Review of Biogas Upgrading
FutureGas project, WP1

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1 Summary

This report was prepared as part of Work Package (WP1) of the project ‘FutureGas’, aiming to improve the common understanding about efficient conditioning and distribution of gas in future energy systems. Here, a summary is given on biogas upgrading technologies and related issues, such as market trends and gas quality requirements, based on a review of recent literature.

The growth potential of biogas upgrading is large. There are about 20,000 biogas plants in Europe today, but only 400 upgrading installations as of 2015. The capacity of new biogas plants tends to increase, resulting in lower specific investment costs of biogas upgrading.

Biomethane has a methane content greater than 95% w/w up to the standard of substitute natural gas (SNG) or compressed natural gas (CNG). In particular, other parameters as Wobbe index, put limits on concentration of some impurities, such as sulfur, oxygen, dust, water, NH₃ and siloxanes. Biomethane can be applied as fuel sources for stove/boilers devices, vehicles, engines and gas turbines to produce heat and electricity. Also, it can be injected into the natural gas distribution system. Moreover, biogas needs to be purified in order to increase the specific heat, minimize corrosion problems caused by acid gases and other impurities. Currently, the biogas upgrading technologies are at the stage of development and performance improvement. Some novel biogas upgrading technologies such as cryogenic separations, in-situ and ex-situ biological upgrading, hydrate separations, are the recent developments. Nevertheless, most of the technical parameters and information have been obtained either in laboratory-scale reactor or pilot tests. Therefore, more research works needs to be performed to bridge the knowledge gap between such tests and large-scale operational biogas plants.

Specifying lower methane contents in the range of 90-98% does not change much in terms of capital expenditure (CAPEX), according to equipment suppliers. More significant parameters in terms of CAPEX are the requirements for pretreatment of the raw gas and quality parameters other than methane content. Obviously, lower methane purity means that more inert carbon dioxide (CO₂) has to be transported and stored in the gas system, and the direct compatibility with natural gas is lost.
Membranes (including membrane hybrids), pressure swing adsorption (PSA), and physical scrubbing all appear to be operationally flexible regarding product gas methane content and operating expense (OPEX), whereas chemical scrubbing has very high CO₂ selectivity.

Only ppm-levels of H₂S, which is corrosive and extremely toxic, can be tolerated in the product gas. Oxygen (O₂) and nitrogen (N₂) are normally an issue with biological sulfur removal only (introduces air into the final step of the anaerobic digester), and when upgrading landfill gas. None of the upgrading technologies will separate nitrogen in their standard configurations. Landfill and sewage gases require special attention to siloxanes and volatile organic compounds (VOC). Siloxanes contain organically bound silicon that is converted to silicon dioxide (SiO₂) deposits during combustion, which may cause serious problems to gas boilers, turbines, and engines.

The most common lean gas treatment technology for low methane concentrations is regenerative thermal oxidation (RTO). Lean gas burners operate autothermally with about 3-6% methane (CH₄) in CO₂. The lean gas may also be cleaned and liquefied to obtain pure CO₂ for e.g. the beverage industry.
2 Market development

The European market for biogas upgrading has been significantly increasing during the last five years. The most recent data from International Energy Agency (IEA) Bioenergy Task 37 indicated that 400 new upgraded biogas plants had been installed during the last decade, out of these approximately 190 installations were in Germany (IEA 2014, 2015). The growth potential is large considering that the total number of biogas plants in Europe currently is close to 20,000, equaling an installed capacity of 9,000 MWₑ, and the number is steadily increasing as shown in Figure 1. (European Biogas Association - EBA 2015, Hoyer et al., 2016). In the middle of 2013, 0.8 billion m³/year biomethane was produced in 14 European Countries with 230 upgrading pant (EBA 2015). The level of biogas production foreseen for 2020 in the National Renewable Energy Action Plans (NREAPs) is approximately 28 billion m³ (natural gas equivalent), and the share of total biogas upgraded to biomethane is projected to increase to 26% in 2020 and 38% in 2030 (EBA 2015). However, the market is challenging due to insufficient national support incentives, subsidies, and lack of cross-border cooperation. Moreover, the compressed natural gas (CNG) and liquefied natural gas (LNG) infrastructure for gas filling stations is insufficient in most regions of Europe.

![Figure 1 Number of biogas plants and total installed capacity in Europe (EBA 2015)](image)

In a biogas upgrading system, methane can be concentrated by removing other impurities to the same standards as natural gas. Afterwards, methane can be injected into the distribution grid. The main constituents of biogas are CH₄ and carbon dioxide (CO₂), but there are significant quantities of undesirable contaminants such as H₂S, NH₃ and siloxanes. Such undesirable impurities are mainly depending upon the feedstock of biogas plants. Fur-
thermore, such impurities have negative impact to any thermal conversion device in the form of corrosion, fouling and harmful environmental emissions. It is also important to remove the water before using it, because it can damage gas compressors, for example. It can also reduce the efficiency of Combined Heat and Power engines. Thus, biogas needs to be cleaned and upgraded to a certain quality such as natural gas. The biogas upgrading and market value have been increasing for six different types of upgrading technologies such as

- Water scrubbing and/or physical absorption
- Pressure swing adsorption (PSA)
- Chemical absorption
- Membrane separation
- Biological and
- Cryogenic technology

Interestingly, chemical (amine) scrubbing and membrane separation are gaining market shares compared to the more conventional PSA and water scrubbing upgrading technology as shown in Figure 1. However, selections of these technologies depend on scale, actual specification and individual requirement of biogas facilities. Membrane separators, for example, should be particularly appropriate in small to medium scale when there is no possibility for heat recovery. O₂ might be a particular concern. Physical scrubbers will not remove O₂, while amines are irreversibly damaged by oxygen. Membranes and PSA have the ability to partially separate the O₂ to the level of 0.2-0.5% by volume. Further reduction requires the installation of an oxygen scavenging unit, adding extra costs and increasing operation complexity. None of the upgrading technologies separate nitrogen in their standard configurations, but PSA can remove N₂ with more costly adsorbent bed configurations. Consequently, methane purity is a function of the nitrogen content of the raw biogas.
Figure 2  Development in the number of upgrading plants and installed technology from 2001 to 2015 (IEA Bioenergy Task 37)
3 Process performance

The specific investment cost of biogas upgrading ranges from about 6000 €/(Nm³/h raw gas) for small plants to approximately 1000 €/(Nm³/h raw gas) for large plants as shown in Figure 3. There is no significant difference in capital expenditure (CAPEX) and operating expenditure (OPEX), observed between upgrading technologies, based on data collected from various suppliers given standard project specs/capacity (Hoyer et al., 2016). Furthermore, other operation parameters such as gas quality and pressure requirements, possibility for use of surplus heat and technology availability are also relevant. As shown in Figure 3, biogas upgrading technology with less than 500 Nm³/hr raw biogas has higher specific investment cost. Thus, the investment cost for biogas upgradation technology is economically feasible for large-scale production plants.

![Figure 3](image)

*Figure 3  The specific investment cost for biogas upgrading vs plant capacity (Hoyer et al., 2016).*

Typical unit operation and process flow is described in Figure 4. In case of water scrubber, a separate H₂S removal scrubber can be used. Moreover activated carbon can be applied to remove H₂S along with siloxanes, but methods based on reaction with iron oxide, producing FeS(s), and biofiltration are common as well. Furthermore, many types of adsorbents are suitable, such as silica gel for siloxanes (Soreanu et al., 2011). In case of membrane and PSA, gas dryer and regeneration tower are not necessary. Off-gas treatment is necessary prior to disposal of waste gas to minimize the potential emission of CH₄ from upgrading technology as shown in Figure 4. Typical performance data for upgrading technologies are compared in Table 1.
and Table 2. Notice that chemical absorption is characteristic by having high selectivity (low methane slip) at the expense of higher thermal energy requirement.

**Figure 4** Outline of typical unit operations in biogas upgrading (Union Instruments, 2014).

**Table 1** Typical performance data of upgrading technologies based on supplier information (Fachagentur Nachwachsende Rohstoffe, 2014).

<table>
<thead>
<tr>
<th>Parameter/Supplier</th>
<th>Carbo-tech</th>
<th>Malmberg</th>
<th>Greenlane</th>
<th>Haase</th>
<th>MT Biomethane</th>
<th>Anxiom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>PSA</td>
<td></td>
<td></td>
<td>Physical scrubber with solvent</td>
<td>Amine</td>
<td>Membrane</td>
</tr>
<tr>
<td>Capacity (m³/h raw gas)</td>
<td>400-2,800</td>
<td>350-2,000</td>
<td>400-2,800</td>
<td>250-2,800</td>
<td>400-2,000</td>
<td>400-700</td>
</tr>
<tr>
<td>Footprint (m²)</td>
<td>200-300</td>
<td>80-250</td>
<td>36-60</td>
<td>100-555</td>
<td>107-230</td>
<td>105-166</td>
</tr>
<tr>
<td>Electricity consumption (kWh/m³ raw gas)</td>
<td>&lt;0.19</td>
<td>0.2-0.23</td>
<td>0.17-0.22</td>
<td>0.23-0.27</td>
<td>0.09</td>
<td>0.24</td>
</tr>
<tr>
<td>Thermal energy consumption (kWh/m³ raw gas)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Internal heat</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>Pressure after process (barg)</td>
<td>2</td>
<td>4.5-5.5</td>
<td>7-8</td>
<td>5-7</td>
<td>1.2</td>
<td>6</td>
</tr>
<tr>
<td>Maximum surplus heat (kWh/m³ raw gas)</td>
<td>&lt;0.1</td>
<td>0.06-0.18</td>
<td>0.1-0.12</td>
<td>0.12-0.13</td>
<td>0.3</td>
<td>0.36</td>
</tr>
<tr>
<td>Methane slip in off-gas (% of methane in raw gas)</td>
<td>&lt;1.5%</td>
<td>≤1%</td>
<td>&lt;1%</td>
<td>≤1%</td>
<td>≤0.1%</td>
<td>≤5%</td>
</tr>
</tbody>
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### Table 2  Pros and cons of biogas upgrading technologies adopted from Andriani et al., 2014.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Pros</th>
<th>Cons</th>
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</table>
| **Water Scrubbing** | - Simple process, remove both CO₂ and H₂S using water as a solvent  
- More than 97% methane upgradation  
- Low CH₄ loss (>2%) from the system | - Highly energy intensive system to press gas and to pump water  
- Slow process due to physical solubility ability of water  
- Corrosion problem due to H₂S  
- Clogging problem due to bacterial growth  
- Small amount of O₂ left |
| **Chemicals Scrubbing / chemical absorption** | - High CH₄ purities (>95%) and low CH₄ loss (<0.1%)  
- Faster process compared to water scrubber  
- Chemical solvent is easier to regenerated | - Energy intensive because steam has to be supplied to regenerate the chemicals  
- Corrosion problem due to H₂S  
- Further chemical waste treatment is necessary |
| **Physical scrubbing / Physical absorptions** | - Higher absorption rather than water  
- High CH₄ purities (>95%) and low CH₄ loss(<0.1%) | - Solvent regeneration is difficult if H₂S is not removed from system  
- Energy intensive to regenerate solvent |
| **Pressure swing Adsorption (PSA)** | - Capital cost shares moderate  
- Relatively quicker start up and installation  
- High CH₄ purities (95-98%) | - Higher capital cost (affected by number of column in PSA unit)  
- Incomplete scrubbing ( other treatment are needed )  
- High CH₄ loss might be possible due to malfunctioning of valves |
| **Membrane based techniques** | - Fast installations and startup  
- Flexible production output  
- Purity and flow rate can vary  
- Low energy required  
- High CH₄ purities (>96%)  
- Low methane loss | - Low membrane selectivity  
- Consume relatively more electricity per unit of gas production  
- Often yields lower methane concentration though high purity is possible |
| **Biological techniques** | - Low energy requirements  
- No unwanted end products  
- Enrichment of CH₄ (>99%) | - Additional nutrients are required for bacterial growth  
- Small amount of O₂ and N₂ are left in treated biogas  
- Low cost process |
| **Cryogenic separation** | - High CH₄ purities (90-98%)  
- Relative pure CO₂ can be separated for further utilization  
- Liquid methane reduces gas volume, thus can be packaged in the tube and can be easily distributed  
- Low methane loss | - Lot of devices are required such as compressor, heat exchanger and cooler,  
- High operating and maintenance cost |
4 Physical absorption / Water scrubber

Physical absorption makes use of the different solubility of gases in a liquid scrubbing solution. Predominantly, water is used as a scrubbing liquid of biogas at an industrial scale, with 41% share of the global biogas upgrading market because of availability, cost effectiveness and low sensitivity to biogas impurities (Kadam et. al., 2017).

Figure 5 Outline of typical water scrubbing process (Bauer, SGC 2013).

Water scrubbing (Figure 5) takes advantage of the higher solubility (approximately 26 times at 25 °C) of CO₂ than CH₄ in water, operating at 6-10 bar pressure. Furthermore, H₂S can be simultaneously removed due to higher solubility in water. However, dissolved H₂S is corrosive, and odor nuisance can burden plant operation, thus it is recommended to remove H₂S prior to CO₂. Due to the use of air for the desorption process, some H₂S is oxidized to elemental sulfur and sulfuric acid, which in turn lowers the pH value. Water is purged to avoid accumulation of impurities and pH decrease (approx. 0.5-5 m³/day). Unfortunately, neither N₂ nor O₂ is removed in the process because they are non-condensable gases.

The performance of a water scrubber depends on the water flow, height of absorber column, type of packing, column pressure and temperature and specification of outlet carbon dioxide concentration. With given absorber column design and outlet CO₂ concentration, the required water flow, Qₘ, is calculated by using equation 1,

\[ Q_w = \frac{Q_{gas}}{K_h \cdot P_{tot}} \quad \text{(equation 1)} \]
where, $Q_{\text{gas}}$ is the total biogas flow, $K_h$ is Henry’s (solubility) constant and $P_{\text{tot}}$ the absorber pressure. $Q_w$ is inversely related to the solubility of CO$_2$, which increases significantly with decreasing absorber temperature, as shown in Figure 6 (range 10-40 °C). Typically, about 0.2 m$^3$$_{\text{water}}$/Nm$^3$_{biogas} is required for outlet CO$_2$ concentrations below 2% (Bauer, SGC 2013). A flash column (no packing) must be installed to limit the methane slip by reducing the pressure to around 2.5-3.5 bar (abs). The composition of the gas released in the flash column is typically 80-90% CO$_2$ and 10-20% CH$_4$, which is recycled to the compressor as shown in Figure 5 (Bauer, SGC 2013). The electricity consumption of water scrubbing is primarily related to compression (0.10-0.15 kWh/Nm$^3$ raw gas), water circulation (0.05-0.10 kWh/Nm$^3$ raw gas) and cooling (0.01-0.05 kWh/Nm$^3$ raw gas). A heat recovery system can be installed to recover heat for the anaerobic reactor.

Figure 6 Relative solubility of carbon dioxide in water versus temperature (Bauer, SGC 2013).

An organic solvent such as methanol and dimethyl ethers of polyethylene glycol (DMPEG) can also be an effective absorber for CO$_2$ and H$_2$ since they have relatively higher solubility. The solubility of CO$_2$ in the commercial solvents Selexol® and Genosorb® is approximately five times higher than in water (Tock, et. al., 2010).
5 Chemical scrubbing

In principle, chemical scrubbing is almost similar to water scrubbing for biogas cleaning (Figure 7), except that chemical reaction takes place between solvent and absorbed substances. The efficiency mainly relies on the reactivity of the absorbent, such as alkanol amines, aqueous alkali solutions mainly KOH, K₂CO₃, NaOH and Fe(OH)₃ (Lasocki et al., 2015).

Chemical scrubbing of sour gases (i.e. gas sweetening) like CO₂ and H₂S is carried out using aqueous amine solutions, such as 30% w/w diethanolamine (DEA). The pH value of the solution is approximately 12, at which about 40% w/w of the absorbed CO₂ is present as HCO₃⁻ and about 55% w/w as DEACOO⁻. H₂S is commonly separated prior to scrubbing; if not an additional 10% heat consumption may occur. CH₄, N₂ and O₂ are practically not absorbed. Due to the high selectivity of the process, the CH₄ slip is low at about 0.1% (Ryckebosch et al., 2011).

![Figure 7 Biogas upgrading by chemical absorption adopted from Awe et al., 2017.](image)

The amine solution enters the absorber at 20-40 °C and leaves at 45-65 °C, being heated due to the exothermal reaction. The amine concentration is in stoichiometric excess to avoid equilibrium constraints. The operating pressure of the absorber is 1-2 bar (abs). The (rich) solution exiting the absorber is heat exchanged with the (lean) exit stream from the stripping process before entering a stripper or series of flash drums. Additional heat is supplied, typically as 120-150 °C steam, to push the chemical equilibrium strongly...
towards the lean amine. The stripper pressure is usually 1.5-3 bar (abs), however, desorption in a vacuum is feasible for using district heating (90 °C) as heat supply. Amine scrubbing may be subject to various operational issues, such as foaming, corrosion, thermal/chemical degradation, and losses. Amines react irreversibly with O₂ and CO₂, and the degradation products, such as e.g. formaldehyde, may be emitted to the atmosphere (Awe et al., 2017).

Figure 8  Calculated influence of amine solution flow rate (liter/Nm³ gas) on the methane content in product gas (PG) and methane slip, respectively (Götz et al., 2012).

Figure 9  Calculated influence of the inlet temperature of the amine solution on the methane content of the product gas (Götz et al., 2012).
6 Membrane separation

Biogas membrane separation is based on the different permeability of gases in polymer materials, such as polyimides and polysulfones. Gas–gas membrane separation can be operated at relatively high pressures in the range of 20–40 bar, whereas lower pressures of 8–10 bar is appropriate for 92–97% methane purity (Bauer et al., 2013). Typically, the CO₂/CH₄ selectivity (ratio of permeability or separation factor) is in the range of 20–50. Membranes for biogas upgrading are mainly hollow fibers (outer diam. 50–3000 µm) with a high effective surface area per unit volume (Persson M. et al. 2007).

![Figure 10 Two-stage cascade with recycling membrane separator design (Makaruk et. al., 2010).](image)

Membranes offer relatively high energy efficiency (<0.4 kWₑ/ Nm³ bio-methane) and is easily scalable for capacities ranging from 10 Nm³/h to more than 1000 Nm³/h. Turn down of the plant is possible at short intervals. Notice that water vapor permeates as well, implying that the product gas is dry and may be injected directly into the grid. A membrane lifetime of 8 to 12 years may be expected. Some of the trace compounds might have adverse effects on the membrane performance, and condensable water, solid particles, and H₂S are in general removed.
The methane recovery depends on the total surface area of the membrane, the number of stages and membrane configuration inside the reactor. Commonly, the simplest single-stage design can achieve up to about 90% purity, whereas multiple-stage systems can produce more than 99% methane. A simulation study from Makaruk et al. 2010 concluded that the two-stage design with permeate recycle was superior regarding minimal membrane area and minimal compression power as shown in Figure 11. Furthermore, two-stage designs allow for a broad range of product recoveries. Interestingly, membrane separation can be integrated with conventional upgrading technologies, so-called hybrid processes, as shown in Figure 12, which are potentially more efficient and cheaper to operate. In the figure, panel A and B, hybrid membrane processes with pressurized water scrubbing are described. Whereas, in figure C and D, membrane processes are integrated with amine scrubbing. Similarly, membrane process can be integrated with cryogenic separation (E), and combined heat and power (F). Furthermore, biogas can be upgraded with three stages membrane configuration system as shown in figure G.

Membranes can also be applied in gas-liquid separation processes, such as amine scrubbing (Persson et al., 2007). In this case, a microporous hydro-
phobic membrane separates the biogas from the countercurrent liquid flow. The amine solution can be regenerated (desorption of CO₂) by heating as with conventional amine scrubbing.

Figure 12 Various proposed hybrid membrane processes with pressurized water scrubbing (A and B), amine scrubbing (C and D), cryogenic separation (E), and combined heat and power (F), A three stage membrane configuration (G) (Chen et al., 2015).
7 Pressure swing adsorption

PSA makes use of a number of columns with solid material(s) that selectively adsorb and desorb CO₂ by cyclic variation of pressure as shown in Figure 13. The most commonly applied adsorbents materials are zeolites (aluminosilicates), modified activated carbon, activated charcoal, silica gel and synthetic resins for the cleaning of biogas (Bauer et al., 2013). The adsorption kinetics and cyclic capacity, i.e. the difference in loading between the high and low pressure of the PSA cycle, depend on physical parameters like porosity, specific surface area and pore size distribution rather than chemical composition (Ryckebosch et al., 2011). The adsorption isotherms of CO₂ and CH₄, respectively, on zeolite 13X are shown in Figure 14 as an example.

The conventional, so-called Skarstrom, a cycle consists of 4 steps using four columns: 1) feed, i.e. CO₂ adsorption, 2) pressure reduction (blowdown), i.e. CO₂ desorption, 3) purge with gas recycle, and 4) pressurization with blowdown gas and feed gas (or gas recycle). In general, CH₄ recovery is 96–98% so lean gas treatment is required in order to reduce methane emissions. However, the PSA cycle and a number of columns can be modified in many ways to increase purity or to reduce methane slip and energy consumption.

For example, the “Smart Cycle PSA” system developed by ETW Energieotechnik GmbH, Germany, is supposed to automatically adjust the pressure swing cycle to varying inlet gas quality and volume flow, giving control of

![Figure 13 Biogas upgrading by PSA (Awe et al., 2017).](image)
the product gas purity up to 99\% (ETW 2017). The supplier states low energy consumption of 0.14 kWh/Nm³. Another example is the fast-cycle, rotary valve PSA from Xebec Adsorption Inc., Canada. The proprietary valve design is claimed to replace up to 36 standard (solenoid) valves, and the product purity/flow rate can be controlled by changing the rotary valve speed.

PSA can be applied for removing H₂S as well. Adsorbents such as iron oxide (Fe₂O₃), iron hydroxide (Fe(OH)₃) or zinc oxide (ZnO) are suitable, but other adsorbents are commercially available, such as Sulphur-Rite®, SulfaTreat®, SOXSIA®, Meda-G2®, and Sulfa-Bind®. Magnesium based metal organics (MOF) have also been synthesized and applied in PSA (Petersson et al., 2009).

![Figure 14 Example of equilibrium adsorption isotherms on zeolite 13X of CO₂ (left) and CH₄ (right) at 303 K (■), 323 K (♦), and 348 K (▲) (Santos, 2011).]
8 Cryogenic separation

Cryogenic separation technology is relatively novel in biogas upgrading and is, to the knowledge of the authors, not yet applied commercially in any larger scale. However, cryo-technology has been used for many years to produce LNG for transportation and distribution of natural gas. The energy consumption is relatively high (about 1.3-1.5 kWh/Nm³ product gas, Johansson, 2009), which is why cryogenic upgrading primarily appears relevant in combination with CBG/LBG production, and where liquid CO₂ is desired as co-product (see also CO₂ utilization, chapter 13).

The phase diagram in Figure 15 illustrates the temperatures and pressures of CO₂ in its solid, liquid and gas phase, respectively. CO₂ has a boiling point of -78 °C, whereas CH₄ has -160 °C. Liquid CO₂ does not exist at pressures below 5.1 atm (~ 5.2 bar) and temperatures below -57 °C. Taking the GPP® system from Gastreatment Services B.V. as an example, the biogas is first compressed to 16-25 bar, and then cooled to -25 °C. CO₂ and CH₄ remains in the gas phase in this step, whereas water, hydrogen sulphide, sulphur dioxide, halogens and siloxanes are removed from the gas. Then CO₂ is removed in two further stages, first by cooling to between -50°C and -59°C, where 30-40% of the CO₂ is removed as a liquid. In the second stage, the remaining CO₂ is removed as a solid, which is why a second column is required while defrosting and removing carbon dioxide from the first column leaving CH₄. (Petersson, 2009, Södermann, ScandinavianGtS).

Figure 15 Phase diagram of CO₂.


9 Biological methanation

In anaerobic digestion, microorganisms (bacteria) consume organic carbon in the absence of oxygen. A series of bio-chemical processes takes place, such as hydrolysis, acidogenesis, acetogenesis and methanogenesis that eventually generate CH₄. In biological methanation, CO₂ is utilized as carbon source and H₂ as electron source by hydrogenotrophic methanogens. Thus, the overall reaction as below:

\[
\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad \Delta H = -164.9 \text{ kJ/mol (equation 2)}
\]

9.1 Hydrogen mediated biological methane enrichment

The enrichment process carried out either in-situ injection of hydrogen into the anaerobic digester or injecting H₂ into ex-situ separate reactor containing methanogenic consortium. Biological methanation has low energy consumption and is less sensitive to gas impurities compared to catalytic methanation. However, a major challenge is that the process is rate limited by the gas to liquid mass transport of H₂. Moreover, due to the stoichiometry of reaction, the gas volume flow is reduced significantly.

Various reactor designs have been proposed to handle this problem, such as the up-flow anaerobic sludge blanket reactor (UASB). Bassani et al., 2016, recently demonstrated an increase in the concentration of CH₄ from 58 to 82%, applying the UASB for anaerobic digestion of potato waste water with H₂ injection (in-situ upgrading), as shown in Figure 16. Similarly, various concepts for ex-situ (separate methanation) are also being investigated (Kougias et al., 2017, Sveinbjörnsson D. et al., 2017).

![Figure 16 In-situ biological biogas upgrading adopted from Bassani et al., 2016.](image-url)
9.2 CO₂ utilisation

The CO₂ gas from biogas upgrading may be processed for various applications, such as greenhouse gas in agriculture, fire extinguishers, carbonated soft drinks, as refrigerant, for dry ice, as liquid solvent for many organic compounds and CO₂ for methane generation. CO₂ utilization is still in its infancy compared to the more well-developed enhanced oil recovery (EOR). However, CO₂ sequestration for EOR is unsustainable due to concerns about possible release associated with earthquake and volcanic eruption. Also, application of CO₂ from biogas plants is not sufficient for EOR. Thus, CO₂ utilization either as industrial feedstock or methane generation has far more positive economic and environmental benefits.

![Figure 17 Biogas CO₂ liquefaction process (Pentair Haffman).](image)

By liquefaction, the CO₂ rich stream is pressurized (about 20 bar) and cleaned/dried using activated carbon. The filtered CO₂ is cooled to -24 °C, whereas remaining methane is stripped and fed back to the membrane unit as shown in Figure 17. CO₂ liquefaction can be retrofitted to existing upgrading units. See also cryogenic separation, chapter 8.

9.3 Power-to-gas (PtG) technology

Power-to-gas (PtG) technology is yet another option to utilize biogas CO₂. By PtG, CH₄ is produced from CO₂ and electrolytically generated H₂, which
in effect links the electricity grid with the gas grid (Fellet and Bach 2016). The currently largest PtG installation in the world with SOEC (solid oxide electrolysis cell) is being demonstrated by Haldor Topsøe A/S and Aarhus University at the Foulum Biogas facility (scale 10 Nm$^3$/h methane) (Bailera M et al., 2017). Further elaboration has been done in a separate report entitled Upgrading of Biogas to Biomethane with the Addition of Hydrogen from Electrolysis prepared by PlanEnergi (Sveinbjörnsson D. et al., 2017).

The company Electrochaea GmbH, Germany, has installed a pilot plant for biological methanation at the BIOFOS Avedøre wastewater treatment plant, Copenhagen, the so called PtG-Biocat process (Sveinbjörnsson D. et al., 2017). The plant includes two Hydrogenics HySTAT$^{TM}$100 alkaline electrolyzers, producing in total up to 200 Nm$^3$/h H$_2$ (power consumption 1 MW) as well as an ex-situ bioreactor (Bailera M et al., 2017). Details of the process are outlined in Figure 18. Electrochaea claims that biological methanation provides operational flexibility and economic viability compared to thermochemical methanation, as listed in Table 3 (Electrochaea 2016).

By so-called gas fermentation, CO$_2$ from biogas upgrading, and/or CO from thermal gasification and various industrial sources, can be utilized as indus-

Figure 18 (A) Outline of biological methanation reactor, (B) biochemistry of biological methanation (Electrochaea 2016)
trial feedstock for the production of chemicals, such as ethanol, acetate, acetone, lactate, n-butanol and 2,3-butanediol and fuels for transportation such as methane, methanol/DME (Keller et al., 2013). The company LanzaTech, New Zealand, seems currently ahead of competition with several technology patents and ethanol production facilities at steel mills, e.g. in Beijing, China. Nevertheless, gas fermentation is still in the development phase (Geppert et al., 2016; Younas et al., 2016).

Table 3 Possible advantages of biological methanation in comparison with thermochemical methanation (Electrochaea, 2016).

<table>
<thead>
<tr>
<th></th>
<th>Thermochemical Methanation</th>
<th>Biological Methanation</th>
<th>Advantage of Biological Methanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Range</td>
<td>300-400°C</td>
<td>60-65°C</td>
<td>Lower engineering complexity, better ramping capability</td>
</tr>
<tr>
<td>Contamination Tolerance (H₂S, O₂, KOH)</td>
<td>Low</td>
<td>High</td>
<td>Ability to use raw biogas and low-purity H₂</td>
</tr>
<tr>
<td>Fuel Produced</td>
<td>CH₄ + intermediates (esp. CO)</td>
<td>CH₄ only</td>
<td>No post-reaction product separation required</td>
</tr>
<tr>
<td>Engineering Complexity</td>
<td>High</td>
<td>Low</td>
<td>Lower CapEx, greater system modularity/mobility</td>
</tr>
<tr>
<td>Scalability</td>
<td>Low</td>
<td>High</td>
<td>Economic viability even at small scales</td>
</tr>
</tbody>
</table>

Simplicity, responsiveness, robustness → lower CapEx and OpEx, higher operating flexibility
10 Biomethane quality

Gas operators are responsible for maintaining the gas quality delivered to end-users as defined in different regulation and standards such as Gasreglementet C-12 (Denmark), DVGW G260/G262 (Germany) and EN 16723-1/16726:2015 (European standards). Part 2 of European standards EN 16723, concerning biomethane application as a vehicle fuel, is currently in the process of approval. Widely acceptable standard development is challenging due to unavailability of data and methods to assess the impact of biomethane quality on the grid system and end user equipment.

Additionally, consumer awareness and consensus are limited regarding the biomethane gas quality. The impact of biomethane components on infrastructure and gas appliances has been studied by the research consortium “EDGaR” with partners from gas companies and universities. The corrosion risk of gas pipeline materials, such as steel (Fe), copper (Cu), aluminum (Al), polyvinyl chloride (PVC) and polyethylene gas (PE) was found to be very low or non-existing with no water present. Thus, thorough gas drying at entry points is strictly recommended as well as increasing the distribution pressure to 100 mbar in order to reduce water ingress by permeation. However, as some water in practice is unavoidable, the recommended limits of the concentrations of O₂, NH₃ and H₂S is 0.01 vol-%, 50 ppm (v) and 34 ppm(v), respectively, for gases in contact with metallic materials. The possible impact of other gases, such as hydrogen cyanide (HCN) and CO₂, or high concentrations of H₂S, i.e. > 160 ppm, was not investigated. Nonetheless, to reduce risks the presence of HCN and CO should be avoided in the gas distribution grid. (Kiwa, 2015).

Further impurities and biogas components, such as siloxanes, terpenes and microbial corrosion via biofilm formation, also need to be assessed. Siloxanes contain organically bound silicon that is converted to SiO₂ deposits during combustion, which may cause serious problems to gas boilers, turbines, and engines. Additionally, terpenes may corrode gaskets and PE piping. They can also mask the odor component such as Tetrahydrothiophene (THT) added to natural gas.
11 Low-methane concentration upgrading

In this study, five different biogas upgrading equipment suppliers have been contacted regarding the cost and prospective of low methane upgrading technology. According to supplier quotations, there is no or very limited savings in CAPEX to be achieved by low-methane upgrading. Requirements for raw gas pretreatment and product gas specifications other than methane content have more impact on CAPEX.

Regarding OPEX, the power consumption of compressors and pumps has a significant impact. Membrane systems can be designed for a high degree of flexibility in terms of product gas methane content. For example, the two-stage membrane system outlined in Figure 19 recycles the permeate stream from the second stage to the compressor. The methane content of the product gas is controlled by a proportional valve, located at the retentive outlet of the second stage, which in turn influences the pressure in the feed channels. Using this control strategy, gases can be produced with 70-99% methane.

![Figure 19 An example of membrane/gas engine system with variable product gas methane content (Biomethane Regions, 2013).](image-url)
12 Lean gas treatment

The lean gas from biogas upgrading may contain from 0.1% to more than 10% by volume CH₄, depending on the upgrading system. Only few countries have specified limits for the methane content of the lean gas, such as Germany with 0.5% by volume. CH₄ is an important climate change forcing greenhouse gas (GHG) with a long-term global warming impact 21 times greater than CO₂. Besides the climatic consequences, a considerable loss of methane from the anaerobic digester or upgrading system will result in an economic loss in itself.

For low methane concentrations, the most common treatment technology is regenerative thermal oxidation (RTO). The RTO contains alternating, fixed beds with ceramic elements that accumulate the heat of combustion from the gas exiting the oxidation chamber(s). The auto-ignition temperature of methane is just below 600 °C but tends to increase as methane and oxygen concentrations drop. Normally, an RTO operation temperature is around 800 °C. The auto thermal operation is possible with methane and oxygen concentrations between 0.2 and 10% by volume, but co-firing is required for start-up. A comparable technology called catalytic beds (RCO) can operate at 400 °C, but H₂S must be removed as it will irreversibly poison the catalysts.

At higher methane concentrations, lean gas treatment must be integrated with the overall Anaerobic Digestion (AD) process in order to achieve optimal performance. This is particularly relevant in case of low-methane upgrading. There are several technologies of choice, such as lean gas burners, gas engines, micro turbines or co-combustion. Biological treatment is under development as well (Dröge, 2014). Recently, the e-flox burner, shown in Figure 20, was commercialized, which operates autothermally with 3-6% by volume of CH₄.

*Figure 20 Recuperative, flameless oxidation burner (e-flox, Germany)*
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European biogas Association


Union Instruments


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