

# Techno-economic evaluation of biogas upgrading process using CO<sub>2</sub> facilitated transport membrane

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## ABSTRACT

The biogas upgrading by membrane separation process using a highly efficient CO<sub>2</sub>-selective polyvinylamine/polyvinylalcohol (PVAm/PVA) blend membrane was investigated by experimental study and simulation with respect to process design, operation optimization and economic evaluation. This blend membrane takes advantages of the unique CO<sub>2</sub> facilitated transport from PVAm and the robust mechanical properties from PVA, exhibits both high CO<sub>2</sub>/CH<sub>4</sub> separation efficiency and very good stability. CO<sub>2</sub> transports through the water swollen membrane matrix in the form of bicarbonate. CO<sub>2</sub>/CH<sub>4</sub> selectivity up to 40 and CO<sub>2</sub> permeance up to 0.55 m<sup>3</sup>(STP)/m<sup>2</sup> h bar at 2 bar were documented in lab with synthesized biogas (35% CO<sub>2</sub> and 65% CH<sub>4</sub>). Membrane performances at varying feed pressures were recorded and used as the simulation basis in this work. The process simulation of an on-farm scale biogas upgrading plant (1000 Nm<sup>3</sup>/h) was conducted. Processes with four different membrane module configurations with or without recycle were evaluated technically and economically, and the 2-stage in cascade with recycle configuration was proven optimal among the four processes. The sensitivity of the process to various operation parameters was analyzed and the operation conditions were optimized.

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## 1. Introduction

To secure a sustainable long-term energy supply, our exploitation of the earth's finite resource such as fossil fuel, must be reduced, while renewable energy must be developed as alternatives. The proportion of energy generated from renewable resources is expected to increase to >20% by 2020. During the same period, the greenhouse gas should decrease by 14% in 2020 compared with 2005 (Anon, 2008). The use of upgraded biogas is considered as one of the most efficient means of utilizing the renewable energy and reducing greenhouse gas emission.

Biogas is a mixture of gases generated from anaerobic microbial digestion from organic wastes such as manure, landfill or sewage. The composition of biogas varies depending on the source. Typically biogas contains 60–65% CH<sub>4</sub>, 35–40% CO<sub>2</sub>, small amounts of hydrogen sulfide (H<sub>2</sub>S), water vapour and traces of other gases. Depending on the source, nitrogen (N<sub>2</sub>) may be present in a larger amount. The content of methane, carbon dioxide, oxygen, nitrogen and hydrogen sulfide in three biogas sources and the variation within them are listed in Table 1. The highest methane content, 65%, was detected in the gas from the sewage digester and the

lowest, 47%, in the landfill gas, while biogas from a typical farm biogas plant contains 55–58% methane and 37–38% CO<sub>2</sub>. The amount of hydrogen sulfide in the farm biogas varied from 32 to 169 ppm (Rasi et al., 2007; Maltesson, 1997).

Raw biogas of above-listed composition exhibits a significantly lower Wobbe index (heating value) compared to natural gas. The conventional way to directly burn biogas for heating is apparently low energy efficient. The removal of carbon dioxide (CO<sub>2</sub>) from biogas to a level of methane (CH<sub>4</sub>) >90%, termed “upgrading”, can not only effectively increase the Wobbe index, but also reduce corrosion caused by acid gas and therefore extend the biogas utilization as a renewable energy resource. Upgraded biogas containing 98% of CH<sub>4</sub> may be compressed and liquefied for vehicle fuel or injected into a public natural gas grid. In addition, by preventing the unnecessary emissions of carbon dioxide and methane gas, upgrading of biogas also helps towards both Kyoto and EU greenhouse gas abatement commitments: CO<sub>2</sub> is well known as greenhouse gas, while CH<sub>4</sub> is approximately 21 times more harmful as a greenhouse gas than CO<sub>2</sub> (NESDIS, 2009). Today more and more attentions were paid on the exploitation and upgrading of biogas.

Water washing, membrane separation, chemical absorption and pressure swing adsorption (PSA) are the four techniques which may be used for biogas upgrading. Membrane separation method exhibits many advantages, including low operation cost, easy to maintain with high process flexibility and no pollution. According

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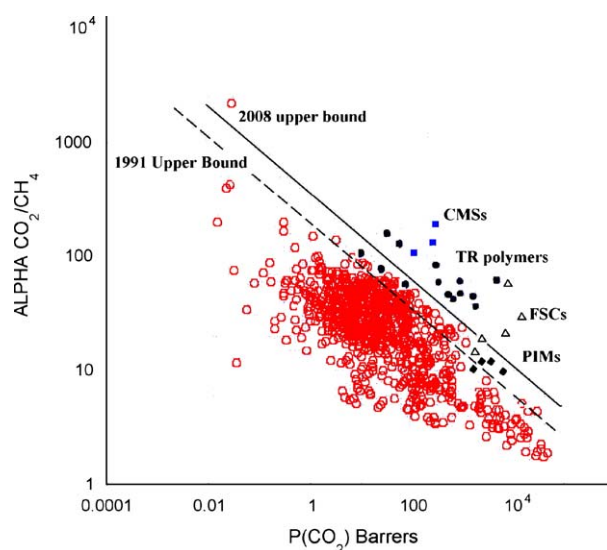
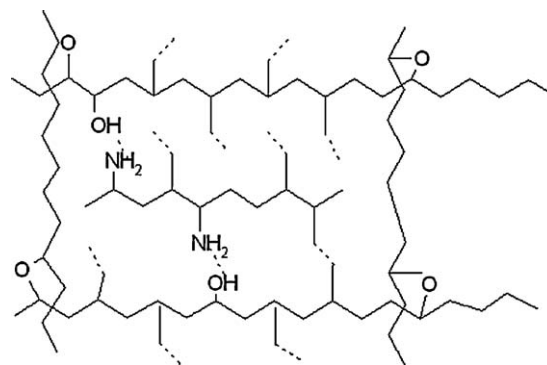
**Table 1**

Composition of biogas from different sources (Rasi et al., 2007; Maltesson, 1997).

Component	Farm biogas plant	Sewage digester	Landfill
CH <sub>4</sub>	55–58	61–65	47–57
CO <sub>2</sub>	37–38	34–38	37–41
N <sub>2</sub>	Trace	Trace	1–17
O <sub>2</sub>	Trace	Trace	0–2
H <sub>2</sub> S	<1	<1	<1
H <sub>2</sub> O	4–7	4–7	4–7
Aromatic hydrocarbon	Trace	Trace	Trace

to the 'Biogas from manure and waste products - Swedish case studies' published by the Swedish Gas Association in May 2008 (Anon, 2008), however, 25 out of 34 biogas upgrading plants in Sweden were using the water washing process based on physical absorption, which produced a big amount of waste water, required high capital investment and energy consumption while showed very low CO<sub>2</sub> capture efficient—it was difficult to reach the methane concentration for the direct usage of biogas as a natural gas substitute. Other plants were using chemical absorption or PSA in order to increase CO<sub>2</sub> capture efficiency although they obviously brought in more pollution problems and consumed more energy—none upgrading plant employed membrane technology as yet might be due to the low separation efficiency of the currently commercially available membranes: the CH<sub>4</sub> recovery of the membrane separation units was the lowest among the listed four techniques. Moreover, the pre-treatment is normally required for a membrane process to remove the water vapour and hydrogen sulfide, which considerably increases the process cost.

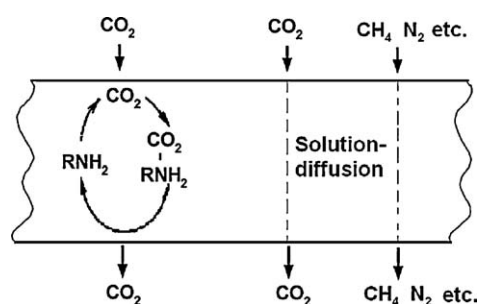
Today commercial membranes for CO<sub>2</sub>/CH<sub>4</sub> separation are in general conventional polymeric dense membranes based on the solution-diffusion mechanism, which are subject to a trade-off between the CO<sub>2</sub> separation selectivity and the flux, as illustrated in Robeson plot in Fig. 1 (Robeson, 1991, 2008). A membrane with high CO<sub>2</sub> selectivity is inevitably suffering a poor permeance of CO<sub>2</sub> and vice versa. For example, limited by the solution-diffusion mechanism, the cellulose acetate (CA) membrane, the most commonly used commercial CO<sub>2</sub> separation membrane, exhibits a CO<sub>2</sub>/CH<sub>4</sub> selectivity of only about 12–15 under operating conditions, which is too low to compete with the amine absorption process according to simulations by Baker (2002). Baker also stated that membrane technology is advantageous in small (less than 6000 Nm<sup>3</sup>/h) and medium scale (6000–50,000 Nm<sup>3</sup>/h) separations

**Fig. 1.** Robeson upper bounds for the CO<sub>2</sub>/CH<sub>4</sub> membrane separation (Robeson, 1991, 2008).**Fig. 2.** Schematic illustration of the PVAm/PVA blend network (Deng et al., 2009).

if product purity requirements are not extremely stringent. An on-farm biogas upgrading is usually a small-scale process according to this definition and therefore is technically preferable to use membrane separation. Membranes with both high selectivity and CO<sub>2</sub> permeance are desired for this process to minimize the CH<sub>4</sub> loss and achieve high CH<sub>4</sub> purity. The membranes are also required to operate at high pressure with the presence of water vapour.

The aim of this work has been to design and optimize a highly efficient biogas upgrading membrane process by using a CO<sub>2</sub> facilitated transport PVAm/PVA blend membrane with both high CO<sub>2</sub> permeance and selectivity. The schematic illustration of the PVAm/PVA blend polymer matrix is given in Fig. 2. Benefited from the reversible reaction between CO<sub>2</sub> and the amino groups (carriers) fixed in the membrane polymer matrix, CO<sub>2</sub> could transport through this membrane by carrier-mediated diffusion (facilitated transport) and in the form of HCO<sub>3</sub><sup>-</sup>, hence water vapour in raw biogas favours the CO<sub>2</sub> separation. The PVAm/PVA blend membrane exhibited excellent intrinsic CO<sub>2</sub>/CH<sub>4</sub> separation properties that could overcome the Robeson upper bound. In addition, robust mechanical properties of the blended hydrogel polymers make it capable of withstanding relatively high-pressure biogas feed as well as being tolerant to water vapour. The membrane works in water swollen condition, and hence no pre-treatment is required to remove water vapour, which simplified the process. The transport mechanism of the PVAm/PVA blend membrane is illustrated in Fig. 3 (Deng et al., 2009). More discussion about the facilitated transport mechanism and effects of operating conditions can be found in (Deng et al., 2009; Hägg and Quinn, 2006; Kim et al., 2004).

In the current study, CO<sub>2</sub>/CH<sub>4</sub> selectivity up to 40 and CO<sub>2</sub> permeance of 0.55 m<sup>3</sup>(STP)/(m<sup>2</sup> h bar) at 2 bar, and selectivity up to 32 and CO<sub>2</sub> permeance of 0.18 m<sup>3</sup>(STP)/(m<sup>2</sup> h bar) at 20 bar were obtained in simulated separation conditions with water saturated biogas (35% CO<sub>2</sub> and 65% CH<sub>4</sub>). Experiments showed that the relative humidity and feed pressure strongly affected the separation performances, and operation with or without sweep gas

**Fig. 3.** Gas transport through PVAm/PVA blend FSC membrane.

at permeate side did not exhibit significant difference on the CO<sub>2</sub> separation performance at high pressures (>10 bar). The CO<sub>2</sub> separation using this membrane was therefore possible to operate with no sweep gas flow, which may significantly simplify the process. The simulation of an on-farm scale biogas upgrading plant (1000 Nm<sup>3</sup>/h) was conducted. Processes with four different membrane configurations with or without recycle were evaluated. The sensitivity of the optimal process using 2-stage cascade configuration with recycle was analyzed and the operating conditions were optimized technically and economically. The simulation result with CH<sub>4</sub> recovery of 99% at a low cost of 0.17 \$/Nm<sup>3</sup> was achieved by using the FSC membrane and the 2-stage recycled process.

## 2. Experimental results

The defect-free homogenous PVAm/PVA blend membrane with a thin selective layer (0.3–2.5 μm) on a polysulfone (PSf) ultrafiltration membrane was developed and tested with synthetic biogas (35 vol.% CO<sub>2</sub> in CO<sub>2</sub>/CH<sub>4</sub> gas mixture, AGA AS). Most experiments were carried out without supplying sweep gas on permeate side. The permeate gas composition were analyzed on line with a micro-GC equipped with auto-sampling. Details of the preparation and characterization techniques of this membrane had been reported elsewhere (Deng et al., 2009). CO<sub>2</sub> permeance ( $P_{\text{CO}_2}$ ) in the unit of m<sup>3</sup>(STP)/(m<sup>2</sup> h bar) and CO<sub>2</sub>/CH<sub>4</sub> selectivity ( $\alpha$ ) are the two key indices for the evaluation of membrane separation performance and can be calculated by Eqs. (1) and (2).

$$P_i = \frac{J_i}{\Delta p_i} = \frac{q_i}{A \times \Delta p_i} \quad (1)$$

$$\alpha = \frac{P_{\text{CO}_2}}{P_{\text{CH}_4}} \quad (2)$$

where  $J_i$  is the flux of component  $i$  (m<sup>3</sup>(STP)/m<sup>2</sup> h) and  $q_i$  is its standard volume flow rate (m<sup>3</sup>(STP)/h).

Effects of operation parameters were investigated in a lab scale membrane unit with the synthetic biogas. Due to the unique hydrogel feature and CO<sub>2</sub> facilitated transport mechanism in the PVAm/PVA blend membrane, CO<sub>2</sub> separation performance of this membrane is strongly dependent on the relative humidity of the separation environment. Feed pressure also significantly influenced the CO<sub>2</sub> transport and consequently the separation performance of the membrane. Room temperature was found the optimal temperature for CO<sub>2</sub>-selective separation of this membrane, so all experimental results for this study were taken at room temperature. Details about the effects of operating conditions on separation performance of the PVAm/PVA membrane can be found in (Deng et al., 2009). A selectivity of CO<sub>2</sub>/CH<sub>4</sub> up to 40 and CO<sub>2</sub> permeance up to 0.55 m<sup>3</sup>(STP)/(m<sup>2</sup> h bar) have been documented at 2 bar and 25 °C with a relative humidity of 92%. Table 2 lists the separation performance of the PVAm/PVA membrane at different feed pressures with maximum relative humidity that

could be reached at the given pressure. The CO<sub>2</sub> purity in the permeate was measured directly by GC except for experiments at 2 bar and 3 bar, which were carried out with sweep gas on the permeate side, hence CO<sub>2</sub> in permeate gas was diluted. However, since biogas is carbon neutral (i.e. part of the natural carbon cycle) and therefore the purity of CO<sub>2</sub> may be of less concern; it will most likely not be sequestered. Sweep gas on the membrane permeate side may thus be used in biogas upgrading process.

## 3. Simulation basis

ChemBrane was employed for the simulations of this biogas upgrading process. This is an in-house simulation membrane module (Grainger, 2007; Grainger and Hagg, 2008) interfaced to Aspen HYSYS<sup>®</sup> and hence has the strong capacity of HYSYS. The Peng–Robinson property package in ChemBrane was used. Cross-flow, co-current and counter-current flow with or without sweep gas on the permeate side are considered in this program. Users can choose a spiral-wound module or hollow fiber module with or without a sweep gas. Cross-flow is typical for a spiral-wound module, while counter current is typically used for hollow fibers. Here the membrane module was assumed as hollow fiber module with the counter-current flow. Hollow fiber membrane module is well known to be the most efficient and practical membrane module design with the highest packing density (up to 30,000 m<sup>2</sup>/m<sup>3</sup>) while countercurrent flow exhibits the best separation and requires the lowest membrane area in hollow fiber modules (Grainger and Hagg, 2008; Lie et al., 2007; Hägg and Lindbrathen, 2005). A hollow fiber membrane module is illustrated in Fig. 4. The separation performance of the hollow fiber membrane module was simulated based on the data obtained from flat sheet membrane experiments.

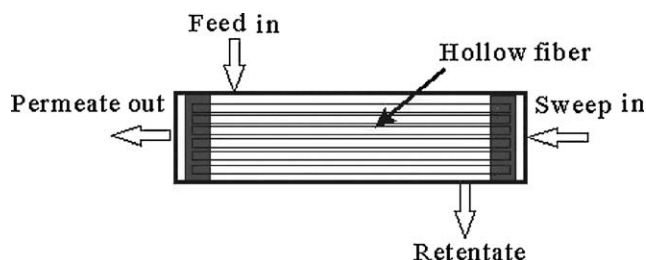
### 3.1. Process description

The schematic diagram in Fig. 5 gives a concept of an on-farm biogas generating system integrated with membrane separation unit for biogas upgrading. Raw biogas from the bioreactor containing CH<sub>4</sub> and CO<sub>2</sub> was saturated with water vapour. As indicated with the desulfurization agent FeCl<sub>2</sub> in Fig. 5, the desulfurization process was integrated within the bioreactor, and most part of hydrogen sulfide could be removed as precipitates. According to the durability test on the PVAm/PVA blend membrane already performed in-house, H<sub>2</sub>S did not seem to affect the membrane performance, hence the effect of H<sub>2</sub>S was not considered in this study. In this process, raw biogas was firstly compressed to 20 bar and then filtered at room temperature to capture liquid impurities before biogas was feed into the membrane separation unit. The upgraded biogas – the retentate gas from the membrane unit – was delivered into a natural gas network after being compressed to 40 bar. The CO<sub>2</sub> enriched permeate gas (CO<sub>2</sub> >80%) was recompressed to 10 bar from atmospheric pressure and then sent to a 2nd stage membrane module to recover CH<sub>4</sub>. The operating pressures at the 1st and 2nd

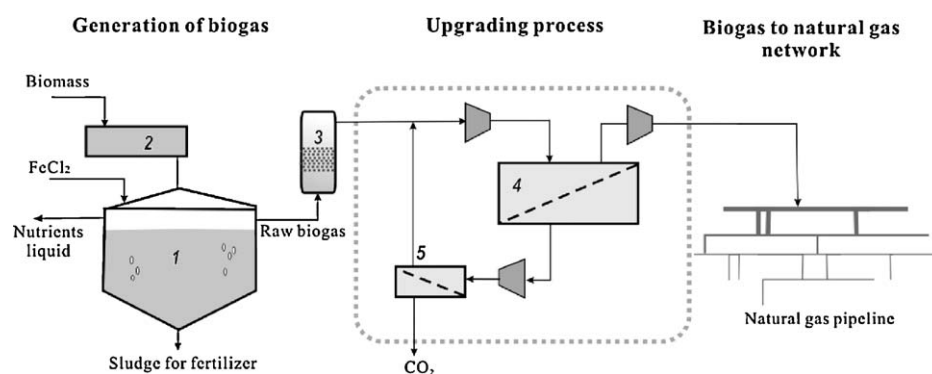
**Table 2**  
Experimental results at various operation conditions<sup>a</sup>.

Pressure (bar)	CO <sub>2</sub> permeance (m <sup>3</sup> (STP)/m <sup>2</sup> h bar)	CO <sub>2</sub> /CH <sub>4</sub> selectivity
2	0.55	40
3	0.48	38
5	0.3	35
10	0.2	30
15	0.18	31
20	0.18	32

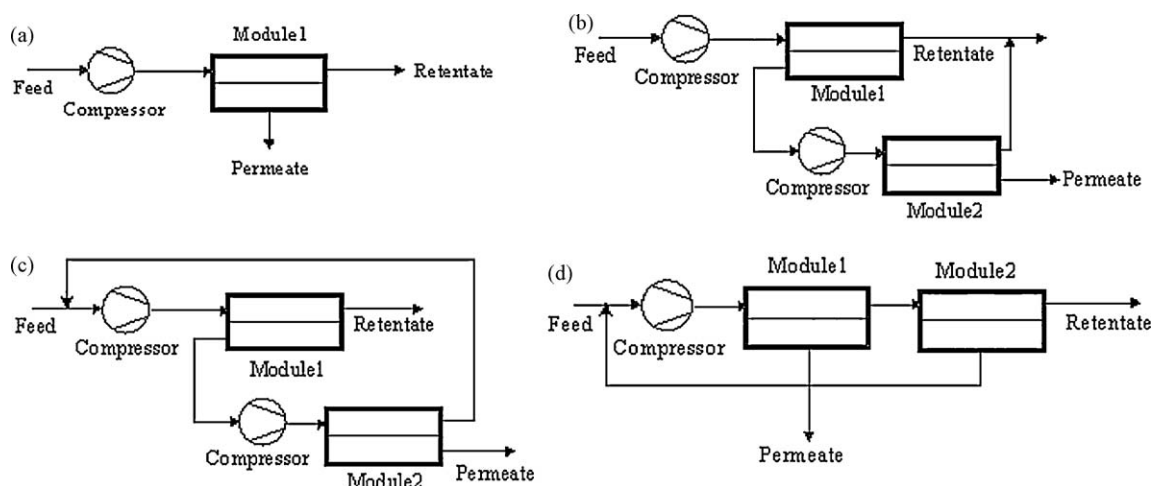
<sup>a</sup> Feed gas: CO<sub>2</sub> 35%, CH<sub>4</sub> 65% and saturated with water vapour.



**Fig. 4.** Schematic drawing of a hollow fiber membrane module.



**Fig. 5.** Conceptual schematic diagram of an on-farm biogas upgrading system providing fuel gas to natural gas network. 1: Bioreactor; 2: thickener; 3: filter; 4: 1st stage membrane module; 5: 2nd stage membrane module.



**Fig. 6.** Proposed membrane module configurations for biogas upgrading process.

stages were chosen based on the process optimization by simulation results.

The simulation of an on-farm scale biogas upgrading plant using PVAm/PVA blend membrane was performed with respect to required membrane area, capital and operation cost, energy demands for compression and the purity and recovery of  $\text{CH}_4$ .

### 3.2. Process configurations

Processes with 2-stage configurations are the most commonly used multi-stage processes; 3-stage configurations may result in better separation (Kaldis et al., 2004), but the complexity of the process variable control and the extra costs limited its applications, thus it will not be discussed in this study.

Fig. 6 illustrates the flow sheets of four simulated module arrangements using the PVAm/PVA blend membrane for biogas upgrading, including a single stage configuration (a) and a 2-stage configuration (b) without recycle as well as two 2-stage configurations with recycle: symmetric cascade (c) and asymmetric cascade (d). In configuration (b), the  $\text{CO}_2$  concentration in the retentate streams from the 1st and 2nd stages was fixed at the same value, and the required membrane area for each stage thus found by simulation. In the symmetric 2-stage cascade configuration (c), the permeate stream of the 1st stage is the feed of the 2nd stage, and the retentate of the 2nd stage is recycled. While in case (d) the feed of the 2nd stage is the retentate of the 1st stage, and the permeate flow of the 2nd stage is recycled (Stern et al., 1998; Bhidé and Stern, 1993a,b;

Hao et al., 2008, 2002; Rautenbach and Dahm, 1987). In all four cases, the retentate stream will be the upgraded biogas ( $\text{CH}_4$ ) and the permeate will be the  $\text{CO}_2$ -rich stream.

### 3.3. Base-case conditions and general assumptions

The base-case conditions for the four biogas upgrading processes are summarized in Table 3. The input membrane gas permeation data were based on the experimental results listed in Table 2, obtained at 25 °C and pressures in a 2–20 bar range. The capacity of the simulated plant was approximately 1000  $\text{Nm}^3/\text{h}$  raw biogas containing 35 vol.%  $\text{CO}_2$  and 65 vol.%  $\text{CH}_4$ -impurities and minor components present were neglected in the simulations. The raw biogas pressure from bioreactor was set as 1.2 bar.

**Table 3**  
Base-case conditions for the biogas upgrading process.

Parameters	Case			
	a	b	c	d
Feed raw biogas ( $\text{Nm}^3/\text{h}$ )	1000	1000	1000	1000
Feed pressure (bar)	1.2	1.2	1.2	1.2
Feed $\text{CO}_2$ concentration (vol.%)	35	35	35	35
Permeate $T$ and $P$ at 1st stage (°C, bar)	25, 1	25, 1	25, 1	25, 1
Permeate $T$ and $P$ at 2nd stage (°C, bar)	–	25, 1	25, 1	25, 1
$\text{CH}_4$ purity (%)	98	98	98	98
$\text{CH}_4$ recovery (%)	–	98	98	–
Upgraded biogas delivery pressure (bar)	40	40	40	40



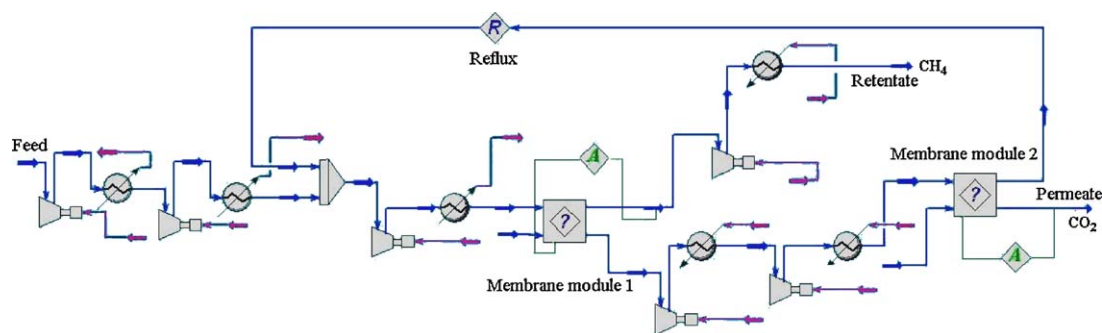


Fig. 7. Flow sheet of the simulated process of case (c) in Aspen HYSYS®.

Following assumptions were made to simplify the simulation:

- Outlet temperature in the compressors was maximum 150 °C. Accordingly, the compression ratio over each compressor stage is limited to 3.5.
- Compressors were assigned an adiabatic efficiency of 75%.
- The pressure drop through exchangers and membrane feed to retentate were assumed to be 0.5 bar.
- The compression duty includes the compression to 40 bar.

As an example of the simulation using Aspen HYSYS® with ChemBrane interfaced, a flow sheet is shown in Fig. 7 for process configuration (c).

### 3.4. Economic evaluation

In principle, the optimization of a process is based on the economic considerations, including reducing the capital cost and operating cost of the process. A rough economic evaluation was performed to find the best membrane configuration based on the operating cost and the capital cost of the main equipments, e.g. membrane modules and compressors in this process. The membrane was not a standard equipment item (Turton et al., 2003), thus an assumption was made to be 20 \$/m<sup>2</sup> for the cost of the membranes module fabrication according to an estimation given by Lie et al. (2007) and Koros (2003). Some other assumptions were made to simplify the evaluation, including the life time of the membrane as 5 years, the compressors material as stainless steel, the interest rate of 6%, the operating cost as 1.1% of capital investment, maintenance as 2.3% of capital investment, insurance of 2% capital investment and 5% discount rate of the capital investment. The total cost per tonne of upgraded biogas could be calculated from the annualized yearly capital cost, the yearly operating costs and the number of tonnes of upgraded biogas produced. Since biogas from farms is usually used locally for heat and power production, the cost of the raw biogas was estimated as 0.087 \$/Nm<sup>3</sup>, calculated from the low heat value (LHV) of 65% CH<sub>4</sub> (36 MJ/Nm<sup>3</sup> CH<sub>4</sub>) with fuel cost as 2.4 \$/GJ<sub>LHV</sub>. The electricity price is set as the average of 0.05 \$/kWh (Grainger and Hagg, 2008).

CAPCOST, a capital cost estimation software based on the equipment module approach and developed by Turton et al. (2003)

and Baker (2002), was used to estimate the total capital cost of the plant. The capital cost calculated with CAPCOST includes the direct and indirect project expenses by multiplying a bare module factor with the equipment cost. The bare module factor associated with the installation of equipment includes the material and labor for installation, the freight, insurance and taxes, construction overhead, contractor engineering expenses. The contingency and fee are included in calculating the total module cost, and the auxiliary facilities are included in the total grass roots cost of plant. The scaling-up factor has been taken into account by CAPCOST with a six-tenth rule in calculating equipment cost. In this case, the major equipment items were the membrane modules and the compressors. The compressors were assumed to be constructed mainly from carbon steel. The bare module factor was 3.5 for the compressors and 3 for the membrane modules in calculating equipment costs. Since the membrane life is set as 5 years, the total membrane area is hence four times of the process required membrane area for a project designed as 20-year lifetime.

Since the CAPCOST results are given in 1996 US\$, the inflation factor is considered using the Chemical Engineering Plant Cost Index (CEPCI). The total capital cost including inflation can be calculated from Eq. (3).

$$C_2 = C_1 \left( \frac{I_2}{I_1} \right) \quad (3)$$

where  $C_2$  is the current total capital cost including the inflation factor,  $C_1$  is the total cost calculated by CAPCOST software,  $I_2$  is the latest CEPCI value (575.4 for 2008 in this case) (Chemical Engineering, 2009) and  $I_1$  for 1996 (382 in the software). A sample for the calculation is given in Table 4.

## 4. Simulation results and discussion

### 4.1. Optimization of membrane process configurations

#### 4.1.1. Parameter study in a basic membrane process

In a biogas upgrading process, CH<sub>4</sub> purity and recovery are the most important technical factors in determining an optimal module arrangement in order to ensure a low CH<sub>4</sub> loss and meet the gas product specifications, while the required membrane area

Table 4

A sample for the capital cost calculation with CAPCOST (CEPCI=382, CEPCI<sub>2008</sub>=575.4).

Equipment list	Amount	Key design parameters	Bare module factor	Equipment cost	Bare module cost
Axial compressor	6	200 kw carbon steel	3.5	\$288,904	\$1,011,164
Membrane module (m <sup>2</sup> )	1297 × 4	Hollow fiber 5-year lifetime	3.0	\$103,760	\$311,280
Total bare module cost					\$1,322,000
Total module cost					\$1,560,000
Total grass roots cost of plant ( $C_1$ )					\$2,030,000
Total capital cost in 2008 ( $C_2$ )					\$3,060,000

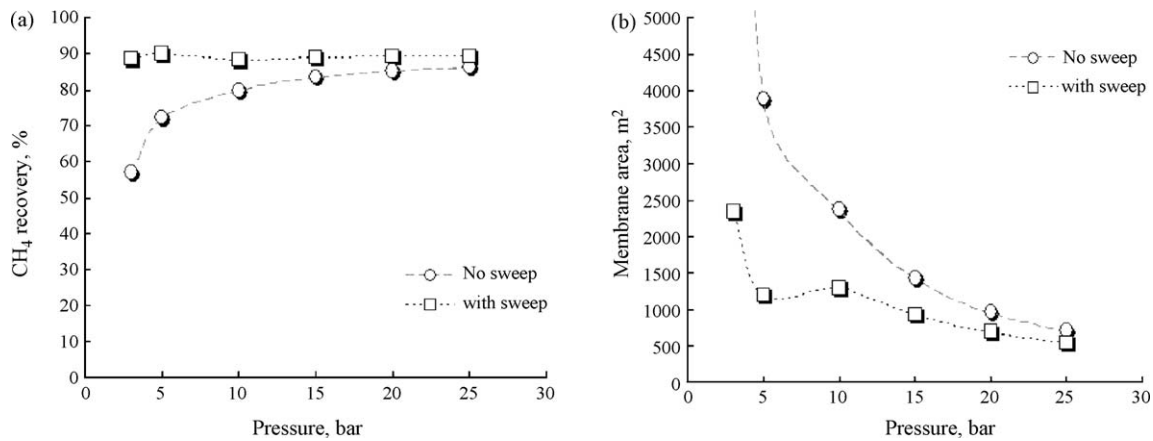


Fig. 8. Effect of operating pressure on CH<sub>4</sub> recovery and required membrane area in single stage process.

and compression energy are critical economic factors. In this study, the influence of operating pressure was simulated to optimize the operating condition with respect to the separation performance and economics in a basic single stage membrane process. CH<sub>4</sub> purity was set as 98% to meet the product specification, and the gas permeation data at different pressures were input from the experimental data listed in Table 2. The process was simulated in the conditions of with sweep gas and without sweep gas, respectively. The simulated CH<sub>4</sub> recovery and required membrane area are plotted as a function of operating pressure in Fig. 8. In the process without sweep gas, the increase of the operating pressure reduces considerably the required membrane area while increases the CH<sub>4</sub> recovery. The required membrane area of the operation at 3 bar is >10 times more than that at 20 bar, and the CH<sub>4</sub> recovery is much lower. The use of sweep gas on the permeate side remarkably improved the separation, especially to the low-pressure operations. However, even though the membrane has a higher CO<sub>2</sub> permeance at 3 bar (0.48 m<sup>3</sup>/(m<sup>2</sup> h bar)) than 20 bar (0.18 m<sup>3</sup>/(m<sup>2</sup> h bar)), the simulated CH<sub>4</sub> recovers are still higher and the required membrane area still lower for high-pressure operations, in both processes with or without sweep gas. Table 5 lists the simulation results of the processes at 3 bar and 20 bar with and without sweep gas. The feed raw biogas flow is set as 1000 Nm<sup>3</sup>/h. Since it needs one more compressor stage to operate at 5 bar, while process at 2 bar has too low energy efficiency, the operating pressure of 3 bar was chosen to represent low-pressure process as a comparison with 20 bar (representing high pressure). The table shows that the operation at 20 bar without sweep gas has the lower cost for per cubic meter product, and the process is simpler and its footprint is smaller than the operation at low pressure or/and with sweep gas. Since the total compression duty

in this case must include the compression of the upgraded biogas to 40 bar (the injection pressure for the natural gas network), the membrane separation at higher pressure does not necessarily lead to higher energy consumption. The pressure of 20 bar without sweep gas exhibits the best performance and lowest cost, thus has been defined as the optimal condition of the membrane process for further simulation.

#### 4.1.2. Comparison of configurations

In principle, any CH<sub>4</sub> purity can be achieved for binary mixtures of CO<sub>2</sub> and CH<sub>4</sub>, but in a single stage membrane process, it has to be at the expense of the recovery rate, exhibiting a trade-off between CH<sub>4</sub> purity and recovery, as can be seen from the trend of plot (a) in Fig. 9. By using the 2nd stage, however, process can achieve both high CH<sub>4</sub> purity and recovery, since the 2nd stage can recover CH<sub>4</sub> from the permeate side of the 1st stage. The separation performances of the processes with the four configurations have been simulated and are presented in Fig. 9. The simulations of these processes are at the optimal operating pressures of 20 bar. The plots of CH<sub>4</sub> recovery as a function of CH<sub>4</sub> purity exhibits apparently different trends for the processes without recycle (a and b) and with recycle (c and d), while the plot for the single stage configuration (a) exhibits much lower recovery than a 2-stage process (b).

Since the capital cost in a membrane separation process is roughly determined by the required membrane area while the operating cost depends to a large extent on the compression

Table 5  
Simulation results of single stage process.

Parameters	3 bar		20 bar	
	No sweep	Sweep	No sweep	Sweep
Upgraded biogas flow rate (Nm <sup>3</sup> /h)	378	588	566	593
CH <sub>4</sub> purity (vol.%)	98.0	98.0	98.0	98.0
CO <sub>2</sub> purity (vol.%)	55	82	78	83
CH <sub>4</sub> recovery (vol.%)	57	88.8	85.5	89.5
Required membrane area (m <sup>2</sup> )	12,780	2344	956	685
Compression duty (kw)	99	127	157	158
Capital cost (M\$)	8.39	2.78	1.86	1.86
Running cost (\$/Nm <sup>3</sup> biogas upgraded)	0.419	0.089	0.062	0.059

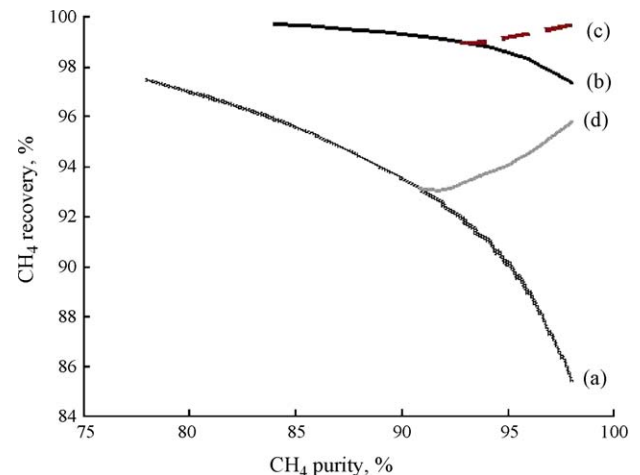


Fig. 9. Comparison of the simulated separation performance of the processes with the four configurations, at 20 bar.

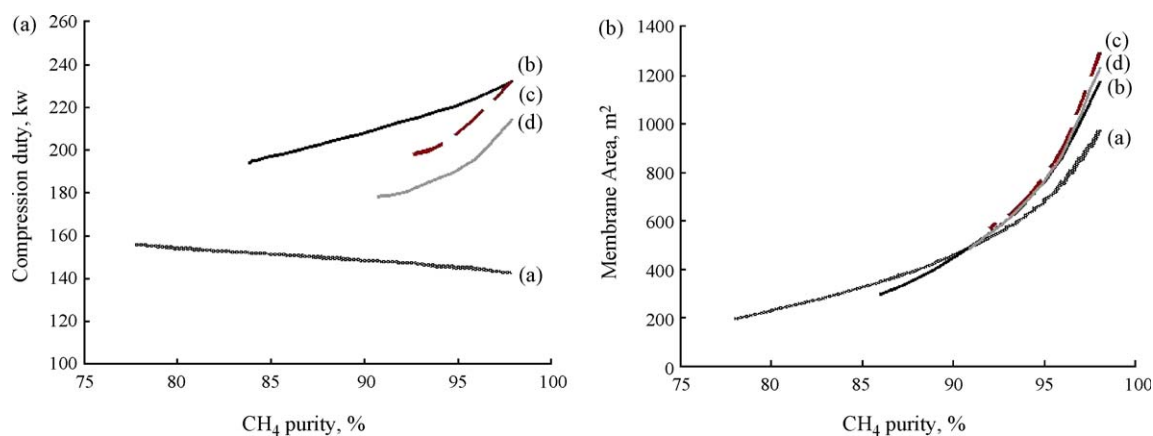


Fig. 10. Comparison of required membrane area (a) and compression duty (b) of the processes with the four configurations.

expense, these two factors are crucial to evaluate the process. The extra process cost for the recycle and the 2nd stage is concerned in the process evaluation for the four configurations. The simulation of the required membrane area and compression duty of the four configurations is presented in Fig. 10, showing that a larger membrane area is required to obtain a higher CH<sub>4</sub> purity, and consequently larger compression due to a higher recycle ratio.

Table 6 summarizes the simulation results of the biogas upgrading processes using the four configurations with the CH<sub>4</sub> purity in upgraded biogas set as 98% to meet the product specifications. The single stage configuration (a) shows the lowest capital costs, but the CH<sub>4</sub> recovery in this process is the lowest. The approx. 15% CH<sub>4</sub> lost is the main disadvantage for this process. In addition, since the upgraded biogas of the single stage process is low due to the low CH<sub>4</sub> recovery, the total running cost per unit product for the single stage process is the highest, especially when considering the raw biogas value. For the three 2-stage processes, the main criteria to evaluate these processes are the CH<sub>4</sub> recovery and the total running cost per unit product, and the process of the 2-stage cascade configuration (c) with recycle shows to be optimal for the biogas upgrading process according to the separation performance and the cost of the four processes listed.

Table 6  
Simulation results of the four cases presented in Fig. 6.

Parameters	Case			
	a	b	c	d
Feed raw biogas flow rate (Nm <sup>3</sup> /h)	1000	1000	1000	1000
Feed pressure at 1st and 2nd stages (bar)	20, –	20, 20	20, 20	20, 19.5
Upgraded biogas flow rate (Nm <sup>3</sup> /h)	566	745	769	638
CH <sub>4</sub> purity (vol.%)	98.0	98.0	98.0	98.0
CO <sub>2</sub> purity (vol.%)	78.0	92.2	98.1	92.5
CH <sub>4</sub> recovery (vol.%)	85.5	97.3	99.7	95.7
Recycle ratio	–	–	0.24	0.26
Total membrane area (m <sup>2</sup> )	956	1167	1297	1226
Compression duty (kw)	157	220	220	203
Capital cost (M\$)	1.86	2.99	3.06	2.34
Energy cost (\$/Nm <sup>3</sup> biogas upgraded)	0.013	0.013	0.013	0.012
Running cost (\$/Nm <sup>3</sup> biogas upgraded)	0.062	0.089	0.088	0.084
Total cost including raw biogas value (\$/Nm <sup>3</sup> biogas upgraded)	0.228	0.206	0.201	0.220

Table 7  
Variable ranges for the sensitivity study.

Parameters	Range
2nd stage pressure (bar)	5–20
Feed flow rate (Nm <sup>3</sup> /h)	250–1500
CO <sub>2</sub> concentration in feed (vol.%)	25–50

## 4.2. Sensitivity analysis

The operating pressure, the raw biogas feed flow rate (plant capacity) and composition are the most critical parameters that affect the upgraded biogas quality and CH<sub>4</sub> recovery in the biogas upgrading process. A sensitivity analysis of the variations of these parameters was made to evaluate the effects of these factors to specify the limits of operation parameters. The variable ranges for the sensitivity study are given in Table 7.

### 4.2.1. Effect of the 2nd stage pressure

The simulation of the influence of the 2nd stage pressure was made with the 1st stage pressure fixed at 20 bar. The required total membrane area and compression duty are plotted as a function of the 2nd stage pressure in Fig. 11. The plot shows that the higher operating pressure in the 2nd stage results in a lower required total membrane area as expected. According to the simulation, operation at a pressure less than 10 bar requires a dramatic increase in membrane area, and the minimal compression duty will be at around 10 bar, since a larger recycle flow must be given at low pressures to ensure a sufficient CH<sub>4</sub> recovery, hence the higher compression energy consumption is required. The increasing of the 2nd stage pressure to more than 10 bar might also result in extra energy consumption and must have one more compressor stage, which would largely increase the capital costs. The optimal 2nd stage pressure was therefore chosen as 10 bar in this study.

### 4.2.2. Effect of feed flow rate

Effect of feed flow rate on separation performance was simulated with the optimal membrane area fixed as 1080 m<sup>2</sup> in

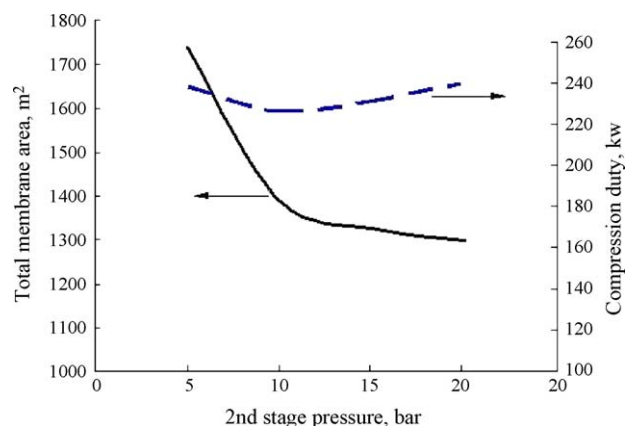


Fig. 11. Influence of 2nd stage pressure on required membrane area and compression duty, CH<sub>4</sub> and CO<sub>2</sub> purity 98%, 1st stage at 20 bar, in configuration (c).

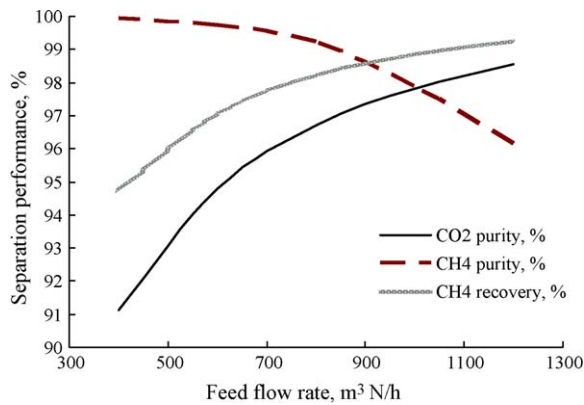


Fig. 12. Influence of feed flow rate on separation performance and total membrane area 1440 m<sup>2</sup>.

the 1st stage and 360 m<sup>2</sup> in the 2nd stage. As shown in Fig. 12, when the feed flow rate decreases under the design capacity of 1000 Nm<sup>3</sup>/h, CH<sub>4</sub> purity would increase, so the upgraded biogas quality could still meet the product specifications. However, CH<sub>4</sub> recovery would decrease due to the loss of CH<sub>4</sub> through the extra membrane area. When the feed flow increases over the design capacity, the membrane area is no longer sufficient for the separation. As a consequence, the increase of the feed flow rate would result in the decrease of the CH<sub>4</sub> purity and hence the product quality could not meet the specifications. An increase of the 1st stage feed pressure could partly solve the problem in this situation, but the new operation parameters must be given accordingly to meet the capacity change.

The capital cost and the total running cost per normal cubic meter upgraded biogas are plotted in Fig. 13 as the function of the plant capacity in a practical range from 200 Nm<sup>3</sup>/h to 1500 Nm<sup>3</sup>/h for on-farm biogas plants to investigate the influences of the plant capacity on economic factors. As shown in Fig. 13, the running costs per normal cubic meter upgraded biogas for the plants over 500 Nm<sup>3</sup>/h show a nearly linear decrease with the capacity increasing. However, the running cost plot for smaller plant (<500 Nm<sup>3</sup>/h) shows a quick increase with the decrease of the plant capacity, which suggests that for smaller plants it will be more expensive to produce the same quality of upgraded biogas to the natural gas network.

#### 4.2.3. Effect of CO<sub>2</sub> concentration in feed

The effect of CO<sub>2</sub> concentration in the feed gas varying from 25% to 50% was simulated in a designed process with a fixed membrane area of 1440 m<sup>2</sup> and 35% CO<sub>2</sub> in feed raw biogas. As shown in

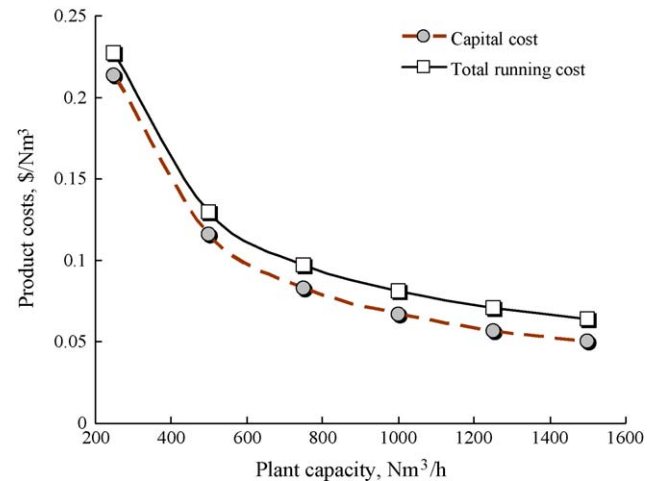


Fig. 13. Effect of plant capacity on economics factors.

Fig. 14(a), CH<sub>4</sub> purity monotonously decreases with the increasing CO<sub>2</sub> concentration in feed while CH<sub>4</sub> recovery slightly increases, since the CH<sub>4</sub> recovery is mainly determined by the loss of CH<sub>4</sub> in the 2nd stage, which increases with the increasing of the CO<sub>2</sub> purity. It suggests that if the CO<sub>2</sub> concentration in the feed were higher than designed (>35%), it would result in a lower CH<sub>4</sub> purity than the product specification (<98%), and should be avoided. When CO<sub>2</sub> concentration decreases to be lower than the design value, the CH<sub>4</sub> purity would be higher than the product specification, but CO<sub>2</sub> purity would decrease and hence the CH<sub>4</sub> recovery decreases. Fig. 14(b) shows the simulation on the compression duty and recycle flow with respect to the influence of the feed CO<sub>2</sub> concentration. The recycle flow increases with the increasing CO<sub>2</sub> concentration in feed. When CO<sub>2</sub> concentration is over 40%, the recycle flow dramatically increases, resulted in a quick increase of the compression duty. The simulation suggested that a variation of CO<sub>2</sub> concentration in the range of 30–40% might lose separation efficiency but not cause serious problems. When the CO<sub>2</sub> concentration in feed was out of this range, however, the membrane process must be redesigned to ensure a sufficient separation.

#### 4.3. Simulation results for optimal process

From the comparison of the processes with four configurations and the optimization of the operating pressures, it can be concluded that the most efficient membrane process for biogas upgrading using the PVAm/PVA membrane was the process with a

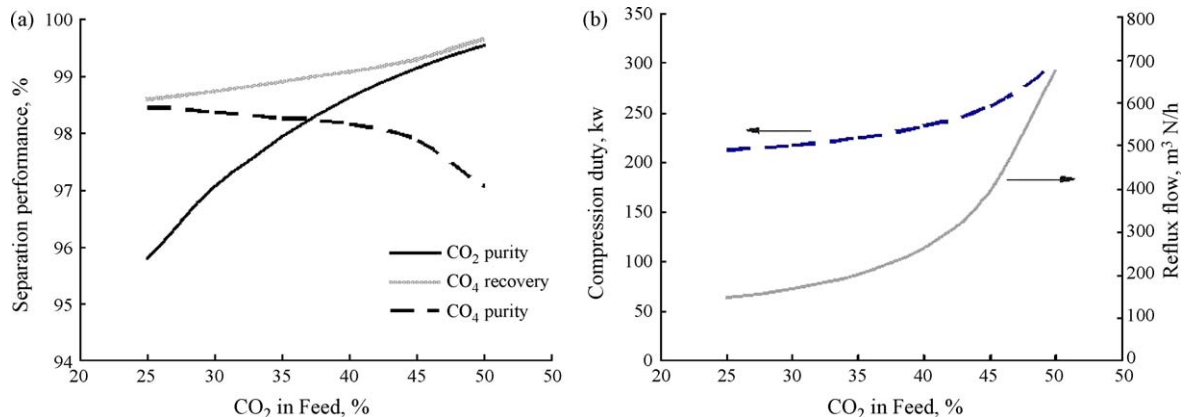


Fig. 14. Influence of feed composition on separation performance (a), the required compression duty and recycle flow rate (b), total membrane area 1440 m<sup>2</sup>.



**Table 8**

Simulation results of the optimal process.

Parameters	Simulation results
Total membrane area (m <sup>2</sup> )	1440
Feed pressure at 1st stage and 2nd stage (bar)	20, 10
Temperature and Pressure at permeate (°C, bar)	25, 1.0
Upgraded biogas flow rate (Nm <sup>3</sup> /h)	761
CH <sub>4</sub> purity (vol.%)	98.0
CO <sub>2</sub> purity (vol.%)	98.0
CH <sub>4</sub> recovery (vol.%)	99.0
Compression duty (kw)	234
Capital cost (M\$)	2.73
Energy cost (\$/Nm <sup>3</sup> biogas upgraded)	0.015
Running cost (\$/Nm <sup>3</sup> biogas upgraded)	0.081
Total cost (\$/Nm <sup>3</sup> biogas upgraded, including raw biogas cost)	0.194

symmetric 2-stage-in-cascade configuration with recycle (case c). A proposed optimal operation condition for this process and the simulation results are listed in Table 8. The optimal operating pressures in the 1st stage and 2nd stage were 20 bar and 10 bar, respectively. The operating temperature was defined as room temperature according to experimental results. Other operating parameters, such as feed gas flow rate and composition, were determined by the raw biogas sources. The process was simulated for a biogas plant with a capacity of 1000 Nm<sup>3</sup>/h raw biogas and a CO<sub>2</sub> concentration of 35 vol.%.

The cost of biogas upgrading process varies considerably on biogas resource, upgrading technology, plant capacity, location, etc., roughly in the range 0.18–0.7 \$/Nm<sup>3</sup> (Lie, 2009). Very few 'hard numbers' are available in the literature. In this study, the cost for producing upgraded biogas is approximately 0.17 \$/Nm<sup>3</sup> for a plant capacity of 1000 Nm<sup>3</sup>/h, including the raw biogas value and the compression of the upgraded biogas to the natural gas network pressure, which is lower than the natural gas price: the international market price for natural gas was fluctuating in the range of 0.25–0.55 \$/Nm<sup>3</sup> during 2005–2009 (U.S. Energy Information Administration, 2009).

## 5. Conclusion

By using the PVAm/PVA blend FSC membrane and the 2-stage recycled process, a CH<sub>4</sub> recovery of 99% at a low running cost could be obtained to upgrade biogas to meet the natural gas network specification, which makes this green process more competitive compared with other conventional technologies currently used. In addition, due to the unique facilitated transport mechanism of this FSC membrane, water vapour saturated in biogas is an advantage rather than a problem to CO<sub>2</sub> permeation, the pre-treatment to remove water vapour is not required. The simulation study based on experimental results for a PVAm/PVA blend FSC membrane was conducted with Aspen HYSYS®. The simulation results using 1000 Nm<sup>3</sup>/h raw biogas demonstrated the potential of a biogas upgrading process. According to the simulation, the process with 2-stage-in-cascade configuration exhibits the highest separation efficiency. The operation pressure, capacity and feed composition were studied on their respective effect on separation performance. The total costs including the raw biogas value for the upgraded biogas was found to be approximately 0.17 \$/Nm<sup>3</sup> which is lower than the natural gas price in the market. Nevertheless, a further durability study towards H<sub>2</sub>S and other impurities is crucial to bring this membrane into industrial applications. Durability tests

of the membrane in a gas stream containing H<sub>2</sub>S and heavy hydrocarbon are ongoing.

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## References

- Anon, 2008. Biogas from Manure and Waste Products—Swedish Case Studies. Swedish Gas Association.
- Chemical Engineering, 2009. Economic indicators. In: Chemical Engineering, May <http://www.che.com>.
- Baker, R.W., 2002. Future directions of membrane gas separation technology. *Industrial & Engineering Chemistry Research* 41, 1393–1411.
- Bhide, B.D., Stern, S.A., 1993a. Membrane processes for the removal of acid gases from natural gas. I. Process configurations and optimization of operating conditions. *Journal of Membrane Science* 81, 209–237.
- Bhide, B.D., Stern, S.A., 1993b. Membrane processes for the removal of acid gases from natural gas. II. Effects of operating conditions, economic parameters, and membrane properties. *Journal of Membrane Science* 81, 239–252.
- Deng, L., Kim, T.-J., Hägg, M.-B., 2009. Facilitated transport of CO<sub>2</sub> in novel PVAm/PVA blend membrane. *Journal of Membrane Science* 340, 154–163.
- Grainger, D., 2007. Carbon Membranes for Hydrogen Separation, in Department of Chemical Engineering. Norwegian University of Science and Technology, Trondheim, p. 150.
- Grainger, D., Hägg, M.-B., 2008. Techno-economic evaluation of a PVAm CO<sub>2</sub>-selective membrane in an IGCC power plant with CO<sub>2</sub> capture. *Fuel* 87, 14–24.
- Hägg, M.B., Lindbräthen, A., 2005. CO<sub>2</sub> capture from natural gas fired power plants by using membrane technology. *Industrial & Engineering Chemistry Research* 44, 7668–7675.
- Hägg, M.B., Quinn, R., 2006. Polymeric facilitated transport membranes for hydrogen purification. *MRS Bulletin* 31, 750–755.
- Hao, J., Rice, P.A., Stern, S.A., 2002. Upgrading low-quality natural gas with H<sub>2</sub>S- and CO<sub>2</sub>-selective polymer membranes: Part I. Process design and economics of membrane stages without recycle streams. *Journal of Membrane Science* 209, 177–206.
- Hao, J., Rice, P.A., Stern, S.A., 2008. Upgrading low-quality natural gas with H<sub>2</sub>S- and CO<sub>2</sub>-selective polymer membranes: Part II. Process design, economics, and sensitivity study of membrane stages with recycle streams. *Journal of Membrane Science* 320, 108–122.
- Kaldis, S.P., Skodras, G., Sakellariopoulos, G.P., 2004. Energy and capital cost analysis of CO<sub>2</sub> capture in coal IGCC processes via gas separation membranes. *Fuel Processing Technology* 85, 337–346.
- Kim, T.J., Li, B.A., Hägg, M.B., 2004. Novel fixed-site-carrier polyvinylamine membrane for carbon dioxide capture. *Journal of Polymer Science Part B—Polymer Physics* 42, 4326–4336.
- Koros, W.J., 2003. Membrane opportunities and challenges for large capacity gas and vapour feeds. In: Presentation at Norway (2003) in European Membrane Society's 20th Summer School, NTNU, Trondheim.
- Lie, J.A., 2009. Carbon membrane for biogas upgrading. In: ECI, Advanced Membrane Technology IV, Trondheim, Norway.
- Lie, J.A., Vassbotn, T., Hägg, M.-B., Grainger, D., Kim, T.-J., Mejdell, T., 2007. Optimization of a membrane process for CO<sub>2</sub> capture in the steel-making industry. *International Journal of Greenhouse Gas Control* 1, 309–317.
- Maltesson, H.Å., 1997. Biogas for fordonsdrift—kvalitetsspecifikation in Kommunikationsforsknings-beredningen (KFB4), Stockholm.
- NESDIS, 2009. Global Warming. <http://lwf.ncdc.noaa.gov>.
- Rasi, S., Veijanen, A., Rintala, J., 2007. Trace compounds of biogas from different biogas production plants. *Energy* 32, 1375–1380.
- Rautenbach, R., Dahm, W., 1987. Gas permeation—module design and arrangement. *Chemical Engineering and Processing* 21, 141–150.
- Robeson, L.M., 1991. Correlation of separation factor versus permeability for polymeric membranes. *Journal of Membrane Science* 62, 165–185.
- Robeson, L.M., 2008. The upper bound revisited. *Journal of Membrane Science* 320, 390–400.
- Stern, S.A., Krishnakumar, B., Charati, S.G., Amato, W.S., Friedman, A.A., Fuess, D.J., 1998. Performance of a bench-scale membrane pilot plant for the upgrading of biogas in a wastewater treatment plant. *Journal of Membrane Science* 151, 63–74.
- Turton, R., Bailie, R.C., Whiting, W.B., Shaeiwitz, J.A., 2003. Analysis, Synthesis, and Design of Chemical Processes, second ed. Prentice Hall, New Jersey.
- U.S. Energy Information Administration, 2009. Natural Gas Prices. [http://tonto.eia.doe.gov/dnav/ng/ng\\_pri\\_sum\\_dcu\\_nus\\_m.htm](http://tonto.eia.doe.gov/dnav/ng/ng_pri_sum_dcu_nus_m.htm).