Explanatory Pages

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Conference Topic 3:
Biomass conversion technologies for fuels, chemicals and materials
3.4 Biomethane
Upgrading of methane rich gases (biologically and thermochemically produced); Biomethane injection into the grid; Technological improvements; Measurement and control systems.

Is Bio-P2G technologically attractive as contribution towards balancing the supply and demand of renewable energy?

Gert Hofstede, Emile Apol, Ronald Wedema, Jan Peter Nap and Folkert Faber
Hanze University of Applied Sciences, Institute for Life Sciences and Technology, Zernikeplein 11, 9747 AS, Groningen, the Netherlands,

correspondence:
Gert Hofstede (g.j.h.hofstede@pl.hanze.nl), The Netherlands, Tel.: +31 631968208

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Nomenclature:

Bio-P2G	: Bio-Power to Gas
RH	: bioreactor administered with hydrogen gas
RC	: control bioreactor
MMB	: Methanomicrobiales (hydrogenotrophic methanogens)
MSL	: Methanosarcinales (acetoclastic methanogens)

1. Introduction

The Bio-P2G-program (Bio-Power to Gas) at the Hanze University of Applied Sciences evaluates the technologic feasibility of the biological reduction of carbon dioxide with hydrogen to methane (biomethanation: $1\ CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$) Chemically, this process is known as the Sabatier reaction, but within anaerobic digestion the biological methanation is catalyzed by a specific group of microorganisms: the hydrogenotrophic methanogens. [5]
In Figure 1, the Bio-P2G process is shown, in which excess of renewable electricity from wind turbines and solar panels is used for electrolysis to store energy as H_2. Subsequently, this renewable H_2 might be administered to an anaerobic digester in which biogas is produced, to stimulate biological methanation by hydrogenotrophic methanogens. As a result, biogas with an increased methane concentration (higher

calorific value) is produced. This concept might be an attractive contribution towards balancing the supply and demand of renewable energy. It develops the necessary further technological development, along with detailed assessments of the microbial community.

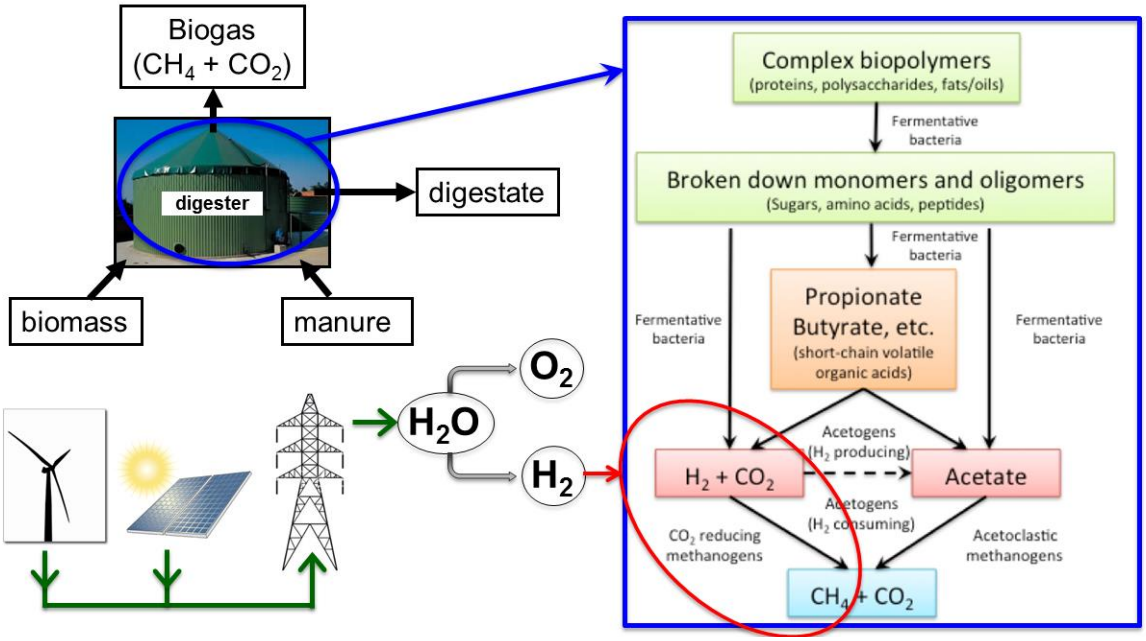

Figure 1. Principle of Bio-P2G. Water (H_2O) is electrolyzed into hydrogen (H_2) and oxygen (O_2); hydrogenotrophic methanogens combine the hydrogen with carbon dioxide (CO_2) to form methane (CH_4).

A major issue in Bio-P2G is solubility of hydrogen when it is added to the digester. Due to the low mass transfer rates of hydrogen from the gas to liquid phase, the overall process rate of biological methanation might be impaired. So, technological innovations to the bioreactors in which anaerobic digestion is performed, will be studied in order to increase these mass transfer rates of hydrogen.
In addition, the choice and efficacy of the micro-organisms performing the biological methanation in the digester is of interest. This may involve communities of microorganisms or can be accomplished with pure cultures. Based on the experiments and data from the literature, the composition and change in composition of the microbial communities as a results of hydrogen addition will be monitored with modern DNA techniques, such as next generation sequencing (metagenomics) of PCR based identification technologies (Taqman-PCR).

Explanatory Pages

2. Methodology

Comparisons of Lab-Scale Bio-P2G technologies: Assessment of the reactor configuration that is best to apply

Biological methanation was studied at mesophilic conditions (42°C) in two 10 litre bioreactors (Infors) in an "in situ" setup, in which hydrogen was added directly to the continuously stirred bioreactor in which anaerobic digestion was performed. The bioreactors were operated in a fed-batch mode continuously feeding the bioreactors with only a concentrated artificial substrate mixture (containing glucose (0,67M), acetic acid (0,98M), propionic acid (0,44M) and butyric Acid (0,53M)) using a syringe pump. This setup made it possible to vary the rate of biogas production by varying the rate of substrate injection.
Hydrogen was added to only one of the bioreactors. This bioreactor (RH) was equipped with a submerged 10-metre silicone tube, through which the hydrogen was added using a Mass Flow Controller (EL-FLOW® Select Series Mass Flow Controller, Bronckhorst®) to control the rate of H_2 addition. Silicone tubing is permeable to hydrogen-gas; silicone rubber has one of the highest permeation rates among all types of rubber [1]. In the control bioreactor (RC) no hydrogen was added. The bioreactors were operated for approximately 3 months, in which both the substrate addition rate and the hydrogen addition rate were varied independently. Biogas production rate was monitored using the AMPTSII (Bioprocess Control), which measured the methane production (total volume and methane production rate). Biogas composition was measured regularly by taking gas samples from the head space of the bioreactors through a rubber septum using a gas tight syringe and injecting in a Gas Chromatograph (GC-2014 - Shimadzu Scientific Instruments, Restek® Shin Carbon ST Column, Molecular Sieve)
To study the changes in the methanogenic communities a duplex Taqman® assay was developed in order to investigate the ratio between the methane production from acetate by **acetogenotrophic** methanogens (Methanosarcinales, MSL), and the methane production from CO_2 and H_2 by and **hydrogenotrophic** methanogens (Methanomicrobiales, MMB).

3. Results and Discussion

Anaerobic digestion of the artificial substrate mixture was studied over the time course of approximately 3 months. Addition of hydrogen clearly resulted in the conversion of carbon dioxide to methane: with an input rate of the substrate mixture of 1,0 ml/hr, theoretically, a methane production rate of approximately 119 ml/hr of CH_4 could be expected if all substrate was converted to biogas (using the Buswell equation [ref 3]). In reactor containing hydrogen (reactor RH), the CH_4 flow-rate of the biogas was about 104,8 +/- 12,2 ml/hr in RH, compared to the control bioreactor (RC) 75,4 +/- 14,4 ml/hr. Theoretically, biogas would contain 53% of CH_4 and 46% of CO_2.The relative amount of CH_4 increased up to approximately 28% relative to the

Explanatory Pages

bioreactor without adding hydrogen gas, as shown in Figure 2. There was a clear correlation between the amount of H_2 being added, and the increase in the percentage of CH_4. No H_2 was observed in the headspace of RH, which means that all added H_2 was consumed. Increasing the addition rate of the hydrogen from 1 to 5 ml/min showed that the all hydrogen was utilized up to 2 ml/min.
A further increase of the hydrogen addition rate, in combination with a substrate addition rate of 1 ml/min, resulted in the appearance of hydrogen in the head space. In addition, this increased hydrogen addition rate also resulted in an increase of pH (from 8.0 to 9.3). This was probably due to the depletion of bicarbonate, which resulted in a decrease in alkalinity with a subsequent increase in pH [2]. Addition of ammonium chloride (2,24M) in the substrate mixture resulted in a stabilization of the pH at pH 8.3. The results obtained are summarized in Table I.

Table 1: Comparisons of Lab-Scale Bio-P2G technologies: Assessment of the reactor configuration that is best to apply

	RH (plus hydrogen)	RC (without)
Substrate ($C_1H_2O_{0,87}N_{0,24}$), (ml/hr)	1,0	1,0
Hydrogen addition (ml/min)	1,0	-
Theoretical (Buswell) CH_4 production (ml/hr)	134	119
Experimental CH_4 Production (ml/hr)	104,8 +/- 12,2	75,4 +/- 14,4
pH	8,0	8,1
Stirring (rpm)	75	75

In Figure 2, the results are shown of the methane levels in 2 lab scale-bioreactors both fed with the same substrate (the same composition and the same quantity). On day "null" the percentage of CH_4 measured in both reactors (sample taken from headspaces of both reactors and analysed with Gas Chromatography). There was no significant difference is at t = 0, in both reactors. Hydrogen gas was added to only one of the reactors (RH) at a flow rate of 1 ml/min (controlled with Mass Flow Controller, Bronckhorst). During 20 days, the percentage of CH_4 was measured in both reactors. The blue line represents the reactor (RH) to which Hydrogen is added, the orange line represents the control reactor (RC).
From Figure 2, a clear difference was observed in the percentage of CH_4 between reactor RH (with hydrogen) and reactor RC (without hydrogen). The difference in CH_4 was ~28%. This difference was accompanied by a decrease in CO_2 in reactor RH with respect to reactor RC (data not shown). Based on this it was concluded that CO_2 was reduced with hydrogen to CH_4.

Explanatory Pages

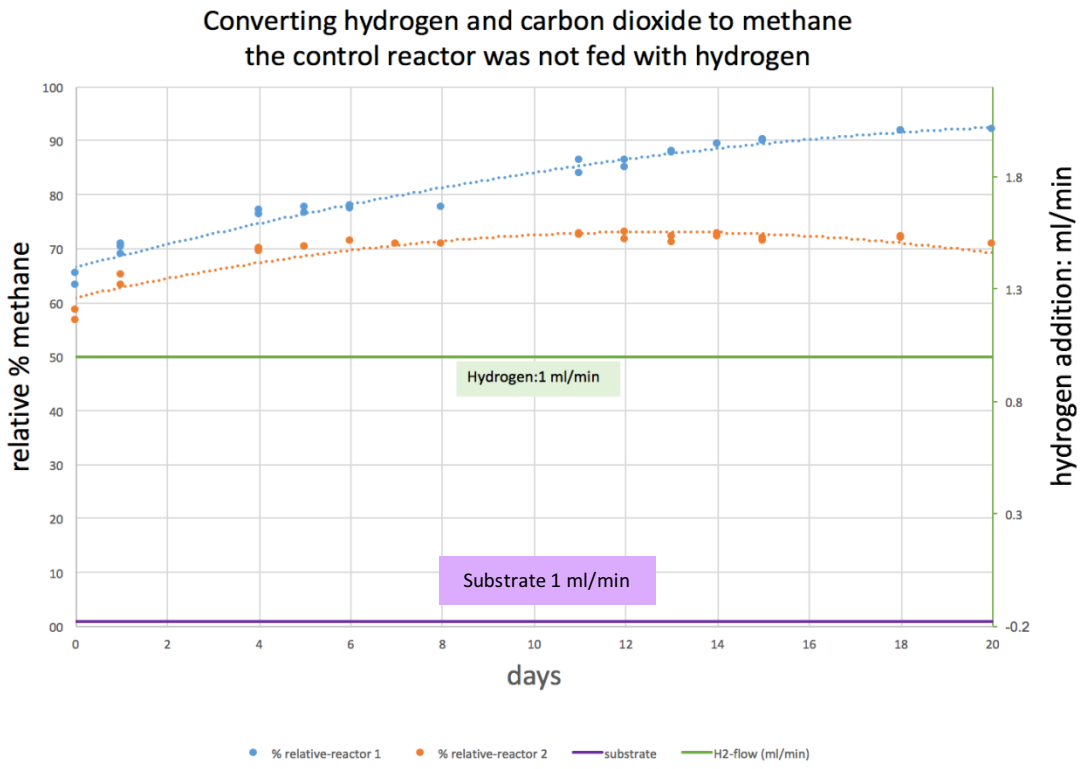

Figure 2: the relative percentages of CH_4 in reactors RH (blue) and RC (orange). Hydrogen (1 ml/min) is only added to reactor RH. Substrate (1 ml/hour) is added to both reactors (RH and R-) The percentage CH_4 is measured (GC, molecular Sieve) during 20 days.

In order to be sure that the increased CH_4 production rate was a consequence of the addition of the hydrogen, the hydrogen-flow was reduced to 0 ml per minute (Figure 3). In Figure 3 we see that the percentages of methane are equal after 23 days: the percentage of CH_4 in both reactors (RH & RC) after 23 days are 53% in reactor RH and reactor 50.5% in RC.

Explanatory Pages

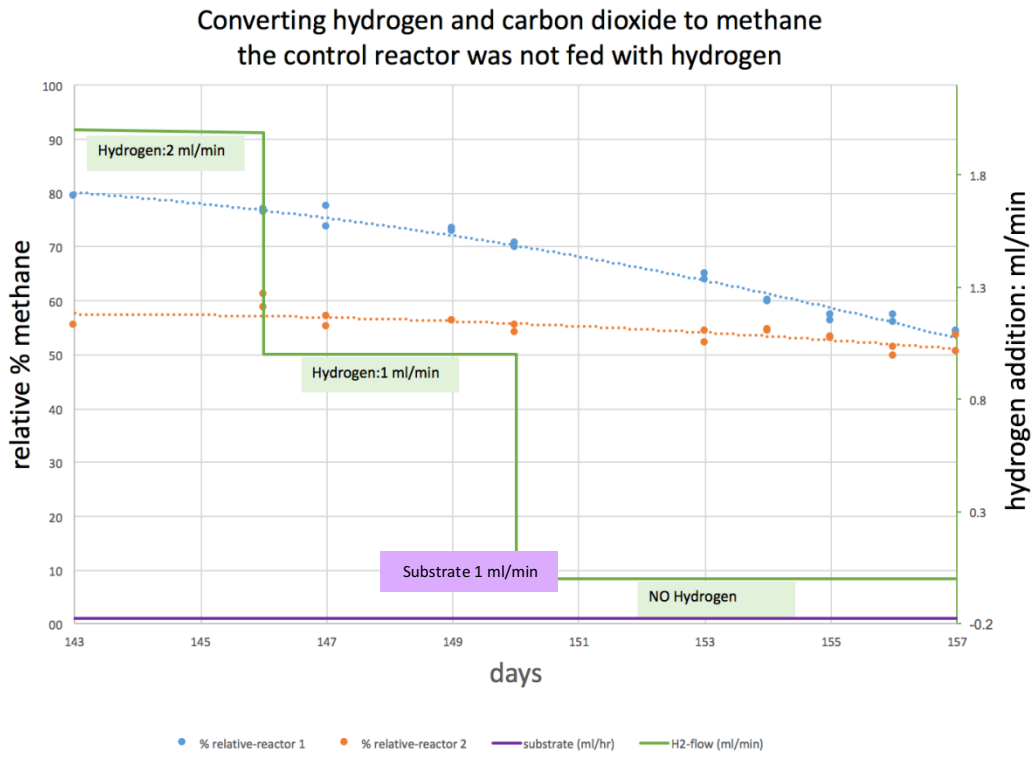

Figure 3 relative percentages of CH_4 in reactor RH (blue) and R- (orange). Substrate (1 ml/hour) is added to both reactors (RH and R-) The percentage CH_4 is measured (GC, molecular Sieve) during 20 days.

The development of a new Taqman-assay to study the changes in the methanogenic communities is ongoing. In the new designed Taqman-assay, an internal control of phage lambda DNA is used to for relative quatification of hydrogenotrophic methanogens (MMB) and acetoclastic methanogens (MSL). Using a new developed R-script the statistical program R was used to calculate the ratios MSL and MMB in each individual reactor at each different time points. The first results showed an increase of the hydrogenotrophic methanogens relative to the acetoclatic methanogens in the reactor administered with H_2 (RH).

4. Conclusion

It is anticipated that the hydrogen supply to the methanogens may be a limiting factor. Hydrogen gas has a low solubility in water and the concentration of dissolved hydrogen is likely to be an important factor determining the overall rate of methane production. Therefore, research has been done to a ‘new’ method of hydrogen administration. The current setup makes use of the high permeability of silicone-tubing. In the “in situ” bioreactor setup, addition of 2 ml/min of hydrogen resulted in sufficient diffusion and solubilisation to convert the produced CO_2 in the biogas by

biomethanation. It is possible to administer hydrogen in a relatively inexpensive and simple way. Currently, experiments are ungoing to increase the biogas production by increased substrate addition rate, combined with increased H_2 addition rate, to study the limits of hydrogen diffusion in the silicone tubing.

Furthermore, as expected, preliminary results with a newly developed Taqman assay clearly showed a relative increase of hydrogenotrophic methanogens compared to acetoclastic methanogens in the bioreactor in which hydrogen was added.

Future experiments will also focus on development of an “ex situ” bioreactor setup, in which hydrogen and carbon dioxide will be added using silicone tubing. In these bioreactors, enrichment cultures on hydrogen and carbon dioxide, as well as pure cultures of hydrogenotrofic methanogens will studied.

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