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Article

Optimization of Thermodynamic Parameters of the Biological Hydrogen Methanation in a Trickle-Bed Reactor for the Conditioning of Biogas to Biomethane

Elena Holl [1,*], Anastasia Oskina [2], Urs Baier [3] and Andreas Lemmer [4]

[1] University of Hohenheim, State Institute of Agricultural Engineering and Bioenergy; elena.holl@uni-hohenheim.de
[2] University of Hohenheim, State Institute of Agricultural Engineering and Bioenergy; anastasia.oskina@uni-hohenheim.de
[3] ZHAW Zurich University of Applied Sciences, School of Life Sciences and Facility Management, Specialist Department for Biocatalysis and Process Technology; u.baier@bluewin.ch
[4] University of Hohenheim, State Institute of Agricultural Engineering and Bioenergy; andreas.lemmer@uni-hohenheim.de
* Correspondence: elena.holl@uni-hohenheim.de

Abstract: The increased demand for resources and energy that is developing with rising global consumption represents a key challenge for our generation. Biogas production can contribute to sustainable energy production and closing nutrient cycles using organic residues or as part of a utilization cascade in the case of energy crops. Compared to hydrogen (H_2), biogas with a high methane (CH_4) content can be fed into the gas grid without restrictions. For this purpose, the CH_4 content of the biogas must be increased from 52 to 60 % after anaerobic digestion to more than 96 %. In this study, biological hydrogen methanation (BHM) in trickling-bed reactors (TBR) is used to upgrade biogas. Design of experiments (DoE) is used to determine the optimal process parameters. The performance of the reactors is stable under all given conditions, reaching a "low" gas grid quality of over 90 %. The highest CH_4 content of 95.626 ± 0.563 % is achieved at 55 °C and 4 bar, with a methane formation rate (MFR) of 5.111 ± 0.167 $m^3/(m^3 \cdot d)$. The process performance is highly dependent on the H_2:CO_2 ratio in the educts, which should be as close as possible to the stochiometric ratio of 4. In conclusion, BHM is a viable approach to upgrade biogas to biomethane quality and can contribute to a sustainable energy grid.

Keywords: Biological methanation; trickle-bed reactor; biogas upgrading; high pressure; biomethane; optimization of thermodynamic parameters

1. Introduction

Biogas is a natural secondary energy source produced by the microbial degradation of biomass under anaerobic conditions, the combustion of which does not lead to an accumulation of CO_2 in the atmosphere. Biogas consists of 50 - 75 % CH_4 and about 25 - 50 % CO_2, less than 10 % water vapor, and trace amounts of H_2 (< 1 %) and hydrogen sulfide (< 3 %) [1], which corresponds to a calorific value of the gas at standard temperature and pressure of 17.95 to 25.12 MJ/m^3 [2]. Currently, desulphurized and dried biogas is mostly used as a fuel in combined heat and power units (CHP) in Germany to generate electrical and thermal energy [3]. The role of biogas in power generation and distribution can be significantly expanded if the quality of biogas is brought up to the standards of natural gas fed into to the gas grid. The natural gas grid in Germany is divided into low-calorific gas (L-gas) with an energy content of 28.8 to 32.4 MJ/m^3 and high calorific gas (H-gas) with an energy content of 36.0 – 43.2 MJ/m^3. To be fed into the natural gas grid, the calorific value of the biogas must first be raised – which is usually done by removing CO_2. At a CH_4 content of 95% - the threshold value for feeding into the H-gas grid biogas reaches an energy content of 34.1 MJ/m^3 [4]. In a second step, the calorific value of this biomethane has to be adjusted to the calorific value of the natural gas in the gas pipeline, usually by adding propane or butane. There are already several CO_2 removal technologies on the market: amine scrubbing, pressure swing absorption, water scrubbing, organic physical scrubbing, cryogenic distillation, and membrane separation [5]. Another promising approach for biomethane production is biological hydrogen methanation (BHM). Following the concept of power-to-gas (PtG), the excess electrical energy from renewable energy sources is used in an electrolyzer that produces "green" H_2. It is then fed into a trickling-bed reactor (TBR) together with CO_2, which is an integral part of a biogas mixture. In the TBR, hydrogenotrophic microorganisms immobilized on plastic carrier bodies will convert both gases into CH_4. Previously conducted studies on CO_2-methanation have shown the influence of operating parameters such as pressure, temperature, and drip interval on process performance in TBRs [6–10]. Researchers found, that when the pressure was increased from 1.5 to 9 bar, the CH_4 content increased simultaneously at mesophilic temperatures of 41 °C [6]. The effect of temperature was investigated by [7] using the same experimental setup. It showed that the conversion rates of H_2 and CO_2 increase, leading to an increasing CH_4 content at increasing temperatures from 40 to 55 °C. The analysis of [10] and [9] achieved CH_4 concentrations above 98 % at ambient pressure and argued the H_2:CO_2 ratio, pH control, and sufficient nutrient supply as limiting factors. At the same time, it was shown in [9] that CH_4 concentrations above 90 % can be achieved in TBR with established microbial culture under thermophilic conditions (55 °C) and ambient pressure at H_2 gas feed rate above 23.2 $m^3/(m^3 \cdot d)$.

Since previous studies focused mainly on CO_2-methanation, which was later referred to as mono-methanation, this study analyzes the co-methanation of biogas and H_2 in a TBR. The objective of the study was to verify the possibility of upgrading biogas with 55 % CH_4 to biomethane with 95 % CH_4 with BHM, and to optimize the thermodynamic parameters of the operating process by applying a design of experiments (DoE).

2. Materials and Methods

2.1. Experimental Setup

The experiments were carried out in the laboratory of the State Institute of Agricultural Engineering and Bioenergy at the University of Hohenheim. The methanation plant was described in detail in [6] and a simplified process schematic of the experimental plant is shown in Figure 1. The plant consists of identical TBRs sharing a single circulation pump that moves the process liquid from the bottom of the reactor to the sprayer at the top. Instead of the mono-methanation of CO_2 and H_2, co-methanation of a standard biogas mixture consisting of 45 % CO_2 and 55 % CH_4 together with H_2 was used (Quality 3.0, Westfalen AG, Germany). The incoming gases were fed to the reactors via mass flow controllers (MFC Type 8742, Buerkert, France) at flow rates of 11.25 L/h for H_2 and 6.25 L/h for the biogas, which met the stoichiometric ratio of 4:1 according to the Sabatier reaction. The flow rates of the educts were adjusted so that the total hourly flow rate of the reacting gases H_2 (11.25 L/h) and CO_2 (2.81 L/h) is comparable to the total volume of the reactors (14.5 L), which consist of 13 L of gaseous main body and 1.5 L of liquid sump together with the periphery. In this case, the gas production at varying operating parameters becomes clear, since the measurement of the product gas quality was performed once per hour and per reactor. During the experiments, the main thermodynamic parameters, namely temperature and pressure, were varied in a certain range to find the optimal operating point.

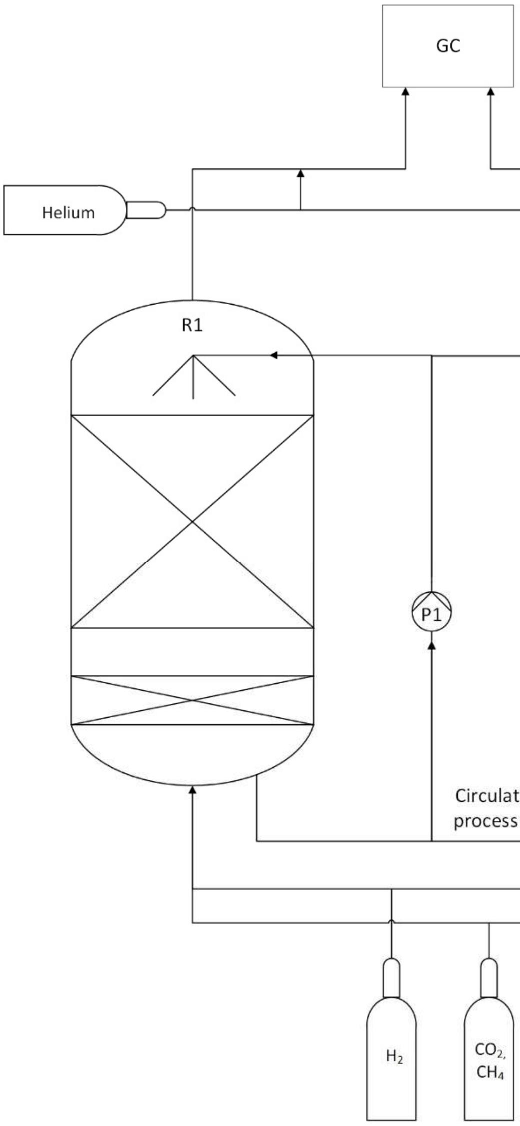

Figure 1. Simplified process scheme of the experimental plant.

As a feed liquid, the effluent from the methanogenic stage of a two-stage anaerobic digestion (AD) plant, as described in [11], was introduced into the periphery of the experimental plant to regularly trickle onto the plastic supports with immobilized biofilm inside the methanation column. According to [12], the composition of nutrients required for the BHM is similar to that required for the AD process, allowing liquid transfer between the two plants. Beyond the microbial nutrient removal, the process liquid was constantly diluted by water formation in accordance with the Sabatier reaction. Thus, at the beginning of each experimental phase, the liquid collected in the sump (about 1.3 L) – the lowest point of the experimental plant – was replaced by the fresh feed liquid containing planktonic microorganisms, nutrients and trace elements [13]. Trickling of the carrier bodies occurred once per hour for three minutes.

The product gases leaving the reactors were cooled to remove water vapor. In addition, helium gas (Quality 3.0, Westfalen AG, Germany) was supplied as a tracer gas at a flow rate of 1 L/h and the percentage of each gas component in the gas mixture was measured using a gas chromatograph (micro-GC FUSION Gas Analyzer (Inficon, USA)). Measurements were performed continuously, once per hour for each reactor, resulting in 24 gas quality measurements per day per reactor. Based on the measured content of the tracer gas supplied at a known flow rate, it was possible to calculate the flow rates of all gas components (H_2, CO_2, CH_4, O_2, N_2, H_2S) potentially present in the produced gas mixture.

2.2. Design of Experiment

A DoE was prepared for the study of co-methanation of biogas and H_2 to optimize the thermodynamic parameters using JMP Pro software (SAS Institute, USA). Since [7] recommended experiments at higher temperatures, a temperature in the range of 50 to 60 °C was set, as first predictor variable. Second, a pressure in the range of 2 to 9 bar was chosen. The maximum values are limited by the reactor design. Therefore, the optimal production point can be estimated using a second-order response surface model. Since methanogens are slow to adapt to a changing temperature [14,15], the parameter was set as a "hard-to-change factor", resulting in a split-plot design, that can be seen in the temperature blocks in **Error! Reference source not found.**. The different series of experiments are abbreviated as T and the corresponding temperature and P with the corresponding pressure. The minimum number of runs for the given specifications in the custom design is six. However, to minimize the probability of error, the number of runs was set to the number of possible combinations: $3^2 = 9$. I-optimality was chosen as the optimality criterion, which aims to minimize the variance of the predictions over the relevant range of predictor variables, offering significant advantages in terms of improved prediction compared to the commonly used D-optimality criterion [16]. The odd pressure in the sixth run is dictated by the experimental design, which attempts to minimize prediction errors.

Table 1. This is a table. Tables should be placed in the main text near to the first time they are cited.

Run ID	Temperature [°C]	Pressure [bar]
T50P9	50	9
T50P2	50	2
T50P5.5	50	5.5
T55P5.5	55	5.5
T55P9	55	9
T55P4.275	55	4.275
T60P2	60	2
T60P9	60	9
T60P5.5	60	5.5

The duration of each experimental phase was set at 144 hours (six complete days), including an adjustment period of 48 hours. After 48 hours, pH and CH_4 production were stabilized, and the above measurements were considered for further analysis.

2.3 Analytical

During each experimental phase, samples of the process liquid were taken three times and further analyzed in the local laboratory of the state institute. The samples were analyzed for volatile fatty acids (VFA) content (acetic acid, n-butyric acid, iso-butyric acid, propionic acid, n-valeric acid, iso-valeric acid, and caproic acid) in the analytical laboratory to exclude or confirm the activity of acetoclastic microorganisms in the methanation process. At the same time, the measurement of chemical oxygen demand (COD) was carried out to determine the percentage of organic degradable material. In practice, the COD of the BHM effluent should ideally be as low as possible, so that it can be discharged into nature without any problems. Total carbon (TC) and total organic carbon (TOC) analysis of the process fluid was performed to balance the amount of carbon involved in the BHM reaction.

VFA concentration was measured using gas chromatography (GC 2100Plus, Shimadzu with an FID-detector and a capillary column WCOT Fused Silica, Varian, Palo Alto USA). COD content was measured using a sensor array photometer (Hach Lange Type LASA 20). A TOC/TNb analyzer (Analytik Jena AG Type multi N/C®, Jena, Germany) was used to measure TC and TOC.

The pH was measured separately in the sump of each reactor using combined pH and Redox sensors (Endress and Hauser AG, Reinach, Switzerland). Pressure in each reactor was measured using an absolute pressure transmitter (ABB Ltd., Minden, Germany). Temperature was determined using compact thermometers (Endress and Hauser AG, Reinach, Switzerland). All sensor data were recorded once per minute and logged in the database.

2.4 Calculations

Both analog sensor data and gas quality measurements were evaluated for the analysis. Since no significant difference in reactor performance was found, average and median values of the process parameters are reported in this study. To evaluate the performance of the reactors, the following key values were determined based on the collected data:

- Methane formation rate (MFR);
- Gas hourly space velocity (GHSV);
- Retention time (RT);
- and the conversion rates of H2 and CO2.

As defined in [17] and [18], the GHSV represents the ratio between the flow rate of the incoming gases at STP and the volume of the reactor or its catalyst content. In the experimental conditions studied, only the reactant gas components fed into the reactor were considered:

$$GHSV = \frac{F_{CO_2} + F_{H_2}}{V_r} \; [1/h] \tag{1}$$

Where F_{CO2} and F_{H2} are the flow rates of CO_2 and H_2 at STP in m^3/h and V_r is the reaction volume, $V_r = 0.013$ m^3. RT refers to the time required for the incoming gases to pass through the reactor volume from the inlet at the bottom of the reactor to the outlet at the top [6]:

$$RT = \frac{V_r}{F_{CO_2} + F_{H_2} + F_{CH_4}} \; [h] \tag{2}$$

Where F_{CO2}, F_{H2}, and F_{CH4} are the flow rates of CO_2, H_2, and inert CH_4 supplied to the reactor in m^3/h at the reactor temperature and pressure [19]. One of the most important parameters related to the performance of the reactor is the MFR, which is determined by the daily flow rate of the product gas and the volume of the reactor [6,19]:

$$MFR = \frac{F_{CH_{4out}} - F_{CH_{4in}}}{V_r} \; [m^3/(m^3 \cdot d)] \tag{3}$$

Where F_{CH4in} is the daily flow rate of CH_4 entering the reactor and F_{CH4out} is the daily flow rate of CH_4 leaving the reactor in m^3/d. Compared to [6], in the present study, the daily flow rate of microbially produced CH_4 was defined as the difference between the measured volumetric flow rate of CH_4 in the product gas and the volumetric flow rate of CH_4 injected into the reactors.

3. Results and discussion

3.1 Operation and performance parameters

The data on the measured parameters as well as the key parameters related to the performance of the reactors during all experimental phases are shown in Table 2. Both temperature and pressure were stable in each experimental phase and did not vary significantly during the experiments. Since the GHSV is related to the fixed parameters of the experimental procedure, its value was kept constant throughout the experiment: GHSV = 1.082 1/h.

Table 2. Operation and performance parameters for all experimental phases.

Parameters	**T50P9**	**T50P2**	**T50P5.5**	**T55P5.5**	**T55P9**	**T55P4.275**	**T60P2**	**T60P9**	**T60P5.5**
Temperature [°C]	49.801 ± 0.284	50.065 ± 0.231	50.145 ± 0.201	54.983 ± 0.250	54.879 ± 0.264	54.952 ± 0.253	59.742 ± 0.297	59.990 ± 0.0	59.99 ± 0.0
Pressure [bar]	9.012 ± 0.018	2.061 ± 0.016	5.512 ± 0.013	5.480 ± 0.022	8.998 ± 0.018	4.288 ± 0.016	2.028 ± 0.011	9.046 ± 0.018	5.535 ± 0.013
pH	8.921 ± 0.128	8.458 ± 0.101	8.689 ± 0.131	8.745 ± 0.106	8.837 ± 0.082	8.762 ± 0.111	8.673 ± 0.106	9.013 ± 0.088	8.949 ± 0.138
Flow rate H_2 [L/h]	11.250	11.250	11.250	11.250	11.250	11.250	11.250	11.250	11.250
Flow rate CO_2 [L/h]	2.81	2.81	2.81	2.81	2.81	2.81	2.81	2.81	2.81
Flow rate CH_4 [L/h]	3.44	3.44	3.44	3.44	3.44	3.44	3.44	3.44	3.44
MFR [$m^3/(m^3 \cdot d)$]	6.376 ± 0.369	5.545 ± 0.224	5.687 ± 0.266	5.701 ± 0.186	5.755 ± 0.337	5.794 ± 0.363	6.076 ± 0.229	5.906 ± 0.241	6.001 ± 0.386
CH_{4total}[1] [%]	95.614 ± 0.151	93.675 ± 0.452	95.614 ± 1.632	94.386 ± 1.137	94.784 ± 0.781	95.626 ± 0.563	95.015 ± 0.714	94.929 ± 0.992	94.214 ± 0.360
CH_{4conv}[2] [%]	48.102 ± 1.017	46.574 ± 0.996	47.425 ± 1.543	47.584 ± 1.670	48.483 ± 1.657	47.285 ± 0.834	47.203 ± 1.201	50.000 ± 1.443	48.873 ± 0.965
H_2:CO_2	4.072 ± 0.003	4.106 ± 0.009	4.068 ± 0.031	4.095 ± 0.024	4.089 ± 0.015	4.070 ± 0.013	4.083 ± 0.014	4.087 ± 0.0719	4.100 ± 0.007
H_{2conv} [%]	97.535 ± 0.166	96.394 ± 0.274	97.288 ± 0.579	96.790 ± 0.827	97.042 ± 0.525	97.608 ± 0.382	97.127 ± 0.354	97.115 ± 0.679	96.616 ± 0.264
CO_{2conv} [%]	99.767 ± 0.026	99.600 ± 0.137	99.569 ± 0.164	99.820 ± 0.085	99.884 ± 0.033	99.784 ± 0.081	99.811 ± 0.037	99.942 ± 0.008	99.895 ± 0.021
RT [h]	5.579	1.240	3.409	3.357	5.494	2.610	1.203	5.411	3.307
GHSV [1/h]	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082

[1] CH_{4total} is the share of methane in the product gas mixture.

[2] CH_{4conv} is the share of the microbiologically produced methane in the amount of total methane CH_{4total}.

The analysis of the flow rates of the incoming and outgoing gases showed some deviation of the H_2:CO_2 ratio from the set stoichiometric value: during all experimental phases there was a slight overshoot of H_2 content. This could be due either to the inaccuracy of the instruments, as reported in [6], or to the fluctuating ratio between CO_2 and CH_4 in the gas mixture supplied to the reactors from the same cylinder. This over-stoichiometric ratio resulted in a better conversion rate of CO_2 compared to the conversion of H_2. On average, the conversion rate of H_2 was 97.124 ± 0.176 % and the conversion rate of CO_2 was 99.941 ± 0.011 % throughout the experiment.

The results of the experiments showed a clear correlation between the quality of biomethane and the H_2:CO_2 ratio (Figure 2**Error! Reference source not found.**). Thus, the purity of the biomethane is determined by the ratio of feed gases, resulting in higher quality the closer the ratio is to 4.

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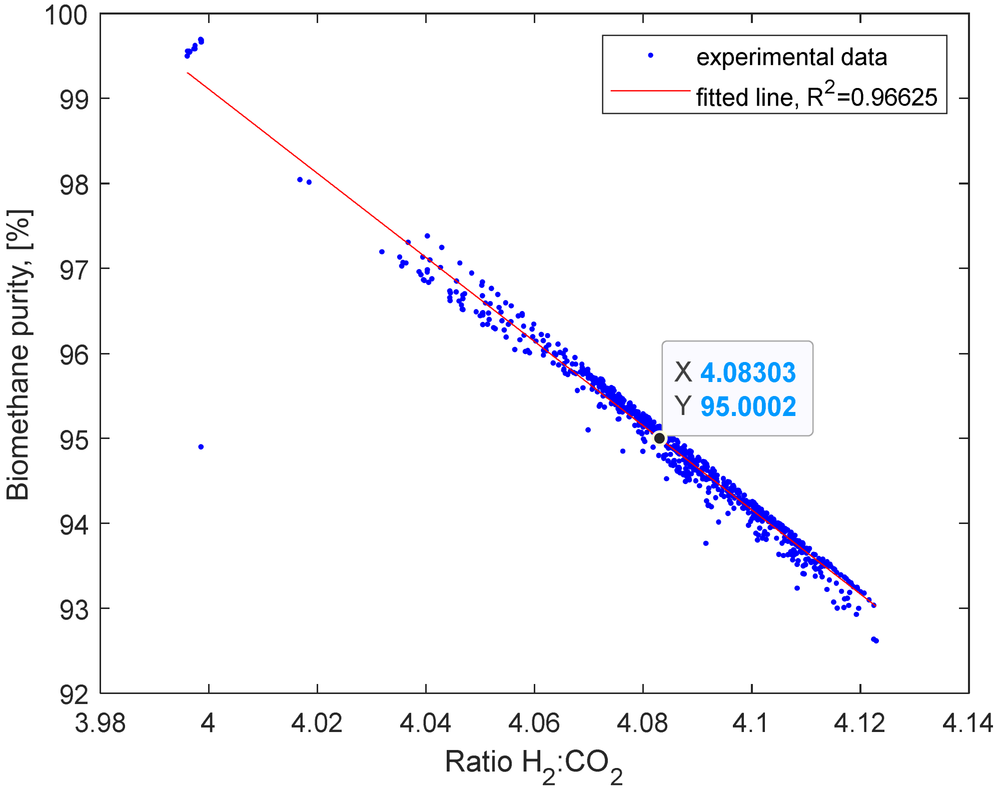


Figure 2. Scatter plot demonstrating the correlation between the H_2:CO_2 ratio and the methane content of the product gas showing biomethane purity.

In the experiments where the H_2:CO_2 ratio was 4.123, the content of CH_4 in the product gas was the lowest. This result indicates a threshold value for the ratio of the reaction gases for their successful conversion into biomethane: The H_2:CO_2 ratio should not exceed 4.083 to achieve a biomethane quality of at least 95 %. On the other hand, the conversion of H_2 shows an obvious linear correlation with the purity of biomethane, with higher conversion rates of H_2 leading to higher purity of biomethane (R^2 = 0.925, see supplementary Materials, Figure S1). At the same time, no obvious correlation was found between the purity of biomethane and the conversion of CO_2 (see supplementary Materials, Figure S2). Since the coefficient of determination of the correlation between the H_2:CO_2 ratio is higher than the H_2 conversion, in practice the dosage of the reaction gases should be controlled and kept as close as possible to the stoichiometric ratio in order to achieve optimal conversion rates of the reactants and maximally reduce the fraction of their residues in the product gas.

The MFR exhibited a relatively constant trend during the experiments confirming the stability of the process and a robust BHM of the injected gases in the presence of inert CH_4 gas. It is worth noting that the MFR increases slightly with increasing pressure and temperature in the reactors, and the obtained results are comparable to the results of [6,8]. At a H_2 gas feed rate of 22.77 $m^3/(m^3 \cdot d)$ (at a flow rate of 11.25 L/h based on the trickle-bed volume V_r = 13 L), the MFR obtained in our study was comparable to the results of [9] for a similar H_2 feed rate. However, the median CH_4 concentration at a temperature of 55 °C was sufficiently higher in our experiments than in [9]: it was above 94 % for all experimental setups and reached 95.494 % at a pressure of 4.275 bar. These results underline the importance of pressure for biogas upgrading in TBRs. Overall, the increase in MFR and the percentage of bacterially converted methane CH_{4conv} demonstrate the higher bacterial activity with increasing temperature and pressure, with the temperature effect being more significant than the pressure increase (see supplementary Materials, Figure S3).

Regarding the quality of the upgraded biogas, the highest biomethane purity was obtained at a pressure of 4.275 bar and a temperature of 55 °C, and at a pressure of 9 bar and a temperature of 50 °C

(Figure 3). In all experimental setups the lowest biomethane quality for “low standard” gas grid is achieved, and in the two cases mentioned, the median value of the quality for “high standard” gas grid is achieved.

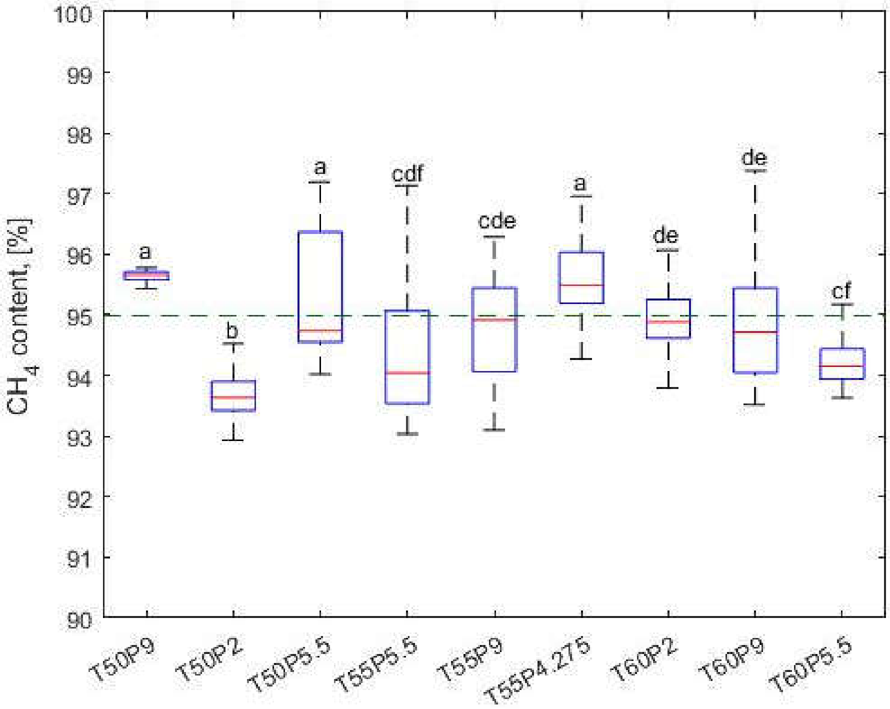


Figure 3. Methane (CH_4) content in the product gas at the different experimental setups. The significant differences among CH_4 content are marked with letters ($p < 0.05$, Tukey’s test).

3.2 Optimizing operating parameters

To evaluate the optimal operating parameters in JMP Pro, three key process performance values were added to the custom design. Biomethane quality, H_2 conversion and MFR were set as equally weighted variables. The standard least square model is chosen to analyze the DoE and the desirability function is optimized over all responses. The maximum desirability is obtained at 50 °C and 9 bar. However, Figure 4 shows no maximum of a key value in the specified intervals of temperature and pressure. The prediction formula shows a negative correlation between biomethane quality, H_2 conversion and increasing temperature, which contradicts the conclusion of [7]. On the other hand, there is a positive correlation between increasing pressure and both variables. As for MFR, both temperature and pressure show a parabolic correlation with this performance parameter. This indicates that further experiments with higher pressure and wider temperature interval are needed to validate the prediction formula found. Furthermore, when the fluctuating ratio of H_2:CO_2 in the reactants is included in the prediction formula, an effect on the biomethane quality and H_2 conversion rate, but not on the MFR can be seen. This shifts the optimal process temperature to 60 °C, which underlines the previous conclusion to use a wider temperature interval in further experiments. On the other hand, ensuring a constant H_2:CO_2 ratio must be considered when planning future experiments.

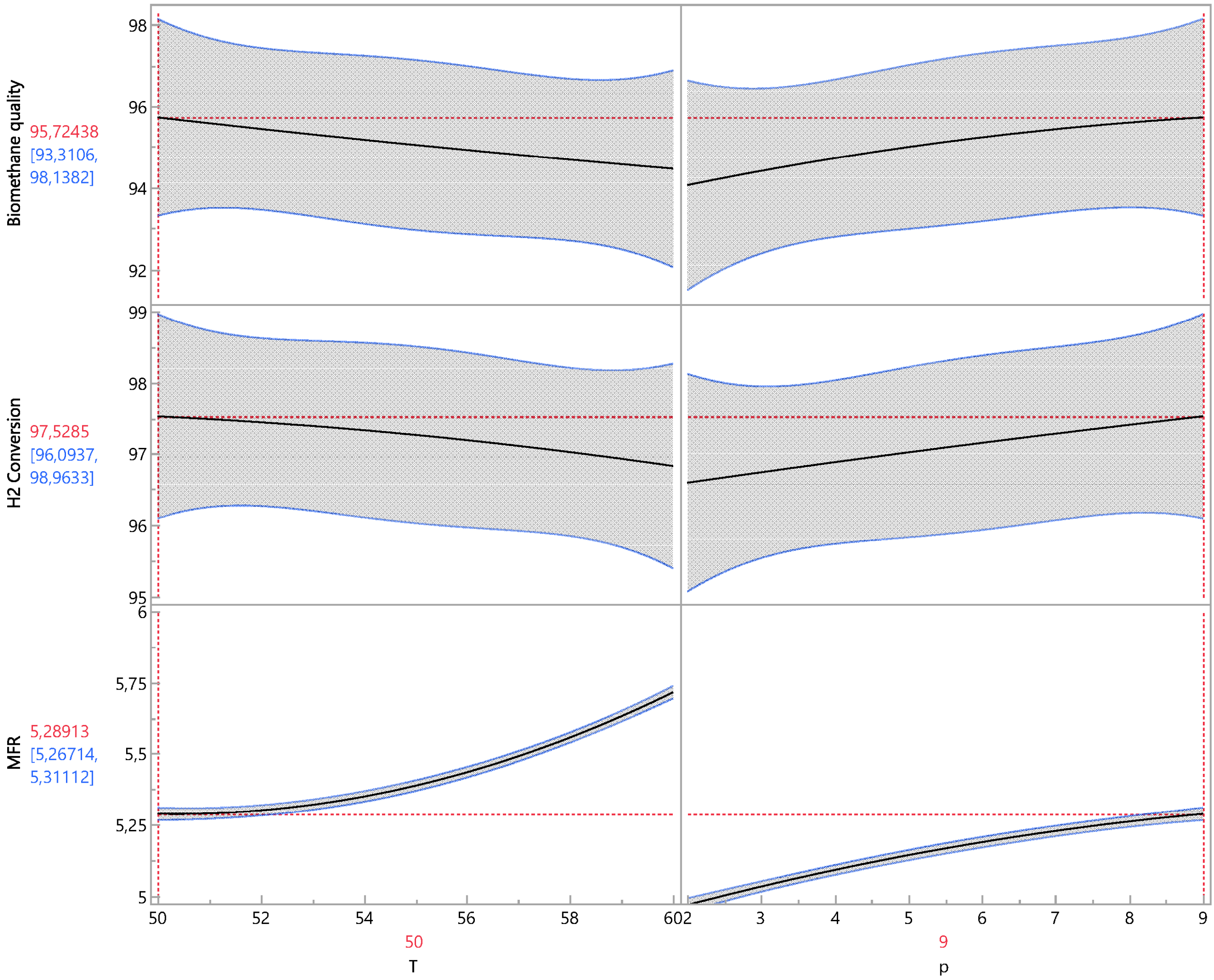
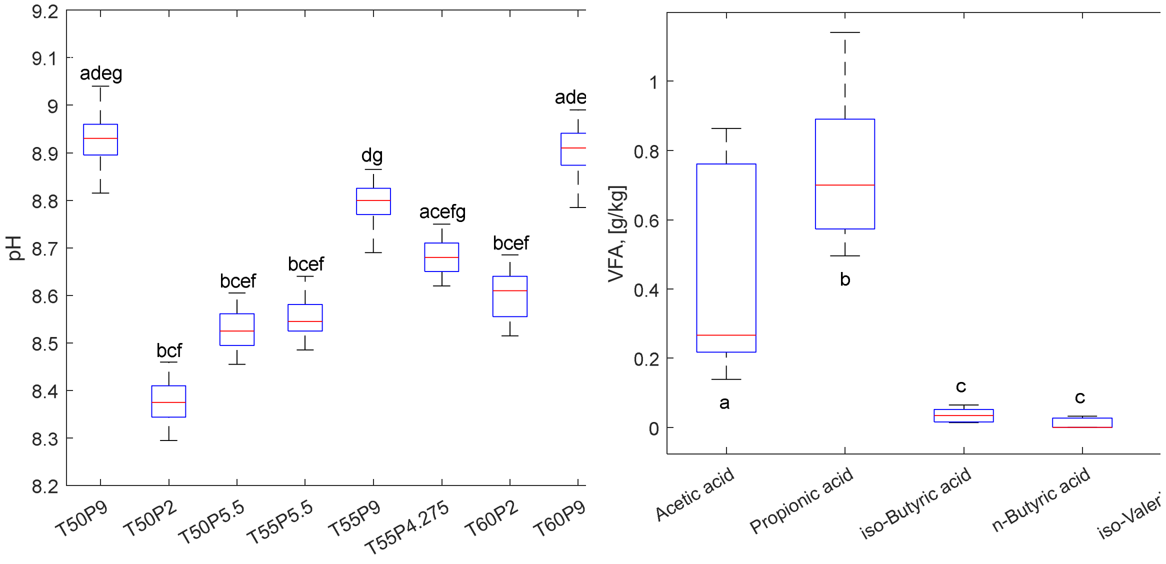


Figure 4. Prediction profiler of JMP Pro showing the maximized desirability function for methane content (biomethane quality), hydrogen conversion and methane formation rate (MFR); where the red dotted lines indicate the calculated maximum at the optimum operating parameters.

3.3 Analysis of the process liquid

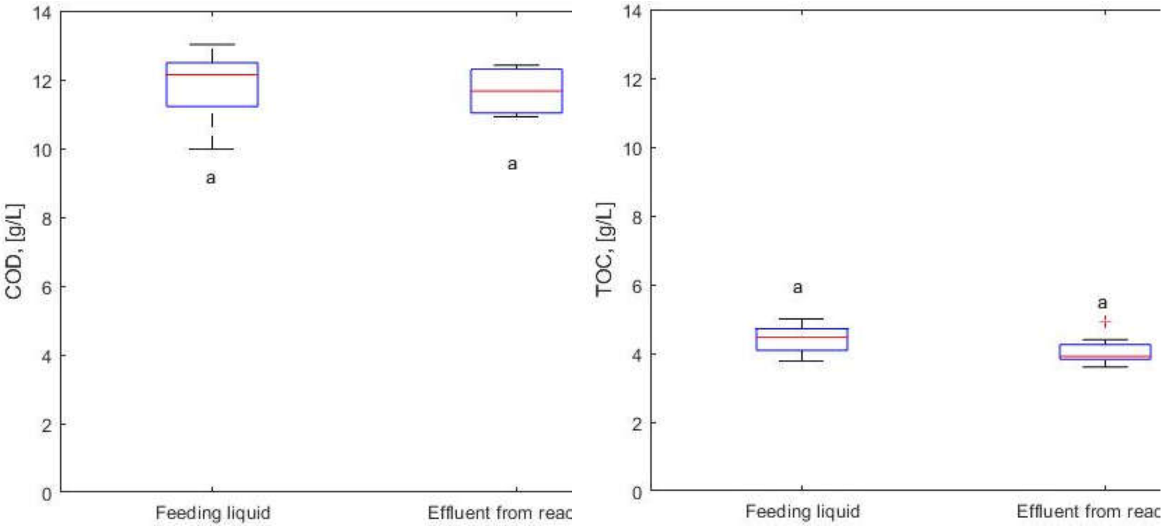
Laboratory analyses of the process liquid show an increase in pH with increasing temperature and pressure (Figure 5 (**a**)). These results are in contrast to the results of [6], where the pH decreased with increased pressure due to the formation of carbonic acid. This may be due to the amount of inert CH_4 in the reactor, which leads to a lower partial pressure of CO_2. The result of [20] also show the importance of pH for process stability, including microbial growth. Since the solubility of CO_2 increases not only with pressure but also with increasing pH, an over stochiometric feed could lead to process disturbances and inhibition of methanogenesis [21].

Since the formation of VFAs occurred in all reactors, the activity of acetoclastic methanogens could not be excluded. The predominant acids found in the reactors were acetic and propionic acids (Figure 5 (**b**)). In addition, both COD and TOC analyses show no significant difference between the effluents from the reactors and the feed liquid (Figure 6 (**a**) and (**b**)). The TC and TN analyses also showed that the inorganic carbon and TN content in the reactor effluent is significantly lower compared to the feed liquid (Figure 6 (**c**) and (**d**)). The depletion of both nutrients from the process liquid over time may indicate biomass growth, as carbon serves as an energy source and nitrogen compounds are required for protein synthesis [22]. At the same time, the relatively low C/N ratio (below 30, as mentioned by [22]) could also be related to VFA formation within the reactors.



(**a**) (**b**)

Figure 5. The parameters of the process liquid characterizing the homeostasis within reactors: (**a**) Boxplots of pH for each experimental phase; (**b**) graph reflecting fluctuations in the volatile fatty acids (VFA) concentration in the reactors´ effluent during the experimental phases; letters mark significance according to Tukey's test ($p < 0.05$).



(**a**) (**b**)

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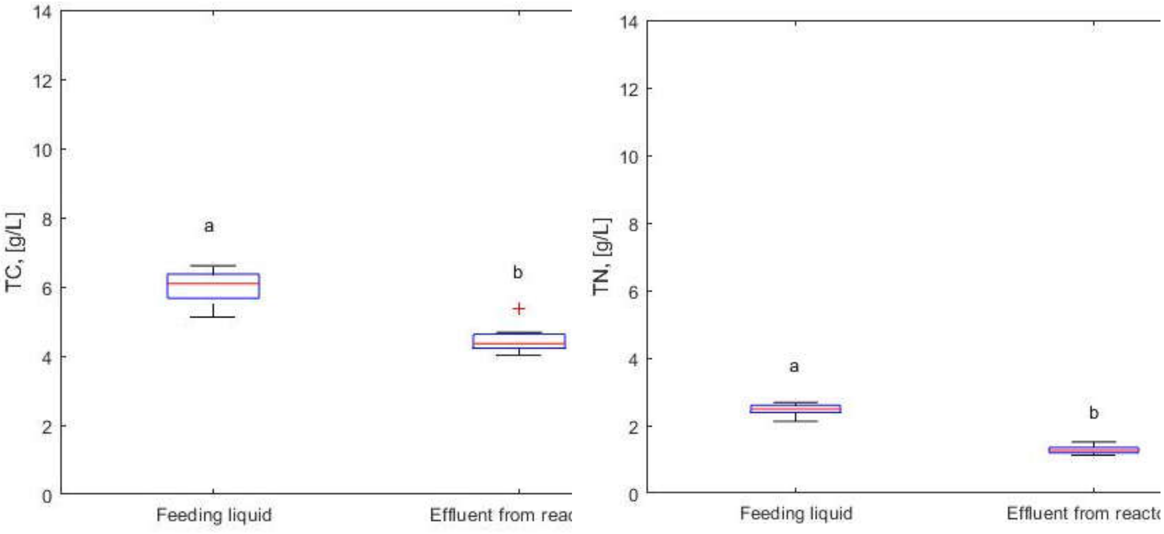

(c) (d)

Figure 6. Boxplots for different process parameters in the liquid: (**a**) Chemical oxygen demand (COD), (**b**) Total organic carbon (TOC), (**c**) Total carbon (TC), (**d**) Total nitrogen (TN); letters mark significance according to Tukey's test ($p < 0.05$).

5. Conclusions and outlook

The present study shows that biogas can be upgraded to biomethane quality by using BHM. By applying a DoE, the optimum process parameters in terms of pressure and temperature were determined with the given experimental setup. At 50 °C and 9 bar, the MFR was 5.295 ± 0.216 $m^3/(m^3 \cdot d)$, CH_4 content was 95.614 ± 0.151 % and H_2 conversion was 97.535 ± 0.166 %. However, no maximum value was obtained in the prediction formula for the key values, suggesting that further experiments with longer intervals are needed. In addition, a quality of over 93 % CH_4 in the product gas was achieved in all experimental runs, which is sufficient for injection into the "low" gas grid. However, under real industrial conditions, the ratio between CO_2 and CH_4 in the biogas may vary, depending on the type of substrates fed or the conditions in the digester. In order to maintain the quality of biomethane fed into the gas grid, the H_2:CO_2 ratio in the educts should be controlled. According to the results of the present study, the H_2:CO_2 ratio should not exceed 4.083:1. At the same time, in the works of [6,9,10] for mono-methanation of CO_2, the lower limits for this parameter were 3.75:1. Therefore, an optimal H_2:CO_2 ratio must be ensured in practice. In addition, an economic analysis weighing the benefits of higher temperature and pressure against manufacturing and operating costs could improve process optimization.

Supplementary Materials: The following supporting information can be downloaded: Figure S1: Interrelation between conversion of H_2 and purity of biomethane; Figure S2: Interrelation between conversion of CO_2 and purity of biomethane; Figure S3: Methane formation rate (MFR) depending on pressure and temperature (grouped by pressure).

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