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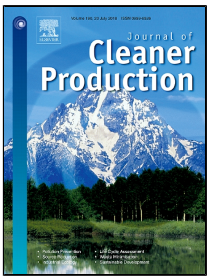

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Carbon Molecular Sieve Membranes for Biogas Upgrading: Techno-economic Feasibility Analysis

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Abstract: Biomethane, produced by biogas upgrading, has a great potential to replace part of the fossil fuel natural gas, and may be injected into a gas grid or used as compressed biomethane as vehicle fuel. The state-of-the-art technologies for biogas upgrading in the European region are water scrubbing, pressure swing adsorption and chemical absorption, however, high performance carbon membranes may also have a great potential in this application. In this work, cellulose-derived hollow fiber carbon membranes were tested for CO_2/CH_4 separation at moderate pressures (5-20 bar), and a CO_2/CH_4 permeance selectivity >60 was obtained. The developed membranes were evaluated for biogas upgrading in a 1000 m^3(STP)/h biogas plant based on HYSYS simulation and cost estimation. The results indicated that carbon membranes can be a promising candidate for biogas upgrading with a low processing cost of 0.078 \$/m^3 at the feed pressure of 8.5 bar. Increased membrane performance can further reduce the cost. Moreover, a carbon membrane system can be very cost-effective for upgrading of biogas in small-scale plants of around 350 m^3(STP)/h.

Keywords: Biogas upgrading; carbon molecular sieve membrane; process simulation; cost estimation; technology feasibility

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Abbreviations

ADJ: adjustor

CRC: annual capital related cost

E: heat exchanger

GWP: global warming potential

K: compressor

Mix: mixer

op: membrane unit

OPEX: operating expenditure

PSA: pressure swing adsorption

RCY: recycling

TEE: distribution unit

TRL: technology readiness levels

VOCs: volatile organic compounds

Nomenclature

A: membrane area, m^2

C_{BM}: bare module cost, $

C_{GR}: grassroots cost, $

C_M: membrane skid cost, $

C_p^0: purchase cost, $

C_{TM}: total module cost, $

J: gas flux, m^3(STP)/(m^2·h)

N: the number of hollow fibers in a module

n: mole flow, kmol/h

P: feed pressure, bar

p: permeate pressure, bar

Pe: permeance, m^3(STP)/(m^2·h·bar)

Q: compressor size or capacity, kW

q: gas volumetric flow rate, m^3(STP)/h

x: mole fraction in feed side

y: mole fraction in permeate side

α: selectivity

θ: stage-cut, %

Superscripts

F: feed

P: permeate

R: retentate

l: one end of hollow fiber module

Subscripts

F: feed

P: permeate

70 *i:* the i^{th} component

71 *m:* membrane

72 1. Introduction

73 The European Commission has launched a set of energy and climate goals for 2030 where the aim
74 in one of the key targets is to reach at least 27 % renewable energy by 2030, and where biomass
75 based biofuels should replace at least 10 % of petroleum-derived fuels for road transport. Upgraded
76 biogas represents a good transition fuel for renewable energy systems and may be converted to
77 other fuels by steam reforming and catalytic processing (Ferella et al., 2017), and it is thus a
78 valuable source with respect to renewable energy production. Biogas is usually produced from
79 anaerobic digestion of biodegradable wastes such as sewage sludge, animal manure, organic
80 fraction of household and industrial waste. Biogas is mainly composed of methane (CH_4) and
81 carbon dioxide (CO_2), and may also contain volatile organic compounds (VOCs), H_2O, H_2S and
82 NH_3 depending on the origin of the anaerobic digestion process. Biogas may be purified and
83 upgraded to have a content of methane higher than 98 vol.%, and hence a very high content of
84 energy. Many countries (e.g., Germany, Denmark, and the Netherland) have shown an interest in
85 the use of upgraded biogas to substitute petroleum-derived fuels for road transport in order to
86 reduce CO_2 emissions. However, depending on the end usage various biogas treatments may be
87 implemented to increase the calorific value. It is thus important to find a suitable technology for
88 purification with low energy consumption, high efficiency and low CH_4 loss. The most common
89 techniques for biogas upgrading include water scrubbing, pressure swing adsorption (PSA),
90 chemical absorption (e.g., amines) and gas separation membranes. The choice of suitable
91 technology is mainly dependent on the specific conditions at a plant, such as the availability of
92 low price of thermal energy, electricity and water, as well as the amount of gas to be purified. In

the European region, water scrubbing is the most prevailing technology at biogas plants (40 %), and membrane has 4 % of the market today (Niesner et al., 2013). Most biogas plants in Sweden are using PSA technology for biogas upgrading even though CH_4 loss is high (3-10 %). The biogas plants using water scrubbing technology can get high purity CH_4 (>99 vol.%), but also produces a lot of wastewater and has high power demands. The amine scrubbing technology presents high selectivity and will produce high purity methane, but the process is energy intensive, and considered not so environmentally friendly due to the needs of organic solvents (amines). Comparing to the other state-of-the-art technologies, gas separation membrane technology presents a more energy- and space-saving process with lower environmental impacts. Membrane processes are preferable for small-scale biogas plants < 1000 m^3(STP)/h (Miltner et al., 2017). However, the main challenge of a membrane system for biogas upgrading is to get high CH_4 purity and low CH_4 loss simultaneously – this is related to that there is too low selectivity between the two main components CO_2 and CH_4. The latest reported single stage polyimide membrane system can only reach a CH_4 purity of 80.7 vol.% with a high CH_4 loss of 24 %, which is unacceptable in any biogas production plants (Nemestóthy et al., 2018). Using a multi-stage polyimide membrane system in series can get high purity CH_4, but the CH_4 loss will be higher. A CH_4 loss to atmosphere of more than 4 % leads to a non-sustainable process according to carbon footprint life cycle assessment (Ravina and Genon, 2015), which is negative related to economy and environment impact due to the high global warming potential (GWP) of methane. Therefore, seeking a high CO_2/CH_4 selective membrane (at least >30) is crucial to reduce CH_4 loss, simplify process design, and reduce energy consumption. Although the commercial polymeric membranes (e.g., SEPURAN®, Carborex®, Prism®) are dominating the current industrial membrane-based biogas upgrading processes, the main challenges are the trade-off between permeability and selectivity,

as well as limitations at higher operating pressures and adverse conditions such as the presence of H_2S in biogas. These facts may direct the development of polymeric membranes to alternative nanocomposite/mixed matrix membranes or carbon membranes to be used for biogas upgrading. The carbon nanotubes reinforced fixed-site-carrier membranes reported to effectively improve membrane performance, especially at high pressure operation (He et al., 2014), but the membranes needs to be operated at a high water vapor content environment which is a challenge for the engineering design. Carbon membranes are usually prepared by carbonization of polymeric precursors such as polyimides, polyacrylonitiles, poly(phthalazinone ether sulfone ketone), poly(phenylene oxide) and cellulose derivatives, and can be used for different gas separation processes. Among them, the cellulose-derived hollow fiber carbon molecular sieve membranes have been tested for CO_2/CH_4 separation, and presented a high CO_2/CH_4 selectivity over 100 (Haider et al., 2016; He et al., 2011, Haider et al., 2018a), which showed a nice potential for biogas upgrading. Several carbon membrane modules (each one with an area of 2 m^2) of this type were exposed to a real biogas (63 vol.% CH_4, 1 ppm H_2S, balance CO_2) over 200 days at a biogas plant in Southern Norway (Haider et al., 2018b). Approximately 1 m^3 (STP)/h biogas was processed by these modules at 15-20 °C and 20 bar feed pressure. High purity methane was achieved, and the membranes showed stable performance over the testing period. The membrane system was judged to be at TRL 5.

To investigate the feasibility of using carbon membrane for biogas upgrading, process simulation at plant scale should be conducted. Although the previous work reported carbon membranes for biogas upgrading (Haider et al., 2016), the optimal operating condition as well as the influences of CH_4 loss and plant capacity have not been systematically investigated - these are critical issues for future commercialization. Thus, in this work, a two-stage carbon membrane system was designed

for a biogas upgrading system based on the experimental data obtained from a bench-scale membrane system testing at high pressure up to 20 bar. HYSYS simulation together with cost estimation was also performed to evaluate the economic competition compared to the state-of-the-art technologies.

2. Method

2.1 Gas permeation testing

The cellulose-derived hollow fiber carbon molecular sieve membranes were provided by MemfoACT for testing (the company closed in 2014). For the gas permeation measurements, a high pressure gas permeation rig with design pressure up to 100 bar and feed gas capacity of 0.33 m^3(STP)/h was used (He et al., 2014). The carbon membranes were fabricated by the carbonization of the regenerated cellulose hollow fibers under a well-controlled procedure described by Haider et al. (Haider et al., 2016; Haider et al., 2018a). The average outer diameter and thickness of the carbon membranes are 200 μm and 25 μm, respectively, and the material characteristics were reported in the previous work (He and Hägg, 2012; He et al., 2011). In total 106 hollow fiber carbon membranes were mounted into a small-scale (stainless steel tube with the outer diameter of 0.0127 m) module with the effective membrane area of 0.02 m^2, which can be tested up to 40 bar and 100 ℃. In this work, the module was tested with a 40 vol.% CO_2/60 vol.% CH_4 gas mixture at different feed pressure of 5-20 bar and 25 ℃. The sweep gas of nitrogen is used in the permeate side at 1 bar. The pre-mixed gas was fed from the bore side of the module, and the fast gas molecules permeated through the membranes to the shell side. The permeate gas composition and flow rate were measured by a SRI gas chromatograph and a mass flow meter (EL-Flow®, Bronkhorst High-Tech B.V.) to calculate membrane separation performances (mainly gas permeance (Pe) and selectivity (α)) by Eq. (1),

$$Pe_i = \frac{J_i}{\Delta p_i} = \frac{q_i}{A \cdot \Delta p_i};\ \alpha_{CO_2/CH_4} = \frac{Pe_{CO_2}}{Pe_{CH_4}} \quad (1)$$

where J_i (m^3(STP)/(m^2·h) and q_i (m^3(STP)/h) are the permeate flux and volumetric flow rate of the gas component i. A and Δp_i are the membrane area (m^2) and trans-membrane partial pressure difference (bar) of the component i, respectively.

2.2 Process design

Biogas produced from an anaerobic digestion process contains CH_4 and CO_2 where CH_4 content is usually 65 vol.%, and the gas may also contain VOCs, H_2O, H_2S and NH_3. Proper pre-treatment is required to remove water, particles and other impurities before feeding the biogas into a membrane system for CO_2 removal. The previous MemfoACT company tested a pilot carbon membrane system (designed capacity: 50 m^3(STP)/h) for biogas upgrading. The high purity biomethane was produced in the retentate side, which was compressed to 220 bar for transportation to a storage site (Haider et al. 2018b). The pilot was, however, overengineered regarding the level of gas pre-treatment as it applied activated charcoal adsorption (in the inlet of the biogas feed compressor) to reduce the H_2S to be in compliance with the Swedish gas standard for vehicles. Moreover, the water level of the feed biogas was controlled to the gas standard (the biogas dew point is low than -40 °C at 250 bar) ahead of the carbon membrane system.

Membrane system performance mainly depends on process configuration and operating condition. Some literature has already reported on the optimization of process configuration in a specific separation process (He, 2017; Hussain and Hägg, 2010; Peters et al., 2011). A single-stage membrane unit was conducted to investigate the influences of process operating parameters such as pressure ratio, feed composition and capacity on membrane system performances, and validated via the membrane model of ChemBrane (He et al., 2014). Those results indicated that single-stage

membrane system cannot achieve both high methane purity and low CH_4 loss simultaneously. Thus, a two-stage cascade carbon membrane system related to the recycling of the permeate from the 2nd stage was designed for biogas upgrading from a gas stream containing 35 vol.% CO_2 (see Fig. 1). It was found that when the raw biogas was compressed (K-100 in the figure) to a given feed pressure (5-20 bar) before being fed into the 1st stage membrane unit (op-100), the CO_2 purity in the 1st stage permeate stream (permeate 1) could achieve >90 vol.%, given the membrane had a CO_2/CH_4 selectivity >30. The stream of *Retentate 1* was fed into the 2nd stage membrane unit (op-101 in flowsheet figure 1) for further purification. The permeate stream in the 2nd stage (permeate 2) recompressed (K-101) and recycled (RCY-1) back to the feed stream of the 1st stage to achieve low CH_4 loss (< 2 %). The high purity methane will then be produced in the retentate stream of the 2nd stage unit (Retentate 2). It is worth noting that the 1st stage membrane area may be adjusted by ADJ-1 to control the overall CH_4 loss, and the 2nd stage membrane area may be adjusted by ADJ-2 to reach the required CH_4 purity. The designed system can thus produce high CH_4 purity using a two-stage cascade membrane unit and achieve low CH_4 loss with the 2nd stage permeate recycling.

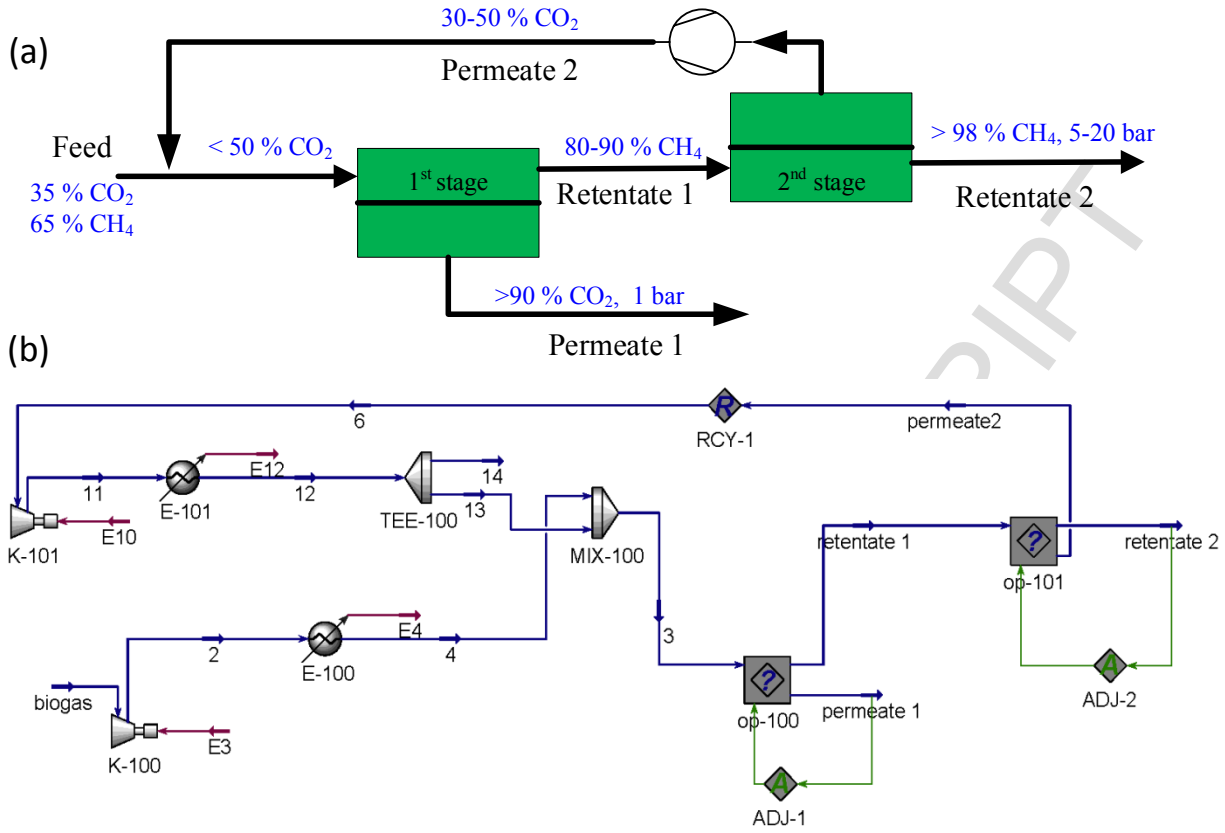


Fig. 1 The illustration (a) and HYSYS process flow diagram (b) of a two-stage membrane system with related to the 2nd stage permeate recycling for biogas upgrading (K: compressor, E: heat exchanger, ADJ: adjustor, RCY: recycling, TEE: distribution unit, Mix: mixer, op: membrane unit)

2.3 Simulation basis

The following assumptions were made for the process simulations.

1. A counter-current configuration without sweep in the permeate side was applied to model the hollow fiber carbon membrane modules (which presents the best separation performance compared to the co-current mode and the cross-flow mode (He et al., 2014)).
2. The Sour Peng-Robinson fluid package was used for the calculation of physicochemical properties of gas mixture. To simplify the simulation, only the main components of CO_2

and CH_4 were considered in the feed gas stream, and biogas pre-treatment was not included in this work.

3. The adiabatic efficiency of 75 % was used for rotary compressors.
4. No temperature and pressure drop were applied in both feed and permeate side of membrane module.

The simulation basis (see Table 1) chosen was based on the experimental data obtained in this work, and the moderate feed pressure of 5-20 bar was investigated in the simulation. The designed two-stage carbon membrane system was employed to document the technology feasibility of the carbon membrane system for biogas upgrading from a 1000 m^3(STP)/h biogas plant (with 35 vol.% CO_2 in feed). The CH_4 purity (> 98 vol.%) and CH_4 loss (< 2 %) were chosen as the separation requirements. The membrane unit was simulated at 30 °C and permeate pressure of 1 bar.

Table 1 The simulation basis for biogas upgrading using a carbon membrane system

Parameters	Values
Feed flow, m^3(STP)/h	200-1500
Feed gas composition	35 vol.% CO_2/65 vol.% CH_4
1st stage feed pressure (P), bar	5-20
Feed temperature, °C	30
CO_2 permeance, m^3(STP)/(m^2·h·bar)	based on experimental data[a]
CO_2/CH_4 selectivity	based on experimental data[a]
CH_4 purity, vol.%	> 98
CH_4 loss, %	< 2
Membrane area, m^2	optimized

[a]: experimental data were obtained at a 40% CO_2 feed gas, but the sensitivity analysis was based on the assumed membrane performance

2.4 Membrane modelling and simulation

The counter-current plug flow pattern with shell side feeding is shown in Fig. 2, and the permeation of multicomponent gas mixture through a hollow fiber membrane module can be described by the following set of equations. The local flow rate of permeation is defined in terms of a differential mass balance by Eq. (2) (Chowdhury et al., 2005; Davis, 2002):

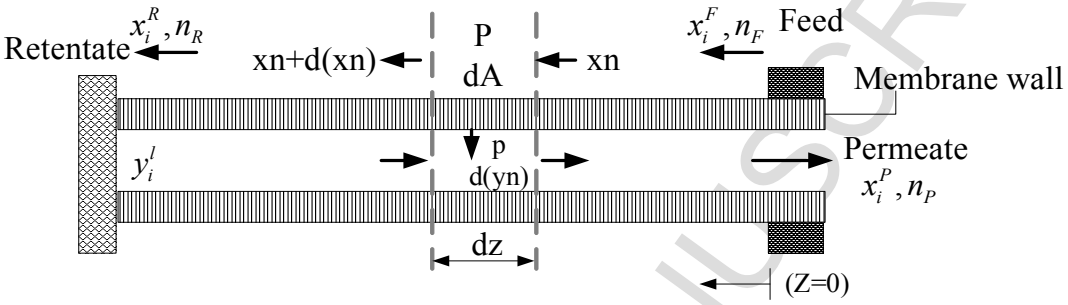


Fig. 2 A counter-current flow configuration for membrane gas separation

$$d(xn)_i = -Pe_i(x_i P - y_i p)dA \tag{2}$$

where n is the molar flow rate of the retentate side; x and y are the component mole fractions on feed and permeate side; P and p the feed and permeate pressure, respectively and dA the differential membrane area ($dA=N\pi d_o dz$, d_o and dz are the outside diameter and differential length of the hollow fibers, respectively, N is the number of hollow fibers in the module). The integration of Eq. (2) gives Eq. (3):

$$x_i^F n_F - x_i^R n_R = Pe_i(\overline{x_i P - y_i p})A_m \tag{3}$$

Davis (2002) reported that logarithmic-mean driving force can be used to estimate the average component trans-membrane partial pressure when the feed composition variation is less than 50 %. This method may be used to simplify the model solution process, and the logarithmic-mean trans-membrane partial pressure for a counter- current flow configuration is defined as:

$$\left(\overline{x_i P - y_i p}\right) = \frac{(x_i^F P - y_i^P p) - (x_i^R P - y_i^l p)}{\ln(\frac{x_i^F P - y_i^P p}{x_i^R P - y_i^l p})} \tag{4}$$

where y_i^l is the permeate composition of the component *i* at the end of the hollow fibers. The y_i^l can be calculated by the assumption of local perfect mixing in Eq. (5) (Davis, 2002):

$$y_i^l n_P = Pe_i (x_i^R P - y_i^l p) A_m \tag{5}$$

If the composition or flow rate of feed stream changes more than 50 %, the membrane unit may be split into several subunits. Therefore, the Eq. (4) is still applicable for the estimation of the trans-membrane partial pressure. In order to simplify the model, the pressure and temperature drop along the module length are neglected here. The stage-cut of the component *i* (θ_i) is calculated by Eq. (6),

$$\theta_i = \frac{y_i^P n_P}{x_i^F n_F} = \frac{Pe_i \left(\overline{x_i P - y_i p}\right) A_m}{x_i^F n_F} \tag{6}$$

Giving the feed compositions and flow rate, the permeate and retentate compositions can be calculated by iterating a stage-cut of each component. In order to accelerate the convergence rate, the non-linear objective function in Eq. (7) is applied. The θ_i can be determined when the objective function reaches the minimum.

$$f_{\min} = \sum_i \left[Pe_i \left(\overline{x_i P - y_i p}\right) A_m - \theta_i x_i^F n_F \right]^2 \tag{7}$$

The logarithm-mean approximation in Eq. (4) is problematic for iterative optimization techniques due to the potential of computational errors caused by division by zero or evaluating the logarithm of a negative number. Thus, a modified logarithm-mean approximation method reported by Chen (1987) was employed to overcome this limitation, and the Eq. (4) can be rewritten as:

$$\left(\overline{x_i P - y_i p}\right) = \frac{\Delta_1 - \Delta_2}{\ln(\Delta_1/\Delta_2)} \cong \left[\Delta_1 \Delta_2 \left(\frac{\Delta_1 + \Delta_2}{2}\right)\right]^{1/3} \quad (8)$$

$$\Delta_1 = (x_i^F P - y_i^P p); \quad \Delta_2 = (x_i^R P - y_i^l p)$$

Chen's approximation is crucial for the implementation of the optimization of Eq. (7) in the gas membrane separation simulator to avoid any divergent solutions. The model was implemented in a HYSYS customized unit - ChemBrane (Grainger, 2007) which has been widely used for in-house process simulation of membrane systems for gas separations (He, 2017; Hussain and Hägg, 2010).

2.5 Cost estimation

Cost estimation of major equipment (e.g., compressor and membrane unit) was implemented for feasibility analysis of a carbon membrane processes operated at different conditions. The cost model as reported in our previous work (He, 2017) was employed to estimate biogas upgrading cost. The project time was set to 15 years, and the purchased cost of the rotary compressor estimated by (Turton et al., 2013):

$$log_{10} C_p^0 = K_1 + K_2 log_{10}(Q) + K_3 \left[log_{10}(Q)\right]^2 \quad (9)$$

where Q is compressor capacity (kW), and K_1, K_2, and K_3 are given in Table 2.

Table 2 Parameters for cost estimation on rotary compressors (Turton et al., 2013)

Compressor Type	K_1	K_2	K_3	F_{BMSS}[a]	W_{min}, kW	W_{max}, kW
Rotary	5.0355	-1.8002	0.8253	5.0	18	900

[a]: the bare module factor using stainless steel material

The grassroots cost (C_{GR}) was used to calculate total capital cost which is considering the auxiliary facilities cost (site development, auxiliary buildings, off-sites, etc.) in addition to the total module cost, and estimated by Eq. (10)

$$C_{GR} = C_{TM} + 0.5\sum_{i=1}^{n} C_{BM,i}^{0} \quad (10)$$

where n is the total number of individual equipment (only compressor here, lifetime 15 years), C_{BM}^{0} and C_{TM} are the bare module cost in the base condition and the total module cost, respectively. The chemical engineering plant cost index (CEPCI) for the equipment of 541.7 (2016) was used to adopt all inflation adjustments. A \$50 cost per m^2 membrane surface area was employed to estimate membrane skid cost (C_M). The membrane lifetime was set to 5 years (He, 2017). The annual capital related cost (CRC) was estimated by Eq. (11),

$$CRC = 0.2 \cdot (C_{GR} + C_M) \quad (11)$$

For the annual operating expenditure (OPEX), only electricity cost was considered to simplify cost estimation (price based on (Zhang et al., 2013)). The specific biogas upgrading cost (\$/m^3 upgraded biogas) was then estimated according to Eq. (12)

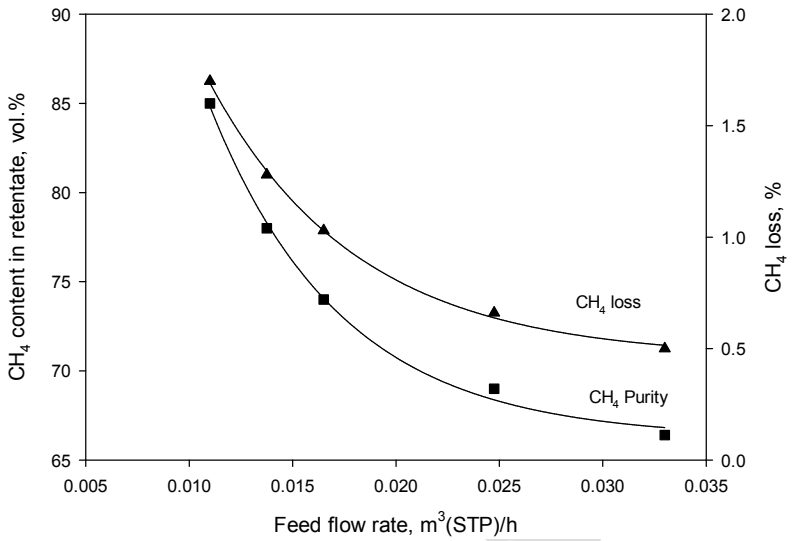
$$Specific\ biogas\ upgrading\ cost = \frac{CRC + OPEX}{Annual\ total\ upgraded\ biogas} \quad (12)$$

3. Results and discussions

3.1 Membrane module performance

Fig. 3 shows the influences of feed flow rate on membrane module performances. It can be seen that the CH_4 purity in the retentate increases with the decrease of the feed flow rate, but the CH_4 loss in the permeate increases as well (as expected). Thus, there is a trade-off to achieve high CH_4 purity and low CH_4 loss using a single-stage membrane system. It was worth noting that feed capacity (i.e., biogas feed flow rate) is usually given at the biogas plants, and the membrane system should thus be operated at a high stage-cut to achieve high purity CH_4 in the retentate; this will however increase the CH_4 loss as can be understood from the definition of stage-cut. Both process

300 design and optimization are hence crucial to achieve both high CH_4 purity and low CH_4 loss in
301 real applications.



302

303 Fig. 3 The influences of feed flow rate on the CH_4 purity in the retentate and CH_4 loss

304 The feed pressure influence was investigated by testing the small-scale membrane module at
305 different feed pressures from 5 bar to 20 bar. A constant feed flow of 0.017 m^3(STP)/h and
306 temperature of 25 ℃ was employed, and the results are shown in Table 3. The CO_2 permeance and
307 CO_2/CH_4 selectivity decreased with the increase of feed pressure. The dependences of gas
308 separation performances on feed pressure were predicted by dynamic data fitting of these results
309 hence the following two equations could be stated:

310 $$P_{CO2} = 0.314 \cdot P^{-0.650} \quad (13)$$

311 $$S_{CO2/CH4} = 176 \cdot P^{-0.323} \quad (14)$$

312 It is worth noting that CO_2 flux increased due to the significant increase of the driving force (i.e.,
313 partial pressure difference across membrane) when operating at higher pressure. Moreover, higher
314 CH_4 purity was obtained at the higher feed pressure, but the energy consumption was naturally

315 also higher. Therefore, process simulation must be performed in order to identify the optimal
316 operating condition based on these experimental data.

317 Table 3 The membrane separation performance tested at different feed pressure

Feed pressure, bar	CO_2 permeance, $m^3(STP)/(m^2 \cdot h \cdot bar)$	CO_2/CH_4 selectivity	CO_2 flux, $m^3(STP)/(m^2 \cdot h)$	CH_4 purity in the retentate, vol.%
5	0.111	104.2	0.15	65.5
10	0.069	84.4	0.21	67.6
15	0.054	73.1	0.25	69.4
20	0.045	66.7	0.28	70.9

318

319 ## 3.2 Technology feasibility analysis

320 Process simulation was conducted using HYSYS integrated with ChemBrane to document the
321 technology feasibility. The two-stage carbon membrane system (see the process flow diagram in
322 Fig. 1) was designed to purify a 1000 $m^3(STP)/h$ biogas stream produced in a biomass digestion
323 process. A feed pressure of 10 bar and a permeate pressure of 1 bar was simulated, and the detailed
324 simulation results and key performance indicators are shown in Table 4 and 5. The proposed two-
325 stage carbon membrane system is, according to our evaluation, technically feasible for producing
326 high purity CH_4 (98 vol.%) with low CH_4 loss (< 2 %) at the given operating condition.

327 Table 4 The mass balances of the simulation results

Gas stream		Component volume flow, $m^3(STP)/h$		
		CO_2	CH_4	Overall
Feed biogas		350	650	1000
1st stage	Feed (including recycling)	525.2	719.8	1245.0

	Retentate	188.1	707.0	895.1
	Permeate	337.1	12.8	349.9
	Stage-cut, %	64.9	1.8	28.1
2nd stage	Feed	188.1	707.0	895.1
	Retentate	12.9	637.1	650.0
	Permeate (recycling)	175.2	69.9	245.1
	Stage-cut, %	93.2	9.9	27.4

328

329 Table 5 The simulated key performance indicators of the process operated at 10 bar feed pressure

Power demand, kW	Membrane area, m^2	CH_4 purity, %	CH_4 loss, %
152.8	11586.7	98.0	1.97

330

331 3.3 Feed pressure influence

332 The first stage feed gas pressure was varied from 5-20 bar to investigate its influence on power
333 demand and required membrane area. Fig. 4 shows the dependences of the first stage feed pressure
334 on power demand for compressors and the required membrane area. Increasing feed pressure will
335 increase the power demand of the compressors, and the dependence was found to be according to
336 Eq. (15).

337 $$Q = 61.517 \cdot P^{0.371} \quad (15)$$

338 The required membrane area which is reduced at higher pressure, can thus be expressed as in Eq.
339 (16)

340 $$A = 9.307 \cdot 10^{5} \cdot P^{-1.917} \quad (16)$$

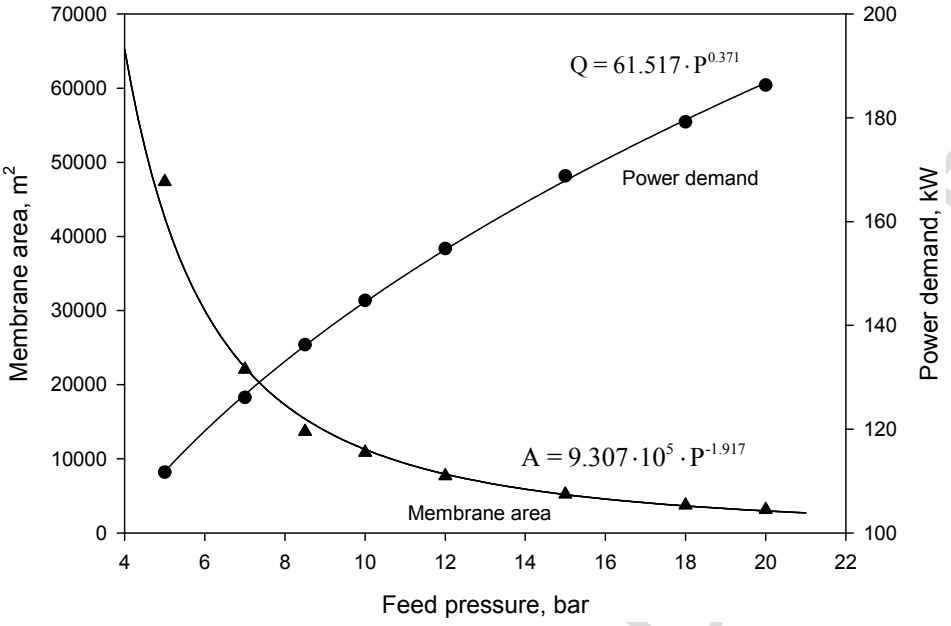
Thus, the optimal operating conditions should be identified based on the specific cost estimated by Eq. (12) considering the electricity price and the membrane skid cost. Fig. 5 shows the dependence of OPEX and CRC on the first stage feed pressure. It was found that annual CRC is more dominating compared to annual OPEX. The total annual cost decreases up to a certain feed pressure (here slightly above 8 bar) and then increases again for higher pressures. The dependence was found to be (Eq. (17)),

$$Total\ annual\ cost = 6.673 \cdot 10^5 - \frac{5.562 \cdot 10^6}{P} + \frac{2.764 \cdot 10^7}{P^2} \quad (17)$$

Moreover, the dependence of specific biogas upgrading cost on feed pressure is shown in Fig. 6. The minimum cost of 0.078 \$/m^3 was found to be at the feed pressure of ca. 8.5 bar (Eq. (18)):

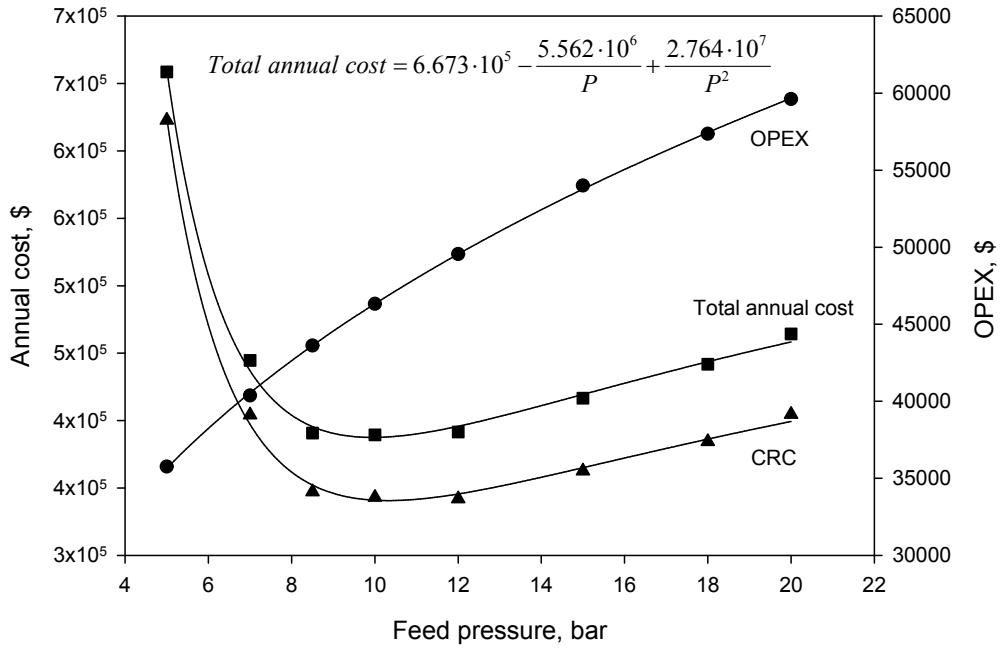
$$\text{Specific biogas upgrading cost} = 0.134 - \frac{1.113}{P} + \frac{5.533}{P^2} \quad (18)$$

which is lower than 0.15 €/m^3 of the cost of the state-of-the-art technologies (i.e., amine absorption, water scrubbing) as reported by Miltner et al. (2017). It should be noticed that the compression cost (usually up to 200 bar for transportation) of the upgraded biogas (biomethane) is not included in our work. The cost of these additional compressors will be significantly reduced if the inlet pressure is 20 bar compared to 5 bar. Moreover, the carbon membrane cost needs to be further investigated, and a pilot-scale demonstration system is required to test membrane performance in the relevant environment at a higher TRL.



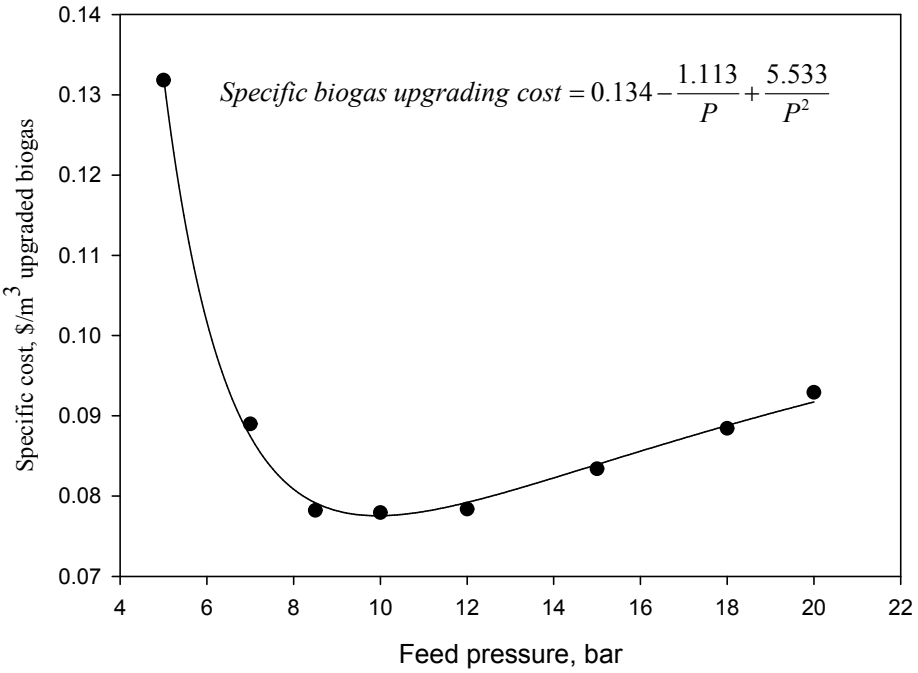
360

361 Fig. 4 The influence of feed pressure on the power demands and the required membrane area



362

363 Fig. 5 The influences of feed pressure on the CRC, OPEX, and total annual cost



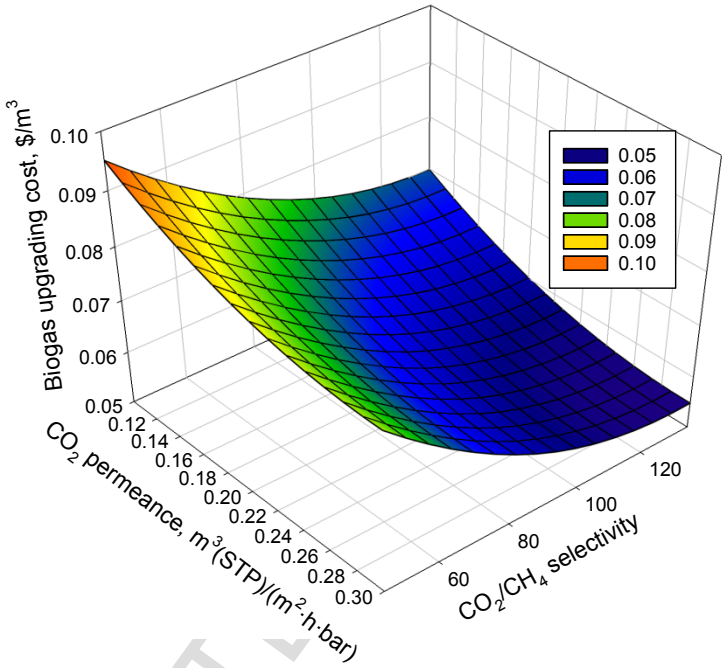
364

365 Fig. 6 The influence of feed pressure on the biogas upgrading cost

366 3.4 Membrane material performance influence

367 From the equation (1), one can see that the increase of gas permeance reduces the required
368 membrane area to process a given amount of biogas. Thus, membranes with high gas permeance
369 are always preferred to bring down membrane unit cost. Moreover, higher selectivity can enhance
370 the separation efficiency and reduce the CH_4 loss per module (or making the system more efficient
371 to achieve the specific separation requirement). It is well known that a given separation problem
372 may be operated in selectivity controlled region or in a pressure ratio controlled mode (Stookey et
373 al., 1986). Therefore, the sensitivity analysis of both CO_2 permeance (0.1-0.3 m^3(STP)/(m^2·h·bar))
374 and CO_2/CH_4 selectivity (45-135) on the biogas upgrading cost were investigated to identify the
375 optimal membrane performances. The process simulations were conducted with a 1000 m^3(STP)/h
376 feed biogas at the feed pressure of 8.5 bar and 30 ℃ to achieve the CH_4 purity of 98 % and the
377 CH_4 loss of < 2 %. The dependence of biogas upgrading cost on membrane performance is shown
378 in Fig. 7. It can be seen that increasing CO_2 permeance and CO_2/CH_4 selectivity can reduce the

379 cost. Selectivity presents a more significant effect as high selectivity improves the separation
380 process and reduce the energy consumption dramatically, and future development should therefore
381 focus on the improvement of CO_2/CH_4 selectivity of carbon membranes. It should also be
382 remembered that the cost of the membrane material combined with the expected lifetime of the
383 module and likewise the compressor cost may shift the optima - these considerations have not been
384 included in the current work.



385

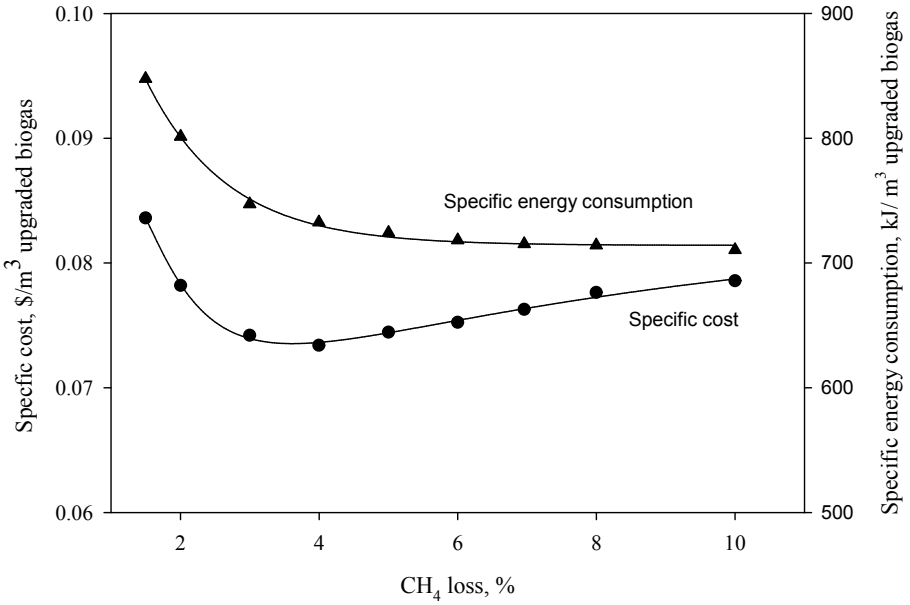
386 Fig. 7 The dependence of biogas upgrading cost on the membrane material performances

387

388 ## 3.5 CH_4 loss influence

389 CH_4 loss is critical at biogas plants both due to loss in energy and the significant greenhouse effect
390 of methane; hence it should be well controlled at a low level. Thus, a varying CH_4 loss from 1.5-
391 10 % operated at a feed pressure of 8.5 bar was investigated, and the specific biogas upgrading
392 costs were estimated as shown in Fig. 8. It can be seen that biogas upgrading cost decreases
393 dramatically in the beginning, but increases at higher CH_4 loss > 4 %. Moreover, the specific

394 energy consumption of 801 kJ/m^3 upgraded biogas at an acceptable CH_4 loss of 2 % was found to
395 be much lower compared to a typical amine absorption process (1807 kJ/m^3 upgraded biogas
396 including power energy and thermal energy (Oreggioni et al., 2017)). It is also worth noting that
397 pursuing extremely low CH_4 loss will dramatically increase biogas membrane upgrading cost, and
398 the enhanced methane recovery may not be able to offset the incremental cost. Thus, 2 % of CH_4
399 loss is the highest which can be recommended for the carbon membrane system in biogas
400 upgrading.



401

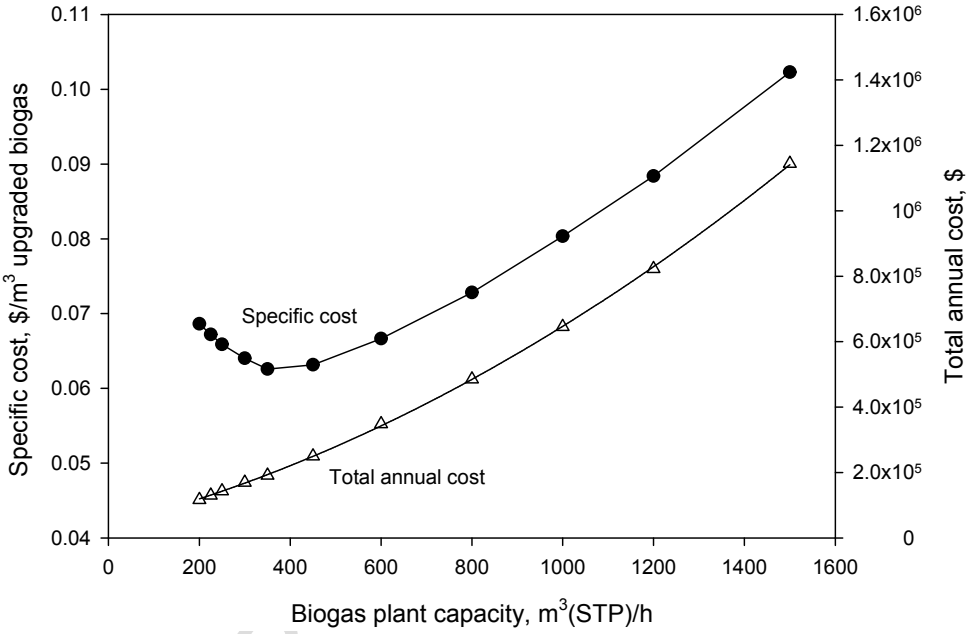
402 Fig. 8 The influences of CH_4 loss on the specific energy consumption and biogas upgrading cost

403

404 ## 3.6 Biogas plant capacity influence

405 Miltner et al. (2017) reported that biogas plant capacity would significant influence the cost, and
406 they found that membrane separation and amine scrubbing technologies were slightly
407 advantageous for plant size below 1000 m^3(STP)/h, while water scrubbing was relatively cheaper
408 for capacities exceeding 1500 m^3(STP)/h. In this work, the biogas plants with the capacities of
409 200-1500 m^3(STP)/h were investigated at 10 bar for the influence on the cost of carbon membrane

410 system for biogas upgrading. Fig. 9 shows the dependence of specific biogas upgrading cost on
411 biogas plant capacity. The main conclusion from this analysis is that the high cost-intensity of
412 large-scale biogas upgrading plants is due to the significant increase of rotary compressor cost
413 (compressor cost is a polynomial function of capacity as described in Eq. (9)). Thus, carbon
414 membrane system is preferable for small-scale biogas plants (ca. 350 m^3(STP)/h), which can also
415 avoid the high cost of feedstock transportation from different supply chains and expand the
416 business of biomass based biofuels to achieve EU 27 % renewable energy by 2030.



417

418 Fig. 9 The influence of biogas plant capacity on the specific biogas upgrading cost

419 ## 4. Conclusions

420 The cellulose-derived hollow fiber carbon membranes showed a high CO_2/CH_4 selectivity (>60)
421 at pressures up to 20 bar, which is much higher compared to the commercial polymeric
422 membranes. The HYSYS simulation results indicated that a two-stage carbon membrane system
423 with recycling of the second-stage permeate can produce high purity of CH_4 (98 vol.%) at a low
424 CH_4 loss of < 2 %. The specific biogas upgrading costs were found to be significantly dependent

425 on the CRC, and thus reduction of the membrane skid cost is crucial to bring down the biogas
426 upgrading cost further. The developed carbon membranes were found to be more cost-effective
427 for small-scale biogas plants (e.g., around 350 m^3(STP)/h) due to a polynomial increase of rotary
428 compressor cost for high capacity requirement. The feed pressure of 8.5 bar was identified as the
429 optimal operating pressure to reach the lowest biogas upgrading cost of 0.078 \$/m^3 for a 1000
430 m^3(STP)/h biogas plant. Moreover, further improving carbon membrane performance by increased
431 CO_2 permeance and/or CO_2/CH_4 selectivity can reduce biogas upgrading cost. The current work
432 documented the technology feasibility of carbon membranes for biogas upgrading, but membrane
433 upscaling and pilot-scale demonstration should be conducted to bring this membrane to future
434 commercialization.
435

436 ## Acknowledgements

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439 the hollow fiber carbon membranes for gas permeation testing.
440
441

442 ## References

443 2030 Energy Strategy. https://ec.europa.eu/energy/en/topics/energy-strategy-and-
444 energy-union/2030-energy-strategy. (Accessed December 12 2017).
445 Chen, J.J.J., 1987. Comments in Improvements on a Replacement for the logarithm Mean.
446 Chemical Engineering Science. 42(10), 2048.
447 Chowdhury, M.H.M., Feng, X., Douglas, P., Croiset, E., 2005. A New Numerical Approach
448 for a Detailed Multicomponent Gas Separation Membrane Model and AspenPlus
449 Simulation. Chemical Engineering & Technology 28(7), 773-782.

Davis, R.A., 2002. Simple Gas Permeation and Pervaporation Membrane Unit Operation Models for Process Simulators. Chemical Engineering & Technology 25(7), 717-722.

Ferella, F., Puca, A., Taglieri, G., Rossi, L., Gallucci, K., 2017. Separation of carbon dioxide for biogas upgrading to biomethane. Journal of Cleaner Production 164, 1205-1218.

Grainger, D., 2007. Development of carbon membranes for hydrogen recovery, Department of Chemical Engineering. Norwegian University of Science and technology, Trondheim.

Haider, S., Lindbråthen, A., Hägg, M.-B., 2016. Techno-economical evaluation of membrane based biogas upgrading system: A comparison between polymeric membrane and carbon membrane technology. Green Energy & Environment 1(3), 222-234.

Haider, S., Lindbråthen, A., Lie, J.A., Andersen, I.C.T., Hägg, M.-B., 2018a. CO_2 separation with carbon membranes in high pressure and elevated temperature applications. Separation & Purification Technology 190, 177-189.

Haider, S., Lindbråthen, A., Lie, J.A., Vattekar Carstensen, P., Johannessen, T., Hägg, M.-B., 2018b. Vehicle fuel from biogas with carbon membranes; a comparison between simulation predictions and actual field demonstration. Green Energy & Environment doi: 10.1016/j.gee.2018.03.003.

He, X., 2017. Techno-economic feasibility analysis on carbon membranes for hydrogen purification. Separation & Purification Technology 186, 117-124.

He, X., Hägg, M.-B., 2012. Structural, kinetic and performance characterization of hollow fiber carbon membranes. Journal of Membrane Science 390–391(0), 23-31.

He, X., Hägg, M.-B., Kim, T.-J., 2014. Hybrid FSC membrane for CO_2 removal from natural gas: Experimental, process simulation, and economic feasibility analysis. AlChE Journal 60(12), 4174-4184.

He, X., Lie, J.A., Sheridan, E., Hägg, M.-B., 2011. Preparation and Characterization of Hollow Fiber Carbon Membranes from Cellulose Acetate Precursors. Industrial & Engineering Chemistry Research 50(4), 2080-2087.

Hussain, A., Hägg, M.-B., 2010. A feasibility study of CO_2 capture from flue gas by a facilitated transport membrane. Journal Membrane Science 359(1-2), 140-148.

Miltner, M., Makaruk, A., Harasek, M., 2017. Review on available biogas upgrading technologies and innovations towards advanced solutions. Journal of Cleaner Production 161, 1329-1337.

Nemestóthy, N., Bakonyi, P., Szentgyörgyi, E., Kumar, G., Nguyen, D.D., Chang, S.W., Kim, S.-H., Bélafi-Bakó, K., 2018. Evaluation of a membrane permeation system for biogas upgrading using model and real gaseous mixtures: The effect of operating conditions on separation behaviour, methane recovery and process stability. Journal of Cleaner Production 185, 44-51.

Niesner J., Jecha D., Stehlik P., 2013. Biogas upgrading techniques: state of art review in european region. Chemical Engineering Transactions 35, 517-522.

Oreggioni, G.D., Luberti, M., Reilly, M., Kirby, M.E., Toop, T., Theodorou, M., Tassou, S.A., 2017. Techno-economic analysis of bio-methane production from agriculture and food industry waste. Energy Procedia 123, 81-88.

Peters, L., Hussain, A., Follmann, M., Melin, T., Hägg, M.B., 2011. CO_2 removal from natural gas by employing amine absorption and membrane technology—A technical and economical analysis. Chemical Engineering Journal 172(2–3), 952-960.

Ravina, M., Genon, G., 2015. Global and local emissions of a biogas plant considering the production of biomethane as an alternative end-use solution. Journal of Cleaner Production 102, 115-126.

Stookey, J., Patton, C.J., Malcolm, G.L., 1986. Membrane Separate Gases Selectively. Chemial Engineering Progress 82(11), 36-40.

Turton, R., Bailie, R.C., Whiting, W.B., Shaeiwitz, J.A., Bhattacharyya, D., 2013. Analysis, synthesis, and design of chemical processes, Fourth Edition. Pearson Education, Upper Saddle River, NJ.

Zhang, X., He, X., Gundersen, T., 2013. Post-combustion Carbon Capture with a Gas Separation Membrane: Parametric Study, Capture Cost, and Exergy Analysis. Energy & Fuels 27(8), 4137-4149.

List of figure captions

Fig. 1 The illustration (a) and HYSYS process flow diagram (b) of a two-stage membrane system with related to the 2nd stage permeate recycling for biogas upgrading (K: compressor, E: heat exchanger, ADJ: adjustor, RCY: recycling, TEE: distribution unit, Mix: mixer, op: membrane unit)

Fig. 2 Counter-current flow configuration for membrane gas separation

Fig. 3 The influences of feed flow rate on the CH_4 purity in the retentate and CH_4 loss

Fig. 4 The influence of feed pressure on the power demands and the required membrane area

Fig. 5 The influences of feed pressure on the CRC, OPEX, and total annual cost

Fig. 6 The influence of feed pressure on the biogas upgrading cost

Fig. 7 The dependence of biogas upgrading cost on the membrane material performances

Fig. 8 The influences of CH_4 loss on the specific energy consumption and biogas upgrading cost

Fig. 9 The influence of biogas plant capacity on the specific biogas upgrading cost

Highlights:

1. A bench-scale carbon membrane module was tested for CO_2/CH_4 separation
2. A two-stage membrane system was designed to achieve 98 % CH_4 at < 2 % CH_4 loss
3. Technology feasibility of carbon membranes for biogas upgrading was documented