Power to Methane

State-of-the-art and future prospects of biological power-to-methane (BioP2M) approaches

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State-of-the-art and future prospects of biological power-to-methane (BioP2M) approaches

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Samenvatting

Het aandeel van wind- en zonne-energie zal blijven groeien in het energie aanbod van de toekomst, maar hun intrinsieke variabele karakter vereisen aanpassingen in energiesystemen voor de opslag en het gebruik van elektriciteit. Opslag van eventueel tijdelijke overschotten aan elektrische energie in de vorm van methaan dat wordt gevormd uit waterstofgas en kooldioxide is een veelbelovende mogelijkheid Met elektrolyse kan uit (duurzame) elektriciteit waterstofgas gemaakt worden. De combinatie van dat waterstof met kooldioxide resulteert in de goed te hanteren energiedrager methaan, dat tevens als koolstofbron voor de toekomst kan dienen. Biogas uit biomassa levert naast methaan ook dat kooldioxide. Anaërobe micro-organismen kunnen extra methaan uit waterstof en koolstofdioxide maken in een proces van methaanvorming dat vergeleken met zijn chemische tegenhanger duidelijke voordelen biedt. Biologisch gevormd methaan zorgt voor duurzame opslag van energie en maakt gepast gebruik van de bestaande infrastructuur voor en kennis van aardgas. Het toevoegen van waterstof aan een aparte bioreactor na vergisting optimaliseert de omstandigheden voor het maken van methaan en geeft de meeste flexibiliteit. De lage oplosbaarheid in water van waterstofgas beperkt de productiesnelheid van methaan. Het gebruik van holle vezels, nano-bellen of beter toegeruste methaan-vormende micro-organismen kan dat knelpunt waarschijnlijk wegnemen. Analyses van de octrooiaanvragen op biomethaanvorming laten zien dat er een aanzienlijke handelingsvrijheid is. Beoordeling van de biologische vorming van biomethaan met betrekking tot zijn economische haalbaarheid en de ecologische waarde is lastig en vereist nieuwe gegevens en ervaringen. Momenteel is biomethaanvorming waarschijnlijk nog niet economisch haalbaar, maar dit kan anders worden in de energiesystemen van de nabije toekomst.

Executive summary

Wind and solar power generation will continue to grow in the energy supply of the future, but its inherent variability (intermittency) requires appropriate energy systems for storing and using power. Storage of possibly temporary excess of power as methane from hydrogen gas and carbon dioxide is a promising option. With electrolysis hydrogen gas can be generated from (renewable) power. The combination of such hydrogen with carbon dioxide results in the energy carrier methane that can be handled well and may may serve as carbon feedstock of the future. Biogas from biomass delivers both methane and carbon dioxide. Anaerobic microorganisms can make additional methane from hydrogen and carbon dioxide in a biomethanation process that compares favourably with its chemical counterpart. Biomethanation for renewable power storage and use makes appropriate use of the existing infrastructure and knowledge base for natural gas. Addition of hydrogen to a dedicated biogas reactor after fermentation optimizes the biomethanation conditions and gives maximum flexibility. The low water solubility of hydrogen gas limits the methane production rate. The use of hollow fibers, nano-bubbles or better-tailored methane-forming microorganisms may overcome this bottleneck. Analyses of patent applications on biomethanation suggest a lot of freedom to operate. Assessment of biomethanation for economic feasibility and environmental value is extremely challenging and will require future data and experiences. Currently biomethanation is not yet economically feasible, but this may be different in the energy systems of the near future.

Summary

In the transition to a more sustainable energy supply, wind and solar energy generation are rapidly replacing fossil fuel-based power and are expected to grow even faster in the not-too-distant future. The inherent discontinuity in wind and solar power generation, known as intermittency, urges the development of appropriate future energy systems for storing and using electrical energy. Chemical storage as gas or liquid allows storage over long periods in large volumes. Next to hydrogen gas methane is considered a suitable storage medium with less safety issues than hydrogen. Methane is formed from hydrogen gas and carbon dioxide and various ways exist to obtain these two substrates. Many different ways to produce hydrogen from power exist or are in development. Different types of electrolysis are most advanced relative to fossil-fuel dependent steam reforming of methane or coal or gasification of biomass, but these are relatively costly and energy inefficient, so innovations are desired. Biophotolysis or microbial electrolysis may be future bio-based alternatives for hydrogen production. Carbon dioxide is the greenhouse gas that contributes to climate and change and global warming, but also presents an abundant carbon feedstock for the future, possibly via methane. Most technologies to produce industrial carbon dioxide heavily rely on fossil resources. An interesting exception is biogas, the mixture of methane and carbon dioxide that is produced from biomass by a complex mixture of anaerobic microorganisms involving archaea. The so-called hydrogenotrophic methanogenic archaea make methane from hydrogen and carbon dioxide (biomethanation) at ambient to moderately high temperature and atmospheric or moderately high pressure, in contrast to chemical methanation (Sabatier reaction) that also involves expensive and impurity-sensitive catalysts and requires purified carbon dioxide and hydrogen gas as input. The amount of biogas per unit of biomass is almost doubled when the carbon dioxide is converted into methane, increasing the effective availability of biomass and obviating the need for further upgrading to natural gas quality. Moreover, in the transition towards renewable energy use, biomethanation for power storage and use makes good use of the existing infrastructure and knowledge base for natural gas, notably in the Netherlands. Biomethanation is however in the research phase. Different reactor set-ups are considered on lab-scale and in few pilot plants. Adding hydrogen to the biogas reactor (*in-situ*) may make best use of prior investments, but is likely less efficient in methane formation than a set-up with a second reactor for the biomethanation reaction (*ex-situ*) that allows better optimization of biomethanation conditions and gives more flexibility towards the source of carbon dioxide. A major challenge in either set-up is the delivery of hydrogen into the microbe. The low water solubility of hydrogen gas relative to carbon dioxide determines the rate of methane production. Various strategies are suggested to overcome this bottleneck and may involve the use of hollow fibers or nanobubbles. Comparative analyses of many more methane-forming species may also prove advantageous. Analyses of patent applications on biomethanation suggest a lot of freedom to operate as well as ample room for improvement. Assessment of biomethanation in terms of economic feasibility (cost-benefit analysis) and environmental value (energy efficiency, greenhouse gas balance) is extremely challenging and requires more data, experiments and experience. Of particular interest are the flexibility and possibilities of scale of biomethanation in view of the intermittency of wind and solar energy production. In the current energy system biomethanation is not yet economically feasible, but this may be different in a future system with more emphasis on flexibility and carbon dioxide taxation. The connection between power and methane is likely to develop into the connection between power and anything.

Contents

1. Introduction

The anticipated pressure on the use of fossil energy in view of climate concerns, global warming and availability of resources has fuelled the need for an alternative energy future for human activity and well-being. The 2015 Paris agreement on climate change (COP21) was heralded as a great success [110], yet may still not be ambitious enough [177]. Efforts include the better efficiency and conservation of energy, as well as the development and use of a wide variety of renewable energy technologies to replace fossil sources. Currently the most advanced renewable energy sources are wind and solar energy. However, the increase in capacity to produce power from wind and solar energy is predicted to present a serious issue: the stochastic, therefore inherently unpredictable and sometimes large variation in wind and solar power production, known as intermittency [31,108,188], does not synchronize well with the fluctuations in power demand and the current set-up of power grids. As a result, the unbalance between production and consumption of power is likely to increase. With the rise of renewable or sustainable power, the periods of such unbalance are likely to increase in frequency, severity and duration in such a way that it threatens the security of supply of energy to individual households and industry [49,93,108]. Different strategies are considered as options to safeguard the future energy supply and alleviate or circumvent the issue of intermittency [53,161].

One of the options to create a large and flexible buffering capacity for wind and solar power is the conversion of power to gas. Gas can be stored relatively easy and cheap compared to electricity and the strategy of storing electricity in the form of gas is known as power-to-gas, or power-2-gas [64,115], generally abbreviated as P2G. However, P2G is becoming an ambiguous term as different gasses can be implied. The gas primarily considered is hydrogen gas, H_2, as strategy also known as power-to-hydrogen Electricity is converted to hydrogen gas by the well-established process of electrolysis [223]. Hydrogen gas is regarded as a promising fuel for the future [12,64]. It burns cleanly without emission of carbon dioxide, CO_2. Hydrogen gas, however, is relatively difficult to handle, as it is extremely explosive, may cause embrittlement and diffuses very easily, causing leaking and all concomitant issues with safety [171]. Therefore, we here focus on the alternative of methane (CH_4) gas as option for storage of renewable power, from here on referred to as power-to-methane or P2M. Methane gas is much easier to handle than hydrogen gas. Because of its current and former fossil methane reserves, notably The Netherlands has developed and is maintaining excellent infrastructure and ample expertise for the transport, storage and safe exploitation of methane gas [190].

Methane gas can be produced from hydrogen gas and carbon dioxide in either chemical (chP2M) or biological processes (bioP2M) that will be reviewed in detail below, with emphasis on the biological pathway. Such production of methane gas requires carbon dioxide, therefore an additional advantage of methane as storage of electricity may be the contribution to a reduced carbon footprint. Different sources of CO_2 are feasible and below we give an overview of the possibilities, with emphasis on CO_2 from biogas. Using CO_2 from biogas to make methane from electricity-generated hydrogen may not only create a suitable buffer for sustainable power, but may also produce biogas with markedly higher methane concentrations.

The sections below are organized along the motivations for and paths of bioP2M. First, the trends in sustainable power developments are briefly summarized (section 2), with emphasis on increases in production, fluctuation, energy storage and future security of energy supply. In section 3, the characteristics, production technologies, uses and future outlook of hydrogen are outlined. In section 4, the same is done for the second substrate, carbon dioxide. In section 5, chemical production of

methane from hydrogen and carbon dioxide is reviewed. This is followed by an overview of the complex biological pathways towards methane in section 6, from the anaerobic decomposition of biomass into biogas to the microbiological conversion of hydrogen and carbon dioxide to methane. Research into the economic feasibility and sustainability of the new technologies is summarized in section 7. We refer mainly to the many excellent reviews and/or reports that have been published in recent years. These references should direct the interested reader to the primary literature.

2. Trends in sustainable power production

Globally, power production from non-fossil sources is increasing tremendously *[28,29]* and is expected to rise even harder in the coming years *[97,195]*. This growth in sustainable power production is almost exclusively due to technological developments in both solar and wind energy generation.

2.1. Wind power

The energy in wind is converted to electrical power by means of a wind turbine, a highly modernized version of the earlier windmill that generated mechanical energy. Arrays of wind turbines, known as wind farms, are an increasingly important source of renewable energy. Offshore wind power is now considered a reliable and affordable source of renewable energy, as long as there is wind *[60]*. The many developments and trends with respect to wind energy conversion aiming at a reduction of costs and improving both efficiency and reliability *[42]* are beyond the scope of this report. Worldwide, the growth of wind power capacity is growing rapidly (Table *2.1*) with a 6-fold increase over the last ten years.

Table *2.1*. Increase in wind and solar energy

	Wind energy (turbine power)			Solar energy (PV power)		
	2006	2016	Fold increase	2006	2016	Fold increase
Installed capacity (GW)						
World	74.0	469.0	6.3	5.8	301.5	52.0
Europe*	48.3	155.2	3.2	3.3	103.6	31.3
Netherlands	1.6	4.2	2.6	0.05	2.1	42.0
Electricity generated (TWh)**						
World	132.4	955.2	7.2	5.7	331.8	58.0
Europe*	82.7	301.8	3.6	2.2	112.6	51.2
Netherlands	2.6	7.9	3.0	<0.22	1.3	6.0

Data from *[29]*;
* minus data from Turkey and Ukraine, if given.
** Data are presented in tonnes oil equivalent (TOE), here converted to electricity based on 10^6 TOE = 4.4 TWh of electricity. Other sources with statistics may differ (slightly) in the data presented.

Also in Europe and the Netherlands the capacity to generate power from wind is increasing (Table *2.1*). The installed capacity of wind power in the Netherlands is currently ca. 4 GW, which is about 7% of the overall installed power capacity. In 2010, the European electricity transmission system operator TENNET projected a total wind capacity of 10 GW for the Netherlands for 2030 *[211]*, whereas a more recent projection comes to 12.6 GW *[61]*.

2.2. Solar power

Solar power is the conversion of sunlight into electricity using so-called solar or photovoltaic (PV) cells. The conversion is based on the photovoltaic effect, the creation of an electric current in material upon exposure to light. Crystalline silicon is currently the material used most *[15]*, but new materials are being considered continuously, such as perovskite *[210]*. The many developments and trends in PV energy conversion with respect to materials, efficiency and costs *[15,163,210]* are beyond the scope of this report. The growth in capacity of power from solar cells increases more dramatically than the growth of wind power (Table *2.1*). Worldwide, capacity increased about 52 fold in the last 10 years. In

Table **2.2**. Overview of energy storage systems.

Main	Subclass	Technology	maturity*
mechanical	Potential	- pumped hydro storage	+++++
		- compressed air energy storage	++++
		- small scale compressed air energy Storage	+++(+)
	Kinetic	- flywheel energy storage	+++(+)
		- floating railway	+
electrical	Electrostatic	- capacitor	++++
		- supercapacitor	++++
	Magnetic	- superconducting magnetic energy Storage	++++
	Electrochemical	- fuel cell (many types)	++(+)
chemical	battery energy storage systems	- lead acid	+++++
		- bromide (zinc, sodium, vanadium)	++++
		- sodium nickel chloride	++++
		- nickel cadmium	++++(+)
		- nickel metal (hydride)	+
		- lithium ion	++++(+)
		- sodium sulfur	++
		- metal air	+
	Chemicals	- hydrogen	++(+)
		- methane (synthetic natural gas)	++(+)
		- methanol	++
		- ammonia	+
thermal	high temperature	- sensible heat water, sand, molten salt, underground	+++++
		- latent heat - phase change materials *e.g.* ice, salts (NaOH), wax	++(+)
		- thermochemical (ad)sorption systems *e.g.* LiCl, zeolites, salt hydrates	++++
	low temperature	- Aquiferous low temperature	+++
		- cryogenic energy storage	++(+)

*+++++, mature; +++, developed; + in development (and all stages in between).

Data assembled and interpreted from various literature *[40,92,95,188,251]*.

the Netherlands the increase was about 42 fold. The installed capacity of solar power in the Netherlands is currently ca. 2 GW, which is about 4% of the overall installed power capacity. In 2010, TENNET, the operator of the European power grid, predicted a solar energy capacity of 4 GW for the Netherlands in 2030 *[211]*. Others predicted a total capacity of 6 GW for solar power in the Netherlands by 2020 *[49]*, with an upper value of 12 GW. Such estimates are likely to be conservative: the rise in solar power may outperform expectations manifold.

2.3. Intermittency
A major issue with both wind and solar power production is the generally unpredictable large variation, both annually and on a daily basis. This inherent fluctuation is known as intermittency *[31,108,128]*. Also power demand fluctuates and when they do not synchronize with the fluctuations in production, periods with great over-production and great underproduction may follow each other. In Germany, this unbalance has already resulted in negative electricity prices *[66,158]*. The introduction of intermittent energy sources will increase the need for overall flexibility in the future energy system *[74]*. Such overall flexibility should enable matching supply and demand at all times and on all scales.

Simulations demonstrate how variable the production of electricity through wind and solar PV can be *[221]*. Although it is tentatively concluded that with the current projections power overproduction is not likely to occur frequently in the Netherlands or Belgium *[221]*, with the rise of solar and wind power, the situation will become more urgent in the foreseeable future (~2030) of Europe. In that case, there is great need for a buffering capacity of wind- and solar power. It is expected that no less than about 20-25% of the total capacity of wind and solar power will have to be buffered in the future *[251]*.

2.4. Power storage

Storage systems are considered the appropriate approach to create buffers to deal with the intrinsic intermittency of sustainable power production and the unbalance between production and demand. Different propositions for Energy Storage Systems (ESSs) are intensively studied, evaluated and reviewed *[40,74,92,188,251]*. In Table **2.2**, the various systems are outlined, categorized on type and system. The various systems are in different stages of development *[251]*. Of these, only pumped hydro storage and the lead acid battery are considered sufficiently mature *[40,251]*. Issues important for storage systems are storage time and storage capacity. Energy storage systems differ in terms of storage duration and storage capacity *[188]*. Of all possibilities, the battery energy storage systems are most versatile, but are limited in storage capacity *[188]*. The recently commercialized Tesla Powerwall uses Li-ion technology *[162]*. For any technology, a combination of affordable long-term storage and high storage capacity will be important for sustainable energy applications in the future.

Chemically stored energy carriers such as hydrogen and substitute natural gas can be stored for long (months to years) periods and have a large storage capacity of 5 GWh to 5 TWh for hydrogen and 20 GWh – 50 TWh for SNG *[188]*. Therefore, chemically stored energy carriers are good options, especially when they can be integrated in the existing infrastructure (*e.g.* the gas grid). Excess electricity could also be stored as liquid, such as diesel, gasoline or methanol *[48,65,199]*. Currently, pumped hydro storage and compressed air energy storage are considered as the more cost-effective large scale approaches *[49]*. There is currently increased interest in so-called hybrid energy storage systems that may perform better *[86]*.

2.5. Future energy system(s)

The future of P2M will depend on the energy system it plays a role in. An energy system is here defined as the combination of components or technologies that converts an available energy source (biomass, solar) to a desired energy carrier for use (power, heat or fuel) or chemical feedstock. An energy system that uses different energy sources is also referred to as a hybrid system *[161]*. The outline of a possible hybrid energy system with a central role for hydrogen and power to methane is depicted in Figure **2.1**. In the Netherlands, energy is currently supplied by

1- the electricity or power grid. This consists of the main grid and sub grids. Because of the intrinsic challenges in storing electricity, power grid plants are ramped up and down to provide the electricity as needed throughout a day. Wind and solar power are among the input for the power grid.

2- the (natural) gas grid. This is organized for transport (high pressure; 40-60 bar) and distribution (low pressure; < 8 bar). Natural gas is currently mainly used to produce heat in the built environment and for industry. In addition it serves as a backup for electricity demand. Biomass is used to produce biogas, that can be upgraded to so-called 'green' gas, *i.e.* biogas with characteristics of natural gas *[17]*. Green gas can be injected into the appropriate gas grid.

The growth of wind and solar power as outlined above is expected to result in a surplus of power in terms of demand relative to supply. This surplus is challenging the energy system. It may be used to produce hydrogen via electrolysis, that can be stored and (re)converted into electricity and/or heat upon demand or used for other purposes either directly or indirectly. An option is to feed hydrogen into a digester to generate methane in different technological set-ups that are discussed below. In this route of power to methane (P2M), wind and solar power become connected to the gas grid.

The different components of this energy system should balance supply and demand to safeguard security of supply to end users. Initially this will be accomplished by a combination of renewable energy sources and storage systems with gradually diminishing conventional sources in a process that is generally referred to as energy transition [233]. Scale is an important consideration. Most components of the current energy system operate centralized at large(r) scale, such as a conventional power plant, or decentralized at small(er) scale, such as a digester on a farm. When biogas produced on a farm is transported to hubs where it is upgraded to green gas, the hub is the linking pin between centralized and decentralized components of the system [87]. P2M has to find its position in the several options of the future hybrid energy system.
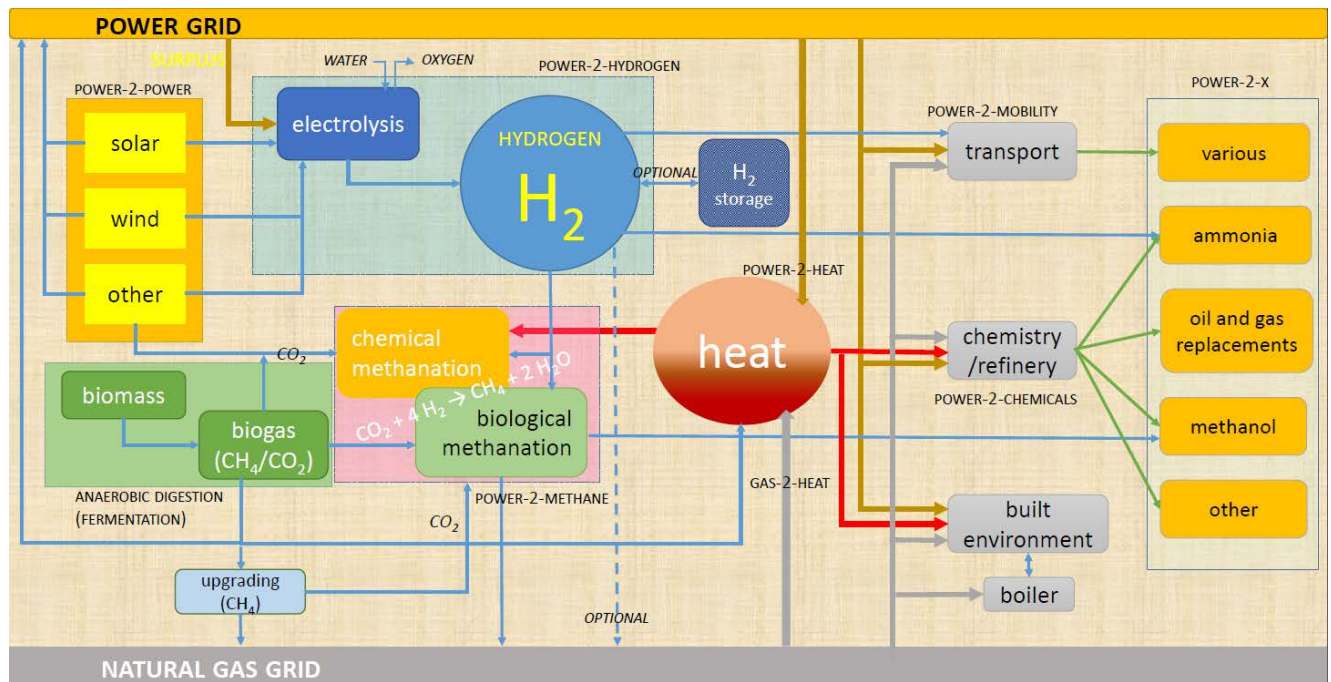
Figure *2.1* Layout of a possible future hybrid energy system with a central position for hydrogen. Simplified and modified after literature *[52]* and discussions.

Possible uses of P2M could include:

(a) **Storage of electricity**. Hydrogen or methane are options for long(er) term storage of (excess) electricity, the latter possibly in the gas grid. Storage of electricity is currently the driving force for research into electrolysis and P2M . It will have to compete with other storage options (see section 2.4) that are in development.

(b) **Management of electricity grid infrastructure.** Appropriate storage of excess power will reduce electricity transport and may help managing the required expansion of the electricity grid in the context of an all-electric supply system. Power storage either as hydrogen or methane (P2M) is an option considered for such developments.

(c) **Upgrade of electricity.** Converting electricity into methane or other components as feedstock for the chemical industry adds value beyond energy. It will result in the production of green chemicals. Current chemistry is almost exclusively carbon-based and most carbon originates from fossil oil. The concept of power-to-chemicals (P2C), or power-to-anything (P2X), combined with advanced use of biogas *[249]*, are promising developments *[227]*. Properly developed electrolysis and P2M technology will be the forerunner of such developments.

(d) **Management of the gas grid infrastructure.** P2M may facilitate the production and direct injection of green gas in the gas grid. This may strengthen and develop the role of the gas grid as storage and back-up system for renewable energy, assuming technological issues and demands with respect to gas properties (pressure, composition, volumes) are addressed and can be adjusted.

(e) **Contribution to system flexibility.** If in the future natural gas is replaced by electricity and possibly green gas, flexible biogas supply chains play an important role *[18,78]*. P2M may contribute to the desired flexibility.

(f) **Biomass availability.** A major issue in the contribution of biomass to a renewable-based energy system is the availability of biomass for such purposes. The availability of biomass is often a limiting factor, depending on assumptions and models used *[19]*. When fully converting carbon dioxide from biogas to methane, the effective availability of biomass will nearly double, assuming ~40% carbon dioxide in biogas. This way, P2M may help to increase the relative biomass availability.

(g) **Carbon dioxide capture.** The future energy system should consider climate effects and comply with agreements on combatting climate change. P2M may be used to capture the greenhouse gas carbon dioxide beyond biogas production. This way it could contribute to the better management of atmospheric carbon dioxide, safeguarding that the resulting methane, as more potent greenhouse gas than carbon dioxide, is not released in the atmosphere.
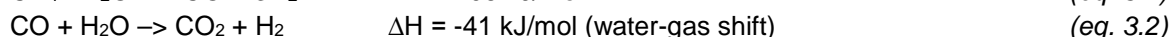
3. P2M substrate: hydrogen gas

3.1. Basic characteristics

Hydrogen is the most abundant element in our universe, comprising about 70% of the universe by mass. In the earth atmosphere, there is only about 0.5 ppm. A comprehensive summary of the characteristics of hydrogen is given in the PubChem database *[171]*. As diatomic gas, it is odourless, colourless and tasteless. It reacts generally slow at room temperature, but is easily activated to react quickly with many substrates. It is extremely flammable over a range of vapour/air concentrations and auto-ignites at 500 °C. Its vapours are lighter than air. Once ignited, its flame is poorly visible. The water solubility of hydrogen is poor at 1.62 mg/L (at 21 °C). It is non-corrosive, but is known to cause embrittlement of metals *[24]*. 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). Hydrogen is used industrially to produce ammonia (Haber process) and a variety of other chemicals. It is also used in welding of steel and other metals. The world annual production was over 50 million tonnes (3.76 EJ) in 2011 and is expected to increase significantly in the coming years *[75]*. Liquid and compressed hydrogen are considered possible fuels for the future. Hydrogen burns 'clean', producing only water. The so-called ' hydrogen (fuel) cell' produces electricity and water from hydrogen and oxygen *[200,216]*, and is being commercialized for use in vehicles *[43]* and possibly aviation *[102]*. Hydrogen gas is produced from fossil or renewable resources with a wide variety of technologies and approaches in different states of development. We here summarize the more important developments.

3.2. Hydrogen from fossil sources

There are several ways to produce hydrogen from methane or hydrocarbon compounds, such as steam reforming, partial oxidation and autothermal reforming *[89]* and for details we refer to overviews published earlier *[89,156]*. The most common method in current commercial industrial use is the treatment of methane gas with steam in a process known as (methane) steam reforming. This occurs in centralized plants because of efficiency of scale *[75]*. Although intrinsically unsustainable, it is still used at a large scale in the chemical industry. It is estimated that currently up to 96% of the world hydrogen production is based on fossil resources, of which 48% via methane steam reforming and 18% via gasification of coal *[26]*.

The reactions of methane steam reforming are *[75]*:

$CH_4 + H_2O \rightarrow CO + 3H_2$	ΔH = 206 kJ/mol	*(eq. 3.1)*
$CO + H_2O \rightarrow CO_2 + H_2$	ΔH = -41 kJ/mol (water-gas shift)	*(eq. 3.2)*

The two reactions (eqs *3.1* and *3.2*) occur simultaneously at high temperatures (~ 800-1200 °C).

Reactors are designed to maximise hydrogen formation and the process uses catalysts such as nickel or costly metals. Catalysts and reactor design are investigated intensively and are seeing progress in recent years *[96,157]*. Steam reforming generally results in gas with about 75% hydrogen. To increase the amount of hydrogen, so-called water-gas shift (eq. *3.2*) reactors and others are used in various set-ups *[89]*. Pure hydrogen is obtained by upgrading over membranes or adsorbents *[75]*. A membrane reactor may produce and separate hydrogen in a single step *[96]*.

An alternative for methane steam reforming is gasification of coal or coke *[156]*. This accounts for an estimated 18% of the world hydrogen production *[26]*. Gasification involves high temperature of about 1000 ˚C and up as well as moderate pressure. The reaction has a complex chemistry *[156]* to produce synthesis gas known as syngas, a mixture of hydrogen, carbon oxides (mono and di), methane and others, depending on gasification temperature and other process parameters *[89]*.

3.3. Hydrogen from water: electrolysis

Arguably the purest form of H_2 results from electrolysis of water, H_2O, the most common hydrogen compound on Earth. Electrolysis is the conversion of electrical energy to chemical energy in the form of hydrogen *[223]*, with oxygen as potentially useful by-product *[89]*. In its simplest form electrolysis is an electrical current between electrodes in water that splits water into hydrogen and oxygen (eq. 3.3).

$$2H_2O + 2e^- \rightarrow 2H_2 + O_2 \qquad \Delta H = -288 \text{ kJ/mol} \qquad \qquad \textit{(eq. 3.3)}$$

The electrodes ensure the flow of an electrical current. Electrolysis requires a significant amount of energy, so it is not necessarily sustainable if fossil resources are used to make the electricity for the electrolysis *[89]*. Electrolysis driven by nuclear energy is problematic because of the radioactive waste associated with nuclear energy and the need for many nuclear reactors *[217]*. Commercial use of electrolysis dates back to the 1890s *[89]*. There has been and still is a huge body of research in splitting water to make hydrogen and oxygen. For further details we refer to overviews published earlier *[26,89,123,223]*. An overwhelming multitude of set-ups for electrolysis cells is present in the literature, accompanied with a wide range of subsequent suggestions for improvements and adjustments *[26]*. A common distinction is in three different technologies *[89]*: alkaline water electrolysis (AWE), proton exchange membrane (PEM) electrolysis and solid oxide electrolysis cells (SOEC), but other ways of classification, such as by operating conditions (temperature, pressure) or substrate type (water, otherwise) are feasible *[26]*.

3.3.1. Alkaline water electrolysis (AWE)

AWE is the oldest and most mature technology. An alkaline electrolysis cell consists of electrodes in an aqueous alkaline electrolyte (usually KOH or NaOH). At the cathode, water is split into hydrogen gas and the hydroxide ion (OH^-). The latter ion travels to the anode, where oxygen gas is formed. The formation of gas phases is troublesome as it hinders electron transfer and power density is relatively low *[26]*. Many technological developments attempt to minimize these negative effects. To prevent re-formation of water from hydrogen and oxygen, a microporous separator is placed between the electrodes. The combination with anion–exchange membranes is considered promising *[26]*. The hydrogen is separated from the alkaline solution in a gas-liquid separation unit outside the electrolyser *[26]*. Alkaline electrolysis typically achieves efficiencies of 50–60%. Yet, alkaline systems have difficulties with intermittent power sources of energy *[223,224]*.

Resistance to electrolyte (KOH)-induced corrosion is a major criterion for the electrodes. The most common cathode material is nickel, often with a catalytic coating, such as platinum. For the anode, also nickel or copper is used, often coated with metal oxides often from manganese, tungsten or ruthenium *[89]*. The relatively low cost of the electrode material is one of the major advantages of AWE relative to other systems. A lot of research is presented on the stability and activity of nickel-based electrodes *[26]*. The electrodes, the separator and the electrolyte are the key elements of the electrolytic cell and predominantly affect the performance of the process. Commercial AWE units are generally operated at temperatures below 100°C, but high temperature electrolysis in alkaline cells is actively investigated *[59]*. Additional advantages of AWE are robustness and lifetime *[26]*. Such electrolysis unit is relatively robust, safe and flexible and therefore able to accommodate the rapid shifts in power supply: it takes approximately 4 minutes to start-up the electrolyser *[234]*. However, assessment and improvement of efficiency continues to be a topic of research interest *[225]*. It may be advantageous to combine electrolysis with battery technology as demonstrated in a recent set-up coined 'battolyser' *[154]*.

3.3.2. Proton-exchange membrane (PEM) electrolysis

PEM electrolysis uses expensive metals such as platinum or iridium for electrodes because of the high acidity in the cells [223,224]. For more details, we refer to the overview that was presented earlier [38]. The separator is a solid thin polymeric membrane which not only separates the electrodes, but acts as a gas separator as well [89]. Water is split into protons and oxygen at the anode. The protons travel to the cathode, where they form hydrogen. PEM electrolysers have efficiencies of 55–70% [38]. The purity of the produced hydrogen is high when compared to alkaline systems. PEM systems are currently getting renewed interest because they deal better with intermittent power sources of energy than alkaline systems [223,224].

3.3.3. Solid oxide electrolysis cells (SOEC)

Solid oxide electrolysis involves a solid polymer electrolyte and high temperatures (750-950 °C). The higher temperature increases the efficiency of the electrolysis: the electrical energy demand to produce hydrogen from water is reduced by approximately 25% [71,223]. Moreover, a solid electrolyte is non-corrosive and it does not present any of the issues with liquid and flow distribution. For more details, we refer to the overviews that were presented earlier [59,69,89]. As in AWE, oxygen is formed at the anode. The electrodes are porous to ensure contact between the gases and the electrodes. The gas stream from the cathode is a mixture of hydrogen and steam, which makes it necessary to add an extra gas cleaning step. The higher temperature also requires the use of costly materials and fabrication methods, in addition to a heat source. The efficiency as a function of electrical input alone can be very high with efficiencies of 85–90% [89] and efficiencies up to 98% have been reported for SOEC at 650°C [69], but when the thermal source is included, efficiencies can drop significantly [89].

In recent years, the interest in SOEC is growing and research focuses on increased durability and lowered costs [38,69]. SOEC are essentially solid oxide fuel cells operating in reverse. Combining these in what is known as Reversible Solid Oxide Fuel Cells for co-generation of hydrogen and electricity is in a relatively early stage of commercial development [69,89]. It may result in savings, when one device can be used for both applications, but dedicated electrolysers are optimised for maximum efficiency, while the reversible system cannot operate at maximum efficiency in both modes. In addition to SOEC also solid proton conducting electrolysis cells are being investigated for high temperature electrolysis, predominantly using perovskites [59].

3.3.4. Ultra-short power electrolysis

Ultra-short pulse voltages of about 300 ns cause hydrogen ions to diffuse faster compared to conventional electrolysis [202]. Such pulsed power applied to electrolysis may offer novel methods for more efficient hydrogen production [152].

3.3.5. Photo-electrolysis

In photo-electrolysis, also referred to as water photolysis, light is used to split water in hydrogen and oxygen. It was demonstrated as early as 1972 [63]. Photo-electrolysis requires semiconductors that are similar to the materials used in photovoltaics [89] The chemistry of that semiconductor material and/or other photochemical catalysts such as water-suspended metal complexes is not trivial, nor is the physics involved [89,169]. Stability, efficiency and costs are the obvious targets for research into photo-electrochemical cells. Despite impressively efficient systems developed in laboratories, these issues are still bottlenecks for practical use [169]. Photo-electrochemical cells and photovoltaics should be considered equivalent approaches for which crossbreeding may benefit both [98].

3.4. Hydrogen from water: alternative routes

In addition to the electrolysis-related technologies discussed above, there are several technologies proposed in the literature as methods to produce hydrogen from water.

3.4.1. Thermolysis

Thermolysis or thermochemical water splitting is the decomposition of water in hydrogen and oxygen by heat alone [89,205]. When water is heated well over 2000 °C a small percentage of the chemical

bonds start to decompose. By using appropriate catalysts that withstand the high temperatures and/or higher pressures, the process is managed [89]. There are very many water splitting cycles suggested in the scientific literature, but costs and efficiencies are still challenging [89].The energy for thermochemical water-splitting could come from solar high-temperature heat. Yet, conventional industrial thermolysis is generally not considered suitable for solar-driven processes, because of intermittency: solar energy supply is not constant enough [112].

3.4.2. Plasmolysis
The technology of plasma reforming of fossil gas or plasmolysis is closely related to thermolysis and well known [89,151] and the chemistry resembles steam reforming (see section 3.2). A plasma (ionised gas) is produced by microwaves. This results in electron acceleration and vibration through which water molecules dissociate into hydrogen and oxygen. Plasmolysis may offer advantages in rapid responses to intermittent power supply and does not use scarce materials. Energy efficiency, when translated into costs, is comparable with electrolysis [215]. The plasma technology for splitting carbon dioxide could be applied to water and may be interesting because of the attractive response time [68]. In the Netherlands, plasmolysis of water is investigated in the project HyPlasma [215].

3.4.3. Biophotolysis
A small group of photosynthetic organisms are able to produce hydrogen gas from water: green (micro)algae and cyanobacteria [217]. The process is known as (direct) (bio)photolysis of water and is closely related to the process of photosynthesis: hydrogen production may be considered as the route chosen in case of excess solar energy [89]. In biophotolysis the electron-carrying ferredoxin protein that is also active in photosynthesis activates hydrogenases (in green microalgae) and/or nitrogenases (in cyanobacteria) to produce the hydrogen [117]. Most biophotolysis research is focussed on microalgae that have the highest photosynthetic capability, such as *Chlamydomonas* spp, for which strategies involving selection of high-yielding strains, genetic engineering and bioprocess engineering are combined [217]. Development of a cost-effective process for biophotolysis is however still considered a major challenge.

3.5. Hydrogen from biomass: gasification
Biomass is the umbrella term for a wide variety of organic sources, often associated with waste (municipal, agricultural, industrial), dedicated production (short rotation woody crops, switchgrass, biomass crops) or a combination of both (roadside flora). Hydrogen can be produced from biomass using thermochemical and biological processes. Pyrolysis and gasification are feasible thermo-chemical routes for hydrogen production. The technology used to produce hydrogen from coal (see section 3.2) is also used to produce hydrogen from biomass. Gasification is heating without combusting at high temperature, generally under limited oxygen application and with the help of catalysts. As such it is a form of pyrolysis [89]. It results in a mixture of hydrogen, methane, carbon monoxide, carbon dioxide, and nitrogen, as such known as 'producer gas'. Biomass tends to contain appreciable amounts of water, which is also vaporized and lowers the thermal efficiency. If the water contents exceeds 35%, gasification can take place in supercritical water at either low or high temperature [156]. In all cases, even at temperatures as high as 1000 °C, significant amounts of tar are formed. An impressive body of research is devoted to catalysts and tar reduction [1,164], as well as and reactor design [47]. Addition of steam or oxygen produces syngas as in steam reforming (see section 3,2) and the water-gas shift reaction (eq. *3.2*) followed by upgrading to hydrogen. Relatively high hydrogen yields are reported with superheated steam and dried biomass [89]. A second reactor is generally necessary to clean the product gas from tar. Gasification technology is mature and commercially used. As a rule, gasification reactors are large and need a continuous supply of massive amounts of biomass. They achieve energy efficiencies of 35–50% [89].

3.6. Hydrogen gas from biomass: bio-hydrogen
In addition to the thermochemical routes, there are several biological routes to produce hydrogen from biomass. A route is here considered 'biological' if it involves organisms or enzymes.

3.6.1. Dark and photo-fermentation

Microbes and some algae harbour the enzymes for a variety of fermentative processes that can produce hydrogen. An overview of possibilities and state of the art is presented in various chapters of a fairly recent book [248]. The two most important routes for microbial production of hydrogen are dark fermentation [67,80] and photofermentation [2,79,228].

Dark fermentation resembles in essence anaerobic biomass fermentation to biogas [80] and is discussed below (see section 4.4.1). It relies on matured bioprocess technology and may be used in combination with a variety of waste streams, notably wastewater [11]. The shift of dark fermentation from methane and carbon dioxide to hydrogen and carbon dioxide to achieve acceptable yields of hydrogen, for example by blocking methanogenesis, presents a major bottleneck for application. Success, often referred to as 'methane-free biogas', was reported with specific waste streams [143,160,250] or a defined component as glycerol [218,219], thermophilic conditions [83], acid pre-treatment [120] or bacterial pre-treatment [124]. In other cases, however, generally a variety of products is generated, lowering yield and requiring expensive upgrading technologies [67,80].

In photofermentation, purple non-sulphur photosynthetic bacteria, such as *Rhodobacter* spp., utilize light energy to convert organic acids to hydrogen gas under anaerobic conditions. Their enzyme nitrogenase reduces protons to molecular hydrogen under nitrogen-limiting conditions [79]. A major issue is efficiency, both in terms of energy consumption and of hydrogen production, resulting in many discussions on optimal reactor design [2,228]. The use of photofermentation for biological hydrogen production awaits practical, let alone commercial, application [248]. Combinations of dark and photofermentation [89], combined with strain selection [218] and use of mixed strains of photosynthetic purple non-sulphur bacteria [153], may result in higher yields of hydrogen in the future [247]. Engineering of the enzymes responsible for hydrogen generation is also considered, targeting efficient hydrogenases that function well under aerobic conditions [180].

3.6.2. Biological water-gas shift

A selected number of microorganisms can metabolize carbon monoxide (CO) and water at ambient temperature and pressure to produce hydrogen gas and carbon dioxide [240] in what is the enzymatic equivalent of the water-gas shift reaction (Eq. 3.2). This reaction occurs in some photoheterotrophic bacteria, such as *e.g. Rhodospirillum rubrum*, that can grow in the dark with carbon monoxide as only carbon source. In addition, a suite of thermophilic bacteria and archaea is reported to be able to make hydrogen from carbon monoxide [55]. Despite favourable thermodynamics and a relatively high conversion rate to hydrogen [89], the application of the biological water-gas shift has not seen much progress over the years [57,90].

3.6.3. Bioelectrohydrogenesis

Hydrogen can be generated from organic material by means of microbial electrohydrogenesis, one of the many applications in the growing field of microbial electrochemistry [194]. A microbial electrolysis cell is a bio-electrochemical reactor in which chemical energy stored in organic compounds is converted into hydrogen via catalytic oxidation by microbes [82,111,118]. Microorganisms generate electrons and protons by the oxidative decomposition of organic compounds and produce CO_2 as by-product. The cathodic chamber is anaerobic, and the transferred protons are reduced to hydrogen. Reduction of protons to hydrogen is thermodynamically non-spontaneous and requires external energy input. A small voltage on the microbial electrolysis cell forces the oxidation of the organic material at the anode and drives the chemical reduction of hydrogen protons at the cathode [242]. Direct combination of a microbial electrolysis cell with anaerobic digestion was reported to generate more methane [25]. Although generally considered promising [136,137], microbial electrolysis cells are not generally seen as very robust and many parameters warrant attention prior to large-scale commercial use, such as reactor design, biofilm composition and substrate characteristics [111,118].

4. P2M substrate: carbon dioxide

4.1. Basic characteristics

Carbon dioxide (CO_2) is an odourless, colourless and incombustible gas with a slightly acid taste. As liquid it is also colourless; solid it is known as dry ice and comes as white, snow-like flakes or cubes. CO_2 is relatively nontoxic, showing toxic effects above ~7%, highly soluble in water, 1.5 times heavier than air and may asphyxiate by displacement of air. A comprehensive summary of various characteristics of carbon dioxide is given in the PubChem database *[170]* as well as in other sources *[172,222]*. CO_2 is an important component in both the carbon cycle of the earth's atmosphere and in the respiration cycle of life. It is formed by combustion as well as by decomposition of organic material. In photosynthesis, plants remove carbon dioxide from the atmosphere and convert it into sugars with the help of the sun *[117]*. Carbon dioxide is an extremely versatile commodity that is used in a multitude of processes and applications *[222]*. Commercially, carbon dioxide is available as high pressure gas (cylinders), relatively low-pressure refrigerated liquid, or as dry ice. Commercial production of carbon dioxide requires relatively high volumes of CO_2-rich gas, which is often a by-product of a large-scale chemical production or biological process *[222]*.

4.2. Carbon dioxide from industry

A major source for carbon dioxide is industry which produces hydrogen or ammonia from natural gas, coal, or other hydrocarbon feedstock. The chemistry of that hydrogen production is presented above. Large quantities of CO_2 are produced by burning limestone (primarily calcium carbonate) to produce calcium oxide (lime) as well as in the production of magnesium from the calcium magnesium carbonate known as dolomite *[155,222]*. Another important source for carbon dioxide is large-volume fermentation in which biological material from plants is converted into ethanol for human consumption or transportation fuel, such as in breweries producing beer from grain or in ethanol plants *[155,222]*. Ethanol plants in the USA (using corn) and Brazil (using sugar cane) are estimated to emit in the order of 0.1–0.14 $MtCO_2$ annually, each *[109,155]*.

Carbon dioxide is generally seen as the unavoidable by-product of energy generation and a main concern in global warming. The concentration of carbon dioxide in air is currently about 0.04%, with a distinct seasonal variation. The concentration of CO_2 in air has been steadily increasing from about 0.028% due to human activities since the industrial revolution (~1800). Without efforts taken, worrisome projections are for concentrations to continue to rise to as much as 0.05 - 0.15% or over by the year 2100 and beyond, depending on models used, with serious consequences for global climate (global warming), weather and agriculture *[94]*. Therefore, a lot of research attention is now focussed on development and use of large-scale carbon dioxide capture, storage and conversion technologies *[246]*. Slowly the view of carbon dioxide as the culprit of global warming is changing into carbon dioxide as the abundant carbon feedstock for the future production of hydrocarbon chemicals and fuels. A description of all carbon dioxide conversion technologies except P2M is beyond the scope of this overview and we refer to the many reviews available *[113,246]*.

4.3. Carbon dioxide from methane

Methane (either fossil or from biogas) itself is an important energy source. It is used for the production of electricity and heat as well as transportation fuel. It is also used as building block in chemical synthesis. Combustion (complete oxidation; eqs. 4.1 and 4.2) of methane to generate heat and electricity is an obvious method to generate carbon dioxide. The same holds for coal (C).

Bacteria known as methanotrophs [81] are also able to generate carbon dioxide from methane by oxidizing it either aerobically [35] or anaerobically using sulphate or nitrite as oxygen donor [46,189]. The biochemical mechanisms, possible applications and relative contribution (up to a global scale) of these microbial conversions are being investigated and discussed [46,105,181].

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \hspace{4cm} \textit{(eq. 4.1)}$$
$$C + O_2 \rightarrow CO_2 \hspace{6cm} \textit{(eq. 4.2)}$$

4.4. Carbon dioxide from biomass (biogas)

Anaerobic decomposition, also called digestion or fermentation, of organic matter known as biomass results in biogas, a mixture of predominantly methane (CH_4;50-75%) and carbon dioxide (CO_2;25-45%), plus water (H_2O) vapour (2-7%) and trace amounts (0-2%) of ammonia (NH_3), carbon monoxide (CO), hydrogen sulphide (H_2S), nitrogen (N_2) and oxygen (O_2) [9,197]. The amount of biogas produced, as well as its composition, varies considerably between different biomass sources and installations [235]. The main interest in biomass fermentation from the application point of view has obviously always been the methane as it is the major energy carrier. Anaerobic production of a renewable energy source is an attractive and efficient way to treat and reduce the load of organic waste. It can be produced and used locally, which facilitates communities all over the world to use biogas as source of energy. The associated carbon dioxide is generally considered the unavoidable by-product of biogas production. It is less common to consider biogas as a source of carbon dioxide as we do here. The utilization of biogas is considered a way to reduce the emission of carbon dioxide into the atmosphere relative to fossil fuel. Data to estimate the amounts of CO_2 produced in biomass fermentation can therefore only be indirectly inferred from methane production.

4.4.1. Microbial digestion: overall process

Biogas is produced in four subsequent stages, [76,182,197,235]: hydrolysis, acidogenesis, acetogenesis and methanogenesis or methanation (Figure *4.1*). The overall process produces little heat because most of the chemical energy stored in the organic feed stock is stored in the methane and carbon dioxide produced, although for practical purposes, the energy content of carbon dioxide is generally set to zero. In all stages, reactor conditions (pH, temperature, design) play an important role, as do different consortia of micro-organisms, some of which act in mutual dependence in so-called syntrophic relationships [189]. The overall process is highly dynamic; small changes influence the microbial community and activity, yet overall efficiency is buffered [213]. Different mathematical models are proposed to describe and optimize the process [119,245]. The 4 stages of anaerobic decomposition of biomass (Figure *4.1*) are studied in considerable detail:

1.**Hydrolysis**, the breaking up of large complex organic polymers into smaller components, such as simple sugars like glucose from carbohydrates, long-chain fatty acids from fats and oils as well as amino acids from proteins. Hydrolysis is catalysed by a variety of hydrolytic enzymes excreted by microorganisms. Diverse groups of usually facultatively anaerobic bacteria are responsible for hydrolysis, commonly referred to as 'fermentative' [197] or 'primary fermentative' [189] bacteria. Hydrolysis can be the rate-limiting step in the overall anaerobic decomposition of biomass [142], notably in case of complex compounds that are difficult -if not impossible- to hydrolyse, such as lignocellulose. In biogas research, there is therefore much attention for pre-treatment technology [9,165] to make biomass easier accessible for microbial hydrolysis.

2. **Acidogenesis**, the conversion of the smaller molecules into various (largely volatile) fatty acids and alcohols, as well as hydrogen and carbon dioxide. Products of this step are for example propionic acid, butyric acid, methanol and ethanol [104], as well as hydrogen. Also the undesired products ammonia and hydrogen sulfide can be generated in this phase. Overall acidogenesis results in a wide variety of compounds produced by complex microbial populations, which are often considered together with the fermentative bacteria responsible for hydrolysis.
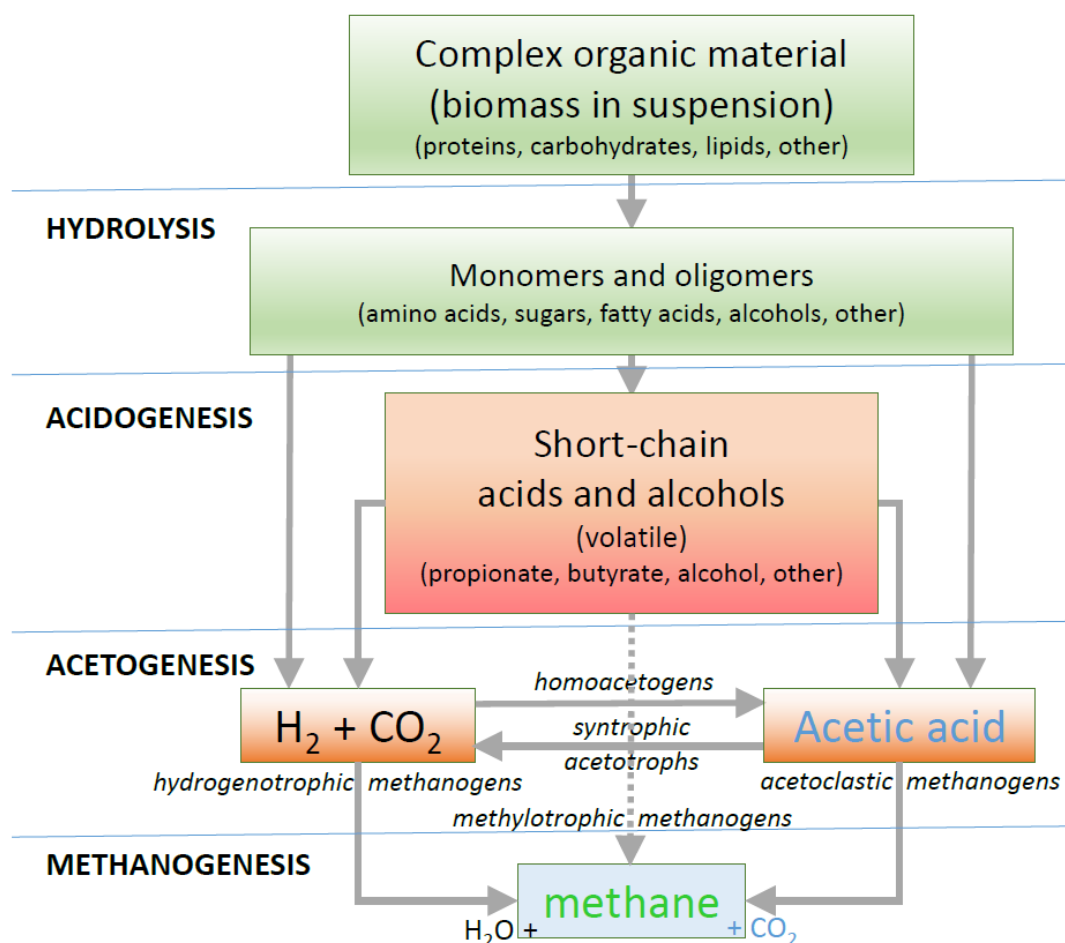
Figure *4.1.* Stages in anaerobic biomethane formation. Modified after literature *[10,51,76,235]*.

.3. **Acetogenesis**, the conversion of the products of acidogenesis (step 2) into the key metabolites acetic acid, carbon dioxide and hydrogen, in addition to various other metabolites. The formation of acetic acid is reported to be inhibited by hydrogen *[56,134]*, possibly due to toxic effects of hydrogen in acetogenic bacteria. So-called syntropic relationships with the methane-forming bacteria in the next phase determine the outcome of this phase: high H_2 partial pressure leads to propionate and butyrate accumulation, while low H_2 partial pressure enhances CO_2 and CH_4 production *[134]*. In addition, bacterial species exist that can oxidize acetate to hydrogen and CO_2 *[84]* This reaction is energetically costly, therefore it only occurs when the hydrogen is utilized by methanogens in what is called syntrophic acetate oxidation. Some syntrophic acetate-oxidizing bacteria can grow in pure culture on H_2 and CO_2 to produce acetate, so the oxidation of acetate must be reversible *[84]*. The relative importance of either route in biogas formation is currently not known.

4. **Methanogenesis**, the conversion of the products of acetogenesis (step 3) into methane, carbon dioxide and water *[91]*. Two main routes for methane formation exist, one from acetate (acetoclastic methanogenesis) which also produces carbon dioxide, and one from hydrogen that consumes carbon dioxide (hydrogenotrophic methanogenesis), the latter possibly preceded by syntrophic acetate oxidation (see above). Different groups of methane-forming or methanogenic bacteria are responsible for these routes (see below). Typically 70% of the methane and all of the carbon dioxide is formed from acetate (acetoclastic) and the remaining 30% of methane is produced hydrogenotrophically from H_2 and CO_2 *[10,193]*. In addition there is the possibility to form methane from methylated C1 compounds such as methanol or methylamines, known as methylotrophic methanogenesis *[10,231]*. The relative contribution of methylotrophic methanogenesis to biogas production remains to be established, but it is unlikely to be as large as it is in some particular ecosystems *[252]*.

4.4.2. Biogas reactors

To accommodate all complexities of biogas formation, biogas reactors are available in a large number of designs, configurations and combinations, ranging from remarkably small and simple for domestic use [88,226] to industrially large and complex as at Attero (formerly Vagron) Groningen [51], each with its own characteristics, advantages and drawbacks. Classification of biogas reactors is generally based on several criteria that can be combined in actual design [51,159,198]:

- (a) **substrate characteristics**: wet fermentation, i.e. low total solids (2-25%), or dry fermentation, i.e. high total solids (>30%);
- (b) **substrate feeding**: batch, fed-batch or continuous;
- (c) **substrate retention time**: low rate (long retention times) or high rate (relatively short retention times);
- (d) **mixing regime**: completely mixed with free living bacteria or fixed film with bacteria attached to each other (flocks) or to a solid substrate;
- (e) **number of units or stages**: single, double or even multi, aimed at optimizing the individual stages of anaerobic decomposition. Two-stage anaerobic digestion systems are often considered to be advantageous compared to one-stage systems, but results can depend considerably on substrates [133] that differ in methane potential [7];
- (f) **operating temperature**: psychrophilic (<20 $^{\circ}$C), mesophilic (20-~45 $^{\circ}$C) or thermophilic (>45 $^{\circ}$C);
- (g) **pressure:** atmospheric or higher;
- (h) **dimensions**: small and local up to large and centralized.

On top of these classifications come engineering issues (material choice, circular design and more) as well as process management parameters such as organic loading rate, use of remaining digestate and waste disposal, all aimed at a good yet complex combination of process efficiency (biogas yield) and economic feasibility (return on investment).

Common reactor types are the completely stirred tank reactor (CSTR; completely mixed type) for wet fermentation with relatively high solids biomass such as manure [27] and the upflow anaerobic sludge bed (or blanket; UASB; fixed film type) reactor [126] for wastewater or low solid input. Generally, fixed film reactors allow a broader range of retention times [203] and are used as second stage reactor in a two-phase configuration in which the liquid effluent is transferred to the fixed film reactor, but many more configurations are feasible. Mesophilic conditions at atmospheric pressure prevail, due to the higher operational stability of such systems, despite the potentially higher efficiency of biogas production in thermophilic conditions and/or higher pressure. Detailed comparisons and analyses of the merits and drawbacks of various reactor types are presented in the literature [51,159,198].

4.4.3. Biogas trends

Relative to liquid biofuels (biodiesel and bioethanol), biogas is still a small contributor, but the numbers continue to be on the rise. In the EU there are currently 17.376 biogas plants (agriculture, industrial, sewage sludge, landfill) installed, with a total capacity of 60.6 TWh electricity [58]. In addition, there are 459 biomethane plants generating green gas, of which many are injecting the methane into the gas grid. In the Netherlands, there are now 268 biogas plants with very different characteristics in terms of size and biomass use. In addition, there are 23 biomethane plants that generated 87 million Nm^3 green gas in 2016. Incentives to double this till 2013 are formulated. The use of biomass for bioenergy/biogas production has however also met concerns with respect to overexploitation, use of agricultural resources for energy crops (food versus fuel), local issues (acceptation, not in my back yard) and other possible negative effects. Sustainability standards are being developing and implemented.
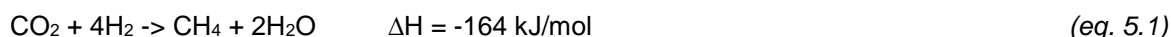
5. P2M technology: chemical methanation

Chemical, or catalytic methane formation, also known as the Sabatier reaction, is the conversion of hydrogen and carbon (mono- or di-) oxide to methane by chemical means. These reactions were discovered in the early 20th century and have seen investigations, uses and developments ever since [178]. For further details on CO and CO_2 methanation, we refer to earlier overviews [71,114,178,188] and a short summary is presented below.

5.1. Chemistry
The overall reaction for the chemical methanation of carbon dioxide is given in eq. 5.1. It is the reverse of the methane steam reforming discussed above (see eq. 3.1). Four moles of hydrogen are needed to create 1 mole methane from CO_2. The methanation of carbon monoxide is given in eq. 5.2. Three moles of hydrogen are needed to create 1 mole methane from CO [178].

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $\quad\quad \Delta H = -164$ kJ/mol $\qquad\qquad\qquad\qquad\qquad$ *(eq. 5.1)*
$CO + 3H_2 \rightarrow CH_4 + H_2O$ $\;\; \Delta H = -206$ kJ/mol $\qquad\qquad\qquad\qquad\qquad\qquad\;$ *(eq. 5.2)*

The two reactions are closely connected via the reverse water gas shift reaction, eq. 5.3 [178,234]. The water gas shift reaction is given in eq. 3.2 above.

$CO_2 + H_2 \rightarrow CO + H_2O$ $\quad \Delta H = 41$ kJ/mol $\qquad\qquad\qquad\qquad\qquad\qquad\;$ *(eq. 5.3)*

Both eq. 5.1 and 5.3 are exothermic. Depending on process conditions, also undesired higher hydrocarbons and solid carbon (C) are formed [188]. The reactions proceed at elevated temperatures and, despite being exothermic, require a catalyst [21] that among other requirements is able to withstand rapid temperature changes. Nickel, ruthenium, platinum, and others meet the requirements [21]. A detailed overview of all issues with respect to catalysts in chemical methanation is presented elsewhere [178]. Most commonly nickel is used because of its high activity and relatively low cost. The nickel catalyst, however, should not be used at temperatures below 200°C, as highly toxic nickel carbonyl can then be formed [188]. The catalyst makes chemical methanation moderately to highly sensitive to impurities in the feed gasses hydrogen and carbon (di or mono) oxide. Especially sulphur or sulphur-containing components deactivate the nickel catalyst [21].

All three reactions (eqs 5.1 – 5.3) are markedly influenced by both pressure and temperature, for which a solid body of literature exists [178]. Notably, temperature control is important for methane formation [188]. Methane formation is favoured up to 600 °C. High conversion leads to high temperatures because of the exothermal reaction and the produced heat needs to be removed from the reactor continuously. Use of the heat that is retrieved in the form of steam for other purposes may increase the overall energy efficiency of the process [188]. Temperatures above 550°C lead to deactivation and sintering of the catalyst [70,188]. High pressure up to 20 bar increases the conversion rate and shifts the equilibrium towards the products [188]. Given appropriate process control, the conversion efficiency of chemical methanation approximates 70% to 85% [74]. It can approach 100% when multiple reactors are operated in series.

5.2. Reactor design

A wide variety of reactor concepts exists for chemical methanation. Reactor design has a large influence on thermal control of the reaction. Multiple reactors in series are recommended to enable cooling of the reactants and obtain optimal conversion rates [188]. Currently in use are mainly fixed-bed methanation, fluidized-bed methanation and three-phase reactors [178].

In a fixed-bed reactor, the reactor is packed with the catalyst that consists of small particles. Mass and heat transfer is limited and adiabatic conditions (no temperature exchange with surroundings) are approached. To remove heat from the reactor, generally two adiabatic reactors are connected in series. Temperature control is realized by intermediate gas cooling steps and recirculation of the reactor outlet. At higher temperatures (above 500°C) in a fixed-bed reactor, hydrocarbons decompose and deposit carbon on the catalyst [70].A demonstration plant in Rozenburg consists of four fixed-bed reactors in series [234]. A comprehensive overview of other fixed-bed methanation set-ups can be found elsewhere [178].

A fluidized-bed reactor contains a solid substrate divided in small particles (usually the catalyst). A gas is led into the reactor with a specific flux, which causes the solid particles and the gas to mix and act like a fluid. The fluidization enables high heat and mass transfer. In this reactor design almost isothermal (constant temperature) conditions are achieved. Losses of and damage to the catalyst and hence pollution of the gas products is still an issue [188].

The three-phase reactor is based on a fine powder catalyst suspended in an inert liquid medium such as mineral oil [178] or dibenzyltoluene [70]. The liquid medium enables high heat transfer and allows good heat control of the reaction. A major issue of this technology is the relatively low conversion rate because of limited mass transfer by the liquid phase [70].

Microreactor designs for chemical methanation are in development [135] to be able to incorporate chemical methanaton in a more decentralized energy infrastructure [178]. These may involve the use of ultra-short-channel-length and/or catalytically coated metal meshes with very small channel diameters known as Microlith substrate. The mesh-like substrates provide high heat and mass transfer coefficients, low thermal mass, and extremely high reaction rates. The Microlith substrates are combined with catalyst coatings to permit CO_2 methanation that favours high reactant conversion, high selectivity and durability [100,101].

5.3. Scale, flexibility and pilot projects

Current chemical methanation plants are based on continuous operation, using syngas. The plants are typically of a size up to 500 MW. Power-to-methane set-ups should however respond to fluctuating sustainable energy supplies (see above). The flexibility of a chemical methanation plant is therefore of concern. The cold start time of a methanation plant can be in the order of several hours, depending on plant size [74,207]. Therefore, smaller plants, aimed to integrate in the P2M system are tested. Three-phase reactors may be more promising because of the high heat capacity of the liquid phase [70].

In Rozenburg, The Netherlands, a small scale chemical P2M (chP2M) installation with a capacity of 1 m^3 CH_4/hour aims at for demonstrating the P2G technology in a realistic environment that considers the value chain from production to end use [234]. Electricity that was generated with solar panels was converted into hydrogen and subsequently methane with natural gas quality is applied in a gas-fired boiler of nearby flat buildings. It requires only 35 minutes for a cold start [234]. In Germany, multiple chemical P2H (chP2H) demo projects are realised, most focus on the production of H_2 and the direct use of H_2. The Eucolino project by Schmack and Viessmann is a demo plant that produces 20m^3/ h H_2 in the first step and 5 m^3/ h methane by use of CO_2 from a biogas production plant in the second step.

The Audi E-gas project is a demo plant producing 1300 m^3/h H_2 that is converted to 300 m^3/h methane for fuel use in cars. In the Netherlands, the Interreg project 'Power-to-FleX' aims at formation of methane from H_2, produced by electrolysis, and CO_2 from a biogas installation using the Sabatier reaction. An overview of current chP2M plants is shown in Table **5.1**.

Table **5.1.** Current chemical P2M plants.

Project name	Country (place)	Electrolysis method	Input (kWe)	Application	Schedule
Tohoku/ Hashimoto	Japan (Sendai)	Alkaline	-	research, electric power generation	built in 1995
ALPHA	Germany (various)	-*	25	Pilot	2009-2012
E-Gas	Germany (Werlte)	-	6.300	natural gas grid injection	2013-
CO$_2$RRECT	Germany	PEM	100	chemical industry	2009-2014
MeGa-stoRE	Denmark	Alkaline	-	biogas upgrading	2013-2015
DEMETER	France	SOEC	-	natural gas grid injection	2012-2020
Rapperswil	Switzerland (Rapperswil)	-	-	Mobility	2015-
Rozenburg	Netherlands (Rozenbrug)	PEM	7	natural gas grid injection	2013-2018
Store&Go	Italy (Puglia)	Alkaline	200	virtual pipeline (LNG trucks)	2016-
Store&Go	Germany (Falkenhagen)	Alkaline	1000	Connection to transport grid	2016-

*-, not specified in public literature.
Data assembled and interpreted from various literature [178,209,232,234].

5.4. Future prospects

Future improvements of the Sabatier process should focus on reducing power requirements and making the process more flexible by shortening the reaction and regeneration time [21]. With reduced reaction and regeneration time the process will be better suitable to react to shifts in power supply and demand. This way it would present a better option for converting sustainable energy [101]. The efficiency of resource use should increase with reduced power requirements and the operational cost should decrease for making it into a more viable technology. Microreactor designs would seem to warrant more consideration in the context of a (distributed) renewable energy system.

6. P2M technology: biological methanation

Biological P2M is based on the ability of microbes to make methane from hydrogen and carbon dioxide. The overall reaction is not different from the reaction in chemical methanation (eq. 5.1),

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \text{(eq. 6.1)}$$

but in a biological system the reaction is catalysed by enzymes at ambient to moderately high (thermophilic) temperatures and atmospheric or higher pressure. Moreover, the biological system is likely to be considerably less sensitive to impurities in either carbon dioxide or hydrogen gas [168]. The likely origin of research into biological methanation started with careful observations in the very first PhD thesis of Delft University in The Netherlands in 1906 [204]. For quite some time hydrogen-consuming methanation was considered the main pathway for energy production by (hydrogenotrophic) methanogenic bacteria [237]. Yet, the acetate route now known to be predominant was already considered in 1906. An early analysis of this reaction aimed at application in view of limited fossil energy resources was presented in 1978 [237], followed by various studies over the years [34,36,37], gaining insight in the underlying microbiology and biochemistry to steer technological development and application.

6.1. Microbiology of biological methanation

6.1.1. Overall characteristics of methanogenic microorganisms
Methanogenic (i.e. methane forming) microorganisms belong to the domain of Archaea or Archeaebacteria, the third branch of life next to the (Eu)Bacteria and the Eukarya [236,238]. Originally identified on the basis of their rRNA sequence, archaea also differ considerably in cell wall structure [4] and biochemistry from (eu)bacteria. Initially thought to be limited to extreme environments, molecular analyses indicated a common presence of archaea in normal habitats, such as ocean waters, lakes and soil [39,212]. Methanogens are free living species in almost any strictly anaerobic environment [45,212], from cold to very hot (>100 ^{o}C) temperatures, in either fresh water or marine environments. Methanogens are also found in the rumen of cattle, deer and other ruminants, in the hindgut of horses, and also in the intestine organs of insects such as termites, whereas they also live as endo- or ectosymbionts of other organisms [77]. Methanogens are mostly active at a neutral pH, but methanogenic activity has been observed at levels as low as pH 3 or as high as pH 10 [39,229]. Seven phylogenetic orders are currently distinguished [121]. The accepted taxonomic classification of all methanogens in seven orders is however being challenged by new discoveries [166] and it was recently predicted that divergent methanogenic lineages await discovery [231]. Three different types of methanogens can be distinguished, based on the pathway for methane formation (see section 4.4.1.):

6.1.2. Hydrogenotrophic methanogens
Hydrogenotrophic methanogenesis is widespread among methanogens, found in six of the seven orders [231] and the vast majority of known methanogens is also classified as hydrogenotrophic [122,127]: they use H_2 as the electron donor to drive the reduction of CO_2 [187]. Many species could therefore be of use in bioP2M applications. Also facultatively hydrogenotrophic methanogens exist [212] that may primarily be methane (methylotrophs) or acetate (acetotrophs) consumers [187].

Hydrogenotrophic methanogens generally maintain a low dissolved hydrogen concentration by close contact with hydrogen producers [206]. Biological methane formation therefore occurs predominantly in flocks or biofilms that facilitate the syntrophic transfer of hydrogen between the two. The biochemistry of hydrogenotrophic methane formation is well studied. It involves several coenzymes as C-1 moiety carrier [134] and the actual methane formation is catalysed by the enzyme methyl-coenzyme M reductase (EC 2.8.4.1), involving a methyl radical intermediate [201]. The gene encoding methyl-coenzyme M reductase, *mcrA*, is often used as biomarker for the analyses of methanogenic communities [8,141].

The isolation and cultivation of the obligate anaerobic hydrogenotropic methanogens requires completely O_2-free conditions and appropriate technologies [239]. Over 40 pure strains of methanogens have been reported as isolated in 1997 [150], whereas the current (February 2017) ATCC (Oregon Collection of Methanogens) has 134 entries on the key word methanogens (https://www.lgcstandards-atcc.org) and many more may be available in individual laboratories. In the current GOLD: Genomes Online Database [173] version 6 maintained by the US DOE-JGI (http://jgi.doe.gov/ accessed 25-feb-2017), the genome sequences of over 250 methanogens are available, most of which are likely to be hydrogenotrophic.

Remarkably few of these have been evaluated for laboratory or industrial-scale bioP2M-related research [174]. For example, *Methanococcus maripaludis* (Order Methanococcales) is a rapidly growing mesophilic facultative autotroph [220] that is extensively used as model organism for molecular and genetic studies [186]. Although a plethora of studies with this organism have contributed to insight in the overall biochemistry and genetics of hydrogenotrophic methanogens [72], *Methanococcus maripaludis* has not been used for laboratory-scale or industrial bio-P2M applications, despite its obvious potential for such use [72].

In biomethanation experiments, predominantly thermophilic Methanothermobacter species have been used, notably *Methanothermobacter thermoautotrophicus* and *Methanothermobacter marburgensis* (both Order Methanobacteriales), likely because they are easily mass cultured with a high growth rate and have resilience towards mixing in reactors as result of their more robust pseudomurein-type cell envelope [174]. The organisms also alter their physiology in response to hydrogen availability and environmental conditions [167]. Genome analyses of these two strains showed overall synteny and identified about 200 genes that are thought to be involved in the generation of methane from carbon dioxide and hydrogen [106,130].

The current limitation to *Methanothermobacter* strains implies that a large group of potentially useful microorganisms has not yet been investigated. Research into the performance of other hydrogeno-trophs may identify new strains that show more efficient biological methane production [174]. Similar to current research into understanding and use of methane consumption [103,214], the better under-standing of biological methane formation is likely to steer metabolic and/or synthetic bioengineering of hydrogenotrophic methanogens for enhanced biological methane production in the future.

6.1.3. Acetoclastic and methylotrophic methanogens

At present, only two genera in the order Methanosarcinales (Methanosarcina and Methanosaeta) are known to be able to make methane via the route of acetoclastic methanogenesis. The first genus can use multiple carbon sources [10], the second genus may not be strictly acetoclastic as it also contains the genes for hydrogenotrophic methanogenesis [179]. Methylotrophic methanogens are so far found in three orders, including the Methanosarcinales, some of which depend on H_2 [121]. The possible stimulating or inhibiting role and therefore application of these types of methanogens in bioP2M approaches is at present unclear..

6.2. Reactor design

Microbiological methanation of CO_2 from biogas with hydrogen can be achieved in at least four different set-ups, three of which are discussed in earlier literature *[168,175]*, although different terminologies are used. In all of these set-ups, bioP2M is combined with conventional methane formation in biogas plants, yet the moment and/or the way hydrogen is introduced differ.

In so-called one-phase or *in situ* systems, the hydrogen is added to a biogas plant (anaerobic digester) directly. Two *in situ* systems are worth considering, (1) a conventional biogas plant at atmospheric pressure, or (2) a plant at higher pressure. In two-phase or *ex situ* systems, the biogas formed in anaerobic digestion goes to a separate bioreactor together with H_2, either without (a) or after upgrading and separation (removal) of the methane (b). Although the second reactor could be a chemical methanation reactor (essentially combining biological and chemical P2M strategies), in the context of bioP2M, we will here only consider bioreactors. It is by far not decided yet what the better set-up is from either technical or economic or combined perspectives *[168,175]*. In Solothurn, Switserland, a 700 kW demonstration plant is scheduled *[209]*.

6.2.1. Hydrogen supply

In all set-ups outlined above, the supply of hydrogen to the microbes is thought to be the rate-limiting step. Hydrogen must be dissolved in the liquid phase of the reactor before it can be utilized by the microorganisms. Sufficient transfer of hydrogen is necessary to produce appreciable amounts of methane. In technology terms, this is known as gas-liquid mass transfer *[168]*. The solubility of hydrogen in water depends on pH and pressure, but is orders of magnitude lower than the solubility of the other feedstock for the microbes, carbon dioxide *[170,171]*.

Several strategies are proposed in the scientific literature to overcome the limitation of the problematic H_2 gas–liquid mass transfer. The use of hollow fibre membranes or various diffusers (ceramic diffusers or column diffusers) is thought to result in hydrogen transfer with less bubbles, which was shown to promote dissolving hydrogen, possibly in combination with optimised agitation. Higher methane yields were achieved in this set-up compared to controls *[13,14,138,139]*. In addition, it is recommended to maximize the residence time of hydrogen in the reactor *[175]*. Hydrogen is therefore best added at the bottom of the digester. Higher viscosity in the digester slows down transport and a small bubble size with increased bubble surface area both prolong the residence time. Hydrogen mass transfer may further be improved by decreasing the bubble size by more forceful mixing. However, this can result in undesired back-mixing, i.e. return of produced methane from the gas phase into the liquid phase resulting in the reversed reaction, formation of CO_2 and H_2. Generally there is a trade-off between mass transfer rate and back-mixing. Stronger mixing to improve the mass transfer rate tends to increase back-mixing and results in lower methane yields *[71]*. Higher H_2 pressures resulted in more methane *[196]*.

Another option to increase hydrogen gas transfer is the application of microfluidic-based hydrogen-containing microbubbles *[176]* as earlier considered for syngas fermentation *[30]*, or the smaller nanobubbles *[5]*. Both are small surfactant-stabilized bubbles with different sizes (micro: ~10-50 μm in diameter; nano: < 1-0.2 μm), that offer orders of magnitude more surface area than conventional bubbles *[3]*. Both types of bubbles have great potential and expectation in various engineering applications *[3]*. Hydrogen-filled bubbles are formed during electrolysis of water *[5]* and their generation and stabilization is an active area of research *[44,176]*. The use of such bubbles deserves more detailed evaluations in bioP2M applications.

6.2.2. One-phase (*in-situ*) bioP2M

In a one-phase system hydrogen is directly fed into the existing biogas reactor. Direct addition of hydrogen to an existing biogas plant using the coproduced carbon dioxide to make more methane is intuitively a simple and therefore attractive option. It makes best use of existing infrastructure and investments. Yet, only few reports on one-phase bioP2M are presented in the literature, mainly for laboratory-scale bioreactors with a volume of 0.1-10 litre *[71,175]*. The experimental set-ups vary

considerably, making comparisons and generalizations difficult. One-phase systems tend to show relatively low increased methane production, likely due to limited CO_2 production and may suffer from too high H_2 concentrations in the resulting gas [138].

In a thermophilic (55°C) lab-scale bioreactor, hydrogen was added using ceramic gas diffusers. Supposedly due to a low gassing rate and low agitation speed, only little CH_4 was produced [138]. In a continuously stirred tank reactor with manure, operated at 55°C, a better methane yield was achieved with either higher reactor mixing or the use of ceramic diffusers to introduce the hydrogen [139]. With ceramic diffusers, the lower mixing speed was however sufficient [138]. The use of so-called anaerobic granules in batch systems was shown to result in higher methane production [243], but the CO_2 balance in the reactor is an issue to consider: the CO_2 production rate may be problematic and CO_2 removal may lead to increase in pH that affects biogas production [71]. In addition, the local hydrogen concentration in bubbles could result in a local over-concentration. As a result, the amount of hydrogen within the bioreactor available for methanation is (or may be) difficult to measure and can (or may be) easily be underestimated [175]. However, direct addition of hydrogen increased the rate of methane formation, which suggested that hydrogenotrophic methanogenesis may not be the rate-limiting step during biogas formation after all [107].

Overall it is clear that direct hydrogen application to an existing biogas reactor poses several challenges. In one-phase reactors not only the process conditions for anaerobic decomposition must be controlled, but also the methanation conditions [168,175]. The fine balance between anaerobic digestion and bioP2M processes is likely the major factor for good performance in one-phase systems [243] and process conditions cannot (easily?) be met for optimal conditions for both.

A new approach for hydrogen supply in a one phase set-up is the combination with a microbial electrolysis cell. It is reported to generate sufficient hydrogen for bioP2M at the expense of a small voltage [25]. How this approach performs when scaled up warrants investigation.
A novel one phase system is the system in which anaerobic fermentation is allowed to build up pressure inside the reactor. At higher pressure, CO_2 has a higher solubility in liquid than CH_4, separating the two. Such autogenerative high pressure digestion [131,132], also referred to as pressurized anaerobic digestion [33], produces biogas with notably higher methane concentrations, possibly directly qualifying as 'green gas' suitable for injection in the gas grid. Exploratory reactors showed a pressure increase upto 90 bar [132], but current scaled-up installations aim at about 20 bar to reduce investments in pressure-proof materials. The system is targeted towards sludge biomass streams and semi-commercial trials were positive (Zagt, personal communication). A seemingly similar high-pressure approach is presented as a two-stage system [41,145,241], because it aims to separate the methanogenic stage of biogas formation from the other steps.

As far as is known or in the public domain, only the autogenerative high pressure digestion system is currently combined with direct hydrogen addition to expand use and further improve the efficiency of the system (Zagt, personal communication). The higher pressure is supposed to promote the presence and activity of the desired methanogens and contribute to higher hydrogen conversion and methane yield than comparable one phase systems at ambient pressure. The set-up is owned and being commercialized by the Dutch SME Bareau (http://www.bareau.nl), where more information is available. More data should however be made available in the scientific and public domain to be able to compare and assess this system in more detail.

6.2.3. Two-phase (*ex-situ*) bioP2M
In a two-phase system the biological methanation takes place in a separate reactor. Two-phase bioP2M reactors have the obvious advantage that in the second reactor the conditions can be fully optimized for methanation [168,175]. Moreover, the CO_2 can come from other sources than biogas [71]. There is, however, a disconcertingly large array of variation possible and present in current technological set-ups. The main variations concern the reactor type, the microbial inoculum and the

gas feed. In all cases, the temperature (mesophilic or thermophilic conditions) is an additional source of variation, in addition to pressure. The large differences between reactor designs and process settings result in large variation in methane formation, both with respect to rate and efficiency [71,175], making comparisons and generalizations difficult. Examples that highlight the more important parameters are given below.

(a) **reactor type**. Various technologies are in use or possible for the second bioreactor: fixed-bed, solid-state, trickle-bed and membrane reactors [71]. Details of these reactor types are outlined above. The type of reactor influences the efficiency of methane formation given the poor gas/liquid mass transfer of hydrogen in liquid environments. For all investigated reactor designs, the supply of hydrogen to the liquid phase with micro-organisms seems rate limiting. In a CSTR, mechanical agitation or stirring is the most common way of enhancing the transfer of gases, but this tends to require large amounts of energy and therefore results in maintenance and high operational costs. Use of polymeric hollow-fiber membranes may improve the transfer of hydrogen [54].

(b) **microbial inoculum**. Hydrogenotropic methanogenic bacteria are derived from either sludge, enriched (mixed) cultures or pure strains. Sludge from an anaerobic digester contains hydrogenotropic methanogenic bacteria (see above). Enrichment cultures are thought to require a pre-adaptation period to adjust the culture to the conditions in the second bioreactor with respect to gassing rates and/or temperature [237]. An enriched hydrogenotrophic mixed culture was reported that had been adapted for half a year with a H_2/CO_2 ratio of 4:1. Enrichment at the thermophilic ($55^{\circ}C$) temperature gave considerably (about 1,6 fold) better yield than enrichment at mesophilic ($37^{0}C$) temperature [140]. A laboratory-adapted pure culture of *M. thermautotrophicus* was able to convert carbon dioxide from industrial, untreated biogas into methane with an external source of hydrogen gas. Analyses showed that optimization of hydrogen gas transfer is needed to balance the hydrogen conversion efficiencies with a high enough conversion rate of carbon dioxide into methane [144]. With pure cultures of another *Methanothermobacter* species similar limitations in hydrogen gas supply were observed [196].

(c) **gas substrate**. Either the biogas from the biogas plant is used directly, or first the methane is separated from the carbon dioxide and the latter is used in combination with hydrogen. Obviously the second reactor can also be fed with purified industrial hydrogen or biohydrogen, or syngas from other sources. For such a set-up, models for optimisation are being developed and validated [23,125].

Feeding a second CSTR reactor with effluent and biogas from cattle manure and additional hydrogen resulted in 89% CH_4 in the mesophilic reactor and 85% in the thermophilic reactor, while the biogas rate increased by almost a factor of 4 in the latter [14]. In a two-phase system with a fixed bed reactor in the second step, higher efficiency of CH_4 production and CO_2 conversion was observed in thermophilic conditions with a CH_4 content up to 82% [13]. In a trickle bed reactor, microorganisms are immobilized on the surface of a packed bed inside a reactor chamber to improve gas transfer. This creates a three phase system of biofilm–liquid phase–gas phase that should improve gas transport due to the high surface area of the packed bed. The system delivered high quality (>98%) methane [37]. In solid state bioreactors microorganisms are immobilized on solid particles inside the reactor [175]. Complete conversion of hydrogen was observed in a fixed-bed reactor inoculated with a slurry of methanogens [6], but stability of this high efficiency is an issue.

In a reverse membrane reactor microorganisms obtained from digested sludge from a biogas fermenter were encased in membrane sachets (made of polyvinylidene difluoride), which were placed in the reactor and examined in batch mode at different temperatures [244]. Methane was produced at both mesophilic and thermophilic conditions. Continuous protocols for application on industrial scale await development. Anaerobic granules for hydrogenotrophic methane formation were used in in an up-flow anaerobic sludge blanket reactor with H_2/CO_2 as sole substrate. They were more efficient in this two-phase set-up than in a one-phase set-up mentioned above [243]. Overall, two-phase reactors

have optimized reactor conditions to maintain a high microbial density. Moreover, they offer the easier possibilities to apply non-biogas CO_2 compared to one-phase reactors. Whether all these advantages outweigh the additional costs remains to be established.

6.3. Scale, flexibility and pilot projects

Few bioP2M pilot projects are presented in the literature (Table **6.1.**), illustrating that the technology is only at the beginning of its commercial application. Data from these projects have to be taken into account for assessment of the technical and economic feasibility of the technology.

Table **6.1.** Current biological P2M plants.

Project name	Country	Electrolysis method	Input (kWe)	Application	Schedule
BioPower2Gas	Germany	PEM	400	natural gas grid injection	2013-2016
Stuttgart	Germany	Alkaline	250	-	2012-
Scwandorf	Germany	-*	-	-	2014-
MicroPyros	Germany	-	-	-	2014-2017
Foulum	Denmark	-	n/a	pre-commercial	2011-2013
BioCat	Denmark	Alkaline	1.000	natural gas grid injection	-
Bareau	Netherlands	-	-	pre-commercial	-
Store&Go	Switzerland	PEM	700	Demonstration	2016-

*-, not specified in public literature.
Data assembled and interpreted from various literature [209,232], see also [71].

6.4. Intellectual property with respect to bioP2M

Patents are a rich and often neglected source of information. They give a good overview of the freedom to operate or restrictions in the field investigated. The concept of Bio-P2G as discussed here has been subject of various patent applications from various parts of the world over the last decades. In total, we have identified 12 such patents (Table **6.2**) using Espacenet of the European Patent Office (www.epo.org), freepatents online (www.freepatentsonline.com) and the Orbit database (www.orbit.com).

The basic idea of bioP2M is already described as *'high-yield methane production process by culture of* Methanobacterium thermoautotrophicum *or any other methanogenic bacterium having the same physiological growth properties'* (US4883753, *[20]*). Methane is obtained by adding a mixture of H_2 and CO_2 to thermophilic methanogenic bacteria. This patent has expired and as a result it could be argued that the bioP2M field has basic freedom to operate*.*

Few applications are granted as EP, but are pending as WO. *The 'process for the biological generation of methane'* (WO2008071175; *[185]*) provides a method for the production of hydrogen by algae and feeding the hydrogen together with CO_2 to methanogenic bacteria.

The *'Energy supply unit'* (WO2014000731; *[191]*) provides a system where the bioreactor is built into the shaft of a wind energy turbine. Hydrogen is produced on site and the high bioreactor (height >5 m) ensures better solubility of the hydrogen gas, resulting in higher efficiency. The application comes from the German company Microbenergy GmbH, belonging to the Viessmann Group, which opened its first Bio-P2G (test)installation in Allendorf (Germany) in March 2015 (press release at http://www.biopower2gas.de).

Currently three new applications are still under review from the University of Chicago (Mets). These are developed in close collaboration with the company Electrochaea (www.electrochaea.com), which seems to be the most active party in establishing an IP position in the field of bioP2M. The application '*A system for the production of methane from CO_2*' (WO2008/094282; *[146]*) provides an industrial system that converts CO_2 into methane via a reaction catalysed by Archaea. The claims of this

application are formulated in fairly general terms. The '*Method and system for converting electricity into alternative energy resources*' (WO2011003081A1; *[147]*) describes a system to convert electric power into methane using a biological reactor that contains a cathode where hydrogen is formed. Carbon dioxide is added to this reactor where it is combined with hydrogen to methane by archaea. The methane formation occurs at temperatures above 50°C and hydrogen is made by electrolysis in the bioreactor itself. The third application, '*Methanothermobacter thermoautotrophicus strain and variants thereof*' (WO2012094538A1; *[148]*) discloses the features of the micro-organism that gives high conversion yield. These three applications are all pending (WO application) and have been amended several times. It is currently unclear if these applications will actually lead to any IP rights and if so, when and for what parts of the applications.

Table *6.2* Inventory of patents on bioP2M.

country of origin	number*	legal status**	year of filing - reference	filing organisation
France	US4883753 EP0253744	R R	1986 - *[20]*	Gaz de France
Netherlands	EP1574581	R	2004 - *[230]*	E M Engineering
Italy	WO2006108532 EP1984098	R R	2005 - *[183]*	Inventors (private)
Germany	WO2008071175 EP2099921	P G	2007 - *[185]*	Inventor (private)
Italy	WO2008099252	R	2007 - *[184]*	Busi Impianti
USA	WO2008094282 EP2032709	P P	2007 - *[146]*	Univ. Chicago
USA	WO2011003081 EP2449084	P P	2010 - *[147]*	Univ Chicago
China	CN103045318	R	2012 - *[85]*	Univ Zhejiang
China	CN102925492	R	2012 - *[129]*	Chengdu Inst CAS
Germany	WO2014000731 EP2867354	P G	2012 - *[191]*	Microbenergy GmbH
USA	WO2012094538 EP2661511	P G	2012 - *[148]*	Univ Chicago
United Kingdom	GB2521808	P	2013 - *[62]*	Oxford Renewable Fuel

* If available, the EP and WO numbers are given separately.

** G, granted; P, pending; R, revoked, expired, not continued, lapsed or withdrawn (*i.e.* not alive). Information applies to the corresponding number. Legal status may be different in different countries.

Information assembled from Espacenet (www.epo.org), freepatents online (www.freepatentsonline.com) and the Orbit database (www.orbit.com).

In *'Biological production of methane utilising the molecular mechanisms and proliferation in methanogenic archaea for uses as a renewable fuel'* (GB2521808; *[62]*) CO_2 from calcium carbonate is combined with hydrogen via electrolysis.

The other patents identified do not reflect any protection of intellectual property anymore. The Chinese application *'Solar energy hydrogen biogas generation device'* (CN103045318; *[85]*) addresses the problem of excess of hydrogen while facing shortage in biogas. The inventor proposed an installation to balance these quantities. The application is withdrawn. The *'Method for restoring carbon dioxide to produce methane and acetic acid by utilizing biological electrochemical system'* (CN102925492; *[129]*) that describes the concept of adding CO_2 to a reactor where an electrode produces hydrogen and electrons for bacterial activity to form acetic acid in addition to methane, was rejected.

A Dutch patent *'Method and apparatus for preparing methane gas'* (EP1574581A3; *[230]*) describes how to produce methane by addition of carbon dioxide to a bacterial culture. It includes the concept of creating hydrogen via electrolysis and adding the hydrogen gas. The application was revoked in 2007.

Two Italian patent applications, *'CO$_2$ capture and use in organic matter digestion for methane production'* (WO2006108532; *[183]*) and *'Conversion of CO$_2$ captured from combustion systems or other industrial processes into methane through anaerobic digestion combined with biomasses'* (WO2008099252; *[184]*) describe the addition of CO$_2$ to a bioreactor. Part of the CO$_2$ is converted to additional methane, depending on the composition of the feed in the bioreactor. However, adding hydrogen to produce more methane is not part of the applications. Both applications are lapsed.

Overall, there seems to be ample freedom to operate in bioP2M research and applications, notably for bioP2M at ambient (mesophilic) temperature. Most patent applications focus on sources for green electricity and/or hydrogen and/or on microbes (archaea) that reach high(er) methane yields. It is surprising that the poor solubility of hydrogen so far is only addressed in the German application *[191]*. Either the game-changing solution of better hydrogen supply has not been found yet, is hidden in patents covering other fields or inventions, or simply does not exist.

6.5. Future prospects
In view of developments with respect to understanding the detailed mechanisms of methane formation from biomass as well as from carbon dioxide and hydrogen gas, as well as reactor design, biological methanation is likely to develop into a mature technology that will have its place in the overall transition to renewable energy, assuming its economics will allow viable business cases. Biological methanation is likely to allow relatively small-scale set-ups that are less demanding than its chemical equivalent. New and possibly more efficient hydrogenotrophic methanogens are likely to be awaiting identification or should be constructed in the laboratory. Major developments in the coming years should focus on novel reactor concepts that optimize the conditions for biomass degradation and hydrogenotropic methane formation in either one or two-phase set-ups. Hydrogen transfer should be tackled by reactor design and possibly bubble application. Aim should be as short a distance as possible between the gas phase and the microbial cells. There is no need for very high hydrogen concentrations to achieve high reaction rates due to relatively high affinity for hydrogen of the methanogens. On the basis of current literature, two stage, fixed bed reactors should be considered the most promising.

7. Economic and environmental sustainability of bioP2M

It is extremely challenging to make accurate economic assessments on any bioP2M implementation, especially when sustainability in terms of the effects on climate and environment should be taken into account. There are (too) many technologies and energy supply chains feasible, mature, maturing as well as in development. Each of the technologies or innovations discussed in the previous chapters comes with its own parameters, challenges and experiences. Yet, any new technology or development needs demonstration pilots and viable business cases in order to be adopted successfully.

In numerous papers and reports the (future) roles of notably chemical P2M (chP2M) in the projected energy transition towards the generation and use of renewable energy have been analysed or reviewed [50,64,149,253]. Studies tend to focus on chP2G or chP2M, because of the considerably larger experience with technology that is already commercially available and used [71]. Yet it is difficult to make comparisons between these analyses as the assumptions made in the various studies vary and also the data used or available for assessment differ considerably. In these studies, chP2G is generally considered as a promising and robust component in the mix of future energy options [74], likely necessary for reaching the desired reduction of CO_2 emission at acceptable societal costs. It is thought to improve the environmental sustainability of sectors such as industry and mobility by supplying carbon-free hydrogen (P2H) or derivatives thereof (P2M). Yet, it is suggested that chP2G should better be considered a long term development, with only few relatively short-term business cases worth considering [50].

7.1. Flexibility

P2M technology (either chemical or biological) is of particular interest because it promises to provide further flexibility to energy systems and contribute to the implementation of intermittent energy sources. In energy systems, flexibility can be defined as the ability to cope with fluctuating supply and demand in a way that demand is always met or to adapt demand to what is available [116]. Flexibility requires energy systems that are dynamic in the quantities produced and/or in the rate at which they can change their production. P2M responds to intermittent energy supplies as it stores electrical energy (wind, solar) in a gaseous form via electrolysis. A conventional electrolysis unit is relatively robust and flexible and therefore able to accommodate rapid shifts in power supply [234]. New developments in electrolysis may target such flexibility even more, but whether these can accommodate the anticipated excess of electrical energy in manageable ways is not yet clear. It is also unclear how the dynamics of electrolysis compares to the dynamics of methanation. The cold start time of a chemical methanation reactor is in the order of one to several hours, depending on its size [74,207,234]. In addition, it requires a deliberately dosed inlet of reactants. The process is sensitive to changes in the inlet because these affect the temperature in the reactor. For fixed-bed reactors a minimum load of 40 % is recommended. Lower loads are possible, but require modifications of the reactor. Three phase chemical methanation units can operate within 10 % to 20 % load [70]. Little is documented about the flexibility of bioreactors. The sentiment in the biogas digester field can probably best be summarized as 'if it runs, let it run'. The minimum load for bioP2M will depend on the size, type of biomass and type of reactor [73]. More data on and research into the flexibility and process sensitivity of bioP2M plants is warranted to be able to assess their contribution to flexibility. To ensure a steady hydrogen supply, hydrogen storage may be advantageous for the flexibility of chP2M as well as bioP2M, depending on the scale of operations and the scale of electrolysis that is available for hydrogen production [64,74].

7.2. Economy

Hydrogen produced with electrolysis is currently (considerably) more expensive than production through steam reforming. A viable business case would require additional (financial) benefits such as avoidance of grid investments, added value of grid balancing for sustainable energy producers or higher CO_2 pricing [50]. At present, the added value of flexibility in the electricity system is too low for a viable P2M business case [32]. Yet, P2M is a technology for storage of expected surpluses of electrical energy. Compared to other storage technologies, chP2M is considered promising, especially when combined with a fully operational gas grid. One of the main advantages is the potential to store large amounts of energy over longer time. It is expected that an energy system including chP2M is cheaper than a system without chP2M the moment the renewable energy production reaches 70% of the total production (per year). This situation is expected to occur in Germany in 2035 [208]. In shorter time frames than a year, it may be even more advantageous (see flexibility). How bioP2M fits in that scenario needs further attention. An obvious issue is the appropriate size of bioP2M plants. Obviously bioP2M should be linked to the amount of carbon dioxide originating from anaerobic digestion and may be considered to increase the relative availability of biomass.

In The Netherlands bioP2M was assessed as one of several options, none of which was deemed viable in the current market [99]. In order to achieve economic feasibility, mobility, balancing services and CO_2 certificates may have to be combined [21,73] and trade in the side products of electrolysis (heat and oxygen) warrants consideration. As hydrogen storage contributes considerably to the cost of any P2M system [71], the dynamics of bioP2M needs to be taken into account as well. In such economic assessments of bioP2M also the alternatives have to be considered, depending on scale and aim of bioP2M in the energy system. Others ways of storage of power may be or become competitive and P2M may have to compete with other uses of power, such as power-to-ammonia [16,22], or other power-to-X applications [227].

7.3. Environment

In addition to the economic aspects of P2M, also the environmental consequences of P2M technology need to be addressed. The scope of the full environmental analysis of an energy system including P2M can be very wide, including different ways of life cycle analyses. Energy efficiency and greenhouse gas emissions are important aspects of such an environmental analysis. The energy input of a P2M system obviously depends on the source of hydrogen and the source of carbon dioxide [192], as outlined above. The relatively modest quantities of CO_2 produced in biogas plants seem to agree well with the scale of current electrolysers available [71]. The optimization of energy supply chains in terms of overall energy efficiency and greenhouse gas emission reduction is useful [17,18] and needs to be investigated for selected bioP2M chains.

7.4. Future prospects

In many aspects bioP2M is not yet as matured as chP2M. It would however be erroneous to translate the assessments from these systems to bioP2M. In the current literature it is unfortunately not always clear which flavor of P2M is discussed. BioP2M is an opportunity to optimize energy systems in a dynamic way. How such dynamic bioP2M energy systems should be modeled is part of future research. At present, energy systems with bioP2M do not yet seem economically viable, but this is likely to change in the future, depending on carbon dioxide policies, the energy carrier and/or the chemical feedstock produced. The market characteristics of the anaerobic digestion sector have to be taken into consideration in order to derive the appropriate scale for the application of bioP2M. It remains to be seen whether chP2M is more suited for large scale applications. The added value of using the oxygen and heat produced should be part of future assessments, together with other applications of hydrogen. BioP2M clearly contributes to further converting the CO_2 in digesters to CH_4, but the quantitative effects on energy efficiency and reduction of CO_2 should be quantified.

8. Conclusions and recommendations

In the ongoing transition to the sustainable energy system of the future, the generation of wind and solar power is likely to increase dramatically for many decades to come. Direct consequences of this increased production of renewable power are the challenges of intermittency and grid management for security of supply. Sustainable large-scale storage of power is necessary. Next to the development of affordable, long-life high capacity storage in batteries, storage of power in the form of gas or liquid has the higher capacity in terms of volume, energy density and time. Most efforts are currently focussed on hydrogen gas as power storage system (power-2-hydrogen). Hydrogen is produced in the electrolysis of water. This is a relatively costly step, therefore developments in the field of electrolysis of water should be followed carefully and alternative routes, such as biological hydrogen generation, warrant attention.

In view of the potential risks associated with hydrogen storage and use, methane qualifies as a good alternative for hydrogen, notably for The Netherlands where the infrastructure and knowledge base are readily available for large volumes of methane. Methane is obtained from the reaction of hydrogen gas with carbon dioxide, either with chemical catalysts (Sabatier; chemical methanation or chP2M) or with the help of methane-forming microorganisms (biological methanation or bioP2M). Assuming proper management of the methane generated, the capture of carbon dioxide in methane could develop into an additional advantage of this approach in view of greenhouse gas emissions and the anticipated future carbon dioxide taxation schemes. In the Netherlands, consideration could be given to the changing perspective of methane as earthquake-related fossil natural gas harvested from large underground gas fields, to (bio)methane as renewable storage of wind and solar energy, possibly presented as 'windsolar' gas.

An overwhelming array of technological designs and options are proposed for both chP2M and bioP2M, indicating that such methanation is still a field very much in development. It makes comparisons difficult if not impossible, yet a 'one-size-fits-all' scenario would seem unlikely. The overall suggestion that chP2M is favoured for large(r) scale applications and bioP2M for small(er) scale applications needs backup with actual data and more experience with application. The documented sensitivity of chP2M to (traces of) impurities in the feedstocks hydrogen and carbon dioxide, as well as the need for high temperatures and pressures, may be good reasons to favour the biological route also for large(r) scale applications.

An attractive option for bioP2M is a combination with biogas production, in which biomass is converted into methane and carbon dioxide. Adding hydrogen to an existing biogas plant (in situ system) would seem attractive and generate most added value for investments already made, resulting in more methane per unit biomass. Yet appropriate delivery of hydrogen to the micro-organisms that convert it to methane is challenging. Therefore, a separate reactor (ex situ system) is considered more promising because the conditions for methanation can more easily be optimized and high concentrations of methane-forming microbes can be used when fixed on solid substrates. Moreover, it would allow using other sources of carbon dioxide than biomass. Biomass is generally considered as a relatively constant and reliable source of renewable energy and carbon dioxide, although the increasing pressure of the biobased economy on biomass to first deliver components with added value

will challenge energy production via fermentation of biomass to the more recalcitrant types of biomass and waste. The concept of bioP2M may prove advantageous in such cases as well.

In either case, however, efficient transfer of hydrogen from the gas phase into the hydrogen-consuming and methane-forming microorganisms requires transport into the liquid phase, an issue that warrants much more research. Higher pressure reactors and/or nano-bubble technology to promote solubilisation of hydrogen in the liquid phase are worth studying. More attention is also warranted towards the particular microbes used for methanation. Whereas they seem omnipresent in anaerobic environments, remarkably few have been tested in the set-ups considered for bioP2M. It is likely that these microbes differ considerably in their bio-catalytic efficiency and hydrogen requirements. In the longer run, metabolic engineering of the methane-forming steps may further improve efficiency.

In the context of all technological possibilities and unknowns it will be extremely challenging to develop possible business cases for bioP2M and assess economic feasibility and environmental sustainability of such cases. At present such cases do not seem economically feasible, but in the context of a changing energy system detailed (life cycle) assessments of the various aspects of bioP2M should be able to define the more promising ways to go. Comparative reassessment of the available data, assumptions and conclusions on chP2M is recommended to include the (technological) differences between chP2M and bioP2M.

Finally, an issue of concern for the future of the hydrocarbon-dependent chemical industry is that hydrogen gas does not contain a carbon moiety. Methanation adds a carbon atom to hydrogen, making it suitable for hydrocarbon-dependent chemistry, in addition to the use for storage of electrical energy and the contribution to preventing the negative effects of intermittency. Methane may be used as feedstock for the synthesis of other feedstocks for the chemical industry without redefining all hydrocarbon-based synthesis routes. Such developments will further contribute to the feasibility and sustainability of bioP2M and broaden the scope from power-to-methane to power-to-anything.

List of acronyms and abbreviations used

AWE	alkaline water electrolysis
bioP2M	biological power-to-methane
chP2M	chemical power-to-methane
ESS(s)	energy storage system(s)
MEC	microbial electrolysis cell
P2C	power-to-chemicals
P2G	power-to-gas
P2H	power-to-hydrogen
P2M	power-to-methane
P2X	power-to-anything
PEM	proton exchange electrolysis
PV	Photovoltaic
SOEC	solid oxide electrolysis cell

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