

## Article

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

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**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<sub>2</sub>), biogas with a high methane (CH<sub>4</sub>) content can be fed into the gas grid without restrictions. For this purpose, the CH<sub>4</sub> 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<sub>4</sub> 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<sup>3</sup>/(m<sup>3</sup>·d). The process performance is highly dependent on the H<sub>2</sub>:CO<sub>2</sub> ratio in the educts, which should be as close as possible to the stoichiometric ratio of 4. In conclusion, BHM is a viable approach to upgrade biogas to biomethane quality and can contribute to a sustainable energy grid.



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**Keywords:** biological methanation; trickle-bed reactor; biogas upgrading; biomethane; optimization of operating 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<sub>2</sub> in the atmosphere. Biogas consists of 50–75% CH<sub>4</sub> and about 25–50% CO<sub>2</sub>, less than 10% water vapor, and trace amounts of H<sub>2</sub> (<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<sup>3</sup> [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 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<sup>3</sup> and high-calorific gas (H-gas) with an energy content of 36.0–43.2 MJ/m<sup>3</sup>. To be fed into the natural gas grid, the calorific value of the biogas must first be raised—which is usually achieved by removing CO<sub>2</sub>. At a CH<sub>4</sub> content of 95%, the threshold value for feeding into the H-gas grid biogas reaches an energy content of 34.1 MJ/m<sup>3</sup> [4]. In the 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<sub>2</sub> 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<sub>2</sub>. It is then fed into a trickling-bed reactor (TBR) together with CO<sub>2</sub>, 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<sub>4</sub>. Then, high-quality biomethane can be injected into the gas grid and is therefore a storage system for excess electrical energy [6]. Previously conducted studies on CO<sub>2</sub> methanation have shown the influence of operating parameters such as pressure, temperature, and drip interval on process performance in TBRs [7–10]. Researchers found that when the pressure was increased from 1.5 to 9 bar, the CH<sub>4</sub> content increased simultaneously at mesophilic temperatures of 41 °C [7]. The effect of temperature was investigated in [8] using the same experimental setup. It showed that the conversion rates of H<sub>2</sub> and CO<sub>2</sub> increase, leading to an increasing CH<sub>4</sub> content at increasing temperatures from 40 to 55 °C. The analysis in [9,10] achieved CH<sub>4</sub> concentrations above 98% at ambient pressure and argued the H<sub>2</sub>:CO<sub>2</sub> ratio, pH control, and sufficient nutrient supply as limiting factors. At the same time, it was shown in [9] that CH<sub>4</sub> concentrations above 90% can be achieved in TBR with established microbial culture under thermophilic conditions (55 °C) and ambient pressure at H<sub>2</sub> gas feed rate above 23.2 m<sup>3</sup>/(m<sup>3</sup>·d).

Since previous studies focused mainly on CO<sub>2</sub> methanation, which was later referred to as mono-methanation, this study analyzes the co-methanation of biogas and H<sub>2</sub> in a TBR. As it was shown in [11], at optimized conditions biomethane could be produced with mono-methanation in a TBR by thermophilic microorganisms with a maximum CH<sub>4</sub> content of 95.3%. Therefore, the objective of this study was to verify the possibility of upgrading biogas with a 55% CH<sub>4</sub> to biomethane above 95% CH<sub>4</sub> with BHM, and to optimize the thermodynamic parameters of the operating process by applying design of experiments (DoE).

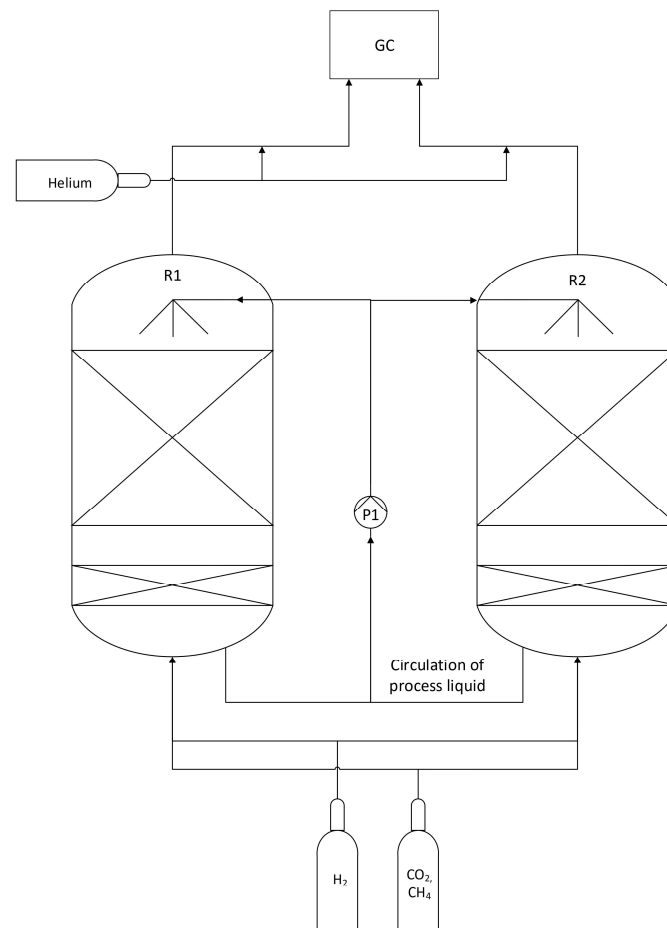
## 2. Materials and Methods

### 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 [7] 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<sub>2</sub> and H<sub>2</sub>, co-methanation of a standard biogas mixture consisting of 45% CO<sub>2</sub> and 55% CH<sub>4</sub> together with H<sub>2</sub> was used (Quality 3.0, Westfalen AG, Münster, Germany). The incoming gases were fed to the reactors via mass flow controllers (MFC Type 8742, Buerkert, Triembach-au-Val, France) at flow rates of 11.25 L/h for H<sub>2</sub> 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<sub>2</sub> (11.25 L/h) and CO<sub>2</sub> (2.81 L/h) was 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 became 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 the range of 50 to 60 °C and 2 to 9 bar to find the optimal operating point.

As a feed liquid, the effluent from the methanogenic stage of a two-stage anaerobic digestion (AD) plant, as described in [12], 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 [13], 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 [14]. Trickling of the carrier bodies occurred once per hour for three minutes.



**Figure 1.** Simplified process scheme of the experimental plant.

The product gases leaving the reactors were cooled to remove water vapor. In addition, helium gas (Quality 3.0, Westfalen AG, Münster, 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, East Syracuse, NY, 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<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>S) 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<sub>2</sub> to optimize the thermodynamic parameters using JMP Pro 15 software (SAS Institute, Cary, NC, USA). Since [8] recommended experiments at higher temperatures, a temperature in the range of 50 to 60 °C was set as the first predictor variable. Then, 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 [15,16], 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 Table 1. 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 [17]. The odd pressure in the sixth run is dictated by the experimental design, which attempts to minimize prediction errors.

**Table 1.** Generated design of experiment by JMP Pro varying temperature and pressure.

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 h (six complete days), including an adjustment period of 48 h. After 48 h, pH and CH<sub>4</sub> production were stabilized, and the above measurements were considered for further analysis.

### 2.3. Analytical Section

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 acid (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, CA, USA). COD content was measured using a sensor array photometer (Hach Lange Type LASA 20). A TOC/TN analyzer (Analytik Jena AG Type multi N/C<sup>®</sup>, Jena, Germany) was used to measure TC and TOC.

The pH level 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

The sensor data logged during the experiment and stored in the database, as well as results of gas measurement, were evaluated and processed with the help of MATLAB R2022b software package. The statistical analysis of the gas measurement data and lab analysis data was performed with Tukey's test ( $p < 0.05$ ).

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);
- The conversion rates of H<sub>2</sub> and CO<sub>2</sub>.

As defined in [18,19], 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:

$$\text{GHSV} = \frac{F_{\text{CO}_2} + F_{\text{H}_2}}{V_r} [1/\text{h}], \quad (1)$$

where  $F_{\text{CO}_2}$  and  $F_{\text{H}_2}$  are the flow rates of CO<sub>2</sub> and H<sub>2</sub> at STP in m<sup>3</sup>/h and  $V_r$  is the reaction volume,  $V_r = 0.013 \text{ m}^3$ . 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 [7]:

$$\text{RT} = \frac{V_r}{F_{\text{CO}_2} + F_{\text{H}_2} + F_{\text{CH}_4}} [\text{h}], \quad (2)$$

where  $F_{\text{CO}_2}$ ,  $F_{\text{H}_2}$ , and  $F_{\text{CH}_4}$  are the flow rates of CO<sub>2</sub>, H<sub>2</sub>, and inert CH<sub>4</sub> supplied to the reactor in m<sup>3</sup>/h at the reactor temperature and pressure [20]. 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 [7,20]:

$$\text{MFR} = \frac{F_{\text{CH}_4\text{out}} - F_{\text{CH}_4\text{in}}}{V_r} \left[ \text{m}^3 / \left( \text{m}^3 \cdot \text{d} \right) \right], \quad (3)$$

where  $F_{\text{CH}_4\text{in}}$  is the daily flow rate of CH<sub>4</sub> entering the reactor and  $F_{\text{CH}_4\text{out}}$  is the daily flow rate of CH<sub>4</sub> leaving the reactor in m<sup>3</sup>/d. Compared to [7], in the present study, the daily flow rate of microbially produced CH<sub>4</sub> was defined as the difference between the measured volumetric flow rate of CH<sub>4</sub> in the product gas and the volumetric flow rate of CH<sub>4</sub> 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:  $\text{GHSV} = 1.082 \text{ h}^{-1}$ .

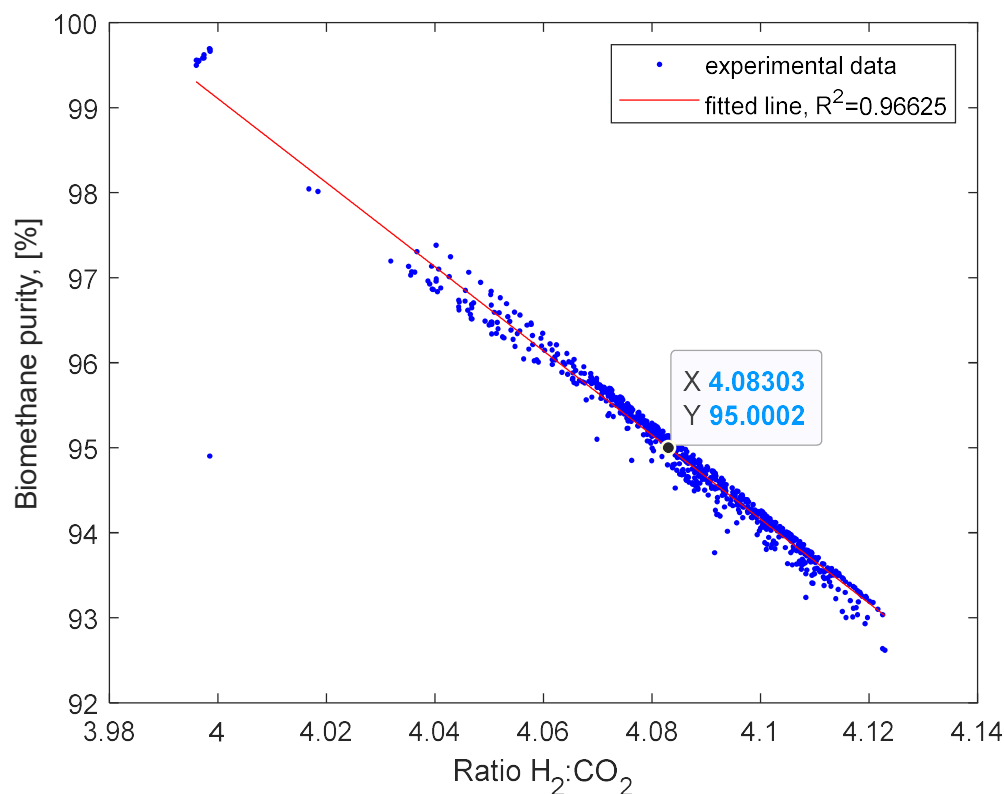
The analysis of the flow rates of the incoming and outgoing gases showed some deviation of the H<sub>2</sub>:CO<sub>2</sub> ratio from the set stoichiometric value: during all experimental phases, there was a slight overshoot of H<sub>2</sub> content. This could be due either to the inaccuracy of the instruments, as reported in [7], or to the fluctuating ratio between CO<sub>2</sub> and CH<sub>4</sub> in the gas mixture supplied to the reactors from the same cylinder. This over-stoichiometric ratio resulted in a better conversion rate of CO<sub>2</sub> compared to the conversion of H<sub>2</sub>. On average, the conversion rate of H<sub>2</sub> was  $97.124 \pm 0.176\%$  and the conversion rate of CO<sub>2</sub> was  $99.941 \pm 0.011\%$  throughout the experiment.

The results of the experiments showed a clear correlation between the quality of biomethane and the H<sub>2</sub>:CO<sub>2</sub> ratio (Figure 2). 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.

**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 <sub>2</sub> (L/h)	11.250	11.250	11.250	11.250	11.250	11.250	11.250	11.250	11.250
Flow rate CO <sub>2</sub> (L/h)	2.810	2.810	2.810	2.810	2.810	2.810	2.810	2.810	2.810
Flow rate CH <sub>4</sub> (L/h)	3.440	3.440	3.440	3.440	3.440	3.440	3.440	3.440	3.440
MFR (m <sup>3</sup> /(m <sup>3</sup> ·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 <sub>4total</sub> <sup>1</sup> (%)	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 <sub>4conv</sub> <sup>2</sup> (%)	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 <sub>2</sub> :CO <sub>2</sub>	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 <sub>2conv</sub> (%)	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 <sub>2conv</sub> (%)	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 (h <sup>-1</sup> )	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082	1.082

<sup>1</sup> CH<sub>4total</sub> is the share of methane in the product gas mixture. <sup>2</sup> CH<sub>4conv</sub> is the share of the microbiologically produced methane in the amount of total methane CH<sub>4total</sub>.

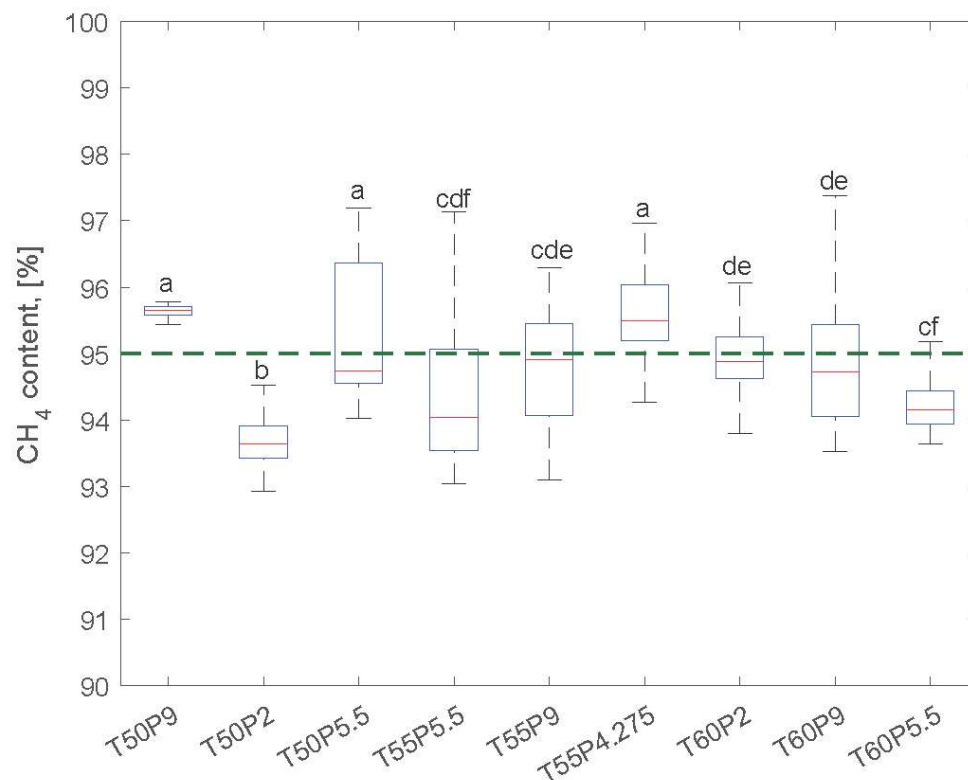


**Figure 2.** Scatter plot demonstrating the correlation between the  $H_2:CO_2$  ratio and the methane content of the product gas showing biomethane purity.

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 that of 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 [7]. At a  $H_2$  gas feed rate of  $22.77 \text{ m}^3/(\text{m}^3 \cdot \text{d})$  (at a flow rate of 11.25 L/h based on the trickle-bed volume  $V_r = 13 \text{ L}$ ), 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  $55 \text{ }^\circ\text{C}$  was sufficiently higher in our experiments than in results shown by D. Strübing et al. [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  $CH_{4\text{conv}}$  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 was achieved, and in the two cases mentioned, the median value of the quality for “high-standard” gas grid was achieved.

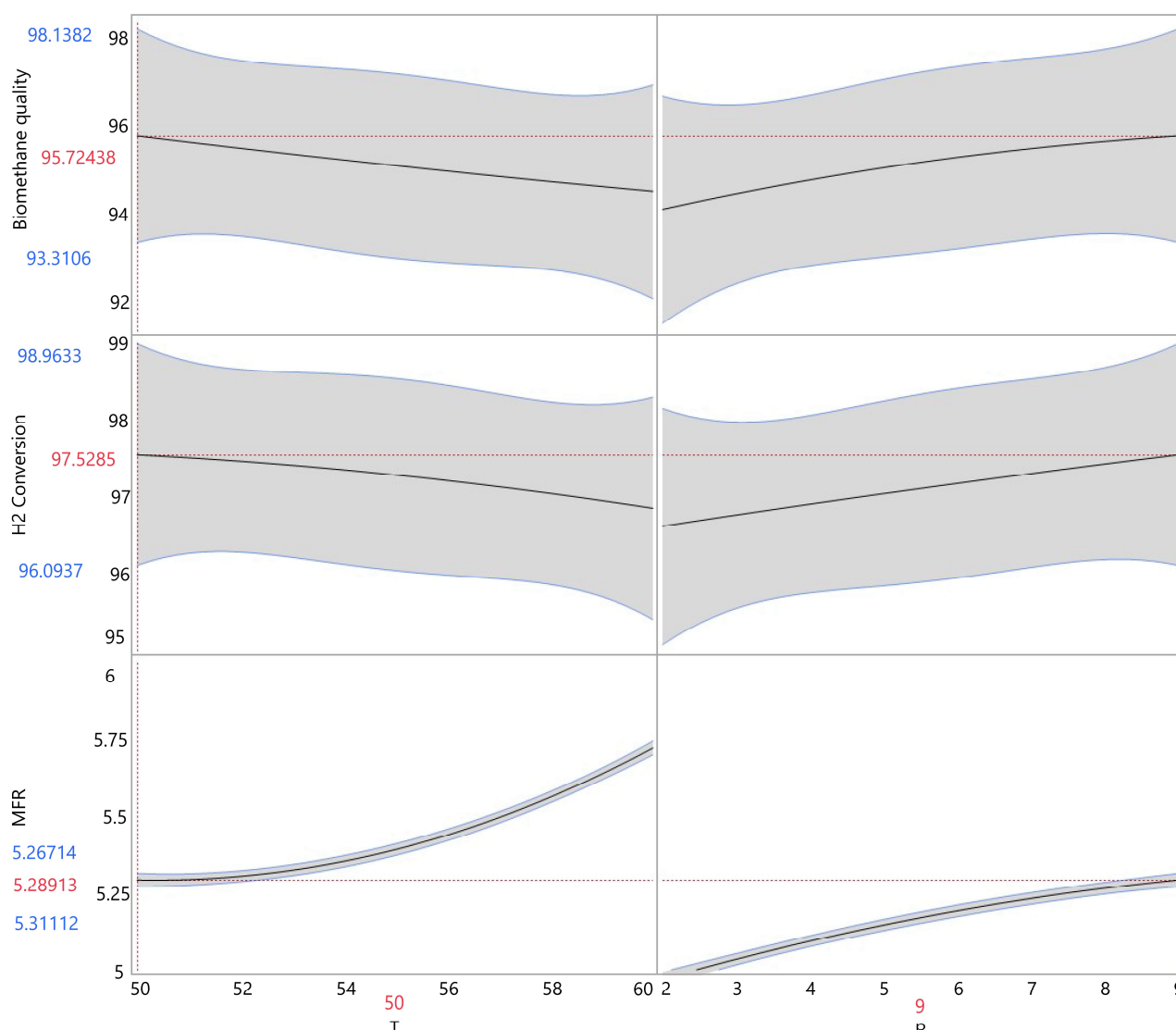


**Figure 3.** Methane content in the product gas at the different experimental setups, where the green line shows the threshold for high gas grid. The significant differences among methane content are marked with letters ( $p < 0.05$ , Tukey’s test).

### 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 was chosen to analyze the DoE and the desirability function was optimized over all responses. The maximum desirability was 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 [8]. 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.

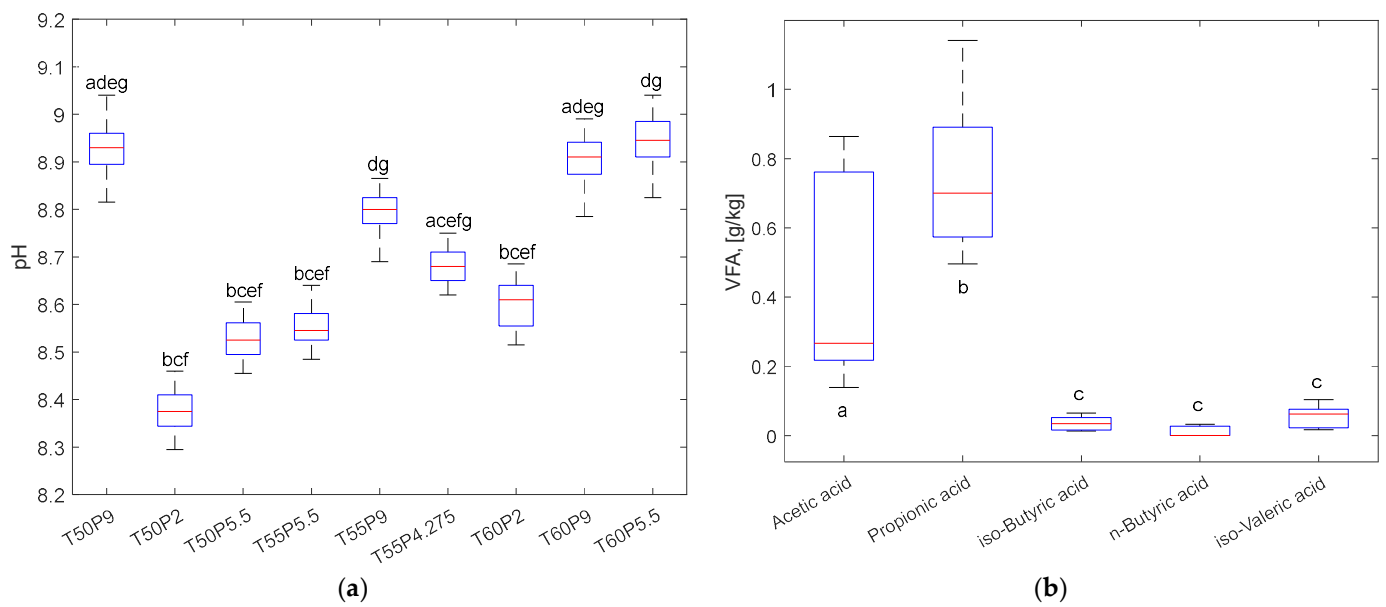




**Figure 4.** Prediction profiler of JMP Pro showing the maximized desirability function for methane content (biomethane quality), hydrogen conversion and methane formation rate (MFR), where the red dotted lines indicate the calculated maximum (given as a red number on the y axis) at the optimum operating parameters (given as a red number on the x axis) and the blue lines indicate the confidence interval on the mean response (given as blue numbers on the y axis).

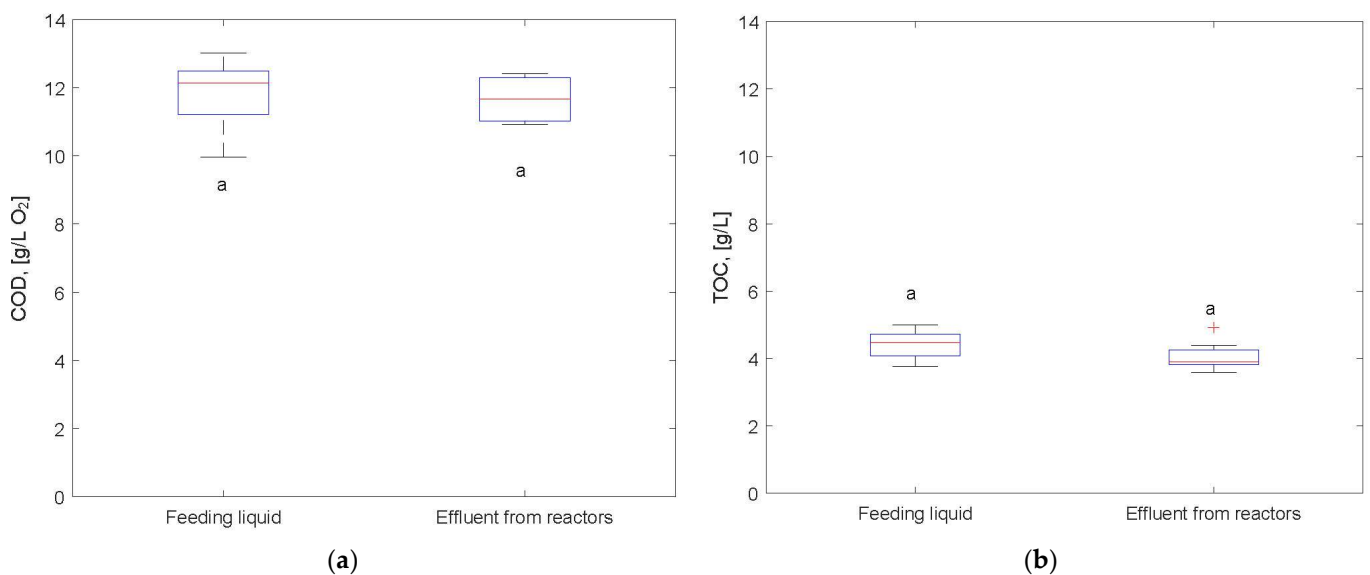
### 3.3. Analysis of the Process Liquid

Laboratory analyses of the process liquid show an increase in pH with increasing temperature and pressure (Figure 5a). These results are in contrast to the results of [7], where the pH decreased with increased pressure due to the formation of carbonic acid. This may be due to the amount of inert  $\text{CH}_4$  in the reactor, which leads to a lower partial pressure of  $\text{CO}_2$ . The results of [21] also show the importance of pH for process stability, including microbial growth. Since the solubility of  $\text{CO}_2$  increases not only with pressure but also with increasing pH, an over stoichiometric feed could lead to process disturbances and inhibition of methanogenesis [22].

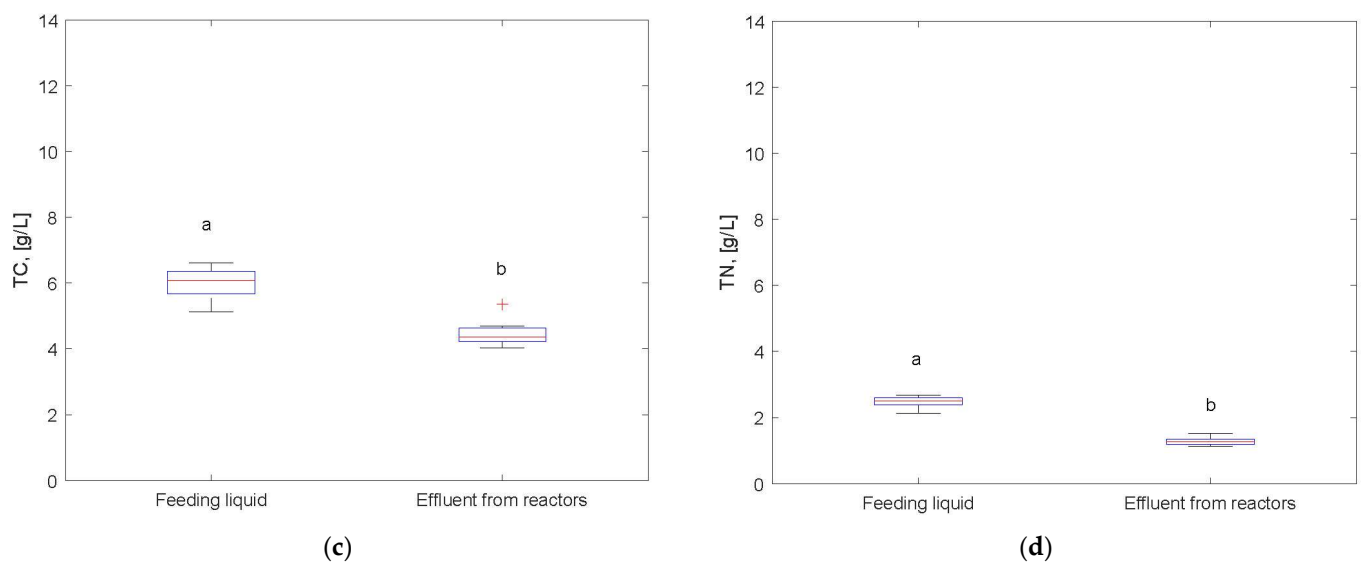


**Figure 5.** The parameters of the process liquid characterizing the homeostasis within reactors: (a) Boxplots of pH for each experimental phase; (b) graph reflecting fluctuations in the volatile fatty acid concentration in the reactors' effluent during the experimental phases; letters mark significance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

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 5b). In addition, both COD and TOC analyses show no significant difference between the effluents from the reactors and the feed liquid (Figure 6a,b). The TC and TN analyses also show that the inorganic carbon and TN content in the reactor effluent is significantly lower compared to the feed liquid (Figure 6c,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 [23]. At the same time, the relatively low C/N ratio (below 30, as mentioned by [23]) could also be related to VFA formation within the reactors.



**Figure 6.** Cont.



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

#### 4. Conclusions and Outlook

The present study shows that biogas can be upgraded to biomethane quality by using BHM. By applying 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  $5.295 \pm 0.216 \text{ m}^3 / (\text{m}^3 \cdot \text{d})$ , the  $\text{CH}_4$  content was  $95.614 \pm 0.151\%$  and the  $\text{H}_2$  conversion was  $97.535 \pm 0.166\%$ . 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%  $\text{CH}_4$  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  $\text{CO}_2$  and  $\text{CH}_4$  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  $\text{H}_2:\text{CO}_2$  ratio in the educts should be controlled. According to the results of the present study, the  $\text{H}_2:\text{CO}_2$  ratio should not exceed 4.083:1. At the same time, in the works of [7,9,10] for mono-methanation of  $\text{CO}_2$ , the lower limits for this parameter were 3.75:1. Therefore, an optimal  $\text{H}_2:\text{CO}_2$  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 at: <https://www.mdpi.com/article/10.3390/en16124720/s1>, Figure S1: Interrelation between conversion of  $\text{H}_2$  and purity of biomethane; Figure S2: Interrelation between conversion of  $\text{CO}_2$  and purity of biomethane; Figure S3: Methane formation rate (MFR) depending on pressure and temperature (grouped by pressure).

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### Abbreviations

Anaerobic digestion	AD
Biological hydrogen methanation	BHM
Chemical oxygen demand	COD
Combined heat and power units	CHP
Design of experiment	DoE
Gas hourly space velocity	GHSV
High-calorific gas	H-gas
Methane formation rate	MFR
Low-calorific gas	L-gas
Power-to-gas	PtG
Retention time	RT
Total carbon	TC
Total nitrogen	TN
Total organic carbon	TOC
Trickling-bed reactor	TBR
Volatile fatty acid	VFA

### References

- Wellinger, A.; Murphy, J.; Baxter, D. *The Biogas Handbook: Science, Production and Applications*; Wellinger, A., Murphy, J., Baxter, D., Eds.; Woodhead Publishing Limited: Oxford, UK, 2013; ISBN 9780857097415.
- Miltner, M.; Makaruk, A.; Harasek, M. Review on available biogas upgrading technologies and innovations towards advanced solutions. *J. Clean. Prod.* **2017**, *161*, 1329–1337. [[CrossRef](#)]
- Pelkmans, L. *Implementation of Bioenergy in Germany 2021*; Country Reports; IEA Bioenergy: Paris, France, 2021.
- German Technical and Scientific Association for Gas and Water. *Technical Rule—Standard: Gas Quality, A*; (G 260); Economic and Publishing Company Gas and Water: Bonn, Germany, 2021. Available online: <https://shop.wvgw.de/G-260-Technical-Rule-09-2021/511831> (accessed on 3 April 2023).
- Adnan, A.I.; Ong, M.Y.; Nomanbhay, S.; Chew, K.W.; Show, P.L. Technologies for Biogas Upgrading to Biomethane: A Review. *Bioengineering* **2019**, *6*, 92. [[CrossRef](#)] [[PubMed](#)]
- Burkhardt, M.; Busch, G. Methanation of hydrogen and carbon dioxide. *Appl. Energy* **2013**, *111*, 74–79. [[CrossRef](#)]
- Ullrich, T.; Lindner, J.; Bär, K.; Mörs, F.; Graf, F.; Lemmer, A. Influence of operating pressure on the biological hydrogen methanation in trickle-bed reactors. *Bioresour. Technol.* **2018**, *247*, 7–13. [[CrossRef](#)] [[PubMed](#)]
- Lemmer, A.; Ullrich, T. Effect of Different Operating Temperatures on the Biological Hydrogen Methanation in Trickle Bed Reactors. *Energies* **2018**, *11*, 1344. [[CrossRef](#)]
- Strübing, D.; Huber, B.; Leuhn, M.; Drewes, J.E.; Koch, K. High performance biological methanation in a thermophilic anaerobic trickle bed reactor. *Bioresour. Technol.* **2017**, *245*, 1176–1183. [[CrossRef](#)] [[PubMed](#)]
- Burkhardt, M.; Koschack, T.; Busch, G. Biocatalytic methanation of hydrogen and carbon dioxide in an anaerobic three-phase system. *Bioresour. Technol.* **2015**, *178*, 330–333. [[CrossRef](#)] [[PubMed](#)]
- Thema, M.; Weidlich, T.; Kaul, A.; Böllmann, A.; Huber, H.; Bellack, A.; Karl, J.; Sterner, M. Optimized biological CO<sub>2</sub>-methanation with a pure culture of thermophilic methanogenic archaea in a trickle-bed reactor. *Bioresour. Technol.* **2021**, *333*, 125135. [[CrossRef](#)] [[PubMed](#)]
- Ravi, P.P.; Lindner, J.; Oechsner, H.; Lemmer, A. Effects of target pH-value on organic acids and methane production in two-stage anaerobic digestion of vegetable waste. *Bioresour. Technol.* **2018**, *247*, 96–102. [[CrossRef](#)] [[PubMed](#)]
- Rusmanis, D.; O’Shea, R.; Wall, D.M.; Murphy, J.D. Biological hydrogen methanation systems—An overview of design and efficiency. *Bioengineered* **2019**, *10*, 604–634. [[CrossRef](#)] [[PubMed](#)]
- Jarrell, K.F.; Kalmokoff, M.L. Nutritional requirements of the methanogenic archaebacteria. *Can. J. Microbiol.* **1988**, *34*, 557–576. [[CrossRef](#)]
- Westerholm, M.; Isaksson, S.; Karlsson Lindsjö, O.; Schnürer, A. Microbial community adaptability to altered temperature conditions determines the potential for process optimisation in biogas production. *Appl. Energy* **2018**, *226*, 838–848. [[CrossRef](#)]
- Chen, H.; Chang, S. Dissecting methanogenesis for temperature-phased anaerobic digestion: Impact of temperature on community structure, correlation, and fate of methanogens. *Bioresour. Technol.* **2020**, *306*, 123104. [[CrossRef](#)] [[PubMed](#)]

17. Jones, B.; Goos, P. I-Optimal Versus D-Optimal Split-Plot Response Surface Designs. *J. Qual. Technol.* **2012**, *44*, 85–101. [[CrossRef](#)]
18. Götz, M.; Lefebvre, J.; Mörs, F.; McDaniel Koch, A.; Graf, F.; Bajohr, S.; Reimert, R.; Kolb, T. Renewable Power-to-Gas: A technological and economic review. *Renew. Energy* **2016**, *85*, 1371–1390. [[CrossRef](#)]
19. Froment, G.F.; Bischoff, K.B.; De Wilde, J. *Chemical Reactor Analysis and Design*; Wiley: New York, NY, USA, 1979.
20. Thema, M.; Weidlich, T.; Hörl, M.; Bellack, A.; Mörs, F.; Hackl, F.; Kohlmayer, M.; Gleich, J.; Stabenau, C.; Trabold, T.; et al. Biological CO<sub>2</sub>-Methanation: An Approach to Standardization. *Energies* **2019**, *12*, 1670. [[CrossRef](#)]
21. Sposob, M.; Wahid, R.; Fischer, K. Ex-Situ biological CO<sub>2</sub> methanation using trickle bed reactor: Review and recent advances. *Rev. Environ. Sci. Biotechnol.* **2021**, *20*, 1087–1102. [[CrossRef](#)]
22. Luo, G.; Angelidaki, I. Integrated biogas upgrading and hydrogen utilization in an anaerobic reactor containing enriched hydrogenotrophic methanogenic culture. *Biotechnol. Bioeng.* **2012**, *109*, 2729–2736. [[CrossRef](#)] [[PubMed](#)]
23. Lin, L.; Xu, F.; Ge, X.; Li, Y. *Biological Treatment of Organic Materials for Energy and Nutrients Production—Anaerobic Digestion and Composting*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 121–181, ISBN 9780128177105.

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