THE REVOLUTION IN BIOGAS UPGRADING UTILIZING GREEN GAS TO ITS FULL POTENTIAL USING HIGHLY SELECTIVE GAS SEPARATION MEMBRANES

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Abstract

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

Biogas was first seen as a nuisance at e.g. landfills, creating odour problems and methane emissions. Flaring has always been a cheap and simple solution. With time, more and more biogas was produced intentionally from bio-solids to generate energy. First in the form of heat and power, but now with the new renewable heat (energy) incentive, it is becoming increasingly attractive to upgrade biogas to natural gas quality and inject it into the natural gas grid. In this way, the gas can be utilized with the best energy efficiency.

There are several biogas upgrading technologies, ranging from old-fashioned water scrubbing to highly sophisticated cryogenic techniques. Each process has its advantages and disadvantages, depending on the biogas origin, composition and plant location. However, with the latest developments in membrane separation, DMT has developed the Carborex® MS system. This system, based on an ingenious, multi-stage, highly selective membrane system, is a perfect fit for almost all situations, especially for plants up to 750 Nm^3/h.

In this article it is shown that the DMT Carborex® MS is a compact modular unit built into a container. The biogas upgrading is performed with highly selective gas membranes. The upgraded gas with a methane concentration of 97-99% CH_4 can be used in the local gas grid, or can be further compressed to 220 bar and used as vehicle fuel (known as compressed biogas or CBG). The system has the highest energy recovery on the market (>98%) with only 0.15-0.20 kWh/Nm^3 energy consumption and <0.5% methane loss. The CO_2 is recovered as >99,5% pure. After an optional liquefaction step, the CO_2 can be obtained as a liquid at food grade purity (>99.9998%). Moreover, due to the liquefaction step the methane loss will be reduced to virtually zero.

Key words

Carborex® MS, CO_2 liquefaction, Biogas, Bio-methane, CBG, Car fuel, Gas separation, Green gas, Highly selective gas membrane, Membrane separation, Upgrading

Introduction

The transition from 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 by various processes. Upgraded biogas can be used as vehicle fuel or injected into the gas grid (Figure 1). Biogas used as vehicle fuel is one of the cleanest possible fuels, with hardly any CO_2 emissions and very low local pollutants.

Upgrading of biogas mainly involves the removal of CO_2, H_2S and H_2O from the raw gas. The CO_2 is removed to increase the energy content of the gas. For vehicle fuel this is important, because it increases the mileage of vehicles. When injecting biogas into the gas grid, a similar energy content will be required as that of the gas already present in the grid. The CO_2 concentration is also important to ensure flame stability and energetic value for the end users. H_2S needs to be removed to prolong the life time of the equipment, piping and burners since it is a very corrosive gas. If H_2O is present in a gas stream, condensation can occur, which is highly able, and therefore, should be completely avoided. Table 1 shows the composition of raw biogas and the requirements of upgraded gas.

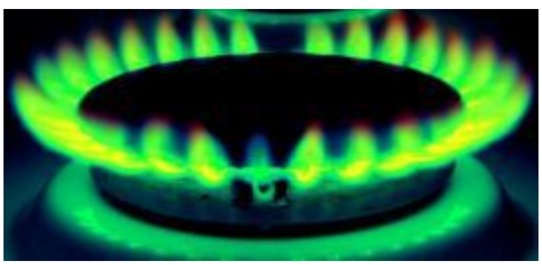

Figure 1: Green natural gas

Table 1: Raw biogas versus biogas of natural gas quality (The Netherlands / UK / Germany) and biogas of maximum quality for vehicle fuel use.[i, ii]

Component	Unit	Biogas	Natural gas Dutch	Natural gas German / UK	Vehicle fuel
CH_4	v/v %	45 -70	90 - 95	> 95	> 97
CO_2	v/v %	30 - 45	< 8	< 5	< 1
N_2	v/v %	1 - 10	< 10	< 5	< 3
O_2	v/v %	0.2 - 1	< 0.1	< 0.2 - 0.5	< 0.5
H_2S	mg/Nm^3	10 - 15.000	< 5	< 5	< 5
CF	mg/Nm^3	0 - 3000	< dew point	< dew point	< dew point
H_2O (dew point)	^{o}C@8 bar	Saturated	< -8	< -8	< -169
Caloric value	kWh/Nm^3	5 - 7.7	8.8 - 10.8	8.4 - 13.1	10.7 - 11.6
Wobbe index	kWh/Nm^3	4.8 - 8.4	12.0 - 12.3	12.8 - 15.7	14.1 - 14.8

There are several biogas upgrading technologies, ranging from old-fashioned but highly reliable water scrubbing to highly sophisticated cryogenic techniques. Each process has its advantages and disadvantages, depending on the biogas origin, composition and plant location. However, with the latest developments in membrane separation DMT has developed the Carborex® MS system, which the perfect solution for almost all situations, especially for plants up to 750 Nm^3/hr.

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, which is coated on a porous layer (Figure 2, bottom pictures). The level of separation is determined by the flux of CO_2 through the membrane which is given by Fick's law:[iii]

$$J = (k * D * \Delta p) / l$$

J = Flux
k = Solubility of CO_2 in the polymer
D = Diffusion coefficient of CO_2 through the polymer
Δp = The pressure difference over the membrane
l = The thickness of the membrane

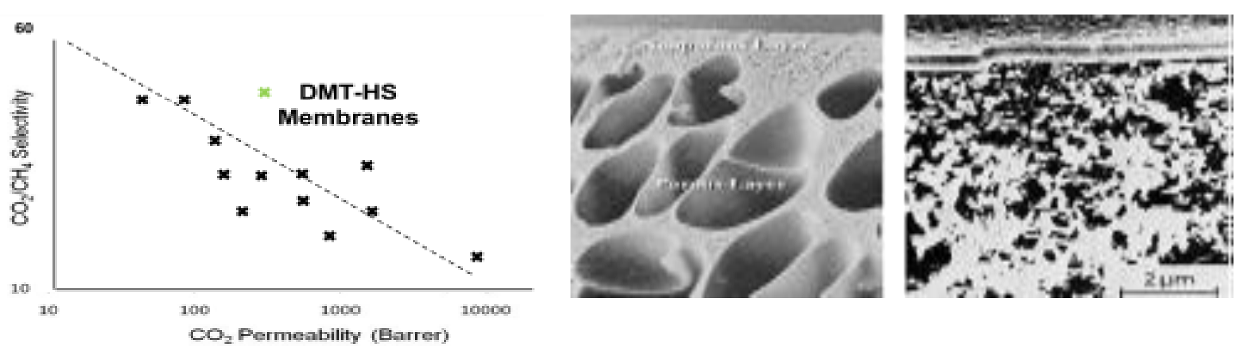

Figure 2 : Relation selectivity – permeability (left) and membrane surface (SEM microscope) (right)

k*D is also known as the permeability (P) and is an indication of the required membrane surface area per gas volume treated. The permeability is a characteristic of the polymer used, but it is also greatly influenced by operating conditions such as pressure and temperature. The permeability of various components such as CO_2, H_2O and H_2S compared to CH_4 gives the selectivity (α) of the membrane. This tells how much faster CO_2, H_2O and H_2S will travel through the polymer compared to CH_4. The selectivity mainly depends on the characteristics of the polymer used for the membrane. In Figure 3, a relative indication is given for the diffusion speed of the various components found in biogas. With a higher purity of the upgraded gas (longer time in the membrane) more methane will slip through the membrane and ends up in the CO_2 stream.

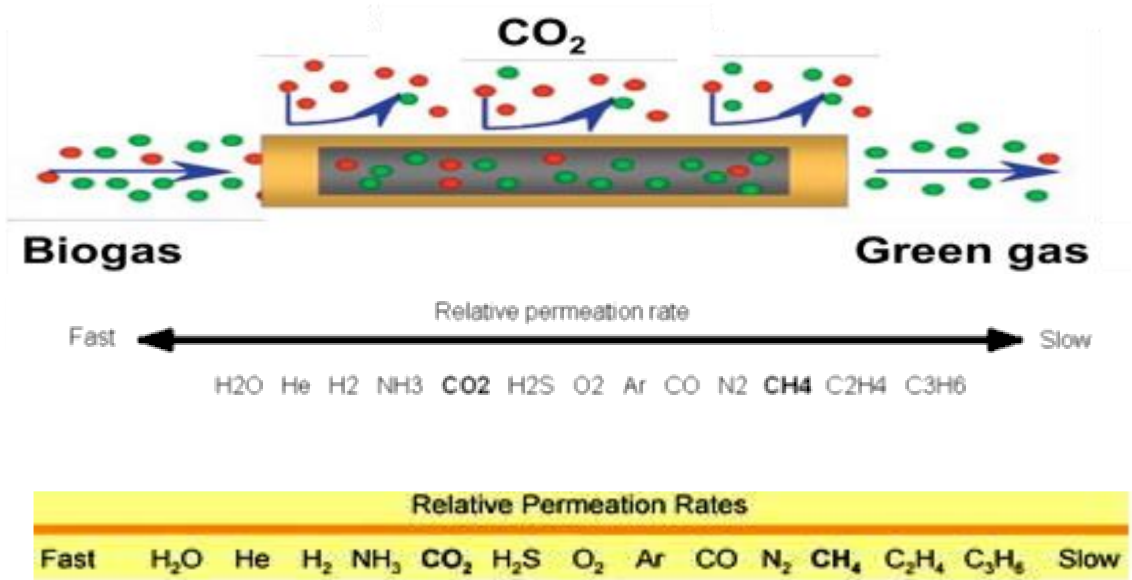

Figure 3: Relative permeation rate of various gas components.

Usually a higher permeability corresponds to a lower required membrane area and vice versa. Higher selectivity corresponds to better methane recovery. Since these forces work counter-effective (see Figure 2, top), until recently a choice had to be made between high permeability and high selectivity. Now DMT and a skilled polymer manufacturer have succeeded, in a close collaboration, to develop a membrane polymer with high selectivity as well as good permeability characteristics.

Multi-stage

As mentioned before, an important aspect of membrane separation systems is the total recovery rate of the methane. Through the use of membranes, the gas is separated into a CH_4-rich stream and a CO_2-rich stream. For a single-stage, low-selective membrane, the CO_2-rich stream may contain methane concentrations up to 25 v% compared to highly selective membranes, for which the methane loss has already decreased to 13 v% for a single pass system. Methane loss can be limited by using a second membrane in series, and feeding the CO_2-rich gas from the second membrane into the feed of the system. If this configuration is used, extra energy is needed to recompress the CO_2-rich stream from the second membrane stage, but the methane loss can be significantly reduced (see Figure 4). Various other configurations (serial, parallel and combinations) for multiple-stage membrane systems are possible.

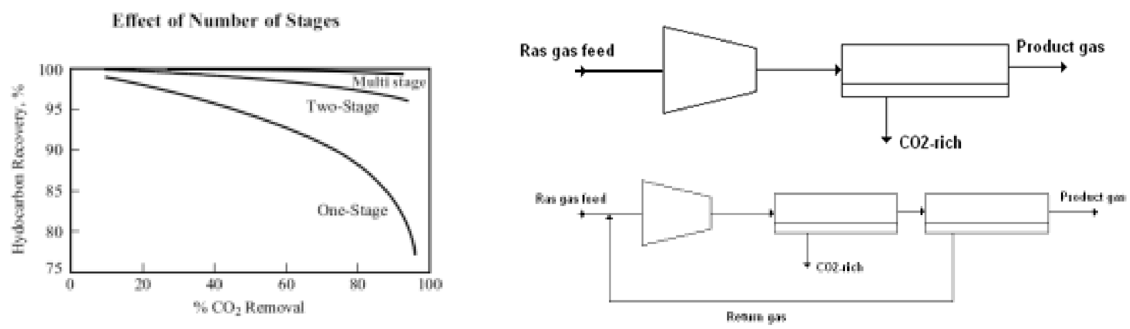

Figure 4: **One-stage, two-stage and multi-stage systems.**
Left: influence on methane recovery.
Right: examples of single-stage and two-stage system.

The most common configurations are shown in Figure 4. In two-stage configurations the methane loss can be greatly reduced, but is still ± 10% for low selective membranes and ± 5% for highly selective membranes. However, with the Carborex® MS system, DMT is using an unique advanced multi-stage system in combination with the developed polymer for highly selective membranes. Consequently, the methane loss is reduced to values below 0.5% and almost pure CO_2 is recovered with only 35% recompression energy.

	CH4 recover	CH4 in off gas	Recycle	
Single stage S=20	69,9	25,8	-	%
Single stage S=50	87,1	13,1	-	%
Dual stage S=20	90,4	10,1	+35,3	%
Dual stage S=50	96,1	4,3	+25,0	%
Multi stage S=20*	95,2	5,1	+156,3	%
Multi stage S=50	**99,6**	**0,5**	**+33,7**	**%**

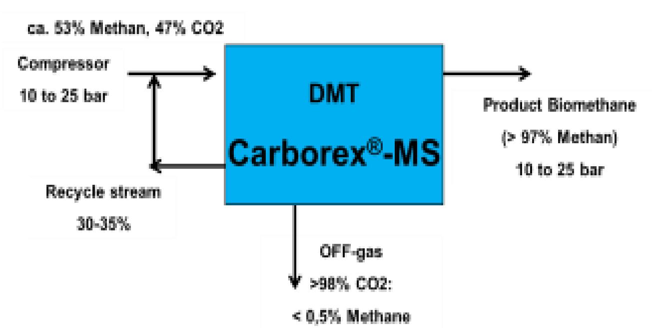

Figure 5: **Relation single-stage / multi-stage and low selective (S=20) and high selective (S=50) membranes. On the right: flow streams for the Carborex® MS system**

Carborex® MS system configuration

The idea of a simple, cheap and robust plant for biogas upgrading implemented with highly selective membranes has resulted in the DMT Carborex® MS system (see Figure 6 for schematic flow diagram). The first step of the upgrading system consists of the removal of H_2S from the raw biogas, which, depending on flow and concentration, can be done by activated carbon, chemical oxidation/ scrubbing or biological oxidation. The biogas is subsequently compressed, which creates the driving force for membrane separation. After compression the biogas is partly dried to prevent any condensation in the membrane and to obtain the desired dew point in the produced gas. At the multi-stage membrane system CO_2, H_2O and H_2S are separated from CH_4. After the final addition of THT odorant, nitrogen and or propane (depending on the gas quality requirements), the CH_4-rich stream can be directly injected in the grid (no additional drying is needed). The gas composition is analysed by the quality control system. An extra drying step is needed when the gas is used as vehicle fuel. The membranes can remove the CO_2 content in the upgraded bio-methane to concentrations < 1%. The CO_2 - off gas stream is > 99% pure. The total methane efficiency is 99.7% with just 0.3 % methane slip. The recycle stream back to the compressor is about 30%, which results in a total power consumption of +/- 0.2 kWh per Nm^3 biogas. The bio-methane can be produced between 9-20 bara. As seen in the next paragraph, these figures are unique in the biogas upgrading world.

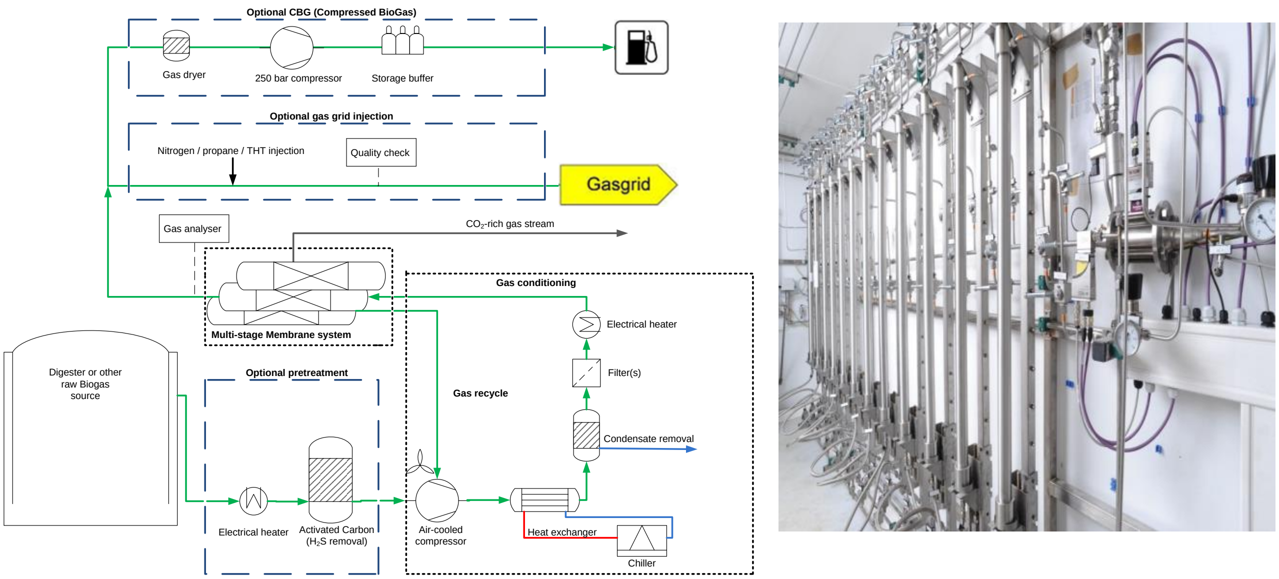

Figure 6: **PFD Carborex® MS system and picture of membrane container.**

CO_2 reuse by liquefaction

The off-gas contains over 99% CO_2. The remainder is mainly water vapour and traces of methane. The gas can be used directly in e.g. green houses. But it is relatively easy to further treat the CO_2 stream by drying, compression to ± 15 bar and cooling to about -35 °C. At this point the CO_2 turns into a liquid, whereas, the methane remains as a gas. The methane can be recycled to the membrane system, reducing the methane slip to 0! The CO_2 can be purified to food grade quality. The liquid CO_2 is easily stored and transported in bottles or bigger tanks.

Choosing the right upgrading process for the job

Besides the membrane systems, there are several upgrading technologies on the market today. Each method has its advantages and disadvantages. A short comparison of the characteristics of the different upgrading techniques is presented in Table 2. The different upgrading systems taken into account are pressurized water scrubbing (PWS), catalytic absorption (CA), pressure swing absorption (PSA), membrane separation (MS), highly selective membrane separation (MS-HS) and cryogenic liquefaction (CL). [iv,v]

Table 2: Comparison of demands for various upgrading techniques. (@ 9 barg)

	PWS	CA	PSA	MS	MS-HS	CL	
Produced gas quality	98	**99**	97	95	**99**	**99.5**	%
Methane slip	1	0.1/0.8[1]	3	15	**0.3**	**0.5**	%
Energy efficiency	**96/99[2]**	93-96	93	85	**98**	93	%
Electrical use	0.23	0.15/0.35[3]	0.25	**0.2**	**0.2**	0.35	kWh/m(3) biogas
Reliability / up time	96	94	94	**98**	**98**	94	%
Gas fluctuation allowed	50-100	50-100	85-100	**0-100**	**0-100**	75-100	%
CAPEX	2000	2150	2250	**1700**	**1800**	2300	€/m³ (4)
OPEX	6.1	6.5	6.7	**5.0**	**5.5**	7.1	Euro ct/m³ (4)
Bio Methane loss	110.000	95.000[1]	194.000	679.000	**55.000**	91.670	€/year
Foot print x height	0.15 x 12	0.17 x 12	0.18 x 4	0.09 x 2.5	**0.1 x 2.5**	0.12 x 3	m²/m³xm(6)
Maintenance needed	Medium	Medium+	Medium+	**Low**	**Low**	High	
Operation ease	Medium	Medium+	Complex	**Easy**	**Easy**	Complex	
Waste streams	**Water**	Chemicals	Carbon	**None**	**None**	None	

[1] 0.8 = Including methane slip/ use from CHP or CO_2 emissions/ energy from required heat source
[2] 99% including heat recovery by heat pump system.
[3] Additional 0.5 - 1 kWh heat is needed (which could be used to produce 0.2 kWh electricity).
[4] At 600 Nm³/hr
[5] compared to 100% recovery and operational time
[6] m²/m³ x m = m² surface per m³ raw biogas times the height of the plant

Highly selective membranes have more advantages in most cases as seen in Table 2. CA will only be the better option in case real excess "free" heat is available and green gas utilization takes place at low pressures. The only inconvenience of the MS-HS system is the scalability of the system. At higher flows (e.g > 1000 Nm³/h) the costs of membrane modules continues to increase the investment and operational costs linearly whereas the other technologies will profit from the benefits of scale. In these larger plants the PWS system remains one of the best options. However, the development of membranes is continuing, resulting in larger modules, higher permeability and better selectivity. Consequently, whitin a few years the membrane system will become feasible for higher flows as well.

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 economically viable. One Nm^3 of upgraded biogas is equivalent to about one liter of diesel and, therefore, worth about €0.65 (natural gas price at the fuel station) to €1.20 (diesel price). The profit per Nm^3 of upgraded gas should be about €0.35 to €0.45 to achieve a pay-back time of 5 years. This means that the cost price for the biogas upgrading should be less than €0.20 to €0.30 per Nm^3.

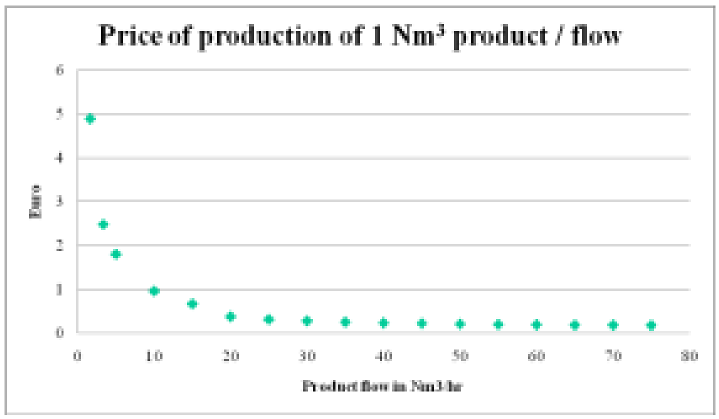

Figure 7: Product price per Nm³ (in Euros) of upgraded gas for various production flows

Figure 7 shows the price per Nm^3 of upgraded vehicle fuel in Euros for the Carborex® MS system. 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 € 0.20 to €0.30 per Nm^3. When the investment only relates to the upgrading, and there is already a fuel station on location, 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.

For larger flows a comparison is made between the Carborex®, PWS and a PSA system for a flow of ± 600Nm^3 of biogas with 55% methane and 500ppm H_2S. For this case study the investment costs for the upgrading, constructions on site and off-gas treatment are taken into account. In most countries a methane slip of about ± 1% may be discharged to the atmosphere. For higher values an RTO or other treatment is needed. The depreciation is taken over 12 years against a 7% interest rate, power costs at €0.07 per kWh and biogas revenues at €0.73 per Nm^3 bio-methane.

The consumables consist of activated carbon for desulphurisation, water for PWS, membranes and molecular sieves for PSA. The methane loss is divided in methane slip and availability. The methane slip is the methane emitted to the atmosphere or flares. The loss due to unavailability is the amount of revenues for bio-methane not produced because of the down time (MS = 2%, PWS = 4%, PSA =6%).

From Table 3 it is shown that by using the highly selective membrane system, additional 1.1 million pounds can be earned compared to PWS and even 2.5 million pounds compared to PSA. For lower flows membrane systems are more profitable, whereas for flows higher than 1000Nm^3/hr the break-even point for PWS is reached. In the near future this economic break-even capacity will increase due to larger membrane units with even better performance.

Table 3: Case study biogas upgrading 600 Nm^3/hr

	MS	PWS	PSA	
Investment (upgrading)	925.600	979.000	1.112.500	£
Investment (constr.)	26.700	48.950	71.200	£
Investment (off gas)	-	222.500	222.500	£
Total Investment	**952.300**	**1.250.450**	**1.406.200**	**£**
Depreciation (12y)	79.359	104.204	117.184	£
Interest (7%)	40.538	53.230	59.860	£/a
Power (0,07 eur/kWh)	65.069	74.364	75.786	£/a
Maintenance	20.737	22.250	25.365	£/a
Staff	3.204	12.994	11.570	£/a
Consumables (AC/MS)	50.730	20.025	24.511	£/a
Methane loss (slip)	9.906	19.309	55.574	£/a
Methane loss (availability)	40.430	80.454	118.243	£/a
Propane addition	157.410	177.724	190.660	£/a
Total	**467.382**	**564.554**	**678.753**	**£/a**

Results and discussion

A big step has been made in the economics for biogas upgrading by introducing multi-stage, highly selective membranes. The Carborex® MS system makes biogas upgrading easy and much more economical. The performance on bio-methane quality and methane efficiency are unique in the biogas world. But to further fuel the conversion of biogas to energy and upgrading of biogas, it is important to lower the costs, especially for small-scale plants. Therefore the quality control and demands have to be adapted for that purpose. When biogas is locally produced and locally used, or injected in small quantities into larger networks, the quality band could be bigger than the current standards so the quality control may be allowed to have a larger error. Not only technology providers but the government and gas transport companies as well should look into the possibilities of biogas utilisation. Legislation and quality specifications are now very strict. There are no standards for biogas utilisation within Europe, which makes it difficult to use the full biogas potential[vi,vii].

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[i]DVFW-G 260 (D), GtS (NL), UKCS (UK)

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