“Next generation biogas upgrading using highly selective gas separation membranes”

Showcasing the Poundbury project

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Abstract

More and more effort is being put into the utilization of organic waste streams in anaerobic digesters, producing useful products such as fertilizers and biogas. DMT has been developing biogas treatment plants for over 25 years, closely following market developments. It is becoming increasingly attractive to upgrade biogas to natural gas quality and inject it into the natural gas grid or use it as transport fuel. In this way, biomethane can be utilized with the highest energy efficiency.

There are several biogas upgrading technologies, ranging from the most commonly used 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 is based on an ingenious, multi-stage, highly selective membrane system and offers the best economics for almost all situations, especially for plants up to 800 Nm^3/h. Besides the economics, it offers several unique technical advantages.

The DMT Carborex® MS is a compact modular unit built into containers. The biogas upgrading is performed with highly selective gas membranes. The upgraded gas has a methane concentration of 97-99% CH_4 which greatly reduces the propane consumption and related costs. The bio-methane can be injected into the local gas grid, or further compressed to 220 bar and used as vehicle fuel. This system has the highest energy recovery available (>98%) with only 0.18-0.22 kWh/Nm^3 energy consumption and <0.5% methane loss, maximizing revenues. The CO_2 is recovered as >99.5% pure. It is the only upgrading technology that also removes significant amounts of oxygen (up to 70%).

In this article the theoretical background of membrane systems is explained along with operation data of the Carborex-MS® plant at Poundbury (largest commercial plant in the UK).

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

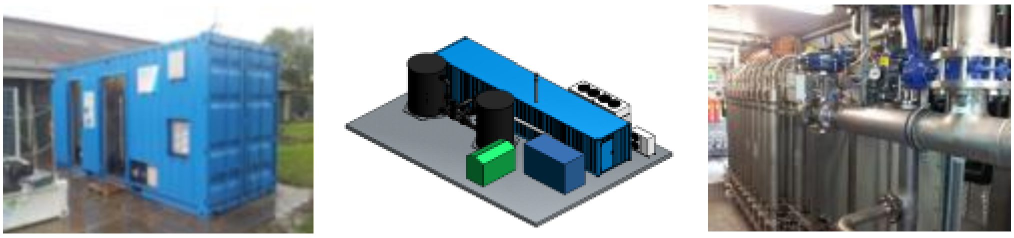


FIGURE 1: Biogas upgrading plants using highly selective membranes.

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 biogas is converted into electrical energy by gas engines with an efficiency of around 40%. Increasing efficiency to levels near 100% will require upgrading of biogas to natural gas quality. This can be done through various processes. Upgraded biogas (bio-methane) can be used as vehicle fuel or injected into the gas grid (Figure 1). Bio-methane 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. 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, an energy content will be required similar to 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 is very likely and therefore should be completely avoided. Table 1 shows the composition of raw biogas and the requirements of upgraded gas for several applications (grid NL/UK/DE and vehicle fuel).

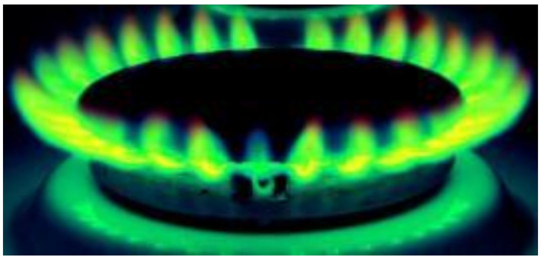


FIGURE 2: Green natural gas

Table 1: Raw biogas, natural gas and CNG (vehicle fuel) gas quality (NML / UK / DE)[i, ii].

Component	Unit	Biogas	Natural gas (NL)	Natural gas (UK/DE)	CNG
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)	^oC@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 provides the perfect solution for almost all situations, especially for plants up to 750 Nm^3/hr.

Choosing the right upgrading process for the job

In addition to the membrane systems, there are several upgrading technologies on the market today each of which has its advantages and disadvantages. A short comparison of the characteristics of the different upgrading techniques is presented in Table 2 and figure 3. The different upgrading systems taken into account are pressurized water scrubbing (PWS), catalytic absorption / amine wash (CA), pressure swing absorption (PSA), membrane separation (MS), highly selective membrane separation (MS-HS) and cryogenic liquefaction (CL)[iii,iv]. There are no standards for biogas utilisation within Europe, which makes it difficult to use the full biogas potential[v,vi].

Table 2: Comparison of performance for various upgrading techniques (result @ 8 barg injection)

	PWS	**CA**	**PSA**	**MS-HS**	**CL**	
Produced gas quality	98	**99**	97	**99**	**99.5**	%
Methane slip	1	0.1/0.8[1]	3	**0.3-0.5**	**0.5**	%
Energy efficiency[7]	**96/99[2]**	93-96	93	**98**	93	%
Electrical use	0.23	0.15/0.35[3]	0.25	**0.21**	0.35	kWh/m(3) biogas
Reliability / up time	96	94	94	**98**	94	%
Gas fluctuation allowed	50-100	50-100	85-100	**0-100**	75-100	%
CAPEX	2000	2150	2250	**1800**	2300	€/m^3 (4)
OPEX	6.1	6.5	6.7	**5.5**	7.1	Euro ct/m^3 (4)
Bio Methane loss	110,000	95,000[1]	194,000	**55,000**	91,670	€/year (4)
Foot print x height	0.15 x 12	0.17 x 12	0.18 x 4	**0.1 x 2.5**	0.12 x 3	m^2/m^3xm(6)
Maintenance needed	Medium	Medium+	Medium+	**Low**	High	
Operation ease	Medium	Medium+	Complex	**Easy**	Complex	
Waste streams	**Water**	Chemicals	Carbon	**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 Nm^3/hr

[5] compared to 100% recovery and operational time

[6] m^2/m^3 x m = m^2 surface per m^3 raw biogas times the height of the plant

[7] Total energy recovery: biogas methane in / (bio-methane out- electric- heat)

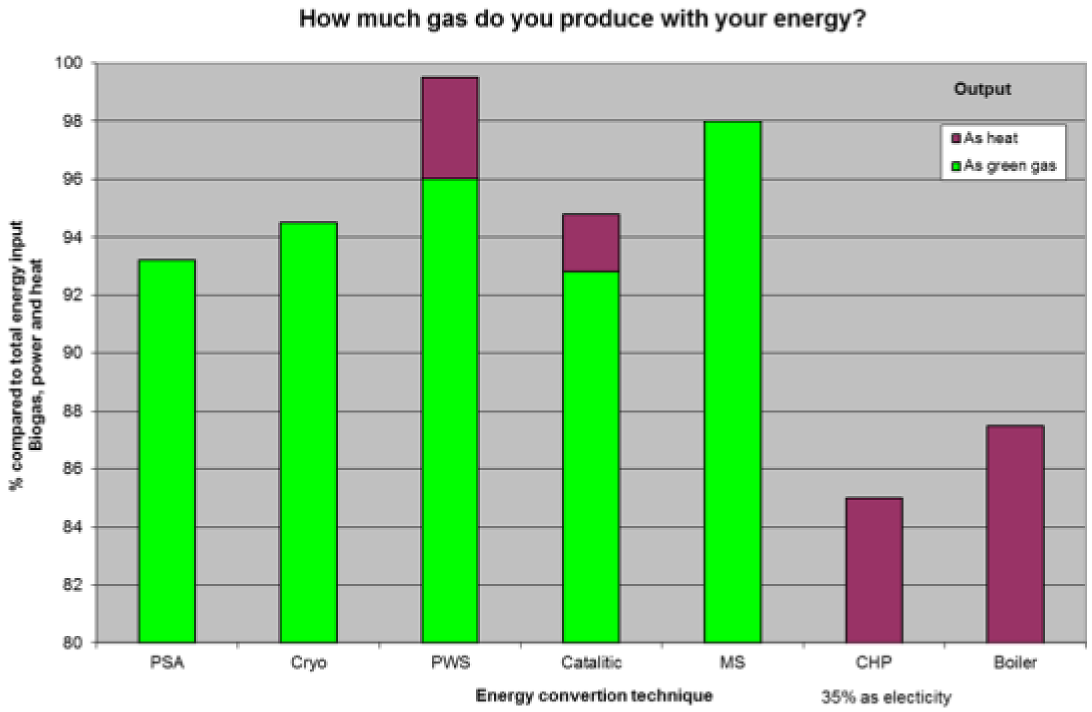


FIGURE 3: Total energy recovery for biogas conversion.

Highly selective membranes have predominantly more advantages, 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 Nm^3/h) the costs of membrane modules continue to increase linearly the investment and operational costs, 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, within a few years the membrane system will become feasible for higher flows as well.

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 4, bottom pictures). The level of separation is determined by the flux of CO_2 through the membrane which is given by Fick’s law[vii] (see Equation 1).

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

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

EQUATION 1 : Fick’s law

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 5, a relative indication is given for the diffusion speed of the various components found in biogas.

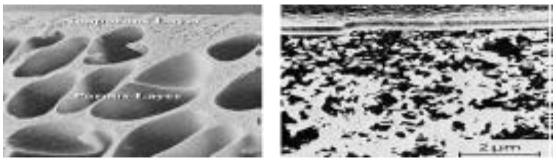


FIGURE 4: Membrane surface (SEM microscope)

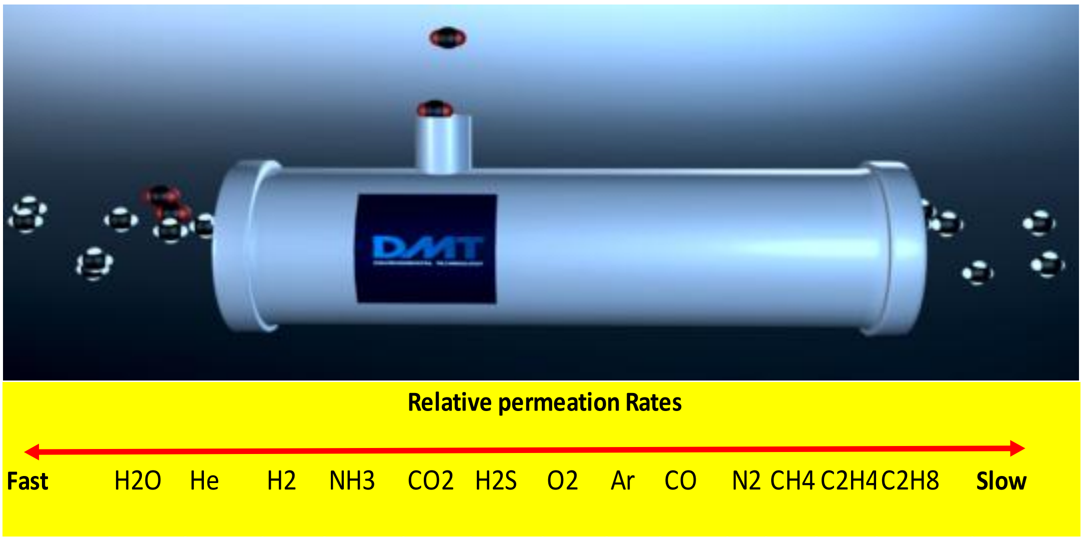


Figure 5: Relative permeation rate of various gas components

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. 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. 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 further limited by using a second membrane in sequence, 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 6). Various other configurations (serial, parallel and combinations) for multiple-stage membrane systems are possible.

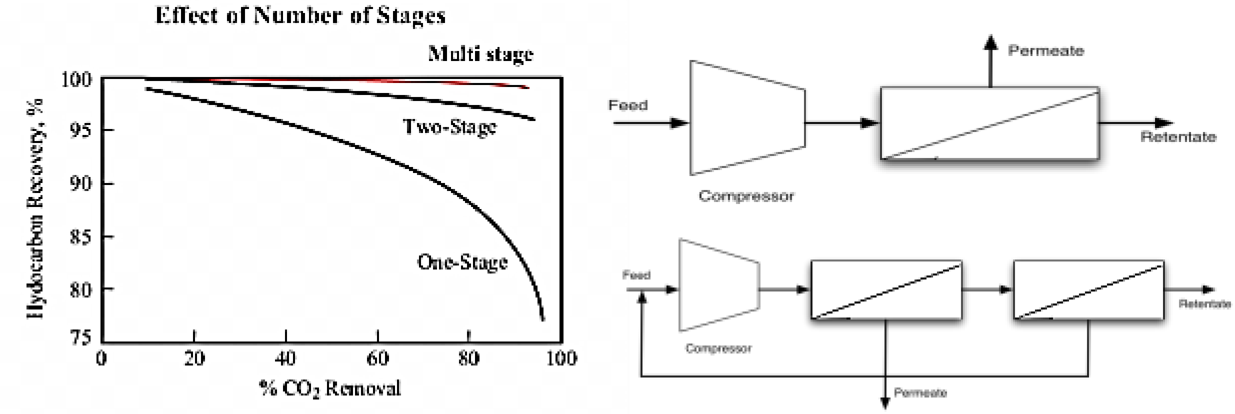
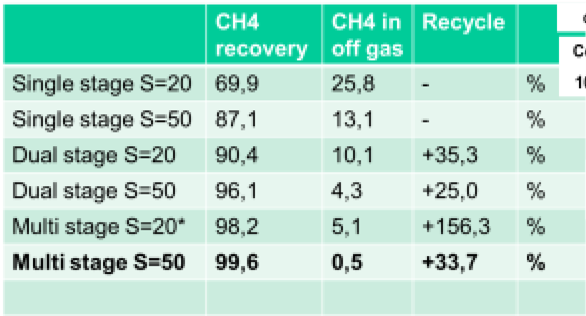


Figure 6: One-stage, two-stage and multi-stage systems.
Left: influence on methane recovery. Right: examples of a single-stage and two-stage system.

The most common configurations are shown in Figure 6. 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 a unique advanced **multi-stage** system in combination with highly selective membranes. Both bio-methane and off-gas streams have a two-stage configuration resulting in bio-methane containing less than 0.5% CO_2 and methane slip reduced to values below 0.5% with only 35% recompression energy.



	CH4 recovery	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*	98,2	5,1	+156,3	%
Multi stage S=50	**99,6**	**0,5**	**+33,7**	**%**

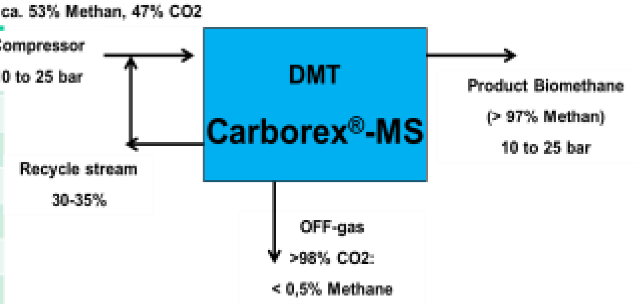


Figure 7: Relation single-stage / multi-stage and low selective (S=20) and highly selective (S=50) membranes. On the right: flow streams for the Carborex® MS system

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 8 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 dew point of the biogas is lowered to prevent any condensation of oil or water in the membrane. An advanced filter system protects the membranes and assures long membrane life-times.

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 into the grid (no additional drying required). The gas composition is analysed by the quality control system. An extra drying step might be needed when the gas is used as vehicle fuel. The membranes can remove the CO_2 content in the upgraded bio-methane to concentrations < 0.5%. The CO_2 - off gas stream is > 99.5% pure. The total methane efficiency can be as high as 99.7% with just 0.3 % methane slip. The recycle stream back to the compressor is about 35%, resulting in a total power consumption of +/- 0.2 kWh per Nm^3 biogas. The bio-methane can be produced between 8-20 bara. As seen in the next paragraph, these figures are unique in the world of biogas upgrading.

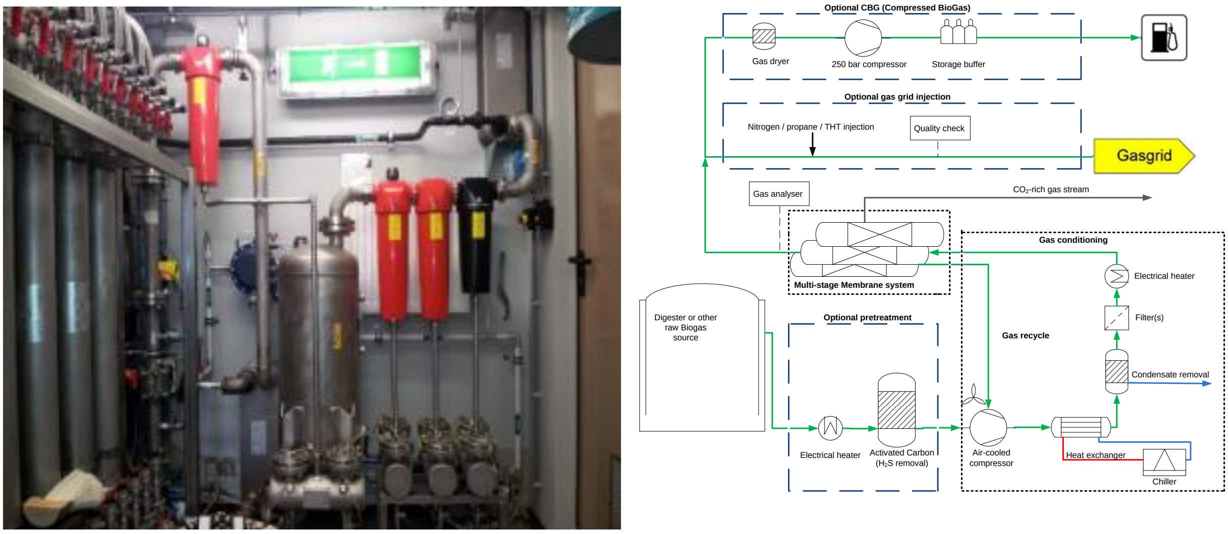


Figure 8: PFD Carborex® MS system and picture of membrane container

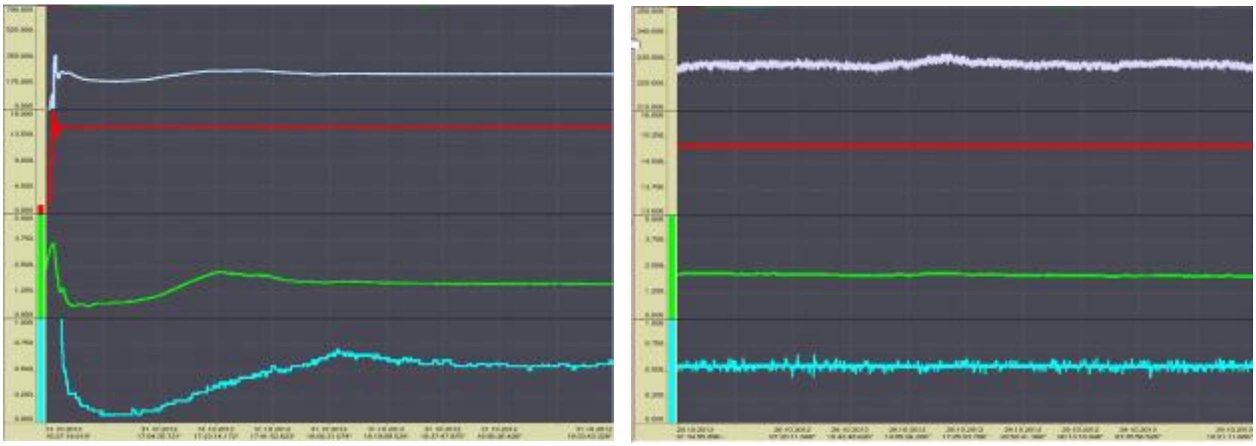
Results

Figure 9: Carborex® MS system for 650Nm^3/h at Poundbury (UK)

The first plants using the advanced three stage system in combination with highly selective membranes have been recently put into operation. Two specific cases give a lot of insight into the performance of the system. The first plant is located at Poundbury and is the biggest bio-methane producer in the UK with a capacity of 650Nm^3/hr of biogas (see Figure 9). The second plant is a small demonstration plant at ACRRES in the Netherlands. At this site new technologies are explored and demonstrated. The plant has a capacity of 50 Nm^3/hr and a maximum flexibility to operate the membranes in various configurations and at different pressures, temperatures, etc.

Most striking about the performance is the ease of operation. The system can be operated with just a single button and is therefore called “green button” technology. The second remarkable achievement is the short start-up time (see Figure 10). After pushing the “green button”, the gas directly reaches a purity of 95% methane or more. Within 2.5 minutes the bio-methane is at specifications and ready for gas-grid injection. These short start-up times make it possible to run the plant at any flow available by the digester with a start-stop system, resulting in a turn-down ratio of 100%!

The control over the system parameters is very stable and very direct. Over a period of 24hrs the CO_2 is kept within a very tight boundary of 2.1% +/- 0.1% and the methane slip is even controlled at 0.55% +/- 0.07%. In the gas to the grid, the caloric value or Wobbe is stable within 0.2MJ/Nm^3. If any other specification is desired the system switches to the new concentration within minutes.



Some other striking results is the achieved dew-point of just -85°C @ 16bara, making any other drying system redundant, which contributes greatly to the stability and robustness of the system. The system also removes over 70% of the oxygen from the biogas. This is a feature not show by any other upgrading technology until now making it possible to apply to strict regulations of several countries (such as e.g. the UK).

The energy consumption of the system depends on the requirements of the bio-methane and off-gas purities. The recycle flow increases from 30% tot over 90% when the methane slip is controlled from 1% down to 0.1%. This shows that an ultra-low methane slip is possible but at a higher power consumption. At the design methane slip of 0.3-0.7% the recycle is about 38-42%, which gives a power consumption of 0.19-0.23kWh/m^3 biogas.

These results give a view into the future, a future in which membranes are becoming more and more selective at lower and lower costs. Our goal is to reach <0.1% methane loss by the end of 2013 and increase the permeability by a factor of 10!

CO_2 reuse by liquefaction

The off-gas contains over 99.5% 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 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.

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.

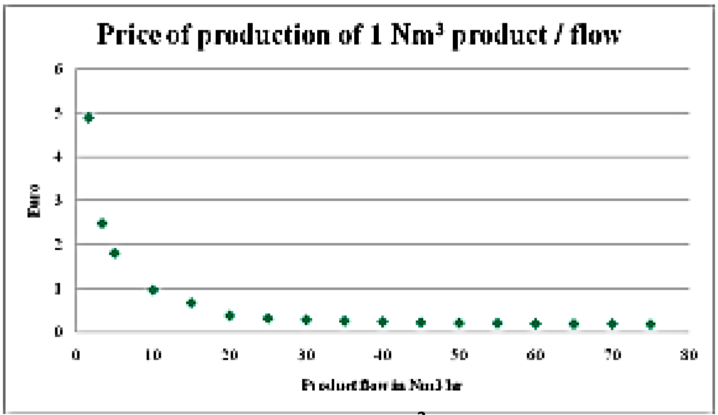
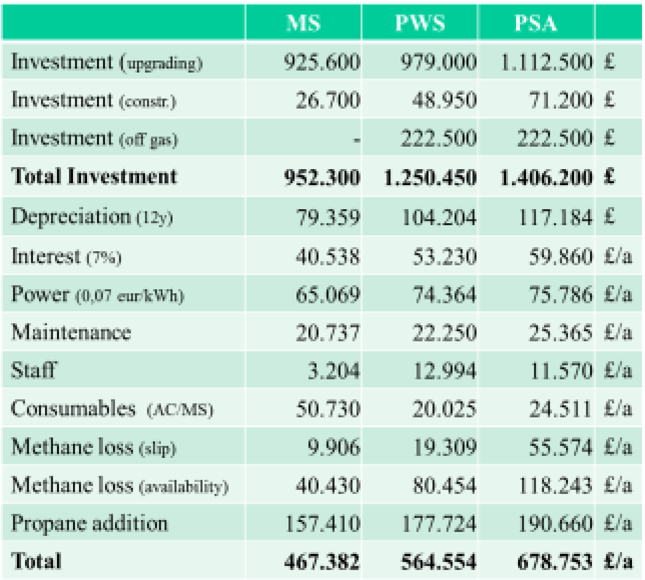


Figure 11: Product price per Nm^3 (in Euros) of upgraded gas for various production flows.

Figure 11 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.



	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**

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 into 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, an additional 1.1 million pounds can be earned (over 12 years) 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.

Conclusions

The developments in the world of biogas upgrading are increasingly fast, especially in the field of membrane separation. Advanced membrane configurations and new highly selective membranes yield the promise of easy biogas upgrading at low cost without methane losses. Already today, DMT shows with the Carborex® MS that it is possible to upgrade to a bio-methane contained of 99.5% with just 0.3% methane slip. This makes the system the most economical system for flows up-to 1000Nm^3/hr. Not only the process performance of the Carborex® MS is without its equal but also the operation of the system is a step in the future. The process can be controlled with a single button and just takes less than 2.5 minutes to reach its specifications. The ease of control also results in up-times of 98-99% or higher, maximizing profits for the user.

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