Ex-situ biomethanation at up-flow reactors

M. Peprah[1], P. Tsapekos[1], P.G. Kougias[2], I. Angelidaki[1]

[1]Department of Environmental Engineering, Technical University of Denmark, Kgs Lyngby, 2800, Denmark
[2]Soil and Water Resources Institute, Hellenic Agricultural Organization – Demeter, 60458 Thermi, Greece
Keywords: Anaerobic digestion, biogas upgrading, hydrogenotrophic methanogenesis, ceramic membranes.
Presenting author email: ptsa@env.dtu.dk

A minimum of 37% renewable energy contribution in the overall energy mixture is one of the main targets of European Commission for 2030. In addition, the sufficient access to reliable, sustainable and modern energy is the core of 7th Sustainable Development Goal of United nations "Affordable and Clean Energy" which should be achieved by 2030. In this context, biological biogas upgrading technologies are gaining increased attention as alternatives for the achievement of the aforementioned targets. In contrast to the traditional upgrading technologies (e.g. amine chemical scrubbing, water physical scrubbing, pressure swing adsorption), biomethanation process does not just separate and discharge CO_2. Specifically, hydrogenotrophic methanogens couple CO_2 derived from biogas with exogenous H_2 to form CH_4 during this biological process. To ensure process sustainability, the exogenous H_2 can be provided at low prices from water electrolysis using off-peak electricity excess from wind mills and/or photovoltaics at windy or sunny periods, respectively.

For biological methanation, H_2 is either supplied in the main biogas reactor (i.e. in-situ or hybrid process) or in a subsequent reactor (i.e. ex-situ or hybrid). When H_2 is injected to the main anaerobic digestion (AD) reactor, operational challenges related to increased pH levels due to the bicarbonate consumption and increased H_2 partial pressure lead to limited process performance. In contrast, ex-situ process is associated with improved efficiency using specialized methanogenic communities and nutrients derived from digested biowaste. Hence, the upgraded CH_4 rich biogas can be utilized not only for heat and power generation, but can be also exploited as an alternative transportation fuel or added in the natural grid for balance in cases of energy fluctuating incidents. Nevertheless, challenges related to low H_2 solubility, practical aspects (i.e. reactor design, diffusion equipment) and gas retention time (GRT) decrease still need to be optimized prior to the industrial scale implementation. Regarding H_2 solubility, novel and efficient diffusion devices are needed in order to increase H_2 poor gas liquid mass transfer. As for practical aspects, the traditionally used continuous stirred-tank reactor cannot lead in efficient gases dispersion and high gas to liquid mass transfer. Also, process sustainability is eliminated if an equally sized to the primary AD reactor should be constructed for the ex-situ concept. In addition, the minimum GRT should be attempted for stable biomethanation to treat more biogas in a fixed amount of time and so, ensure process sustainability.

The main aim of the present research was to investigate the efficiency of different ceramic membranes to increase the gas to liquid mass transfer during ex-situ biomethanation. Four up-flow reactors equipped with dissimilar diffusers were operated and the important biochemical parameters were monitored to elucidate process performance and biomethanation efficiency. Additionally, the composition of microbial communities was investigated to identify the important members for increased biological upgrading efficiency.

The efficiency of ex-situ biomethanation process was evaluated at thermophilic conditions (55 ± 1 °C) in four identical up-flow reactors of 1.0 L working volume. The first reactor (R_1) was equipped with a 1.2 μm aluminum oxide (Al_2O_3) diffuser and was used as a control due to previously sufficient upgrading performance of this membrane (Corbellini et al., 2018). As alternatives, silicon carbide (SiC) membranes with a pore size of 0.5, 7.0 and 14 μm were used to diffuse the gases in R_2, R_3 and R_4, respectively. The effluent of a well-performing biogas reactor fed with cattle manure was used as a nutrient source. To reduce lag phase, mixed hydrogenotrophic inoculum was collected from an efficient upgrading reactor system (Bassani et al., 2015). An artificially prepared synthetic gas mixture (i.e. H_2, CH_4, CO_2 with a ratio 62:23:15) was used to feed the up-flow reactors and replicate a real mixture of biogas supplemented with external H_2. For the initial experimental phase, the gas mixture was continuously diffused through the membranes at a flow rate of 2.4 $L/L_r/d$ and at a gas recirculation rate of 117 $L/L_r/d$. Once steady-state conditions were achieved, the Gas Retention Time (GRT) was decreased to 5 hours. The gas production was measured using an automated displacement gas meter of a 100 mL reversible cycle and the total production was recorded using a gas counter. TRACE 1310 and TRACE 1300 gas chromatographs equipped with a Flame Ionization Detectors (Thermo Scientific, USA) were used every three days to determine the exact biogas composition at the output and the volatile fatty acid accumulation in the up-flow reactor, respectively. Analysis of variance with a Fisher's Least Significant Difference test was conducted to compare the efficiency of reactors at steady-state conditions and reveal significant differences ($p < 0.05$). Moreover, the microbial composition of the mixed cultures was revealed using high-throughput 16s rRNA amplicon sequencing.

A summary of the major experimental results obtained at steady-state conditions is presented in Table 1. After a short lag-phase, the microbial communities adapted to the new environments and started to sufficiently coupling H_2 with CO_2 for CH_4 formation in all up-flow reactors. However, at steady-state operation, only the SiC-filled reactors achieved an output biomethane content that fulfills the highest standard (i.e. CH_4 > 95%) that allows the gas to be injected in the natural gas grid or to be directly used as transportation fuel. Among them, R_3 was associated with the highest biomethanation performance, reaching a value of 99% along with the highest production rate (0.31 ± 0.02 L_{CH4}/L_r/d), H_2 utilization and CO_2 utilization efficiencies (ηH_2, ηCO_2 = 99%). However, the performance of the alternative SiC diffusers was insignificantly different compared to R_3 ($p > 0.05$). Likewise, R_3 was the most efficient reactor at the second experimental phase. The superior performance of the 7.0 μm SiC membrane was shown by the high biomethane output (CH_4 >97%) and also, increased k_La compared to all alternative reactors. Overall, the bubbles generated by the larger pore sizes of the SiC diffusers could possibly led to a more efficient mixing of the liquid media in the up-flow reactors (Bassani et al., 2017). Specifically, sufficient mixing can boost the contact between injected gases and reactor´s liquid media, resulting in increased conversion rates. Furthermore, the positive impact of intense recirculation rate in biological biomethanation is also known (Alfaro et al., 2019; Díaz et al., 2015). The results support the hypothesis that SiC is a more promising material compared to Al_2O_3-based diffusers for gas injection. In addition, the results from 16s rRNA gene analysis revealed high abundance of hydrogenotrophic methanogens (e.g. *Methanothermobacter* genera were detected in the archaeal population) and syntrophic acetate oxidizing bacteria validating the efficient biological biomethanation process in reactors equipped with SiC membranes.

Table 1: Up-flow reactors' performances under steady-state operation

	CH_4 [%]	CO_2 [%]	H_2 [%]	CH_4 rate [L_{CH4}/L_r/d]	ηH_2 [%]	ηCO_2 [%]	k_La [day^{-1}]
GRT: 10 h							
R_1: 1.2 μm Al_2O_3	91 ± 0.5	2 ± 0.1	7 ± 0.1	0.26 ± 0.03	98 ± 0.1	95 ± 1.1	$2.37*10^3$
R_2: 0.5 μm SiC	97 ± 0.5	1 ± 0.1	2 ± 0.5	0.28 ± 0.02	99 ± 0.3	97 ± 0.2	$8.50*10^3$
R_3: 7.0 μm SiC	99 ± 0.1	1 ± 0.1	0 ± 0.1	0.31 ± 0.02	99 ± 0.1	99 ± 0.2	$1.57*10^4$
R_4: 14.0 μm SiC	98 ± 0.5	1 ± 0.1	0 ± 0.1	0.25 ± 0.01	99 ± 0.1	97 ± 1.1	$1.57*10^4$
GRT: 5 h							
R1: 1.2 μm Al_2O_3	84 ± 1.4	2 ± 0.1	14 ± 1.1	0.55 ± 0.04	91 ± 1.1	87 ± 2.2	$2.23*10^3$
R2: 0.5 μm SiC	90 ± 0.2	1 ± 0.1	9 ± 0.2	0.55 ± 0.01	88 ± 0.4	96 ± 0.2	$3.42*10^3$
R3: 7.0 μm SiC	97 ± 1.0	0 ± 0.1	3 ± 0.1	0.66 ± 0.02	96 ± 1.3	98 ± 0.3	$1.16*10^4$
R4: 14.0 μm SiC	71 ± 0.9	5 ± 0.1	24 ± 0.6	0.36 ± 0.07	83 ± 1.0	85 ± 1.0	$5.03*10^3$

To conclude, up-flow reactors equipped with SiC diffusers had improved output-gas quality due to the achievement of better reactor mixing at both experimental phases compared to Al_2O_3 diffusion devices. Microbial analysis showed high abundance of hydrogenotrophic methanogens and proliferated syntrophic bacteria confirming the effect of H_2 to alternate AD microbiome and enhance hydrogenotrophic methanogenesis.

Acknowledgement
This work was supported by Energinet under the ForskEL project "-BioUpgrade-Ex-situ biogas upgrading through biologically mediated CO_2 reduction" and the MUDP project ''VARGA - VAnd Ressource Genvindings Anlægget''.

References

Alfaro, N., Fdz-Polanco, M., Fdz-Polanco, F., Díaz, I., 2019. H2 addition through a submerged membrane for in-situ biogas upgrading in the anaerobic digestion of sewage sludge. Bioresour. Technol. 280, 1–8.

Bassani, I., Kougias, P.G., Treu, L., Angelidaki, I., 2015. Biogas Upgrading via Hydrogenotrophic Methanogenesis in Two-Stage Continuous Stirred Tank Reactors at Mesophilic and Thermophilic Conditions. Environ. Sci. Technol. 49, 12585–12593.

Bassani, I., Kougias, P.G., Treu, L., Porté, H., Campanaro, S., Angelidaki, I., 2017. Optimization of hydrogen dispersion in thermophilic up-flow reactors for ex-situ biogas upgrading. Bioresour. Technol. 234, 310–319.

Corbellini, V., Kougias, P.G., Treu, L., Bassani, I., Malpei, F., Angelidaki, I., 2018. Hybrid biogas upgrading in a two-stage thermophilic reactor. Energy Convers. Manag. 168, 1–10.

Díaz, I., Pérez, C., Alfaro, N., Fdz-Polanco, F., 2015. A feasibility study on the bioconversion of CO2 and H2 to biomethane by gas sparging through polymeric membranes. Bioresour. Technol. 185, 246–253.