CH_4 production at moderate H_2/CO_2 pressures – insights on the specific hydrogenotrophic methanogenic activity

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Abstract
CO_2 is one of the main contributors to greenhouse gases (GHGs), being its emission to the atmosphere one of the major driver of global climate change. Biological methanation of CO_2 using renewable H_2 provides a promising approach to use of superplus renewable electrical power to produce a gaseous fuel. CH_4 is considered an important renewable energy carrier, that has a wide range of applications such as natural gas for distribution. Hydrogenotrophic methanogens are key elements in the CO_2/H_2 methanation process. Thus the importance to study the specific hydrogenotrophic methanogenic activity (SHMA). The effect of the initial substrate (H_2/CO_2) pressure on the SHMA was investigated in two different pressurized bioreactors. The results suggest that in addition to the increase of the initial substrate pressure, also the bioreactor configuration influence the SHMA, which is crucial for the success of biological CO_2 methanation technologies but also in anaerobic bioreactors treating wastewaters.

Keywords: SHMA; Biological CO_2 methanation; Pressurized bioreactors

1. Introduction

Biological methanation of CO_2 with H_2 produced via water electrolysis using the superplus renewable electrical power (*e.g.* wind and solar) offer opportunities to reduce the CO_2 emissions while storing the excess of renewable electrical energy in chemicals/fuels.

During H_2/CO_2 methanogenesis, hydrogenotrophic methanogens are responsible by 95 % to 98 % of the H_2 consumption, thus playing a vital role in maintaining a low H_2 partial pressure in the anaerobic digestion processes (Liu et al., 2016). Therefore, it is of utmost importance to study the specific hydrogenotrophic methanogens activity (SHMA) for a stable and efficient process performance. The SHMA determines the activity of the H_2-consuming microorganisms present in the methanogenic population (Coates et al., 1996). In this work, the effect of initial substrate (H_2/CO_2) pressure, from 100 kPa to 500 kPa, on the SHMA and subsequent conversion to CH_4 was investigated in two different pressurized bioreactors.

2. Material and Methods

H_2/CO_2 bioconversion was carried out in two different pressurized bioreactors: a stirred tank bioreactor (STR) (total volume of 600 mL) and a gas lift bioreactor (GLR) (total volume of 3500 mL). The anaerobic liquid medium was prepared as described previously by (Stams et al., 1993). A synthetic mixture of H_2/CO_2 (80%/20%, v/v) was used as substrate. Five different initial substrate pressures were tested (100 kPa, 200 kPa, 300 kPa, 400 kPa and 500 kPa). All the experiments were conducted in batch mode at 37 ºC.

Anaerobic granular sludge (VS = 82 g_{VS} $kg^{-1}_{biomass}$) collected from a wastewater treatment plant was used as inoculum. The specific methanogenic activity of the inoculum in the presence of acetate (30 mM) reached 144 ± 74 mL CH_4 g^{-1}_{VS} d^{-1}, whereas in the presence of H_2/CO_2 (80:20, v/v) reached 443 ± 26 mL CH_4 g^{-1}_{VS} d^{-1}. Specific methanogenic activity was expressed at STP conditions.

For both reactors, the CH_4 accumulated in the headspace was measured by gas chromatography. The SHMA was determined according to Coates et al. (1996). A modified Gompertz model was applied to describe the evolution of cumulative CH_4 production obtained from the batch experiments (Costa et al., 2012).

3. Results and Conclusions

3.1. Effect of initial H_2/CO_2 pressures on the CH_4 production rate

Figure 1.1 shows the profile of cumulative CH_4 production obtained at each initial substrate pressure tested at STR (Figure 1.1A) and GLR (Figure 1.1 B). As expected, the CH_4 production increase with the increase of initial substrate pressure as a result of the increase on substrate concentration.

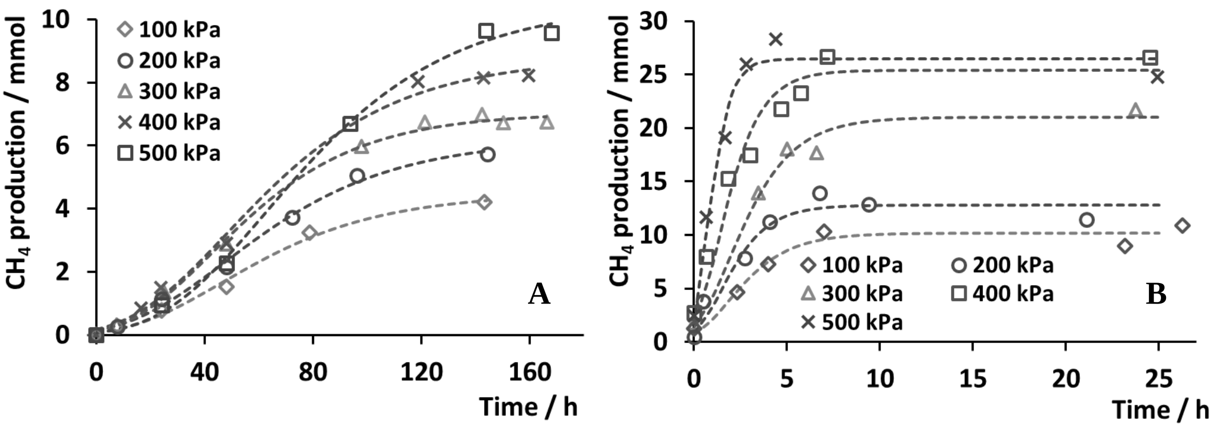

Figure 3.1 - Cumulative CH_4 production obtained for the different initial substrate pressure tested at STR (Figure 1.1A) and GLR (Figure 1.1B) bioreactors.

Table 1.1 reports the results of the dynamic model, CH_4 production rate (R_m), lag phase (λ) and the correlation coefficient (R^2), obtained for the different initial substrate pressures. The correlation coefficients above 0.94 suggest the suitability of the modified Gompertz model. For both bioreactors, an increase on the CH_4 production rate with the increase of the initial substrate pressure was observed. The superior performance of the GLR is evident from the absence of lag phase and from the significantly higher rate of CH_4 production that was 144-fold higher that in the STR at 500 kPa. This suggests that GLR is a promising reactor to perform the hydrogenotrophic reaction aiming at developing an efficient CO_2 capture and utilization process.

Table 1.1 Experimental and predicted CH_4-production parameters obtained at different initial substrate pressures (100 to 500 kPa), at STR and GLR bioreactors.

Initial substrate pressure[a] kPa		100	200	300	400	500
STR	R_m / mmol h^{-1}	0.05	0.06	0.08	0.09	0.10
	λ / h	12.8	11.9	12.1	12.7	24.1
	R^2	0.992	0.995	0.997	0.995	0.997
GLR	R_m / mmol h^{-1}	1.59	3.33	4.09	7.27	14.44
	λ / h	0.00	0.00	0.00	0.00	0.00
	R^2	0.991	0.943	0.984	0.948	0.969

[a]Initial substrate (H_2/CO_2) pressure of the system corresponds to the initial total pressure.

3.2. Effect of initial H_2/CO_2 pressures on hydrogenotrophic activity

Table 1.2 reports the SHMA obtained at each initial substrate pressure tested. The results showed an increase in the SHMAs with the increase in the initial substrate pressure, suggesting as well that: 1) no microbial activity inhibition was observed with the increase in the H_2 partial pressure, and 2) the mass transfer of H_2 from headspace to liquid could be a limiting step. At STR, the SHMA was increased 2-fold with the increase on the initial substrate pressure from 100 kPa to 500 kPa, whereas at GLR the SHMA was increased 9-fold.

The GLR was also able to mimic the condition of the SHMA test that was designed to provide the conditions that allow to assess the maximum potential hydrogenotrophic activity (Coates et al., 1996). The maximum potential SHMA of the inoculum was 443 ± 26 mL CH_4 g^{-1}_{VS} d^{-1}, a value that was also obtained in the GLR for similar pressure conditions. , In a GLR, the gas stream is injected from the bottom of the reactor promoting the agitation as well as the material exchange between the gas phase and the liquid medium (Merchuk and Camacho, 2010).

Table 1.2 - Results of the specific hydrogenotrophic methanogenic activity (SHMA) at different initial substrate pressures, at STR and GLR bioreactors.

Initial substrate pressure[a] kPa	SHMA mL $CH_{4@STP}$ gVS^{-1} d^{-1} STR	GLR
100	64	370
200	87	520
300	107	677
400	112	937
500	146	1612

[a]Initial substrate (H_2/CO_2) pressure of the system corresponds to the initial total pressure.

In conclusion, these results propose that in addition to the increase of the initial substrate pressure, also the bioreactor configuration influence the SHMA. According to the results, for a maximum CO_2 conversion, a GLR should be used. These insights are of utmost importance for the biological CO_2 methanation technologies and to develop efficient CO2 capture and storage processes based on sustainable and green biocatalysts.

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