Comparative assessment of different packing materials in biological methanation

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Keywords: Biological Methanation, Trickle Bed Reactors, Packing Materials, Pressure, Gas-Liquid mass transfer
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Carbon utilization technologies are increasingly drawing attention due to rising CO_2 emissions. Biological methanation (or biomethanation) of H_2 and CO_2, also known as hydrogenotrophic methanogenesis, is an attractive method for capturing CO_2 (Burkhardt et al., 2019). Biomethanation is carried out by hydrogenotrophic methanogens, which utilize induced H_2 as an electron donor to reduce CO_2 to CH_4, according to the chemical equation Eq. 1 (Angelidaki et al., 2011). Several factors influence the reaction rate and efficiency of CH_4 production in this process (Lóránt & Tardy, 2022). Specifically, the mass transfer of H_2 from the gas to the liquid phase has been identified as the main rate-controlling factor (Pauss et al., 1990). Trickle bed reactors (TBR) are one of the most promising types for the biological methanation process. In TBR, packing materials with large surface areas ensure better gas to liquid mass transfer, resulting in higher CH_4 production (Kusnere et al., 2021).

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O, \Delta G^o = -130.7\ KJ/mol \quad \textbf{(Eq. 1)}$$

Pressure, along with other operational conditions, such as pH and temperature, are fundamental for the biological methanation process. These parameters influence the microbial community composition, which in turn affects the process performance (Ebrahimian et al., 2022). According to Henry`s law, the amount of dissolved gas in the liquid phase is proportional to its partial pressure in the gas phase (Ullrich & Lemmer, 2019). Previous research showed that pressurized reactors presented higher gas-liquid mass transfer, with significantly higher CO_2 and H_2 conversion rates (Ullrich et al., 2018). However, while high pressure improves process efficiency, it might create implications during reactor monitoring and operation (Mauerhofer et al., 2021). Thereby, the pressure might present a technical challenge for biological methanation to achieve higher process performance.

Considering that packing materials serve as a means of immobilizing microorganisms and enabling biofilm formation, those with a high specific surface are more efficient at supporting biomethanation process. In view of this aspect, the aim of the study is to evaluate and compare the performance of TBRs packed with three different packing materials with varying surface areas. Along with this, the present study aims to assess how operating pressure affects the biomethanation process.

On accounts of the above, three custom-made stainless steel TBRs of 1L functional volume have been installed. Raschig rings (6 x 6 mm each with a specific surface area of 4.9 x 10^{-3} m^2/g), activated carbon (in the form of pellets; 20 x 4 mm each with a specific surface area of 1100 m^2/g), and biochar (with a particle size exceeding 2 mm) have been placed inside the three reactors denoted as TBR1, TBR2 and TBR3, respectively. Additionally, the TBRs were designed to include custom pressure-struggling valves so as to investigate the influence of various operating pressures on methane production rate. The three gastight TBRs operate at thermophilic conditions (55 ± 1°C) using thermal jackets. Prior to the injection of H_2 and CO_2 gases, enriched hydrogenotrophic inoculum was recirculated within the reactors to wet the packing material and enable the development of sufficient biofilm on its surface. Municipal waste-derived digestate collected from the anaerobic reactor that operates in Thessaloniki's Wastewater Treatment Plant is used as a source of essential nutrients for the microbial community of the reactors. A synthetic gas mixture composed of 80% H_2 and 20% CO_2 is constantly provided to the reactors. This gas mixture is supplied from the top of the TBRs using peristaltic pumps (BT100-3J, Longer Pump, China). The liquid medium contained in the nutrient vessels is also provided to the top of the TBRs with the aid of peristaltic pumps (Sci-Q 300, Watson Marlow, United Kingdom), aiming to trickle the packing materials.

The performance of TBRs will be evaluated under four different Gas Retention Times (GRTs) denoted as phase I (GRT = 4 h), phase II (GRT = 3 h), phase III (GRT= 2 h), and phase IV (GRT= 1 h). The GRT will be

reduced by increasing the gas supply rate. The change of GRT will be applied immediately after achieving steady-state conditions in each phase (i.e., fluctuations in the output-gas composition of less than 5%). Additionally, the impact of pressure on the biological methanation process will be examined for all TBRs in an effort to further reduce GRT while maintaining high methane purity. Quantitative evaluation of the output gases will be performed daily with the use of water displacement gas-metering system. The composition of output gases will be determined twice per week by a gas chromatograph (GC-2014 Pro, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD) with a Porapak Q Column (1.83 m length, 1/8-inch inner diameter, and film thickness 2 mm) and Agilent J&W CP-Molsieve 5Å (1.83 m length, 1/8-inch inner diameter, and film thickness 2 mm) with helium as carrier gas. Liquid samples from the digestate vessels will be collected twice per week for the monitoring the reactors biochemical paramaters (i.e., pH, Volatile Fatty Acids composition, micronutrients concentration (Fe, Ni, Co)) and microbial composition.

Acknowledgments

The "Demonstration of a mobile unit for hybrid energy storage based on CO_2 capture and renewable energy sources (LIFE CO2toCH4 - LIFE 20/CCM/GR/001642)" project has received funding from the LIFE Programme of the European Union.

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