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Biogas upgrade with green hydrogen in a semi-pilot trickle bed reactor

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Abstract The current study investigated the performance of biological methanation of CO_2 using green H_2 in a mesophilic (37°C) trickle bed reactor (TBR) (0.051m^3) at ambient pressure. For both phase A and phase B a synthetic gas feed (60/40 CH_4/CO_2) was used to simulate biogas. Nitrogen was used in phase A for better monitoring of the system. For phase A the average productivity of methane was 3.2 $m^3_{CH_4}/(m^3_{trickle\ bed} * d)$ at methane content of 71.3% with 10.3% N_2. For phase B no Nitrogen was used, and the average productivity of methane was 1.3 $m^3_{CH_4}/(m^3_{trickle\ bed} * d)$ at methane content of 97.9% with less than 0.1% residual H_2.

Keywords: *TBR, Biogas, Biological methanation, mesophilic*

1. Introduction

Due to the fluctuating availability of renewable energy, there is a growing demand for flexible efficient energy conversion and long-term storage technologies that utilize existing infrastructure and distribution networks (Sterner et al., 2021). One promising approach is the concept of Power-to-Gas (PtG) which converts surplus electricity generated from renewable sources to produce H_2 via water electrolysis.

However, hydrogen due to its extremely low density, high diffusivity in combination with inadequate facilities faces serious challenges for its transportation, storage and application (Qyyum et al., 2021). To address these limitations, H_2 can be combined with CO_2, derived from emission streams and produce CH_4 through the reaction

$$4H_2 + CO_2 \rightarrow CH_4 + H_2O$$

The synthetic methane can be directly injected into the existing natural gas grids. Regulations for the required methane concentrations to this end ranges from 80% (Netherlands) (Tauber et al., 2021) to 96% (Austria, Switzerland) (Muñoz et al., 2015). The conversion of CO_2 and H_2 can be achieved by a catalytic chemical reaction (Sabatier process) or by methanogenic microorganisms (Hydrogenotrophic methanogens). Biological methanation offers several advantages, including higher resistance to gas impurities, such as H_2S and NH_4^+ (Lecker et al.,2017) (Calbry-Muzyka et al., 2019) and lower energy requirements, since it operates at 35-75°C compared to the catalytic approach (>250°C)(Götz et.al.,2016). However, the main limitation of the process is the very low solubility of H_2 in water leading to serious gas-liquid mass transfer constraints. Different types of reactors have been studied with the one showing the most promising results being the trickle bed reactor due to their high surface-area per reactor volume increasing the phase boundary interface and mitigating the gas-liquid mass transfer limitations.

While most existing studies focus on CO_2_ and H_2 as feed gases, few of them investigate biogas upgrading under realistic conditions. This study aims to evaluate the performance of a mesophilic trickle bed reactor for synthetic biogas upgrading using green hydrogen, simulating real-world applications.

2. Materials and Methods

2.1. Trickle bed reactor setup

The semi-pilot trickle bed reactor system consisted of a double-walled plexiglass tube with a height of 2000mm and an inner diameter of 212mm and a total volume equal to 70.5L. Thus, the height to diameter ratio was 8.3. The liquid medium was recirculated to the top of the reactor through a perforated stainless-steel sphere with 2mm diameter holes, while the gaseous feed (green H_2, CO_2, CH_4 and N_2) entered at the bottom in a countercurrent flow configuration. The production of green hydrogen was carried out using an Enapter EL 2.1 electrolyzer, powered by photovoltaic panels. Temperature was maintained at mesophilic conditions (37°C) via heated water circulation in the reactor jacket (7L volume) and was monitored in the headspace using a thermocouple. The packing occupied 73% of the total volume and was 51L. Two types of fillers were used, one with a high specific surface area (955m^2/m^3) HXF13KLL+ and one with a low specific surface (420m^2/m^3) HXF25KLL made of polyethylene. The porosity was 0,658 and 0,918 respectively. The fillers were packed in the following alternating configuration: 12L HXF25KLL-7.5L HXF13KLL-12L HXF25KLL-7.5L HXF13KLL-12L

HXF25KLL. The trickling liquid was circulated at an average rate of 10L/h for 7 minutes, 2 times a day.

2.2 Operating Conditions and phases

Table 1 Operational parameters

Phase	Days	Hydrogen gas feed rate $\frac{m^3_{H_2}}{m^3_{tricklebed}*d}$	Methane production rate $\frac{m^3_{CH_4}}{m^3_{tricklebed}*d}$	Methane content [%]	Methane and N_2 content [%]
A	1-11	11.8	3.2	71.3	81.6
B	1-13	4.9	1.3	97.9	-

To validate the accuracy of gas flow and concentration measurements, N_2 was added to the feed at a rate of $1.1m^3_{N_2}/(m^3_{trickle\ bed} * d)$ in Phase A. No Nitrogen was added in phase B. On day 2 of phase A a $NaHCO_3$ solution was added to the liquid media to maintain a pH above 7. Also, on day 8, in order to enrich the hydrogenotrophic methanogens, anaerobic sludge from a full-scale wastewater treatment plant (WTTP) digester (Metamorphosis, Greece) was added to the system. Prior to addition, the sludge was pre-treated with NH_4Cl to restrict the activity of other homoacetogens and acetoclastic microorganisms (Tauber et al., 2023; Wang et al, 2020).

2.3 Analytical methods

The analytical measurements (pH) were performed according to the standard methods for the examination of Water and Wastewater. The volatile fatty acids (VFAs) were measured via Gas Chromatography (Shimadzu GC-2010 plus) and the concentration of ammonia nitrogen was measured using Photometer HI83303.The CH_4, CO_2,H_2,CO and H_2S content of the biogas was measured using a portable gas analyzer (Gas Data-GFM436)

3.Results and discussion

The pH for both phases was kept between 6.6 and 7.18 for phase A and 7.2-7.4 for phase B. ammonia N was kept above 2000mg/L for both phases to restrict side reactions and thus the undesirable production of VFAs instead of methane. Figure (A) demonstrates the reactor's gas product output. The data indicate incomplete conversion of H_2 and CO_2 by the hydrogenotrophic methanogens due to the high inlet gas loading rates. Pre-treated anaerobic sludge (2L) was added into the reactor on day 8 in order to enrich the community of the hydrogenotrophic methanogens and this seems to have had a positive effect on the conversion (further data collection ongoing).

The achieved product gas and the average methane concentration was 71.3% rising to 81.6% when considered that N_2 can simulate the role of CH_4 in biogas while the methane productivity averaged $3.2m^3_{CH_4}/(m^3_{trickle\ bed} * d)$ (excluding input CH_4). Subsequently, as shown in figure (B) a reduction of the feed gas flows significantly improved product quality with average 97.9% methane purity and a productivity of $1.3m^3_{CH_4}/(m^3_{trickle\ bed} * d)$.

4.Conclusions

This study demonstrates the feasibility of biogas upgrading in a trickled bed reactor system with biological methanation under mesophilic conditions using green hydrogen. Highenough gas retention times lead to very high concentration of methane at the gas product. Maintaining a high ammonia N concentration in the feed proves to be a good strategy for avoiding undesirable side conversions to acetic acid by homoacetogenic bacteria.

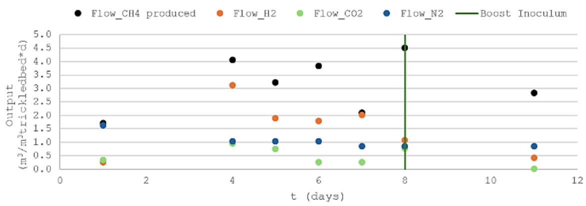

Figure 1 Composition of gas flow in phase A

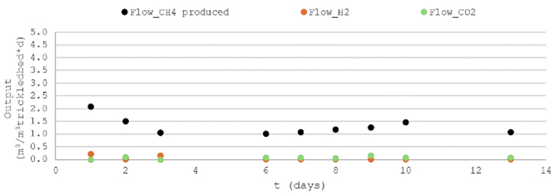

Figure 2 Composition of gas flow in phase B

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