Small scale biogas upgrading: Green gas with the DMT Carborex-MS® system

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Abstract

More and more effort is being put in the utilization of bio-solids. Bio-solids can be an important source for useful products like fertilizers and biogas. DMT has been developing biogas treatment plants for over 20 years following the market developments closely.

Biogas was first seen as a nuisance at e.g. landfills, creating odor problems and methane emissions. A flare has always been a cheap and simple solution. But with time more and more biogas was produced intentional from bio-solids to generate energy.

In the current market the choice for utilization of the biogas is usually a choice for a single technology (e.g. boiler, CHP or upgrading to natural gas/ fuel quality), which is than fixed for the next 10-20 years. At the same time economical feasibility, especially for biogas upgrading, but also the other technologies, is based on “the bigger the better” principle, which is relying on the benefit of scale. This is in contrast to the reality where the biggest potential for biogas production is on small-scale sites.

DMT has developed a biogas upgrading plant with the focus on small scale utilization of bio-solids. In this article it is shown that, also with a biogas production of only 50-200Nm³/h, it is feasible to utilize biogas as a combination of energy sources. The DMT Carborex-MS® is a modular plant built in a sea container(s). The biogas upgrading is performed with gas selective membranes. The upgraded gas with a methane concentration of 96-98% CH₄ can be used in the local gas grid, or can be further compressed to 220 bar and used as vehicle fuel (CBG). To optimize the energy balance and to prevent methane emissions, the off-gas from the membranes is burned in a micro-turbine, to produce electricity and heat.

Keywords

Carborex-MS, CHP, Biogas, Bio-methane, CBG, Car fuel, Gas separation, Green gas, Gas Membrane, Small Scale Upgrading

Introduction

The transition of fossil to renewable fuels is on its way! Biogas produced at landfills and/ or digesters can be considered as renewable fuel since it is produced from organic waste. Most commonly the biogas is converted to electrical energy by gas engines with an efficiency of around 40%. Increasing efficiency to levels near 100% will require upgrading of the biogas. This can be done with various processes. Upgraded biogas can be used as vehicle fuel or injected into the gas grid. Biogas used as vehicle fuel is one of the cleanest possible fuels, with hardly any CO₂ emissions and very low local pollutants. This is shown in figure 1.
Upgrading of biogas mainly evolves the reduction of CO\textsubscript{2}, H\textsubscript{2}S and H\textsubscript{2}O from the raw gas. The CO\textsubscript{2} is removed to increase the energy content of the gas. For vehicle fuel this is important, because it increase the action radius of the vehicles. When injecting the biogas in the gas grid a similar energy content will be required as compared to the gas already present. The CO\textsubscript{2} concentration is also important to ensure flame stability and energetic value for the end users. H\textsubscript{2}S needs to be removed to prolong the life time of the all use equipment, piping and burners since it is a very corrosive gas. When H\textsubscript{2}O is present in a gas stream condensation can occur which is highly undesired, therefore, it should be completely removed. Table 1 shows the composition of raw biogas and the demands of upgraded gas.

Table 1: Raw biogas versus biogas at natural gas quality (The Netherlands/ UK/ German) and biogas at maximum quality for vehicle fuel use.\textsuperscript{1,2}

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>Biogas</th>
<th>Natural gas Dutch</th>
<th>Natural gas German / UK</th>
<th>Vehicle fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{4}</td>
<td>v/v %</td>
<td>45-70</td>
<td>90-95</td>
<td>&gt;95</td>
<td>&gt;97</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>v/v %</td>
<td>30-45</td>
<td>&lt;8%</td>
<td>&lt;5%</td>
<td>&lt;1</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>v/v %</td>
<td>1-10</td>
<td>&lt;10%</td>
<td>&lt;5%</td>
<td>&lt;3</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>v/v %</td>
<td>0.2-1</td>
<td>&lt;0.1%</td>
<td>&lt;0.2-0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>H\textsubscript{2}S</td>
<td>mg/Nm\textsuperscript{3}</td>
<td>10-15.000</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>CF</td>
<td>mg/Nm\textsuperscript{3}</td>
<td>0-3000</td>
<td>&lt;dew point</td>
<td>&lt;dew point</td>
<td>&lt;dew point</td>
</tr>
<tr>
<td>H\textsubscript{2}O (dew point)</td>
<td>°C@8 bar</td>
<td>Saturated</td>
<td>&lt; -8</td>
<td>&lt; -8</td>
<td>&lt; -169</td>
</tr>
<tr>
<td>Caloric value</td>
<td>kWh/Nm\textsuperscript{3}</td>
<td>5-7.7</td>
<td>8.8-10.8</td>
<td>8.4-13.1</td>
<td>10.7-11.6</td>
</tr>
<tr>
<td>Wobbe index</td>
<td>kWh/Nm\textsuperscript{3}</td>
<td>4.8-8.4</td>
<td>12.0-12.3</td>
<td>12.8-15.7</td>
<td>14.1-14.8</td>
</tr>
</tbody>
</table>

Many companies that provide upgrading plants design systems which are suitable and optimized for large scale biogas upgrading. The high investment costs of the installations show that with the present grants and gas prices, approximately 500-1000 Nm\textsuperscript{3}/h of raw gas is needed to make the plant economically viable. However, most of the biogas is produced at farm scale digesters and waste water treatment plants on a much smaller scale. This causes a loss in potential of upgradable biogas. Therefore, DMT developed a system which can upgrade biogas on a small scale in an economical viable way.

**Choosing the right upgrading process for the job**

There are several upgrading technologies on the market today. Each method has its advantages and disadvantages. The choice for the optimal process is influenced by multiple aspects e.g.: the biogas source and quality (e.g. landfill gas, manure digestion or sludge digestion), the desired final quality (gas grid or fuel) and local circumstance like availability of heat, power and space. Most upgrading plants are focused on large scale biogas production sites, and are optimized for maximum methane and energy efficiency. This results in relative high investment costs and a rather complex plant design and operation.
The large scale upgrading plants rely for a large part on the benefits of scale and are becoming more and more profitable at higher flows. However, there is a much larger volume of small scale sites. For these locations the benefit should not come from economics of scale but from mass production. For these sites it is also more important to utilize all the biogas as an energy source than as upgraded gas. Therefore, DMT re-engineered an upgrading plant based on the important aspects for small production sites. The final product is very basic and easy to reproduce as a standard (mass) product.

A short descriptions of the characteristics of the different upgrading techniques are presented in table 2. These parameters are compared to the demands for both small scale and large scale biogas upgrading plants. The different upgrading techniques taken in account are: pressurized water scrubbing (PWS), catalytic absorption (CA), pressure swing absorption (PSA), membrane separation (MS) and cryogenic liquefaction (CL). 

### Table 2: Comparison of demands for various upgrading techniques.

<table>
<thead>
<tr>
<th></th>
<th>PWS</th>
<th>CA</th>
<th>PSA</th>
<th>MS</th>
<th>CL</th>
<th>Large Scale</th>
<th>Small Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas quality</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Gas quantity v.</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Investment</td>
<td>Medium</td>
<td>Medium+</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Maintenance</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium+</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Operation</td>
<td>Medium</td>
<td>Complex</td>
<td>Complex</td>
<td>Easy</td>
<td>Complex</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Compact</td>
<td>Medium</td>
<td>Medium</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Medium</td>
<td>Yes</td>
</tr>
<tr>
<td>Methane eff.</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Emissions</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td>Waste streams</td>
<td>Continues</td>
<td>Continues+</td>
<td>Batch</td>
<td>Batch</td>
<td>Continues</td>
<td>Continues</td>
<td>Batch</td>
</tr>
</tbody>
</table>

**Green:** best match for small scale plants  **Yellow:** best match for large scale plants

**Gas quality:** The most important aspect is that the system needs to be able to convert the raw biogas to high quality upgraded biogas according to table 1. This means that CO₂, H₂S and H₂O removal should be sufficient. All techniques mentioned in table 2 are capable of accomplishing high quality gas with methane concentrations over 95%.

**Gas quantity variations:** There is a big variation in the possibilities of each process to handle fluctuations in the inlet biogas flow compared to the design rate. For large scale plants it is very important to always be able to treat all the gas, even when gas production is hundreds of cuubs lower or higher. For small scale biogas plants production is in most cases not even 100m³/h. Therefore the plant design can be more robust and if in the worst case scenario the gas has to be utilized in a CHP, this will not be a big problem.

**Investment and operational costs:** The production and upgrading of biogas must be profitable. To obtain short payback times for the installations, investment and operational cost should be minimal. For large scale installations the process may be more expensive due to the benefit of scale, high production efficiency and maximum operational availability. Small scale plants have to be much more ‘low budget’, also due to the limited financial possibilities of the investor.
**Complexity of operation:** The end users of the small scale system will most likely have limited knowledge of process technology when compared to larger companies/industries. Furthermore, there will be less working hours available to operate the installation and for maintenance. Therefore, the system should be able to operate fully automatic without any human interaction for weeks. Large scale plants can be more sophisticated and optimized to run at higher efficiency at the cost of a more complex operation and day to day supervision.

**Low maintenance:** As for complexity of operation, the maintenance should take minimum effort, especially for small scale sites. For that reason maintenance should preferable be restricted to 1 or 2 site visits a year.

**Compact:** Space, at for example farms, is often limited. In addition farms often have integrated households, esthetics is, therefore, also important. Consequently, a small footprint and indoors installation is desired. For large scale plants, size is less important, as they are usually located at industrial areas, WWTP or waste handling sites.

**Methane efficiency:** The methane efficiency is the percentage of methane which is converted into upgraded gas. This is very important for large scale plants because a small difference in efficiency means a large difference in output of biogas and, therefore, in profits (e.g. 0.5% less efficiency at 1000Nm³/h means >42.500Nm³/year upgraded gas extra = ± 25.000 euro). For small scale plants the change in output is relative small and the biogas can be easily used for other energy sources e.g. heat and power. This keeps the energy efficiency maximal.

**(Methane) emissions:** Emission of methane is an important issue since methane is a strong green house gas. This results in a significant contribution to the CO₂ footprint at large biogas flows. But for small scale this is slightly less important due to the lower flow amount and the big local emissions in the field coming from the e.g. the stock of cattle.

**Minimal waste streams:** Treatment or disposal of waste streams results in more costly and complicated operation. Waste streams should, therefore, be limited. For large scale system there can be a continuous flow of consumables and discharge streams. For small scale plants it is more important to have batch changes and disposal of consumables at e.g. once or twice a year.

**Conclusions**
Pressurized water scrubbing is the most suitable process for most large scale systems. It is a moderate simple, very robust technology which can be easily regulated to handle big variations in flow and gas quality. PWS has a high energy and methane efficiency and is moderately expensive. However, for small scale plants it is more important to have a cheap and very simple system. Variations in flow and methane efficiency are of less importance. Consequently, the membrane system is a better option, especially when combined with a CHP to provide an increased flexibility of the system and high energy efficiency.
Membrane separation

The principle of membrane separation is that the components of a gas mixture are separated by the difference of solution-diffusion through a polymer. The level of separation is determined by the flux of CO₂ through the membrane which is given by Fick’s law:\(^5\)

\[
J = \frac{k \cdot D \cdot \Delta p}{l}
\]

\(J\) = Flux
\(k\) = Solubility of CO₂ in the polymer
\(D\) = Diffusion coefficient of CO₂ through the polymer
\(\Delta p\) = The pressure difference over the membrane
\(l\) = The thickness of the membrane

\(k \cdot D\) is also known as the permeability (P). This permeability is influenced by operating conditions like pressure and temperature. The permeability of various components like CO₂, H₂O and H₂S compared to CH₄ gives the selectivity (\(\alpha\)) of the membrane. This tells how much faster CO₂, H₂O and H₂S will travel through the polymer compared to CH₄. The selectivity depends on the characteristics of polymer used for the membrane. In figure 6, a relative indication is given for the diffusion speed of the various components found in biogas.

High permeability corresponds to a lower required membrane area. Higher selectivity corresponds to better methane recovery. Since these forces work opposite of each other a choice needs to be made between high permeability and high selectivity. Due to the relatively low gas flows of small upgrading systems, it is better to fixate on high selectivity to obtain the best result.

As mentioned before, an important aspect of membrane separation is the recovery rate of the methane. Through the use of membranes the gas is separated in a CH₄ rich stream and a CO₂ rich stream. The CO₂ rich stream also contains methane, at quantities of approximately 30 v%. The methane recovery of the total ingoing CH₄ feed is around 75%. For full scale membrane systems this can be enhanced by using multiple membranes, and feeding the CO₂ rich gas from the second membrane into the feed of the system. Various other configurations (serial, parallel and combinations) for multiple stage membrane systems are possible. The most common configuration is shown in figure 7.\(^6\)
If this configuration is used, extra energy is needed to recompress the CO₂-rich stream from the second membrane stage. The CO₂-rich stream from the first membrane still contains methane but the result is a total methane recovery close to 95%. This means that the CO₂-rich stream still needs to be treated with for example thermal or catalytic oxidation. This configuration is normally used to optimize large scale plants. The disadvantage for this configuration is that the price and complexity of the plant increases due to a bigger compressor, double amount of membranes and a catalytic oxidizing step.

The advantage of using a single stage membrane system is that the CO₂-rich stream contains enough methane to use it as fuel in an energy recovery unit (e.g. a CHP). For small scale systems the energy from the waste gas can then be easily used for the local energy demand. Implementing this energy recovery unit in the small scale systems has another advantage. It provides a high flexibility in gas utilization, for example, in situations where there is no or less demand of upgraded gas. The simplified membrane configuration is shown in figure 8.

The CarbOrex® system as small scale biogas utilization plant.

The idea of a simple, cheap and robust plant for biogas upgrading implemented with membranes and an energy recovery unit resulted in the DMT Carborex-MS® system (see figure 9 for schematic flow diagram). The first step of the upgrading system consists of a preconditioning step. Here partial removal of water and particles from the gas stream takes place by condensation of the saturated incoming biogas. the Removal of H₂S from the raw biogas is optional for situations in which the inlet concentrations are too high for downstream equipment. Thereafter, the biogas is compressed which creates the driving force for membrane separation. At the membranes CO₂, H₂O and H₂S are separated from CH₄. The CH₄-rich stream goes to a polishing step. The CO₂-rich stream goes to the energy recovery unit. The polishing step will consist of further H₂O and/or H₂S removal depending on the required specifications. Whether the specifications are met is analyzed by the quality control system. When the gas is not within specification it will be send to the energy recovery unit. If the quality is good then the gas will be processed to the desired form of utilization.

Upgraded gas can be utilized in various ways using various options. The most simple, is delivery to a low pressure local gas grid. Reduction valves can be used to lower the pressure of the gas so it can be used for cooking and/or heating. The gas can also be directly injected in the medium pressure grid (6-9barg) or compressed for the high pressure national gas grid. For application as vehicle fuel, the gas can be even further compressed and stored at 220bar. This can be easily combined with a dispenser for local use.
Utilization of the treated gas directly at or nearby the production site is an important aspect for the system design. Especially for the production of vehicle fuel it is important to know if the gas can be bottled and sold to gas stations, in which case maximal fuel production is desired. In situations where the fuel is used for a limited amount of e.g. agricultural vehicles, it will not be wise to produce more than needed to maximize the running time of the installation and lower the investment and operational costs. The cost for quality monitoring and control also highly depends on the final user. If the final user is local then the quality variations are less important, furthermore, accuracy of the used analyzers can be lower. This has a big impact of the investment price for small scale units.

**Gold/Platinum: optimization of energy production or flexibility in upgrading capacity.**

Since membrane separation is a static process it is possible to design a systems with a constant upgraded gas production. Therefore, the small scale systems called the DMT Carborex-MS® gold is supplied in three sizes: 50/100, 100/150 and 150/200 Nm$^3$/h of raw gas per hour.

The gold system is optimized for the designed capacities of 50, 100 and 150Nm$^3$/h. The membranes can not upgrade more or less gas than designed. The possible surplus of maximum 50Nm$^3$/h of biogas can be utilized in the energy recovery unit combined with the off gas of the membrane. The other possibility is upgrading the control system of the small scale unit in combination with installation of multiple parallel membranes, instead of 1 membrane for the total flow. In this way the system can handle a fluctuating incoming gas stream. This system is called the DMT Carborex-MS® platinum system.

The platinum system is designed to handle a maximum raw biogas flow of 100, 150 or 200 Nm$^3$/h and which can always be turned down to a minimum of 50Nm$^3$/h. The results of biogas utilization for both systems are shown schematically in figure 10. The incoming gas flow is plotted versus the utilized gas flows. E.g. for the Gold B system 100-150m$^3$/h of biogas will deliver 50m$^3$/h of upgraded gas, 50m$^3$/h of spec gas from the membranes going to the CHP and 0-50Nm$^3$/h of raw biogas directly to the CHP. While the Platinum B system 100-150m$^3$/h of biogas will deliver 50-75m$^3$/h upgraded gas and 50-75m$^3$/h of off spec membrane gas to the CHP.

**FIGURE 10: DIFFERENCE IN RAW GAS UTILIZATION FOR THE GOLD AND PLATINUM SYSTEM AT AVERAGE BIOGAS COMPOSITION OF 60-65% METHANE.**
Economics
For small scale plants the most economical way to use the upgraded gas is to use the produced gas locally or as car fuel. There is a minimum production rate to make the system economical viable. One Nm$^3$ of upgraded biogas is equivalent to about one liter of diesel and, therefore, worth about 0.70 (natural gas price at the fuel station) to 1.20 euro (diesel price). The profit per Nm$^3$ of upgraded gas should be about 35-45ct to obtain a pay-back time of 5 years, this is without taking profits from the CHP unit in account. This means that the cost price for the biogas upgrading should be less than 20-30ct/Nm$^3$.

Figure 11 shows the price per Nm$^3$ of upgraded vehicle fuel in Euros. It becomes clear that at least 20 to 25 Nm$^3$/h of upgraded gas must be produced to obtain a production price of approximately 20 to 30 Euro cents per Nm$^3$. When the investment only compromises the upgrading, and there is already a CHP on the location, then the payback time for the same situation is just 3-4 years. Moreover, due to depletion of fossil fuel it is likely that fuel prices will increase.

Small scale plant Zalagaerszeg (Hungary)
The first plant build based on the small scale principle, but still with pressurized water scrubbing, is the upgrading plant at the waste water treatment facility of Zalagaerszeg in Hungary. The sludge of the bioreactor (nitrification-denitrification carousels) is being treated in an anaerobic digester, producing 50-100Nm$^3$/h of biogas. This gas is treated in a small scale upgrading unit which starts with a pre-treatment unit to desulphurize and optionally dry the gas. After the pre-treatment the gas can go directly to the CHP or continue to the upgrading. The gas can be upgraded to the desired methane quality which is 93-95% for the local natural gas grid, or >97% for vehicle fuel. The first results show that over 99,5% methane can be reached easily in the upgraded gas. After upgrading the gas pressure is 9 bar, and can be directed to the gas grid or further compressed to 220bar. At 220 bar there is a small gas storage connected to a dispenser at which the car fleet of the plant can directly fill their cars. The total unit is fully automatic and has a footprint of less than 100m$^2$.

In this way the waste water plant can direct the biogas to the process with the highest demand for energy in relation with cost price. This results in the highest efficiency towards energy utilisation both economical and sustainable. The return of investment for this specific plant is less than 3 years based on the current car feet of 10 cars. The maximum amount of cars to be fuelled is about 70 cars.
Discussion

To further fuel the conversion of biogas to energy and upgrading of biogas, it is important to lower the cost, especially for small scale plants. Therefore, also the quality control and demands have to be adapted for that purpose. When biogas is locally produced and locally used, or injected in small qualities into larger networks, the quality band could be bigger than the current standards and also the quality control may be allowed to have a larger error. Not only technology providers but also government and gas transport companies should look into the possibilities of biogas utilisation. Legislation and quality specifications are now very strict. Also there are no standards for biogas utilisation within Europe, which makes it difficult to use the full biogas potential\textsuperscript{7,8}.

Conclusions

The transition of waste to energy becomes more important to fulfill the world’s energy demand. In this article it is shown that biogas upgrading is not only economical viable for large scale installations. With the new small scale design and the usage of membrane technology, gas from the many small farm and WWTP digesters can be utilized to full potential.

References

\textsuperscript{1} DVFW-G 260 (D), GtS (NL), UKCS (UK)
\textsuperscript{2} Aansluit- en transportvoorwaarden gas, RNB, Nma
\textsuperscript{3} Prof. Dr. Ing. E. Weidner (2008) Report: Technologien und Kosten der Biogasaufbereitung und Einspeisung in das Erdgasnetz. Ergebnis der Markterhebung. Fraunhofer Institute:
\textsuperscript{4} Report: Comparing different biogas upgrading techniques; July 2008 \url{http://students.chem.tue.nl/ifp24/}, Technical University of Eindhoven
\textsuperscript{5} D. Dortmunit & K Doshi (1999) Recent developments in CO\textsubscript{2} removal membrane technology. UOP
\textsuperscript{6} E. Van Jarwaarde (2007) Benchmarking Novel Membrane Processes for CO\textsubscript{2} Removal from Contaminated Natural Gas. Technical University of Eindhoven
\textsuperscript{7} M. Persson & A. Wellinger (2006) Biogas upgrading and utilization. IEA Bioenergy
\textsuperscript{8} M. Broeils, Chances for small scale biogas upgrading in Sweden, University of Van Hall Larenstein, Leeuwarden.