gas can be calculated.

The analysis of the volatile fatty acids including acetic acid, propionic acid, n- and iso-valeric acid, n- and iso-butyric acid and caproic acid of the liquid was carried out in a CP-3800 gas chromatograph from Varian Medical Systems.

The chemical oxygen demand (COD) was measured using the Hach Lange cuvette test (LCK014). Because the test has different measuring ranges (LCK 014: 1000–10,000 mg/L O2), the samples were diluted according to the measuring range. Finally, the COD value is determined after cooling in the photometer from Dr. Lange (DR 3900).

The conductivity and salinity were determined with an EC300 from VWR International GmbH by dipping the conductivity tube into the sample.

2.4. Calculations

According to Götz et al. (2016), important parameters for evaluating the reactor efficiency are the methane formation rate (MFR, Eq. (1)), the gas hourly space velocity (GHSV (Eq. (2)) and the methane content Y_{CH4} in the product gas.

$$MFR = \frac{F_{V,CH4,out} - F_{V,CH4,in}}{V_R}\left(\frac{m^3}{m^3 d}\right) \quad (1)$$

With the MFR, the specific methane yields can be calculated as a function of the reactor volume. $F_{V,\ CH4,\ out}$ and $F_{V,\ CH4,\ in}$ is the volumetric flow rate in and out of the reactor. The reactor volume V_R is the volume of the trickle-bed plus the fixed-bed and amounts to 14.5 L.

The GHSV is a typical value for evaluating the performance of a catalyst or a reactor and refers to the incoming gases.

$$GHSV = \frac{F_{V,G,in}}{V_R}(h^{-1}) \quad (2)$$

$F_{V,G,in}$ of the GHSV is the volumetric flow rate at STP of the feed gas without any inert gases.

Furthermore, the conversion rates of H_2 and CO_2 are calculated. The conversion X_i of an educt gas is defined in Eq. (3). $F_{n,\ i,\ in}$ is the incoming, and $F_{n,i,out}$ the outcoming H_2 or CO_2 in L h^{-1}.

$$X_i = \frac{F_{n,i,in} - F_{n,i,out}}{F_{n,i,in}} * 100(\%) \quad (3)$$

Due to the different pressure stages and the associated increase in the gas concentration, the retention time of the reactant gases in the reactors also changes. The retention time (RT) is calculated as a function of the reactor volume (V_R) and the volumetric flow of the incoming gases $F_{V,\ G,\ in}$.

$$RT = \frac{V_R}{F_{V,G,in}}(h) \quad (4)$$

According to Merkle et al. (2017), who also examined the effects of different operating pressures, the data was statistically analyzed using the Kruskal Wallis Test and subsequently Tukey's Test ($p < 0.05$). The statistical software "R Studio" was used for all calculations.

3. Results and discussion

3.1. Operating parameters

The operating parameters temperature, pressure and pH of the test series are shown in Fig. 2. Aggregating the data of the three independent reactors, the arithmetic average is calculated for each operating pressure. It is apparent, that the target operating parameters regarding pressure and temperature had been achieved with high accuracy and constancy. Only slight temperature differences from Reactor 1 with 40.38 ± 0.15–40.56 ± 0.29 °C to Reactor 3 with 41.02 ± 0.34–41.09 ± 0.15 °C could be observed. The measured pressure did not differ essentially from the target values. At the target level 1.5 bar, pressures from 1.43 ± 0.03 to 1.58 ± 0.02 bar, at pressure level 5 bar, values from 5.09 ± 0.04 to 5.16 ± 0.02 bar and at pressure level 9 bar, values from 9.27 ± 0.01 to 9.29 ± 0.02 bar were recorded.

Deviations of up to 15% from the target value could be detected in the flow rates of H_2 − and the CO_2 mass flow controller (Table 1) due to inaccuracies of the instruments. Since the deviations in the CO_2 mass flow controller are significantly larger than in the case of the H_2 mass flow controller, no stoichiometric gas ratios could be set. By that, CO_2 was introduced slightly overstoichiometric in each pressure phase into all reactors, but with a constant ratio over the test phases.

Burkhardt et al. (2015) introduced an overstoichiometric amount of CO_2 into the trickle-bed reactors, too, with a ratio of 1:3.76 of CO_2 to H_2. Similarly, Rachbauer et al., (2016) used different ratios of 1:3.67–1:4.15. The influence of these slight shifts in the feed gas ratios will be subject to further investigations.

The increased operating pressures led to a notable drop of the pH-value in the process liquid from 6.98 ± 0.05 at 1.5 bar to 6.34 ± 0.03 at 9 bar, due to the augmented formation of carbonic acid. The low pH

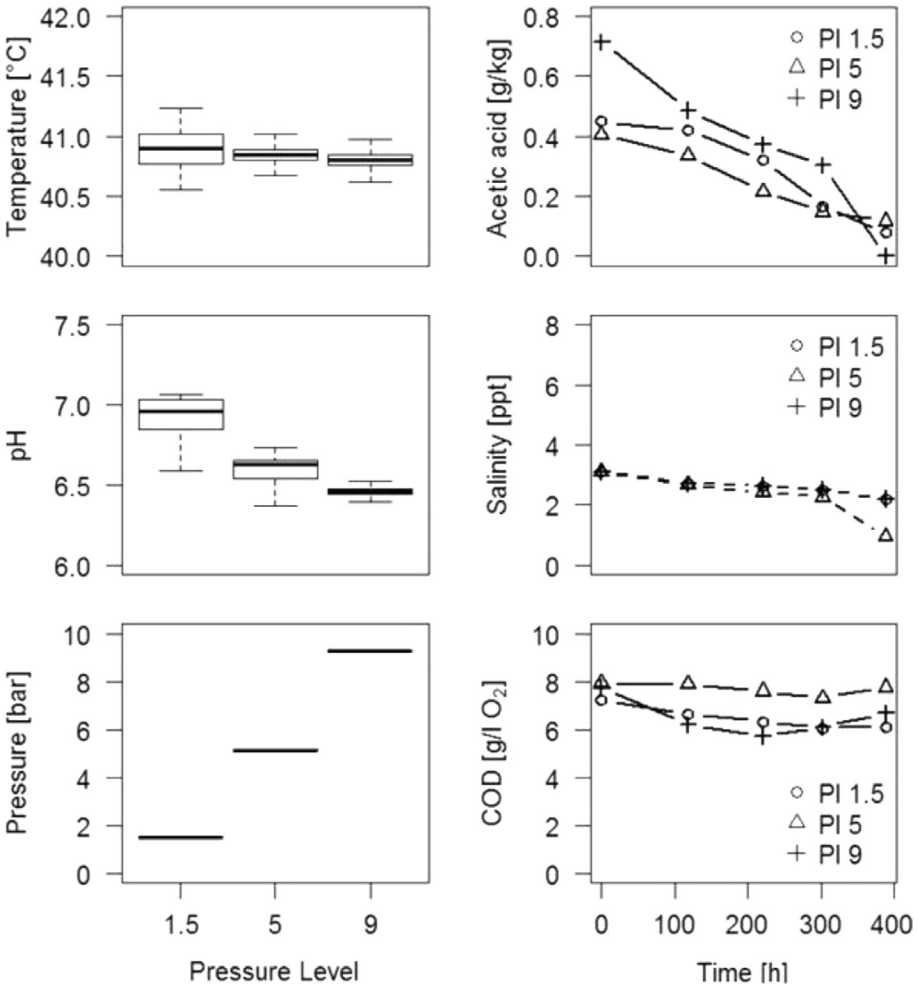

Fig. 2. Operating temperature, pH and pressure parameters as well as the content of the acetic acid, COD and salinity as analysis of the nutrient solution over the experimental period depending on the different pressure levels (Pl 1.5, Pl 5, Pl 9). The results of the three reactors were calculated as an arithmetic average.

Table 1
Overview of the most important operating parameters as well as the set flow rates and gas ratios. The results of the three reactors were calculated as an arithmetic average. The significant differences among the pressure levels are marked with different alphabets ($p < 0.05$, Tukey's test).

Pressure Level	1.5	5	9
Flow H_2 [L h^{-1}]	10.98	10.87	10.92
Flow CO_2 [L h^{-1}]	2.88	2.91	2.82
CO_2:H_2	1:3.81	1:3.74	1:3.87
MFR [m^3 CH_4 m^3 d^{-1}]	4.09 ± 0.10[a]	4.28 ± 0.26[a]	4.20 ± 0.45[a]
GHSV [h^{-1}]	0.86 ± 0.04[a]	0.86 ± 0.01[a]	0.86 ± 0.01[a]
Retention time [h]	1.62	5.40	9.79
Conversion H_2 [%]	93.08 ± 2.64[a]	96.97 ± 1.15[ab]	98.02 ± 1.16[b]
Conversion CO_2 [%]	85.95 ± 1.23[a]	88.93 ± 0.37[a]	90.03 ± 0.42[a]

has no observable essential influence on the performance of the methanation process. Merkle et al. (2017) also measured low pH values up to 6.53 in a stable high pressure anaerobic digestion process. In Chen et al. (2014), the pH dropped to 6.4 at a pressure of 10 bar, using a pressurized anaerobic filter. Moreover, an improvement in conversion and gas quality at this pressure and pH level is achieved.

3.2. Analysis of the process liquid

The results of the analysis of the process liquid are also shown in Fig. 2. For the purpose of improved clarity, only the acetic acid is represented, which constituted the largest share (76% and 91% at a pressure level of 9 bar and 5 bar, respectively) of the acids. At the beginning of each experimental phase, the process liquid was partially replaced by the hydrolysate, which contains 0.36 ± 0.05–0.52 ± 0.05 g kg^{-1} organic acids. It is apparent, that these acids were permanently degraded over the experimental periods. Acid accumulation was never observed at any time, thus indicating a high biological process stability. According to the acid degradation, a slight increase in pH was observed during the experiments. There was no observable influence in pressure since the liquid does not compress like the gases in the reactor.

COD and salinity parameters were investigated to study the stability of the process liquid over the experimental period. Nearly stable values were observed for COD and only slight changes in salinity (3.2 ppt at the beginning of the test at 9 bar to 0.7 ppt at the end of the test at 1.5 bar) were recorded. The salinity decreased marginal as a result of water production during BHM, thus diluting the process liquid.

In Chen et al. (2008), optimal ranges of salinity for methanogenic microorganisms of 0.35 ppt are mentioned, slight inhibitions has been detected at 3.5 ppt. The presented investigation indicted that the performance was not affected by an decrease in salinity, so that process inhibitions due to the continuous dilution of the process liquid can be excluded.

3.3. Conversion rates and gas quality

The conversion of carbon dioxide and hydrogen improved with raising the operating pressure in the conducted experiments, as shown in Table 1. The conversion of CO_2 increased from 85.95 ± 1.23 to 90.03 ± 0.42% with an increasing pressure level from 1.5 to 9 bar. However, these differences are not statistically significant. Overall, the conversion rates of CO_2 are lower than H_2. The reason for this could be

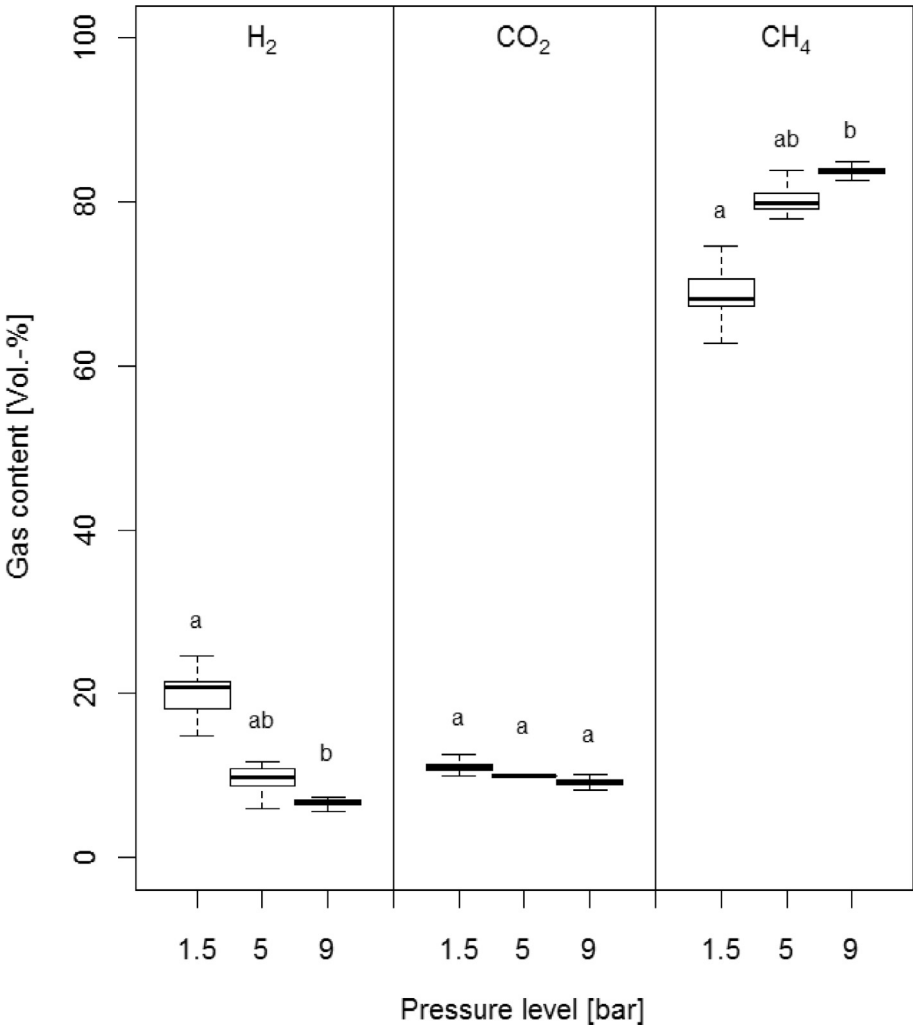

Fig. 3. The gas quality of the product gas depending on the different pressure levels. The significant differences among the pressure levels are marked with different alphabets ($p < 0.05$, Tukey's test).

the overstoichiometric ratio of CO_2. The improvement of the conversion rates of CO_2 with increasing pressure can also be due to the improved availability of H_2.

The gas composition and the conversion rates of Reactor 1 are worth being emphasized separately. Here, the highest methane concentrations and the highest conversion were achieved throughout all pressure levels. This overperformance is the main reason for the quite high standard deviation of the aggregated results, leading to statistically significant differences only between pressure level 1 and 9 for the content of H_2 and CH_4 in the product gas (Fig. 3). In addition, the differences in CO_2 conversion would be statistically significant without reactor 1. Reactor 1 has a performance up to 18% higher than Reactor 2 and 3 regarding the gas quality over all three pressure levels in the test period. However, the improvement of the gas quality as a result of the increased operating pressure was observed in all three reactors and pressure levels. Although it was not possible to obtain quantitative evidence, the overperformance of the first reactor may have resulted from an improved growth of the microorganisms on the packing material of Reactor 1, thus leading to higher concentrations of microorganisms. For a more detailed investigation, the reactors will be opened at the end of all experiments.

The influence of the operating pressure is reflected in the product gas composition, too, as shown in Fig. 3. At a pressure of 1.5 bar, the average hydrogen content was 20.05 ± 6.78 vol-%, compared to a minimum of 6.71 ± 2.29 vol-% at the highest pressure 9.28 bar. Since CO_2 was sub-stoichiometrically injected into the reactors, high conversion rates were achieved, so that the content of CO_2 in the product gas did not vary significantly between the different experimental phases.

According to the decreased content of H_2 and CO_2 and the higher conversion rates with increased pressure, the content of methane in the product gas rises with increasing operating pressure. While the methane content at the pressure level 1.5 bar only amounted to 64.13 ± 3.81 vol-%, the mean values reached 86.51 ± 0.49 vol-% at the pressure level of 9 bar.

As shown in Burkhardt et al. (2015) and Rachbauer et al. (2016), even higher methane contents in the product gas of up to 98% can be reached with trickle-bed reactors. These values were confirmed in preliminary tests with the described reactors of this study. In order to emphasize the influence of the operating pressure, the experiments were conducted at high flow rates to ensure incomplete conversion processes throughout all experimental phases, thus leading to maximum methane contents of up to 86.51 ± 0.49 vol-% in the product gas.

In general, higher methane concentrations are reported for trickle-bed reactors compared to other reactor configurations. Alitalo et al. (2015) could reach in a fixed-bed system methane contents in the product gas of > 90 vol-%. In CSTR reactors, maximum CH_4 concentrations of 85 vol-% were achieved (Seifert et al., 2014).

3.4. Performance parameters and retention time

According to the constant input flow rates, the average methane formation rates (MFR) only varied between 4.09 ± 0.10 and

4.29 ± 0.26 m^3 CH_4 m^{-3} d^{-1}, depending on the process phase, although significant differences in the conversion rates were detected (Table 1). From pressure levels of 1.5–5, the MFR changes from 4.09 ± 0.10 to 4.28 ± 0.26 m^3 CH_4 m^{-3} d^{-1}. But in pressure level 9, the MFR changes to 4.20 ± 0.45 m^3 CH_4 m^{-3} d^{-1}, thus indicating that the improved conversion rates did not lead to a significant change of the MFR. A reason for this could be the reduction in the volume by a factor of 5 at the process of biological methanation, resulting in very similar product gas amounts throughout the experiment. Burkhardt et al. (2015) achieved MFRs of 1.49 m^3 CH_4 m^{-3} d^{-1} with a similar experimental setup. However, in a pressureless state and with a much higher methane content of up to 98 vol-%.

Compared to other studies, the investigated set-up was run at quite low MFRs. Alitalo et al. (2015) described MFRs of up to 6.35 m^3 CH_4 m^{-3} d^{-1} in fixed bed reactors, but with retention times of 144 h. In biological methanation, the highest MFRs are recorded for CSTR-systems. Seifert et al. (2014) reached 137 m^3 CH_4 m^{-3} d^{-1} with a methane content of 85 vol-% at a process temperature of 65 °C and stirrer speeds of 1500 rounds per minute.

In contrast to the MFR, the GHSV is related to the amount of gases, injected into the reactor. Since the flow rates were almost identical over the different pressure levels, the GHSV was nearly identical for all pressure levels with 0.86 h^{-1} showing no statistical differences.

During the microbial conversion of CO_2 and H_2 to CH_4 and H_2O, the volume of the feed-gases is nearly five times higher than the volume of the product gases. However, calculating the retention time of the gaseous substrates in the digesters according to Eq. (4), where the reduced volume was neglected, results in an underestimation of the real retention time of the gases in the reactor. In contrast to the GHSV, the retention time of the gases in the reactor increased.

As shown in Table 1, the retention time increased proportionately with the operating pressure from 1.62 h (1.5 bar) to 9.79 h (9 bar). With regards to the increase in gas quality, the question arises whether the improved conversion rate is caused by the enlarged retention time of the gases in the reactor or by the augmented mass transfer due to the higher operating pressure. This interesting topic will be subject to further investigations.

Overall, the experiments of this study show, that the biological power-to-gas technology is a stable and reliable process, using the proofed reactor concept. These findings are in line with the reports of other studies (Burkhardt et al., 2015; Rachbauer et al., 2016). Based on the results presented and the necessity for feeding the compressed gas into the gas grid, process efficiency can be improved by elevating operating pressures.

4. Conclusion and outlook

The present study shows that by raising operating pressures, higher CO_2 and H_2 conversion rates and higher methane contents in the biological methanation by means of trickle-bed reactors can be achieved. The tests of three different pressure stages 1.5, 5 and 9 bar showed an improvement in the gas quality. The methane content of at least 64.13 ± 3.81 vol-% at a pressure level of 1.5 bar could be increased by up to 86.51 ± 0.49 vol-% at 9 bar with MFR in the range of 4.09 ± 0.10–4.28 ± 0.26 m^3 CH_4 m^{-3} d^{-1}. However, it should be considered that with increasing pressure, higher safety precautions are required, especially regarding full scale applications. Additionally it should be clarified, whether a pressure increase for gas quality enhancement justifies the necessary technical and economical effort.

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