Operation of pilot scale biomethanation system for utilization of CO_2

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Biomethanation, a low-energy biological process, aligns with circular economy principles by valorizing CO_2, particularly from carbon-intensive sectors, and can integrate with carbon capture technologies. Trickle bed reactors (TBRs) excel in producing high-quality methane due to their design, allowing microbial immobilization on high-surface-area packing materials, enhancing gas-liquid mass transfer and methanogenic archaea activity (Chatzis et al., 2023; Tsapekos et al., 2021).

The core of the pilot-scale biomethanation system is a trickle-bed continuous reactor with a 100 L capacity, constructed from stainless steel, featuring three compartments for operational stability against malfunctions (e.g. clogging). Each compartment has its temperature-control thermal jackets (operating at 55 ± 2°C) and temperature sensors, while a pressure meter monitors the reactor's internal pressure. The system also includes an anaerobic vessel for recirculating liquid inoculum, ensuring even wetting of reactor packing material without flooding, thus maintaining a moist environment for microorganisms, supplemented with nutrients and trace elements. The output stream is driven to a gas flow meter for biomethane production monitoring. The gas supply (CO_2 and H_2) to the reactor is managed by mass flow controllers. The system's monitoring and data logging are overseen by a Programmable Logic Controller with remote access, allowing for automated operation, continuous parameter monitoring, and remote-control capabilities (Kontogiannopoulos et al., 2023).

The operational strategy of the pilot biomethanation unit was refined to achieve high biomethane production efficiency through gradual Gas Retention Time (GRT) reductions. Initially stabilizing at a 4 h GRT, the unit's GRT was methodically decreased in half-hour increments. This led to stable performance, with CH_4 concentrations in the output gas consistently exceeding 95% over 300 days (Figure 1a). At a 3 h GRT, the system achieved peak performance, with CH_4 concentration reaching 99.7%, showcasing near-complete conversion of CO_2 to methane. This efficiency persisted even when the GRT was reduced to 2.5 h, maintaining approximately 99% CH_4 content despite a temporary dip that never fell below 95.5%. This demonstrated the system's robustness and its ability to maintain high CO_2 capture and utilization efficiency under varying operational speeds.

The system exhibited high efficiency as GRT was further reduced to 2 h, with CH_4 content remaining above 95%. This period marked the first observation of metabolic water production, a byproduct of hydrogenotrophic methanogenesis, indicating the impact of reduced GRT on water production within the system. The system demonstrated resilience despite a slight decrease in CH_4 concentration to below 90% on the 154th day, possibly due to increased metabolic water. Maintaining the same pattern, when GRT was decreased to 1.5 h, the pilot scale biomethanation system continued to exhibit a CH_4 content exceeding 95% for 10 consecutive days. However, a significant challenge was encountered when the GRT was decreased to 1 h. The CH_4 concentration notably dropped below 70% on the 183rd day, probably due to limited gas-liquid mass transfer of H_2, crucial for efficient methanation. The rapid flow rate at this GRT impeded effective contact between H_2 and the microbial consortia, leading to a marked decrease in methanation efficiency. The system successfully regained its processing efficiency by substituting a considerable portion of metabolic water with filtered digestate from a biogas reactor, achieving a CH_4 concentration greater than 90%.

The analytical monitoring of the pilot unit's performance involved a detailed examination of Volatile Fatty Acids (VFAs) concentrations, which are pivotal for assessing the system's operational stability and methanation efficiency. The elevation of VFA levels, particularly following the reduction of GRT from 4 to 3 hours, highlighted a significant shift in the metabolic pathways within the system, potentially indicating a move towards homoacetogenesis rather than the desired methanogenic process. This unexpected shift, marked by a rapid increase in acetic and propionic acid concentrations, was an early warning of potential instability within the pilot unit's operational dynamics (Figure 1b). Moreover, the operational phase experienced notable fluctuations in pH values, further evidencing the system's instability. Specifically, reductions in pH were observed after the decrease of GRT from 4 to 3 h, directly correlating with the period of unstable operation. In contrast, during stable

operational phases with high methanation efficiency, the pH values consistently remained above 8, establishing a direct link between operational stability and pH levels.

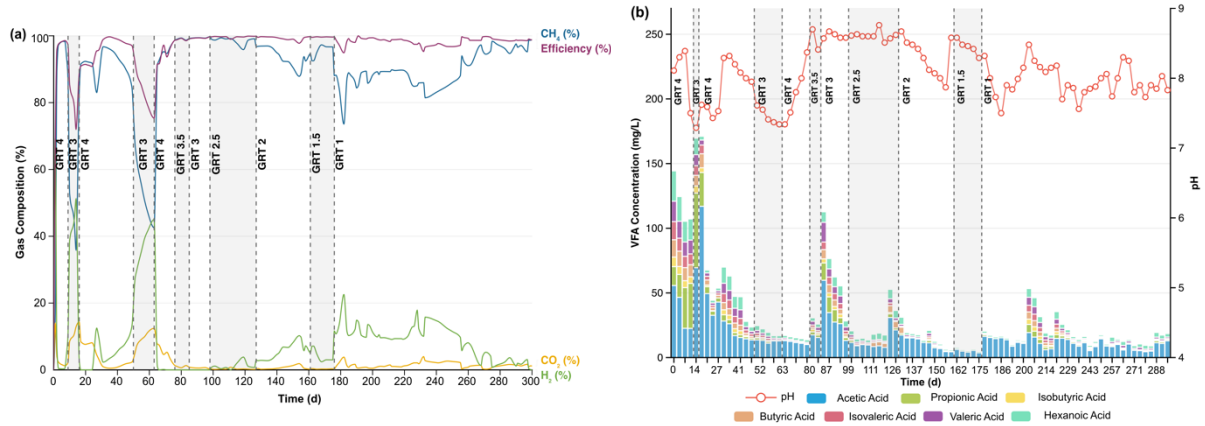

Figure 1. Output gas composition (%) of CH_4, CO_2, and H_2 of the pilot unit during the different GRT of the operation (left); Stacked bar-plot of individual VFA concentrations (mg/L). The red line illustrates the pH values during the different GRTs of the experiment (right). Dashed lines indicate the end of each GRT.

The continuous monitoring of VFAs and pH levels was essential to identify periods of operational instability and optimize performance towards effective biomethanation. In subsequent operational phases, despite the observed temporary spikes in VFA concentrations following GRT adjustments, the system exhibited remarkable resilience, and maintained high methanation efficiency, as evidenced by the stable and high CH_4 content in the output gas. This indicated a well-balanced biomethanation process capable of adapting to nutrient supply variations and operational changes without significant detriment to system stability or efficiency. This was further evidenced by the system's ability to sustain stable pH levels, even slightly outside the conventional optimal range for biological methanation, without adversely affecting the methanation process. The impact of metabolic water production on system pH was notably observed, particularly at reduced GRTs, where the dilution effect in the nutrient liquid contributed to pH variations without a corresponding increase in VFAs. This highlighted the complex interplay between metabolic water production, nutrient dynamics, and pH, underscoring the critical importance of pH management in optimizing biomethanation efficiency. The observed pH fluctuations and their correlation with methanation performance across different GRTs emphasize the necessity of maintaining optimal pH levels to ensure the system's stability and operational efficacy, especially under varying operational conditions.

The main objective of the current study concerns implementing and monitoring the biomethanation process under pilot-scale conditions aiming to convert CO_2 into biomethane, a renewable energy source, thus contributing to a reduction in net CO_2 emissions. For more than 300 days of operation, the pilot unit successfully captured more than 156 kg of CO_2, effectively utilizing it as a feedstock in the biomethanation process. Overall, the pilot scale biomethanation system showcased a robust and adaptable biomethanation efficiency, capable of maintaining efficient performance and high CH_4 output across varying operational conditions. The consistently low levels of VFAs across all GRTs underscored the operational stability of the unit, attributing the challenges encountered at shorter GRTs to factors beyond shifts towards less favorable metabolic pathways.

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References

Chatzis, A., Orellana, E., Gaspari, M., Kontogiannopoulos, K.N., Treu, L., Zouboulis, A., Kougias, G.P., Comparative study on packing materials for improved biological methanation in trickle Bed reactors. Bioresource Technology, 385, 2023, 129456

Kontogiannopoulos, K.N., Antoniadis, A., Roumpos, C., Kougias, P.G., Pilot scale biomethanation system for capturing and utilization of CO_2 from exhaust gases. 10th International Conference on Sustainable Solid Waste Management, Chania, Greece, 21-24 June 2023.

Tsapekos, P., Treu, L., Campanaro, S., Centurion, V.B., Zhu, X., Peprah, M., Zhang, Z., Kougias, P.G., Angelidaki, I., 2021. Pilot-scale biomethanation in a trickle bed reactor: Process performance and microbiome functional reconstruction. Energy Conversion and Management, 244, p.114491.