Membranes for upgrading biogas to natural gas quality

Project Report
February 2012

REPORT

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1 Introduction

This report is written as a part of the ForskNG project 2007-1-6766 “Development of a CO_2-selective biogas membrane”.
Danish Technological Institute is managing the project and the role of the Danish Gas Technology Centre has been to describe requirements to upgraded biogas for gas grid injection and to compare membranes with other technologies for biogas upgrading.

Originally it was planned that DGC should perform laboratory of test a membrane unit. However, at the end of the project the membrane unit is not developed to a stage where it is ready for “proof of concept” testing. A test rig was designed for the membrane tests. A sketch and a brief description are given Appendix A. This report presents a description of the requirements to upgraded biogas distributed by the natural gas grid in Denmark as well as properties and performance of different technologies for upgrading of biogas including membrane technology.

The project is financially supported by Energinet.dk through the ForskNG program.

2 Summary and conclusions

As the title of the project indicates the overall aim of the project is to develop a membrane for upgrading biogas. This report describes the requirements that the biogas must meet in order to be injected into the Danish natural gas network. However, in a market where several different upgrading technologies are commercially available it is not enough to meet the technical requirements. Performance data and prices for competing upgrading technologies are described. Finally, other upgrading units based on membranes are described.

From the survey it is concluded that:

- Biogas must be upgraded to around 98 % methane in order to be injected into the Danish natural gas network.
- It is possible to achieve that using membrane technology. However, the methane loss and/or energy consumption is higher than for other commercially available technologies.
- It is possible to obtain the same performance with different selectivities of the membranes if they are configured differently. The membrane with the lowest selectivity will have the highest energy consumption. Depending on the price of membrane material it might be the most cost efficient solution to choose a cheaper membrane material and accept a higher energy consumption. This must be taken into account when membranes are chosen for a biogas upgrading unit.

This sets the scene for what a new membrane based upgrading unit must match in order to become a commercial success.

3 Gas quality requirements

Biogas that is upgraded for injection into natural gas grid must match certain requirements in order to prevent causing damage to gas grid and to secure safe operation of appliances connected to the grid.
In Denmark the requirements for gas quality in the distribution grid are described by The Danish Safety Technology Authority (Sikkerhedsstyrelsen) /1/, /2/, /3/. The requirements are listed in Table 1.

Table 1 Gas quality requirement for gas distributed in Danish distribution grids

Wobbe-index	50.8 – 55.8 $MJ/m^3(n)$
Relative density	< 0.7
H_2S	< 5 $mg/m^3(n)$
Total sulphur	< 30 $mg/m^3(n)$
Moisture	< 4 bar: < Ground temperature > 4 bar: < 0°C
Particle	Technically free
Ammonia	< 3 $mg/m^3(n)$
Oxygen	< 1 %
CO_2	< 3 %
Siloxanes	< 10 $mg/m^3(n)$
Microorganisms	No health risk is accepted

For gas injected into the high pressure transmissions other requirements must be fulfilled. E.g. the requirement for oxygen content in the transmission system is less than 0.1 % /4/.

From the table it is seen that no CH_4 concentration or heat value limit is stated. Instead a range of acceptable wobbe index is given. Wobbe index is defined as

$$W = \sqrt{\frac{H_u}{\rho_{rel}}}$$

where H_u is the higher heating value and ρ_{rel} is the gas density relative to the density of air. Assuming that the upgraded gas consists of CH_4 and CO_2 only, the relation between methane content and wobbe index is given in

Figure 1. The lower wobbe limit corresponds to 97.3 % of methane if the rest is CO_2. If the composition of the gas is measured with an accuracy of for instance ± 0.5 %, the biogas must be upgraded to a quality corresponding 97.8 % in order to be sure not to violate the lower wobbe index limit. This means that in reality biogas must be upgraded to methane content of around 98 % if it is to be injected into the Danish gas grid. Alternatively, the gas could be enriched by addition of propane in order to increase the wobbe index. However, that is a relatively costly option /8/.

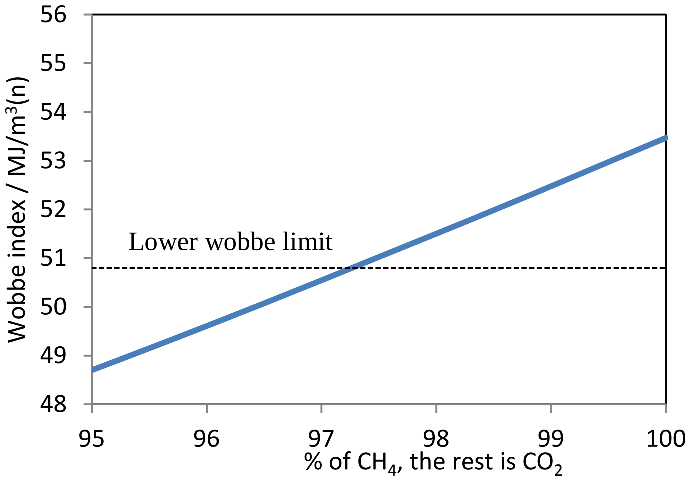

Figure 1. Relation between CH_4 concentration and wobbe index when it is assumed that the rest is CO_2.

4 Comparison of membranes and other technologies

A number of different technologies are commercially available for upgrading biogas to natural gas quality. The threemost common technologies are PSA (Pressure Swing Adsorption), physical absorption in pressurized water and chemical absorption using amines.
In 2008 Fraunhofer UMSICHT published a comparison of different commercial available units for upgrading of biogas to natural gas quality.

Table 2. Properties of different upgrading technologies /5/.

Parameter	PSA	Water scrubbing	Chemical scrubbing
Pre-cleaning needed	Yes	No[1]	Yes
Heat consumption [kWh/m^3 biogas]	0	0	0.55 /6/ 0.47@ 105 °C /7/
Electricity consumption [kWh/m^3 biogas]	0,25	0,25	<0.15 /6/ 0.031 /7/
Working pressure	7 bar	7 bar	Atmospheric
Operation range	+/- 15 % [2]	50-100 %	50-100 %
Methane loss	1-3%	1-2% [3]	<0.1%
Methane slip	<0.2 % [4]	<0.2% [4]	<0.1%

[1] Pre-cleaning needed if H_2S concentration > 500 mg/m^3
[2] CarboTech claims the same controllability performance as the two other technologies.
[3] Malmberg Water garanties less than 2 % methane loss.
[4] By catalytic oxidation of methane.

The costs the membrane upgrading must compete with is given in Figure 2.

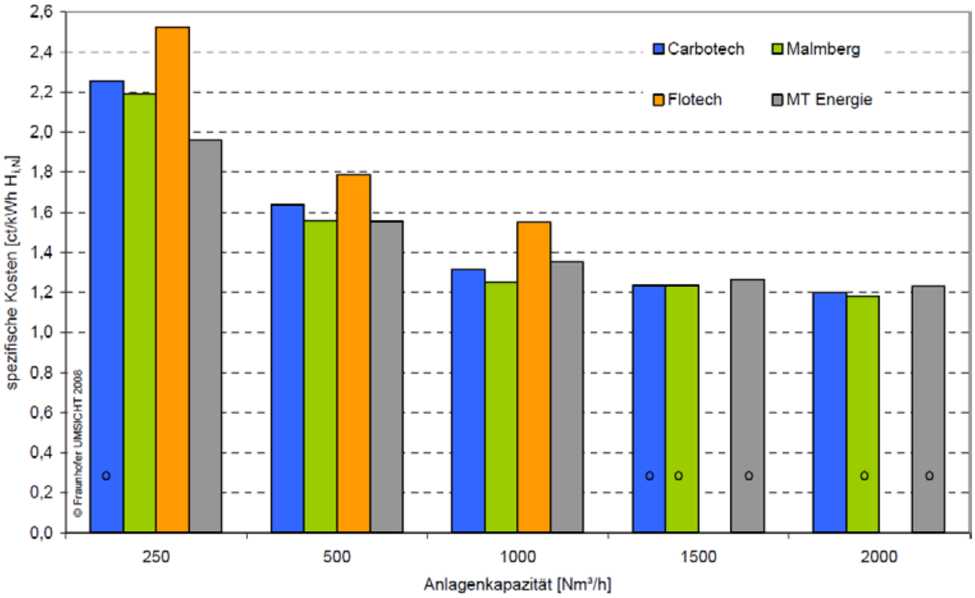

Figure 2. Upgrading cost for upgrading of biogas to natural gas quality. Given for different sizes and from different suppliers. Carbotech unit is based on PSA technology, Malmberg and Flotech are water scrubbing unit and MT Energie unit are based on chemical scrubbing /5/.

A Similar study has been conducted by DGC/8/. However, that study only included detailed information on PSA technology and water scrubber units and for one size only. The two surveys show similar results both regarding performance and costs. IEA refers to the FRAUNHOFER Umsicht survey regarding performance and cost of upgrading /9/.

5 Comparison with other membrane upgrading technologies

As membrane technology for biogas upgrading to natural gas quality is not common or commercial available only sparse information is available.
Table 3 and Table 4 show two different comparisons of different upgrading technologies including membrane technology. Furthermore, a comparison of energy consumption is given in Figure 3. As shown in Figure 2 the amount of gas to be upgraded is of significant importance for the price of upgrading. However, for values given in Table 3 and Table 4 no plant size is stated.
Both of the two tables state that the maximum methane concentration in the product gas is around 90 % and methane loss around 20 %.That is, however, not necessarily the case. It is possible to increase the methane content in the product gas and to reduce to methane loss at the expense of higher power consumption. See section 5.1 and 5.2.

Table 4 states that the upgrading costs to 0.12 €/m^3 of biogas using membrane technology. Table 4 comes from a poster that presents results from multidisciplinary student project at the Technical University of Eindhoven. In the project report on which the poster is based, it is stated that the upgrading cost is 0.22 €/m^3 (biogas) as 0.10 €/m^3 is added to the above mentioned 0.12 €/m^3 for required H_2S removal.

For comparison the table shows that the upgrading costs using water scrubber, PSA technology and chemical absorption is 0,13, 0,17 and 0,25 €/m^3 respectively.
This huge span is unexpected as Figure 2, which is based on information from supplier of commercial available upgrading units, shows the costs only vary modestly for the individual amounts of biogas. Therefore the costs of upgrading using membrane technology should be taken as indicative only.

Table 3 states that the energy consumption is 0.20 kW_e/m^3 biogas. As the subject is energy consumption it is assumed it is 0.20 kWh_e/m^3 biogas that is meant. This is the same as given in Figure 3 for membrane separation (50 kW / 250 m^3/h = 0.20 kWh/m^3).
It should be noted that Table 3 and Table 4 both come from Dutch references and the requirement for methane concentration in Holland is 85 % /9/. The reason for that is that the Dutch natural gas has a significantly lower

heating value than i.e. North Sea or Russian natural gas. Therefore, upgrading to a methane content of 90 % is sufficient in Holland but not in Denmark and most other European countries.

Table 3. Comparison of different upgrading technologies. From /11/.

	FROM BIOGAS TO GREEN GAS: UPGRADING TECHNIQUES			
	GAS CLEANING	CRYOGENIC TECHNIQUES	VPSA	MEMBRANE FILTRATION
	Liquid absorbs CO_2	Separating liquid CO_2	Active carbon adsorbs CO_2	Separating CO_2 via a membrane
Dutch suppliers	• **Cirmac** (LP Cooab-technique) • **DMT** (TS-PWS process) • **See also De Marke project***	• **GTS** (GPP-technique)	• **Cirmac** (VPSA = vacuum swing adsorption)	• **Cirmac** • **Van der Wiel Stortgas**
Methane loss (without using residue gas)	< 0.1% (Cirmac) < 1% (DMT)	< 0,5%	1–3%***	15–20%****
Methane content product gas	max. 99,5% (Cirmac) max. 98% (DMT)	max. 99,5%	max. 98%	max. 90%
Working pressure	atmospheric (Cirmac) 8–10 bar (DMT)	10–18 bar	6–8 bar	6–8 bar
Electricity consumption	0,05–0,12** kWe/Nm³ raw gas (Cirmac) 0,20–0,25 kWe/Nm³ raw gas (DMT)	0,20–0,28 kWe/Nm³ raw gas	0,25 kWe/Nm³ raw gas	0,20 kWe/Nm³ raw gas
Comments	CO_2-exhaust gas can be utilised usefully	Pure CO_2 (liquid) as useful by-product		Equipment is compact, simple and lightweight

The aforementioned figures are indications only, based on information provided by the suppliers.
* This demonstration project (see back page) used a third gas scrubbing technique, developed by TNO, Techno Invent and LTO Noord.
** 0.05 kWe/Nm³ applies if compression is not necessary (such as when injecting into the 100 mbar low-pressure grid). The energy consumption increases if compression is used to inject at higher pressures. Heat is also necessary to regenerate the absorption substance. The advantage of much lower energy consumption therefore only remains if there is residual heat available.
*** Up to 3% of the (strong greenhouse gas) methane ends up in the residual gas. This methane emission may not be acceptable to competent authorities that issue permits, so additional measures may be required.
**** With membrane technology (and from an efficiency point of view), the permeate gas should be used to generate energy.

Table 4. Comparison of different upgrading technologies. From /12/.

Technique	Investment cost €	Running cost €	Cost price upgraded biogas €/Nm^3 biogas	Maximum achievable yield %	Maximum achievable purity %	Advantages	Disadvantages
Chemical absorption	353,000	134,500	0.17	90	98	· Almost complete H_2S removal	· Only removal of one component in column · Expensive catalyst
High pressure water scrubbing	265,000	110,000	0.13	94	98	· Removes gases and particulate matter · High purity, good yield · Simple technique, no special chemicals or equipment required · Neutralization of corrosive gases	· Limitation of H_2S absorption due to changing pH · H_2S damages equipment · Requires a lot of water, even with the regenerative process
Pressure swing adsorption	680,000	187,250	0.25	91	98	· More than 97% CH_4 enrichment · Low power demand · Low level of emissions · Adsorption of N_2 and O_2	· Additional complex H_2S removal step needed
Cryogenic separation	908,500	397,500	0.44	98	91	· Can produce large quantities with high purity · Easy scaling up · No chemicals used in the process	· A lot of equipment is required
Membrane separation	233,000	81,750	0.12	78	89.5	· Compact and light in weight · Low maintenance · Low energy requirements · Easy process	· Relatively low CH_4 yield · H_2S removal step needed · Membranes can be expensive

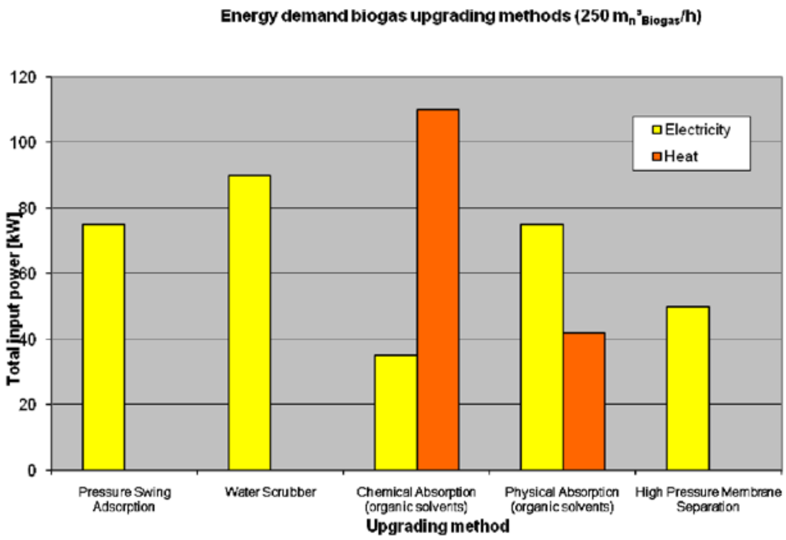

Figure 3. Comparison of energy consumption for different upgrading technologies. From /13/.

5.1 Upgrading by membrane technology

Recently Ryckebosch et al. published a review paper on upgrading of biogas /16/. Here it is stated that due to imperfect separation of CO_2 and CH_4 it is often not possible to obtain a satisfying methane concentration in one step that meets the Wobbe index requirement. However, by applying two or three steps a satisfying CH_4 concentration can be achieved. The drawback is the energy consumption for upgrading increases or the content of CH_4 in permeate (off-gas) increases /16/.

5.1.1 Austrian plants

In Austria two upgrading units based on membranes are in operation.
One is a single-step membrane unit where the CH_4 containing off-gas is mixed with raw biogas and fed to a CHP unit where it is utilized for heat and electricity production. However, despite a relatively large methane slip the retentate is to lean to be used as engine fuel as it is. Therefore the methane containing off-gas is supplied with raw biogas.
The other upgrading unit is a two-stage membrane where the offgas is fed to boiler. The membrane configuration of the two systems is shown in Figure 4 and Figure 5.
The energy consumption and obtained methane concentration in the upgraded gas is

- Single-stage: 0,280 kWh/m^3 of product (96,1 % CH_4)
- two-stage: 0,378 kWh/m^3 of product (98,1 % CH_4) /19/.

The methane recovery was not stated in /19/.

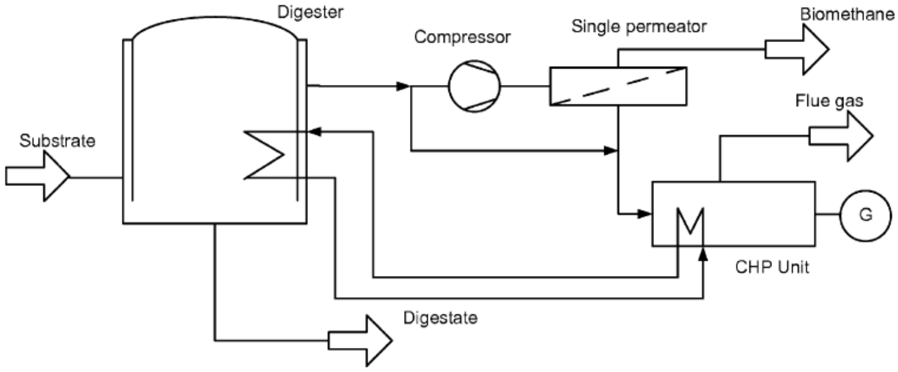

Figure 4. Simplified flowsheet for a single-stage configuration with CHP unit. From /18/.

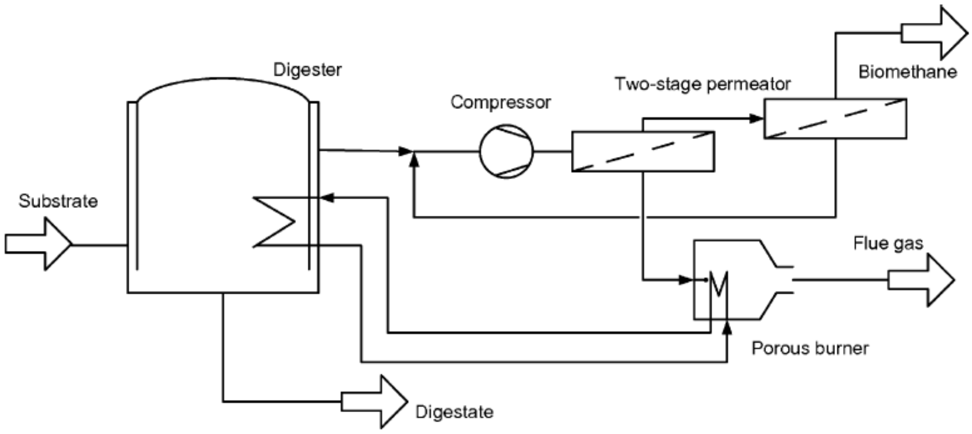

Figure 5. Simplified flowsheet for a two-stage configuration with permeate burner. From /18/.

As a fraction of the permeate from the second stage is recycled and re-compressed the two-stage configuration approach has a higher energy consumption compared to single-stage configuration.

The high methane concentration in the off-gas seems harmless as long as it is utilized for instance as shown in Figure 4 and Figure 5. Instead of using biogas as energy source for the biogas process, it is possible to use a lower quality fuel as straw or wood chips for that purpose and the biogas can be used where a higher fuel quality is required.

5.1.2 German plant

Thüga Energie's Kisslegg Rahmhaus plant is the only membrane based plant in operation in Germany /17/. The membrane itself is based on hollow polyamide fibres. It is a two-stage unit which allow methane concentrations varying from 90-99.9 %. It is designed to upgrade 500 m^3/h of raw biogas to 330 m^3/h of product gas with a content of 97 % of methane. However, the biogas production was only 300-350 m^3/h. The off-gas contains some methane which is subsequently oxidised. This results in 160 kW thermal energy that is used in the biogas production process. The 160 kW corresponds to around 7.5 % of energy in the biogas. The upgraded gas is supplied to a 55 bar natural gas grid. It is stated that the power consumption is 0,4 kWh/m^3 biogas. However, it is expected that it will be lower when the biogas production increases to the design level - 500 m^3/h. The investment costs were 2.1 mio. € for the upgrading unit and 0,7 mio. € for the injection unit including compression and gas quality measurements as well as 5,7 km. of pipe to the natural gas grid.

5.2 Membranes and energy consumption

Results of calculation of methane recovery and energy consumption has been published recently /18/. The methane recovery is defined as the fraction of methane in the biogas that will be present in upgraded gas. Some of the results of these calculations are given in Figure 6 for different selectivities of the membrane material. The area ratio is defined as the membrane area of the second step divided by membrane area of the first step. For all cases the target was a methane content of 98 % in the upgraded gas.

The figure shows that at very low area ratio, which corresponds to a single-stage configuration, it is not possible to achieve a high methane recovery. Even at selectivity as high as 50 the methane recovery is 85 % corresponding or a methane slip of 15 %. The methane slip is not a loss as it can be used for CHP as mentioned above or for producing process heat for the biogas reactor.

It is also possible to obtain 98 % methane in the product gas and a methane recovery of 85 % with membrane material with a lower selectivity if a two-stage configuration is used instead of a single-stage configuration. Figure 6 shows that the specific energy consumption is around 0,18 kWh/m^3 biogas applying a membrane with a selectivity of 50. With a selectivity of 10 and 20 the specific energy consumption will be around 0,21and 0,31, respectively.

This means that it is 15 % more costly from a power consumption point of view to apply a membrane with a selectivity of 20 instead of 50 at the above stated conditions. But on the other hand the 15 % additional power consumption also dictates how much extra it is possible to pay for the more selective membrane materials. This must be taken into account when membranes are chosen for a biogas upgrading unit.

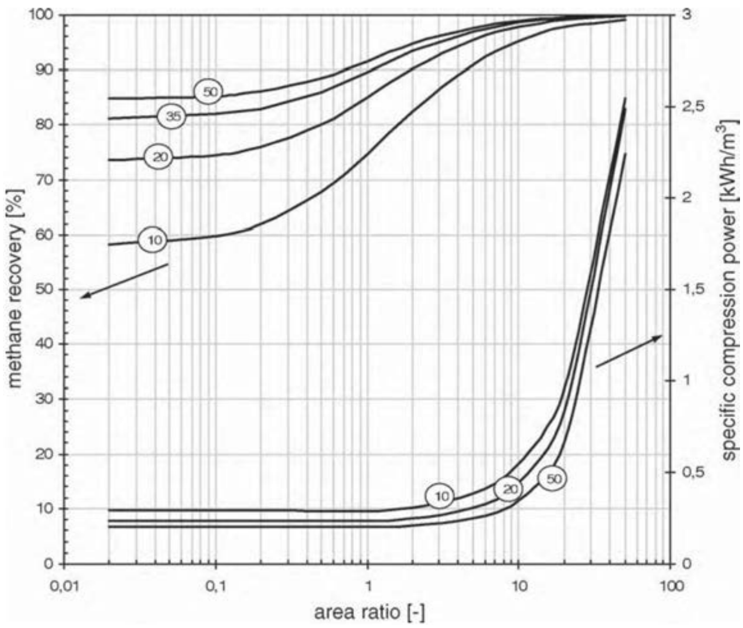

Figure 6. Model calculation of methane recovery and specific energy consumption for different area ratios and membrane selectivities. From /18/.

5.3 Long time performance

Miltner et al. /16/ has reported that some of the trace compounds can have adverse effects on the membrane performance in the gas permeation. The permeation of heavy hydrocarbons can promote temporary and permanent polymer changes like plasticization, swelling and compaction of the membrane material. Therefore the reduction of the concentration of these components is a crucial step in biogas upgrading. Adequate gas pre-treatment must be applied if high process performance needs to be preserved for longer operational times. In Bruck/Leitha pre-treatment is mainly done by cooling to low gas temperatures (freeze drying), filtering and adsorption /16/, see Figure 7. Based on 24 month of operation it was found that application of an adequate gas pre-treatment leads to a prevention of membrane deterioration and to a significant enhancement of the overall plant durability.

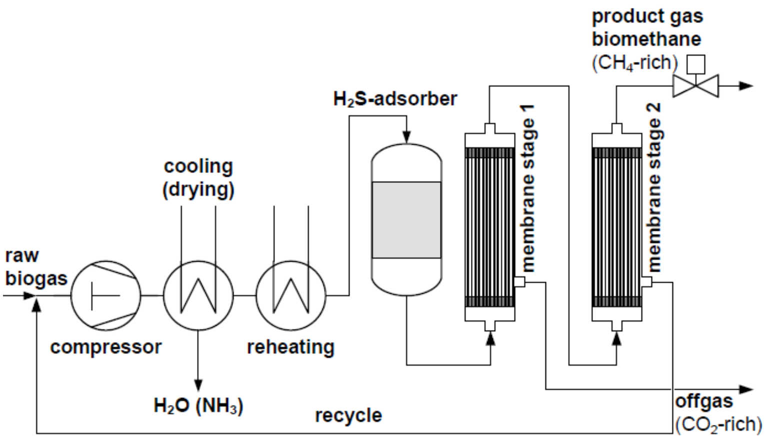

Figure 7. Flowsheet including the pretreatment before separation of the plant in Bruck/Leitha, Austria. The same unit as shown in Figure 5. From /16/.

5.4 Suppliers of upgrading unit based on membranes

According to /15/ the following companies deliver equipment for upgrading of biogas based on biogas membranes.

Air Liquide	www.airliquide.com
Bebra Biogas	www.bebra-biogas.com
Cirmac	www.cirmac.com
DMT	www.dmt-et.nl
Evonik	corporate.evonik.com
Gasrec	www.gasrec.co.uk
Haffmans	www.haffmans.nl
Memfoact	www.memfoact.no
Methapur	www.methapur.at
Terracastus	www.terracastus.com

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Appendix A

Test of biogas membrane

Testing of a biogas membrane unit has been prepared. The test setup is limited to test the separation of CH_4 and CO_2. The influence of other constituents as H_2S and moisture was omitted in the planning.
A simple sketch of the test setup is given below.

Experimental setup

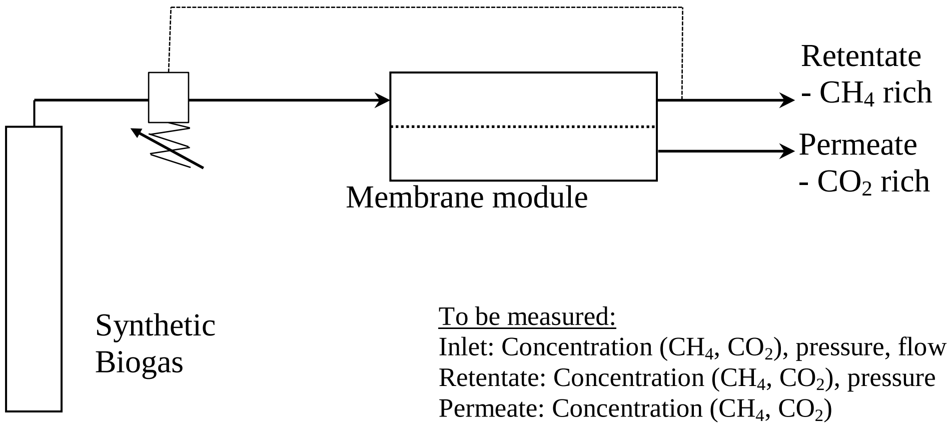

Figure A1. Sketch of the setup for membrane test.

Test gas and gas analysis
The test gas will be a synthetic biogas made from pure CO_2 and CH_4 only. This means that the gas will contain no moisture, H_2S or any other trace components.
This mixture is pressurized and stored in a vessel. The same mixture will be used for all conducted tests. The composition of the test gas as well as retentate and permeate will be determined by gas cromatograph (GC).

Tests will be conducted at different pressures and gas flows.