Membrane separation process for small scaled partial biogas upgrading

Abdessamad Saidi1,a, Fosca Conti1,2,*b, Matthias Sonnleitner1,e and Markus Goldbrunner1,d

1Institute of new Energy Systems, Technische Hochschule Ingolstadt, Esplanade 10, 85049 Ingolstadt, Germany
2Department of Chemical Sciences, University of Padova, via Marzolo 1, 35141 Padova, Italy

Email: aabdessamad.saidi@thi.de, bfosca.conti@unipd.it (*corresponding author), cmatthias.sonnleitner@thi.de, dmarkus.goldbrunner@thi.de

Abstract. Biogas upgrading is actually limited to the production of biomethane as natural gas substitute. To realize the according gas quality a cost intensive methane enrichment is required, wherefore biogas upgrading is actually merely cost-efficient in case of high production rates. Since the energy and cost effort disproportionately increases with the required product gas purity partial biogas upgrading for decentralized utilization represents a promising utilization approach for farm based applications. Among the available technologies for CO2-separation the gas permeable membrane has high potential for small scaled biogas upgrading. Within the present study a model based analysis to determine the savings potential of a membrane based upgrading system is performed.

1. Introduction

To achieve climate protection goals at national and international levels, the expansion of renewable sustainable energies has been quantified with specified obligatory targets initialized by the Kyoto decisions concerning the reduction of greenhouse gases (GHG). In Germany, a GHG emissions reduction by at least 40 % until 2020 as compared to 1990 and by 80 – 90 % until 2050 in comparison to 1990 is pursued [1].

Besides energy efficiency measures, the expansion of energy production from renewable sources is a mainstay to achieve these ambitious goals. The Directive for renewable energy sources of the European Union (2009/28/EG) determines a share of renewable energies of 18 % of the gross energy consumption until 2020 [2].

In Germany the implementation of renewable energy into the structure of energy supply has been expanding continuously within the recent years. In 2016, a total feed-in power of 188.3 TWhel is occurred which implies a share of 31.7 % of the electricity consumption [3]. With 32.37 TWhel, biogas provides about 17.2 % of electricity generation from renewable energy sources and therefore makes a significant contribution to sustainable electricity production besides wind energy and photovoltaics [3].

The massive build-up of biogas plants over the last decade was stimulated by governmental funding and legal framework of the Renewable Energy Sources Act. To preserve the existing plants after the financial funding has expired the economic efficiency of biogas processes has to be increased and new revenue opportunities have to be uncovered.
As an alternative utilization pathway to conventional CHP conversion for electricity and heat production, biogas upgrading has been increasingly applied in the recent years. The product gas, so-called biomethane, can be injected into the natural gas grid. To meet the high quality standards for the use as natural gas substitute various gas treatment steps are required. Mainly biogas upgrading includes gas drying, desulphurization, removal of further harmful trace components and CO$_2$-separation to improve the calorific value [4].

Due to high investment and operating costs, this option is constrained to high production rates. Since the CO$_2$ separation represents the most energy and cost intensive sub process, a reduced methane enrichment enables profitable farm based biogas upgrading on a small scale.

Within the present research project, the approach of decentralized utilization of partially upgraded biogas as fuel for agricultural machinery is investigated. Experimental studies on a reequipped single-cylinder diesel revealed, that performance equivalent engine operation can be realized with a CO$_2$-content up to 25%. This determined concentration represents the superordinate goal for the design of the upgrading system [5].

To remove the CO$_2$ fraction from gas mixtures various methods have been developed and optimized in the gas processing industry within the recent decades. For biogas upgrading the following processes are available [4]:

| Solvent demand | Water scrubbing          |
|----------------|--------------------------|
|                | Organic solvents         |
|                | Amine scrubbing          |
| No solvent demand | Pressure swing          |
|                  | Cryogenic separation     |
|                  | Membrane separation      |

Due to its low complexity and equipment demand the membrane separation shows high potential for small scaled applications among the currently available upgrading technologies and therefore represents a promising option for the present research issue.

The separation mechanism relies on the preferential transfer of one gas fraction from a mixture through a semi-permeable membrane material. Membranes can be grouped into high pressure membranes which have gases present on each side of the membrane, and low pressure systems, which have a liquid adsorbent on one side of the membrane wall. High pressure membranes are widely used for biogas upgrading. In a membrane system, high concentrations of contaminants such as H$_2$S and moisture are generally reduced prior to methane enrichment. High pressure membrane separation is typically undertaken at 8–15 bar [6]. Biogas is generally upgraded in a multi stage process to yield a final CH$_4$ concentration of 96%. Waste gases from the preliminary stages are recycled within the process to enhance CH$_4$ capture whilst waste gas from the final stage, which may contain 10–20% CH$_4$, is either flared, used for heat production [6] or captured catalytically. This technology has been applied for some time for the upgrading of natural gas.

2. Methods

2.1 Upgrading concept
The approach of reduced CO$_2$-separation provides the option for further simplifications of the conventional membrane separation process (e.g. Figure 1).
The most significant process simplification is given by the reduction of the separation stages. In principle, the number of stages does not represent a limiting factor for the product gas purity, since any composition of the product gas can be realized by a single membrane unit. Rather, the multi-stage process provides an option to mitigate the tradeoff between the product gas purity and mass efficiency. Since the methane rich permeate of the final stages is recirculated by the feed flow, the multi stage configuration enables a significant reduction of the methane losses.

Regarding overall process efficiency and after treatment of the waste gas the methane losses define an essential criterion for conventional upgrading systems. However, for small scaled biogas upgrading, the methane content of the permeate flow is of subordinate significance. Taking typical biogas production rates into account, the comparatively low gas flow provided as fuel for agricultural machinery allows the recirculation of the waste gas stream without a significant impact on the raw biogas composition. The impact of the recirculation for different gas flow rates and methane slip values (share of separated methane) can be determined by simple mass balance calculations and is illustrated in Figure 2.

As depicted, the raw biogas plus recirculated gas flow show decreased reduction of the methane content with increased methane slip. However, since the impact on the gas composition is negligibly small, a recirculation of the permeate gas can be performed.

The product gas purity and separation efficiency of the membrane process are strongly related to the operating pressure. The low purity requirements afford the option to reduce the energy demand of the separation process by lowering the compressor capacity.

A disadvantage of the simplified configuration is the reduced degrees of freedom with fewer adjustable process parameters. While the tradeoff between the product gas purity, the operation pressure, and product gas flow rate can be mitigated in multi stage separation with process design and

Figure 1. Simplification options for membrane separation process

Figure 2. Impact of the methane slip on the raw biogas composition with recirculation of the offgas
off gas recirculation, a decoupling of these parameters is not possible in a single membrane unit. This issue is illustrated in detail based on the following explanations.

2.2 Model equations

The permeable separation of gas components represents an established gas processing method in different industry sectors, giving rise to the development of various modelling approaches in recent decades.

| Developer          | Year | Reference |
|--------------------|------|-----------|
| Coker et al.       | 1999 | [7]       |
| Marriott et al.    | 2001 | [8]       |
| Kalids et al.      | 2000 | [9]       |
| Giglia et al.      | 1991 | [10]      |
| Davis              | 2002 | [11]      |
| Katoh et al.       | 2010 | [12]      |
| Makaruk et al.     | 2009 | [13]      |
| Mota et al.        | 2002 | [14]      |
| Rautenbach et al.  | 1996 | [15]      |
| Scholz et al.      | 2012 | [16]      |
| Ohlrogge et al.    | 2005 | [17]      |

Due to the high thematic consistency and appropriate compromise between accuracy and computing time, the model calculations of Makaruk et al. [13] are chosen among these methods for the present research objective. The approach provides a discretization of the continuous separation process. For one component i, the discretization is based on the finite difference method in a domain including the number c of discrete points (Figure 13).

Figure 3. Discretization of the continuous membrane separation process

The corresponding conservation equations of the feed and permeate stream for a co-current separation process are presented as follows [13]:

\[
Q_{P,i,j}^{n+\left(1/2\right)} = Q_{F,i,j}^{n} - \Delta l n_{i,j}^{n} \left( y_{F,i,j}^{n} - y_{P,i,j}^{n} \right) s \pi d
\]  

(1)
The state variables within the iterative solver are characterized by the index \( n \). Since the separation efficiency is strongly related to the operating pressure, an accurate determination of the pressure gradient along the membrane unit is essential to generate a valid separation model. Taking the flow characteristic of membrane processes into account, the dissipative pressure loss has to be considered in addition to the pressure decrease caused by permeation. Under the assumption of a laminar flow, the pressure loss can be calculated via the Hagen-Poiseulle law. The corresponding equation for a discretized system is shown as follows [18].

\[
\Delta p_F = \sum_{i=1}^{k} \frac{Q_{F,i} \mu_{F,i} \Delta l_{p,STP} T_F}{s \pi D^4 p F \rho \mu_{F,STP}}
\]

Besides the separation pressure, which represents a process variable, the permeability as a material property has to be known. While several reported values for membrane materials are available in literature, membrane permeability of commercially available membranes are often concealed. To consider the actual state of the art, the present model is based on simulations provided by a co-developer of the SEPURAN® Green membrane (Evonik industries), which ranks among the most applied products for permeable biogas upgrading in Germany. Since the provided simulations are derived from real operations performed by pilot and commercial plants, validation of the present model is fulfilled to a great extent.

3. Results and discussion

A sensitivity analysis was conducted on the simulation with varying gas flow rate and operating pressure. The gas composition on the permeate and retentate side along the membrane for a feed flow of 10 and 11 m\(^3\) \( \text{STP} \)/h is shown in Figure 4.
As expected, the permeation of the CO\textsubscript{2} fraction is advanced by pressure increase, leading to lower CO\textsubscript{2}-concentrations of the retentate flow (e.g. Figure 4 left). For higher volume flows, an appropriate rise of the operation pressure is required to enable adequate product gas purity. Concomitantly, a pressure increase is also connected to higher methane concentration in the permeate flow (e.g. Figure 4 right), implying lower methane recovery. According to the explanations around Figure 2, the methane content on the retentate side should not be considered as methane losses. Nevertheless, in terms of conservation of mass, an increased methane permeation requires a higher feed demand to reach a targeted product gas amount and composition.

A summarizing illustration of the product gas composition over the entire variation range for flow rate and operation pressure is shown in Figure 5.

![Product gas composition (left) and volume flow (right) depending on the operating pressure](image)

**Figure 5.** Product gas composition (left) and volume flow (right) depending on the operating pressure

For a pre-specified raw biogas flow rate, the operating pressure is the single lever to achieve a targeted gas composition. For example, a gas flow with a CO\textsubscript{2} content of 25% and a flow rate of 10 m\textsuperscript{3}\textsubscript{STP}/h can be realized with an operation pressure of about 12.4 bar and a raw biogas flow of approximately 14 m\textsuperscript{3}\textsubscript{STP}/h. Decoupling of the process parameters is not possible. A single stage membrane separation is severely limited by the degrees of freedom to accommodate fluctuating raw biogas compositions.

4. Conclusions
The membrane separation process shows high potential as economic methane enrichment technology for small scaled applications. The approach of a reduced CO\textsubscript{2}-separation provides the option for further simplifications of the conventional process. Furthermore, the idea enables lower operating pressures and therefore contributes to an increased cost-efficiency. Since the CO\textsubscript{2}-separation merely represents the key step of the upgrading system, an overall model based investigation including the further gas processing steps as well as an economic efficiency calculation has to be performed to determine the total savings potential.

References
[1] Energiekonzept für eine umweltschonende, zuverlässige und bezahlbare Energieversorgung,
Federal Ministry for Economic Affairs and Energy, Berlin 2010.

[2] Directive 2009/28/EC, European Parliament and Council, Brussels 2009.

[3] Erneuerbare Energien in Deutschland, Umweltbundesamt, Dessau-Roßlau 2017.

[4] Poeschl, M., Ward, S., Owende, P. 2010. Prospects for expanded utilization of biogas in Germany, Ren. and Sust. En. Rev. 14, 1782–1797 [1] Davalos J. et. al. 1976 J. Chem. Eng. Data 21 1.

[5] Saidi, A., Beringer, M., Sonnleitner, M., Männl, U., Innerhofer, S., Goldbrunner, M., Combustion and exhaust emission characteristics of a dual fuel engine operated with low caloric biogas, Poster: Progress in Biogas IV, 8-11/03/2017, Stuttgart.

[6] Wellinger, A., Lindberg, A., Biogas Upgrading and Utilisation. IEA Bioenergy Task 24, 2005.

[7] Marriott et al., Detailed mathematical modelling of membrane, Computers & Chemical Engineering, p. 693–700, 2001.

[8] Kalids et al. , Simulation of multicomponent gas separation in a hollow fiber membrane by orthogonal collocation–hydrogen recovery from refinery gases, Journal of Membrane Science, p. 61–71, 2000.

[9] Giglia et al. , Mathematical and experimental analysis of gas separation by hollow fiber membranes, Industrial & Engineering Chemistry, p. 1239–1248, 1991.

[10] Davis et. al. , Simple gas permeation and pervaporation membrane unit operation models for process simulators, Chemical Engineering & Technology, p. 717–722, 2002.

[11] Katoh et al. , Dynamic simulation of multicomponent gas separation by hollow-fiber membrane module: Nonideal mixing flows in permeate and residue sides using the tanks-in-series model. Separation and Purification Technology, 2010.

[12] Makaruk et al. , Numerical algorithm for modelling multicomponent multipermeator systems, “ Journal of Membrane Science. p. 258–265, 2009.

[13] Mota et al. , Simulation of a new hybrid membrane/pressure swing adsorption process for gas separation, Desalination, p. 275–280, 2002.

[14] Rautenbach et al. , Simulation and design of membrane plants with Aspen Plus, Chemical Engineering & Technology, p. 391–397, 1996.

[15] Schoitz et al. , Modeling gas permeation by linking non-ideal effects, Industrial & Engineering Chemistry Research, 2012.

[16] Schoitz et al. , Membranverfahren zur Abtrennung organischer Dämpfe in der chemischen und petrochemischen Industrie, Chemie Ingenieur Technik, p. 527–537, 2005.

[17] James P. Hartnett; Milivoje K., Heat Transfer to Newtonian and Non-Newtonian Fluids in Rectangular Ducts. Advances in Heat Transfer, Volume 19, 1989.

Acknowledgement
The work was financially supported by the German Federal Ministry of Education and Research within the program “Forschung an Fachhochschulen” under the grant “22402215”. FC is grateful to the University of Padova, Italy, for providing the opportunity to spend research periods at the Technische Hochschule Ingolstadt.