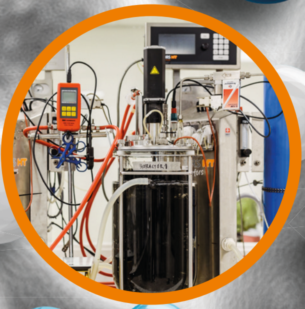
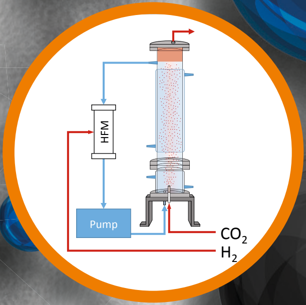
Biomethane from hydrogen and carbon dioxide





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Programma

10.00 – 10.30 uur	**Inloop**
10.30 - 12.00 uur	**Context voor Biologische methanisering** - Inleiding project, Jan Peter Nap (Hanzehogeschool) - Rol van groengas in het Nederlandse energiesysteem, Ruud Paap (GroenGasNL) - CO_2 landschap, Petrus Postma (Bloc) - Energie / CO_2 in Europese context, Grijs Kreeft (Royal HaskoningDHV)
12.00 - 13.30 uur	**Lunch met mogelijkheid tot rondleiding EnTranCe**
13.30 - 14.15 uur	**Verdieping in de resultaten van het Bio-P2M project** - Technisch, Folkert Faber/Gert Hofstede (Hanzehogeschool) - Economisch, Jan Bekkering (Hanzehogeschool) - Toepasbaarheid, Jort Langerak (DMT), Gerard Martinus (GasTerra) - Innovatie Jeroen Tideman (Bioclear earth) - Wrap-up project Jan Peter Nap (Hanzehogeschool)
14.15 – 15.00 uur	**Discussie** o.l.v. moderator Charles van Santvoord met de presentatoren en het publiek over de implicaties van de resultaten, toepasbaarheid en toekomst van biologische methanisering.
15.00 - 16.00 uur	**Netwerkborrel**

Colophon

An ‘EnTranCe - Hanze Expertise Centre of Energy’ publication
‘Biomethane from hydrogen and carbon dioxide’

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Context

SIA-RaakPRO project ‘P2G using biological methanation (Bio-P2G)’, project number 2014-01-21 PRO, 2013 – 2019.

Bio-P2M consortium (2019). **‘Biomethane from hydrogen and carbon dioxide’** Symposium document, Hanze University of Applied Sciences Groningen, Groningen, the Netherlands, 48 pp**.**

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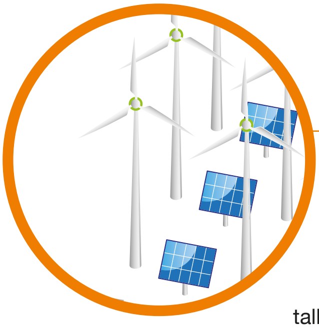
1. Preface



Are we going to make it? To rescue our climate and to prevent further earthquakes in Groningen? All those plans and intentions and agreements and policy directions and meetings and talks and climate tables? Or will we keep on talking? A slight embarrassment would be warranted: in a time that we almost make the Champions League of soccer (again), the Dutch only beat Malta and Luxembourg concerning the implementation of renewable energy. For sure, we don't need to worry about the dialectics of progress.

Is everything all-electric feasible as future energy system (Fig. 1) with predominantly solar panels and wind farms and eventually zero emission of greenhouse gases? How about the dark, cold days without sun and wind? Is storage indeed only a minor issue? After all, green electricity is easily converted to and stored as hydrogen. Are we ready for such green hydrogen? How about the costs? Safety? History of safe use? Infrastructure? Acceptance?

It is with great pleasure and honour that we present you this brochure outlining and presenting the main approaches and results of a 4-year power-to-biomethane project. Power-to-gas technologies are considered promising in the context of the transition to a (more) renewable energy. Such a transition is urgent because of various reasons: climate concerns, European incentives, the Paris Climate agreement, the overly long neglected earthquake issues in parts of Groningen and beyond, as well as the Dutch policy intentions to stop harvesting natural gas from Groningen soils, although counterforces seem to get stronger.

In a consortium of stakeholders in the field of energy transition, we joined the forces of two research universities (Wageningen and Groningen), seven companies (four SME and three larger) and a network organisation, managed by the Hanze University of Applied Sciences

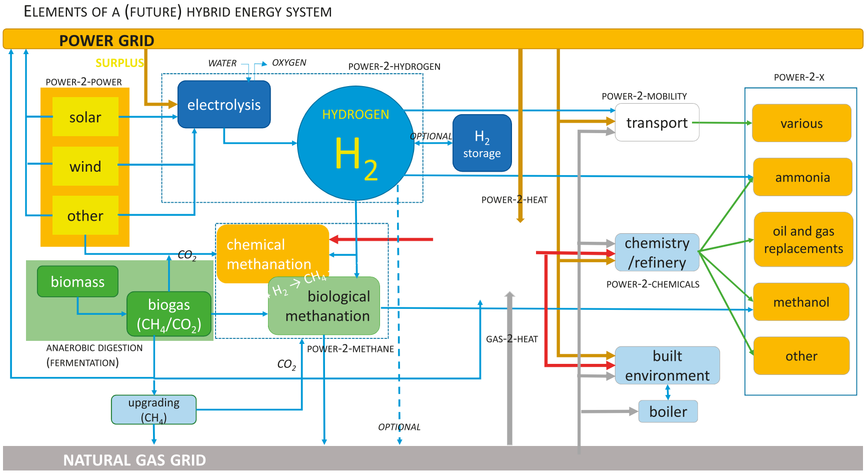


Figure 1. **Possible future hybrid energy system of the Netherlands.** Hydrogen obtained via electrolysis has a central position. The technology considered here in detail is biological methanation or power-2-methane, biomethane formation from carbon dioxide and hydrogen.

(UAS) Groningen. The consortium has been investigating the use and feasibility of an old mate: methane, the molecule in natural gas.

No, this is not old wine in new bottles. Rather, it is new wine in old bottles. The old bottle being the infrastructure and knowledge we have on methane as an energy carrier. The new wine is in the way the methane is produced. Not harvested from age-old gas fields with all the negative consequences the North of the Netherlands is now facing but produced from biomass with the help of bacteria: biological power-to-methane. It can also be achieved chemically (Sabatier), but the biological route has several advantages in a future energy system (Fig. 1) that is going to be more bottom-up and de-centralised. The biology can be combined with existing infrastructure to help valorising biogas plants but can also develop as a stand-alone application. Main issues are technical optimisation, its overall economic feasibility, and upscaling.

The results were obtained in the context of the RaakPRO program of the Taskforce Applied Research (Dutch: Nationaal Regieorgaan Praktijkgericht Onderzoek) SIA, now a division of NWO, the Dutch Organisation for Scientific Research. Many of you may not yet be familiar with SIA as the most important organisation for funding of applied research at Universities of Applied Sciences. The RaakPRO program is the largest, most prestigious and competitive program of SIA for collaborative research groups. Research activities should present a clear focus on developing new knowledge, insights and applications useful for professional practise (i.e. the former students), for the education portfolio, and our knowledge system.

We trust that you will see these aims reflected in the approaches and results presented in the following sections. A new angle to an old mate can and should generate enthusiasm for new and refreshing ideas for innovation and change.

Sabatier (chemical) or bio-P2M (biological): $CO_2 + 4\ H_2 \rightarrow CH_4 + 2H_2O$

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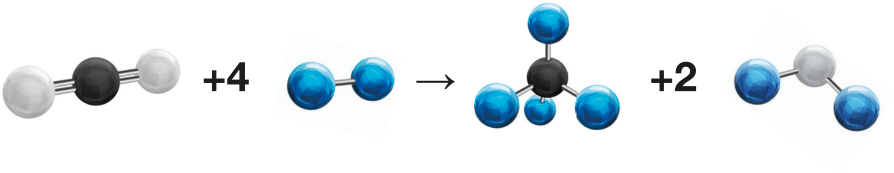
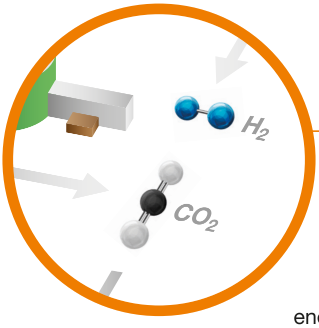


Electrolysis: $2H_2O \rightarrow 2H_2 + O_2$

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

Figure 2**. Methane from carbon dioxide and hydrogen.** The chemical conversion is known as the Sabatier reaction. The biological conversion is identical, but is carried out by microorganisms known as hydrogenotrophic methanogenic archaea. The latter is here referred to as bio-P2M. It is preceded by the formation of hydrogen via electrolysis.

2. Background



Methane from carbon dioxide and hydrogen

The pressure on the use of fossil energy given climate concerns, global warming and availability of resources has fuelled the need for an alternative energy future. The future energy system in the Netherlands will most likely be a hybrid system encompassing different energy sources (Fig. 1), with important contributions of wind and solar energy.

However, both wind and solar power production show an unpredictable and sometimes large variation on both a daily and an annual basis. This variation is known as intermittency. Because of intermittency, production does not necessarily synchronise well with fluctuations in power demand, nor with the current set-up of power grids. Intermittency can be overcome by storage, the required capacity of which may be up to 20-25% of the total installed capacity. Important elements for storage systems are storage time, storage capacity, flexibility and costs. Many systems are being considered.

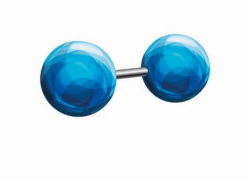
Energy storage systems

For longer-term storage of energy, chemical storage is warranted. A potential buffer of renewable energy is hydrogen gas: power can be converted directly into hydrogen gas via electrolysis of water. Hydrogen has storage capacities of 5 GWh to 5 TWh. Hydrogen gas, however, is relatively difficult to handle, as it is extremely explosive and flammable, may cause embrittlement and diffuses very easily, resulting in leakage and issues with safety.

Methane, or substitute natural gas (SNG), is easier to handle than hydrogen gas. Because of fossil methane reserves, The Netherlands has developed and is maintaining an excellent infrastructure and ample expertise for transport, storage and safe exploitation of methane gas. Methane could, therefore, be an attractive alternative for energy storage.

Methane can be produced from hydrogen, and carbon dioxide in a chemical process called the Sabatier reaction or can be carried out by microorganisms (Fig. 2). The chain from power to biomethane is here called biological power-to-methane (bio-P2M). It results in the storage of renewable energy in the form of biological methane.

Hydrogen (H_2)



Hydrogen is the most abundant element in our universe. Hydrogen is odourless, colourless and tasteless, extremely flammable and auto-ignites at 500 °C. The water solubility of hydrogen is poor at 1.62 mg/L (at 21 °C). It is non-corrosive, but it is known to cause embrittlement of metals. Hydrogen itself is not toxic, but when displacing oxygen in air, it becomes an asphyxiate and can result in dizziness or suffocation. Upon contact with skin or eyes, it causes cold-burn (frostbite). It is used to produce ammonia (Haber-Bosch process) as well as various other chemicals; and it is used in welding of steel and other metals.

Hydrogen gas can be produced from fossil or renewable resources with a wide variety of technologies and approaches. Hydrogen production from renewable sources involves the electrolysis of water. Electrolysis is the conversion of electrical energy into chemical energy in the form of hydrogen, with oxygen as a potentially useful by-product. Electrical current splits two water molecules into two hydrogen molecules and one oxygen molecule. Although the reaction produces heat, electrolysis requires a significant amount of energy and is only sustainable if the renewably produced electricity is used.

Electrolysis currently comprises three major technologies: alkaline water electrolysis (AWE), proton exchange membrane (PEM) electrolysis and solid oxide electrolysis cells (SOEC). AWE is the oldest and most mature technology with efficiencies of 50–60%, but AWE systems have difficulties with intermittency. PEM electrolysis uses expensive metals such as platinum or iridium and achieves efficiencies of 55–70%. PEM systems deal better with intermittent power sources of energy. SOEC involves a solid polymer electrolyte and high temperatures (750-950 °C) that require costly materials and fabrication methods, as well as a heat source. It results in a mixture of hydrogen and steam that needs an extra gas cleaning step. Efficiencies up to 98% have been reported. Many other systems for electrolysis of water exist or are being developed. In addition to electrochemical routes, also biological routes to produce hydrogen are considered.

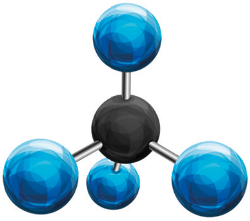
Carbon dioxide (CO_2)

Carbon dioxide is the second substrate for bio-P2M. It is an odourless, colourless and incombustible gas with a slightly acid taste. CO_2 is relatively nontoxic and highly soluble in water. Carbon dioxide is generally seen as the unavoidable by-product of fossil energy generation and is the main concern in global warming. Its concentration in air has been increasing steadily from about 0.028% to a current 0.04%, due to the accumulated human activities since the industrial revolution at around 1800.

Carbon dioxide is an extremely versatile chemical commodity that is used in a multitude of processes and applications. Commercial production of carbon dioxide is often a by-product of large-scale chemical production, e.g. during the production of hydrogen from natural gas, coal, or other hydrocarbon feedstock, or in production of limestone for agriculture. Another important source of carbon dioxide is large-volume production of bio-ethanol for transportation and production of beer and wine for consumption.

During anaerobic decomposition of organic matter known as biomass, a mixture of gases is produced. In a biological system, biogas consisting of predominantly methane (50-75%) and carbon dioxide (25-45%) is formed. During thermal decomposition, a mixture known as syngas consisting of methane, carbon dioxide, carbon monoxide and hydrogen results. In both, water vapour and trace amounts of other components are produced.

Methanation from carbon dioxide and hydrogen: two alternative routes



Catalytic methane formation, or the Sabatier reaction, or gas phase methanation, is the chemical conversion of hydrogen and carbon dioxide into methane. Four molecules of hydrogen gas are needed to convert one CO_2 methane molecule into one molecule of methane and two molecules of water (Fig. 2). About 30% of the energy in hydrogen gas is converted into heat. The reaction requires high temperatures and a catalyst for which mostly nickel is used. Nickel catalysts are easily inactivated, and the gases in the Sabatier must, therefore, be free of contaminants.

The ability of methanogenic archaea to make methane from hydrogen and carbon dioxide was discovered in Delft in 1906. Archaea are the third domain of life, next to Bacteria and

Eukarya. In such microbes, the reaction is catalysed by enzymes at temperatures between 35 and 70 °C at atmospheric or elevated pressure.

The methanogens using hydrogen and carbon dioxide to produce methane are called hydrogenotrophic methanogens. They use hydrogen as the electron donor to drive the reduction of carbon dioxide. In bio-methanation experiments, predominantly thermophilic Methanothermobacter species have been used, likely because they are easily mass cultured with a relatively high growth rate, but hydrogenotrophic methanogens are widespread among methanogens. Many other species could, therefore, be of use for bio-P2M. New and possibly more efficient hydrogenotrophic methanogens are likely to await identification or should be constructed in the laboratory.

A major advantage of the microbial process over the chemical process, in addition to lower temperature and pressure, is the absence of sensitive catalysts. Therefore, less pure substrates can also be used. It makes the process much more flexible and adaptable. The ability to convert also non-pure gases allows bio-P2M to use biogas as a carbon dioxide source. Conversion of the carbon dioxide to methane results in the direct production of nearly 100% methane, or gas that conforms to the Dutch standards for ‘green gas’.

Reactor design for bio-P2M

At least two different systems are conceivable for the combination of anaerobic digestion (biogas formation) and biological methane formation from carbon dioxide and hydrogen (Fig. 3). In a one-phase or *in situ* system, the hydrogen is fed into an existing biogas reactor to convert the carbon dioxide to methane. It is a simple, intuitive and therefore attractive option that makes best use of infrastructure and prior investments. However, not only the process conditions for anaerobic digestion but also for methanation must be controlled. Good performance in one-phase systems requires optimal process conditions for both. That may be difficult to achieve and result in slow methane production or hamper biogas production itself.

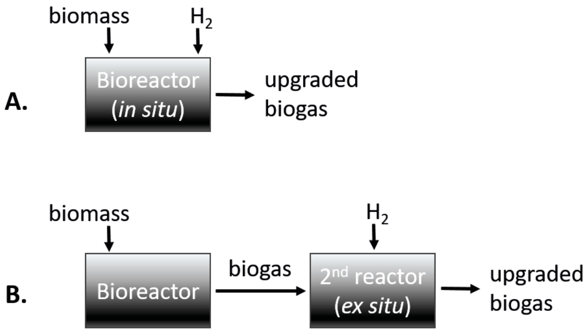


Figure 3. **Reactor concepts for bio-P2M combined with biogas. A.** The *in situ* system, in which hydrogen is directly added to a biogas reactor; **B.** The *ex situ* system, in which biogas (or only carbon dioxide) is led into a second reactor to which hydrogen is added.

In a two-phase or *ex situ* system (Fig. 3), the biogas formed in anaerobic digestion, either as such or only the carbon dioxide after separation from the methane, is fed into a separate bioreactor together with hydrogen. In the second reactor, the conditions can be optimised for the methanation reaction and maintain a high density of methanogens. Moreover, carbon dioxide can come from other sources than biogas.

In both set-ups, the supply of hydrogen to the microbes is thought to be the rate-limiting step. The solubility of hydrogen in water is orders of magnitude lower than the solubility of carbon dioxide. Sufficient hydrogen must be dissolved in the liquid phase to be available for the methanogens. Such transfer of hydrogen is known as gas-liquid mass transfer. Several strategies to overcome the limitation of the problematic hydrogen gas-liquid mass transfer have been proposed for continuously stirred tank reactors (CSTRs). These include the use of forceful mixing, micro- or nanobubbles, hollow fibre membranes, ceramic or column diffusers or process parameters as higher pressure or optimised temperature.

An attractive option is a biofilm reactor. Such a reactor has a solid substrate upon which the microbes are fixed. This set-up offers a very short distance between the gas phase and the biofilm layer, facilitating high hydrogen transfer rates. A trickle-bed reactor is a typical example of such a biofilm reactor. A better understanding of reactor optimisation is warranted. Research should focus on reactor concepts that optimise the conditions for biomass degradation and hydrogenotrophic methane formation in either one or two-phase set-ups.

Considerations of scale and use

Current chemical methanation reactors are generally of a size up to 500 MW based on continuous operation with syngas. The robustness of operation and flexibility to a fluctuating power supply of such a chemical methanation plant is of concern. Sabatier plants are considered more suitable for medium to large scale installations at a rather constant power supply. Improvements focus on power requirements, robustness and flexibility.

In contrast, biological methanation is likely to allow relatively small-scale set-ups that require fewer investments, are less demanding and more robust than its chemical equivalent (Fig. 4). Besides, bio-P2M could play different roles in addition to a storage buffer of electrical power. It may increase the effective biomass availability: if all carbon dioxide in biogas is converted to methane, the total production of green gas (or substitute natural gas) from biomass almost doubles. In addition, the technology can be used to capture carbon dioxide beyond biogas production, possibly as a contribution to better management of atmospheric carbon dioxide. When mature, biomethane from carbon dioxide and hydrogen will add flexibility and have its rightful place in the energy system towards the necessary transition to renewable energy.

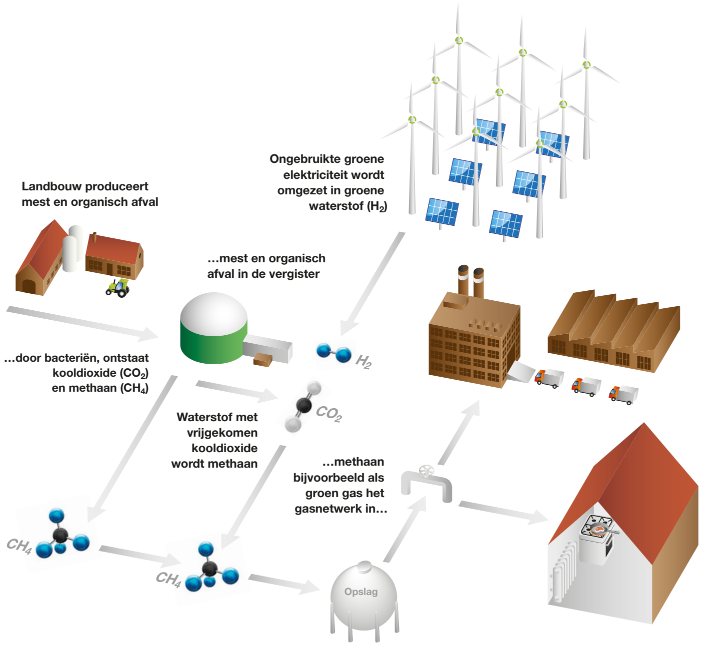


Figure 4. **Possible integration of bio-P2M in a local energy system**.

3. Technology of bio-P2M

Laboratory-scale experimentation

Anaerobic digestion is an attractive technology to produce the carbon dioxide required for bio-P2M (see section 2). The process of anaerobic digestion, in which biomass is converted into methane and carbon dioxide consists of four well-characterised and well-orchestrated steps (Fig. 5). The last step is methanogenesis or methane formation. Methane is either produced by the conversion of acetic acid to methane and carbon dioxide by acetoclastic methanogens, or by hydrogenotrophic methanogens, which combine carbon dioxide and hydrogen to produce methane and water in the process of biological methanation (bio-P2M) here considered (Fig. 2).

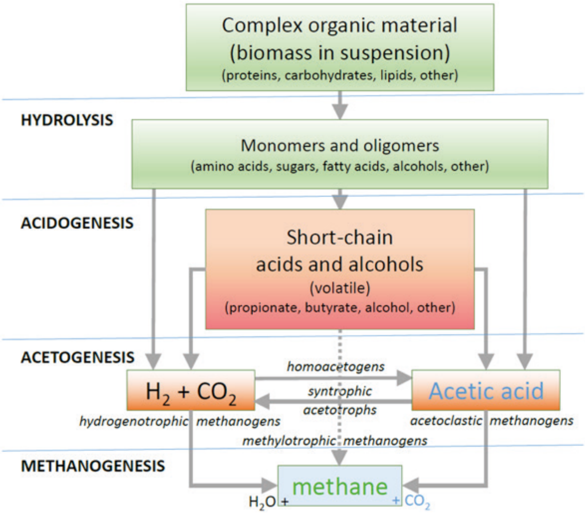
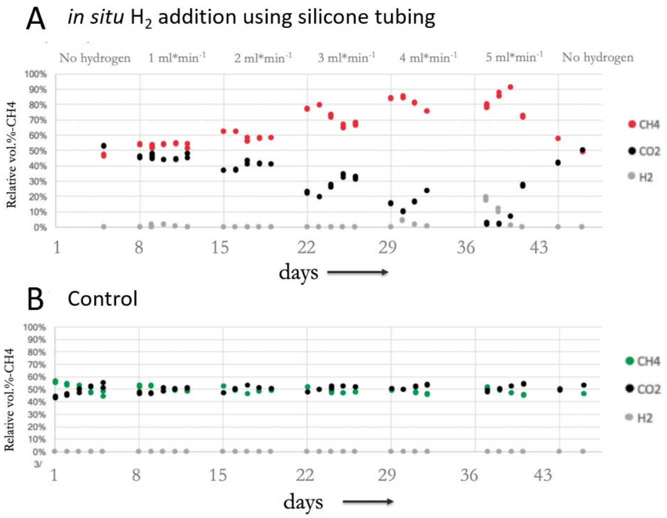


Figure 5. **Stages in anaerobic digestion.** Complex organic compounds such as carbohydrates, proteins and lipids are converted to biogas (methane and carbon dioxide) in four successive steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Methane formation based on the conversion of hydrogen and carbon dioxide is an integral part of this process. All conversions are the result of microbial activities.

Silicon tubing increases the mass transfer rate of hydrogen

Appropriate reactor conditions have been evaluated in the laboratory to facilitate the hydrogenotrophic methanogens to carry out the process of biological methanation. Different small-scale experimental set-ups were established to compare different bioreactor types. Experiments were performed using two 10L continuously stirred tank reactors (CSTRs) in either *in situ* or *ex situ* configurations (see section 2; Fig. 3), as well as in trickle-bed reactors (TBRs) that were newly designed based on the experimental results.



A *in situ* H_2 addition using silicone tubing

B Control

Figure 6. **Addition of hydrogen to a 10 litre biogas reactor *in situ* results in additional methane formation. A.** The *in situ* bioreactor with a constant supply of biomass and increasing addition of hydrogen. **B.** Control reactor with the same supply of biomass without hydrogen addition.

The relatively low solubility of hydrogen in water is responsible for the problematic gas-liquid mass transfer of hydrogen compared to carbon dioxide. Therefore, several strategies were compared for good hydrogen supply, such as conventional bubbling, the use of a gas sparger for much smaller bubbles (see section 6), as well as the use of a silicon tube. Based on experiments with water, a given silicone tube increased the mass transfer rate of hydrogen to the liquid phase considerably. This technology was used in further experimentation. All subsequent experiments were performed with digestate (sludge) from a bioreactor of a wastewater treatment facility.

In situ bio-P2M

For the *in situ* setup, the two 10L CSTRs were run in parallel. The *in situ* bioreactor was fed with defined biomass and hydrogen through silicon tubing. The rate of hydrogen addition increased over time, whereas the amount of biomass added was kept constant. The control bioreactor was fed with the same amount of defined biomass. A typical result is shown in Fig. 6. Addition of hydrogen increases the relative volume of methane to well over 90% (Fig. 6A), compared to the consistent production of biogas with an average composition of 50% methane and 50% carbon dioxide in the control bioreactor (Fig. 6B). This result shows the proof-of-principle of biological methanation of hydrogen and carbon dioxide in an *in situ* reactor set-up.

Further experimentation and modelling showed that the rate of methane formation in the *in situ* CSTR is relatively low. Possibly this is due to a pH increase due to the capture and removal of the carbon dioxide that slows down (inhibits?) the overall process of methane formation. It suggests that *in situ* CSTRs need a fine balance between biomass addition, hydrogen addition and carbon dioxide removal that will require more experimentation at the experimental boundaries (biomass load, hydrogen addition) of the system.

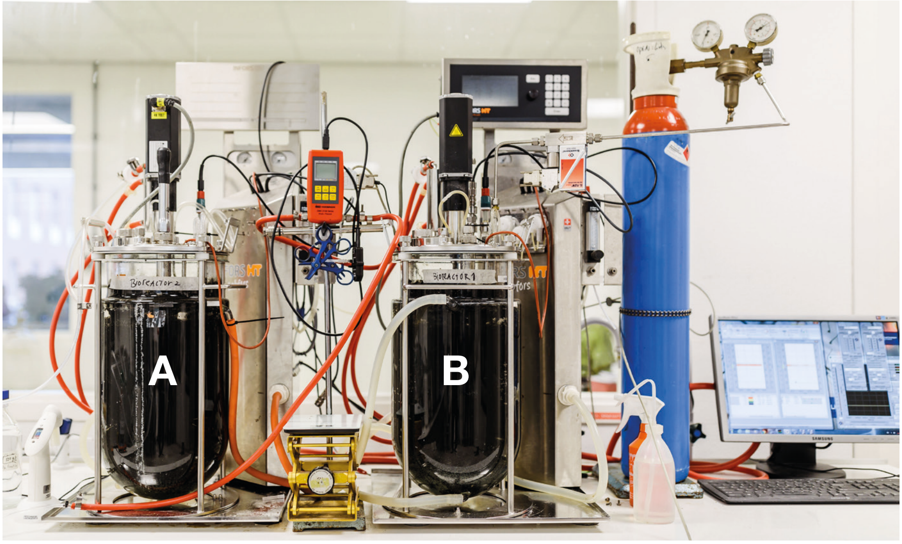


Figure 7. *Ex situ* **configuration of two 10 litre CSTRs for biological methanation.** Bioreactor A is constantly fed with biomass, producing biogas which is led to bioreactor B that is also fed with hydrogen via a silicon tube in the reactor.

Ex situ bio-P2M

Based on theoretical considerations (see section 2), the *ex situ* set-up is likely to offer more flexibility, better control of system parameters and better options to increase the rate of methane formation. The two 10L bioreactors were set up in an *ex situ* configuration (Fig. 7).

The constant addition of a defined mix of biomass results in a constant supply of biogas. This biogas was led into the second *ex situ* bioreactor, supplied in parallel with increasing amounts of hydrogen via a silicon tube (Fig. 7B). Methane, carbon dioxide and hydrogen levels were determined. The results demonstrate the desired formation of methane from hydrogen and carbon dioxide in the *ex situ* set-up.

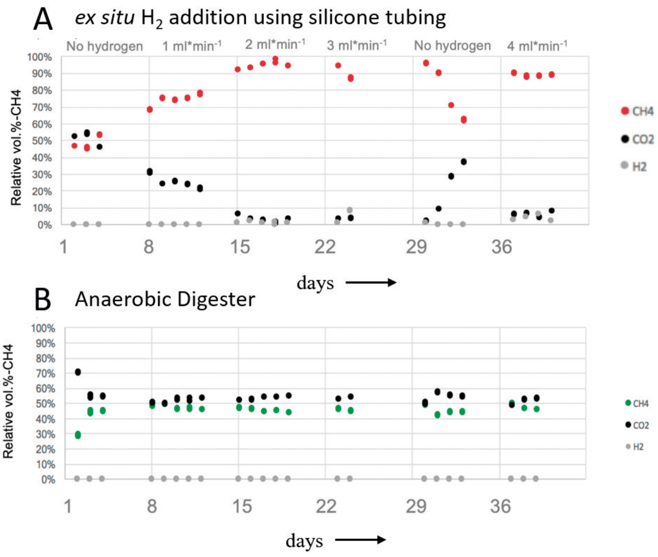


Figure 8. **Addition of hydrogen to a 10 litre *ex situ* biogas reactor results in methane formation. A.** An *ex situ* bioreactor (see Fig. 7) with a constant supply of biogas and increasing addition of hydrogen. **B.** Biogas reactor with a constant supply of biomass.

In separate experiments, also defined mixtures of pure hydrogen and carbon dioxide were used to assess the effect of increased input rates of carbon dioxide and the effect of changing ratios of these gases. Results showed that up to 95% of CO_2 is converted to CH_4, but the hydrogen diffusion through the silicone tubing becomes limiting at higher amounts of CO_2.

The methane production rate (MER) of 0.3 L of CH_4 per litre of bioreactor is still relatively low. It shows that higher H_2 mass transfer rates are desirable for better MER production rates.

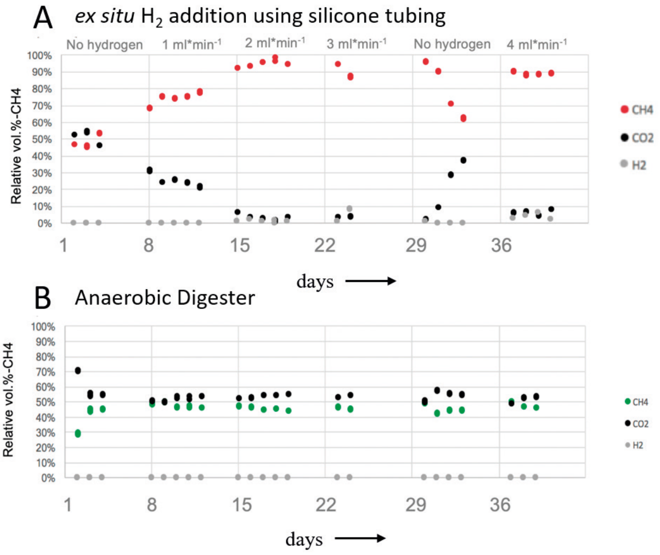


Figure 9**. Methane production in a trickle-bed reactor fed with hydrogen and carbon dioxide.** A. Production rates in ml/day, comparing the theoretical and experimental data. B. Methane formation rate (MER).

Trickle-bed reactor set-up

A trickle-bed reactor (TBR) configuration may result in the desired higher mass transfer rate of hydrogen to the liquid phase, resulting in increased production rates of methane. Therefore, different TBRs were constructed, in which the type of solid phase (metals, plastics or siporax), liquid medium, as well as the ratio of hydrogen and carbon dioxide was investigated in an *ex situ* set-up.

The results of a TBR with the same digestate used before, but adapted for the new conditions, with siporax as solid phase and a hydrogen/carbon dioxide ratio of four (i.e., the theoretical ratio, see Fig. 2) are given in Fig. 9. Methane formation from carbon dioxide and hydrogen is observed (Fig. 9A) and the MER increases almost 10-fold to about four (Fig. 9B).

The difference between the theoretical and the observed yield of methane (Fig. 9A) is due to acetate formation. The system instability observed after about 30 days (Fig. 9AB) may also be due to acetate formation and pH effects. Increased partial pressure of H_2 can promote the activity of homoacetogenic microorganisms that convert carbon dioxide and hydrogen into acetic acid. Current experiments are focused on optimising the conditions which favour the activity of the hydrogenotrophic methanogens.

Based on the results obtained so far, it is concluded that although experimental conditions need further optimisation, an *ex situ* TBR offers the most promising configuration for upscaling of biological methane formation from carbon dioxide and hydrogen.

4. Microbiology of bio-P2M

Community analyses

Biogas formation by anaerobic digestion is the result of the activities of a complex community of microorganisms, which are partly dependent on each other for balancing the consecutive steps in biogas formation (Fig. 5). Any change in a process parameter (e.g. temperature, pH, type of biomass, amount of biomass, and many more) can influence the activity or composition of the community with possibly irreversible detrimental effects on biogas formation. The addition of hydrogen either *in situ* of *ex situ* can be considered such a change in a process parameter. As long as the formation of biomethane from carbon dioxide and hydrogen (bio-P2M) is accomplished by a mixed community of microorganisms, the same considerations apply to the process of bio-P2M.

Therefore, the relative amounts and activities of the microorganisms involved in the community for optimal methane formation should be determined and monitored closely. We aimed to develop and use molecular technologies that would allow the study of the microbial composition and changes therein upon methane formation.

TaqMan qPCR technology for community analyses

Various molecular technologies allow monitoring the change in the relative abundance of microorganisms. We here focus on quantitative polymerase chain reaction (qPCR) technology making use of the TaqMan protocol. Total DNA extraction from digestate samples taken from bioreactors was optimised. Depending on the specificity and selectivity of the primers and probes used, the presence of designated microorganisms belonging to a specific, class, order, family, genus or even species can be identified.

Primers and probes were designed for the genus Methanoculleus (MC), which reflects the presences of hydrogenotrophic methanogens, and for the order Methanosarcinalis (MSL), which reflects the acetoclastic methanogens. qPCR conditions were optimised, and samples taken from the CSTR bioreactors described in section 3 were analysed. TaqMan qPCR analysis clearly showed a significant increase in the relative abundance of hydrogenotrophic methanogens (MC) up to 25-fold after 28 days of adding hydrogen as compared to the control bioreactor to which no hydrogen had been added. Similar results were obtained for the *ex situ* bioreactor (Fig. 7). TaqMan qPCR results show the expected results for changes in the relative abundance of hydrogenotrophic and acetoclastic methanogens. Although such trends could be reproduced, the large variability of the quantitative data on community changes could not be accounted for.

Next-generation sequencing

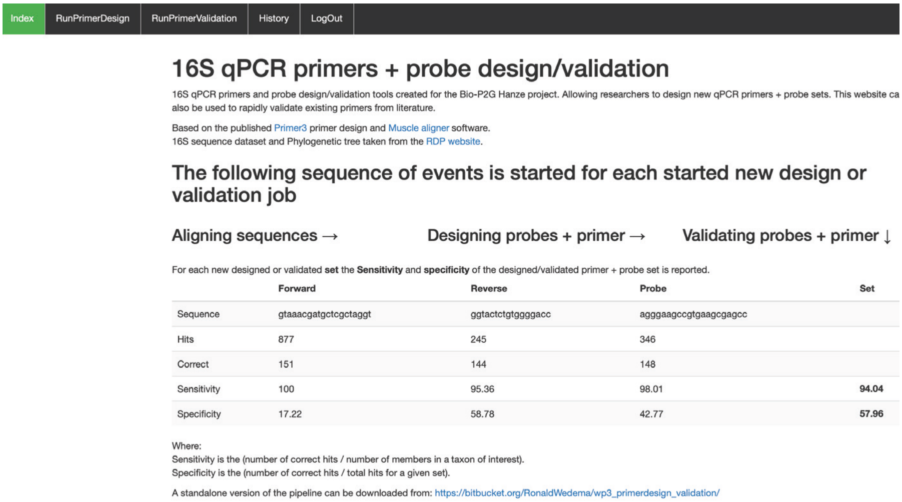
Microbial community analyses were also performed using next-generation sequencing to assess the large variability observed in TaqMan qPCR analyses. Next-generation sequencing can generate a (more) complete overview of the microorganisms that are present, but such a complete metagenomic analysis is expensive. We, therefore, selected a new and promising and relatively cheap, method for metagenomic DNA analysis, MinION nanopore technology (Fig. 10). Although the MinION system is designed for the analysis of pure microbial cultures, or simple bacterial communities, we tried complex community analysis with sophisticated data processing strategies.

Figure 10. **MinION sequencer.** Nanopore technology for DNA sequencing from Oxford Nanopore Technologies.

After optimising the DNA extraction procedure to obtain long-chain DNA fragments from relative contaminated digestate samples, various DNA samples from the experiments described in the previous section were selected and analysed with the MinION. Although differences in microbial communities were observed, the complexity of our microbial communities was unfortunately too high to be analysed properly with MinION data.

Primer design for TaqMan qPCR

The specificity and selectivity of the primes and probes used in TaqMan qPCR assays to study the changes in microbial community changes in anaerobic digesters could be improved upon. No tools are available to design and evaluate desired primers in combination with a selective probe. Therefore, a new software tool was developed which combines various analytical tools, such as Primer3, Muscle aligner and RDP probematcher, integrating this with a user-friendly interface to make it also accessible for non-bioinformaticians (Fig. 11). Currently, we use this tool for the development of new primers and probes.



16S qPCR primers + probe design/validation

16S qPCR primers and probe design/validation tools created for the Bio-P2G Hanze project. Allowing researchers to design new qPCR primers + probe sets. This website ca also be used to rapidly validate existing primers from literature.

Based on the published Primer3 primer design and Muscle aligner software.
16S sequence dataset and Phylogenetic tree taken from the RDP website.

The following sequence of events is started for each started new design or validation job

Aligning sequences → Designing probes + primer → Validating probes + primer ↓

For each new designed or validated **set** the **Sensitivity** and **specificity** of the designed/validated primer + probe set is reported.

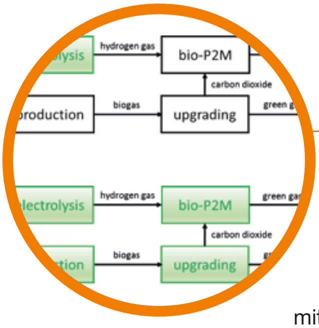
	Forward	Reverse	Probe	Set
Sequence	gtaaacgatgctcgctaggt	ggtactctgtggggacc	agggaagccgtgaagcgagcc	
Hits	877	245	346	
Correct	151	144	148	
Sensitivity	100	95.36	98.01	**94.04**
Specificity	17.22	58.78	42.77	**57.96**

Where:
Sensitivity is the (number of correct hits / number of members in a taxon of interest).
Specificity is the (number of correct hits / total hits for a given set).

A standalone version of the pipeline can be downloaded from: https://bitbucket.org/RonaldWedema/wp3_primerdesign_validation/

Figure 11**. RunPrimerDesign.** A new bioinformatics tool for designing combined primers and probes for highly selective TaqMan qPCR, based on a selected set of sequences**.**

5. Economy of bio-P2M



Modelling of costs and benefits at farm scale

The biological P2M technology (bio-P2M) as addressed here could be a novel strategy to help to face the challenge of intermittency, the unpredictable and sometimes large variation in electricity production by wind farms and solar panels on both a daily and an annual basis (see section 2). Green methane as energy storage would seem a good transition strategy: Groningen has ample knowledge of methane as an energy carrier, and the Netherlands has the appropriate infrastructure for the distribution of methane.

An important issue in any new or upgraded technology is its sustainability, i.e. its feasibility in terms of economy (investments, costs and benefits), energy efficiency (energy input versus output) and environmental benefits, here narrowly defined as the reduction of greenhouse gas (GHG) emission. Such analyses make use of and should be compared to, existing models for chemical methanation and be part of the assessment of the hydrogen economy of the future.

Assessment of economic feasibility is, however, a complex issue which in the context of climate change, earthquake risks and security of energy supply, should not focus on price only, but on environmental issues as well. We have assessed the requirements and economic consequences of bio-P2M technology in various ways. Essential data required for such assessments are the availability of sufficient electricity for hydrogen gas production, appropriate production of green hydrogen, as well as sufficient biomass -or alternatives- for carbon dioxide, i.e. the necessary substrates for the bio-P2M technology we aim to assess.

Availability of electricity

In a scenario based on generic data on energy consumption anticipating full accomplishment of the EU climate targets in the Netherlands, in 2035 about 13 TWh a-1 is estimated to be in excess, which would be 9,4% of all the electricity generated, about two times the excess electricity calculated for a reference scenario. In the province of Groningen, about 550 GWh of excess electricity would be available in 2035. As the scale of renewable energy in the overall electricity generation increases, also the estimates of the amount of electricity that becomes available increases. Such estimates do not, however, include major changes in export of (excess) electricity to neighbouring and interconnected countries, nor does it account for major changes in electricity consumption that may occur in the future of an all-electric society. As the scale of renewable energy in the overall electricity generation increases, also the estimates of the amounts of electricity that become available increase.

Production of green hydrogen

The amount of hydrogen that can be produced depends on the energy efficiency of the electrolyser, as well as the overcapacity desired for peak electricity production. Overall, appreciable amounts of green hydrogen will be available for bio-P2M, although the various competing uses of this hydrogen are difficult to assess at this moment. As a biological process, bio-P2M technology can cope with lower-quality hydrogen gas than needed for applications such as transportation. Classification of green or residual hydrogen streams and associated appropriate use warrants more attention.

Availability of biomass and carbon dioxide

Biogas from biomass generally consists of 50-60% methane and 50-40% carbon dioxide, with minor pollutants. In Europe, most biogas originates from farm-based installations, next to a few industrial-sized digesters. For the latter, logistics and storage of biomass are bigger issues. Any organic material now used for biogas production could profit from bio-P2M technology to produce more green gas. Promising sources of biomass are sewage sludge from wastewater treatment plants, food and beverage waste, possibly aquatic biomass as well as animal manure, either co- or mono-digested. More efficient use of largely unused biomass such as roadside grass would be attractive, although better digestion technologies for grass should be considered. Various industrial processes produce large amounts of carbon dioxide that could be converted into methane. The availability of carbon dioxide suitable for bio-P2M does not seem to be an issue of concern.

Bio-P2M at farm-scale biogas plants

Bio-P2M technology is likely most appropriate in a de-centralised set-up at small-to-intermediate scales (Fig. 4). Biogas plants in the Netherlands produce up to 1.200 $Nm^3\ h^{-1}$ green gas, with an average of about 200 $Nm^3\ h^{-1}$. We have developed a model for a detailed bio-P2M production chain based on a medium-sized farm-scale digester of 500 Nm^3 h^{-1} biogas that produces 4.10^6 Nm^3 biogas per year in 8.000 operational hours (i.e. 91% productive hours). Such a chain allows quantitative assessment of the feasibility of the bio-P2M technology in terms of levelised costs of energy, energy efficiency as fossil primary energy input and output, as well as sustainability expressed as a reduction of the emission of greenhouse gases compared to a natural gas mix.

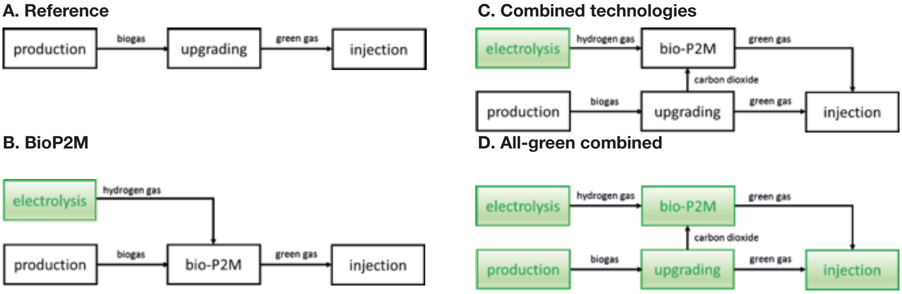


Figure 12. **Bio-P2M scenarios considered for economic feasibility and viability.** Each scenario is given as a sequence input-to-output transformation blocks. A green block indicates that all electricity used is renewable (solar, wind). Otherwise, the energy is from fossil origin. The production and injection blocks were detailed previously and are identical in all four scenarios. See text for more details **(A)** The reference scenario. **(B)** The bio-P2M block involves an *ex situ* trickle-bed reactor; the electrolysis block involves a PEM electrolyser. **(C)** A combination of A and B, in which the carbon dioxide obtained after membrane separation is fed into an *ex situ* bio-P2M trickle-bed reactor. **(D)** Same as C, but now all the electricity used is renewable. The calculations in the model are based on an average Dutch biogas plant. Other assumptions and all quantitative data used are detailed elsewhere.

Four scenarios are compared (Fig. 12). Electricity costs are set at the marginal costs of electricity generated by wind turbines. Electrolysis uses a Proton Exchange Membrane (PEM) electrolyser for which the energy efficiency is estimated to be 71% (5 kWh Nm^3). At a biogas production rate of 500 Nm^3 h^{-1}, a 3.4 MW electrolyser would be sufficient to produce the hydrogen gas for all the carbon dioxide to be converted to green gas (with 10.3 % residual carbon dioxide). Two or three state-of-the-art wind turbines are required for generating the amount of electricity required. It shows that a considerable amount of electrical energy can be stored as green gas, adding to the notion of building up a suitable buffer to balance supply and demand in case of intermittency. Typical costs of hydrogen of 1.0 € kg-1 to 2.0 € kg-1 are foreseen for the future. Detailed data, calculations and assumptions are presented elsewhere.

Table 1. **Comparative analysis of the four scenarios**[1]

Parameter **Scenario**	**A**	**B**	**C**	**D**
Levelised costs of energy (€ct.Nm^{-3} green gas)	55	73	80	77
Proportion of fossil energy use	33	23	27	10
Reduction of GHG emission (%)	55	68	65	80

[1] See Figure 12 for the details of the scenarios and text for an explanation of the parameters used for comparisons. GHG = greenhouse gas.

Main results are presented in Table 1. The production costs of green gas in the reference scenario are lowest because no additional investments and costs have to be made for electrolysis and bio-P2M. The costs of electrolysis add to the higher costs for the newer bio-P2M technologies. Reduction of the production costs of green hydrogen, either by improving electrolysis or by the development of more efficient alternative technologies would boost the economic viability of bio-P2M technology.

In contrast, the bio-P2M scenarios show better energy efficiencies and higher environmental benefits (Table 1). The environmental benefits are due to the use of renewable electricity. Only the all-green scenario (D) meets the future EU goal of 80% reduction of greenhouse gas emissions. More detailed environmental assessments, using, for example, the concept of eco points, are thinkable and are being evaluated. These analyses show that bio-P2M technology is economically viable if the assessments include sustainability goals: it can reach a considerable reduction in greenhouse gas emissions.

Additional analysis shows that it would require a carbon dioxide price of 200 € t-1 to achieve the current levelised cost of energy of 65 €ct Nm^{-3} of the reference scenario A. Whether such pricing is realistic will depend on policies and decision making. Higher costs of renewable energy and carbon dioxide compared to the current costs of fossil energy and carbon dioxide seem necessary and unavoidable. Inclusion of a simple model of the intermittency of renewable energy in the scenarios increases the costs substantially. How intermittency is best considered in models like these, as well as in practical set-ups in the future, need further experimentation, investigation and modelling. If temporary financial losses are compensated for by sufficient yields at other times, intermittency may become an acceptable part of the business model of any future renewable energy technology, including bio-P2M.

6. Upscaling of bio-P2M

Novel reactor concepts

Conversion of hydrogen to methane on the lab scale is well-established technology (see section 3), although optimisation of process parameters is still an issue. The *ex situ* reactor concept has higher methane productions rates, with possibilities of fixed-bed, trickle-bed and hollow fibre membrane (HFM) reactors. It is currently not clear which of these reactor concepts is most suitable for achieving the desired methane formation rate (MER, expressed in litre methane per litre reactor volume per day).

Reactor design

A multipurpose reactor was designed with a flexibility of reactor concepts in mind. From the start, the option of using the reactor in three different operation modes was part of the philosophy of design. This set-up enables experiments for identifying the most suitable reactor concept for scale-up. The reactor in the configuration of a bubble column, a hollow fibre membrane reactor and a trickle-bed reactor is shown in Fig. 13.

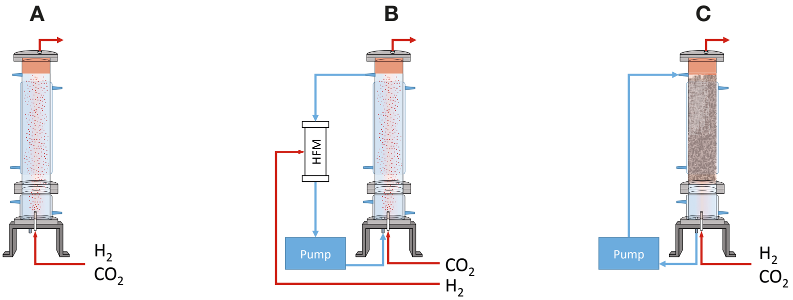


Figure 13. **Reactor configurations. A.** Bubble column, **B.** hollow fibre membrane and **C.** trickle-bed configuration, as combined in a single design. The volume is 7.5 litre.

As outlined above (section 2 and 3), the conversion to be established involves the transfer of the gases CO_2 and H_2 to the reaction phase (water), uptake by the microorganisms and enzymatic conversion. The solubility of hydrogen in (pure) water is poor and declines with increasing temperature (Table 2). These solubility data imply that 1 m^3 of fully hydrogen-saturated water at 20°C has the potential of producing 4.5 L of gaseous methane. Continuous supply of hydrogen to the aqueous phase is therefore essential for achieving high MERs.

Table 2. **Solubility of hydrogen in water**

T [°C]	Solubility [mg/litre]
20	1.61
30	1.52
40	1.47
50	1,44

Hydrogen transfer to the liquid phase

First, the bubble column reactor configuration (Fig. 13A) was used to assess the best reactor configuration for hydrogen transfer. Hydrogen transfer measurements at 20 °C and 7.5 L of water in the reactor were based on a gas sparger constructed of sintered metal without additional mixing. The hydrogen concentration in water was determined by titration. Results are given in Table 3.

Table 3. **Hydrogen concentration in pure water**. Measurements in the bubble column set-up with gas sparger

$\Omega_{v,H2}$ [ml/min]	t [hour]	c_{H2} [mg/l]
4	30	0
20	8	0
40	6	0.1

[1] $\Omega v_{,H2}$: hydrogen flow rate [Nml/min]; [2] t: hydrogen supply time [hour]; [3] c_{H2}: hydrogen concentration [mg/l].

Although the combination of the hydrogen flow rate and supply time could theoretically result in achieving saturation of the water with hydrogen at 1.61 mg/l (Table 2), the results show that the transfer of hydrogen from the gas bubbles to the liquid is negligible. Observation of individual gas bubbles (Fig. 14) showed that even small bubbles reached the surface without dissolving. It is not clear why this experimental set-up performed so poor. As a result, gas sparger experiments were stopped.

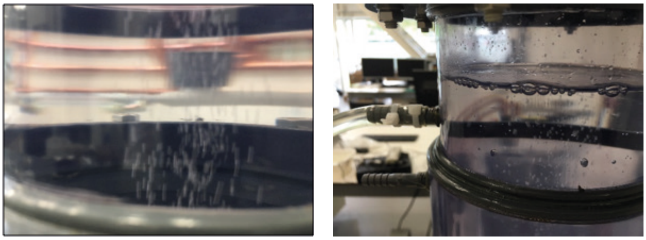


Figure 14. **Hydrogen from the gas sparger (left) reaching the surface (right).**

Focus shifted to the transfer of hydrogen using the Hollow Fibre Membrane unit (HFM). The HFM reactor configuration (Fig.13B) was used in hydrogen transfer measurements using an HFM module obtained from PermSelect (Fig. 15).

Figure 15. **PermDMSXA-7500 Hollow Fibre Membrane module.** Estimated membrane transfer area is 7500 cm^2.

All assays were carried out with continuous water flow of pure water through the HFM module. Quantitative analysis of the hydrogen was carried out by titration. The results in Table 4 show that in all cases, the saturation achieved is considerably lower than the theoretical saturation calculated from the hydrogen and water flow rates.

At conditions of oversaturation (assay 2) or near saturation (assays 1 and 3) hydrogen gas bubbles may form if the water flow rate is too low. Such a gas bubble does not contribute to the hydrogen transfer to the water phase. However, also in assays carried out at low theoretical saturation (assays 4, 5, 6), the experimental saturation was significantly lower than the values calculated and expected. Possibly the HFM unit was less robust than hoped for: if partly damaged (e.g. by too high pressures), the membrane transfer area may be lower than expected.

Table 4. **Hydrogen transfer measurements using the HFM module**

Experiment	Water flow rate [l/min]	Hydrogen flow rate [Nml/min]	Theoretical saturation @100 % absorbed	Measured saturation [%]	MFR max
1	1.2	20	92	19	0.19
2	0.6	20	184	12	0,06
3	0.6	10	92	21	0,11
4	1.2	10	46	12	0,13
5	1.38	10	40	14	0,15
6	1.38	5	20	11	0,13

For insight into the feasibility of membrane hydrogen transfer in a full-scale bio-P2M reactor, the hydrogen transfer rates were used to calculate the theoretical maximal MER (Table 4). The calculated MER values are based on the volume of the reactor in combination with the Perm-Select HFM module (liquid volume in reactor = 7.5 litre and membrane transfer area = 7500 cm^2). Results show that theoretical MERs are low compared to MERs achieved experimentally (see section 3). It can be concluded, therefore, that also the HFM membrane set-up does not deliver. More experimentation with possibly a new HFM would be necessary to get more insight in why this set-up performs so unexpectedly poor.

Methane formation rates in the trickle-bed configuration

A trickle-bed reactor configuration offers the advantage of the gas phase being the continuous phase. Therefore, the limitations of the hydrogen gas-to-liquid mass transfer are compensated for by the large gas-liquid transfer area that is available. Experiments were carried out using the reactor set-up (Fig. 13C; see also section 3). MERs obtained using this set-up reach 3-4 m^3/m^3 reactor×day. These are in general agreement with literature data on trickle-bed methanation. Current experimental work evaluates conversion of hydrogen to methane at close to 100% efficiency with high MERs at varying hydrogen feeding rates and hydrogen/carbon dioxide ratios.

7. Outlook

The end of the beginning?

The organisation and management of a large, multi-partner, multi-market and multi-disciplinary research project as the one here presented has been an interesting learning experience. To bring together different fields of study, fields of expertise and research cultures to generate added value has been and still is an encouraging and remarkable challenge. With sadness, we remember Hans Banning, CEO of our valued partner PROCES Groningen, who passed away halfway the project, far too soon.

On the go, contents and results have been leading and rewarding. Regularly, external parties hearing about the approach and results have reacted with ‘hey, this is cool; something new. Let’s try’. They see the added value, understand the bonus of capturing carbon dioxide, the added value of more efficient use of biomass, and they acknowledge the important role that green gas is supposed to play in the midterm energy supply and future energy transition.

But subsequent calculations tend to kill the enthusiasm: costs and scale are serious issues. The more experts/professionals are used to large scale installations and volumes (consider the volumes of natural gas that go around in the Netherlands on a cold day), the more sceptic they seem. The feeling is that biology cannot deliver on the necessary scale and will never be able to do so. Well, look at beer production, a process of large scale fermentation, or sewage treatment, that also is a large scale multistep biological process. Both examples show that any hesitations towards biological approaches need reappraisal.

Green hydrogen, i.e. hydrogen from renewable energy sources, is still relatively expensive, and many alternative uses and applications lurk. The overall attraction of biology to convert the hydrogen to methane is among others that it deals better with impurities and pollution. The chemical Sabatier alternative requires expensive catalysts that are easily ruined by pollutants. The use of less-than-pure (green) hydrogen in the biological set-up warrants more attention in the laboratory, also assuming there will be sufficient supply of such hydrogen.

Better mastering of hydrogen supply to microbes, better assessment of recalcitrant biomass types and more grasp of the implications and importance of the issue of intermittency in relationship to buffering and balancing are still on the menu. Indirectly, these issues touch the security of supply, the capacity of the local and national electricity net, the legal system regarding energy production and many more issues that all must converge to whatever future energy system we are going to put in place. Renewable energy, as here investigated, can only outcompete fossil energy on price if all environmental issues are also considered.

A welcome and noteworthy appreciation for the project you here have seen the results from was its nomination (among six out of 23 projects considered) in June 2018 for the prestigious Raak AWARD 2018 as an example of leading, innovative and trendsetting research at a University of Applied Sciences in the Netherlands. The project did not win. According to the report of the jury, ‘it was too far from the market’. Such a verdict shows the tragedy of our type of innovation: if it is new, people ask why it is not applied. If it is applied, people will comment that it is not new. Projects and technologies such as biological power to methane have a complexity that will result in a long time-to-market. Besides, there are competing technologies on the market, and researchers in other countries are continuously developing and improving.

Has this project performed? Yes, beyond expectations. Has it contributed to the research culture and infrastructure at Hanze? No doubt. Does that mean ‘mission accomplished’? No way. As upscaling is an issue, Hanze is investing in a semi-industrial environment (Zernike Advanced Processing Facility). It should facilitate addressing upscaling issues to produce energy as well as biologicals and biochemicals. Larger investments are now necessary and sought after to test at a much larger scale the concepts we have here developed. The future of the energy landscape in the Netherlands is far from clear; there are many viewpoints, many stakeholders, many interests and, therefore, many uncertainties. Such uncertainties hamper decisions, investments and progress. Overall, answers have been generated; questions have become clearer, approaches are defined as well, So, I think I can conclude with confidence and pride that we are at the end of the beginning. Thanks to all partners and stakeholders for input, discussion and funding.

To be continued.

Hanze University of Applied Sciences Groningen

EnTranCe - Centre of Expertise Energy

Hanze University of Applied Sciences Groningen is overall manager of and main contributor to the project. Main project members are Marije Nienhuis (project manager), dr. Jan Bekkering (economy), dr. Folkert Faber (bioprocess & reactor technology), Gert Hofstede MSc (bioprocess technology; PhD student), dr. ir. Gerard Lammers (reactor technology) and dr. ir. Jan Peter Nap (project leader).

Jan Bekkering

Folkert Faber

Gert Hofstede

Gerard Lammers

Jan Peter Nap

Marije Nienhuis

Bioclear earth

Bioclear earth is a consultancy and innovation agency whose mission is to make the world cleaner and more sustainable. We achieve this by creating “with the power of nature”. In our vision (and that of many others), green gas plays an important role in the global transition to a sustainable energy system. With our initiatives we therefore focus on maximizing methane production from residual biomass.

However, biomass is scarce. There is not enough biomass in the world to be able to meet our energy and green gas needs without undermining food production, biodiversity and / or soil quality. That is why we want to use carbon from the available residual flows as efficiently as possible. With green gas production through fermentation, half of the converted carbon is lost in the form of (short-cyclic) carbon dioxide. By converting this carbon dioxide with sustainably produced hydrogen into methane, the green gas yield from the available residual flows can be doubled. This immediately shows the potential of Bio-P2M.

Within the RaakPRO project we have gained a lot of knowledge about Bio-P2M. We have thus obtained a proper understanding of the added value, the possibilities and impossibilities of this technology and we have gained knowlegde of which synergies can be used in the production of green gas. Furthermore we have researched the further optimization of the process based on the characteristics of the archaea; these “primordial bacteria” are the workhorses of biomethanation. A key result of this project is that we were able to demonstrate on lab scale in a prototype Trickle Bed Reactor that continuous biomethanation is possible. With this relatively compact process (approximately 10x smaller than the corresponding digester), an output of 100% methane was generated under mild conditions (30 °C, no excess pressure).

What is the future prospect for biomethanation?

Bioclear earth, together with stakeholder in het production chains, aims to refine the biomethanation technology, as a market-ready technology through further development, upscaling and integration. From an economic point of view, the relationship between the cost of sustainably produced hydrogen and the value of green gas is the key for a successful implementation. Smart synergies such as the use of the produced oxygen and the produced residual heat, the replacement of green gas reprocessing, the reduction of CO_2 emissions per Nm^3 of green gas can subsequently be decisive in the preparation of feasible cases.

Finally, we believe that CO_2 may become a scarce resource in the future. In the atmosphere, however, it is abundantly available. Therefore, Bioclear earth is working together with SkyTree (Amsterdam) on a concept to integrate biomethanation with Direct Air Capture. It would be fantastic to demonstrate at Entrance that we can produce green methane from only air, water and green electricity so we could use biomass for other things!

We have greatly enjoyed the interaction with all project partners. The mutual cooperation and discussions have led to better project results and effective networking. Within our organization, the project was widely supported through the involvement of several employees: Jeroen Tideman, Emiel Elferink, Cirsten Zwaagstra, Sytze Keuning and trainees Julian Zamudio (WUR), Thirza van den Berg (Van Hall), and Harmen Sikkema (RUG).

Jeroen Tideman

Teammanager technology & innovation

After Jeroen graduated in Chemical Engineering at the University of Groningen, he worked at the R&D department of Procter & Gamble in Brussels for six years. To follow his dream to make the world a better place, he moved to Bioclear earth in 2012. Jeroen is working on the development of new technologies based on biological processes, for instance bio-fuels from waste, the production of green materials and enhancing treatments of manure.

DMT

Our main contribution to the project has been the technical and economical validation of the P2M technology. This has been done by sharing our knowledge on process technical equipment, engineering and biogas upgrading processes and supply chains and providing input on the different technological configurations and utilizations routes.

With respect to this project we expected to gain additional fundamental knowledge on the biological methanation processes and to enhance our understanding on its potential role within society.

For our product development activities, it is crucial to collaborate with different knowledge partners as well as end users (such as Gasterra, Enexis etc.) By participating in this project, we gained insight in the political landscape surrounding the energy transition and the hurdles that still lay ahead for applying the Bio-P2M technology.

A critical note on economic feasibility.

Within the first part of the project the focus was rather academic and less relevant for DMT. Only at the end of the project, where the validation and discussions on end use were initiated, added value to DMT was created.
The most important result is that our view on the business cases and timelines related to Bio-P2M have been confirmed.

We highly value the collaboration with the educational institute and other partners, not only does it provide us with access to lab facilities it also allows us to keep in contact with young professionals that could potential become new DMT employees.

The results of the project are used for our strategic decision making. Especially the input on social and political conditions will help us in setting timelines and priorities with respect to CO_2 capture and utilization.

For a follow-up project I would like to see an extension towards P2X.

Jort Langerak is a product development manager with a master degree in Industrial Engineering and Management and a BSc degree in Chemical Technology. He works at DMT Environmental technology where he is responsible for the development of new products. DMT Environmental technology is an engineering company with more than 30 years of experience in the field of water and gas treatment. We specialize in developing clean tech solutions such as biogas upgrading installations. We do this for industry, utilities and agricultural industry. It is our passion to shape a green economy. In this we are a leading company. Our specialists monitor market developments closely and translate them into opportunities for the development of new products and product improvements.

Enki Energy

Enki Energy, a Dutch SME specialized in small scale biogas production, became partner in the Bio-P2G -project (“P2M using biological methanation”) in 2015. Enki Energy has been interested in increasing methane content in biogas for a long time. Without the addition of hydrogen to the reactor, the maximum methane concentration does not exceed 70%. For many feedstocks (e.g. swill, greenery waste) the methane concentration is even considerably lower. The Bio-P2M project offered us a perfect opportunity to explore ways of improving methane yields. As we focus on systems at atmospheric pressure, the biogas from our processes always contains considerable amounts of CO_2. The Bio-P2M project gave us the chance to investigate higher methane production while simultaneously reducing CO_2-concentration in the final biogas.
The biological process investigated in Bio-P2M works at atmospheric pressure and ambient temperature, making it an ideal candidate for Enki’s small-scale digesters.

At the start of the project we assumed that there would be many ways to get to the desired results. The first impression after our initial patent searches seemingly confirmed this. Deeper research however made clear that many things have been tried to increase methane production but only few do have the potential to be something real.

In order to facilitate technical research and development in this project, Enki Energy introduced a 500 dm^3 digester.

An important result after two years was the Internal Report. This report, that can be used as the basis for a review in the public literature, gives an extensive overview of Bio-P2M , not only focussing on technical issues, but also paying attention to market studies, Intellectual Property and Energy mix.

The next stage in the project did comprise a technical and biological study whereby hydrogen was added to an anaerobic digester, leading to a large increase in methane content in the biogas. Methane enrichment was successful at laboratory scale. It is still a challenge to bring the process to an industrial scale.

At the start of the process our expectations were that cheap electricity could be stored as chemical energy in methane, via the electrolysis of water for hydrogen production and the subsequent bio-methanation. We thought the project would mainly focus on solving technical and economic issues. During the project itself we observed that other questions emerged, leading to new insights. In the first years of the project it became quite clear that bio-methanation is only economically feasible if there is a surplus of electricity that would otherwise be lost. Slowly we started to realize that the process of bio-methanation is also a very important way to produce organic chemicals in a sustainable way. In the next decade, this production of basic chemicals probably will become more important than the storage of energy itself.

HanzeHogeschool Groningen (University of Applied Science) made considerable contributions to the understanding of the bio-methanation process and addressed a number of technical issues. Thanks to their comprehensive laboratory studies we know now what is needed for (economically) successful bio-methanation.

We hope that within 2 years it will be possible to enrich the biogas form our installations via bio-methanation. The electricity needed for the production of hydrogen (through electricity) can be from wind energy (large scale hydrogen production) or from solar panels (small-scale hydrogen production). Due to changing rules, in a few years excess solar power will be more suited for the production of hydrogen than for delivery into the grid.

Dr Stefan Blankenborg (1965) studied Biology at Wageningen University and Physical Chemistry at Free University in Amsterdam. He finished his PhD in 1995 on an electrochemical subject. During the next 15 years he worked in chemical industry. In 2010 he started Enki Energy. Since then he has been involved with the development of anaerobic processes and has developed stand-alone digesters, biogas filters as well as anaerobic filters. His main interest is the application of anaerobic processes as a means of chemical processing.

GasTerra

The Bio-P2G project offered GasTerra the opportunity to participate in research into a new approach for increasing green gas production in the Netherlands. For us, the project was supposed to make it clear that biomethanation technology is technically and, to a certain extent, economically, feasible. This in turn is important to us, because we want to increase the limited potential of Dutch biomass for green gas. Bio-P2G is a way to achieve this, by converting CO_2 from biogas into additional green gas.

In GasTerra's view, green gas plays an important role in reducing Dutch CO_2 emissions. We can introduce green gas without having to change the existing energy infrastructure, in order to reduce emissions in places where there is no good alternative to gas.

GasTerra has contributed knowledge about the functioning of the energy markets in the Netherlands, and in particular about the role of flexibility. We initiated a study into the role of biomethanation on a regional and national scale. We also provided financial support for the development of laboratory-scale pilot installations for biomethanation.

For us, the project has made it clear that, in theory at least, biomethanation is a viable technology for producing considerably more green gas in the Netherlands. We would have liked to have seen this, as part of the project, translated into a working demonstration model in EnTranCe's living lab. What was interesting for GasTerra was that the project reveals a preference for biomethanation as a separate process step. This means that the technology can also be retrofitted, in other words, biomethanation is also suitable for existing installations to increase the production of green gas.

For GasTerra, the next most important step now is to translate the results into a technique that can be tested under realistic conditions. It must also be developed into an affordable concept. What is ‘affordable’ depends, among other things, on the way in which a technology is marketed. It may be necessary for us to look at new business models. Once these next steps have been taken, GasTerra will actively promote the technology among its green gas producers, in order to serve the goal of generating more Dutch green gas.

GasTerra is a wholesaler of natural gas and green gas. We buy gas from domestic and foreign producers and on the open gas market. Our customer base consists of energy companies, industry and other large customers in Western Europe.

GasTerra’s contribution to the project was coordinated by Gerard Martinus. He has been the Energy Transition Project Leader for the company since 2012.

Gasunie

Gasunie aims at contributing to the energy transition, accelerating the transition to a carbon-neutral energy supply. Important steps to accelerate the energy transition are development and sharing of knowledge, and further research on promising techniques that could contribute to a future carbon-neutral energy supply. As Bio-P2M could possibly be an interesting and relevant technique in the energy transition, it is important to further study the possibilities and hurdles of this technique. Gasunie has been working already for quite some years on innovative renewable gas and related infrastructure solutions, and has publicized the survey 2050 for the Netherlands, showing that a CO_2-neutral future can be achieved. Thus Gasunie has to offer quite some knowledge in the area of sustainable solutions including green gas and hydrogen related solutions, and is well situated to value these techniques in the overall context of the energy transition. This knowledge and insights has been shared within the Bio-P2M project, increasing the quality of the research.

The main results of the project are a to be published article on the technique of BioP2G, the enrichment of knowledge at Hanze University, which was not only of importance for the Bio-P2M project, but could also increase quality of future research projects at Hanze University. Furthermore, the exchange of ideas and strengthening of relationships between the project partners can be seen a relevant result of this project. As a company serving the public interest, Gasunie is happy to be able to support scientific institutions working on energy transition issues.

Company profile N.V. Nederlandse Gasunie

Gasunie is a leading European energy infrastructure company whose core activities are gas transport and gas storage. We serve the public interest and facilitate the energy transition by providing integrated infrastructure services. We focus on value creation for our shareholder(s) and other stakeholders and apply the highest safety and business standards used in the sector. We believe in a sustainable future with a balanced energy mix and a lasting role for diversified gas. We believe that we serve our customers best with innovative gas and related infrastructure solutions.

Gasunie

For the Bio-P2M project, Gasunie was represented by Tineke van der Meij (up to mid 2018) and Kees Alberts (mid 2018 – end of project). Gasunie’s contribution relates to knowledge sharing on the energy transition in general and aspects related to Bio-P2M in particular, advise, as well as contributions to an article on BioP2M.

Energy Valley

part of New Energy Coalition

New Energy Coalition is a knowledge and network organisation striving for a sustainable world by boosting the acceleration of the energy transition. This system transformation requires business enterprises, (knowledge) institutes and policy makers to innovate in close collaboration in order to achieve breakthroughs in technology and knowledge, in economic and societal implementations and in people’s mindset and behaviour. As a catalyst, New Energy Coalition drives innovation and education by bringing together knowledge, policy and entrepreneurship.

Greening the gassystem

New Energy Coalition is working with five themes, one of which is ´greening the gas system’. Within this theme New Energy Coalition wants to contribute to the goals as set in the Dutch climate agreements. One of the routes to achieve this is by increasing green gas production. The northern part of the Netherlands already contributes significantly to the total green gas volume. Bio-P2M is one of the innovative technologies that have the potential to almost double the green gas volumes with the same input volume.

Additionally one of the pillars of New Energy Coalition is developing knowledge and education in the energy transition field. The Bio-P2G project has increased the understanding of the Bio-P2G gas system in the Hanze University and introduced many students to the topic.

Machiel van Steenis holds a Bachelor and Master Degree in Agricultural and Environmental Sciences. He received his PhD at Wageningen University & Research.
At present he is business developer BioEnergy & Green Chemistry at the New Energy Coalition in Groningen, the Netherlands. At New Energy Coalition he is coordinating the theme

Industrial Transformation and is amongst others involved in projects on biomass gasification, power to gas, CO_2-reuse and sustainable chemistry. Before that he worked as policy advisor at the province of Groningen, was marketing and research manager in the horticultural sector and researcher at Wageningen University & Research.

Wageningen Environmental Research

Wageningen University & Research (WUR)

Wageningen Environmental Research contributes by qualified and independent research to the realization of a high quality and sustainable green living environment. The results are used for policy, nature conservation and design of the green space on local, national and international level. The Environmental Sciences Group provided the knowledge on the process of bacterial methanation. This created the realization of the importance of hydrogen mass transfer to the liquid medium, needed in a biogas reactor.

For the Environmental Sciences Group the cooperation with SME's and bigger companies was very important. Even though ESG expected the project would succeed in producing methane from hydrogen and CO2, the application in practice can only be realized when companies and knowledge institutions work together closely. The project was a true success in this respect. Also the collaboration between Wageningen University as 'thinkers' and Hanze Applied University as 'do-ers' was very productive and complementary.

The project demonstrated clearly the potential of using bacteria for capturing CO_2 and transforming it into methane. The knowledge gathered can also be used for producing other valuable organic compounds with CO_2. ESG will use the results in scientific publications and is looking forward to a further collaboration with the consortium partners in the future.

Dr. Kor Zwart is a microbiologist with large experience in (an)aerobic fermentation and biogas production

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