Biogas upgrade to biomethane in trickling bed reactors: Process optimization under mesophilic conditions

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Abstract. The biomethane sector is rapidly expanding due to the compelling advantages of renewable biomethane, which closely resembles non-renewable natural gas. In this work, we present a novel study on trickling bed reactors (TBR) under mesophilic conditions, demonstrating their robustness in producing biomethane with a content of 96% in methane (CH_4) at low gas retention times of 1 h. Our research brings a fresh perspective to the field of biomethane production.

Keywords: biogas, biomethane, trickling bed reactor, biological upgrade, *Methanobacter*

1. Introduction

Biomethane is a methane-rich fuel similar to natural gas, with over 1,400 operational plants in Europe. Upgrading biogas to biomethane primarily involves removing carbon dioxide (CO_2) through physicochemical methods, while biological methods using hydrogenotrophic methanogens are gaining interest. These methanogens convert CO_2 to CH_4 using hydrogen (H_2), which can be produced via water electrolysis powered by surplus green energy. Though this process enables the storage of renewable energy as CH_4, the low solubility of H_2 in water poses challenges. Ex-situ hydrogenotrophic methanogenesis in TBRs offers a more efficient approach under thermophilic conditions, although thermophilic conditions may cause instability due to volatile fatty acid accumulation (Spyridonidis et al 2024).

This study aimed to develop efficient mesophilic TBR and evaluate various operating conditions, including packing material, gas retention time (GRT), nutrient recirculation rate, nutrient addition, and pressure. Microbial analysis during the long-term TBR operation revealed insights into the prevailing microbial community.

2. Methods

Two lab-scale TBRs with a capacity of 1 liter each were set up and operated in parallel at a temperature of 39°C. The gas feed entered the TBRs from the bottom, while the liquid nutrient and trace metal supply was introduced from the top. This liquid trickled through the bed's supporting material, was collected in a bottle, and recirculated back to the top. The feeding mixture contained argon (Ar) instead of CH_4 because argon was more readily available. H_2 and CO_2 were supplied in various proportions, with the H_2/CO_2 ratio ranging from 3.5 to 4. Both TBRs were inoculated with digested material taken from a mesophilic digester. Samples were collected from both the liquid medium and the supporting material, and their DNA was extracted using an automated nucleic acid extractor (MagCore®). Microbial diversity in the samples was investigated through Nanopore sequencing of the full 16S rRNA gene. A bioinformatic pipeline was implemented to process the raw sequencing reads (Porechop, NanoFilt, Canu). The processed reads were subsequently mapped to the SILVA 138.1 SSU reference database using minimap2 with the map-ont preset, suppressing secondary alignments.

3. Results

3.1. Effect of the packing material

Two packing materials were tested: Bioceramax and Kaldness K1, which have specific surfaces of 1600 m^2/m^3 and 800 m^2/m^3, respectively. Despite its higher specific surface area, the efficiency of the TBR filled with the ceramic material (Bioceramax) was not superior. At a GRT of 2.2 hours, the BTR filled with Bioceramax produced biomethane with a total CH_4 content of 89.4 ± 1.4% (this accounts for both the produced CH_4 and the argon representing the biogas CH_4 contained in the feed but not reacting in the TBR). In contrast, the BTR filled with Kaldness K1 resulted in biomethane with a total CH_4 content of 95.1 ± 2.2% (see Figure 1). This suggests that the inoculum derived from digestate may be more effectively trapped and attached to the plastic material.

3.2. Effect of nutrient supply and liquid recirculation

After proving that the Kaldanes K1 was a suitable filling material, it was selected for both TBRs, which operated at a GRT of 2.2 hours. During the operation of the TBRs, the ammonia concentration in the recirculating medium fluctuated, reaching highs of 280 mg/L and lows of 1 mg/L. The total CH_4 in the outlet mixture was recorded at 97±1% and 87±5%, respectively. Supplementing with fresh digestate effectively maintained the ammonia levels above 20 mg/L, which was the lower threshold. Additionally, it was observed that reducing the liquid recirculation rate led to a deterioration in process efficiency.

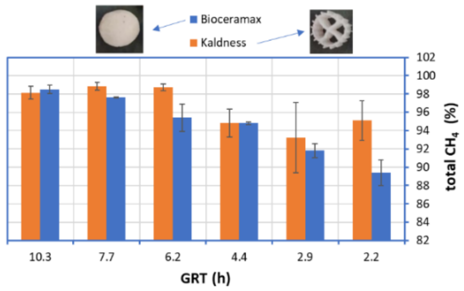

Figure 1. Effect of packing material on the total CH_4 content of biomethane produced from TBRs operated under various GRTs.

3.3. Effect of pressure

The headspace of one of the TBRs was connected to a 1-meter-high water column, creating an overpressure of 100 millibars. In contrast, the second TBR operated at atmospheric pressure. The GRT decreased from 2.2 hours to 1 hour in a stepwise manner (see Figure 2). Both TBRs were taken offline between the 80th and 110th days to evaluate the restart process after 30 days of inactivity. Upon restarting, both reactors quickly resumed operations. It appeared that the overpressure slightly enhanced process performance and stability.

The biomethane composition closely approached the maximum expected based on the stoichiometry of the reaction $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ until the 150th day, when the CH_4 content decreased in both reactors due to trace metal deficiency. After appropriate supplementation was provided to both reactors, the TBR with overpressure recovered and achieved a CH_4 content of 96% under a GRT of 1 hour. In contrast, the TBR operating at atmospheric pressure deteriorated, with total CH_4 content dropping to 60%. The overpressure seems to favor performance by positively influencing H_2 solubility and the diffusion of gases to the biofilm.

3.4. Microbial analysis

Analysis of the sequencing data revealed a relatively high bacterial diversity dominated by Firmicutes and Proteobacteria in all the samples. The genus *Proteiniclasticum* prevailed in the inoculum maintaining reduced stable levels in the supporting material and liquid medium. Although *Proteiniclasticum* is not a methanogen, it supports methanogenesis by degrading proteins and releasing metabolites that methanogens can use. Regarding the archaeal diversity, Euryarchaeota was the dominant phylum and the genus *Methanobacterium* predominated in the supporting material. Species belonging to the genus *Methanobacterium* are hydrogenotrophic methanogens.

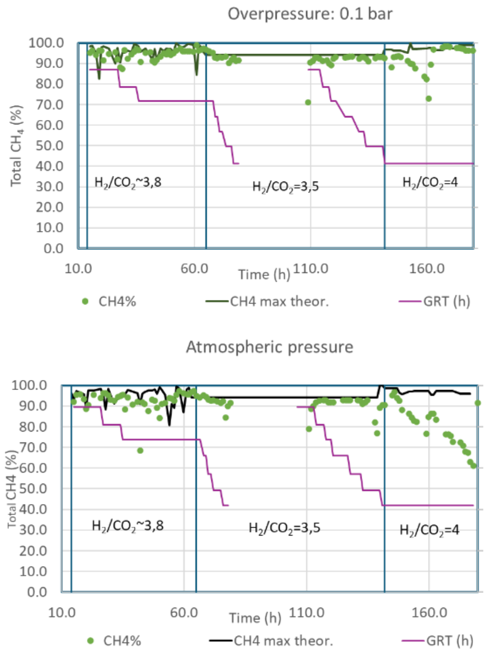

Figure 2. Effect of a slight overpressure on the total CH_4 content of biomethane produced from TBRs operated under various GRTs and gas influent composition

4. Conclusions

This study highlights the effectiveness of mesophilic TBRs in upgrading biogas to high-quality biomethane. Key factors, including packing material selection, nutrient management, and pressure conditions, significantly affect conversion efficiency and methane purity. Notably, Kaldness K1 produced more methane than Bioceramax despite its smaller surface area, underscoring the importance of microbial interactions. Maintaining optimal ammonia levels was crucial, and applying overpressure enhanced reactor performance and stability, enabling efficient biomethane production with shorter gas retention times. These findings support the development of stronger renewable energy strategies and the potential for biomethane as a sustainable energy source. Future research should focus on refining operational parameters and scaling these approaches for larger systems..

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