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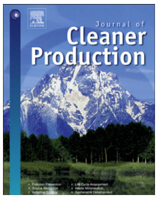

Carbon molecular sieve membranes for biogas upgrading: Techno-economic feasibility analysis

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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.

1. Introduction

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

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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.

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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$^2\cdot$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$^2\cdot$h$\cdot$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
i	the ith component
m	membrane

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, 2018a; He et al., 2011), 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., 2016, 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 °C. 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 °C. 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