Guidelines for the implementation and operation of biogas upgrading systems

Keywords:
Biogas, upgrading, biomethane, carbon dioxide, water scrubber, pressure swing adsorption, PSA, chemical absorption, physical absorption, membrane separation, cryogenic upgrading

Abstract:
This report gives stakeholders willing to implement a biogas upgrading plant an overview about the state-of-the-art of all technologies that are available for cleaning and upgrading of biogas to biomethane. It includes experiences of BIOGASMAX and project external plant operators as well as technology providers, and gives recommendations to avoid faults in both the planning and operating stages of plants.

Written by:
Michael Beil and Uwe Hoffstede, Fraunhofer IWES
reviewed by:
Henning Hahn, Fraunhofer IWES

September 2010

www.biogasmx.eu
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1 Introduction

This deliverable “Guidelines for the implementation and operation of biogas upgrading systems” has been prepared within the European project BIOGASMAX.

This guideline will focus on the part of the process chain: “Upgrading of raw biogas to biomethane”.

1.1 The EU-project BIOGASMAX

The BIOGASMAX project is a European research project for sustainable development with the objective to develop alternative fuels by improving the management and use of waste and urban transportation.

One of the main fields which are focused by the project is the upgrading of biogas to biomethane for grid injection and/or the direct use as vehicle fuel. For this a network of biogas upgrading demonstration plants is created in Europe with the aim of sharing experiences.

The overall goal of the project is to support the European Community in reducing dependency on oil, reducing greenhouse gases and direct emissions through knowledge about more efficient production, distribution and use of biogas in the transport sector generated from a wide variety of feedstock available in urban areas and regions in Europe.

The specific objectives of the project are:

• to prove the technical reliability, cost-effectiveness, environmental and societal benefits of biogas fuels;

• to perform large-scale demonstrations to optimise industrial processes, experiment and benchmark new and near-to-market techniques and expand biogas fleets;

• to identify and assess ways to remove existing technical, operational, organisational and institutional barriers, which can inhibit or prevent alternative motor fuels and energy efficient vehicles from entering the market in significant quantities;

• to widely spread knowledge about the demonstration experience and results to European cities and stakeholders in a transferable manner, with particular emphasis on New Member States, with training, decision tools and knowledge network support actions.
1.2 Biogas upgrading history and current status

Upgrading of biogas to biomethane was not developed during the last few years. First, large scale plants were installed in Europe about 25 years ago. Currently there are more than 100 upgrading plants in Europe in operation. Figure 1 describes the overall raw biogas capacity of all biogas upgrading plants installed in Europe with status 2009. In Northern America and Asia there are about 20 plants in operation in total.

![Figure 1: Plant capacity of biogas upgrading (status: in operation) in Europe in 2009 [ISET, 2009].](image)
2 Basics and background information on biogas upgrading

To implement a biogas upgrading project it is essential to know the available technologies for cleaning and upgrading the biogas to biomethane.

This chapter will give a common overview of the state-of-the-art of all available cleaning and upgrading technologies.

2.1 Biogas upgrading technologies for CO₂ removal

The main step of the production of biomethane is the removal of CO₂. These upgrading technologies can be separated in 4 groups shown in Figure 2:

1. Adsorption
2. Absorption
3. (Gas) Permeation
4. Cryogenic upgrading (to LBG or CBG)

![Diagram of biogas upgrading technologies for CO₂ removal](image)

Figure 2: Overview biogas upgrading technologies for CO₂ removal.

In the following sub-chapters, all relevant technologies will be described and plant manufacturers will be shown.
2.1.1 Pressure Swing Adsorption (PSA)

The pressure swing adsorption (PSA) is an adsorptive upgrading technology. For the central unit there are mostly used carbon molecular sieves. Besides CO₂, other compounds like H₂O, H₂S, N₂ and O₂ can also be separated from the gas stream. In a practical use it's required to do a desulfurization and drying of the raw biogas before it enters the molecular sieve. Typical pressures are in the range from 4 to 7 bar. Typical CH₄ concentrations in the product gas stream are >96%. Because the exhaust gas stream includes >1% CH₄ (related to the CH₄ mass flow of the biogas) an exhaust gas cleaning is required. Because the exhaust gas does not include any sulphur the following exhaust gas treatment technologies are possible:

- Catalytic Oxidation
- Regenerative Thermal Oxidation
- Flameless Oxidation

Figure 3 describes the PSA process and shows the places in the process where H₂S, H₂O and CO₂ are separated.

![Figure 3: Flow chart pressure swing adsorption.](image)
Table 1 shows plant manufacturers that provide PSA upgrading plants for the production of biomethane.

### Table 1: Plant manufacturers PSA technology.

<table>
<thead>
<tr>
<th>Company</th>
<th>Technology</th>
<th>Internet</th>
</tr>
</thead>
<tbody>
<tr>
<td>CarboTech Engineering GmbH</td>
<td>PSA</td>
<td><a href="http://www.carbotech.info">www.carbotech.info</a></td>
</tr>
<tr>
<td>Xebec</td>
<td>PSA</td>
<td><a href="http://www.xebecinc.com">www.xebecinc.com</a></td>
</tr>
<tr>
<td>Acrona-Systems</td>
<td>PSA</td>
<td><a href="http://www.acrona-systems.com">www.acrona-systems.com</a></td>
</tr>
<tr>
<td>Cirmac</td>
<td>PSA</td>
<td><a href="http://www.cirmac.com">www.cirmac.com</a></td>
</tr>
<tr>
<td>Gasrec</td>
<td>PSA</td>
<td><a href="http://www.gasrec.co.uk">www.gasrec.co.uk</a></td>
</tr>
</tbody>
</table>

### Recommendations:

- Avoid H$_2$S, siloxanes and organic solvents on the molecular sieve.
- Be aware of high H$_2$S concentrations by using two activated carbon filters for desulfurisation to be able to change one filter without having to stop the whole process.
- If sewage gas is cleaned/upgraded, be aware of possible organic solvent peaks in the raw gas by the installation of an extra cleaning step for this.
- If there are siloxanes in the raw gas (especially if using sewage gas, biogas from waste or landfill gas), choose a special cleaning step for this.
- If using an activated carbon filter for siloxane removal, note that there are special charcoals available for H$_2$S removal and others for siloxane removal.
- A biological desulfurisation (by using air) in the digester is theoretically possible because the PSA system can also adsorb N$_2$.
- Use an exhaust gas treatment technology to avoid CH$_4$ emissions to the atmosphere.
2.1.2 Water Scrubber

The water scrubber technology is an absorptive method for separating CO\(_2\) from the gas stream. Besides CO\(_2\), H\(_2\)S and NH\(_3\) can also be separated. Normally it is not required (and also not constructed in current plants) to schedule a desulfurisation step before the raw gas enters the absorption column. But it can be helpful to avoid significant H\(_2\)S emissions to the atmosphere by the exhaust gas or alternatively if there is an exhaust gas treatment technology installed, it will avoid SO\(_2\) emissions. Pressures in the absorption column are in the range from 7 – 10 bar. Typical CH\(_4\) concentrations in the product gas stream are ~97%.

Because the exhaust gas stream includes >1% CH\(_4\) (related to the CH\(_4\) mass flow of the biogas) an exhaust gas cleaning is required. Because the exhaust gas normally contains H\(_2\)S the following exhaust gas treatment technologies are possible:

- Regenerative Thermal Oxidation
- Flameless Oxidation

Figure 4 describes the water scrubber process and shows the places in the process where H\(_2\)S, H\(_2\)O and CO\(_2\) are separated.

![Flow chart water scrubber (with regeneration).](image)
Table 2 shows plant manufacturers that provide water scrubber upgrading plants for the production of biomethane.

**Table 2: Plant manufacturers water scrubber technology.**

<table>
<thead>
<tr>
<th>Company</th>
<th>Technology</th>
<th>Internet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malmberg</td>
<td>Water scrubber</td>
<td><a href="http://www.malmberg.se">www.malmberg.se</a></td>
</tr>
<tr>
<td>Flotech</td>
<td>Water scrubber</td>
<td><a href="http://www.flotech.com">www.flotech.com</a></td>
</tr>
<tr>
<td>Rosroca</td>
<td>Water scrubber</td>
<td><a href="http://www.rosroca.de">www.rosroca.de</a></td>
</tr>
</tbody>
</table>

**Recommendations:**

- Avoid N\textsubscript{2} and O\textsubscript{2} in the raw gas stream because the system can not separate these gas compounds. It would cause a decrease of the heating value of the biomethane.

- Therefore a biological desulfurisation (by using air) in the digester is not recommended.

- If sewage gas is cleaned/upgraded be aware of possible organic solvent peaks in the raw gas by the installation of an extra cleaning step for this. It could cause a damage of your gas drying system if a PSA/TSA is used for this.

- Use an exhaust gas treatment technology to avoid CH\textsubscript{4} emissions to the atmosphere.
2.1.3 Physical Absorption (organic solvents)

The physical absorption technology using organic solvents (mostly Selexol or Genosorb) is basically comparable to the water scrubber technology. Besides CO$_2$ also H$_2$S, NH$_3$ and H$_2$O can be separated. Normally it is not required (and also not constructed in current plants) to schedule a desulfurisation step before the raw gas enters the absorption column. But it can be helpful to avoid significant H$_2$S emissions to the atmosphere by the exhaust gas or alternatively if there is an exhaust gas treatment technology installed, it will avoid SO$_2$ emissions. The pressures in the absorption column are normally ~ 8 bar. For regeneration in the desorption column, a temperature level of ~50°C is required. Typical CH$_4$ concentrations in the product gas stream are in the range from 93 – 98 %.

Because the exhaust gas stream includes >2% CH$_4$ (related to the CH$_4$ mass flow of the biogas) an exhaust gas cleaning is required. Because the exhaust gas normally contains H$_2$S the following exhaust gas treatment technologies are possible:

- Regenerative Thermal Oxidation
- Flameless Oxidation

Figure 5 describes the process and shows the places in the process where H$_2$S, H$_2$O and CO$_2$ are separated.
Figure 5: Flow chart physical absorption (using organic solvents).

Table 3 shows plant manufacturers that provide physical absorption upgrading plants using organic solvents for the production of biomethane.

Table 3: Plant manufacturers physical absorption (organic solvents) technology.

<table>
<thead>
<tr>
<th>Company</th>
<th>Technology</th>
<th>Internet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haase Energietechnik AG</td>
<td>Physical absorption (organic solvents)</td>
<td><a href="http://www.haase-energietechnik.de">www.haase-energietechnik.de</a></td>
</tr>
</tbody>
</table>

**Recommendations:**

- Avoid N\textsubscript{2} and O\textsubscript{2} in the raw gas stream because the system can not separate these gas compounds. It would cause a decrease of the heating value of the biomethane.
- Therefore a biological desulfurisation (by using air) in the digester is not recommended.
- Use an exhaust gas treatment technology to avoid CH\textsubscript{4} emissions to the atmosphere
2.1.4 Chemical Absorption (organic solvents)

The chemical absorption technology using organic solvents (mostly MEA or DEA) is a combination of a physisorption and a chemisorption. Besides CO\(_2\), H\(_2\)S and NH\(_3\) can also be theoretically separated. In practical use, a desulfurization step before the biogas enters the absorption column is required to avoid unwanted reactions in the process. The pressure in the absorption column is normally only a few mbar. For regeneration in the desorption column a temperature level of 120 - 160°C is required. Typical CH\(_4\) concentrations in the product gas stream are in the range from ~99 % if there is no N\(_2\) and/or O\(_2\) in the biogas flow. An exhaust gas treatment is not necessary.

Figure 6 describes the process and shows the places in the process where H\(_2\)S, H\(_2\)O and CO\(_2\) are separated.

![Flow chart chemical absorption (using organic solvents).](image-url)
Table 4 shows plant manufacturers that provide chemical absorption upgrading plants using organic solvents for the production of biomethane.

### Table 4: Plant manufacturers chemical absorption (organic solvents) technology.

<table>
<thead>
<tr>
<th>Company</th>
<th>Technology</th>
<th>Internet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cirmac</td>
<td>Chemical absorption (organic solvents)</td>
<td><a href="http://www.cirmac.com">www.cirmac.com</a></td>
</tr>
<tr>
<td>MT Energie GmbH &amp; Co. KG</td>
<td>Chemical absorption (organic solvents)</td>
<td><a href="http://www.mt-energie.com">www.mt-energie.com</a></td>
</tr>
<tr>
<td>Läckeby Water Group AB</td>
<td>Chemical absorption (organic solvents)</td>
<td><a href="http://www.lackebywater.se">www.lackebywater.se</a></td>
</tr>
<tr>
<td>Köhler&amp;Ziegler Anlagentechnik</td>
<td>Chemical absorption (organic solvents)</td>
<td><a href="http://www.koehler-ziegler.de">www.koehler-ziegler.de</a></td>
</tr>
<tr>
<td>DGE GmbH</td>
<td>Chemical absorption (organic solvents)</td>
<td><a href="http://www.dge-wittenberg.de">www.dge-wittenberg.de</a></td>
</tr>
<tr>
<td>Dreyer &amp; Bosse</td>
<td>Chemical absorption (organic solvents)</td>
<td><a href="http://www.dreyer-bosse.de">www.dreyer-bosse.de</a></td>
</tr>
</tbody>
</table>

**Recommendations:**

- Avoid N2 and O2 in the raw gas stream because the system cannot separate these gas compounds. It would cause a decrease in the heating value of the biomethane.
- Therefore a biological desulfurization (by using air) in the digester is not recommended.
- Be aware of high H₂S concentrations by using two activated carbon filters for desulfurization to be able to change one filter without having to stop the whole process.
- If sewage gas is cleaned/upgraded be aware of possible organic solvent peaks in the raw gas by the installation of an extra cleaning step for this.
- If there are siloxanes in the raw gas (especially if using sewage gas, biogas from waste or landfill gas) choose a special cleaning step for this.
- If using an activated carbon filter for siloxane removal, note that there are special charcoals available for H₂S removal and others for siloxane removal.
2.1.5 Membrane separation

Basically there are two different membrane separation technologies available: a dry high-pressure one and a low-pressure one. They are a combination of permeation and chemical absorption using organic solvents. For the practical use, only dry high pressure systems are currently relevant. CO₂, H₂O, H₂S and NH₃ pass the membrane nearly complete and will be found in the permeate stream. The retentate stream consists mainly of CH₄. In practical use, mostly two stage systems will be found. To increase lifetimes of the membrane modules it is mostly required to install a desulfurisation and drying step before the raw gas enters the membrane.

![Diagram of membrane separation](image)

**Figure 7:** Description of the CO₂ separation step of membrane systems.

Table 5 shows plant manufacturers that provide membrane upgrading plants for the production of biomethane.

**Table 5: Plant manufacturers membrane separation technology.**

<table>
<thead>
<tr>
<th>Company</th>
<th>Technology</th>
<th>Internet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Liquide</td>
<td>Membrane</td>
<td><a href="http://www.airliquide.com">www.airliquide.com</a></td>
</tr>
<tr>
<td>Cirmac</td>
<td>Membrane</td>
<td><a href="http://www.cirmac.com">www.cirmac.com</a></td>
</tr>
<tr>
<td>Gasrec</td>
<td>Membrane</td>
<td><a href="http://www.gasrec.co.uk">www.gasrec.co.uk</a></td>
</tr>
<tr>
<td>Terracastus Technologies</td>
<td>Membrane</td>
<td><a href="http://www.terracastus.com">www.terracastus.com</a></td>
</tr>
</tbody>
</table>
2.1.6 **Cryogenic upgrading**

The cryogenic biogas upgrading shown in figure 8 is an example of the Dutch company GtS. The process is separated in 5 steps:

Step 1: Gasdrying.
Step 2: Compression.
Step 3: Gascleaning – siloxane removal.
Step 4: Desulfurisation.
Step 5: Carbon dioxide removal.

![Cryogenic upgrading process](GTS, 2008)

**Figure 8: Overview cryogenic upgrading process (Example: GPP® of GtS).**

Table 6 shows plant manufacturers that provide cryogenic upgrading plants for the production of biomethane.

**Table 6: Plant manufacturers cryogenic upgrading technology.**

<table>
<thead>
<tr>
<th>Company</th>
<th>Technology</th>
<th>Internet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gastreatment Services bv</td>
<td>Cryogenic</td>
<td><a href="http://www.gastreatmentservices.com">www.gastreatmentservices.com</a></td>
</tr>
<tr>
<td>Prometheus</td>
<td>Cryogenic</td>
<td><a href="http://www.prometheus-energy.com">www.prometheus-energy.com</a></td>
</tr>
</tbody>
</table>

---
2.1.7 Other technologies
Contribution not available in time for inclusion in this report.

2.1.8 Comparison of upgrading technologies

Figures 9 and 10 show the total input power of PSA, water scrubber, chemical scrubber using organic solvents, physical scrubber using organic solvents and membrane systems – shown as installed capacity separated in electricity (yellow) and heat (orange).

![Energy demand biogas upgrading methods (250 m₃ biogas/h)](image)

Figure 9: Energy demand biogas upgrading systems as total input power in kW of all electricity and heat consumers (yellow: electricity; orange: heat), plant capacity 250 m₃/h [ISET, Bell; Dalkia, Schwalbenbach/Lange, 2008]
Figure 10: Energy demand biogas upgrading systems as total input power in kW of all electricity and heat consumers (yellow: electricity; orange: heat), plant capacity 1,000 m³/h [ISET, Beil; Dalkia, Schwalbenbach/Lange, 2008]

Figure 11: Plant availabilities (blue) in % based on manufacturer information [ISET, Beil; Dalkia, Schwalbenbach/Lange, 2008].

Figure 11 shows the plant availabilities (blue) of chemical scrubber using organic solvents, water scrubber, membrane system, physical scrubber using organic solvents and PSA systems.
2.2 Biogas cleaning technologies for \( \text{H}_2\text{S} \) reduction/removal

For biomethane grid injection as well as for vehicle fuel provision it’s necessary to clean the biogas of \( \text{H}_2\text{S} \).

The following table gives an overview about 8 different cleaning technologies for \( \text{H}_2\text{S} \)-reduction or nearly removal. Those methods are separated in methods for primary desulphurization and for precision desulphurization. The allocation takes place because of the reachable \( \text{H}_2\text{S} \) output concentration after the process. Furthermore the table shows if there is a necessity of \( \text{O}_2 \) for the process and if it takes place inside (internal) or outside (external) the digester.

The green marked methods are the most important ones for biogas upgrading systems.

Table 7: Overview of methods for desulphurization.

<table>
<thead>
<tr>
<th>No.</th>
<th>Method</th>
<th>( \text{H}_2\text{S} ) - Output-concentration</th>
<th>Necessity of ( \text{O}_2 )</th>
<th>Internal / External</th>
<th>Primary desulph.</th>
<th>Precision desulph.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Internal biological ( \text{H}_2\text{S} ) reduction (in the digester)</td>
<td>50 - 200 ppm</td>
<td>Yes</td>
<td>Internal</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>2</td>
<td>External biological ( \text{H}_2\text{S} ) reduction (out of the digester in a sprinkling filter)</td>
<td>50 - 200 ppm</td>
<td>Yes</td>
<td>External</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>3</td>
<td>Combination of external biological ( \text{H}_2\text{S} ) reduction with lye scrubber</td>
<td>20 - 100 ppm</td>
<td>(Yes)</td>
<td>External</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>4</td>
<td>Chemical precipitation using iron salts (sulphide precipitation)</td>
<td>100 - 150 ppm</td>
<td>No</td>
<td>Internal</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>5</td>
<td>Chemical precipitation using iron hydroxide</td>
<td>100 - 150 ppm</td>
<td>No</td>
<td>Internal</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>6</td>
<td>Iron oxide or iron hydroxide (in an external column)</td>
<td>&lt; 1 ppm</td>
<td>(Yes)</td>
<td>External</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>7</td>
<td>Adsorption / catalytic oxidation using impregnated activated carbon</td>
<td>&lt; 1 ppm</td>
<td>Ja</td>
<td>External</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>8</td>
<td>Zinc oxide</td>
<td>&lt; 1 ppm</td>
<td>No</td>
<td>External</td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

2.2.1 Internal biological \( \text{H}_2\text{S} \) reduction (in the digester)

The internal biological desulphurization inside the digester is the most applied method for primary desulphurization at agricultural biogas plants using CHPs.

An air injection into the gas phase of the digester takes place using a concentration of 2-12 % air.

The advantage of this method is its cost efficiency – regarding investment costs as well as operational costs.

Disadvantageous is the insufficient controllability. Furthermore \( \text{H}_2\text{S} \)-peaks can’t be reduced sufficiently. A further disadvantage is the accumulation of \( \text{O}_2 \) and \( \text{N}_2 \) in the biogas stream.

Therefore this method can mostly not applied as pretreatment for biogas upgrading systems because most upgrading technologies are not able to remove \( \text{O}_2 \) and \( \text{N}_2 \) out of the gas stream. It’s only possible if the biomethane will be injected in a natural gas grid that contains natural gas with L-gas-quality (low calorific value and mostly significant amounts of \( \text{N}_2 \) in the natural gas).
problem is the dilution of biomethane with N₂. To minimize or avoid these dilution effects there is the possibility to inject pure O₂ into the digester. Because the buying of bottled pure O₂ is mostly too expensive there is the possibility to generate pure oxygen directly at the biogas plant. For this e.g. a small Pressure Swing Adsorption (molecular sieve) can be used. This strategy is sporadic applied in large scale biogas upgrading plants.

Figure 12: A view into a digester shows the typical web used as surface for bacteria for a biological desulfurization in the digester [Jean Corell, 2008].

Figure 13: Sulphur precipitation on a digester web - view of an opened digester [Jean Corell, 2008].
2.2.2 External biological H\textsubscript{2}S-reduction (out of the digester in a sprinkling filter)

At this method the H\textsubscript{2}S-reduction takes place in an external column by fixed microorganisms. An air dosing (5 – 10%) into the system is required. Furthermore the provision of a nutrient solution for the bacteria has to be ensured.

The advantage compared to the internal biological desulphurization is the better controllability. If pure oxygen is injected into the system, the accumulation of N\textsubscript{2} in the biogas can be avoided and of O\textsubscript{2} reduced to a minimum.

Using conventional methods the main problem is the dilution of biomethane with the inert gas N\textsubscript{2} and with atmospheric oxygen. Due to the more comprehensive systems engineering compared to the internal biological desulphurization this method generates higher specific costs.

2.2.3 Combination of external biological H\textsubscript{2}S-reduction with lye scrubber

This technology is often called a “bio scrubber” or “bio washer” but it’s a combination of a lye scrubber (e.g. NaOH) and a biological desulphurization. It’s a two step process. In the first step H\textsubscript{2}S is bonded by the lye. In the second air is injected and the biological degradation takes place.

The following figures show the THIOPAQ® process.

The working principle is according to Paques bv:

- The H\textsubscript{2}S containing gas enters the absorption section and is washed by scrubbing liquid.
- The liquid has an alkaline nature and absorbs the H\textsubscript{2}S.
- The biogas exits the top of the absorber virtually free of H\textsubscript{2}S.
- The sulfide containing liquid flows into the bioreactor.
- In the reactor bacteria oxidize the sulfide with oxygen.
- The sulfur is then removed by use of a settler.
• The sulfide free liquid returns to the absorption section.

Compared to the methods described above there can be achieved higher purities and there is no accumulation of oxygen or nitrogen in the gas stream.

Disadvantageous compared to the above mentioned methods are higher specific costs and minor practical experience (especially compared to 2.2.1).

Figure 15: A THIOPAQ® plant for H₂S-reduction: Combination of external biological H₂S-reduction with lye scrubber [www.paques.nl].
2.2.4 Chemical precipitation using iron salts (sulphide precipitation)

Here an addition of soluted iron salts in the digester takes place. Sulfur ions are bonded under generation of iron sulfide.

Advantageous are low investment costs, high service experiences and the fact that no air and therefore no oxygen has to be injected into the biogas stream. Especially in agricultural biogas plants and sewage treatment plants this method has been applied successfully.

Disadvantageous are – depending on the H$_2$S concentration – high operational costs.

Currently it’s a typical primary desulfurization method for biogas upgrading plants if it’s not allowed to inject air into the gas stream.

2.2.5 Chemical precipitation using iron hydroxide

This method is comparable to 2.2.4 but here the iron hydroxide is added in solid form into the digester where the following reactions take place:

\[
2 \text{Fe(OH)}_3 + \text{H}_2\text{S} \rightarrow 2 \text{Fe(OH)}_2 + \text{S} + \text{H}_2\text{O} \\
\text{Fe(OH)}_2 + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2\text{O}
\]

Advantageous are low investment costs, high service experiences and the fact that no air and therefore no oxygen has to be injected into the biogas stream.

Compared to the iron salt dosing this method has lower operational costs and the handling of iron hydroxide is easier as of iron salts.
2.2.6 Iron oxide or iron hydroxide (in an external column)

Iron hydroxide reacts with H$_2$S to Fe$_2$S$_3$ and water. If using single-stage systems the regeneration can be applied by injecting 1-5% air into the reaction column. Here Fe$_2$S$_3$ reacts with oxygen and water again to iron hydroxide and elemental sulfur. The with elemental sulfur saturated material has to be removed out of the column. H$_2$S-output-concentrations < 1 ppm (related to 1000 ppm H$_2$S in the raw gas stream) are possible.

If the system is designed as two-stage system (2 columns) the injection of air (and therefore oxygen) in the biogas stream can be avoided. The raw biogas streams through the first column and iron sulfide is generated. In parallel in the second column air is injected and the regeneration takes place.

2.2.7 Adsorption / catalytic oxidation using impregnated activated carbon

Here first a catalytic oxidation of H$_2$S takes place and following the adsorption at the activated carbon. As typical impregnations potassium iodide (KI) or potassium carbonate are used (K$_2$CO$_3$).

For an efficient operation of this method water (~ 60% relative humidity) as well as oxygen is required. The impregnation of the activated carbon operates as catalyst. H$_2$S and oxygen are soluted in a water film that’s placed on the surface of the activated carbon. O$_2$ reacts at a temperature level of 70 – 80 °C with H$_2$S to elemental sulfur (if KI is used as catalyst). If K$_2$CO$_3$ is used oxygen is also required. Here CO$_2$, H$_2$O und K$_2$SO$_4$ are generated.

Because of high operational costs it should be only used for precision desulphurization. If low H$_2$S-concentrations for the upgrading plant are required, this method is the most applied desulphurization technology.

A redundant design – normal operation in series connection (second one as police filter) - is recommended. When the first filter is saturated it’s possible to change the flow to the second filter without stopping the process.

2.2.8 Zinc oxide

At this method a reaction of H$_2$S together with ZnO to H$_2$O and ZnS takes place.

The main advantages very low outlet concentrations of H$_2$S (in the literature H$_2$S-concentrations in the area of ppb are mentioned) and there is also no injection of oxygen in the biogas stream necessary. Disadvantageous are high process temperatures (200 – 400 °C) and high costs for ZnO because there is no regeneration possible.

For biogas upgrading this method had no relevance by now - there could not be any practical applications identified.
2.3 Biogas cleaning technologies for H₂O, NH₃, N₂, O₂ removal
Contributions not available in time for inclusion in this report.

2.4 Biogas cleaning technologies for siloxane removal
Siloxanes are organic silicon compounds that are completely synthetic and don’t occur in nature.

How siloxanes can get in the biogas stream, is depending on the kind of biogas:

- By wastewater at wastewater treatment plants
- By waste at biogas plants that use waste as feedstock
- By waste in landfill gas

If siloxanes can cause problems in the biogas upgrading plant or also the grid is not known by now. But of course it’s depending on the concentration in the biogas. What is well known is, that siloxanes can cause damages in engines like CHPs that are operated with biogas.

The following table shows relevant organic silicon compounds with their key data. The orange marked ones are the most analyzed ones for the above mentioned biogases. Of them the most importance have Octamethylcyclotetrasiloxane D₄ and Decamethylcyclopentasiloxane D₅.

TMS and MOH occur mainly in landfill gases. Normally you won’t find TMS in sewage gas – because of its good solubility it remains in the digester mostly in the sludge or water phase.

Table 8: Overview key data of organic silicon compounds in biogases.

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbrev.</th>
<th>Formula</th>
<th>M [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethyisilan</td>
<td>TMS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethylsilanol</td>
<td>MOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexamethydisiloxane</td>
<td>L2</td>
<td>C₆H₁₄O₃Si₂</td>
<td>162</td>
</tr>
<tr>
<td>Octamethyltrisiloxane</td>
<td>L3</td>
<td>C₈H₁₈O₂Si₃</td>
<td>236</td>
</tr>
<tr>
<td>Decamethyldisiloxane</td>
<td>L4</td>
<td>C₁₀H₃₀O₂Si₄</td>
<td>310</td>
</tr>
<tr>
<td>Dodecamethylpentasiloxane</td>
<td>L5</td>
<td>C₁₂H₃₈O₄Si₅</td>
<td>384</td>
</tr>
<tr>
<td>Tetradecamethyhexasiloxane</td>
<td>L6</td>
<td>C₁₄H₄₂O₅Si₆</td>
<td>459</td>
</tr>
<tr>
<td>Hexadecamethylheptasiloxane</td>
<td>L7</td>
<td>C₁₆H₄₈O₆Si₇</td>
<td>533</td>
</tr>
<tr>
<td>Octadecamethyloctasiloxane</td>
<td>L8</td>
<td>C₁₈H₅₄O₇Si₈</td>
<td>607</td>
</tr>
<tr>
<td>Hexamethylcyclotrisiloxane</td>
<td>D₃</td>
<td>C₁₂H₃₈O₂Si₃</td>
<td>222</td>
</tr>
<tr>
<td>Octamethylcyclotetrasiloxane</td>
<td>D₄</td>
<td>C₈H₁₈O₄Si₄</td>
<td>297</td>
</tr>
<tr>
<td>Decamethylcyclopentasiloxane</td>
<td>D₅</td>
<td>C₁₀H₃₀O₂Si₅</td>
<td>371</td>
</tr>
<tr>
<td>Dodecamethylcyclohexasiloxane</td>
<td>D₆</td>
<td>C₁₂H₃₈O₆Si₆</td>
<td>445</td>
</tr>
<tr>
<td>Tetradecamethylcycloheptasiloxane</td>
<td>D₇</td>
<td>C₁₄H₄₂O₇Si₇</td>
<td>519</td>
</tr>
<tr>
<td>Hexadecamethylcycloctasiloxane</td>
<td>D₈</td>
<td>C₁₆H₄₈O₈Si₈</td>
<td>593</td>
</tr>
</tbody>
</table>

Because siloxanes are a sum parameter and concentrations are normally not given for one single substance the following table shows the conversion factor for a mixture of 50% D₄ and 50% D₅ mass related.
Table 9: Siloxane concentration conversion mg/m³ <-> ppmv (ml/m³).

<table>
<thead>
<tr>
<th></th>
<th>Molecular Volume (standard cond.)</th>
<th>Molecular weight (50% D4 + 50% D5)</th>
<th>Mass concentration (averaged)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22.41 l/mol</td>
<td>334 g/mol</td>
<td>14.90 mg/ml</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mass concentration</th>
<th>Conversion in ppm (volume related)</th>
<th>Conversion in ppb (volume related)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 mg/m³</td>
<td>0.067 ppmv</td>
<td>67.108 ppbv</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Volume concentration</th>
<th>Conversion in mass concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 ppmv</td>
<td>14.901 mg/m³</td>
</tr>
</tbody>
</table>

2.5 Biogas cleaning technologies for particulate removal
Contribution not available in time for inclusion in this report.

2.6 Exhaust gas treatment technologies for reduction of CH₄ emissions
There are different technologies available for reduction of CH₄ emissions to the atmosphere. The most applied technologies are the RTO (regenerative thermal oxidation), the catalytic oxidation and the FloxBurner described in the following sub chapters.

2.6.1 Regenerative thermal oxidation RTO
This technology is well known for treatment of gas streams contaminated with VOCs (volatile organic compounds). But it’s also possible to use it for the oxidation of low methane concentrations in gas streams like the exhaust gas of water scrubbers or from physical absorption using organic solvents (Genosorb / Selexol scrubbers). In a first step the exhaust gas is heated up to process temperature. It’s now possible to oxidize the CH₄ and also other gas ingredients like H₂S. If there are high concentrations of H₂S in the exhaust gas it causes SO₂ in the off gas after the exhaust gas treatment. The main advantage of this technology is that it can run autotherm with minimum CH4 concentrations of ~1.5 g CH₄/m³. Basically a heat recovery is also possible. In the following figures there are described two chamber and three chamber systems. The decision for a two or three chamber system depends on CH₄ load in the treated gas stream.
2.6.2 Catalytic oxidation
Contribution not available in time for inclusion in this report.

2.6.3 Flox Burner
Contribution not available in time for inclusion in this report.
3 Experiences and Recommendations

- Do site visits of currently running biogas upgrading facilities
- Use the experiences of plant operators
- Check references (reference plants)
- Call for tenders to get an overview of the “Who is delivering what for which price?”
- Exact specification of raw gas (biogas) quality
- Start early talks to your gas company (grid injection)
- Evaluate the legislative situation in your country for biogas upgrading
- Evaluate the legislative situation in your country for biomethane distribution
- Evaluate the requirements (biomethane quality) for grid injection
- Clarify: Which gas quality has to be reached and where (at the place of injection or at the place of the outlet of the natural gas grid)?
- Clarify: Which concentrations of which gas compounds are allowed?
- Clarify: Is it generally allowed to inject (also upgraded biogas) to the grid (not in each country it’s allowed to inject also upgraded landfill gas)?
- Note that biological desulphurization (addition of air into the digester or a reaction column) can cause N₂ and O₂ in the biogas → Not each upgrading technology can remove these compounds
- Be aware of the quality of process water for water scrubbers (fouling)
- Training of operators by the manufacturer is recommended

4 Conclusions

This report gives stakeholders willing to implement a biogas upgrading plant an overview about the state-of-the-art of technologies that are available for cleaning and upgrading of biogas to biomethane. It includes experiences of BIOGASMAX and project external plant operators as well as technology providers and gives recommendations to avoid faults in both the planning and the operating stages of plants.