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A membrane based process for the upgrading of biogas to substituted natural gas (SNG) and recovery of carbondioxide for industrial use

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Abstract

A low pressure carbon molecular sieve (CMS) membrane based process to upgrade biogas from anaerobic digestion of agricultural waste to a substitute natural gas (SNG) has been tested on a pilot scale. The data extracted from the pilot plant was used to estimate membrane permeance and ideal selectivity of the CO2/CH4 gas pair. Four semi-commercial modules were tested. The results show that by using a membrane cascade and by carefully choosing the CMS modules, it is possible to produce a stream containing at least 90 vol-% CH_4 and a by-product containing at least 60 vol-% CO2. The substituted natural gas can be mixed with NG in the national grid and the latter by-product is intended for the production of liquified CO_2, suitable for use in greenhouses. At a pressure level of 8-16 barg, this process could offer simplicity and less investment and maintenance than other technologies.
Keywords: Substituted Natural Gas, Carbon Molecular Sieves, Gas separation, Biogas

1. **Introduction**

The use of biogas, a mixture of CO_2 and CH_4, as a high quality fuel, requires the removal of CO_2 as to increase its calorific value to that comparable to NG. There are three main technologies available for this duty: Water absorption (WA), pressure swing adsorption (PSA) using activated carbon and membrane gas separation (MGS) employing hollow fibre based membranes (polymers) or inorganic (carbons, zeolites etc.) materials. MGS for the upgrading of biogas is still in its infancy with less than 20 years of serious R&D behind the technology, but recent advances in MGS technology has revealed enormous potential by using pyrolyses as a technique to render precursor commercial polymer fibres into inorganic carbon molecular sieves with excellent strength, heat and chemical resistance. The membrane properties are controlled by pyrolysis techniques. By tailoring membrane properties, the manufacturer is able to deliver membranes, which suit the client. Another important advantage of CMS membranes is that they are in theory regenerable which would drastically decrease membrane replacement as is the case employing polymeric membranes.
The MGS based process aims at upgrading the biogas to SNG using low pressure (8-16 barg) and distributing the SNG in the natural gas network. The main advantage here is no energy loss so that apart from process heating, the net loss is zero. Polymer based MGS processes often use pressures up to 35 barg as the driving force. A prerequisite however is the proximity of a natural gas pipeline and the prior

acceptance of a sub-standard natural gas in the pipeline. The by-product of the MGS process is a stream rich in CO_2 which could be liquified to produce very pure, industrial CO2. After liquefaction, the remaining biogas components, which includes CH_4 are recycled to the MGS process, thereby minimising the loss of biogas. Other possibilities also exist like using the CO2, in gaseous form, directly in greenhouses if within proximity of the biogas plant.

Process design

An MGS pilot plant used in previous studies, was retrofitted with CMS membranes handling biogas flowrates of up to 30 Nm3.h-1. The plant was situated at a centralised biogas plant in Denmark, which produces 400 Nm3.h-1 biogas containing, on a dry basis, 69 vol-% CH4, 31 vol-% CO2 and trace amounts of ammonia (NH3) and hydrogensulfide (H2S). The plant could intermittently produce SNG containing up to 95 vol-% CH_4 with minimal amounts of CO_2 and residual H_2S. The SNG was returned to the main biogas network by means of a pressure reduction station.
The biogas was biologically desulfurised in a bioscrubber reducing the H_2S content from 2000 ppm to 5 ppm before the pilot plant. The gas, at 20 mbarg, enters the pilot plant where the gas is compressed by a roots blower to 0,7 barg. A PSA unit operating at 0,6 barg removes excess watervapour and the gas is then compressed to 6-10 barg in a reciprocating piston compressor. A final treatment step consists of a activated carbon bed which removes traces of H_2S and NH_3.

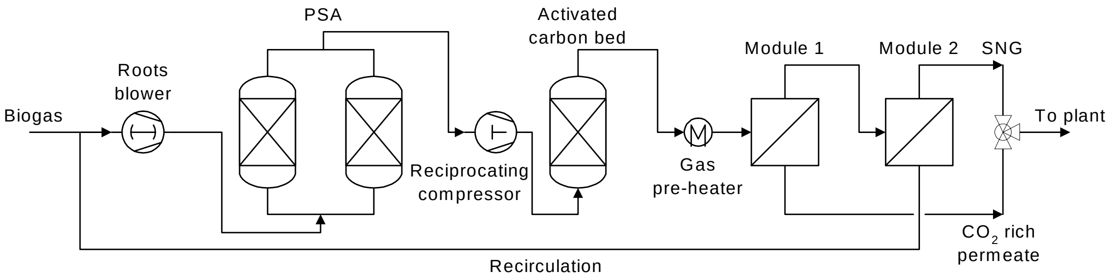

Fig. 1: Flowdiagram of MGS pilot plant.

The membrane stage consisted of a PLC controlled gas pre-heater and a membrane stack consisting of two CMS membranes operated as a cascade. The first membrane module produced a slightly CH_4 enriched retentate which became the feed to the second module. Permeate of the first module was highly enriched in CO_2 and after CO_2 sampling, sent to the main biogas network. The highly CH_4 enriched retentate from the second module was also sampled for CO_2 and sent to the main biogas network. Permeate from the second module was recycled to the blower suction and enriched the feed with CO_2 as to produce a first stage permeate with a high concentration of CO_2. A PC-based data acquisition system collected data such as CO_2 content in all streams, membrane operating temperatures, feed pressure to the first module, permeate pressure of the first module, and SNG flow rate. Gas chromatography (GC) samples were taken manually and analysed. The modules with a total of 8 m^2 were acquired from CML ltd, Israel.

Fundamentals of the carbon molecular sieve MGS process

Molecular sieving is a mechanism whereby different molecules are separated because of their different size. The aim of the project was however not to investigate the actual molecular sieving mechanism, but rather to prove the technology as a possible competitor in the biogas MGS industry. The material transport used in this study was sufficiently described by the equation

$$J_i = Q_i \cdot \left(p_f x_i - p_p y_i\right) \qquad (1)$$

where J_i is the flux in liter.m^{-2}.hr^{-1}, Q is the permeance in liter.m^{-2}.hr^{-1}.bar^{-1}, p_f and p_p are the feed and permeate absolute pressures in bar respectively and x_i and y_i are the feed and permeate concentration as a volumetric fraction of a gas at a local point on the membrane axis. Eq. (1) was used throughout to compare different membrane modules by calculating Q_i. The ideal selectivity of a membrane towards CH4 and CO2 results from different permeances for each gas and is written as

$$\alpha_{ij} = \frac{Q_i}{Q_j} \qquad (2)$$

where α_{ij} is the ideal selectivity of the membrane. The subscript i and j are for the fast and slow gas respectively. The ideal selectivity in eq. (2) was also calculated from the ratio of permeances as per eq. (1).

Simulation of a membrane cascade operation

After membrane permeance and selectivity was estimated, these parameters were in turn used to estimate large scale MGS plant economics. The model is based on eq. (1) and (2), but modified to allow calculation for a crossflow pattern on the feedside of the membrane as this is more realistic, especially when calculating the necessary membrane area for a given separation. The model also includes the possibility for simulating gas separation for multicomponent mixtures according to numerical and analytical techniques devised by Shindo et. al., 1985. In terms of dimensionless variables, the governing equations for the crossflow pattern are

$$\frac{df}{ds} = -\sum_{k=1}^{n} q_k \left(x_k - \gamma y_k\right) \qquad (3)$$

$$\frac{dx_i}{ds} = -\frac{q_i}{f}\left(x_i - \gamma y_i\right) + \frac{x_i}{f}\sum_{k=1}^{n} q_k \left(x_k - \gamma y_k\right) \qquad \left(i = 1,...,n-1\right) \qquad (4)$$

The simultaneous equations (3) and (4) were solved numerically, using a Runge-Kutta fourth order numerical routine.

Experimental results and discussion

Typical experimental runs to see whether the membranes could produce SNG of suitable quality lasted approximately two hours after which the compressor feed pressure would become excessive due to the large pressure drop over the equipment in general. An example is shown on figure 1.

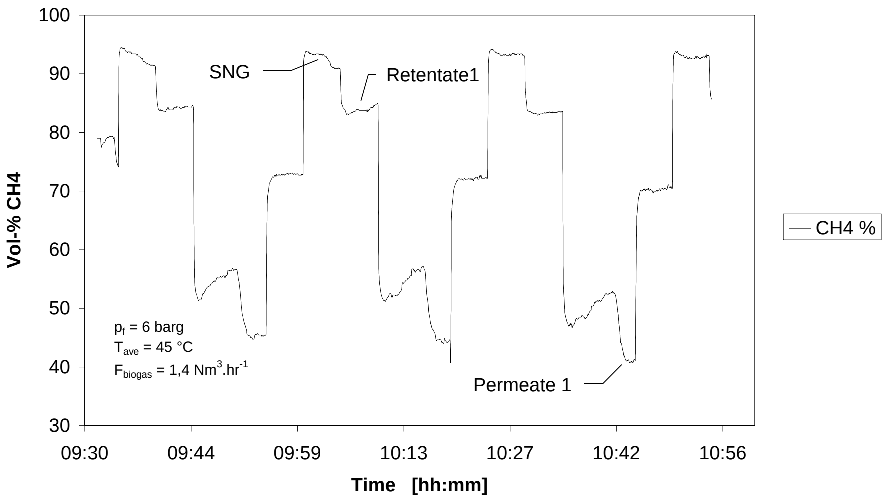

Fig 1: Methane content in pilot plant streams as a function of time

GC analysis of the raw biogas and the SNG revealed nitrogen levels of between 0-0,5 and 1-2 vol-% respectively. All the experimental results therefore indicate that the achievable methane content in the SNG is only limited by the nitrogen content of the feed. Thus infiltration of air into the process has to be avoided in the production of SNG with over 95 vol-% CH4. As membrane area and product purity both are strong functions of the membrane properties, a series of experiments were conducted as to estimate membrane parameters. Four membrane modules were tested. The results, using eq. (1) and (2) are shown in table 1.

Membrane ID	**Permeance**		**Ideal selectivity**	**Process parameters**	
	Q_{CO2}	**Q_{CH4}**	**α_{ij}**	**T_{ave}**	**$p_{f,ave}$**
	$[L_{STP}.m^{-2}h^{-1}.bar^{-1}]$	$[L_{STP}.m^{-2}h^{-1}.bar^{-1}]$	[1]	[°C]	[bara]
B-193	96,9	2,6	36,9	48,8	7,9
B-195	228,4	7,5	30,3	48,2	7,1
B-203	113,9	1,7	67,5	49,5	7,5
B-205*	853,5/601,8	115,7/159,7	7,4/4	49,5/49,5	7,5/4,6

Table 1 Average permeance and ideal selectivity of CMS modules tested

No knowledge regarding the permeance of CO_2 and CH_4 in the above membranes was available for comparison and the validity of the found values have not been corroborated. Membrane parameters for all modules were estimated from a number of runs under slightly varying conditions with large deviations especially when calculating ideal selectivity. One example shows that a CO_2 measurement error of 1 vol-% in the permeate caused a 15% error in calculating ideal selectivity. The highly permeable module B-205 showed a significant difference in permeance at varying pressures as can be seen in table 4.1. The other modules showed a less significant difference. By inspection it seems that pressure driving force has a notable effect on the more permeable membranes. The data in table 4.1 will subsequently be used as is.

Simulation and plant economics

Large scale application of the concept described above has been simulated with the following requirements:

1. Biogas flowrate 625 $Nm^3.hr^{-1}$.
2. CH_4 in the retentate or SNG should be ***93 %*** by volume.
3. CO_2 in the permeate will vary according to the modules used.
4. Pre-treated biogas consists of 29% CO_2, 0,5% O_2, 69,5% CH_4 og 1% N_2.
5. The feed pressure to the first and second stage is 15 and 14 barg respectively.
6. Membrane properties as in table 4.1 will be used. O_2 permeance is set to 50% of CO_2's and N_2's at 20% of O_2's.
7. CO_2 liquifaction will be taken into account

A sensitivity analysis, fig. 2 using the most optimal configuration, shows the influence on investment and operating costs if one would want to increase the CH_4 content of the SNG.

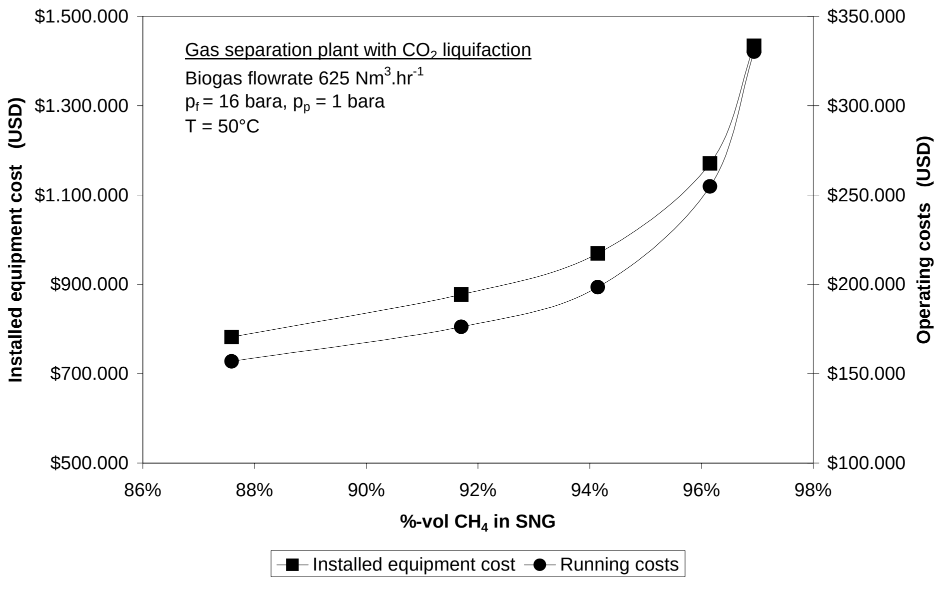

Fig. 6.1: Annual installed equipment and operating costs as a function of CH_4 content of produced SNG.

Conclusion

Four carbon molecular sieve membrane modules, based on the same pre-cursor polymer, were tested and yielded permeance and selectivity data enabling cross-flow, multicomponent simulation of a full-scale MGS plant. In the process economy SNG quality and feed pressure are the most important to this application. SNG quality is highly dependant on the air present in the biogas which limits the content of CH_4. Pretreatment of the feed gas is very important especially the removal of particulates, moisture, oil and toxins like H_2S and NH_3.
Total regeneration of membrane flux was possible after a module became saturated with watervapour which caused condensation within the module.
The technology could also sucessfully be used to upgrade landfill gas to a high quality fuel.

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