

Chapter 6

Upgrading anaerobic digestion within the energy economy – the methane platform

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6.1 INTRODUCTION

Anaerobic digestion is a mature biotechnology production platform that is mainly used in a decentralized manner at many wastewater treatment plants, industrial sites, and farms all over the world (Angenent *et al.*, 2004; Lettinga, 1995; also see Chapter 5 of this book). The produced biogas contains approximately 35–50% carbon dioxide besides methane. The carbon dioxide at such high concentrations reduces the energetic density of biogas and renders it to be utilized on-site in a low-efficiency way. However, this carbon dioxide can be removed or even converted into methane. The resulting renewable natural gas containing primarily methane (~97–98%; only little carbon dioxide and other minor gaseous impurities), which is also referred to as biomethane, can be injected into the existing natural gas grid.

The conversion of carbon dioxide from biogas into more methane within a power-to-gas (PtG) system could almost double the methane yields from anaerobic digesters. Pumping this renewable natural gas into the existing natural gas grid would connect all decentralized anaerobic digesters and use the total amount of produced methane as an important energy carrier in the energy economy. For example, this methane can be used as a preferred low-carbon fuel for trucks, buses, and other heavy vehicles. Alternatively, the carbon in biomethane from a centralized system can also be used as a source for chemical production or for alternative energy carriers, such as carbon monoxide or hydrogen, after post-treatment (Verbeeck *et al.*, 2018).

Even though injecting biomethane from biogas into the natural gas grid has been technically feasible for quite some time, this has yet to become an economically attractive proposition. Here, we will discuss and explain the recent technological advances that can make such a proposition more attractive in the future. Of course, regulatory constraints, the absence of political will, and cheap fossil fuels have also been very important deterrents in addition to the lack of technological advances, but

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we will not discuss these here. We would like to refer the reader to Chapter 13, where the regulatory aspects are discussed in more detail.

We will start this chapter by explaining why carbon dioxide is produced in anaerobic digestion in the first place. Then, we will focus on how to possibly increase the amount of methane and carbon dioxide (biogas) from biomass conversion with anaerobic digestion. This increase can be achieved by biological means, such as by increasing the temperature to improve biomass breakdown, or non-biological means, such as by integrating thermochemical process units upstream or downstream of the anaerobic digester. The resulting increase in the amount of methane (the energy carrier) will make it more attractive in the future to invest in technologies to remove or convert carbon dioxide from the biogas, and is, therefore, important here.

The integration of abiotic processes with anaerobic digestion to improve its economic feasibility was also recently described in a review paper (Angeles *et al.*, 2018). We continue the chapter by describing three mature abiotic examples (water scrubbing, amine scrubbing, and pressure-swing adsorption) to remove carbon dioxide and other impurities from biogas. The removed carbon dioxide is either: (1) released into the atmosphere; or (2) converted into more methane in a downstream carbon dioxide conversion system with the opportunity to almost double the methane yields.

One of the systems to convert carbon dioxide into more methane is with ex-situ biomethanation (in a separate bioreactor from the anaerobic digester) with thermophilic (65°C) methanogenic archaea (Martin *et al.*, 2013). Archaea are single-cellular microbes from a different domain of life than bacteria and eukarya and are therefore not closely related to bacteria (Pace, 1997). Engineers have performed carbon dioxide conversion by introducing hydrogen gas (from an abiotic electrolyzer by water splitting) together with the carbon dioxide (from biogas) into a bioreactor. Because the hydrogen gas would be produced from renewable electric power (i.e., windmills, photo-voltaic), the biomethanation system, which is also referred to as power-to-gas (PtG), becomes a storage-enabling technology for renewable electric power. The existing storage capacity for this renewable natural gas in natural gas grids exceeds several months during peak demand. We will discuss and explain the PtG technology by introducing the electrolyzer, the bioreactor, and the biocatalyst. Finally, we end this chapter with a perspective on some future considerations.

6.2 LEARNING OBJECTIVES

At the completion of this chapter you should be able to:

- Discuss the technological advances that are needed to connect anaerobic digesters to biogas upgrading and thermochemical processes, and to make it a major player in the energy economy.
- Explain why anaerobic digesters have been characterized by a high methane yield and have been referred to as extreme fermentation.
- Explain the fundamental principles of scrubbing, membrane separation, and pressure-swing adsorption for carbon dioxide removal from biogas.
- Name and explain the fundamental principle of two hydrothermal technologies that can increase the methane yield from biomass conversion and place them in their optimum location before or after the anaerobic digester.
- Discuss why it is advantageous to perform PtG with a thermophilic bioreactor compared to a mesophilic bioreactor.
- Synthesize all the knowledge in this chapter and describe how you would make the connected anaerobic digestion system produce the most methane.
- Characterize and explain specific challenges for the connected anaerobic digesters and biomethanation systems in a society that runs on renewable electric power and renewable natural gas.

This implies that, upon completion, any other type of fermentation (e.g., to lactate, butyrate, caproate) will produce less free energy for the microbes compared to AD, and thus a lower yield of the carbon end product. Furthermore, since both methane and carbon dioxide bubble out from the bioreactor broth when they are produced, there is no product accumulation (no additional thermodynamic limitations). When the conditions are favourable, such as a neutral pH in the fermentation broth, a very long residence time of the substrate, and in the presence of methanogens, the desired carbon product will be primarily methane, and not, for example, lactate, butyrate, or caproate. As a result, the methane yield (the methane formed compared to the degraded organic substrate) will be high, and the carbon product yield will be higher than for any other fermentation. This also implies that AD should never be underestimated as a biotechnology production platform, because it is a way of steering the conversion of a complex substrate into one carbon product with the highest yield possible.

6.3.2 Why carbon dioxide is produced besides methane – electron balance

Biogas is composed of a mixture of gases for which methane and carbon dioxide are the main constituents. Although biogas from complex organic substrates is typically composed of ~60% methane and ~40% carbon dioxide (v/v), the exact proportion between the two gases is entirely dependent on the mixture of organic compounds within the AD influent (substrate). For example, carbohydrates, such as the sugar glucose (with carbon at an oxidation state of zero), will produce equal molar parts of methane (50%) and carbon dioxide (Equation (6.3)):



Proteins and lipids will produce higher proportions of methane (69 and 70% methane [v/v], respectively).

The explanation why there is always carbon dioxide being formed from organic carbon compounds during AD lies again in the understanding that life is based on redox reactions within a completely anaerobic and closed-off vessel. In the case of methane fermentation, this involves both the reduction of carbon in the organic compound to form methane (gaining electrons); and the oxidation of carbon in the organic compound to form carbon dioxide (using up electrons). Since besides a carbon balance we also need an electron balance, carbon dioxide has to be formed besides methane, otherwise we would end up with more electrons in the product compared to the organic substrate, and that is not possible. Only by adding electrons, for example, in the form of hydrogen gas and by utilizing hydrogenotrophic methanogens (Equation (6.2)), can we reduce the amount of carbon dioxide in the biogas.

6.3.3 How to improve methane yields with biology – thermophilic AD

As temperature increases, microbial rates, and therefore methane production rates of AD, also increase. This, however, does not occur in a temperature continuum – there are three main temperature ranges for optimal microbial growth: psychrophilic (<20°C), mesophilic (30–40°C), and thermophilic (55–65°C). With each incremental temperature range, both the thermodynamics and the kinetics of methane production improve. Better thermodynamics, however, has little impact on methane yields. Why? Because thermodynamics only dictates if a reaction will proceed, and thermodynamics for the two main biochemical pathways of methane production in AD are already well favoured, even at psychrophilic temperatures. Conversely, improved kinetics has a significant impact on the methane production rates. Essentially, a digester operated at thermophilic temperatures can achieve higher volumetric methane production rates (in m³ methane per m³ reactor volume per day) than the same digester operated at mesophilic temperatures when all other conditions are held equal.

Still, operators of anaerobic digesters can look forward to higher methane yields due to the faster kinetic rates of certain biochemical reactions (Labatut *et al.*, 2011). This is because hydrolysis (solubilization) of non-soluble organic waste biomass is the rate-limiting step in AD, resulting in a

non-complete degradation. Because of a considerable faster reaction rate for thermophilic bacteria that perform this hydrolysis compared to their mesophilic counterparts in similar bioreactor volumes (the residence times are similar), more of the non-soluble substrate is solubilized, resulting in higher methane yields. Despite this advantage, most anaerobic digesters are operated under mesophilic conditions because of the higher energy input required and poorer process stability observed in thermophilic AD (Labatut *et al.*, 2014). Therefore, a chance exists at most AD locations to improve the methane yields by increasing the operating temperature of the digester.

6.4 HOW TO IMPROVE METHANE YIELDS OR PRODUCE OTHER ENERGY-CARRIERS WITH HYDROTHERMAL SYSTEMS

6.4.1 What are hydrothermal systems?

One of the emerging technologies that can be coupled with AD to improve the overall energy return is hydrothermal processing – an attractive option for the production of energy and bio-based chemicals from organic substrates. The main advantage of hydrothermal processes is the use of water as the reaction media, in contrast to dry thermochemical processes (i.e., pyrolysis or gasification) which require the removal of water *prior* to the process. Thus, hydrothermal processes offer opportunities for an energy efficient valorization of wet biomass, such as animal manure and food wastes, before or after AD (Posmanik *et al.*, 2018). The hydrothermal reaction is based on substantial changes in the properties of water, occurring between the boiling temperature and the critical point ($T_c = 374^\circ\text{C}$; $P_c = 22 \text{ MPa}$) (Figure 6.2). Water above its saturation pressure (dark line in Figure 6.2) remains in a liquid state at elevated temperatures (usually referred to as subcritical water or subcritical liquid). Under such conditions, several properties of water rapidly change and turn the water into an

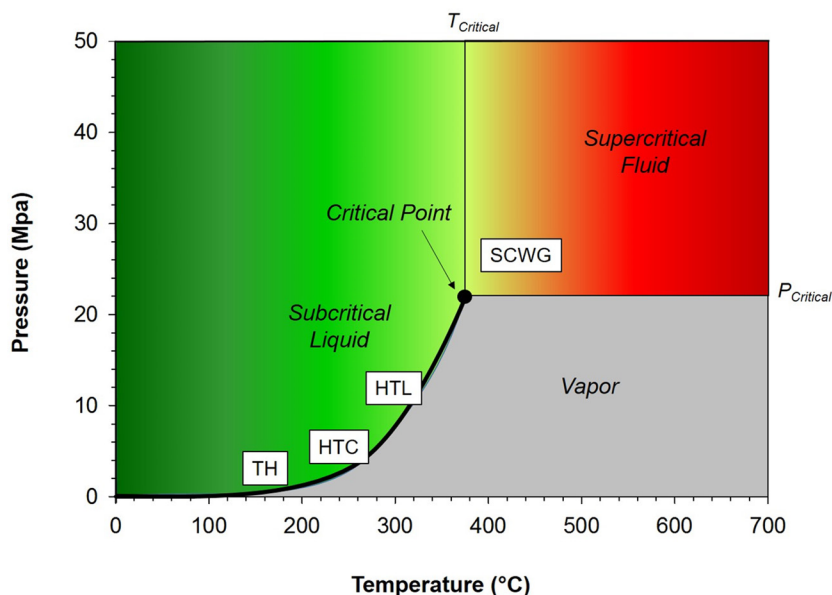


Figure 6.2 Phase diagram of water with the environmental conditions pressure and temperature, showing where specific hydrothermal processes occur in subcritical and supercritical regions. From low to high temperature and pressure, the hydrothermal processes are: thermal hydrolysis (TH), hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and supercritical water gasification (SCWG).

attractive media for chemical conversion processes, including fast hydrolysis, phase fractionation, and re-polymerization reactions (Peterson *et al.*, 2008; Tekin *et al.*, 2014).

Hydrothermal processes can be classified depending on their processing temperature and pressure, yielding different product distributions. A reaction at relatively low temperatures (up to 170°C) is referred to as thermal hydrolysis (TH) and generally results in hydrolysis of carbohydrates. Hydrothermal carbonization (HTC) occurs at mild temperatures (170–250°C) and pressures around 2.5 MPa to generate a solid product (char) that can be used as an energy product or for agricultural purposes. Between 250 and 370°C and operating pressures between 5 and 22 MPa, hydrothermal liquefaction (HTL) is favoured, generating an energy-dense bio-crude oil, which can be used as a liquid fuel. Beyond the critical point of water, supercritical water gasification (SCWG) typically takes place to convert the feedstock into a combustible gas: methane-rich in the near-critical region and H₂-rich at temperatures above 600°C (Figure 6.2).

6.4.2 Thermal hydrolysis (TH) as a pre-treatment to AD

Thermal hydrolysis (TH) of sludge *prior* to AD is an established mature technology which has been commercially available for more than 20 years. TH combines sterilization of the biomass (e.g., waste activated sludge at a domestic wastewater treatment plant) with improving its biodegradability to favour AD performance, resulting in higher methane yields (Barber, 2016). The main advantages of TH are: (1) increasing the organic loading rates (i.e., minimizing the size of the digester) due to a better degradability of the biomass; (2) increasing the yield of biogas from the biomass; (3) improving the dewaterability of the sludge (i.e., reducing the downstream processing costs); and (4) sterilization of the sludge, possibly allowing downstream land application.

The optimal operating conditions involve temperatures between 160 and 180°C for 20–40 minutes (Bougrier *et al.*, 2008; Stuckey & McCarty, 1984). TH is generally favoured to treat carbohydrate- or protein-rich sludge and has little influence on the lipids. Therefore, it is more suitable to treat waste activated sludge, rather than primary sludge (Wilson & Novak, 2009). Because TH increases the solubility of proteins and improves the breakdown by the digester microbiome, an increase in free ammonia and alkalinity is a major challenge of the technology. Currently, ammonia toxicity is the rate-limiting design consideration, requiring dilution of the hydrolyzed sludge *prior* to feeding it to the anaerobic digester. Regardless, full-scale systems exist, including the TH system at the Blue Plains wastewater treatment facility in Washington, DC, USA.

6.4.3 Hydrothermal liquefaction (HTL) as a pre- or post-treatment for AD

HTL is an emerging technology, yet very promising, due to the valuable product (bio-crude oil) it generates within a relatively short reaction time (<60 minutes). Therefore, HTL can be coupled to an AD to yield additional valuable products, to recover nutrients, to stabilize the waste, and to expand the overall efficiency of the waste management system. One process integration option is by using the HTL aqueous product as a substrate for a high-rate AD system such as an upflow anaerobic sludge blanket (UASB) reactor – thus the HTL system as a pre-treatment for AD. Researchers demonstrated that combining HTL and AD indeed increased the recovery of the total energy from food waste (Posmanik *et al.*, 2017). However, the total energy balance of such process integration provides a trade-off between bio-oil (gained from HTL) and biogas (gained from AD).

Another process integration option is by using AD effluent as the feedstock for HTL – thus as a post-treatment for AD. Looking into that scenario, researchers showed that changing the hydraulic retention times (the length of time that the liquid waste remains in the vessel) in the AD directly affected the yield of the bio-oil that was produced in the HTL, with the highest yield at a residence time of 38 days and the lowest yield at a residence time of 60 days (Eboibi *et al.*, 2015). Of course, a longer residence time in the AD resulted in less substrate for HTL.

6.5 REMOVING CARBON DIOXIDE FROM BIOGAS

6.5.1 The basic principle of carbon dioxide separation

To introduce renewable natural gas into the natural gas, grid each jurisdiction has different regulations and standards, but as a general rule the gas should consist of ~97–98% methane. Carbon dioxide can be separated and removed from biogas using a variety of techniques. The techniques described in this section will include: (1) physical absorption; (2) chemical absorption; and (3) adsorption. Although the specific mechanisms involved with each technique are different, they all rely on the same basic principle, which is the preferential retention or exclusion of one or more components in a fluid, based on differences in its physical and chemical properties. Specifically, we want to produce a concentrated (or enriched) stream of methane gas by selectively removing carbon dioxide from biogas.

6.5.2 Physical and chemical absorption

Absorption is a process involving the entrainment or incorporation of a fluid component (liquid or gas) into the bulk phase of a liquid or solid. The bulk phase material responsible for entraining the fluid component is called the sorbent. Absorption is achieved via two main mechanisms: (1) physical absorption; and (2) chemical absorption. In physical absorption, the fluid component is physically trapped inside the matrix of the bulk phase material without the aid of chemical bond formation. Physical absorption could be the entrapment of H₂ gas molecules between the interstitial spaces of liquid water, for example, or the diffusion of oil into the pores of a clay mineral. Chemical absorption, on the other hand, involves the formation of chemical bonds between the fluid component and the bulk phase of the material. For example, hydrogen sulphide (H₂S) in a gas stream can be chemically absorbed and precipitated by exposing it to a bed of steel shavings, which contain ~99% iron (II), in the solid-state reaction (Equation (6.4)):



6.5.3 Physical absorption of carbon dioxide using water scrubbing

The most common application of physical absorption for carbon dioxide removal from biogas is water scrubbing. In this process, carbon dioxide from the biogas is readily absorbed by water (sorbent) with minimal absorption of methane. This preferential absorption of carbon dioxide is due to the high solubility of carbon dioxide in water (1.45 g L⁻¹, at 25°C and 100 kPa [1 atm]) compared to methane (0.022 g L⁻¹, at 25°C and 100 kPa). The solubility of carbon dioxide and methane is also greatly affected by temperature and pressure. Solubility of these gases will decrease (S↓) at higher temperatures (T↑), and increase (S↑) at higher pressures (P↑). In other words, solubility is indirectly related with temperature (S↓ · T↑; S↑ · T↓), and directly related with pressure (S↑ · P↑; S↓ · P↓).

Another important parameter in gas absorption is the mass transfer rate of the gas into the bulk medium. Overall mass transfer is directly related to the concentration gradient, the interface contact area, and the contact time. For example, we know intuitively that mixing will increase the absorption rate of carbon dioxide into water. This is because mixing prevents accumulation of dissolved carbon dioxide at the gas/liquid interface, thereby maintaining a high concentration gradient. Another way to increase mass transfer is to create small gas bubbles at the bottom of a water column using diffusers. The small gas bubbles have a higher surface area per unit volume compared to larger gas bubbles, thereby increasing the interface contact area. Small gas bubbles also experience higher drag forces compared to large gas bubbles, which slows their ascent through the water column and increases the contact time between the gas bubble and the water. Now that we have explained these basis concepts, we can describe a typical water scrubbing system.

Most water scrubber systems are configured as tall, vertical columns (Figure 6.3). Water is sprayed into the top of the column, while the biogas is introduced at the bottom of the column. The biogas (at

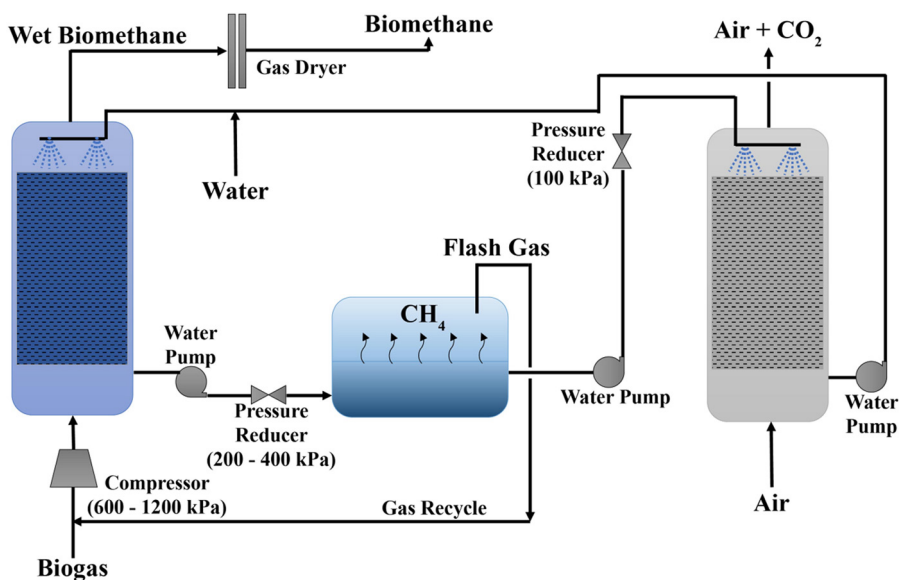


Figure 6.3 Diagram of a typical water scrubbing system for biogas upgrading. The system contains three main components: (1) a carbon dioxide absorption column (left block); (2) a flash tank (middle block); and (3) a carbon dioxide stripping column (right block). Compressed biogas is injected into the carbon dioxide absorption column while air is directed through the carbon dioxide stripping column. Water is recirculated between the three components and introduced to the top of each column via sprayers. Wet biomethane leaving the carbon dioxide absorption column is passed through a gas dryer (depicted here as a plate heat exchanger).

approximately 35°C) is usually pressurized (i.e., 600–1200 kPa) to promote carbon dioxide absorption as it rises through the column. Packing material is often added to the column as well to increase turbulence and better mix the biogas and water streams as they pass each other in a counter-current flow. As they interact, proportionally more carbon dioxide is absorbed compared to methane. By the time the gas stream leaves the top of the column it is almost completely depleted of carbon dioxide and enriched with methane (e.g., >97%).

The gas leaving the column, which can now be called biomethane, will then be transferred to a drying process (e.g., cooled in a heat exchanger) to remove the moisture picked up during the scrubbing process (Figure 6.3). On the other end of the column, the water leaving the bottom is now rich in dissolved carbon dioxide, with only low levels of dissolved methane. This carbon dioxide-laden water is sent to a low-pressure flash tank (i.e., 200–400 kPa), which causes a quick dissolution of the dissolved methane while at the same time retaining most of the carbon dioxide. The off-gas from the flash tank is then recycled back to the water scrubber and combined with fresh biogas. Finally, the carbon dioxide-laden water is transferred to the top of a stripping column at low pressure (i.e., 100 kPa), where the carbon dioxide is *desorbed* or driven-off from the water using an upward-flowing air stream. The regenerated water is then returned to the water-scrubbing column to complete the cycle (Figure 6.3).

6.5.4 Chemical absorption of carbon dioxide using amines

Amines are compounds similar to ammonia (NH₃). In both cases, nitrogen serves as the central atom and allows the formation of three chemical bonds. However, unlike ammonia, which has three hydrogen bonds, amines replace one or more of the hydrogen bonds with an organic functional group

(e.g. methylamine is basically an ammonia molecule with one H-bond replaced with a methyl group). Amino acids, which are the building blocks of proteins, are classified as amines. In the context of carbon dioxide scrubbing, amines, such as diethanolamine (DEA) and methyldiethanolamine (MDEA), are typically used due to their high selectivity for carbon dioxide compared to methane.

Because of this, they can treat gas streams containing very low concentrations of carbon dioxide, and thereby achieve higher biomethane purity levels (e.g., >99.9%). An amine scrubber system is very analogous to a water scrubbing system, consisting of an absorption column and stripping column, but rather than using water in the absorption column and air in the desorption column, they use an amine solution and heat, respectively. The heat is required to break the chemical bonds formed between the carbon dioxide and amine molecules, with the goal to release the carbon dioxide at the end of the process. Finally, unlike water scrubbing systems, amine scrubber systems do not require a flash tank to recover methane because the amine solution absorbs very little methane.

6.5.5 Adsorption

Unlike absorption processes, which entrain the fluid inside a liquid or solid bulk phase material, adsorption processes involve the retention of a fluid on the surface of a solid substratum. The solid materials are typically selected to have high surface area and porosity to help separate the components in a fluid mixture based on molecular size and surface-related interactions such as Van der Waals forces and polar bonds. Typical examples of solid materials that are used for adsorption include silica gels, activated carbon, carbon molecular sieves, and zeolites. Selective retention of fluid components can be achieved using two different approaches. The first approach, known as equilibrium-based adsorption, relies on differences in surface interactions between the fluid components and the adsorbent material to selectively retain a component (or components) based on the strength of its interaction. For example, fluid components with large molecular size can be separated from small molecular components because the Van der Waals forces holding the large molecules to the solid surface are stronger than the forces holding the small molecules. At equilibrium, a higher concentration of large molecules will be adsorbed to the surface compared to small molecules.

The second approach, known as kinetic adsorption, relies on differential rates of adsorption between fluid components onto the solid surface. For example, solid materials can be selected based on the pore size to control the diffusion rate of fluid components into the solid matrix. In the case of methane and carbon dioxide, which have a kinetic diameter of 3.8 and 3.4 Angstroms (Å), a solid substratum (e.g., carbon molecular sieve) with an intermediate pore size could be used to promote faster diffusion of carbon dioxide (3.4 Å) into the pore matrix compared to methane (3.8 Å), which effectively concentrates the carbon dioxide. Finally, like absorption, the process of adsorption depends strongly on the applied temperature, pressure, and contact time. These parameters can be manipulated to improve the selectivity of the adsorption process, taking into account the specific physical/chemical properties of the fluid components.

6.5.6 Biogas upgrading using pressure-swing adsorption

Within the field of adsorption technology, pressure-swing adsorption (PSA) is very common and is often used for biogas upgrading. As indicated in the name, differential adsorption is achieved by alternating (swinging) between pressure levels. It works on the principle that at higher pressures relatively more adsorption occurs, and when the pressure is reduced, the fluid component will detach or *desorb*. A typical biogas PSA system is carried out in four steps: (1) pressurization; (2) feeding; (3) blow-down; and (4) purging. In the first step, the biogas is pressurized to approximately 400–1000 kPa and delivered to the bottom of an adsorption column where carbon dioxide is selectively adsorbed. Meanwhile, methane passes through the column with minimal retention. During the feeding step, the column is fed with pressurized biogas until the adsorption material reaches its carbon dioxide saturation point. At this stage, the blow-down step begins, which involves shunting the inflow of biogas to allow the pressure within the column to dissipate. As the pressure decreases, carbon dioxide

desorbs from the adsorption material, and regenerates the column. Once the minimum pressure is reached, the remaining carbon dioxide is driven off by purging the column with some of the processed biomethane to further regenerate the column and complete the cycle. The PSA process can be configured to run continuously using two or more adsorption columns, where each column is at a different stage of adsorption or regeneration.

6.6 EX-SITU BIOMETHANATION

6.6.1 PtG concept

The basic concept of PtG is to utilize renewable electric power to produce gaseous energy carriers (Schiebahn *et al.*, 2015). Currently, two PtG approaches exist (i.e., power-to-hydrogen and power-to-methane). Both use electric power in a first step to split water into hydrogen and oxygen with an electrolyzer. In the case of a power-to-hydrogen system, hydrogen is the final energy carrier. In contrast, the hydrogen is further converted into methane with a power-to-methane system in a second step by introducing it together with carbon dioxide (from biogas or other CO₂ sources) into a reactor. The individual reaction steps are:

- (1) electrolysis (Equation (6.5)):



- (2) *plus* methanation (Equation (6.2)), resulting in a net reaction (Equation (6.6)):



The methanation can be performed with methanogenic archaea (biomethanation) or chemical catalysis (Sabatier process). Biomethanation can use biogas directly without methane separation and purification because the methanogens can withstand impurities, or even profit from, for example, sulphur contaminants (hydrogen sulphide) as a growth nutrient. This is different for the abiotic Sabatier process (thermo-chemical methanation). There, a solid metal catalyst (usually nickel) is present inside the reactor and catalyzes the methanation reaction. However, the catalyst can be easily poisoned by impurities. This process is operated at high temperatures to activate the catalyst (300–550°C) and also at a high pressure (up to 10 000 kPa) to shift the equilibrium of the methanation reaction towards the products. The Sabatier process, therefore, requires highly purified carbon dioxide. It seems likely that for systems that are connected to decentralized anaerobic digesters for which stringent biogas cleaning is difficult, the biological route of PtG will be chosen (Figure 6.4) (Bailera *et al.*, 2017).

PtG is a storage technology for renewable energy, where electric power that is generated by wind mills or photo-voltaic systems is used to produce gaseous energy carriers (Götz *et al.*, 2016). In the case of methane, the gas can be injected and stored as renewable natural gas in the existing natural gas grid, which offers a storage capacity for methane that exceeds the energy consumption needs for several months. Although hydrogen could also be stored in the natural gas grid after certain changes are made, the amount of pure hydrogen that can be injected is strictly limited by regulations, which restricts the theoretical storage capacity of the power-to-hydrogen technology. Of course, the natural gas grid could be updated and changed to handle higher concentrations of hydrogen gas, which is a highly diffusive gas due to its relatively small molecule size. An additional advantage of the power-to-methane technology is that it can circumvent the release of carbon dioxide at the decentralized anaerobic digester sites. Carbon dioxide, which would have otherwise been released into the atmosphere, is converted into methane and used at central locations.

6.6.2 Hydrogen supply via electrolysis

How to transform liquid water to gas? Vaporization is obviously one answer. However, we can also employ another physicochemical process to split liquid water into more useful and valuable hydrogen and

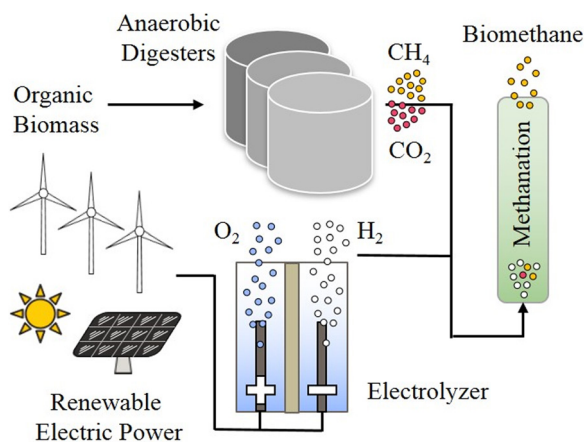


Figure 6.4 Schematic of a PtG system to upgrade biogas into biomethane. The process includes an electrolyzer and a biomethanation reactor for untreated biogas from an anaerobic digester. When the biogas is first cleaned and without methane, an abiotic methanation reactor is also possible based on the Sabatier process.

oxygen gases. This process is called electrolysis for which electric current drives chemical reactions to complete the separation of its elements. An electrical circuit, which consists of working electrodes (anode and cathode) and supporting electrolyte, achieves electrolysis by passing of an electric current (Figure 6.5). Electrons are current carriers in electrodes, whereas charged ionic species carry current through the electrolyte solution. Chemical reactions are induced by the passage of current but occur only at the electrode/electrolyte interfaces and not in the bulk of either electrodes or electrolyte. The products of electrolysis vary depending on the type of electrolyte and the utilized materials for the electrodes.

In alkaline solutions that are electrolyzed by inert carbon or metal electrodes, hydroxide ions (OH^-) will migrate as major current carriers in the solution, and oxidize at the anode to produce oxygen.

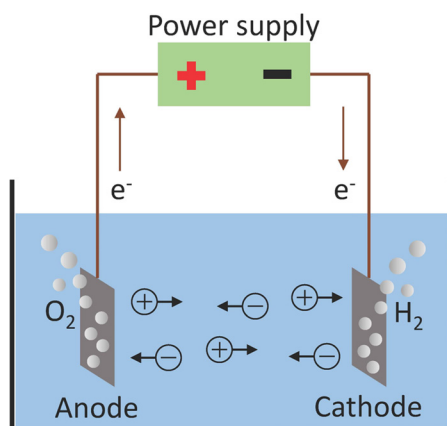


Figure 6.5 Schematic of an electrolysis cell. A power supply generates an electric current that sustains chemical reactions at the electrode/electrolyte interfaces. At the anode, oxygen gas is produced which could be used at the wastewater treatment plant to boost aerobic bioprocesses. At the cathode, hydrogen gas is produced at pressure that can be introduced into the methanation process. Finally, heat is produced, which can be utilized to heat the digester or for other applications.

At the cathode, water reduction occurs, which produces hydrogen. The overall required energy that drives electrolysis must equal the free energy changes of the chemical reactions *plus* the over-potential that sustains the reactions to proceed in a certain rate *plus* the heating loss of electrical resistance such as the electromigration of ionic species in the solution. With the depletion of electrolyte, more and more heat will be generated in the solution. Due to the production of both gases, pressure will build up during electrolysis.

6.6.3 Bioreactor technology

Methanogenic archaea are present in an aqueous matrix within the ex-situ biomethanation reactor, and water is being produced as a side product of the biological reaction to methane (Equation (6.2)). The nomenclature of ex-situ is used here to indicate that the hydrogenotrophic methanogenic reaction for PtG is taking place outside of the main anaerobic digester. When hydrogen gas is introduced into the main anaerobic digester to sustain this biological reaction (Equation (6.2)), the nomenclature is in-situ biomethanation. You can read why in-situ biomethanation is not deemed feasible for a commercial system in another review of our group (Angenent *et al.*, 2018). Once hydrogen and carbon dioxide have been introduced into the ex-situ biomethanation reactor, for example, via bubble formation, the gases first need to dissolve before they can be taken up and converted into methane by the archaea. Since the solubility of hydrogen is low compared to carbon dioxide, the rate of hydrogen transfer into the liquid is the rate-limiting step of the biomethanation process (Schill *et al.*, 1996). Increasing the hydrogen partial pressure can enhance the solubility of hydrogen gas. Therefore, most ex-situ biomethanation reactors are operated at overpressure.

In addition, the gas-to-liquid transfer rate can be improved by increasing the gas/liquid interfacial area. Therefore, special reactor types that provide large gas/liquid interfaces are being developed, resulting in volumetric methane production rates that can be larger than the 50 m³ per m³ volume per day that was achieved with real biogas in bench-scale bioreactors (Martin *et al.*, 2013). For example, the demonstration plant in Denmark (stirred bubble-column bioreactor) is operating at 250 m³ per m³ volume per day (Figure 6.6). That is much higher than for anaerobic digestion for biosolids treatment at a wastewater treatment plant (0.25 m³ per m³ volume per day) (Uman *et al.*, 2018), resulting in about 1000 times smaller volumes for biomethanation reactors compared to these anaerobic digesters. Stirred bubble-column bioreactors are applied to create very small gas bubbles through bubbling and mixing, which increases the specific surface area of the gas/liquid interface (Figure 6.6).



Figure 6.6 Picture of a 1-MW power-to-methane system at a wastewater treatment plant. The stirred bioreactor with bubble formation in a column is on the left. This picture was taken at Electrochaea's patented BioCat plant in Avedøre, Denmark, which is a demonstration-scale system to store biogas as renewable natural gas in the Danish natural gas grid.

An alternative concept is to create high specific liquid surface areas by creating thin liquid films in a trickle-bed reactor. Trickle-bed reactors use a solid matrix on which microbes grow as a biofilm. A liquid solution is then recycled from the bottom to the top of the bioreactor, while it trickles down over the biofilm without immersing the matrix into standing liquid. Basically, the gas within the anaerobic bioreactor surrounds the liquid on the biofilm to allow a proper gas/liquid transfer. Currently, the demonstration- and full-scale plants are built as stirred bubble-column bioreactors or trickle-bed reactors for ex-situ biomethanation (Bailera *et al.*, 2017).

6.6.4 Why operate at 65°C rather than 37°C

One very important parameter for ex-situ biomethanation is the temperature at which the bioreactor is operated. Often it is assumed that a bioreactor has to be heated to maintain a given temperature such as 37°C. Following this logic, it seems obvious that a process that has to be heated to 65°C consumes more energy compared to a process that only has to be heated to 35°C. While this is true in many cases for traditional bioprocesses including anaerobic digestion, in the case of biomethanation we need to look more closely at the underlying reaction for hydrogenotrophic methanogenesis again (Equation (6.2)). The energy gain from this reaction is relatively low, given by the overall Gibb's free energy change of -131 kJ mol^{-1} under biological standard conditions (pH = 7; temperature = 25°C; pressure is 100 kPa). Therefore, the cell has to maintain a high rate of methane formation to produce enough cellular energy in the form of ATP to sustain growth (Schill *et al.*, 1999). The resulting high ratio of methane (product) to biomass is an advantage of anaerobic bioprocesses.

What we also see from Equation (6.2) is that the methanogens produce one mole of gas and two moles of water from five moles of gas. This results in a considerable decrease of the system's entropy (negative ΔS), which means, in easy terms, that the system reaches a higher state of order. To maintain the driving force for energy conservation (negative ΔG ; $\Delta G = \Delta H - T \Delta S$; and with $- = +$ for ΔS), the reaction must be accompanied with a decrease in the enthalpy (negative ΔH) by energy dissipation in the form of heat–exothermic conditions (Schill *et al.*, 1999). Taken together, it follows that due to the high methane production rate and heat generation during the metabolism, the reactor has to be cooled rather than heated. Therefore, an operating temperature of 65°C is beneficial compared to an operating temperature of 37°C. Furthermore, the higher operating temperature results in reduced chances for contamination and more efficient stripping of product gas (methane).

6.6.5 Thermophilic methanogen – *Methanothermobacter thermautotrophicus*

For the biomethanation step in PtG systems, *Methanothermobacter thermautotrophicus* (*M. thermautotrophicus*) is being used as the methanogen. It is a rod-shaped microbe with a length of 3–7 μm and a diameter around 0.5 μm (Figure 6.7). The optimal growing temperature is 65°C, which makes it a thermophilic (warm-loving) microbe (Zeikus & Wolfe, 1972). All methanogens belong to the domain of archaea, which is the third domain of life besides bacteria and eukarya (Pace, 1997). Typically, methanogens must be kept under strictly anaerobic conditions (oxygen-free) since they lack mechanisms for oxygen detoxification. *M. thermautotrophicus* is a hydrogenotrophic methanogen using anaerobic respiration (Equation (6.2)).

This anaerobic respiration process occurs via the Wolfe cycle, which is a pathway with several consecutive steps: (1) carbon dioxide is reduced to formate and connected to a one-carbon-carrier cofactor; (2) the resulting complex molecule is further reduced in several steps to a methyl-group; and (3) methane is formed. One of the reasons why *M. thermautotrophicus* is utilized in biomethanation is the fast growth rate, which is 8–10 times faster compared to most other methanogens. This makes it easier to maintain a well-grown biocatalyst in the bioreactor. Because the energy gain per molecule methane produced is relatively low, the methane production rate of *M. thermautotrophicus* has to be relatively high, which is beneficial for the biomethanation process (Martin *et al.*, 2013; Schill *et al.*, 1999). Another reason why this microbe is used for biomethanation is because it is not as sensitive to oxygen compared to other methanogens, which makes the biomethanation system easier to operate.

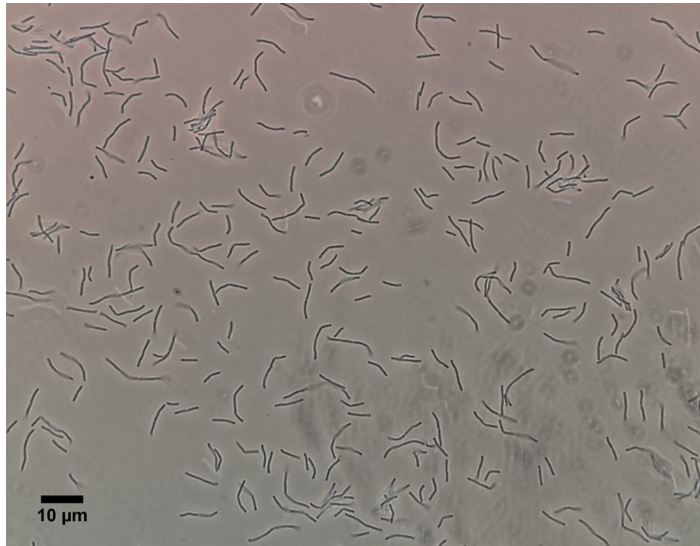


Figure 6.7 Light microscope view of living cells of *M. thermotrophicus* in the exponential growth phase. Magnification 1000 \times . The reference is 10 μm .

6.7 PERSPECTIVES AND FUTURE NEEDS

Decentralized anaerobic digesters have been built all over the world but are mostly seen as a biomass and wastewater treatment technology, rather than an important energy provider for societies. With localized subsidies to boost the income from electric power production with combined heat and power systems, the digesters have become somewhat connected via the electric grid. However, these subsidies are often temporary. In addition, the conversion efficiency from methane to electric power is relatively low, resulting in a high heat production compared to heat demand in, for example, rural areas. By placing abiotic or biological systems close to the anaerobic digester, carbon dioxide can be removed or converted to produce more biomethane, which can be stored and transported into the existing natural gas grid. After transportation of the product (biomethane), a centralized chemical plant can utilize the energy or even the carbon from biomethane at a large scale. Distributing the methane directly to decentralized users can also promote the use of methane as a low-carbon fuel for vehicles. Both possibilities would make AD a much more important energy-production partner and boost AD implementation for carbon recovery.

By almost doubling the methane yield of digester through PtG, methane as a low-carbon fuel can have a real impact in the future energy economy. An increase in the total volume of anaerobic digesters is also required to increase this impact. When finally most organic waste will be treated with anaerobic digesters, this will likely occur through co-digestion of several different wastes together, such as food waste and animal wastes, possibly in large centralized digesters. However, a massive increase in digester capacity requires the smart reuse and recovery of nutrients (in addition to the carbon) from anaerobic digesters because otherwise the resulting biosolids from digesters would leak these nutrients into the environment after land application, resulting in uncontrolled nutrient runoff and eutrophication of surface waters (lakes, oceans). Thus, a systems-oriented approach is necessary that ties agriculture, food-waste management, land management, nutrient recovery, energy production, and water. This has also been referred to as the food energy water (FEW) nexus. Research is now necessary on how to combine all these aspects together without causing further environmental harm.

6.8 CHAPTER SUMMARY

In this chapter, we have introduced and explained several systems to improve the methane yield in AD, remove carbon dioxide from biogas, and increase the overall biomethane production. In addition, we have also introduced a possibly compatible thermochemical system to produce bio-oil and biomethane. Some of the systems are commercially available, while others are being developed as an operating-unit next to the decentralized anaerobic digester. We cannot predict yet which of these technologies will actually be used. However, it is clear that for AD to play an important role during the transition from a fossil fuel-based economy towards a renewable energy-based economy, some of these technologies will be necessary to connect all digesters with the existing natural gas grid.

6.9 EXERCISES

Exercise 6.1: If you have an anaerobic digester with an infinite volume, resulting in an infinite residence time for the substrate, would you produce more methane under mesophilic or thermophilic temperatures? Discuss the reason

Exercise 6.2: Why is there a thermodynamic advantage of anaerobic digestion as compared to other types of fermentation?

Exercise 6.3: A large dairy farm is using anaerobic digestion to produce biogas from cattle manure with a capacity of $6\,000\,000\text{ m}^3\cdot\text{yr}^{-1}$. The farm is considering adding a PSA system to convert the biogas into biomethane, which qualifies for renewable energy credits. However, their biogas contains 450 ppm(v) of hydrogen sulphide (H_2S), which is detrimental to the adsorption column (e.g. it forms irreversible bonds with the sorbent), and needs to be removed prior to PSA. A local industry produces iron-oxide impregnated wood chips, which could be used as an H_2S scrubbing material. The absorptive capacity of the wood chips is related to its iron oxide content, which is $190\text{ kg Fe}_2\text{O}_3\cdot\text{m}^{-3}$. To complete their economic analysis of the proposed system, they need to calculate the amount of woods chips required for H_2S scrubbing. Calculate the annual consumption of wood chips in cubic meters. Assume the wood chips have a 90% capacity factor relative to the theoretical maximum absorption. Note: the molecular weight of $\text{Fe}_2\text{O}_3 = 159.687\text{ g mol}^{-1}$, and $\text{H}_2\text{S} = 34.1\text{ g mol}^{-1}$.

Exercise 6.4: A dairy farm with 3000 cows has a manure waste flow of $500\text{ m}^3/\text{d}$ (10% solids). The total organic carbon (TOC) concentration in manure is 60 g/L. The hydraulic retention time (HRT) in AD is 20 days. The TOC removal efficiency in AD is 80% and for each kg of TOC removed, the digester generates 0.25 m^3 of CH_4 . The residual TOC is then subjected to hydrothermal liquefaction (HTL), which converts 60% of the carbon into bio-crude oil carbon. Assume manure has the density of water.

- What should be the size of the AD?
- What is the CH_4 production per unit of digester?
- What is the effluent carbon flow from the AD to HTL?
- How much carbon (as CH_4 and bio-crude oil) can be recovered per cow per day.
- Describe the advantages and disadvantages for each one of the following integrated process sequences: (1) TH-AD; and (2) AD-HTL.

Exercise 6.5: Calculate the composition of the product gas leaving the PtG bioreactor if pure carbon dioxide (no biogas) is introduced with hydrogen at a ratio of 1:4 and assuming that (i) 25%, (ii) 50%, (iii) 75%, or (iv) 100% of the carbon dioxide are consumed by biomethanation. All the water generated by methanation can be assumed to remain as liquid.

Exercise 6.6: (A) Compare power-to-methane and power-to-hydrogen and name two advantages of each technology; and (B) Can you think of reasons, why the hydrogen content in the natural gas grid is restricted?

Exercise 6.7: Performing electrolysis in an electrolyte solution (50 mL) that contains 1 M NaOH by passing 1 mmol e^- :

- Discuss which species will be oxidized at the anode based on the standard reduction potential, OH^- ions or water?
- Calculate how much oxygen will be produced at the anode?
- Discuss which species will be reduced at the cathode based on the standard reduction potential, Na^+ ions or water (assuming H^+ reduction is negligible)?
- Calculate how much hydrogen will be produced at the cathode?

Exercise 6.8: Considering the information you have from this chapter and given that $\Delta G = \Delta H - T \Delta S$, conclude whether the change in Gibb's free energy is more negative at 37°C or at 65°C for hydrogenotrophic methanogenesis? Evaluate what this implies for the maximum biomass yield per methane of thermophilic hydrogenotrophic methanogens compared to mesophilic species?

6.10 DISCUSSION QUESTIONS

Question 6.1: Is it possible to avoid the formation of carbon dioxide by biological means? How would you do it?

Question 6.2: In each of the technologies described in this chapter, carbon dioxide was considered a valueless by-product. However, given that many of the off-streams have been enriched in CO_2 , should these off-streams really be considered valueless? Can you think of a particular application where this CO_2 maybe be useful? If so, which biogas upgrading technology would be the most advantageous for the proposed application?

Question 6.3: As the lead engineer of a WWTP, you are in charge to integrate a PtG system to treat the biogas stream (50% carbon dioxide, 50% methane) of the WWTP's anaerobic digester. You are asked to give a presentation to the board of directors in which you provide a concept on how the process will be integrated with all its mass and energy streams into the WWTP's infrastructure. Can you identify synergistic effects?

Question 6.4: After reading about the thermophilic methanogens,

- Do you think the thermophilic character of *M. thermautotrophicus* is an advantage or disadvantage for biomethanation applications?
- Which are the only substrates that *M. thermautotrophicus* can metabolize?
- Do you need to add a carbon source to the growth medium of *M. thermautotrophicus*? If yes, which one. If no, why not?

Question 6.5: With the biochemical reaction of carbon dioxide and hydrogen gas into methane and water at a high production rate, would you need to heat or cool the reactor if you want to operate at a temperature of 65°C, and why?

Question 6.6: Can you think of another way to convert a liquid into a gas besides vaporization?

FURTHER READING MATERIALS

Blanco H. and Faaij A. (2018). A review at the role of storage in energy systems with a focus on power to gas and long-term storage. *Renewable and Sustainable Energy Reviews*, **81**, 1049–1086.

Ghaib K. and Ben-Fares F.-Z. (2018). Power-to-methane: a state-of-the-art review. *Renewable and Sustainable Energy Reviews*, **81**, 433–446.

- The German Solar Energy Society and Ecofys. (2004). *Chapter 3: Anaerobic Digestion. Planning and Installing Bioenergy Systems: A Guide for Installers, Architects and Engineers*. James & James/Earthscan, London, UK.
- Weiland P. (2006). Biomass digestion in agriculture: a successful pathway for the energy production and waste treatment in Germany. *Engineering in Life Sciences*, **6**, 302–309.

REFERENCES

- Angenent L. T., Karim K., Al-Dahhan M. H., Wrenn B. A. and Domínguez-Espinosa R. (2004). Production of bioenergy and biochemicals from industrial and agricultural wastewater. *Trends in Biotechnology*, **22**, 477–485.
- Angenent L. T., Usack J. G., Xu J., Hafenbradl D., Posmanik R. and Tester J. W. (2018). Integrating electrochemical, biological, physical, and thermochemical process units to expand the applicability of anaerobic digestion. *Bioresource Technology*, **247**(Supplement C), 1085–1094.
- Bailera M., Lisbona P., Romeo L. M. and Espartero S. (2017). Power to gas projects review: lab, pilot and demo plants for storing renewable energy and CO₂. *Renewable and Sustainable Energy Reviews*, **69**, 292–312.
- Barber W. P. F. (2016). Thermal hydrolysis for sewage treatment: a critical review. *Water Research*, **104**, 53–71.
- Bougrier C., Delgenès J. P. and Carrère H. (2008). Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion. *Chemical Engineering Journal*, **139**, 236–244.
- Eboibi B. E., Lewis D. M., Ashman P. J. and Chinnasamy S. (2015). Integrating anaerobic digestion and hydrothermal liquefaction for renewable energy production: an experimental investigation. *Environmental Progress & Sustainable Energy*, **34**, 1662–1673.
- Götz M., Lefebvre J., Mörs F., McDaniel Koch A., Graf F., Bajohr S., Reimert R. and Kolb T. (2016). Renewable power-to-gas: a technological and economic review. *Renewable Energy*, **85**, 1371–1390.
- Hanselmann K. W. (1991). Microbial energetics applied to waste repositories. *Cellular and Molecular Life Sciences*, **47**, 645–687.
- Labatut R. A., Angenent L. T. and Scott N. R. (2011). Biochemical methane potential and biodegradability of complex organic substrates. *Bioresource Technology*, **102**, 2255–2264.
- Labatut R. A., Angenent L. T. and Scott N. R. (2014). Conventional mesophilic vs. Thermophilic anaerobic digestion: a trade-off between performance and stability? *Water Research*, **53**, 249–258.
- Lettinga G. (1995). Anaerobic digestion and wastewater treatment systems. *Antonie Van Leeuwenhoek*, **67**, 3–28.
- Martin M. R., Fornero J. J., Stark R., Mets L. and Angenent L. T. (2013). A single-culture bioprocess of *methanothermobacter thermoautotrophicus* to upgrade digester biogas by CO₂-to-CH₄ conversion with H₂. *Archaea* **2013**, 1–11 (Article ID 157529).
- Pace N. R. (1997). A molecular view of microbial diversity and the biosphere. *Science*, **276**, 734–740.
- Peterson A. A., Vogel F., Lachance R. P., Fröling M., Antal M. J., Jr and Tester J. W. (2008). Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. *Energy & Environmental Science*, **1**, 32–65.
- Posmanik R., Labatut R. A., Kim A. H., Usack J. G., Tester J. W. and Angenent L. T. (2017). Coupling hydrothermal liquefaction and anaerobic digestion for energy valorization from model biomass feedstocks. *Bioresource Technology*, **233**, 134–143.
- Posmanik R., Martinez C. M., Cantero-Tubilla B., Cantero D. A., Sills D. L., Cocero M. J. and Tester J. W. (2018). Acid and alkali catalyzed hydrothermal liquefaction of dairy manure digestate and food waste. *ACS Sustainable Chemistry & Engineering*, **6**, 2724–2732.
- Schiebahn S., Grube T., Robinius M., Tietze V., Kumar B. and Stolten D. (2015). Power to gas: technological overview, systems analysis and economic assessment for a case study in Germany. *International Journal of Hydrogen Energy*, **40**, 4285–4294.
- Schill N., van Gulik W. M., Voisard D. and von Stockar U. (1996). Continuous cultures limited by a gaseous substrate: development of a simple, unstructured mathematical model and experimental verification with *Methanobacterium thermoautotrophicum*. *Biotechnology and Bioengineering*, **51**, 645–658.
- Schill N. A., Liu J. S. and Stockar U. (1999). Thermodynamic analysis of growth of *methanobacterium thermoautotrophicum*. *Biotechnology and Bioengineering*, **64**(1), 74–81.
- Stuckey D. C. and McCarty P. L. (1984). The effect of thermal pretreatment on the anaerobic biodegradability and toxicity of waste activated sludge. *Water Research*, **18**(11), 1343–1353.

- Tekin K., Karagöz S. and Bektaş S. (2014). A review of hydrothermal biomass processing. *Renewable and Sustainable Energy Reviews*, **40**, 673–687.
- Uman A. E., Usack J. G., Lozano J. L. and Angenent L. T. (2018). Controlled experiment contradicts the apparent benefits of the Fenton reaction during anaerobic digestion at a municipal wastewater treatment plant. *Water Science and Technology*, **78**(9), 1861–1870.
- van Haandel A. and van der Lubbe J. (2012). *Handbook of Biological Wastewater Treatment*, 2nd edn. IWA Publishing, London, UK.
- Verbeeck K., Buelens L. C., Galvita V. V., Marin G. B., Van Geem K. M. and Rabaey K. (2018). Upgrading the value of anaerobic digestion via chemical production from grid injected biomethane. *Energy & Environmental Science*, **11**, 1788–1802.
- Wilson C. A. and Novak J. T. (2009). Hydrolysis of macromolecular components of primary and secondary wastewater sludge by thermal hydrolytic pretreatment. *Water Research*, **43**, 4489–4498.
- Zeikus J. G. and Wolfe R. S. (1972). *Methanobacterium thermoautotrophicus* sp. n., an anaerobic, autotrophic, extreme thermophile. *Journal of Bacteriology*, **109**, 707–713.