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Published in:
Bioresource Technology

Link to article, DOI:
10.1016/j.biortech.2022.128160

Publication date:
2022

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Pilot-scale study of biomethanation in biological trickle bed reactors converting impure CO₂ from a Full-scale biogas plant

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HIGHLIGHTS

- Successful implementation of biomethanation on full-scale biogas plant.
- Validated biomethanation technology by upscaling of biological trickling filters.
- Parallel operation obtained 9.44 Nm\textsuperscript{3}CH\textsubscript{4}/m\textsuperscript{3}R day\textsuperscript{-1} with a product gas of 95.7 \% CH\textsubscript{4}.
- Serial operation exceeded parallel operation with 10.6 Nm\textsuperscript{3}CH\textsubscript{4}/m\textsuperscript{3}R day\textsuperscript{-1} at 97.4 \% CH\textsubscript{4}.
- Flexibility proven by intermittent feeding of H\textsubscript{2} to biological trickling filters.

GRAPHICAL ABSTRACT

ARTICLE INFO

Keywords:
Biogas
Biomethanation
Biomethane
Pilot scale
Power-to-x

ABSTRACT

Research within biological methanation has been a great development using biotrickling filters (BTF), as a power-to-x solution, but research within up scaling is missing. This study investigates the commercial potential of biomethanation in BTF by operating two 1 m\textsuperscript{3} reactors which was implemented into a full-scale biogas plant. Several areas were investigated, such as enrichment and start-up, long-term steady state operation, serial operation, and intermittent feed. A methane productivity of 9.44 Nm\textsuperscript{3}CH\textsubscript{4}/m\textsuperscript{3}R day\textsuperscript{-1} with a product gas of 95.7 \% CH\textsubscript{4} was obtained for parallel operation, whereas during serial operation a methane productivity of 10.6 Nm\textsuperscript{3}CH\textsubscript{4}/m\textsuperscript{3}R day\textsuperscript{-1} at 97.4 \% CH\textsubscript{4} was achieved. The flexibility of the biomethanation was demonstrated with unintentional loss of H\textsubscript{2} feed in periods of 12 to 72 h, where initial performance was regained within 6 to 12 h. The results from this study demonstrate the potential for commercial use of biomethanation in BTF for future Power-to-X solutions.

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https://doi.org/10.1016/j.biortech.2022.128160
Received 29 August 2022; Received in revised form 12 October 2022; Accepted 14 October 2022
Available online 20 October 2022
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1. Introduction

With the current state of greenhouse gas (GHG) emissions, a solution for carbon capture storage and utilization (CCS and CCU) is needed. The GHG emissions have been increasing since the 1960s and in 2015 it resolved in the climate agreement, the Paris Agreement (United Nations Framework Convention on Climate Change (UNFCC), 2015). This has been regularly updated, but the main goal still exists. The temperature increase must not exceed 1.5 °C compared to pre-industrial levels. With an increasing interest in CO\textsubscript{2} reductions, such as EU2030 and EU2050 goals (European Commission, 2020a; b), there has become a great need for solutions that can store or utilize CO\textsubscript{2}, which are known as CCU and CCS solutions. Along with the increasing GHG emissions, the current state of energy supply in the world has shifted throughout 2022. To solve these issues, along with stability of natural gas supply, power-to-x technologies could be utilized. These technologies utilize electricity, to produce H\textsubscript{2} by electrolysis, with CO\textsubscript{2} to form e-fuels. These fuels are capable of substituting fossil fuels, i.e., natural gas can be substituted by e-methane. Conversion of H\textsubscript{2} and CO\textsubscript{2} can be done catalytic and biologically, where the process will produce CH\textsubscript{4} and H\textsubscript{2}O. A stoichiometric reaction of 4:1 of H\textsubscript{2}:CO\textsubscript{2} will produce the e-methane and H\textsubscript{2}O in ratio 1:2, respectively.

Moreover, CO\textsubscript{2} credits and unified carbon tax are ongoing incentives that can accelerate the implementation of e-methane across various industries. For example, the C-rich inlet stream can be taken from bio-manufacturing (i.e. biogenic CO\textsubscript{2}) or intensive GHG releasing chemical industries (e.g. cement, steel, lime). On the other hand, the forthcoming huge implementation of solar and wind energy along with advances in water electrolysis are expected to trigger the H\textsubscript{2} at lower prices. Methanation technology has been researched widely at laboratory scale, where a biological approach utilizing a biological trickling filter (BTF) has shown great potential. The use of BTFs has shown a potential for lower operational costs and ability to use less purified feed gases than catalytic methanation which requires high purity gas, and higher operating temperatures and pressures, up to 250 °C and 90 bar, respectively (Younas et al., 2016). Other types of large scales of biomethanation have been demonstrated before. One of these have been in Denmark and Switzerland (Electrocha, 2022), where a biological methanation have been demonstrated with a pure culture of methanogens in a CSTR reactor. The results from these operations are strictly limited, but they have operated at 63 °C and at 10 bar of pressure.

Several studies have tested biological methanation using BTF at lab-scale with promising results of production capacity, from 0.2 L (Dunnock and Deshusses, 2017) up to 14.5 L (Lemmer and Ullrich, 2018). Some studies have also performed biological methanation (bio-methanation) at a relatively larger scales than the lab-scale i.e., semi-pilot scale. For example, Strübing et al. (2017) used a pilot scale trickle bed reactor with packed volume of 58.1 L and used pure CO\textsubscript{2} and H\textsubscript{2} gases as feed. They reported CH\textsubscript{4} production capacity of 15.4 Nm\textsuperscript{3} m\textsuperscript{-3} d\textsuperscript{-1} with 98 % CH\textsubscript{4} at the reactor outlet. Recent studies from Tsepokos et al. (2021) and Cheng et al. (2022) used a semi pilot-scale trickle bed reactor with a packed volume of 68 L and 35 L. However, the focus in both studies was on the microbial communities applying metagenomics and the reactors were operated at low gas feed rates. Asimakopoulos et al. (2021) conducted a scale up study for syngas biomethanation in semi-pilot trickle bed reactor with a packed volume of 5 L. They reported 100 % H\textsubscript{2} conversion and CH\textsubscript{4} production capacity of 10.7 Nm\textsuperscript{3} m\textsuperscript{-3} d\textsuperscript{-1} at a gas retention time (GRT) of 0.6 h.

While these semi-pilot scale studies were performed in a larger BTF than laboratory scale, the upscaling was minimum a 4-fold, compared to the study of Lemmer and Ullrich (2018), which is not enough to encounter unknown challenges from upscaling to a larger scale. Moreover, it is imperative for the future development and implementation of biomethanation to investigate how the operation and process performance of a BTF will be affected at larger scales, especially when the BTF is operated continuously using raw biogas containing traces of ammonia, hydrogen sulphur, etc., from a biogas plant. Without this upscaling, it will be impossible to predict the potential for larger scale biomethanation. Therefore, this study aimed to achieve steady-state and high-rate biomethanation, exposing and solving potential upscaling challenges during the demonstration at operational scale. A pilot scale biomethanation system consisting of two 1 m\textsuperscript{3} BTF reactors was designed and built. This upscaling of biomethanation was a 15-fold increase from the study of Cheng et al. (2022) and a 69-fold increase from the laboratory scale of Lemmer and Ullrich (2018). The pilot BTFs was placed in a full-scale biogas plant utilizing raw biogas to show the real potential of this technology. Parallel and series operation, effect of packing material, and effect of intermittent supply of H\textsubscript{2} were investigated. Furthermore, this study validated the results from the pilot-scale against the results from earlier lab-scale studies. This study provides a fundamental reference for the assessment and potential of biomethanation using BTF in larger scale.

2. Materials and methods

2.1. Reactor configuration of pilot BTFs

The pilot plant consisted of two BTFs (BTF-1 & BTF-2) with a packed volume of 1 m\textsuperscript{3} each. The reactors have inner diameter of 1 m, and a packed height of 1.3 m, giving a low height:diameter ratio of 1.3:1. The complete pilot plant setup was constructed inside a 20 ft. container. Fig. 1 shows an illustration of the reactor configuration.

The BTFs were built accordingly to given regulations from the Danish Safety Technology Authority regarding H\textsubscript{2} safety. Given H\textsubscript{2} is highly permeable through materials (Abohamzeh et al., 2021), the BTFs and all piping for gases were built in stainless steel. All welding was done by certified welders and followed Danish regulations. Fig. 1 shows the BTFs are built with piping arrangements that allows switching between parallel and serial operation of the two BTF units and allows gas recirculation to the first BTF. Both BTFs were fully insulated to minimize heat loss to surroundings from the BTFs.

Each BTF reactor has a sump volume of 0.4 m\textsuperscript{3} at the bottom of packed volume to contain nutrient media. Two liquid pumps (SHB 20–100 horizontal pump, Stibbe GmbH & Co. KG) were placed to pump the sump with nutrients at a trickling flow rate of 0.7 m\textsuperscript{3} m\textsuperscript{-3} m\textsuperscript{-1}. A nozzle was installed to ensure even distribution of trickled media. The sumps were actively cooled to keep a steady operating temperature of 54–57 °C throughout the BTFs, which was observed by 7 temperature points located throughout each BTFs. To keep a steady operating temperature, a regulation loop was put in place with a minimum and maximum temperature of the sump at which the cooling would stop or start, respectively. Both reactors were initial packed with a high surface area (>3500 m\textsuperscript{2}/m\textsuperscript{3}) packing material (5x10mm) with 76 % void space (MBBR PE08, Tongxiang Small Boss Special Plastic Products Co., Ltd). The same packing material have been used previously in a different study as well (Ashraf et al., 2021).

2.2. Operational parameters

2.2.1. Inoculum and inoculation

Prior to the inoculation, the BTFs were heated up to the thermophilic operating temperature and continuously trickled with water to wet the packing material. The liquid fraction obtained from a decanter separation process of digestate at Nature Energy Videbæk A/S was used as inoculum for the BTFs. This decanted liquid was free of particles >500 μm and was sampled at the inoculation day. A direct inoculation method was applied, as used in (Dahl Jenson et al., 2020), by flooding the reactors packed volume with the inoculum. After the inoculation process, the feeding of gases was started.
2.2.2. Gas supply

The pilot BTFs were installed onsite at Nature Energy Holsted A/S for utilization of raw, non-upgraded biogas. The biogas was supplied directly from the main gas pipe transporting the raw biogas from the primary and secondary digesters to the biogas upgrading. The raw biogas varied in composition but averaged at ~58% CH4 and ~42% CO2, 3000 ppm H2S and unknown amounts of volatile organic compounds (VOC). The H2 was supplied from a 58 kW alkaline electrolyzer (Green Hydrogen Systems) with a purity of >99.9%.

The flow of the biogas and H2 into the BTFs, and the product gas out, was measured and controlled by mass flow meters and controllers (Deltaflow DFS, Systec Controls Messtechnik GmbH). The flow of biogas was based on the CO2 concentration which was provided from Nature Energy Holsted A/S onsite measurements. The flow of H2 was then supplied in a ratio of 3.8–3.9:1 of H2 and CO2, respectively. A lower ratio than the stoichiometric was applied for improved pH control in the system, as described in (Ashraf et al., 2020). For series operation, the outlet gas from BTF1 was fed at the inlet of BTF2. For parallel operation, the feed gas mixture was split into the two reactors and distributed naturally between the two reactors. A valve was added for manually adjustments of the feed flow, which would ensure equal feed for both BTFs. Gas sampling was done automatically from the bottom of both BTF1 and BTF2, with a gas analyser (Pronova SSM6000 LT). The product gas from both BTFs was analysed alternating every 5th min between the two BTFs product gas.

2.2.3. Gas retention time reduction

The initial GRT for each BTF was 45 min, equal to a flow of 0.21 m3CO2 h−1, and it was decreased by 6% every second day, until a GRT target of 20 min was reached. The decrease of 6% in GRT happened if the operation was at steady state and did not start to drop in CH4 in the product gas. At times with loss of H2 supply the reduction was postponed until the supply was steady again. The H2 loading rate was increased from 9.6 m3H2 m−3reactor d−1 (GRT 45 min) to 41 m3H2 m−3reactor d−1 (GRT 20 min) to reach the targeted operational conditions.

2.2.4. Liquid sample analysis

To ensure optimal operating conditions, various liquid sample analyses were performed on the trickling medium from the sump. From previous study (Ashraf et al., 2021) it was found that biomethanation performance was depending on sufficient supply of N and Fe. In this study, NH4+ was measured with distillation (Vapodest 500C, Gerhardt GmbH & Co. KG) two times a week, to ensure a concentration above 0.8 g/L. Fe content was measured along other trace elements by ICP (inductively coupled plasma), to ensure sufficient concentrations above 50 mg/L. If NH4+ or Fe was below the set concentration limits, the nutrient supply was increased. Volatile fatty acid (VFA) concentrations were measured on gas chromatograph (GC) with the same method as in Jonson et al. (2022). Continuously online measurement of pH (MAC 100, KROHNE Messtechnik GmbH) from both BTFs was implemented from day 1.

2.2.5. Nutrients

To supply sufficient nutrient, a mixture of NPK fertilizer (Flex Bio – NPK 10-2-5 + nitrate, Flex Fertilizer System) and trace element solution (BC.TEplex AKUT, Shaumann Bioenergie) was supplied. The mixture was in a ratio of 25:1 of NPK and trace elements, respectively. The concentrated nutrient mixture was supplied in a low flowrate of 90–120 mL d−1 m−3reactor. To ensure enough buffer capacity in the system during steady state operation, 25 L week−1 m−3reactor of decanter liquid from Nature Energy Videbæk A/S was added to the sump.

2.2.6. Production capacity and elimination capacity

For calculations on the performance of the BTFs, two equations are used. The first parameter is production capacity (PC), which gives the efficiency of the biomethanation on how much CH4 is produced per packed volume of reactor per unit of time (Eq. (1)).

\[
\text{PC} \left( \text{m}^2 \text{CH}_4 \text{m}^{-3} \text{reactor} \text{day}^{-1} \right) = \frac{F_{\text{CH}_4, \text{out}} - F_{\text{CH}_4, \text{in}}}{V_{\text{reactor}}} \left( \frac{\text{m}^3 \text{h}^{-1}}{\text{m}^3} \right) \left( \frac{24 \text{ h day}^{-1}}{} \right)
\]  

(1)

The PC is based on the increase of CH4 flow, per packed volume of the reactor and then multiplied to be expressed daily.

The other parameter is the elimination of CO2, measuring the conversion of CO2 based on the concentration at the inlet and outlet (Eq. (2)).

\[
e\text{CO}_2[\%] = \frac{F_{\text{out}} - F_{\text{in}}}{F_{\text{in}}} \times \text{eCO}_2 \times 100%\]

(2)

Both PC and eCO2 indicate the performance of the biomethanation in the BTF.
2.3. Experimental periods

In this study, the reactors were designed to assess a real-life operation of a biological methanation system, which would reflect on the commercial aspect of the technology. Hence, four major areas were investigated.

Parallel operation: The focus was to validate the technology in operational environment, compared to the previous laboratory scale studies (Ashraf et al., 2021, 2020; Dahl Jonsen et al., 2020; Ebrahimian et al., 2022; Ghofrani-Ishafani et al., 2022; Jonsen et al., 2022; Tsapekos et al., 2021). The BTFs were operated under identical conditions of temperature, flow, and trickling.

Serial operation: Serial operation of the BTFs was tested to elucidate if the methanation process would become more efficient. The feed gas would enter the first BTF and output would enter the second BTF. The overall gas load to the system was kept unchanged.

Intermittent feeding: Previous studies (Jonsen et al., 2022; Strübing et al., 2018) have shown the potential of this type of biomethanation technology to work under an intermittent energy system, where H2 production would be fluctuating. The intermittent feeding, or dynamic operation, is an important parameter for implementation of this technology into the current energy system which have been described more in Jonsen et al. (2022). The results from Jonsen et al. (2022) was going to be validated herein, to show the scalability of the optimized parameters for downtime operation of the BTFs. This flexible operation is one of the most important areas to be investigated to assess the applicability of this technology.

3. Results and discussion

3.1. Operational performance from pilot scale BTFs

Due to equipment calibrations and sensor challenges, H2 was periodically added in a higher ratio than 4, and therefore H2 output is neglected on all figures while the outlet ratio of CH4 and CO2 were used instead. The BTFs have been operated for >500 days, not all data will be shown here, as some was commissioning, and others was steady state operation during the experimental periods. The commissioning of the BTFs took around 100 days (data not shown) due to the equipment and signals that needed to be between the pilot container, the electrolyser unit and the biogas plant, along with safety installations and signals. The results during this period were used for calibration and adjustments of the equipment.

The BTFs were started in parallel operation to ensure uniform performance. 10 days after inoculation, the outlet gas of the BTFs had CH4 > 90 %. This CH4 content is lower than gas grid requirements in Denmark (Erhvervsmimisteriet - Sikkerhedsstyrelsen, 2018), but it is known the product gas from the BTFs will undergo further upgrading to remove residues of CO2 and H2S from the raw biogas. Therefore, this study does not have a target of gas grid gas quality in the product gas. After 45 days of steady-state operation the GRT was lowered to increase the PC of BTFs. This ramp-up technique of gas flow was mimicked from commercial scale biogas digester ramp-ups and being based upon studies (Aramrueang et al., 2016; Babaei and Shayaneg, 2011; Wijekoon et al., 2011), investigating organic loading rate (OLR) changes in anaerobic digestions. Specifically, an increment in the OLR could have negative impacts on the performance due to over-feeding. With this ramp-up, the GRT was lowered to 20 min after 28 days. However, due to challenges with the H2 supply from the electrolyser unit and equipment difficulties, the stable operation at the GRT of 20 min was reached after 112 days after initial ramp-up start. GRT of 20 min, on average, resulted in PC of 10 m3CH4 m3reactor day−1, with a H2 loading of 41 m3 m3reactor d−1, and the BTFs were kept at this GRT during the parallel operation trials.

3.1.1. Parallel operation

From day 188 to day 266, the BTFs were operated in parallel at steady state with a flow of 0.48 m3CO2 m3reactor h−1 per BTF, giving a GRT of 20 min. The outlet ratio of CH4 and CO2 is illustrated in Fig. 2, where H2 was neglected as previously mentioned.

For the whole period, an average between both BTFs showed 95.7 ± 2.2 % CH4 and an eCO2 of 89.8 ± 5.2 % with a peak in eCO2 of 97.3 %. A mean PC of 9.44 ± 2.37 m3CH4 m3reactor day−1 was reached with a maximum of 11.1 m3CH4 m3reactor day−1. During the 78-day parallel operation (Day 188–263), three occasions with loss of H2 supply happened that were related to the operation of the electrolyzer unit. The occasions with loss of H2 was at day 197, 230 and 250, and the periods without H2 supply had a duration of 1.5 days, 6 days, and 0.6 days, respectively. During the loss of H2 the outlet switched to raw biogas concentrations and when H2 feeding was reintiated, the performance was regained within a day of operation. This regain of performance was unexpected, as no strategy was implemented for this loss of H2, but the relative fast recovery was a clear sign for the potential of flexibility of the technology. Neglecting the periods with loss of H2 the averaged concentration of CH4 in the outlet was 95.73 ± 2.17 %.

3.1.2. Serial operation

In the serial operational, the total gas flow was not changed from 0.48 m3CO2 m3reactor h−1 per BTF, but instead of dividing the flow between the reactors, the total inlet flow was directed into BTF-1 and that outlet gas was directed into BTF-2. Fig. 2 shows the output concentrations of CH4 and CO2 for both BTF in the serial operation mode from day 266 to day 322. With all flow going through BTF-1, the GRT was halved to 10 min, while the precise inlet flow and GRT of BTF-2 was unknown due to equipment failure on the inlet flowmeter in this period. Besides this, the product gas quality from BTF-1 was used to estimate and calculate a flow, which could then be used for calculations of PC. The outlet of BTF-2 expressed the total CO2 conversion.

When the operation was switched to serial operation a significant change in the product gases were observed. This was due to BTF-1 receiving an increased load of feed. This stabilized until day 292, where it was observed that a malfunction had happen and with the switch in operational mode, had lowered the inlet feed gases. At day 292–295 the malfunction was fixed, and the initial feed used for parallel operation was used for serial operation. During the last 28 days, smaller fluctuations were observed, but overall performance of BTF-1 increased slowly.

During the whole 58-day period of serial operation, BTF-1 had a PC of 16.8 ± 2.6 m3CH4 m3reactor day−1, but a lower CH4 content at 89.0 ± 4.6 %. The PC was higher than the results obtained during parallel operation due to increased feed. The eCO2 was 73.5 ± 11.4 % and the high variation was due to feed flow adjustments at day 293, which lowered the conversion of BTF-1 for the rest of the period. For the whole biomethanation system, the PC during the 58 days was 10.6 ± 0.6 m3CH4 m3reactor day−1 at 97.4 ± 1.4 % CH4, corresponding to a 10 % increase compared to the parallel BTFs operation. The eCO2 increased to 93.4 ± 5.33 % in serial operation, which was also higher than during the value achieved during the parallel operation of the BTFs. With the serial operation, an enhanced operation was observed compared to the parallel operation, and more stability was observed in the quality gas of BTF-2 compared to the parallel operation from both BTF-1 and BTF-2.

3.1.3. Intermittent feeding

With the importance of dynamic operation due to the intermittent energy system, a validation test was performed. The first test was unintentional, where downtimes occurred due to the loss of H2 have occurred. As mentioned previously, a loss of H2 was not uncommon as the electrolyzer unit was not performing optimally. In the period from day 90 to day 120 there had been multiple occasions with losses of H2.
Fig. 2. Operation of the pilot BTFs with outlet concentrations of CH$_4$ and CO$_2$, from day 188 to day 322. Parallel operation: Day 188 to 266. Serial operation: Day 266 to 322.

Fig. 3. A comparison of the output concentrations of CH$_4$ and H$_2$ from different downtime periods and the effect of refeeding strategy within pilot scale operation. The downtimes were mostly controlled, except for (a). (a) Spontaneous downtime of 18 h with instantaneously H$_2$ refeeding from 0% to 100%; (b) Controlled downtime of 24 h with usage of successful refeeding strategy of H$_2$ from laboratory scale. (c) Controlled downtimes of 3 h with instantaneously H$_2$ refeeding from 0% to 100%; (d) Controlled downtime experiment of 3 h with controlled refeeding of H$_2$, focused on lowest output of H$_2$ possible.
ranging from 12 to 72 h (data not shown). For these periods the regain of performance after H$_2$ was reinitiated took between 6 and 12 h. Common for these downtimes was no strategy for refeeding of the H$_2$, which could be a reason for the relatively longer time to regain conversion. Therefore, a downtime period of 24 h was tested with a refeeding strategy, as was used in Strübing et al. (2018), and the results were compared to the earlier lab-scale study from Jönson et al. (2022).

For the second test, a method was investigated for the development of a refeeding strategy. A 3-hour downtime was used for testing no refeeding strategy and a strategy where the H$_2$ refeeding was increased slowly and gradually to avoid high H$_2$ concentrations in the product gas. This was done due to limitations of the Wobble index in the gas grid (Erthversministeriet - Sikkerversdyrelsen, 2018). The results from both tests of refeeding strategy in a pilot scale operation are shown in Fig. 3.

By comparison of the unintentional downtime at Fig. 3a with the intentional downtime of Fig. 3b, a significant difference in product gas development is noticed. With the controlled refeeding strategy, a H$_2$ peak of 19.0 % was noticed after 2 h but dropped to 2.2 % after 7 h. Compared to no refeeding strategy, 16.8 % H$_2$ was noticed in the product gas after 2 h, which was lower than with the refeeding strategy, but no signs of improvements were noticed as 17 % of H$_2$ was still in the outlet after 7 h. This significant difference was a clear result of proper implementation of a refeeding strategy.

A shorter downtime was tested with no refeeding strategy (Fig. 3c) and peaked with 10.1 % H$_2$ in the outlet, whereas the gradually increasing H$_2$ input reduced this peak to 4.4 % H$_2$ in the product gas. Besides this, the time to regain < 0.5 % H$_2$ in the outlet was reduced with > 3 h, as 0.4 % H$_2$ was achieved 5 h after refeeding (Fig. 3d) while after 7 h the H$_2$ concentration was still 2.6 % without a refeeding strategy (Fig. 3c). The comparison of all results from Fig. 3 highlighted the influence and importance of optimizing the refeeding strategy.

3.2. Validation of pilot scale results

With the overall objective of this study to validate the use of BTFs for biomethanation in larger scales, the results obtained in this study needs to be compared with laboratory scale studies. To meet this target, the laboratory studies from the groups within this project were used (Ashraf et al., 2021, 2020; Dahl Jönson et al., 2020; Ebrahimian et al., 2022; Ghofrani-Isfahani et al., 2022; Jönson et al., 2022; Tsapekos et al., 2021). The studies were all precursor to this pilot-scale study. All studies were of laboratory scales ranging between 0.8 L and 8 L of packed volume, besides Tsapekos et al. (2021) which was of semi-pilot-scale at 68.8 L packed volume. The laboratory studies used an artificial biogas composition, whereas Tsapekos et al. (2021) and this study, both used real biogas as feed.

3.2.1. Non-enriched inoculum vs pre-enriched inoculum

The method for inoculation differs between the studies presented. The inoculum used for inoculation in the studies of Ashraf et al. (2020), Ghofrani-Isfahani et al. (2022), Ebrahimian et al. (2022) and Tsapekos et al. (2021) was pre-enriched inoculum for hydrogenotrophic methanogens in a two-stage system from Bassani et al. (2015). The method for inoculation of the BTFs in these studies were by trickling. This study, Jönson et al. (2022), Dahl Jönson et al. (2020), and Ashraf et al. (2021) used non-enriched inoculum (direct inoculation), which was liquid fraction of digestate from full-scale biogas plants, and the inoculation methods were both trickling and flooding.

As this study was focused on the potential of biomethanation in a BTF for larger scale operations, the enrichment phase was important. For larger scale operations, to pre-enrich inoculum with the same method as used for the studies of Ashraf et al. (2020), Ghofrani-Isfahani et al. (2022), Ebrahimian et al. (2022) and Tsapekos et al. (2021) would be expensive in terms of operating cost and time. Using a direct inoculation with non-enriched inoculum would reduce the expenses for enrichment of the BTF. Comparing the pre-enriched and non-enriched studies, it was found that the pre-enriched BTF would require between 7 and 16 days in the BTF to reach >90 % CH$_4$ in the product gas. Including the time period for the pre-enrichment period from Bassani et al. (2015), which was 35 days for thermophilic enrichment, the total enrichment time would take between 42 and 51 days to reach >90 % CH$_4$ in the outlet of a BTF. With the non-enriched inoculum used in this study, Jönson et al. (2022), Dahl Jönson et al. (2020), and Ashraf et al. (2021) the threshold of >90 % CH$_4$ in the outlet was reached within 5 to 25 days, which have halved the total time for the enrichment process. The same results were found in (Dahl Jönson et al., 2020), and it has now been proven to fit for larger scale biomethanation in BTF by this study. It should be mentioned that the inoculum taken from Bassani et al. (2015) was enriched in planktonic environment and grown at GRTs above 10 h. In the present study, significantly higher gas rates were fed to achieve the targeted GRTs (<0.5 h) and, the utilized BTFs utilized that rely on biofilm formation which is a completely different reactor design. Thus, the microorganisms at the studies of Ashraf et al. (2020), Ghofrani-Isfahani et al. (2022), Ebrahimian et al. (2022) and Tsapekos et al. (2021) were subjected to more intensive operating conditions and completely different environment (i.e., from planktonic to biofilm) leading to relatively prolonged lag phase. Nevertheless, high biomethanation was achieved in all the cited studies of this project. On the long run, syntrophic associations of bacterial and archaeal strains accelerated biofilm formation through the secretion of extracellular polysaccharides aided by both microbial groups. Hence, archaeal strains were enriched over time at the packing materials and strong biofilm was formed to achieve the increased production capacities. The enrichment process chosen for future large scale biomethanation in BTF should be of direct enrichment. This saves operational costs of keeping larger volumes of pre-enriched inoculum active, performance would be equal in long term operation and enrichment time would be faster.

3.2.2. Flooding or trickling for inoculation

Flooding of a BTF has been proved to be an effective strategy for supplying nutrients at high concentrations in the packing material (Ashraf et al., 2021). However, it also had negative impacts on the steady performance afterwards compared to trickling, due to thicker water film formation from flooding. Applying this knowledge to inoculation of a BTF, the flooding would ensure even distribution of inoculum on the packing material and at a faster rate than trickling. Flooding was applied for inoculation in the present study as well as Jönson et al. (2022). Enrichment periods were observed varying between 10 and 14 days, respectively, before reaching >90 % CH$_4$. Comparing this strategy to the inoculation with trickling (section 3.3) the outlet reached >90 % CH$_4$ after 5 days, having a similar performance with the Tsapekos et al. (2021) study which also used trickling for inoculation, and reached >90 % CH$_4$ within 7 days after inoculation using a pre-enriched inoculum. The studies of Dahl Jönson et al. (2020) and Ashraf et al. (2021) also used trickling and non-enriched inoculum and they reported a need of 25 and 22 days to reach >90 % CH$_4$ in the outlet, respectively. This shows that inoculation by flooding in this study resulted in a 3- to 4-fold reduction in the time needed for enrichment of the BTF as compared to lab-scale studies that used inoculation by trickling. For the inoculation using trickling in this study (section 3.3), it should be noted that the packing material (PE08) was previously used but has been cleaned with water. This could leave residues of inactive hydrogenotrophic methanogens or bacteria that can biosynthesise extracellular polymeric substances and improve the biofilm formation on the packing material, which could improve the enrichment period, decreasing the time needed to reach >90 % CH$_4$ in the outlet. Reducing the inoculation process to larger scale operation, the trickling would be preferable over flooding. Flooding a large scale BTF would result in a large water pressure at the bottom of the BTF, which would require more expensive materials, higher operating costs, and more strict safety measurements. Based on the results discussed, there was no substantial difference between flooding and trickling during inoculation to reach >90 % CH$_4$ but with
the requirements of separate tanks, extra pumps, and piping for culture when flooding larger scale BTF, trickling would be the preferable method for inoculation in larger scales.

3.2.3. Buffer capacity in nutrient supply

For most DTU and SDU studies, the nutrient supply was from a biologically origin (i.e., digested manure and pasteurized manure) while only Tsapekos et al. (2021) exploited the effluent of an anaerobic digestion (AD) reactor fed with source separated municipal biowaste. Digested manure contains all needed nutrients, both macro-nutrients and trace elements (Awais et al., 2016) along with natural occurring buffer capacity (Westerholm et al., 2012). Also, all the essential nutrients were available in the digested biowaste (Khoshnevisan et al., 2018) and no shortage of the essential elements was detected during ex-situ upgrading tests (Tsapekos et al., 2021). Comparing the present work in which the nutrient supply was artificial, consisting of N + P + K and trace elements (Fe, Mn, Mo, Cu, etc.), the major difference was the missing buffer capacity. The consequence of the limited buffering capacity was seen from day 201 to 210 (Fig. 2), when the outlet concentration dropped from 96.1 % CH$_4$ to 85.3 % CH$_4$ at day 204 before returning to 95.5 % CH$_4$ at day 210. The drop in CH$_4$ was found to be related to a loss of buffer capacity in the BTFs due to dilution from H$_2$O produced (Eq. (1)) along with no addition of buffer capacity to the system. A similar drop in CH$_4$ was found for Ashraf et al. (2021) where it was linked to insufficient amounts of NH$_4^+$ and Fe, but this was available for this study. After this period, regular addition of decanted liquid from Nature Energy Videbæk A/S was followed to ensure sufficient buffer capacity for the biomethanation process, which would also function as a re-inoculation due to the continuously addition of new microorganisms. Subsequently, a positive effect on the performance stability was detected after day 210 (Fig. 2). The microorganisms added weekly were of same origin as the inoculum used, which showed signs of being beneficial towards performance stability.

3.2.4. Performance parameters (Gas supply, GRT, steady state, PC, purity)

Studies of Jørgensen et al. (2022), Ghofrani-Isfahani et al. (2022), Ebrahimian et al. (2022), Ashraf et al. (2020), Dahl Jørgensen et al. (2020), and Ashraf et al. (2021) all used bottled dry gases of >99.9 % purity, without any impurities. The study of Tsapekos et al. (2021) was implemented on a biogas plant using biogas after H$_2$S removal. A key parameter in the present study was the use of raw and saturated biogas containing 3000 ppm H$_2$S, volatile organic compounds and other trace gases (Rykebosch et al., 2011). Securing a well-performing process at such conditions would be beneficial in larger scale biomethanation implemented on a full-scale biogas plant, as the need for traditional biogas upgrading for removal of CO$_2$ would be reduced. The H$_2$S would still need to be removed.

It is worth mentioning that alternative technologies, which are available in high technological readiness level, explored pure autotrophic archaean cultures to optimize biomethanation (Wegener Kofoed et al., 2021). Previously, a similar technical study examined the scaling-up of biomethanation from lab to field growing Methanothermobacter thermoautotrophicus (Thema et al., 2021). However, the study was only demonstrated using chemicals of analytical grade as nutrients and gases of high purity. Thus, the robustness of the monocoulture at real conditions utilizing gas and liquid streams from a biogas plant as a source of CO$_2$ and nutrients, respectively, cannot be concluded. In contrast, the presented technology utilizes naturally evolved microbially prevailing in biogas plants that can efficiently couple CO$_2$ from biogas with renewable H$_2$ and utilize digestate as nutrients source. Indeed, robust microbiomes were evolved handling gas impurities, pH variation, alternation of nutrients’ content and without the need for sterile conditions.

Furthermore, when comparing the present research to the studies using bottled gas, there have been no significant differences in the obtained GRT at steady state operation. This study has been operated at a GRT of 20 min with steady state performance (Fig. 2), whereas Ebrahimian et al. (2022) and Ashraf et al. (2021) have been operated at 21 min and 25.7 min, respectively, with steady state operation. The studies of Jørgensen et al. (2022), Ebrahimian et al. (2022), Ashraf et al. (2021), and this study, all used the same packing material (PE08), had different reactor dimensions, but reached similar PCs of 7.0 (Ashraf et al., 2021) to 9.44 (this study) $m_{CH}_4^{in}$ $m_{CH}_4^{out}$ day$^{-1}$ with purities of 90.4 % CH$_4$ to 98.9 % CH$_4$, respectively. During the serial operation in this study, an improved overall PC of 10.6 ± 0.6 $m_{CH}_4^{in}$ $m_{CH}_4^{out}$ day$^{-1}$ at 97.4 ± 1.4% was reached, with a specific PC of 16.8 ± 2.6 $m_{CH}_4^{in}$ $m_{CH}_4^{out}$ day$^{-1}$ with 89.0 ± 4.6% CH$_4$. The specific PC of this study was near the obtained PC for the study of Strübing et al. (2017) of 15.4$m_{CH}_4^{in}$ $m_{CH}_4^{out}$ day$^{-1}$ at 98.5 % CH$_4$ but did have significant lower CH$_4$ in the product gas. A reasoning for this could be the GRT which have been lower for this study as raw biogas was used, while Strübing et al. (2017) utilized a mixture of pure CO$_2$ and H$_2$ only.

With a gas grid quality requirement of +97 % CH$_4$ in Denmark (Energiforskningsinstituttet - Sikkerhedsstyrelsen, 2018) these studies reached a steady state operation where the product gas would require minimal gas upgrading for injection to the gas grid. Comparing the GRTs, PCs, and purities, it is proven that this study has validated the results found in lab. This shows great potential for the performance of biomethanation in larger scales, and how implementable it would be to a raw biogas supply.

3.2.5. pH and VFA concentrations

With discussed steady state operation and performance, pH and VFA concentrations can be used as process indicators to retain stability. The most common VFA to measure in biomethanation have been reported to be acetate, as it is also a product of CO$_2$ and H$_2$, while propionate is also accumulated at high partial pressure of H$_2$.

During the parallel and serial operation in this study a pH of 8.47 ± 0.5 was obtained, which was in the range of the previously mentioned studies which were in the range of 7.57 ± 0.2 (Ghofrani-Isfahani et al., 2022) to 8.67 ± 0.1 (Jørgensen et al., 2022). These pH levels are neutral and within the known pH optimum for methanogenesis of pH 6.5–8.5. During this study, a high VFA concentration of 2.12 ± 0.7 $g_{VFA}$ L$^{-1}$ was obtained in contrast to the studies of Ashraf et al. (2020; 2021) which reached 0.07 and 0.09, respectively. The high VFA could limit the methanogenesis by VFA inhibition, but the content of acetate in this study was found to be lower than in the studies of Ghofrani-Isfahani et al. (2022) and Dahl Jørgensen et al. (2020) at 0.51 ± 0.3 $g_{Acetate}$ L$^{-1}$ compared to 1.43 ± 0.3 and 1.55 ± 0.1 $g_{Acetate}$ L$^{-1}$, respectively. This could indicate that the obtained VFA did not inhibit the methanogenesis during this study. The pH in the sump is affected by the VFA concentration as increased concentration of these acids can lower the pH. pH in the sump is connected to the carbonated buffer which is affected by the CO$_2$ partial pressure over the sump (Bassani et al., 2015; Savvas et al., 2017), which in the case of co-flow operation is the CO$_2$ content at the outlet of the reactor. A lower CO$_2$ partial pressure can lower the carbonate and bicarbonate concentrations in the sump causing an increase in the pH. One way to keep the pH from increasing is maintaining the carbonate buffer by keeping the H$_2$ to CO$_2$ ratio slightly lower than the stoichiometric value of 4:1 (Ashraf et al., 2020). The H$_2$ to CO$_2$ ratio used for the pilot-scale unit in this study was 3.8:1 and on average the pH remained lower than 8.5. These results are alike the lab-scale studies where a long-term operation with pH lower than 8.5 was achieved by using H$_2$ to CO$_2$ ratio of 3.8:1 (Ashraf et al., 2021; 2020).

Regarding VFA, a part of the gaseous feedstock can be driven towards acetate at H$_2$/CO$_2$ fuelled reactors (Liu et al., 2016). Indeed, acetic acid was accumulated in the studies of Ghofrani-Isfahani et al. (2022), Ebrahimian et al. (2022) and Tsapekos et al. (2021) in periods with decreased biomethanation efficiency, while in this study no performance instability was observed with the accumulated acetic acid. In addition, propionic acid – which demands a low H$_2$ partial pressure for
its oxidation – is considered as stress indicator (Tsapekos et al., 2022). With the continuously addition of new decanted liquid, a mixed culture is added to the system. In the effluent of a biogas reactor, propionate could be found as process intermediate from the function of AD micro-
biome. During non-efficient ex-situ methanogenesis, H₂ can remain non-utilized, and this will enhance the accumulation of propionate due to non-favourable thermodynamic conditions (Guo et al., 2021). Its degradation requires a syntrophy between propionate-oxidizing bacteria and hydrogenotrophic archaea. However, high H₂ partial pressure inhibits this syntrophy resulting in propionate accumulation (Xu et al., 2016). The degradation can be thermodynamically restricted by high H₂ concentrations and so, the propionate will accumulate. In accordance, propionic acid was the second most abundant VFA in the studies of Ghofrani-Isfahani et al. (2022) and Tsapekos et al. (2021), while also being the most abundant in this study.

3.2.6. Flexibility towards an intermittent energy system

With validation of laboratory results in the pilot scale and showing the potential for biomethanation in larger scales, the successful scalability of dynamic operation was needed. While the steady-state operation of pilot scale biomethanation in BTFs indicated the technology would return to initial performance after variating downtimes at day 196, 230, 250, there was still a need to control and optimize these periods. To compare the scalability and dynamic operation in this study, Table 1 shows a comparison with other studies investigating dynamic operation.

The flexibility obtained in this study have been comparable to multiple laboratory studies. Tsapekos et al. (2021) does not directly compare but do show the potential of having downtimes of a higher order downtime periods. The downside would be the prolonged time to regain performance, but this could be optimized with a refeeding strategy. Comparing the study 24-hour controlled downtime in this study, using the same refeeding strategy as both Strübing et al. (2019) and Jonson et al. (2022), it was observed that pilot scale needed significantly longer time to regain performance (i.e., magnitude of 2-fold to 4.5-fold in time). This observation could be attributed to several reasons. The first one being the GRT of the different systems. This study had 20 min GRT which was around half of the value used in Jonson et al. (2022) which had 45 min. Thereby, the feed loading of this study was higher, which could be a reason of the longer time needed to regain performance. Strübing et al. (2018) had a cooled downtime and a normal operating temperature downtime, which both regained faster than in the present study. While the refeeding method was identical for this study, during the downtime of the 24 h, the constant trickling of both BTFs was kept on. This error led to a difference between the full laboratory method used in Jonson et al. (2022), semi-pilot study of Strübing et al. (2019) and this pilot-scale study. This could be the reasoning for the unexpected result from the 24-hour downtime. Further testing would be needed to validate if this was the reasoning. Another impact could be the time of steady-state operation for the maturing of the biofilm and adaptation to the feed load. Downtimes were performed at day 196, 230 and 250 in this study, after 150 days of operation in Jonson et al. (2022) and 86 days of operation in Strübing et al. (2021). All these studies are of comparable maturing, as the lowest of 86 days have been operated for almost 3 months, which would be relative long time to mature a biofilm, as enrichment periods previously have been shown to vary between 7 and 25 days. Therefore, the maturity of the biofilm was not seen as a reasoning for the unexpected results in this pilot scale study.

The flexibility of biomethanation and dynamic operation have been demonstrated within this study in larger pilot scale. While there have been found areas which needs further investigation and improvements, these results do show the great potential of this technology.

3.3. Assessment of pilot scale study

While the performance of the technology has been shown and discussed the cost aspects of this type of technology has not been mentioned. With this technology utilizing H₂ produced from electricity through e.g., an alkaline electrolysis, the produced H₂ can vary a lot in price, depending on the electrical spot prices. Along with the known low efficiency of alkaline electrolysis, a loss of energy is present. Combining this with the natural gas prices, this technology is of a low interest, in the aspects of the cost versus the product. Therefore, this technology could also be limited to area where electricity is of low enough price and/or the selling price of the biomethane is favourable.

To assess the performance of biomethanation in larger pilot scale, lab-based results have been compared and do validate the scalability and great potential of conducting biomethanation in BTF for future Power-to-X solutions. Nevertheless, there are some areas which needs more in-depth research and development for larger scale operations, to ensure more scalability within the methods used. (i) An area could be deeper understanding for nutrient requirements, with focus on which specifically are the needs for the hydrogenotrophic methanogens and how the nutrient supply could be optimized. Despite the present study demonstrated the use of commercial NPK and micronutrients solutions, optimization of the dosage is still needed. (ii) Another area of focus would be optimization of the methods used for dynamic operations. This study demonstrated that the previously found optimized refeeding strategy (Strübing et al., 2019) of H₂ after downtime periods did not have the same response time as in other studies (Jonson et al., 2022; Strübing et al., 2019; 2018), this could be due to constant trickling which would need further testing. The method also resulted in a higher H₂ output compared to legislation (Erhvervsministeriet - Sikkerhedsstyrelsen, 2018). This was improved with testing of another refeeding strategy which decreased the H₂ in the product gas with a 2.3-fold and was low concentration enough to not interfere with legislations. Research on these areas could contribute towards up scaling of this technology even further.

4. Conclusions

This study successfully demonstrated the implementation of a pilot-scale biomethanation system into a full-scale biogas plant for biogas upgrading. The operation and results obtained were validated by comparison with laboratory results. Under steady state and with GRT of 20 min a PC of approx. 10 m³CH₄ h⁻¹ m⁻³ reactor day⁻¹ was achieved with output gas quality matching the grid requirements of methane composition. The flexibility and dynamic operation of the technology was successfully demonstrated and showed the potential for implementation of larger scale biomethanation in an intermittent energy system, such as solar or wind powered electrolyzers.

Funding

The author was grateful that this study was financially supported by

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the project “eFuel – Electrofuel from a bio-trickling filter”, which is a Energiteknologiskt Udviklings- og Demonstrationsprogram (EUDP) project (Project ID 64018-0559).

CRediT authorship contribution statement

Brian Dahl Jenson: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing—original draft, Writing—review & editing. Panagiotis Tsapekos: Data curation, Visualization, Writing—original draft. schnur: Writing—review & editing. Muhammed Tahir Ashraf: Data curation, Visualization, Writing—original draft. Jens Ebyhe Schmidt: Supervision, Writing—review & editing. Juan-Rodrigo Bastidas-Oyanedel: Supervision, Writing—review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

An exceptional acknowledgement goes to Biogasclean A/S for their help and assistance in building and operating the pilot scale unit. CEO Thorkład Dahlgreen and technical employee Jan Thomsen have done an extraordinary effort to make the project a reality with their knowledge and work during this study.

References


