ORIGINAL RESEARCH

Performance enhancement of biological methanation with trickle bed reactors by liquid flow modulation

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Abstract
Experiments were carried out to investigate the influence of liquid flow modulation of trickle bed reactors (TBR) on biological hydrogen methanation (BHM). The modulation promises to improve the gas-liquid mass transfer and has already been demonstrated in trickle bed reactors of other fields of application. Therefore, the influence of four different circulation intervals with pauses from two to 1,440 min was investigated in TBR for BHM. The results showed that as pause intervals without sprinkling became longer, the methane content increased from 88.61 ± 1.58 vol-% at a circulation interval of 2 min to up to 97.19 ± 0.46 vol-% at a circulation interval of 1,440 min. The analysis of the process liquid indicated a stable biological process at any trial phase. This study demonstrated that the performance of TBR on BHM can be significantly improved by liquid flow modulation, thus significantly reducing operating costs.

KEYWORDS
biological methanation, hydrogen, liquid flow modulation, power-to-gas, renewable energy, trickle-bed-reactor

1 | INTRODUCTION

The volumetric productivity of biological hydrogen methanation (BHM) can be improved by enhancing the gas-liquid mass transfer (Seifert, Rittmann, & Herwig, 2014). Thus, over the past few years, trickle bed reactors (TBRs) have been investigated in order to improve BHM performance (Burkhardt, Koschack, & Busch, 2015; Strübing, Huber, Lebuhn, Drewes, & Koch, 2017; Ullrich et al., 2018).

Trickle bed reactor is one of the classical multiphase packed bed reactor configurations with extensive applications in petroleum industries including hydrocracking, hydrotreating and alkylation. TBRs are also commercially utilized in chemical industries for hydrogenation of aldehydes and reactive animation (Atta, Roy, Larachi, Deo, & Nigam, 2014). In biotechnology, these reactor systems are often used for enabling biological conversion of gaseous substrates under defined conditions, which are performed for multiple purposes. They are characterized by an efficient control of pH, temperature, moisture content and pressure (Ullrich et al., 2018). In biotechnological TBR, also known as biotrickling filters, the source gases pass through a biofilm immobilized on a packed bed, which is normally continuously irrigated with a nutrient solution (Quijano, Miguel-Romera, Bonilla-Morte, & Figueroa-Gonzalez, 2017). The reaction gases are initially absorbed in the trickling aqueous solution and subsequently converted in the fixed biofilm. The packed bed provides a large specific surface area and thus a large phase contact area, which enables high mass transfer rates (Burkhardt et al., 2015). Therefore, improved mass transport is achieved which increases the final productivity of the entire system. In contrast to several other reactor systems such as continuous stirred tank reactors (CSTR), fixed bed or bubble column reactors, the gaseous phase surrounds the packing...
material and the microbial community colonizing them completely. This allows for independent control of the superficial gas velocity (Strübing et al., 2017). However, the presence of a continuous water layer over the biofilm often entails a limited abatement performance for hydrophobic gases as a result of their poor gas-liquid mass transport (Quijano et al., 2017).

Another possibility to enhance the mass transfer from the gaseous to the liquid phase in such systems is to increase the operating pressure of the reactor (Klasson et al., 1990; Vega, Clausen, & Gaddy, 1990). According to Henry’s law, the amount of a dissolved gas in the liquid phase is proportional to its partial pressure in the gas phase. Pressurized TBRs were investigated in Ullrich et al. (2018), where the methane content of the TBR was increased by 34 vol-% with an increase in pressure from one to nine bar absolute.

Many studies have investigated the operating pressure of TBRs in order to increase the gas-liquid mass transfer, thus achieving higher performance. As with the BHM, high operating pressures are commonly used for this purpose (Wongkia, Suriye, Nonkhamwong, & Praserthdam, 2013).

However, recent studies are focusing on the periodic operation of TBRs (Liu & Mi, 2005). In general, TBRs operate under steady-state mode with constant feeding rates under a constant and often a low liquid flow rate (5–10 L m⁻³ reactor volume min⁻¹) (Quijano et al., 2017). Urseauu, Boelhouwer, Bosman, and Schroijen (2004) conclude that there is a poor interaction between the gas and the liquid. Many studies have successfully demonstrated that periodic operation improves TBR catalytic performance for many reactions (Banchero, Manna, Sicardi, & Ferri, 2004; Stradiotto, Hudgins, & Silveston, 1999; Turco et al., 2001; Urseau et al., 2004).

A common approach is a periodic liquid feed modulation with a continuous gas phase (Wongkia et al., 2013). In this case, a distinction is made between two different periodic operation types, commonly known as flow modulation strategies. In the mode of operation base-pulse, the liquid flow rate switches between a low level (base) and a high level (pulse). When the base liquid flow rate is set to zero, it is called an on-off mode. Using such an on-off mode, Liu and Mi (2005) were able to improve conversion and selectivity of hydrogenation of 2-ethylanthaquinone significantly compared with those under steady-state. Wongkia et al. (2013) investigated styrene hydrogenation in a TBR. Using periodic operation of the liquid, a maximum improvement of styrene conversion of 18% was observed.

Ayude, Cassanello, Martínez, and Haure (2005) also described the potential to enhance performance through better supply of reactants to the catalyst and improved fluid dynamics and catalyst wetting. Atta et al. (2014) assumed that periodic operation in a TBR would considerably enhance the mass transfer rate of the gaseous reactant, thus resulting in a higher solubility of the gaseous phase within the liquid. He also states that periodic liquid flow modulation can minimize liquid maldistribution in the TBR, which strongly affects reactor performance. Liu et al. (2009) demonstrated this fact while analysing the transient behaviours of the liquid holdup of an air kerosene system in a periodically operated TBR. Modulation of the liquid flow minimizes the possibilities of hot spot formation. An improved liquid distribution over the catalyst surface using periodic operation was mentioned by Liu and Mi (2005). Catalyst wettings are significantly higher for the periodic operation. In some operating states, a further advantage mentioned is a decrease in liquid film thickness due to drainage in the OFF phase of the on-off mode (Liu & Mi, 2005).

It is widely accepted that unsteady-state operation is becoming a promising intensified technological process and will be implemented on industrial TBRs in the future (Liu, Zhang, Wang, Zhang, & Mi, 2008).

However, the advantages of improved gas–liquid mass transfer by periodic circulation have not yet been investigated for biological TBR. In addition, to improve the conversion, the periodic operation can also reduce the energy consumption of the process. In this biological system, however, it is important to note that the process fluid carries not only the reaction gases, but also the nutrients for the microorganisms. Therefore, a liquid flow modulation should not affect the nutrient supply.

In order to specify this more precisely, various liquid flow modulation strategies were investigated in this study. The aim was to increase the conversion and improve the overall performance of BHM in trickle bed reactors, while maintaining a stable biological process by adequate nutrient supply. For this purpose, a continuous and automated experimental plant was developed and constructed at the University of Hohenheim. The evaluation of the system performance is based on important parameters like gas quality and methane formation rate.

## 2 | MATERIALS AND METHODS

### 2.1 | Experimental setup

As described in detail in Ullrich et al. (2018), the experimental plant was designed with three identical TBRs. The nutrient solution for the microorganisms was sprinkled over the trickle bed in countercurrent with the source gases carbon dioxide (CO₂) and hydrogen (H₂). The structure of the plant is shown as a piping and instrumentation diagram in Figure 1.

The reaction volume for the immobilization of the microorganisms amounts to a total of 14.5 L and consists
of a 13 L trickle bed in the gas phase, as well as a 1.5 L fixed bed in the liquid phase in the sump of the reactors. The remaining volume within the reactors was required for sprinkler and gas entry, which was placed between the fixed bed and the trickle bed.

The trickle bed had a height of 0.74 m with a total surface area of 11.193 m². The packing bed was made of filling elements HX09 from Christian Stöhr GmbH & Co. KG, Germany. The elements are made of high density polyethylene with a diameter of 9 mm and a length of 7 mm. They offer a specific area of 861 m²/m³. Together with the fixed bed in the sump, a surface area of 12.489 m² was available for colonization by microorganisms.

The pressure sensors 261AS from ABB Ltd., Switzerland were mounted on the top blind flange of the reactors. They have a measuring range between 0 and 10 bar absolute with a basic accuracy of 0.1% and are equipped with a gold-coated membrane for protection against aggressive media. The temperature sensor Easytemp TMR31 from Endress + Hauser Messtechnik GmbH + Co.KG., Germany, was attached to the bottom blind flange. This measured the temperature between the sump and the trickle bed of the reactors. The combined pH/redox electrodes Memosens CPS16D from the same manufacturer were installed in the reactor periphery.

The nutrients were supplied with the circulated process liquid. For this purpose, the product liquid of a continuous
two-stage anaerobic digestion experimental plant from Merkle et al. (2017) was used. According to Vintiloiu, Lemmer, Oechsner, and Jungbluth (2012) and Vintiloiu et al. (2013), this predigested process liquid is advantageous because it contains all essential nutrients for the methanogenic microorganisms and nearly no energy rich substances, such as acids and alcohols, that could affect the methane production of the reactors (Table 1).

A by-product of the methanation of hydrogen and carbon dioxide is water, which dilutes the nutrient solution over time. Thus, half of the process liquid needed to be replaced before starting a new modulation. For this purpose, the liquid of the filter was drained during the OFF time, which was half of the total liquid. The shut-off valves upstream and downstream of the filter allowed the liquid to be changed without pressure loss.

### 2.2 | Experimental procedure

The pilot plant had already been used for investigating different operating pressures prior to this study (Ullrich et al., 2018). Thus, the trickle bed was already covered with a biofilm at the beginning of the experiments, so that no separate start-up period was required.

To investigate the influence of the trickling interval on the gas–liquid mass transfer and thus the conversion of $\text{H}_2$ and $\text{CO}_2$ to $\text{CH}_4$, a method involving liquid flow modulation, commonly performed for trickle bed reactors in petrochemical applications, should be used (Banchero et al., 2004; Stradiotto et al., 1999; Turco et al., 2001; Urseanu et al., 2004). Various modulation strategies were examined for this purpose. Within a modulation, the amount and duration (ON) of the circulating liquid can be varied, as well as the intervals (OFF) between them. For the tests carried out in this study, the ON time (1 min) of the circulation and liquid flow rate ($4.1 \, \text{L hr}^{-1} \, \text{L reaction volume}^{-1}$) were kept constant for all modulations. Only the OFF times were varied.

At the beginning of the trial phase, steady-state liquid flow modulation with an ON time of 1 min and an OFF time of 2 min was used. As only one common pump is available for the circulation of the three reactors, this modulation represents the shortest possible interval. Furthermore, modulations with longer OFF times of 240, 480 and 1,440 min were investigated. The tests were carried out in the order 2—480—1440—240 min. This results in an effective “trickling time” of 8 hr/day and reactor in the first trial period which is reduced to 1 min/day and reactor in the last phase. Table 2 gives an overview of the implemented modulations and their specifications.

The modulations were carried out simultaneously in the three reactors for a duration between 130 and 144 hr each. For a clear representation, the results of the reactors were calculated as an arithmetic average.

The flowrates of the mass flow controllers were adjusted to 12 L/hr for $\text{H}_2$ and 3 L/hr for $\text{CO}_2$ for each reactor to achieve a stochiometric ratio. That means that according to the reaction equation (Equation 5), there must be a ratio of $\text{H}_2$ to $\text{CO}_2$ of 4:1 to form one molecule of methane and two molecules of liquid water. Due to the low inaccuracies of the $\text{H}_2$ and $\text{CO}_2$ mass flow controllers, the real quantities fed in were calculated using the results of the gas analysis and the He - tracer gas. Over the entire duration of the experiment, the operating temperature was set to 40°C and the pressure to 5 bar absolute.

The process liquid was sampled at the start and the end of each modulation. The content of volatile fatty acids and total alkalinity, the chemical oxygen demand, conductivity and salinity, as well as the ammonium concentration were measured from the untreated sample.

### 2.3 | Analytical

As described in Ullrich et al. (2018), the quality of the product-gases was analysed by a 3,000 L-Gaschromatograph from Inficon GmbH, Germany. The product gas amount was determined by injecting a defined quantity of tracer gas (Helium) to the gas stream. By analysing the gas proportions by gas chromatography, the amount of the product gas was calculated.

The volatile fatty acids in the liquid were analysed by a 2010plus gas chromatograph with AOC-20i Autoinjector from Shimadzu, Japan. The chemical oxygen demand (COD) was measured using the Hach Lange cuvette test

### TABLE 1 Nutrient composition of the process liquid

|   | Cu (mg/kg DM) | Ni (mg/kg DM) | Zn (mg/kg DM) | Fe (mg/kg DM) | B (mg/kg DM) | Co (mg/kg DM) | Mn (mg/kg DM) | Mo (mg/kg DM) | Se (mg/kg DM) | Al (mg/kg DM) | W (mg/kg DM) | As (mg/kg DM) |
|---|--------------|---------------|---------------|---------------|-------------|--------------|---------------|---------------|--------------|---------------|--------------|--------------|
|   | 4.8          | 13.0          | 156.0         | 1,768.4       | 29.7        | 2.5          | 303.5         | 3.9           | 1.2          | 147.9         | 0.9          | 1.1          |
| Cd (mg/kg DM) | Pb (mg/kg DM) | Sn (mg/kg DM) | V (mg/kg DM) | Cr (mg/kg DM) | Sb (mg/kg DM) | P (% of DM) | K (mg/kg DM) | Mg (mg/kg DM) | Na (mg/kg DM) | Ca (mg/kg DM) | S (mg/kg DM) |
| 0.1 | 0.9          | 0.3           | 0.5           | 1.8           | 0.3         | 1.3          | 12.7          | 0.7           | 0.5          | 1.5           | 0.5          |
the reactor volume.

The methane yield as a function of the produced methane and methane formation rate (MFR, Equation 1). It describes the A parameter for evaluating the reactor efficiency is the 2.4 AG, Switzerland.

Using an automatic titrator 785 DMP Titrino from Metrohm acids and total inorganic carbon (VFA/TIC) was analysed and salinity were determined. The ratio of volatile fatty (LCK014). By inserting the conductivity tube from an EC300 from VWR International GmbH into the liquid sample, taken from the filter of the reactor during the OFF time at the beginning and end of a test phase, the conductivity and salinity were determined. The ratio of volatile fatty acids and total inorganic carbon (VFA/TIC) was analysed using an automatic titrator 785 DMP Titrino from Metrohm AG, Switzerland.

2.4 | Calculations

A parameter for evaluating the reactor efficiency is the methane formation rate (MFR, Equation 1). It describes the methane yield as a function of the produced methane and the reactor volume. \( F_{V,CH_4,\text{out}} \) and \( F_{V,CH_4,\text{in}} \) is the volumetric flow rate in and out of the reactor (Götz et al., 2016).

In this study, the reaction volume \( V_R \) consists of the trickle-bed plus the fixed-bed zone and amounts to 14.5 L.

\[
\text{MFR} = \frac{F_{V,CH_4,\text{out}} - F_{V,CH_4,\text{in}}}{V_R} \left( \frac{m^3}{m^3d} \right) \tag{1}
\]

The gas hourly space velocity (GHSV) is another important parameter. It is a value for evaluating the incoming gases of a catalyst or a reactor. \( F_{V,G,\text{in}} \) of the GHSV is the volumetric flow rate at STP of the source gas without taking any inert gases into account (Götz et al., 2016).

\[
\text{GHSV} = \frac{F_{V,G,\text{in}}}{V_R} \left( \text{hr}^{-1} \right) \tag{2}
\]

Furthermore, the conversion \( X_i \) of both feed gases is defined in Equation 3. \( F_{n,\text{in}} \) is the incoming, and \( F_{n,\text{out}} \) is the outgoing \( H_2 \) or \( CO_2 \) in L/hr.

\[
X_i = \frac{F_{n,\text{in}} - F_{n,\text{out}}}{F_{n,\text{in}}} \times 100 \% \tag{3}
\]

The retention time (RT) describes the time the gases remain in the reactor. It was calculated as a function of the reaction volume \( (V_R) \) and the volumetric flow of the incoming gases \( F_{V,G,\text{in}} \).

\[
RT = \frac{V_R}{F_{V,G,\text{in}}} \left( \text{hr} \right) \tag{4}
\]

The statistical software “R Studio” was used for all calculations, as well as for the statistical analysis with the Kruskal–Wallis test and subsequently Tukey’s test \((p < 0.05)\).

3 | RESULTS AND DISCUSSION

3.1 | Operating parameters

The adjusted pressure was achieved with high constancy over the four modulations in all three reactors. After aggregating the data of the three reactors, the arithmetic average was calculated for each modulation. An overview of the results is presented in Table 3.

The operating pressure of the modulation experiments was set at 5 bar absolute to avoid a possible impairment of the results by low pH values. As shown in Ullrich et al. (2018), the pH value dropped to 6.34 ± 0.03 when the pressure was increased to 9 bar due to the improved solubility of the injected \( CO_2 \).

However, the concern about low pH levels was unfounded. As indicated in Table 2, the pH values varied between 7.31 ± 0.22 at modulation 2 and 7.44 ± 0.21 at modulation 480. A slight decrease in pH was observed with proceeding test duration, which can be explained by the dilution of the process liquid and thus a decrease of the buffer capacity. A similar behaviour was also observed in Strübing et al. (2017), especially with high gas feed rates and associated high metabolic water production. Overall, the pH value was demonstrated to be very stable in this study and varied only slightly within the optimal range of 6.5 and 8.5 for methanogenic microorganisms (Bassani, Kougiás, Treu, & Angelidaki, 2015).

The aimed mesophilic process temperature of 40°C was achieved with a high accuracy and was kept very constant—both between the experiments and the different reactors. A slight increase in temperature can be seen with progressive OFF times. For example, the average temperature for modulation 2 was 40.97 ± 0.18°C, which rose to 41.57 ± 0.10°C for modulation 1,440. Methanation follows the exothermic Sabatier reaction (Equation 5).

\[
CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \Delta H^0 = -165 \text{kJ/mol} \tag{5}
\]

Higher conversion rates at long OFF times may have led to a higher release of reaction energy, thus resulting in higher digester temperatures. Furthermore, the heat can no longer be dissipated as efficiently due to the long OFF time.

The gas flows were adjusted to an overstoichiometric ratio of \( CO_2 \). In other studies on biological methanation in TBR, the advantages of overstoichiometric ratios were mentioned. In Burkhardt et al. (2015), a complete conversion was achieved with a \( CO_2: H_2 \) ratio of 1:3.76 and in Strübing et al. (2017), ratios of 1:3.75–1:4 were used. Due

| Table 2 | The different modulation strategies with the set parameters examined in this study |
|---------|---------------------------------|
| Modulation strategy | 2 | 240 | 480 | 1,440 |
| Liquid flow [L hr⁻¹ 1 reaction volume⁻¹] | 4.1 | 4.1 | 4.1 | 4.1 |
| Circulation time: ON [min] | 1 | 1 | 1 | 1 |
| No circulation: OFF [min] | 2 | 240 | 480 | 1,440 |
to deviations of the mass flow controllers, the ratios were not completely identical between the experiments. There were fluctuations in the range from 1:3.89 to 1:3.93 between modulation 1,440 and 240. By that, the source gas ratio was kept quite stable compared to recently published experimental set-ups (Strübing et al., 2017).

### 3.2 Analysis of the process liquid

The process liquid was sampled at the beginning and the end of an experiment. The VFA/TIC fluctuated in a range of 0.19 ± 0.04 for modulation 480 and 0.27 ± 0.03 for modulation 240. The values were in a small range, and overall the VFA/TIC indicates a continuous stable methanation process (Merkle et al., 2017).

As already suspected during the discussion of the moderately declining pH values, a slightly decreasing TIC was measured, which indicates a dilution of the process liquid by metabolic water production. The largest reduction was observed in modulation 240. Here, the TIC decreased from 2,084 ± 85 mg CaCO₃ L⁻¹ at the beginning of the trial period to 1,795 ± 119 mg CaCO₃ L⁻¹ at the end of the same period.

At the beginning of modulation 480, a low acid concentration was measured in a single reactor. An acetic acid concentration of 0.12 ± 0.07 g/kg and a propionic acid concentration of 0.03 ± 0.002 g/kg was determined. These small acid concentrations were metabolized till the end of the trial period. An influence on the conversion or the product gas quality was not determined in this case. Further acid concentrations could not be measured in any trial period.

The salinity of the process liquid can also be regarded as stable, but at a high level. The lowest values were observed at 2.57 ± 0.06 ppt for modulation 2, and the highest at modulation 240 with 3.03 ± 0.15 ppt. Optimal areas for methanogenic microorganisms are in the range of 0.35–3.5 ppt (Chen, Cheng, & Creamer, 2008). Slightly larger fluctuations were observed in the COD. At modulation 240, the COD was 3.86 ± 0.23 g L⁻¹ O₂⁻¹, in modulation 480, values of 5.23 ± 0.35 g L⁻¹ O₂⁻¹ were detected. Overall, the data indicate high biological process stability throughout all experimental phases.

### 3.3 Performance parameters

The conversion rates of H₂ and CO₂ significantly increased with the modulations and longer OFF times. The conversion of H₂ was raised from 98.33 ± 0.01 to 99.67 ± 0.00% by extending the OFF time from 2 to 1,440 min. The conversion of CO₂ was also significantly improved and increased in the same modulation to 98.62 ± 0.00%. Although there was a slight increase between the modulations 240, 480 and 1,440, they are not statistically significant.

The increasing conversion of H₂ and CO₂ with an increase in OFF times is also reflected in the gas qualities. The highest gas quality was achieved in modulation 1,440. Compared to modulation 2, the content of H₂ in the product gas was reduced from 5.97 ± 1.69 vol-% to 1.29 ± 1.23 vol-% (Figure 2). The values of CO₂ were also significantly reduced from 5.18 ± 0.29 to 1.36 ± 0.32 vol-%.

During the entire duration of the experiment, the product gas contained a noticeably high amount of CO₂, reaching a level close to that of H₂. For a complete conversion of CO₂, however, a four times higher amount of H₂ is required according to Equation 5. Due to these so-called overstoichiometric injection of CO₂, higher conversion rates of hydrogen compared to the carbon source were
achieved, thus indicating that an exact gas ratio of 4:1 leads to higher overall conversion rates and methane contents. A recommended ratio of 1:3.76, as described in Burkhardt et al. (2015), cannot be confirmed in these experiments.

Similar to the decreasing contents of H₂ and CO₂ and the improved conversion rates, the share of CH₄ in the product gas increases in the course of the modulations. There were significant differences only between modulation 2 and modulations 240, 480 and 1,440. Modulations 240, 480 and 1,440 were not significantly different. The largest differences were observed between modulation 2 and 1,440, where the content of CH₄ increased from 88.61 ± 1.58 to 97.19 ± 0.46 vol-%. Thus, the periodic circulation in modulation 1,440 significantly increased the content of CH₄ by 10%.

With regard to the significance, it must be mentioned that the conversion rates of modulations 240, 480 and 1,440 are at a very high level. It is more difficult to achieve significant differences at these high levels than with low conversion rates.

In Figure 3, the direct influence of the process liquid sprinkling on the product gas quality is shown. The CH₄ content decreased and the H₂ and CO₂ content rose immediately after each circulation. After about 2 hr, the gas qualities returned to the previous level.

In modulations with longer OFF times, less gas peaks were found and thus smaller standard deviations were observed. The standard deviations for modulation 2 and modulation 1,440 were 1.58 and 0.46, respectively. By that, longer OFF times contribute to stable high methane contents in the product gas. The slightly larger peak between modulations 480 and 1,440 on day 3 was caused by the fluid change before each new modulation.

Due to the immediate change in circulation, an increased concentration of microorganisms can be excluded as a reason for the rapidly changing gas composition. This would require a longer acclimatization period of the microorganisms.

During the whole trial period, the performance of the three different laboratory scale reactors was very similar, which is indicated by the small standard deviations presented in Figure 2 and Table 3. The largest differences were observed in modulation 2 with small fluctuation ranges of a maximum of 1.3% between reactor 2 and 3. This demonstrates the high reliability and reproducibility of the gained data.

Numerous studies have already proven that high gas qualities are possible with TBR (Burkhardt et al., 2015; Rachbauer, Voitl, Bochmann, & Fuchs, 2016; Strübing et al., 2017). In these studies, methane contents of up to 98 vol-% were achieved. For alternative reactor concepts, methane contents higher than 90 vol-% (fixed-bed systems) (Alitalo, Niskanen, & Aura, 2015) and 85 vol-% (CSTR
systems) (Seifert et al., 2014) are reported. Compared to these results, the chosen set-up of this study led to very high conversion rates of the injected source gases. In this study, the MFR increased from $5.36 \pm 0.12 \text{ m}^3 \text{ m}^{-3} \text{ day}^{-1}$ for modulation 2 to $5.62 \pm 0.10 \text{ m}^3 \text{ m}^{-3} \text{ day}^{-1}$ for modulation 1,440. The differences between modulations 240, 480 and 1,440 were not significant. The MFR in this study had a maximum value of $5.62 \pm 0.10 \text{ m}^3 \text{ m}^{-3} \text{ day}^{-1}$, which is at a high level compared with similar studies.

Burkhardt et al. (2015) reached $1.49 \text{ m}^3 \text{ m}^{-3} \text{ day}^{-1}$ and Rachbauer et al. (2016) $1.9 \text{ m}^3 \text{ m}^{-3} \text{ day}^{-1}$ with methane contents of 98 and 96 vol-%, respectively. Pressures up to 9 bar absolute, an MFR of $4.28 \pm 0.26 \text{ m}^3 \text{ m}^{-3} \text{ day}^{-1}$, and a methane content of $86.51 \pm 0.49$ vol. % were achieved by Ullrich et al. (2018). Only Strübing et al. (2017) reported a methane content of $86.51 \pm 0.49$ vol. % which is at a high level compared with similar studies. Previous studies had maximum values of $88.61 \pm 1.58$ vol.-%.

No significant differences were found in the GHSV and the associated gas flow in the reactors, nor in retention time. Differences in MFR and conversion rates are therefore due to the liquid flow modulation. The tests have shown that by modulating the process liquid flow, the performance of TBR for the biological methanation of hydrogen can be significantly increased. The results are consistent with investigations regarding TBRs in other fields of application (Banchero et al., 2004; Stradiotto et al., 1999; Turco et al., 2001; Urseanu et al., 2004). In addition, this application offers a very simple way to save electrical energy in practice by reducing pumping activity which can help to make the biological methanation process with TBR more cost-efficient.

### 4 | CONCLUSION AND OUTLOOK

Liquid flow modulation in TBR has been shown to increase BHM performance in various experiments. For this purpose, the trickling was suspended for OFF times of 2, 240, 480 and 1,440 min. The analysis of the process liquid revealed that the biological process, which was kept stable during the experimental phase, was not negatively influenced by the modulation. The methane content of at least $88.61 \pm 1.58$ vol.-% at modulation 2 was significantly increased by up to $97.19 \pm 0.46$ vol.-% at modulation 1,440.

It should be mentioned, that the OFF times cannot be extended indefinitely. The microorganisms depend on a sufficient supply of nutrients, which are provided with the liquid. The maximum OFF time could not be identified in this study, but further research investigating this is encouraged. This OFF time is expected to depend on the amount of injected educt gas. In the context of ensuring nutrient supply, the influence of the dilution of the process liquid on the reactor performance is another important topic that is worthy of attention.

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### REFERENCES

Alitalo, A., Niskanen, M., & Aura, E. (2015). Biocatalytic methanation of hydrogen and carbon dioxide in a fixed bed bioreactor. Bioresource Technology, 196, 600–605. [https://doi.org/10.1016/j.biortech.2015.08.021](https://doi.org/10.1016/j.biortech.2015.08.021)

Atta, A., Roy, S., Larachi, F., Deo, K., & Nigam, P. (2014). Cyclic operation of trickling bed reactors: A review. Chemical Engineering Science, 115, 205–218. [https://doi.org/10.1016/j.chemosphere.2013.08.038](https://doi.org/10.1016/j.chemosphere.2013.08.038)

Ayude, M. A., Cassanello, M. C., Martínez, O. M., & Haure, P. M. (2005). Phenomenological approach to interpret the effect of liquid flow modulation in trickling bed reactors at the particle scale. Chemical Engineering Science, 60, 6262–6269. [https://doi.org/10.1016/j.ces.2005.03.019](https://doi.org/10.1016/j.ces.2005.03.019)

Bassani, I., Kougias, P. G., Treu, L., & Angelidaki, I. (2015). Biogas Upgrading via Hydrogenotrophic Methanogenesis in Two-Stage Continuous Stirred Tank Reactors at Mesophilic and Thermophilic Conditions. Environmental Science & Technology, 49, 12585–12593. [https://doi.org/10.1021/acs.est.5b03451](https://doi.org/10.1021/acs.est.5b03451)

Banchero, M., Manna, L., Sicardi, S., & Ferri, A. (2004). Experimental investigation of fast-mode liquid modulation in a trickle-bed reactor. Chemical Engineering Science, 59, 4149–4154. [https://doi.org/10.1016/j.ces.2004.03.048](https://doi.org/10.1016/j.ces.2004.03.048)

Burkhardt, M., Koschack, T., & Busch, G. (2015). Biocatalytic methanation of hydrogen and carbon dioxide in an anaerobic three-phase system. Bioresource Technology, 178, 330–333. [https://doi.org/10.1016/j.biortech.2014.08.023](https://doi.org/10.1016/j.biortech.2014.08.023)

Chen, Y., Cheng, J. J., & Creamer, K. S. (2008). Inhibition of anaerobic digestion process: A review. Bioresource Technology, 99, 4044–4064. [https://doi.org/10.1016/j.biortech.2007.01.057](https://doi.org/10.1016/j.biortech.2007.01.057)

Götz, M., Lefebvre, J., Mörs, F., McDaniel Koch, A., Graf, F., Bajohr, S., ... Kolb, T. (2016). Renewable Power-to-Gas: A technological and economic review. Renewable Energy, 85, 1371–1390. [https://doi.org/10.1016/j.renene.2015.07.066](https://doi.org/10.1016/j.renene.2015.07.066)

Klasson, K. T., Elmore, B. B., Vega, J. L., Ackerson, M. D., Clausen, E. C., & Gaddy, J. L. (1990). Biological production of liquid and gaseous fuels from synthesis gas. Applied Biochemistry and Biotechnology, 24–25, 857–873. [https://doi.org/10.1007/BF02920300](https://doi.org/10.1007/BF02920300)

Liu, G., Lan, J., Cao, Y., Huang, Z., Cheng, Z., & Mi, Z. (2009). New insights into transient behaviors of local liquid-holdup in periodically operated trickle-bed reactors using electrical capacitance tomography (ECT). Chemical Engineering Science, 64, 3329–3343. [https://doi.org/10.1016/j.ces.2009.04.008](https://doi.org/10.1016/j.ces.2009.04.008)

Liu, B. G., & Mi, Z. (2005). Hydrogenation of 2-ethylanthraquinones in a periodically operated trickle-bed reactor. Chemical
Engineering and Technology, 28, 857–862. https://doi.org/10.1002/eat.200407151
Liu, G., Zhang, X., Wang, L., Zhang, S., & Mi, Z. (2008). Unsteady-state operation of trickle-bed reactor for dicyclopentadiene hydrogenation. Chemical Engineering Science, 63, 4991–5002. https://doi.org/10.1016/j.ces.2008.03.008

Merkle, W., Baer, K., Lindner, J., Zielonka, S., Ortloff, F., Graf, F., ... Lemmer, A. (2017). Influence of pressures up to 50 bar on two-stage anaerobic digestion. Bioresource Technology, 232, 72–78. https://doi.org/10.1016/j.biortech.2017.02.013
Quijano, G., Miguel-Romera, J., Bonilla-Morte, L.-M., & Figueroa-Gonzalez, I. (2017). Two-phase partitioning bioreactors for treatment of volatile hydrocarbons. In K. Heimann, O. P. Karthikeyan, & S. S. Muthu (Eds.), Biodegradation and bioconversion of hydrocarbons (pp. 225–258). Singapore, Singapore: Springer Science+Business Media.

Rachbauer, L., Voitl, G., Bochmann, G., & Fuchs, W. (2016). Biological biogas upgrading capacity of a hydrogenotrophic community in a trickle-bed reactor. Applied Energy, 180, 483–490. https://doi.org/10.1016/j.apenergy.2016.07.109
Seifert, A. H., Rittmann, S., & Herwig, C. (2014). Analysis of process related factors to increase volumetric productivity and quality of biomethane with Methanotaerobacter marburgensis. Applied Energy, 132, 155–162. https://doi.org/10.1016/j.apenergy.2014.07.002

Stradiotto, D. A., Hudgins, R. R., & Silveston, P. L. (1999). Hydrogenation of crotonaldehyde under periodic flow interruption in a trickle bed. Chemical Engineering Science, 54, 2561–2568.

Strübing, D., Huber, B., Lebuhn, M., Drewes, J. E., & Koch, K. (2017). High performance biological methanation in a thermophilic anaerobic trickle bed reactor. Bioresource Technology, 245, 1176–1183. https://doi.org/10.1016/j.biortech.2017.08.088
Turco, F., Hudgins, R. R., Silveston, P. L., Sicardi, S., Manna, L., & Banchero, M. (2001). Modelling of trickle-bed reactors in foaming regime. Canadian Journal of Chemical Engineering, 79, 438–443.

Ullrich, T., Lindner, J., Bär, K., Mörs, F., Graf, F., & Lemmer, A. (2018). Influence of operating pressure on the biological hydrogen methanation in trickle-bed reactors. Bioresource Technology, 247, 7–13. https://doi.org/10.1016/j.biortech.2017.07.069
Urseanu, M. I., Boelhouwer, J. G., Bosman, H. J. M., & Schröijen, J. C. (2004). Induced pulse operation of high-pressure trickle bed reactors with organic liquids: Hydrodynamics and reaction study. Chemical Engineering and Processing, 43, 1411–1416. https://doi.org/10.1016/jcep.2003.09.010
Vega, J. L., Clausen, E. C., & Gaddy, J. L. (1990). Design of bioreactors for coal synthesis gas fermentations. Resources, Conservation and Recycling, 3, 149–160. https://doi.org/10.1016/0921-3449(90)90052-6

Vintiloiu, A., Boxriker, M., Lemmer, A., Oechsner, H., Jungbluth, T., Mathies, E., & Ramhold, D. (2013). Effect of ethylenediaminetetraacetic acid (EDTA) on the bioavailability of trace elements during anaerobic digestion. Chemical Engineering Journal, 223, 436–441. https://doi.org/10.1016/j.cej.2013.02.104
Vintiloiu, A., Lemmer, A., Oechsner, H., & Jungbluth, T. (2012). Mineral substances and macronutrients in the anaerobic conversion of biomass: An impact evaluation. Engineering in Life Sciences, 12(3), 287–294. https://doi.org/10.1002/elsc.201100159
Wongkia, A., Suriye, K., Nonkhamwong, A., & Praserthdam, P. (2013). Catalytic performance improvement of styrene hydrogenation in trickle bed reactor by using periodic operation. Korean Journal of Chemical Engineering, 30, 593–597. https://doi.org/10.1007/s11814-012-0220-z

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