

Optimizing the dosing and trickling of nutrient media for thermophilic biomethanation in a biotrickling filter

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Abstract

Ex-situ biomethanation in a biotrickling filter is being developed as a robust technology for the conversion of CO₂ to CH₄ using H₂ generated from renewable power. The technology uses hydrogenotrophic methanogens in a biofilm as the catalyst and the optimum supply of nutrients in the biofilm is imperative for stable and long-term operation. In this study, essential nutrients for the methanogens in the biotrickling filter were highlighted along with a systemic investigation of the nutrient supply methods. The results showed that ammonium and iron were the critical nutrients with a minimum required concentration of 0.3 g/L and 1.5 mg/L, respectively. Furthermore, thoroughly wetting the biofilm with nutrient media, either using flooding or trickling at a high-rate, was needed to maintain an active biofilm; although, these methods temporarily reduce the conversion for a duration of 18 to 24 h due to the formation of the thicker water film.

Keywords: *biomethanation, biogas, hydrogenotrophic methanogens, nutrients, power-to-methane*

1 Introduction

Power-to-methane (PtM) is a potential solution for the storage of excess renewable power [1] and it is a source of low carbon gaseous fuel [2]. The interest in PtM is supported by the fact that the product, methane (CH_4), can be utilized in the existing natural gas infrastructure. For example, the EU has a network of approx. 2 million km of transmission and distribution with 800 TWh of underground storage for natural gas [2]. PtM can be applied for the conversion of industrial and/or biogenic CO_2 to CH_4 . Overall, application of PtM can integrate the renewable power grid with biomethane/natural gas grid, which will offer flexibility to the electricity grid while aiding decarbonization of other sectors [3]. It is estimated that by 2050 about 150 TWh (14 bcm natural gas equivalent) of PtM could be produced in the EU using biogenic CO_2 captured from biogas plants combined with locally produced H_2 using electricity from solar and wind power [4]. The application of PtM at a biogas plant is also a substitute for the conventional biogas upgrading process, where CO_2 is removed from the biogas to increase its heating value. Whereas, using PtM the CO_2 is utilized to produce CH_4 that increases the heating value and the overall CH_4 output from biogas plant.

Several studies have shown the ex-situ biomethanation using biotrickling filter (BTF) as a feasible technology for PtM and for the biogas upgrading [5–8]. The BTF is a 3 phase reactor where the HM are grown over a packing material as biofilm, the gaseous substrates (H_2 and CO_2) pass over the biofilm, and the liquid nutrient media is trickled over the packed bed to supply the nutrients. The solubility of H_2 is approx. 40 times lower than CO_2 and the overall process is mass transfer limited [9]. The arrangement of HM over a packing material offers a relatively large surface area for the mass transfer of gaseous substrates that results in higher mass transfer rates. The main advantage of BTF is the relatively higher volumetric rate of CH_4 production as compared to the other biomethanation technologies. For example, CH_4 production rate of $15.4 \text{ Nm}^3/\text{m}^3 \text{ d}$ was achieved using a lab scale BTF [10] as compared to $3.7 \text{ Nm}^3/\text{m}^3 \text{ d}$ using CSTR [11] and $0.25 \text{ Nm}^3/\text{m}^3 \text{ d}$ using upflow reactor [12]. In addition, the BTF does not require stirring or gas recirculation and hence offers a lower operating cost. The BTF technology can also be applied with other sources of CO_2 , e.g. for biomethanation of syngas [13].

In BTF the conversion of CO_2 and H_2 to CH_4 is carried out by the hydrogenotrophic methanogens (HM), a class of anaerobic archaea found in the anaerobic digester for the biogas production. The HM are enriched and immobilized on a packing material in the form of biofilm and the substrate gases pass over it. The optimal supply of the nutrients is essential for the continuous operation of BTF because

the methanogens are dependent on their availability. Major elements found in the methanogenic microorganism are C, H, N, Na, K, S, P, Ca, and trace elements are Fe, Ni, Co, Mn, Zn, Cu, and Mo [14]. Central to the hydrogenotrophic methanogenesis pathway are enzyme complexes that catalyze redox reactions, and these enzymes contain transition metals as cofactors for electron transport or as catalytic centers at active sites. Important transition metals for methanogenic archaea are Fe, Ni, Co, Mn, and Zn and low bioavailability of transition metals limits the methanogenesis in pure and mixed cultures [15, 16]. The depletion of trace metals results in process imbalances because they are essential in enzyme complexes [17]. Specifically, for the hydrogenotrophic methanogenesis, the hydrogenases are Ni-Fe enzymes that oxidize H_2 and reduce ferredoxin (coenzyme F_{420}) [18]. These energy converting hydrogenases are abundant in Fe and contain a cluster of Fe_4S_4 with a Ni-Fe active site. For example, the membrane-associated hydrogenases contain three Fe_4S_4 clusters and a Ni-Fe active site [14], and can contain additional polyferredoxin subunits with 6, 10, or 14 Fe_4S_4 clusters and a Ni-Fe active site [19]. Another type of hydrogenase contains four Fe_4S_4 clusters and a Ni-Fe active site [20]. Physiological studies of pure cultures have shown that optimal metal concentrations for microbial metabolism are orders of magnitude higher than in situ concentrations [16]. In the case of biofilm reactors, such as BTF, the nutrient concentration required could be higher due to the diffusion resistance in the water and biofilm. In addition, for the biofilm reactors the supply method of the nutrients over the packing materials plays a vital role.

The availability of nutrients is needed for the stability of anaerobic digester for biogas production which is operated with energy crops, animal excreta, crop residues, organic fraction of municipal solid wastes or any other type of organic waste [21], and have been studied in detail [22, 23]. As compared to the anaerobic digestion, the substrate for the ex-situ biomethanation in BTF is simple, i.e. H_2 and CO_2 , hence nutrients supplementation is more essential. However, to the best of our knowledge, analytical investigation of nutrient consumption and the analysis of nutrient dosing and supply methods have not been carried out for BTF, specifically for the long-term continuous operation of the reactor. In this study, an optimization of the nutrients dosing and supply method was studied for stable operation of ex-situ biomethanation in a BTF. Essential nutrients were identified along with their minimum concentration levels, followed by a systematic approach to find the effective method of supplying these nutrients. The dosing method relates to the frequency of supplementation of the nutrients in the nutrient media sump and the supply method relates to the method of trickling the nutrient media over the biofilm in the BTF. After the optimization of the nutrient dosing and supply methods, the maximization of methane production was investigated.

2 Materials and Methods

2.1 Experimental setup

The schematic layout of the BTF reactor and the connections to ancillary equipment are shown in Figure 1. The reactor body was built using a clear polyvinyl chloride pipe. The inner diameter was 5.4 cm, packed length was 22 cm, working volume (V_r) was 503.8 mL, and media sump volume (V_s) was 400 mL. The reactor had a heating jacket that was made by wrapping a silicon tube (6.4 mm inner diameter) around the whole length of the reactor. On top of the heating jacket, a layer of thermal foam insulation was wrapped. Water at 57 °C was circulated from a water bath in the silicon tube to maintain thermophilic conditions in the reactor. The reactor was packed with finned Raschig rings made of polyethylene and had the size of 7 mm x 10 mm (PE08, Tongxiang Small Boss Special Plastic Products Ltd. (<http://www.smallboss.com/>)). One piece of the packing materials had a vendor quoted surface area of 3500 m²/m³. The bed void fraction of the packing material was measured to be 76%.

The feed gas used was a mix of N₂, CO₂, and H₂. The inlet flowrate of these gas components was controlled using thermal conductivity-based mass flow controllers (EL-FLOW Select series, Bronkhorst®).

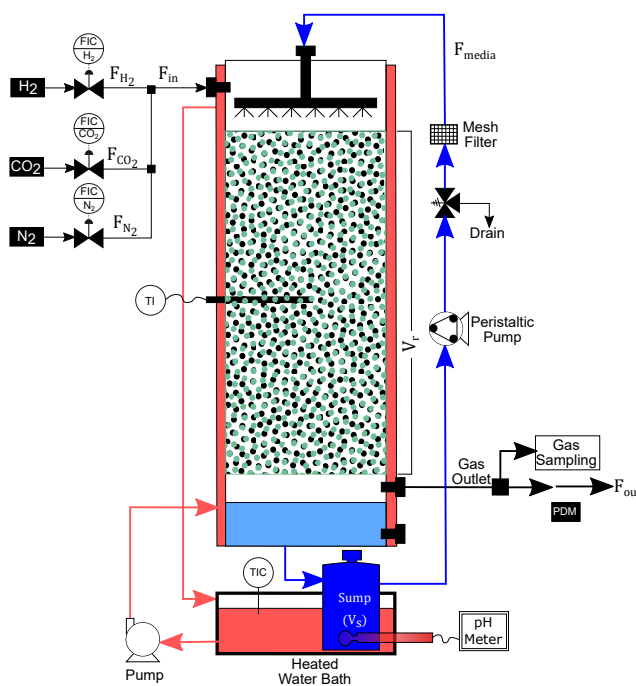


Figure 1: Schematic diagram of biotrickling filter reactor. FIC—flow indicator controller, TIC—temperature indicator controller, TI—temperature indicator, PDM—positive displacement meter.

Nutrient media was trickled from the sump to the top of the reactor using a peristaltic pump (Watson Marlow Qdos30 Universal Pump). A 125-micron mesh filter was installed in the media line connecting the peristaltic pump and the reactor. The filter stops the larger particle size solids from entering the reactor, which was the modification made after the clogging of the BTF reactor in an earlier study [24]. The filter was cleaned regularly. A relief valve with a set point of 100 mbar was installed before the filter. The relief valve provided safety in case the peristaltic pump was running, and the filter got clogged. The pH in the nutrient media sump was measured using a digital pH meter with the probe (INTELLICAL PHC735, HACH Lange) mounted in the sump. The outlet flowrate of the gas was measured using a positive displacement type gas flowmeter (BPC[®] μ Flow, BPC Instruments AB, Sweden).

2.2 Nutrient media

Pasteurized cow manure (PCM) was used as the nutrient media. The use of PCM has been validated as an effective nutrient media in the earlier study [8], however, the presence of solids in PCM led to eventual clogging of the BTF, as reported in [24]. In this study, an improved method of pretreating the manure was adopted that consisted of the following steps: (i) coarse sieving the cow manure to remove large solids and fibers, (ii) filtering through 500 μ m sieve, (iii) centrifugation at 8000 rpm for 10 min, (iv) filtering the supernatant through 125 μ m sieve, (v) and lastly heating the filtrate from 125 μ m sieve till 70 °C for 1 hr. Two different batches of PCM were prepared and their analysis is given in Table 1. PCM Batch 1 was used from the start of reactor operation till day 280 and PCM Batch 2 was used afterward till day 450.

2.3 Inoculation

The reactor was started using the direct inoculation methods as was reported in the earlier study [25]. Mixed anaerobic culture was used as inoculum that was obtained from the primary digester of Nature Energy Midtfyn biogas plant, Denmark. The inoculum was coarsely sieved to remove large solids and straw, afterwards, it was filtered through 125 μ m sieve. The filtered inoculum was degassed for one week at 55 °C in an incubator. The analysis of the filtered and degassed inoculum is given in Table 1.

2.4 Analytical methods

Gas samples were collected in triplicates at the gas outlet of the reactor in 5.9 ml vacuum vials (Exetainer[®] Evacuated Flat Bottom Vial). The composition of H₂, CO₂, N₂, and CH₄ was analyzed using gas chromatography (GC, 7890A, Agilent Technologies, Santa Clara, CA, USA) equipped with a thermal conductivity detector and a fused silica capillary column (Carboxen[®] 1010 PLOT, 30 m \times 0.53 mm). The

Table 1: Composition of the pasteurized cow manure (PCM) and inoculum.

Parameter	PCM Batch 1	PCM Batch 2	Inoculum
Total solids (TS, g/100g)	2.27 ± 0.01	3.08 ± 0.01	4.18 ± 0.14
Volatile solids (g/100g-TS)	72.7 ± 0.30	68.7 ± 0.58	27.4 ± 0.01
pH	7.80	7.86	7.75
<i>Volatile fatty acids (VFA)</i>			
Acetate (g/L)	1.04 ± 0.17	3.32 ± 0.30	0.77 ± 0.002
Propionate (g/L)	0.44 ± 0.03	1.59 ± 0.0	0.42 ± 0.00
Butyrate (g/L)	0.83 ± 0.05	0.28 ± 0.01	0.37 ± 0.003
Valerate (g/L)	0.76 ± 0.02	0.41 ± 0.02	0.39 ± 0.003
<i>Nutrients</i>			
Ammonium (NH ₄ ⁺ , mg/L)	1,771.1 ± 5.3	3,638.6 ± 69.9	3,091.0 ± 15.8
Total nitrogen (TN, mg/L)	2,923.2 ± 8.2	N/A	4,436.9 ± 8.2
Phosphate (PO ₄ ³⁻ , mg/L)	3,425.4 ± 476.8	1,547.8 ± 300.9	5,344.4 ± 266.6
Potassium (K ⁺ , mg/L)	2,137.3 ± 307.6	3,888.6 ± 209.1	2,288.8 ± 80.9
Fe (μg/L)	3,741.6 ± 11.1	13,082.4 ± 334.7	5,415.7 ± 828.9
Co (μg/L)	210.4 ± 26.0	N/A	84.5 ± 11.9
Ni (μg/L)	104.8 ± 3.1	247.1 ± 38.0	126.9 ± 5.1
Mn (μg/L)	628.8 ± 4.7	665.7 ± 295.4	606.3 ± 16.3

temperature of the oven holding the column was maintained at 35 °C with a holding time of 4 min, followed by a ramp of 25 °C/min up to 225 °C, and then maintained with a holding time of 2 min. Ar was used as the carrier gas and certified gas mix standards from Mikrolab Aarhus A/S were used for the calibration of GC.

Liquid samples were collected from the nutrient media sump for the volatile fatty acids (VFA) and nutrient analysis. The nutrient analysis included NH₄⁺, total nitrogen (TN), PO₄³⁻, K⁺, and trace metals Fe, Ni, Co, and Mn. The VFA concentration was measured using GC (7890B, Agilent Technologies, Santa Clara, CA, USA) equipped with a flame ionization detector (FID) and a polyethylene glycol column (HP-INNOWax, Agilent Technologies, Santa Clara, CA, USA; 30 m × 0.25 mm × 0.25 μm). Samples for the VFA analysis were pretreated before the analysis, where 0.10 mL of phosphoric acid (85 wt %) and 0.5 ml of DI water were added with 0.5 mL of the sample. After that, the samples were centrifuged for 15 min (Eppendorf mini Spin), filtered through a 0.5 μm cellulose filter into GC vials, and then injected into the GC. NH₄⁺, TN, PO₄³⁻, and K⁺ were measured using a spectrophotometer and HACH Lange LCK cuvette test system (LCK-303 NH₄⁺, LCK-338 TN, LCK-049 PO₄³⁻, and LCK-228 K⁺). Before the analysis samples were diluted 10-30 times to meet the measuring range of the LCK cuvette. Trace metals were measured by atomic absorption spectrometry equipped with a graphite tube atomizer (AAS, Agilent AA-200 series graphite furnace atomic absorption spectrometer, Agilent Technologies, Santa Clara, CA). AAS was calibrated using standard solutions from Agilent

and hollow cathode lamp also from Agilent were used for each of the metals, Fe, Ni, Co, and Mn.

2.5 Performance parameters

Gas retention time (GRT) was calculated based on the total gas flowrate at the inlet of the reactor and empty bed, as shown in Eq. 1. Here, V_r is the empty packed bed volume and F_{H_2} , F_{CO_2} , and F_{N_2} are the inlet flowrate of the gas components H_2 , CO_2 , and N_2 , respectively, in NmL/min.

$$GRT = \frac{V_r}{F_{H_2} + F_{CO_2} + F_{N_2}} \quad (1)$$

To analyze the reactor performance in terms of methane production, specific methane production capacity (PC, $Nm^3/m^3 d$) was calculated as shown in Eq. 2. Here, F_{out} (NmL/min) is the total gas flowrate at the reactor outlet and C_{CH_4} is the CH_4 composition at the reactor outlet.

$$PC = \frac{1440 F_{out} C_{CH_4}}{V_r} \quad (2)$$

To analyze the conversion of H_2 removal efficiency (RE, %) was calculated, as shown in Eq. 3. Here, C_{H_2} is the H_2 composition at the reactor outlet

$$RE = \frac{F_{H_2} - F_{out} C_{H_2}}{F_{H_2}} 100 \quad (3)$$

2.6 Startup and operating procedures

Details about the input parameters and experimental trials conducted are given in Table 2. The reactor was started using the direct inoculation methods as outlined in [25]. A mix of H_2 , CO_2 , and N_2 was used as the inlet gas to the reactors. N_2 was added in the inlet gas to simulate the feed gas as biogas, where N_2 asserts an equivalent partial pressure in the feed gas as that of CH_4 in the case of a biogas feed. However, during the startup and enrichment period, only H_2 and CO_2 were fed as inlet gas to the reactors. This enables a higher partial pressure of substrate H_2 and CO_2 that assists the enrichment and development of biofilm in the BTF reactors. After the startup period, GRT reduction trials were conducted, where the objective was the incremental increase in the gas feed flowrate and in turn to maximize the PC. After that, the nutrient consumption and supply trials were conducted. Here a distinction needs to be made, the term nutrient dosing is used for the addition and/or supplementation of the nutrients in the nutrient media sump to maintain the concentration of the essential nutrients in the sump. During the nutrient consumption trials the concentrations of the nutrients in the sump were measured, and their consumption was recorded over time. The term nutrient supply

Table 2: Set of experimental trials with details of feed gas flowrate and gas retention time (GRT).

Trial description	Days	Feed gas flowrate	GRT (min)
		H ₂ : CO ₂ : N ₂ (all values in NmL/min)	
Startup and enrichment	0–7	4.0:1.11:0	98.6
GRT Reduction trial	7–64	4.0:1.11:1.0	82.5
	65–85	5.24:1.34:2.0	59.2
	86–115	12.7:3.4:3.5	25.7
	116–281	8.0:1.66:2.0	43.2
Nutrient dosing trial	282–303	12.7:3.4:3.5	25.7
Nutrient supply method trial	304–408	12.7:3.4:3.5	25.7
Biomethanation trial	409–436	16:4.2:0	24.9
	437–450	24:6.22:0	16.7

refers to the method of supplying the media over the packed bed. Three nutrient supply methods were tested, namely, continuous trickling at the top, flushing, and flooding. Flushing was defined as trickling at 400 mL/min (flux 10.5 m³/m² h) for 3 min, a method of a relatively high rate of trickling to wet a larger fraction of the packing. Flooding was the method of filling the whole reactor with the nutrient media till the top of the packing, the nutrient media was completely drained immediately afterward.

3 Results and Discussions

3.1 Enrichment and GRT reduction trail

The reactor started producing CH₄ on the second day and on day 5 its concentration reached a maximum value of 28.5 mole% (C_{CH_4} at the reactor outlet. This showed that the enrichment of the hydrogenotrophic methanogens has started. After that N₂ feed to the reactor was started along with the start of GRT reduction trial. The results of the performance parameters are shown in Figure 2. In the first step, the GRT was 82.5 min and the H₂ concentration at the outlet kept decreasing indicating increased activity of the hydrogenotrophic methanogens. From day 22 there was an almost complete conversion of H₂, this shows that the 7 days of enrichment period was insufficient, and it took 22 days for the development of sufficient biofilm that resulted in the complete conversion of H₂. These results are in agreement with the direct inoculation method reported in [25], where a rapid increase in CH₄ was observed during the first 10 days and a steady production was achieved after 25 days. From day 22 onwards the conversion remained stable with an average PC of 1.7 Nm³/m³ d and average $C_{N_2+CH_4}$ of 87.7%. On day 65 the GRT was decreased to 59.2 min, the reactor performance remained stable at

this trial with an average PC of $3.65 \text{ Nm}^3/\text{m}^3 \text{ d}$ and average $C_{\text{N}_2+\text{CH}_4}$ of 94.2%. The outlet gas quality was improved during this period as the feed gas ratios were adjusted to reduce the unconverted CO_2 at the reactor outlet. During days 86 to 115 the feed gas flowrate was further increased and GRT was set at 25.7 min. The PC increased to $6.7 \text{ Nm}^3/\text{m}^3 \text{ d}$ initially, however, there was an incomplete conversion of H_2 . The C_{H_2} at the reactor outlet kept increasing afterward, Figure 1b, which showed that the activity of the hydrogenotrophic methanogens was decreasing. The average PC achieved during this period was $5.37 \text{ Nm}^3/\text{m}^3 \text{ d}$. As seen in Figure 2c, the pH of the nutrient media sump was within the normal operating range (< 8.5) and the VFA concentration was also insignificant ($< 0.1 \text{ mg/L}$). The temperature of the reactor was also maintained at an average value of 52°C during this period. Before the start of the trial at GRT 25.7 min, nutrient media was added two times to maintain the liquid level in the media sump: 350 mL on day 59 and 200 mL on day 79. The liquid level decreases due to the periodic cleaning of the external mesh filter. On day 109, 150 mL of nutrient media was added that relatively improved the H_2 conversion, and C_{H_2} decreased from 42% to 35%, however, this effect was short-lived and the C_{H_2} increased again to $< 40\%$ on day 114.

The objective of the GRT reduction trial was to find the limits for stable conversion and maximum PC. During this trial the GRT was reduced stepwise and it showed that the supply of the nutrient could be the bottleneck in increasing the PC and maintaining the quality of the upgraded biogas.

3.2 Estimation of nutrient limitation

From day 116 to 281 nutrient limitation trials were conducted, the objective was to find whether the trickling or supply method is the limiting factor or the concentration level of the nutrients in the media sump are the limiting factor. To stabilize the reactor the gas feed flowrate to the reactor was reduced and GRT was increased from 25.7 min to 43.2 min. This temporality improved the H_2 conversion but overall, the C_{H_2} kept increasing at the outlet of the reactor, as shown in Figures 2a and 2b.

3.2.1 Nutrient supply method

The nutrient media was trickled continuously from the top of the reactor at a flowrate of 10 mL/min (flux $0.262 \text{ m}^3/\text{m}^2 \text{ h}$). It might be possible that there was channeling due to which only a limited area of the packing was getting the nutrient supply. To investigate this limitation flushing trials were conducted, where nutrient media was trickled at a high flowrate of 400 mL/min (flux $10.5 \text{ m}^3/\text{m}^2 \text{ h}$) for 3 mins. The idea was to disturb the channeling and to enable the nutrient supply to a wider section of the packing. On day 140 the reactor was flushed, as can be seen in Figure 2b this resulted in decreasing the C_{H_2} from 32% to 19%. However, this improvement in conversion was short-lived and C_{H_2} increased again. This indicated that channeling might be a factor and the nutrient supply could

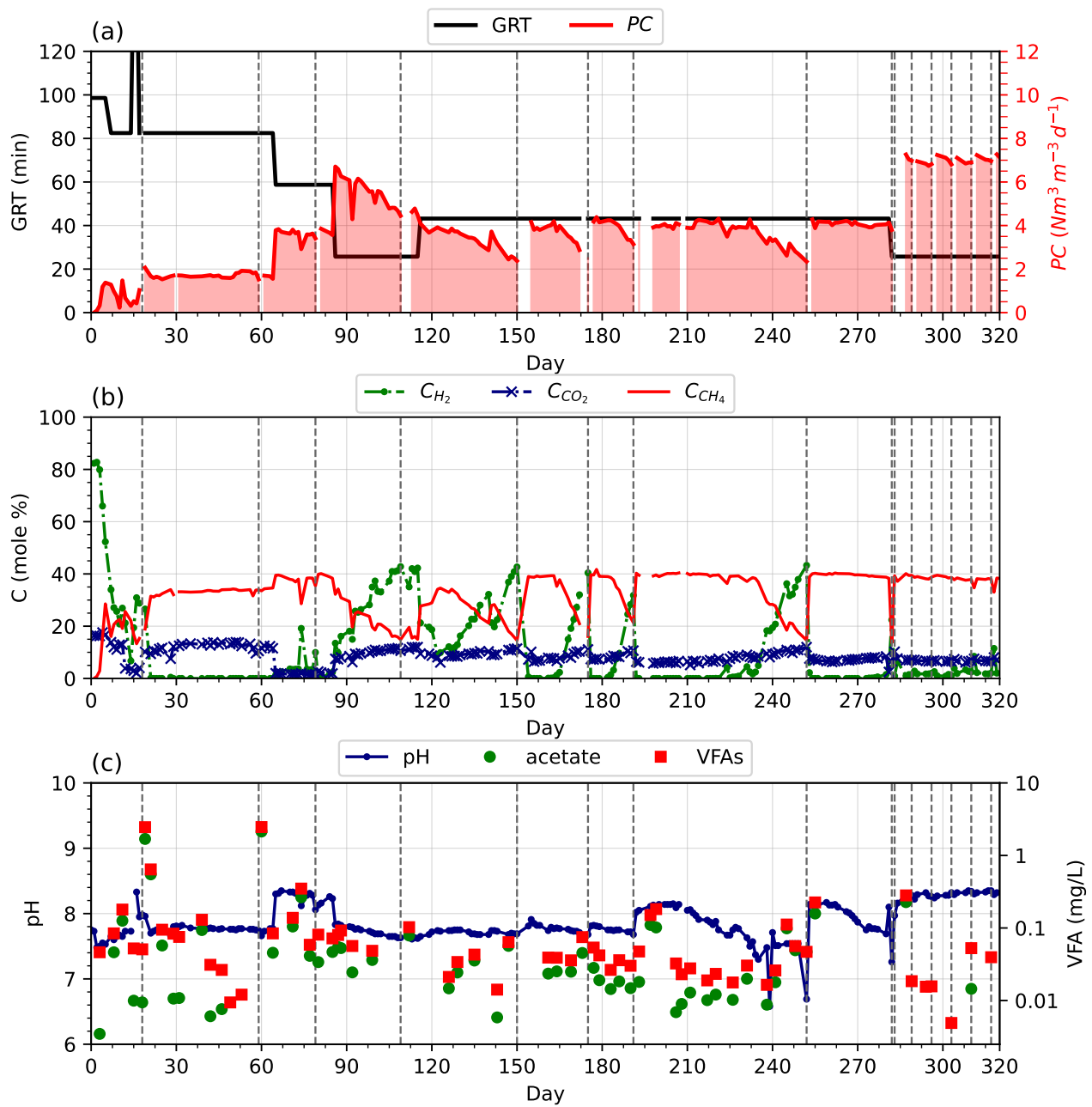


Figure 2: Figure showing the overall performance of the reactor during the GRT reduction and nutrient consumption trials. (a) GRT (min) — gas retention time, PC ($\text{Nm}^3/\text{m}^3 \text{ d}^{-1}$) — specific CH_4 production capacity. (b) C_{H_2} (mole%) — H_2 gas composition at the reactor outlet, C_{CO_2} (mole%) — CO_2 gas composition at the reactor outlet, and $C_{\text{N}_2+\text{CH}_4}$ — sum of N_2 and CH_4 composition at the reactor outlet, as an indicator of the outlet gas quality. (c) VFA (mg/L)—total volatile fatty acids. Vertical dashed lines indicate the events of nutrient media addition in the nutrient media sump.

be improved by routinely flushing the reactor. Hence, from day 150 to 190 the reactor was flushed every second day. During this the fresh media was added on days 150 and 175 with the following

procedure: 100 mL of was removed and 200 mL of the fresh media was added in the sump. As can be seen in Figure 2b, the H_2 conversion improved significantly after media addition on days 150 and 175, the C_{H_2} reduced to almost 0. However, the C_{H_2} remained stable for approx. 10 days and afterward it started increasing again. The routine of flushing the reactor every second day was carried out during this period ensured supply over a wider fraction of the packing. Considering this, the decrease in conversion showed that the concentration of nutrients could have decreased over time that resulted in lowering the activity of methanogens. Hence, the concentration levels of the nutrients were measured over time.

3.2.2 Critical nutrients

From day 191 to 281 nutrient concentrations were routinely measured to identify the essential nutrients and to estimate the minimum or critical concentration of these nutrients. The flushing routine was changed from once every second day to once every week. The media sump was cleaned and refilled twice during this period. First, on day 191 the media sump was cleaned and refilled with a fresh batch of media. The feed gas flowrate and all other parameters were kept the same. From day 211 the concentrations of NH_4^+ , K^+ , PO_4^{3-} , Fe, Ni, Co, and Mn were measured routinely, the results are shown in Figure 3. As can be seen in Figure 3, right after the media replacement activity on day 191, there was an almost complete conversion of H_2 , and it remained stable till day 224. C_{H_2} started increasing afterward and reached 43% by day 252. During this period, i.e. day 211 to 228, there was a relative decrease in the concentration of NH_4^+ and Fe. During these 15 days, the concentration of NH_4^+ reduced by 95% from 0.601 g/L on day 211 to 0.032 g/L on day 224 and Fe concentration dropped from 2.549 mg/L to 1.306 mg/L, a 48% change. On day 252 the media sump and media line filter were cleaned for the second time and 300 mL of the nutrient media mixed with 150 mL of deionized water were added to the sump. H_2 conversion improved after the media addition and remained stable till day 280. Again, NH_4^+ and Fe were the two nutrients with a significant decrease in the concentration level; NH_4^+ concentration dropped from 0.634 g/L to 0.002 mg/L on day 280, a drop of 99%, and Fe concentration dropped from 3.971 mg/L to 0.842 mg/L, a drop of 79%. The concentrations of other measured nutrients remained relatively unchanged, which indicated that the concentration of NH_4^+ and Fe could be the significant parameter for the methanogens in BTF. However, this does not mean that other trace metals are not essential; their significance for the methanogens and for the overall anaerobic digestion process have been reviewed in detail [16, 21, 26].

In this study, the critical level of NH_4^+ and Fe was estimated as a minimum concentration below which the activity of the hydrogenotrophic methanogenesis starts getting affected. For NH_4^+ and Fe, the

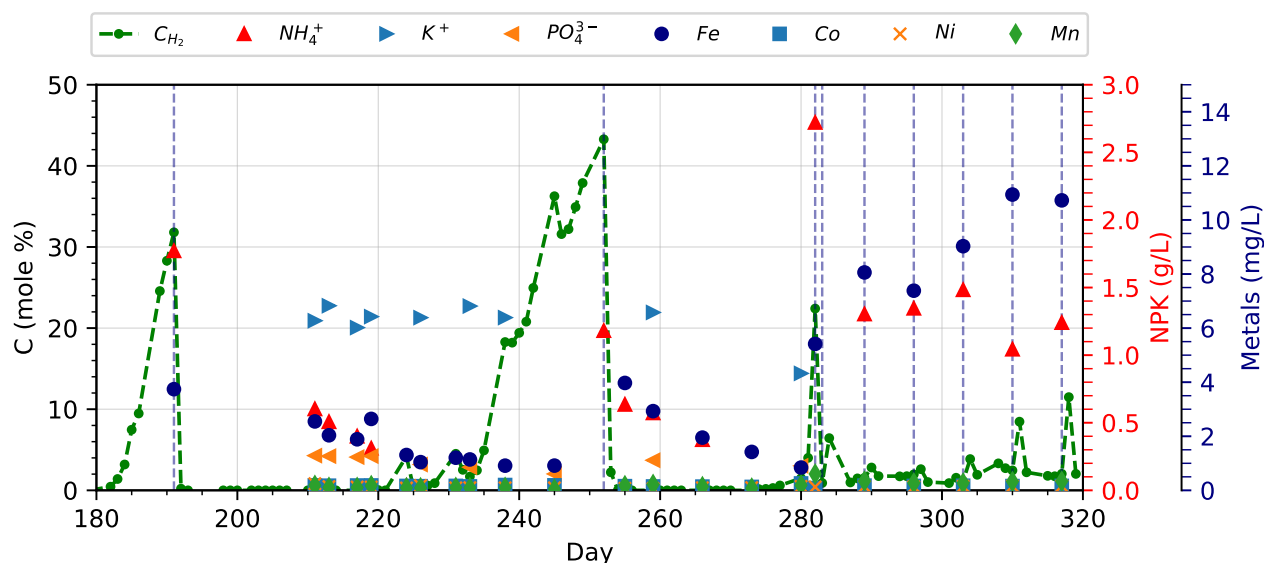


Figure 3: Nutrient composition in the nutrient media sump of the reactor. C_{H_2} (mole%) — H_2 gas composition at the reactor outlet, NPK – stands for nitrogen (NH_4^+), phosphorous (PO_4^{3-}), and potassium (K^+).

critical levels were estimated as 0.3 g/L and 1.5 mg/L, respectively. Dupnock and Deshusses, (2019) used artificial nutrient media in their study for BTF and reported similar values, where NH_4^+ and Fe concentrations higher than 1 g/L and 2 mg/L, respectively were reported as optimal. They reported a 41% increase in PC after the NH_4^+ and Fe concentrations in the nutrient media were optimized. For wastewater treatment by an anaerobic digester, a minimum requirement of Fe was estimated as 1.9 mg/L [15].

3.3 Optimizing the nutrient supply method

As was shown in section 3.2.1, the flushing of the reactor increased the H_2 conversion which indicated that the method of supplying the nutrients over the packing of the BTF has a significant effect on the conversion. An effective nutrient supply method ensures the nutrients supply to a wider section of the packing material that enables a larger active biofilm area. In this section results from the systemic investigation of three different methods of nutrient supply in a BTF setup are reported. The three options for the nutrient supply method were continuous trickling, flushing, and flooding. The term flushing is defined as a high rate of trickling for a short while and the term flooding refers to the method of filling the column with media such that all the packing is submerged. The feed gas flowrate had to be stopped during the flooding activity. The following set of trials were conducted: (i) continuous trickling at different flowrates, (ii) flushing with continuous trickling, (iii) flushing with no trickling, (iv) flooding with continuous trickling, and (v) flooding with no trickling. The routine of

Table 3: Effect of continuous nutrient media trickling flowrate on the BTF performance.

Days	Flowrate of Trickling (mL/min)	Liquid Flux ($\text{m}^3/\text{m}^2 \text{ h}$)	GRT (min)	Average C_{H_2} (mole %)	Average H_2 RE (%)	Average PC ($\text{Nm}^3/\text{m}^3 \text{ d}$)
282 - 302	10	0.262	50.41	1.67	99.15	7.0
303 - 310	30	0.786	16.8	2.57	98.6	6.91
311 - 317	60	1.572	8.4	3.35	98.16	7.06
318 - 324	90	2.358	5.6	4.32	97.54	6.90
325 - 331	120	3.144	4.2	12.69	93.02	6.30
332 - 338	150	3.930	3.4	7.06	96.29	6.70
339 - 345	200	5.240	2.5	15.79	90.82	6.05

weekly nutrient dosing was continued during these trials ensuring the nutrient concentration levels were higher than the minimum levels estimated in section 3.2.2.

3.3.1 Effect of flowrate of continuous trickling

Flowrate of the continuous media trickling was varied from 10 mL/min to 200 mL/min. Each setting of the flowrate was maintained for 7 days and the average values of performance parameters measured are given in Table 3. H_2 conversion reduced with an increase in the trickling flowrate. Taking the 10 mL/min as the base case, the C_{H_2} increased from an average value of 1.96% at 10 mL/min of trickling flowrate to 15.79% at 200 mL/min of trickling flowrate. Similarly, RE of H_2 reduced from 98.9% to 90.82% and PC reduced from 7.0 $\text{Nm}^3/\text{m}^3 \text{ d}$ to 6.05 $\text{Nm}^3/\text{m}^3 \text{ d}$. A similar correlation of decrease in PC with an increase in trickling flowrate was reported by [5]. The increased trickling flowrate results in a thicker water film on top of the hydrogenotrophic biofilm. As a result, it increases the resistance to mass transfer for the feed gases H_2 to reach the active hydrogenotrophic methanogens inside the biofilm.

3.3.2 Flushing vs flooding

Figure 4 shows the results of the flushing and flooding trials, where the total gas flowrate at the reactor outlet, F_{out} , is used as an indicator of reactor performance. The F_{out} was recorded continuously using the BPC[®] μ Flow Gas flowmeter connected with a data logger. Because there was a net reduction of gas moles due to the biomethanation reaction, a lower flowrate at the reactor outlet indicated a higher conversion while higher flowrate values indicated a relatively lower conversion. Right after, either the flooding or flushing there was a transient period of relatively higher flowrate at the reactor outlet that showed that both methods lowered the conversion for a certain duration. This was due to the buildup of a thicker water film that increased the mass transfer resistance. The conversion recovers after the media had drained down the sump. For the case of non-continues trickling, both flooding and flushing showed a transient period that lasted for approx. 24 h, as shown in Figure 4a. For the

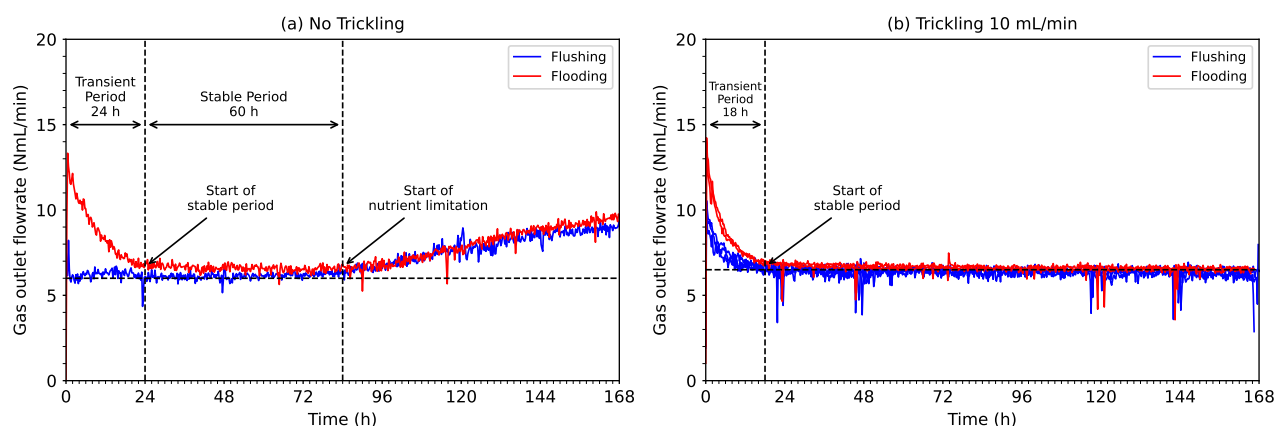


Figure 4: Comparison of two nutrient supply methods—flushing and flooding. (a) no continuous trickling after flushing or flooding, (b) continuous trickling at 10 mL/min after flushing or flooding.

case where continuous trickling was started after the flushing and flooding the transient period was 18 h, as shown in Figure 1b. This indicates that the continuous trickling might facilitate the draining of the liquid media from the packing.

The trials with no trickling after the flushing and flooding showed the efficacy of these nutrient supply methods over time. The results showed that after the transient period is over the conversion in the reactor is stable for a limited time, as shown in Figure 4a. The stable period was approx. 60 h after which the outlet gas flowrate started increasing indicating the beginning of nutrient limitation. In comparison, in the trials where media was continuously trickled after the flushing and flooding the stable period lasted for 150 h, as shown in Figure 1b, after which the flooding or flushing activity was done again. This showed that the combined method of continuous media trickling along with either the flushing or flooding was the best method for the supply of nutrients. Using this combined methodology, the transient period was relatively shorter, and the stable period was increased from 60 h to 150 h.

Comparing the flushing and flooding, no relative difference was found between these two methods of nutrient supply in terms of their efficacy of nutrient supply. However, there are aspects of operating and capital cost that need to be determined to select among these methods of nutrient supply. The flooding method will require a separate vessel of at least equal volume of the BTF reactor to store the nutrient media for flooding. This will increase the capital cost of the biomethanation system. The flushing method does not require additional vessels however, a high flowrate pump will be required. Moreover, the flooding method ensures a complete wetting of the packing material and ensures the supply of nutrients over all the packing material. Hence, inoculation of the BTF with flooding is

recommended as it will ensure the formation of the biofilm over all the packing material.

As was discussed in section 3.2.1, the method of supplying the nutrients with only continuous trickling at a relatively low flowrate could lead to channeling and reduced activity of the biofilm. Hence, ensuring the nutrient media supply using the relatively vigorous method of flushing or flooding is necessary. However, they cause the conversion to reduce for the duration of the transient period. This means that a biomethanation system consisting of a single BTF reactor cannot maintain a steady operation or CH_4 productivity. To overcome this shortcoming, a system of two or more BTF can be designed that undergo the vigorous nutrient supply method of flooding or flushing at alternative times. This system can be operated using a feed gas flowrate control scheme that shifts the feed gas flowrate to the reactor operating at a stable period and reduces the feed gas flowrate from the reactor that is under the transient period. Overall, the feed gas control scheme can ensure a steady conversion and outlet flowrate from the biomethanation system.

The effect of the thickness of water film on BTF performance was investigated by [9] where they compared the PC with continuous nutrient trickling at a flux of $1.36 \text{ m}^3/\text{m}^2 \text{ h}$ and no trickling. They reported a 20% increase in PC without trickling as compared to the trickling. This improvement effect was attributed to direct gas to biofilm contact where the mass transfer resistance due to water film is not present. The results of this study also show the same effect where PC decrease with increasing the trickling rate. It was also shown in this study that the case of no trickling is not sustainable for long period. However, intermittent supply of the nutrient can be adopted, where the reactor is either flushed or flooded at controlled intervals.

3.4 Biomethanation trial

During the biomethanation trial, the feed gas consisted only of H_2 and CO_2 . The objective was to investigate the effect of relatively higher partial pressure of reacting gases, H_2 and CO_2 , in the absence of N_2 which is an inert gas component. The relatively higher partial pressure of the reacting gases could lead to higher absorption of reacting components in the biofilm and higher rates of reaction. The biomethanation trial was conducted at a high gas feed rate to GRT of 24.9 and 16.7 min and the results are shown in Figure 5. On average PC was $8.51 \pm 0.56 \text{ Nm}^3/\text{m}^3 \text{ d}$ at GRT of 24.9 min, which was 21% higher than the PC of $7.0 \pm 0.17 \text{ Nm}^3/\text{m}^3 \text{ d}$ achieved at a similar GRT of 25.7 min but had N_2 the feed gas. This showed the effect of partial pressure of the reacting gases that leads to higher absorption and conversion in the absence of the inert component. The average PC further increased to $9.44 \pm 0.50 \text{ Nm}^3/\text{m}^3 \text{ d}$ at GRT of 16.7.

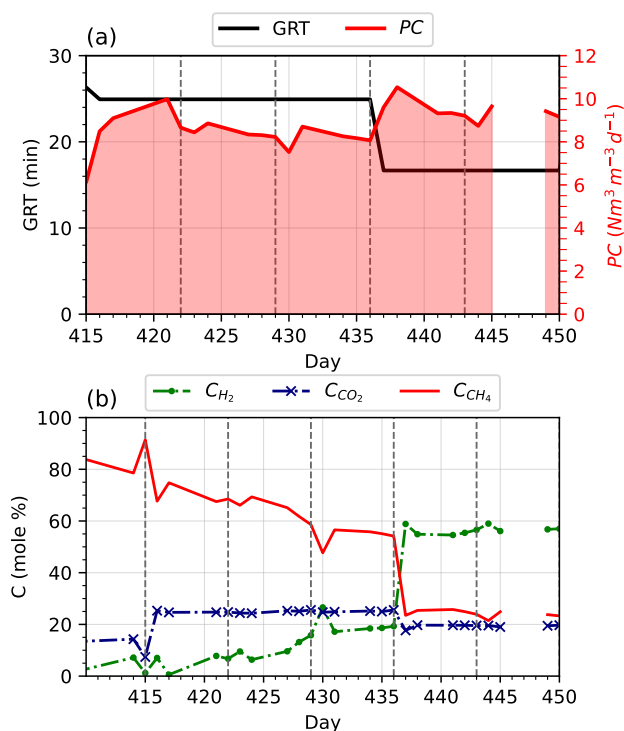


Figure 5: Figure showing the overall performance of the reactor during the biomethanation trials. (a) GRT (min) – gas retention time, PC – specific CH_4 production capacity ($\text{Nm}^3/\text{m}^3 \text{d}$). (b) C_{H_2} (mole%) – H_2 gas composition at the reactor outlet, C_{CO_2} (mole%) – CO_2 gas composition at the reactor outlet, and C_{CH_4} (mole%) – CH_4 gas composition at the reactor outlet.

During the biomethanation trial, there was unreacted H_2 and CO_2 at the reactor outlet, RE was 96.1% and 67.6% at GRT of 24.9 and 16.7 min, respectively. This indicated that the feed gases were available over the whole length of the packing in the reactor, hence the CH_4 formation was not limited by the unavailability of the substrate. This also means that the PC value achieved at GRT of 16.7 was the maximum possible for this size and type of packing material and reactor, considering that the whole packing contained an active biofilm of hydrogenotrophic methanogens. The reason for unconverted H_2 and CO_2 at the same GRT compared to when the feed was H_2 , CO_2 , and N_2 , is the increased H_2 and CO_2 flow due to the same GRT .

3.5 Overall reactor performance

In an earlier study BTF reactor using the PCM and polyurethane foam as packing material was tested. The PCM used was only coarse filtered through $500 \mu\text{m}$ mesh, which resulted in clogging the reactor after 215 days of operation. During this study pretreatment of PCM was carried to filter it through $125 \mu\text{m}$. Also, an external filter was installed in the nutrient media line, as shown in Figure 1, which was cleaned routinely. With these modifications, the reactor was successfully operated for 450 days.

This showed that the continuous operation of the BTF could be extended by adopting a pretreatment method for PCM and with the use of an inline filter. The same approach applies to other solid containing nutrient media, for example, anaerobic digestate.

The maximum average PC achieved in this study was $7.0 \pm 0.17 \text{ Nm}^3/\text{m}^3 \text{ d}$ with the inert gas present in the feed gas and an average outlet gas quality of $C_{N_2+CH_4}$ of $91\% \pm 1.7\%$ was achieved. During the biomethanation trial, the maximum average PC was $9.44 \text{ Nm}^3/\text{m}^3 \text{ d}$, however, this was achieved at GRT of 16 min and without complete conversion of H_2 and CO_2 . These values of PC are lower as compared to the maximum reported in the literature for BTF, for example, PC of $15.4 \text{ Nm}^3/\text{m}^3 \text{ d}$ was reported by [10]. The relatively lower PC achieved in this study could be due to the packing material, as in the earlier study a PC of $8.54 \pm 0.47 \text{ Nm}^3/\text{m}^3 \text{ d}$ was achieved [24], that used a similar BTF design and PCM as nutrient media but had polyurethane foam as the packing material.

4 Conclusion

The installation of an external filter and pretreatment of the pasteurized cow manure led to 450 days of continuous BTF operation without clogging. NH_4^+ and Fe were essential nutrients and their concentration of nutrients can be controlled using either a routine or continuous replacement of the nutrient media. Continuously trickling at a low flowrate together with periodical flushing or flooding was found to be an effective strategy for the nutrient supply; although both flushing and flooding affect the CH_4 productivity in the hours after. This effect needs to be considered at a system level design of BTF.

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Author statement

Muhammad Tahir Ashraf: writing – original draft, conceptualization, methodology, investigation, formal analysis, visualization.

Lars Yde: conceptualization, methodology, resources, writing – review.

Jin Mi Triolo: supervision, writing – review.

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