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EXHIBIT A



Structural optimization of membrane-based biogas upgrading processes

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Received 17 February 2014, Revised 8 August 2014, Accepted 14 August 2014, Available online 28 September 2014.

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<https://doi.org/10.1016/j.memsci.2014.08.032> 

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Highlights

- Process optimization model for gas permeation.
- New biogas upgrading process.
- Identifying optimal membrane materials.

Abstract

Gas permeation membranes are well known for separating CO₂ and CH₄. Single stage processes cannot provide both, high product gas purity and high recovery at the same time, but multistage processes do. Commonly, the design of multistage gas permeation processes relies on heuristics and experience, so that often sub-optimal separation processes are designed. We apply a structural optimization approach to biogas upgrading processes. This systematic method determines the most profitable process layout including membrane areas and pressures required for two commercial membranes. Furthermore, we determine the optimal selectivity and CO₂ permeance

following the upper bound of the Robeson plot. The process model is implemented using General Algebraic Modeling System (GAMS). For commercial membranes a three stage gas permeation process is the most profitable process which operates with only a single compressor. Optimizing the process layout together with the membrane properties a two stage process is the best process configuration. CO_2/CH_4 selectivities of approximately 120 are optimal. The impact of changed feed conditions and required product purity was investigated. The results highlight that for biogas upgrading commercial gas permeation membranes already provide powerful separation characteristics. The optimal membrane processes are capable to economically compete with conventional biogas upgrading techniques.



Previous

Next



Keywords

Process modeling; Structural optimization; Gas permeation; Biogas upgrading

1. Introduction

The depletion of fossil resources triggers the transition to renewable energies. Biogas upgrading will contribute to future energy supply. Contrary to solar and wind power, biogas is produced continuously. Biogas will considerably contribute to future energy supply as it is a renewable resource. Biogas upgrading refers to the separation of CH_4 and CO_2 , where a CH_4 rich gas is polished so that it can be used as natural gas substitute [1]. Gas permeation membranes are well known for separating CO_2 and CH_4 [2], [3], [4]. Their application in biogas upgrading offers several advantages over conventional gas separation techniques. First the gas permeation operates with the upgraded product gas being at elevated pressure so that it can directly be injected into the natural gas grid [1]. Secondly gas permeation modules are robust and the process is simple, which is particularly suitable for on-farm application [5].

The objective of the study at hand is to design a membrane based biogas upgrading process based on structural process optimization. Here, (i) the optimal process configuration, (ii) the required membrane areas in the various stages and (iii) the pressure to drive the gas permeation process for a commercial membrane material are determined simultaneously. In a further step selectivity of the membrane material is optimized together with the process layout and the process conditions.

Process design often relies on heuristics and experience [6] which may result in suboptimal process configurations. The application of systematic methods for process design ensures the identification of the most profitable process configuration. Although superstructure optimization provides a systematic framework for the design of membrane based separation processes only limited work has been published. Sargent and Gaminibandara were the first who introduced the concept of structural optimization in designing distillation sequences. This concept has been adapted by El-Hawagi and Manousiouthakis who optimized mass exchange networks [7].

In the optimization of gas permeation processes Uppaluri et al. [8] studied the enriched oxygen production, hydrogen recovery from synthesis gas, and hydrogen recovery from refinery streams. They obtained new process designs which reduces the costs by 20% compared to process designs previously reported in the literature. They applied stochastic optimization using a simulated annealing algorithm.

Qi and Henson [9], [10] report on CO₂/CH₄ separation in natural gas treatment and enhanced oil recovery. Here, only recycle compressors are investigated as the raw gas is already pressurized. They used GAMS along with the DICOPT++ algorithm to solve the MINLP. They even introduced discrete variables to account for a more realistic process design as membrane modules are available with fixed active membrane areas. They identified a four stage gas permeation process as the process configuration with the lowest gas treatment costs for natural gas polishing. For enhance oil recovery they also determined a four stage process as optimal process configuration as it has the lowest costs. In an additional publication [10] they extend the binary model to multicomponent model. The separation of CH₄, CO₂, H₂S and heavier hydrocarbons in natural gas treatment as well as the separation of CH₄, CO₂, H₂S, C₂H₆ and heavier hydrocarbons in enhanced oil recovery were investigated.

Kookos [11] does not only optimize the process layout and process conditions, but he also determines the best selectivity along with the best permeance for the production of nitrogen and oxygen from air. The upper bound correlation published by Robeson is applied to account for the membrane material performance. For the production of oxygen the comparison of an optimized membrane material and a commercial membrane material leads to the conclusion that impressive cost reductions are obtained.

We adapt the structural optimization approach to identify the most profitable membrane based biogas upgrading system. The process model is implemented in the General Algebraic Modeling System (GAMS). In a first step commercial gas permeation membranes are applied to the process optimization. The best process layout together with the optimal membrane areas and process conditions were calculated. In a second step the membrane's selectivity is an additional optimization parameter. The relation between selectivity and CO₂ permeance is determined according to the upper bound published by Robeson [12]. In contrast to Kookos [11] we applied the updated data for the upper bound correlation published in 2008. A three stage process is the optimal process configuration for the commercial membrane materials while a two stage process is the best layout for optimal membrane materials. An optimal CO₂/CH₄ selectivity in the order of 120 was most profitable for a process in which a single selectivity is applied to all membrane stages. When calculating the optimal selectivity for each membrane stage individually, a first highly selective stage is combined with highly permeable stage cleaning the permeate of the first stage.

The process model can easily be adapted to other gas separation problems such as helium production from natural gas, natural gas upgrading or air separation to determine the most profitable process configurations.

2. Process model

Commonly gas permeation processes include multiple membrane stages to achieve high gas purities and recoveries simultaneously. Favre [13] reported that more than three stages are usually not installed in industrial applications since these processes seem to be less efficient and cost demanding. In biogas upgrading it is rather unsuitable to use more than three stages as the complexity of the system increases rapidly and the application of such a system at a biogas site seems to be less robust. The process model implemented here is not limited to any number of membrane stages, but for the optimization of the biogas upgrading process a maximum number of three membrane stages is defined.

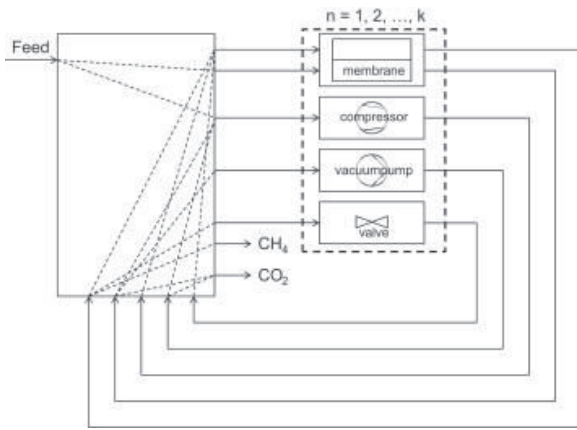
The gas permeation modules considered in the simulations are equipped with polymeric membrane materials to separate CO₂ and CH₄. CO₂ will permeate faster through the membrane so that the permeate is enriched in CO₂. Thus, CH₄ is enriched on the retentate side of the membrane which is particularly advantageous in biogas upgrading as the product gas is pressurized and can thereby directly be injected into the natural gas grid. Table 1 lists the raw gas conditions and the product gas requirements. A membrane CO₂/CH₄ selectivity of 60 is assumed based on a current patent [14] for a polyimide membrane material.

Table 1. Feed and product gas conditions of a common biogas upgrading process. The permeances of the polymeric membrane materials are also listed. PI – polyimide; CA – cellulose acetate; $1 \text{ GPU} = 2.7 \times 10^{-3} \text{ m}^3/\text{m}^2\text{h bar}$.

	Unit	Value
Raw gas mole fraction CH_4	–	0.6
Raw gas mole fraction CO_2	–	0.4
Raw gas flow rate	$\frac{\text{m}^3(\text{STP})}{\text{h}}$	150
Raw gas temperature	$^{\circ}\text{C}$	20
Raw gas pressure	bar	1
Product pressure	bar	16
Product mole fraction CH_4	–	0.96
CH_4 permeance PI	GPU	1
CO_2 permeance PI	GPU	60
CH_4 permeance CA	GPU	3
CO_2 permeance CA	GPU	60

However, no information is given on the permeances of such a membrane material and we assume a CO_2 permeance of 60GPU. In addition, a membrane material with selectivities reflecting the characteristics of a cellulose acetate membrane is investigated. The permeances are also listed in [Table 1](#).

In general, feed gas conditions, product gas requirements and economic parameters such product gas pressure and energy costs considerably determine the optimal process configuration. Consequently, the optimal process configuration presented here, is identified by applying the boundary conditions set here. This process configuration is most likely not optimal for the entire range of parameters to be applied in biogas upgrading and boundary conditions have to be reviewed carefully. The objective of the optimization is to maximize the profit of the biogas upgrading plant. Four different types of unit operations are implemented and could be used in the process model. These are a gas permeation module to perform the separation and equipment to generate the driving force of permeation such as compressors, vacuum pumps, and pressure control valves. [Fig. 1](#) shows the respective unit operations and illustrates the potential connections of the individual unit operation with other unit operations. Here only selected connections are presented. For the gas permeation model it is also possible to use a sweep gas on the permeate side. At the inlet (bottom) of the so called distribution box each stream can be split and connected to all available outlet ports of the distribution box. The inlets are splitters while the various outlet ports on the right side of the distribution box are mixers. Each unit operation can be selected several times, so that multistage processes can be optimized with the process model.



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Fig. 1. Superstructure approach to optimize a membrane based biogas upgrading plant. Note that not all possible connections between the various unit operations are presented.

The gas permeation module itself is the most important piece of process equipment as it performs the separation. The driving force can either be generated by compressing the feed gas, by applying sub-ambient pressure on the permeate side or by diluting the permeate with a sweep gas. The solver selects the compression equipment based on the operational and investment costs since the driving force method determines the pressure levels as well as the recycle flow rates.

The superstructure model including the models for the unit operations and their connections were programmed in the General Algebraic Modeling System (GAMS). GAMS is a modelling system for mathematical programs that are occasionally used in process optimization [15]. In GAMS the mathematical problem is programmed independently of the solver. Various algorithms are available to solve linear programs (LP), nonlinear programs (NLP) and mixed integer nonlinear programs (MINLP). Optimizing the biogas upgrading process is a MINLP as the connections between the unit operations are of integer type and nonlinear equations (e.g. capital cost calculation) are solved.

The Branch-And-Reduce Optimization Navigator (BARON) is used which is a branch and bound type global optimization solver. With this kind of solver, identification of the global optimum is guaranteed even if fairly general assumptions are made [16].

2.1. Unit operation models

The gas permeation module is built as a short cut model based on the fundamental equations for conservation of mass and a simple mass transfer equation. The gas permeation module is discretized in 100 elements j and solved together with the superstructure equations by BARON. The mole balances for counter current flow for each gas species i of the feed side and the permeate side are solved for each element j :

$$\dot{n}_{R,i,j} = \dot{n}_{i,j} + \dot{n}_{R,i,j+1} \quad (1)$$

$$\dot{n}_{P,i,j} = \dot{n}_{i,j} + \dot{n}_{P,i,j+1} \quad (2)$$

Here, $\dot{n}_{R,i,j}$ refers to the flow rate on the feed side and $\dot{n}_{P,i,j}$ is the flow rate on the permeate side, respectively. The mass transfer through the membrane $\dot{n}$ is determined by the partial pressure difference, the permeance of the gas species Q_i , the active membrane area A and it is determined for each discretized element:

$$\dot{n}_{i,j} = Q_i \cdot (x_{i,j} p_F - y_{i,j} p_P) A \quad (3)$$

Mole fractions are determined by

$$x_{i,j} = \frac{\dot{n}_{r,i,j}}{\sum_i \dot{n}_{r,i,j}} \quad (4)$$

$$y_{i,j} = \frac{\dot{n}_{p,i,j}}{\sum_i \dot{n}_{p,i,j}} \quad (5)$$

Simplifying assumptions have been made: (i) no pressure losses are considered, (ii) isothermal operation, (iii) concentration polarization is neglected, (iv) constant permeances and (v) ideal gas behavior are assumed.

The compressors and the vacuum pumps are modeled as single stage isentropic compression units without interstage cooling. The isentropic outlet temperature T_{out} is determined by

$$T_{out} = T_{in} \cdot \left(\frac{p_{out}}{p_{in}} \right)^{(\kappa-1)/\kappa} \quad (6)$$

The isentropic exponent κ is 1.3. T_{in} and p_{in} delineate the inlet temperature and pressure, and p_{out} is the compressor's discharge pressure. The real outlet temperature T_{real} is calculated by

$$\eta_{isent} = \frac{T_{out} - T_{in}}{T_{real} - T_{in}} \quad (7)$$

The isentropic efficiency η_{isent} of the compressor is 0.72. Vacuum equipment has isentropic efficiencies of far less than 0.5, in case of a jet pump it is only 0.1 [17]. Thus, we assume an isentropic efficiency of 0.5 for the vacuum equipment. The net power e , which is the energy supplied to the gas stream, is determined by

$$e = \dot{m} \cdot c_p \cdot (T_{real} - T_{in}) \quad (8)$$

whereby, $\dot{m}$ is the mass flow rate through the compression equipment and c_p is the specific heat capacity of the gas (34.77 J/molK). A simple constraint for the pressure control valve was implemented. Here, the upstream pressure has to be higher than the pressure on the downstream side:

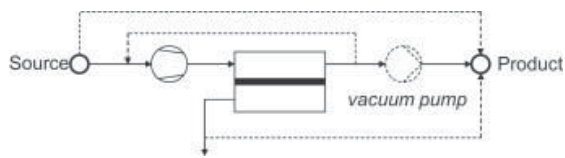
$$p_{in} \geq p_{out} \quad (9)$$

Compared to the costs for compressors and vacuum pumps the costs for a pressure valve can be neglected. Since a pressure valve has to be installed anyway.

Generally any outlet of an unit operation can be connected to any inlet of all available unit operations. Therefore it is possible to optimize membrane cascades including recycle streams. Fig. 1 illustrates a set of connections between the different unit operations. To mix two different process streams the pressure of the streams have to be equal. In case of different stream pressures these are either increased by a compressor or reduced by a pressure control valve.

To reduce the number of process configurations and the calculation effort some connections can be precluded which do not contribute to the separation process or even have a negative impact on process performance. Fig. 2 illustrates these respective connections which are not considered in the optimization. These connections are for instance:

- recycling of a retentate stream and mixing with the feed stream of a membrane module;
- direct connection of the feed and the product stream;
- mixing of permeate streams with the product stream;
- connection of a retentate outlet stream and a vacuum pump inlet.



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Fig.2. Connections which are excluded from the optimization. Excluded connections are labelled with dashed lines.

2.2. Economics

To optimize the process it is more appropriate to determine the economic optimum rather than the energetic optimum, since the membrane based biogas upgrading process has to compete economically with well established gas separation techniques. The energetic optimum can be fairly different from the economic optimum. In this study we determine the most profitable process configuration by taking both, operational cost, mainly caused by electrical energy consumption, and investment costs for the compression equipment and the membrane modules into account.

The membranes lifetime is 4 years and the membranes have to be exchanged after this operation period. Table 3 summarizes the economic parameters chosen for the optimization simulation.

Table3. Economic parameters used for optimization of a membrane based biogas upgrading plant.

Costs	Unit	Value
Membrane module costs	$\frac{\text{Euro}}{\text{m}^2}$	55
Electrical costs	$\frac{\text{Euro}}{\text{kWh}}$	0.08
Commission of purified gas	$\frac{\text{Euro}}{\text{m}^3}$	0.2
Membrane lifetime	year	4
Annual operation	h	8,000
Interest rate	–	0.09
Amortization period	years	8

Investment costs for the compressor and the vacuum pump can be estimated with Guthrie's method [18], [19]. This method enables the calculation of capital costs based on the size of the compression equipment and the process conditions. The method roughly estimates investment cost with an $\pm 25\%$ error [18].

In a first step the bare module costs (BC) are determined:

$$BC = C_0 \cdot \left(\frac{S}{S_0} \right)^\alpha \quad (10)$$

where C_0 are reference costs for the equipment, S is a variable taking the size of the respective equipment into account and S_0 is a reference size of the equipment. In case of compression S is the required compression duty and S_0 is the reference compression duty. The parameter α considers the cost increase with increasing equipment size.

Here, the economy of scale is taken into account since α is generally lower than 1. The required values for C_0 and S_0 are tabulated in Biegler et al. [18].

To determine the capital costs the reference costs have to be updated as the values were determined for the reference year 1969. In addition, the capital costs of the equipment depend on the operating conditions and the materials used. Thus, the capital costs CC are calculated by

$$CC = UF \cdot BC \cdot (MPF + MF - 1) \quad (11)$$

Here UF delineates the update factor which takes the current price level into account. MPF is the material and pressure factor accounting for the material of the equipment. The module factor MF additionally considers the size of the equipment. Hirschberg [20] suggests that 2 should be added to this factor to realistically reflect today's investment costs. The Guthrie parameters used here are listed in Table 2.

Table 2. Parameters to estimate the investment costs for the compression equipment with Guthrie's method [18].

Parameter	Unit	Value
Update factor 2011		4.91
Material and pressure factor		2.9
Module factor		5.11
Conversion bhp* in kW	kW/bhp	0.746
Reference costs for compressor in 1968	US Dollar	23,000
Reference compressor size	bhp	100
Cost function exponent		0.77
Conversion US Dollar in Euro	US Dollar/Euro	1.2719

*

bhp – brake horse power.

2.3. Robeson plot

Many efforts are made to develop new membrane materials which have improved selectivities and permeances. From an operational point of view the application of these membranes in gas permeation processes is limited. High selectivities together with high permeances induce concentration polarization significantly limiting the separation performance of the gas permeation modules. Thus the driving force for the retained gas species increases while the driving force for the fast permeating species reduces [21], [22]. However, the effect of concentration polarization is not accounted for in the model but it is remarkable for membranes with selectivities and permeances as high as 100 and 1000 GPU, respectively [22].

Furthermore, for gas permeation processes high pressure ratios have to be provided to take advantage of high membrane selectivities [23]. The trade-off between permeability and selectivity is well known [12]. In terms of process design low selectivities increase the amount of the retained gas species which permeates through the membrane resulting in increased compression duty. For high selectivity, permeance drops which increases the required membrane area remarkably. As a consequence higher investment costs and membrane replacement costs reduce the profitability of the upgrading process.

Robeson [12] introduced a correlation to determine the permeability as a function of the selectivity for upper bound materials. We implemented the upper bound correlation into the superstructure model, to determine the most profitable selectivity simultaneously with the optimal process layout, the membrane areas and pressures. For CO₂ and CH₄ Robeson published the following correlation:

$$P_{\text{CO}_2} = 5369140(\alpha_{\text{CO}_2/\text{CH}_4})^{-2.636} \text{ Barrer} \quad (12)$$

Assuming a membrane thickness of 30nm transforms permeability into permeance.

$$Q_{\text{CO}_2} = 33.77 \cdot 5369140(\alpha_{\text{CO}_2/\text{CH}_4})^{-2.636} \text{ GPU} \quad (13)$$

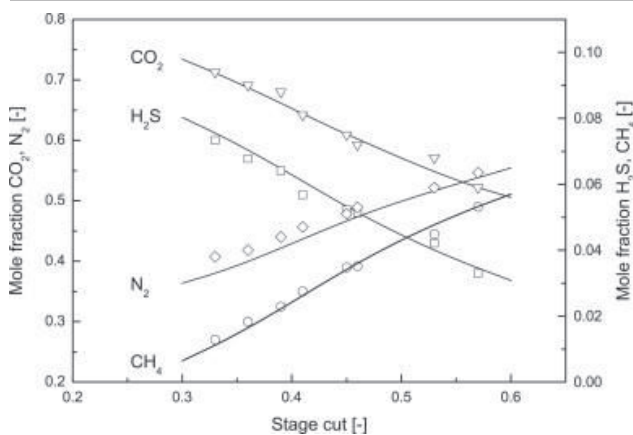
where, $\alpha_{\text{CO}_2/\text{CH}_4}$ is the selectivity:

$$\alpha_{\text{CO}_2/\text{CH}_4} = \frac{Q_{\text{CO}_2}}{Q_{\text{CH}_4}} \quad (14)$$

3. Results and discussion

3.1. Model validation

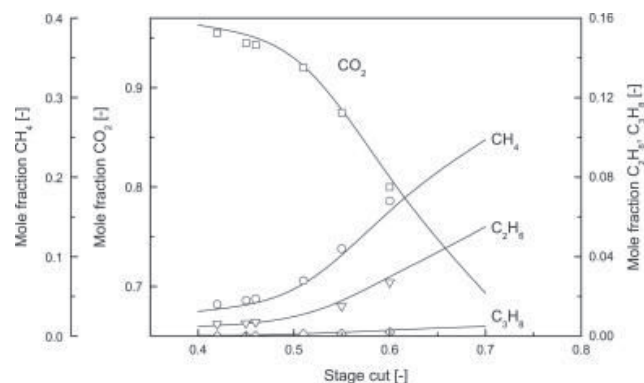
Pan [24] reported experimental data on the separation of CO₂, N₂, H₂S and CH₄, and for the separation of CO₂, CH₄, C₂H₆ and C₃H₈. We compared this data to the simulation results of the gas permeation model. Fig. 3 shows the mole fractions of CO₂, N₂, H₂S and CH₄ as a function of the stage cut. For a wide range of stage cuts the model applied here reflects the experimental data. Analogously, Fig. 4 shows the mole fraction of CO₂, CH₄, C₂H₆ and C₃H₈ as a function of stage cut. Here, the model results agree with the published data.



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Fig.3. Permeate mole fractions as a function of stage cut. The model data (lines) is compared to data reported by Pan (symbols) [24].

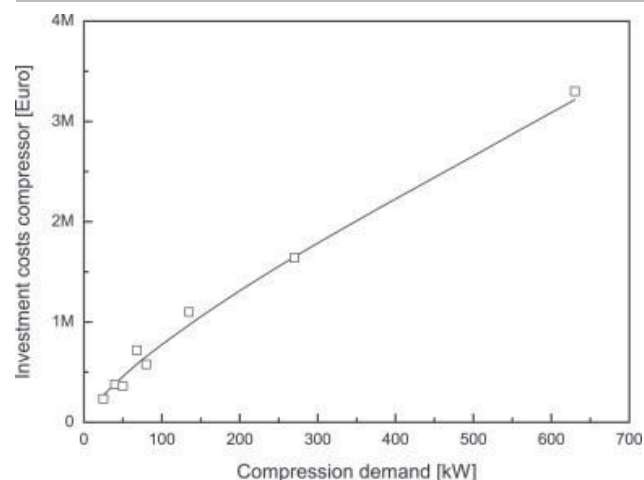


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Fig.4. Permeate mole fractions as a function of stage cut. The model data (lines) is compared to data reported by Pan (symbols) [24].

Fig. 6 depicts the investment costs for a compressor as a function of the compression demand. The line refers to the data obtained by Guthrie's method, while the squares represent data provided by a compressor manufacturer, who does not want to be mentioned here. The difference between the estimated costs and the real compressor costs are less than 20%. In general, Biegler et al. [18] report an error of $\pm 25\%$ for Guthrie's method. It has to be noted that for low compression duties the investment costs for compressors might fluctuate significantly. Compressors with a low discharge pressure can be single stage, while a slight increase in the discharge pressure results in an additional compression stage which increases the costs for the compressor. However, we apply Guthrie's investment cost estimation method to determine investment costs in the superstructure optimization model.



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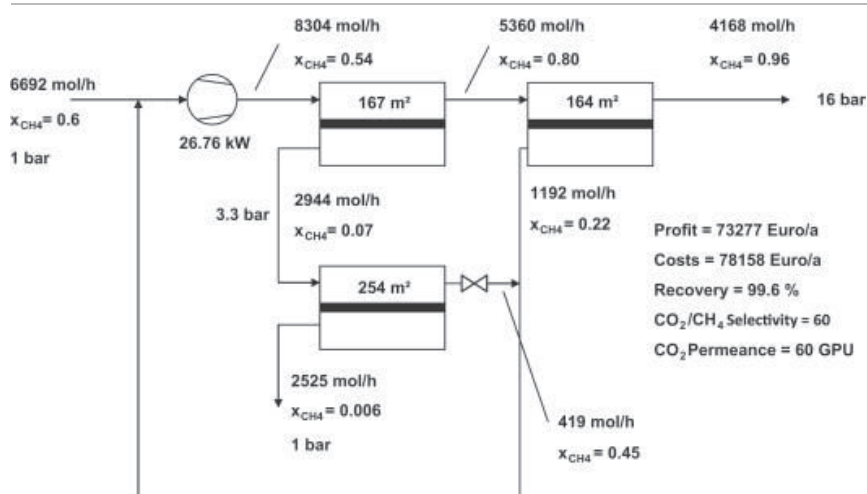
Fig.6. Comparison of real investment costs for compressor (symbols) and investment costs estimated by Guthrie's method as a function of the compression demand.

3.2. Superstructure optimization with commercial membranes

In this section two commercial membrane materials are compared. One with a CO_2/CH_4 selectivity of 60 which is typical for polyimide type of materials and a second materials reflecting the properties of cellulose acetate

membranes with a selectivity of 20. While the cellulose acetate membrane is well established in the gas permeation applications [25], the polyimide membranes considered have recently be launched. Both types of membranes are considered to investigate the impact of selectivity on the process performance. In the optimization a product gas purity of at least 96% together with a CH₄ recovery of more than 95% and 99.5%, respectively, have to be met.

Fig. 5 shows the optimal process layout together with the process parameters for a membrane material with a CO₂/CH₄ selectivity of 60 and a CO₂ permeance of 60 GPU. A three stage membrane process using a single compressor is identified to be the best process configuration. The raw gas is compressed to pipeline pressure of 16 bar and fed to the first membrane stage. The first stage performs a bulk separation of CO₂ and CH₄ and significant amounts of CH₄ also permeate through the gas permeation membrane. The retentate of the first stage is fed to a second stage in which the final product purity is obtained. The permeate of the second stage is recycled and mixed with the raw gas stream to enhance the CH₄ recovery. The third stage polishes the permeate of the first stage and the retentate of the third stage is also recycled to further increase the CH₄ recovery of the process. The pressure valve on the retentate outlet of the third stage controls the feed pressure in the third stage, hence, it provides the driving force for permeation. Accordingly, the elevated pressure on the permeate side of the first stage reduces the driving force in the first stage. The optimal feed pressure in the third membrane stage is 3.3 bar.



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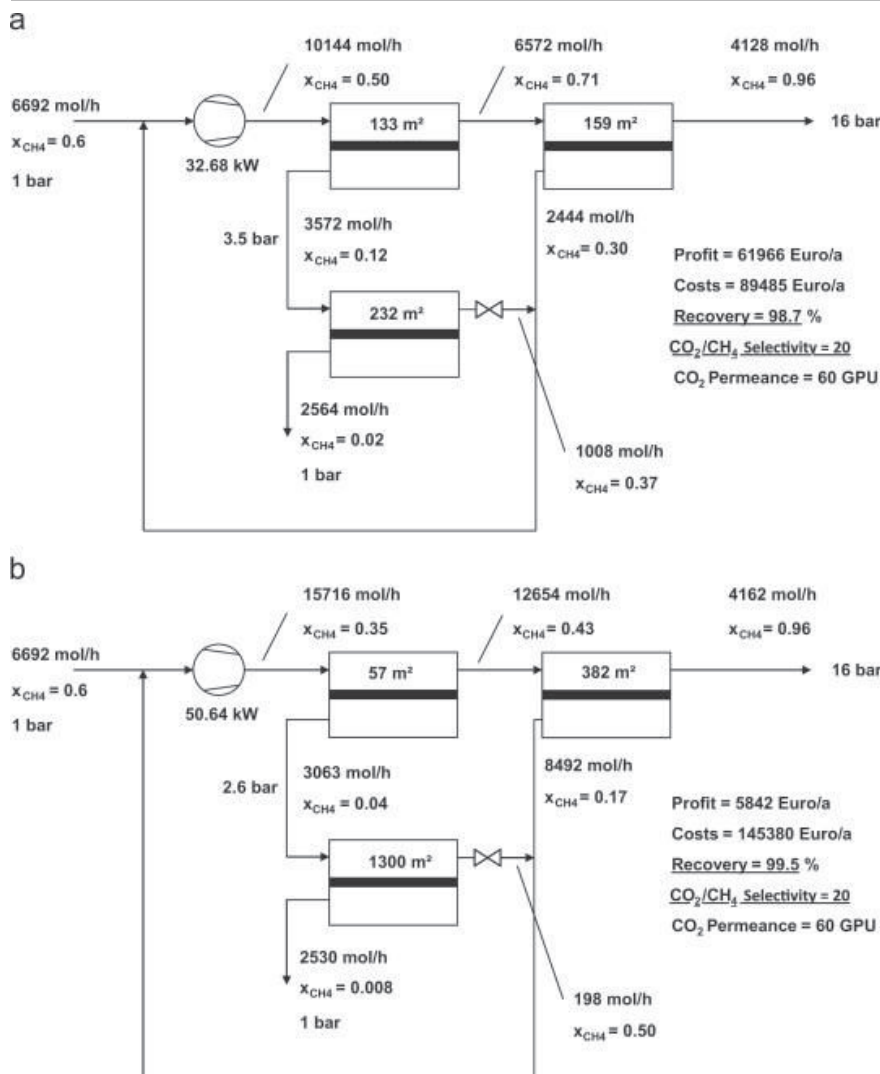
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Fig.5. Optimal process design and process conditions for gas permeation membranes with a CO₂/CH₄ selectivity of 60 and a CO₂ permeance of 60 GPU.

By using this process a CH₄ recovery of 99.6% can be obtained, which is slightly higher than the required recovery of 99.5%. Unsurprisingly, the same process layout as well as the process conditions are chosen for the case in which the lower bound of CH₄ recovery is set to 95%. An annual profit of approximately 73,300 Euro can be realized along with annual upgrading costs of approximately 78,158 Euro. A compressor with a compression duty of 26.76 kW is required to drive the process, which translates to a specific electrical energy demand of 0.178 kWh/m³(STP) with respect to the raw gas flow rate. A total membrane area of 585 m² has to be installed. This results in a specific area demand of 3.9 m²h/m³(STP). Assuming a gas permeation module size of 25 m² per module, 24 modules have to be installed.

For a membrane reflecting the characteristics of a cellulose acetate membrane with a CO₂/CH₄ selectivity of 20 the results are depicted in Fig. 7. In Fig. 7(a) the lower bound for CH₄ recovery is set to 95%. However, a higher CH₄

recovery of 98.7% is identified to be optimal for this constraint. The process layout does not change compared to the case in which more selective membrane materials are applied. An annual profit of approximately 62,000 Euro is obtained and annual costs of approximately 90,000 Euro have to be paid. While the total membrane area (524 m²) is almost constant compared to the process using more selective membranes, the compression demand increases significantly due to the increased recycle flow rate. A specific electrical compression demand of 0.22 kWh/m³(STP) together with a specific area demand of 3.5 m²h/m³(STP) are required. 21 gas permeation modules have to be installed in case that a single module contains 25 m² membrane area.



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Fig.7. Optimal process design and process conditions for gas permeation membranes with a CO_2/CH_4 selectivity of 20 and a CO_2 permeance of 60 GPU. (a) The required CH_4 recovery is higher than 95%. (b) The required CH_4 recovery is higher than 99.5%.

By demanding a CH_4 recovery of at least 99.5%, the profit for a process using membranes with selectivities of 20 drops significantly. The optimal process is still the three stage process describe for the better selective material, while the areas to be installed in the three stages differ remarkably. However, the high recovery can only be obtained on cost of an increased recycle flow rate. The recycle flow rate (9,024 mol/h) is even higher than the raw gas flow rate (6,692 mol/h). This translates to a high compression demand and a high specific energy demand of 0.34 kWh/m³(STP). Since large amounts of gas are recycled, large membrane area is also required to obtain the

required product gas purity. The total membrane area of $1,739\text{m}^2$ results in a specific area demand of $11.6\text{m}^2\text{h}/\text{m}^3(\text{STP})$ with respect to the raw gas. Assuming a module size of 25m^2 per module, 70 modules have to be installed. This poor performance results in low profitability ($\approx 5,800\text{Euro}/\text{a}$) and high annual upgrading cost ($\approx 145,000\text{Euro}/\text{a}$).

Although the solver can select a vacuum pump to generate the driving force for permeation, for each set of parameters considered here, the compression of the feed side is preferred. In any case the gas has to meet the natural gas grid pressure of 16 bar, so that at least a single compressor is needed to provide the natural gas grid pressure.

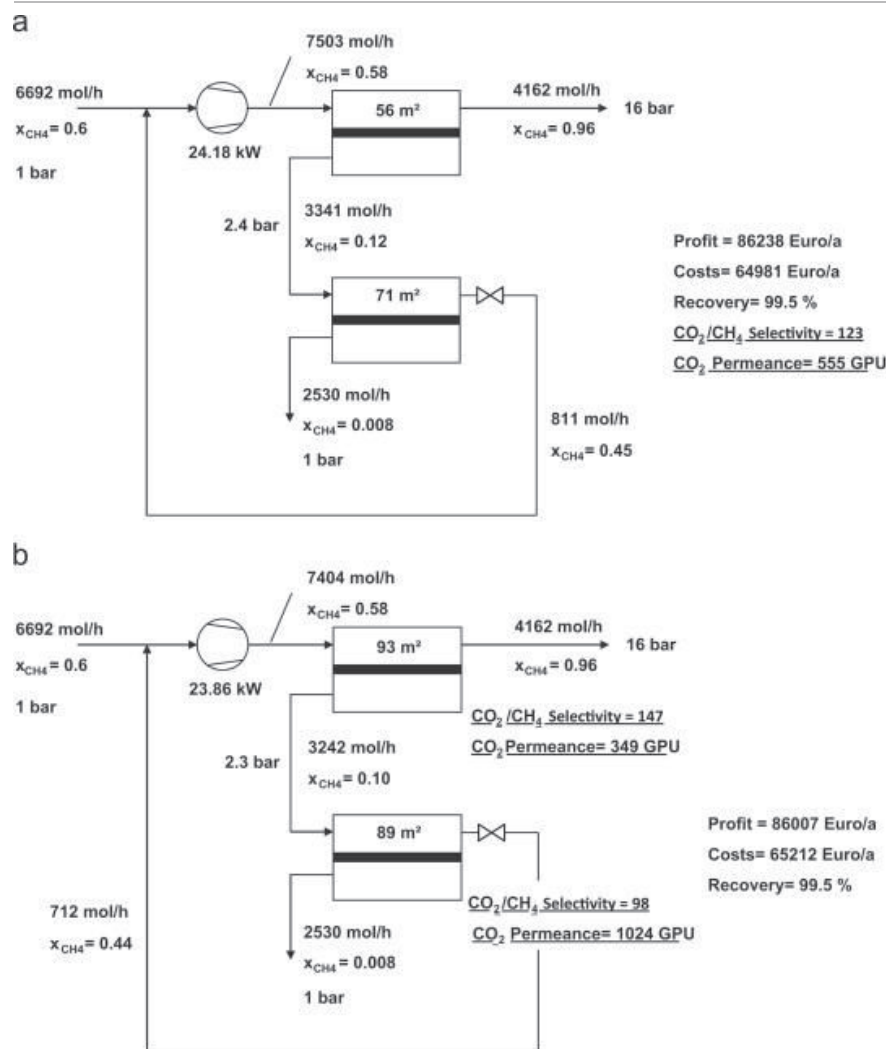
In general, the investment costs for the membranes are 10% of the total investment costs. This agrees well with the data published by Baker [23].

Comparing these results to conventional upgrading techniques such as amine absorption ($e_{elec}=0.15\text{kWh}/\text{m}^3(\text{STP})$, $e_{therm}=0.3\text{--}0.8\text{kWh}/\text{m}^3(\text{STP})$) and pressurized water scrubbing ($e_{elec}=0.25\text{kWh}/\text{m}^3(\text{STP})$) clearly shows that the gas permeation process can compete with these established technologies [1], [26]. Note that the energy demands for the conventional techniques are obtained at a gas grid pressure of 7 bar while the energy demand determined here refers to a grid pressure of 16 bar. In addition, the application of a multistage compressor would further reduce the energy demand for the gas permeation processes.

3.3. Identifying the optimal selectivity and permeance

As material development aims for higher selectivities and permeances, we used both parameters in process optimization. Hence, not only the process layout, the membrane area and the pressures are optimized, but also the optimal selectivity is determined. The optimal CO_2 permeance is calculated with the characteristic of the upper bound correlation of Robeson. For the processes considered here, the CH_4 recovery should be at least 99.5% to minimize the environmental impact caused by extensive CH_4 losses. Two cases are investigated. In the first case a single selectivity is determined for all membrane stages while in the second case an optimal selectivity is calculated for each individual membrane stage.

Fig. 8(a) shows the optimal process flowsheet for the first case in which only a single selectivity is applied to all membrane stages. Here, an optimal CO_2/CH_4 selectivity of 123 together with a CO_2 permeance of 555 GPU is determined. Compared to the processes in which a commercial gas permeation material is applied, the optimal process only consists of two membrane stages. This process design is similar to the three stage process presented in Section 3.2. However, the stage for final purification is not required as the first stage already polishes the raw gas to product grade without generating large CH_4 losses in the permeate. Due to the Robeson's upper bound characteristic the required membrane area reduces significantly compared to the commercial membranes ($585\text{ m}^2 \rightarrow 127\text{ m}^2$). Hence, only 5 gas permeation modules are required, assuming a module size of 25m^2 . Interestingly, the energy demand to drive the process is similar to the case in which commercial materials are applied. Here, a specific energy demand of $0.161\text{kWh}/\text{m}^3(\text{STP})$ is required. Hence, the optimization of the membrane material has the strongest impact on the membrane area rather than on the energy demand. In terms of energy demand the commercial membrane with a CO_2/CH_4 selectivity requires similar energies to drive the gas permeation process (compare Section 3.2). An annual profit of approximately 86,000 Euro with annual cost of approximately 65,000 Euro can be obtained.



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Fig.8. Optimal process design and process conditions for a gas permeation material inherent Robeson's upper bound characteristics. (a) A single optimal selectivity is determined for all membrane stages. (b) Individual optimal selectivities are calculated for each stage.

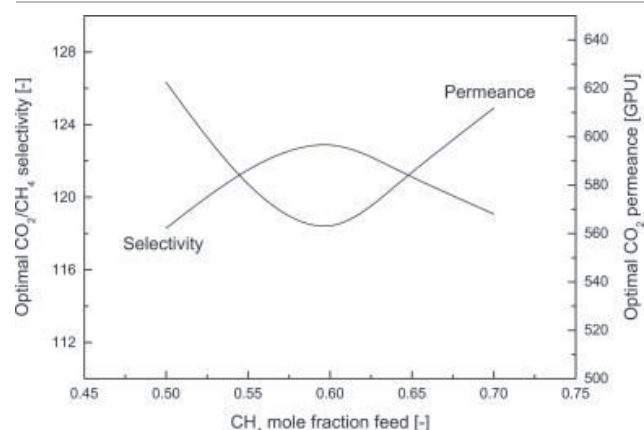
Fig. 8(b) illustrates the process layout for the process optimization in which the membrane properties for each stage are determined individually. Although the selectivities and permeances differ significantly from the case in which only a single selectivity is optimized, the annual profit as well as the annual upgrading costs are almost constant. A small reduction in the energy demand is compensated by providing more membrane area.

3.3.1. Changing the CH₄ feed mole fraction

In this section the impact of the CH₄ feed mole fraction on the process layout and selectivity is analyzed. Here, two effects have to be accounted for. On one hand the CO₂ driving force increases with increasing CO₂ level in the feed gas. On the other hand, the higher the CH₄ mole fraction in the feed gas the less CO₂ has to be removed to meet the gas grid standard.

Fig. 9 shows the optimal selectivity and the permeance of CO₂ as a function of the CH₄ mole fraction in the feed gas. Here, selectivity and CO₂ permeance follow the correlation of Robeson's upper bound. Although the feed mole fraction of CH₄ changes considerably from 50% to 70% the optimal selectivity is in the range between 118 and 123.

The resulting CO₂ permeance ranges between 560 and 600 GPU. Regarding their selectivity polypyrrolones might be an adequate polymer of choice with a selectivity of 130 [27], [12].



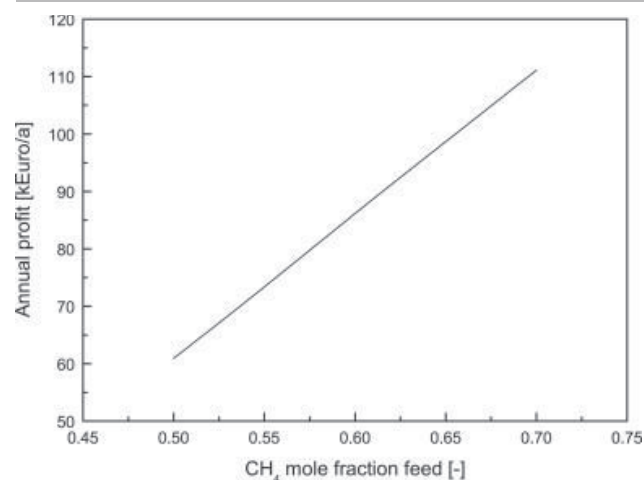
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Fig.9. Optimal selectivity and CO₂ permeance as a function of the CH₄ mole fraction in the feed gas.

The maximum in selectivity and as a consequence the minimum in permeance are caused by a trade-off between recycle ratio and driving force. The recycle ratio, which is the ratio of the recycle flow rate to the feed flow rate, increases with increasing CH₄ feed mole fraction. Increasing the selectivity steers against the increase in recycle ratio. On the other hand driving force decreases with increasing CH₄ feed mole fraction. Thus, larger membrane areas are required to compensate the loss in driving force. To reduce the required membrane area higher permeances have to be applied resulting in reduced selectivities.

The impact of the CH₄ feed mole fraction on annual profit is depicted in Fig. 10. Since the product gas flow rate increases with an increased CH₄ feed mole fraction at a fixed CH₄ recovery, the profit also increases linearly with increasing CH₄ feed mole fraction.



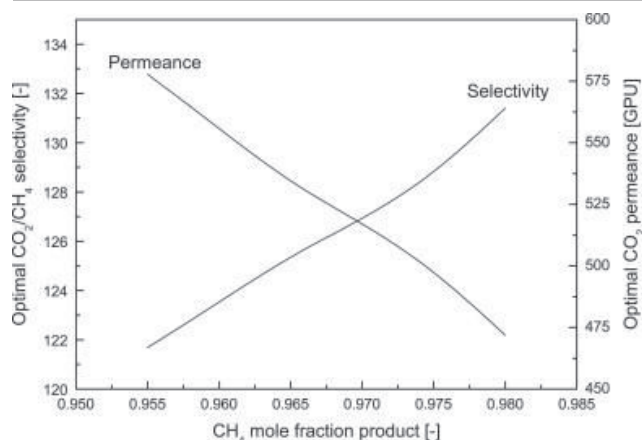
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Fig.10. Profit as a function of the CH₄ mole fraction in the feed gas for an optimal selectivity and CO₂ permeance following the Robeson upper bound.

3.3.2. Changing the required CH_4 product purity

Fig. 11 shows the optimal CO_2/CH_4 selectivity as a function of the required CH_4 mole fraction in the product gas for a CH_4 feed mole fraction of 0.6 for the case in which only a single selectivity is optimized for all membrane stages. Selectivity increases with increasing product purity. Increasing the CH_4 level in the product gas results in increased permeation of CH_4 in the first gas permeation stage which increases the recycle flow rate. As a consequence the energy demand to drive the compressor increases. To reduce the recycle flow rate selectivity increases which also translates to lower permeances.



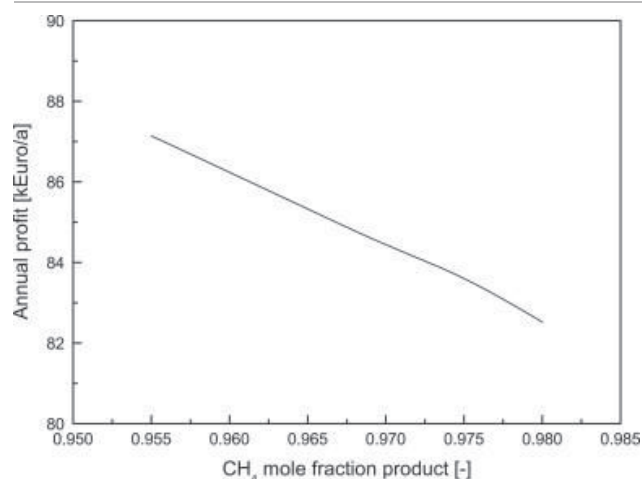
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Fig. 11. Optimal selectivity and CO_2 permeance as a function of CH_4 mole fraction of the product gas. The feed mole fraction of CH_4 is 60%.

Compared to the change in the feed mole fraction of CH_4 the change in the required CH_4 mole fraction of the product gas is more pronounced. The impact of the required product purity on optimal selectivity is more pronounced than the impact of the CH_4 feed mole fraction since the selectivity drops by more than 8% while only increasing the CH_4 mole fraction of the product gas by 3.5% (compare to Fig. 9). This typically reflects the characteristic of gas permeation processes which are good in performing a bulk separation but need a strong effort for providing high purities. Consequently, the required product purity has to be chosen carefully, since it has a tremendous impact on the process performance and only the required natural gas standard should be met.

Fig. 12 illustrates the annual profit as a function of CH_4 mole fraction of the product gas. Due to an increase in the recycle flow rate and required membrane area the annual profit decreases by 3.2%.



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Fig. 12. Profit for an optimal gas permeation process as a function of CH₄ mole fraction of the product gas. The feed mole fraction of CH₄ is 60%.

3.3.3. Does the process benefit from higher selectivity and permeance?

From a technical point of view the process benefits from a better membrane material inherent upper bound characteristics. However, the profit for a process in which the CH₄ product mole fraction of 96% and a CH₄ recovery of 99.5% are achieved is 73,000 Euro for a commercial membrane material ($Q_{CO_2}=60\text{ GPU}$, $\alpha_{CO_2/CH_4}=60$) and 86,000 Euro for a material of the upper bound ($Q_{CO_2}=580\text{ GPU}$, $\alpha_{CO_2/CH_4}=120$), respectively. The annual upgrading costs can be reduced from 78,000 Euro for a current membrane material to 65,000 Euro for an optimal material. Thus, the annual costs decrease by approximately 16%. Taking the material development costs into account and considering that this material has to be manufactured in large quantities it is unlikely that the increase in profitability justifies the effort for material development for this particular separation process. In addition, Baker [23] reported that only nine polymeric membrane materials play a role in large scale application of gas permeation membranes. Furthermore, for selectivities as high as 100 and permeances exceeding 1,000 GPU concentration polarization will have an impact on the module performance. Most likely the increase in profitability will be diminished by concentration polarization.

4. Conclusions

A process model for structural optimization of gas permeation processes is presented and applied to the separation of CH₄ and CO₂ in biogas upgrading. Short cut models for a gas permeation module, a compressor, a vacuum pump and a pressure valve have been implemented in GAMS. Both, commercial membrane materials as well as optimal membrane materials have been investigated. For the commercial gas permeation membranes and for the boundary conditions set here a three stage gas permeation process using only a single compressor is most profitable. Comparing two types of membrane materials the process equipped with membrane materials with CO₂/CH₄ selectivity of 60 has a higher profit and lower costs than the process with low selective materials. Regarding the specific energy demand, the optimized gas permeation processes can compete with established gas separation techniques for biogas upgrading. The simple process layout and the robustness of the process would even favor the application of gas permeation technology in biogas upgrading.

Moreover, we investigated the impact of optimal selectivity on the process performance where the membrane material follows the correlation for Robeson's upper bound. Two cases have been investigated in which a two stage process is identified to be most profitable. First a single optimal selectivity for all gas permeation stages have been determined ($\alpha_{\text{CO}_2/\text{CH}_4}=120$). Subsequently, the selectivity is optimized for each individual membrane stage. Here, a high selective stage ($\alpha_{\text{CO}_2/\text{CH}_4}=147$) is combined with a stage in which high permeances ($\text{CO}_2=1,024\text{GPU}$) are required.

However, the impact of optimized membrane materials on profitability is low, as the CH_4 recovery of the three stage process using commercial membrane modules is already high. Hence, the product gas flow rate cannot be increased significantly. The choice of the membrane material has an impact on the upgrading costs. For the optimal membrane material it is questionable if development and product launching costs justify the application of such a material.

Ultimately, the application of a three stage gas permeation process with current commercial membranes already shows good performance.

Acknowledgments

We are grateful to Mirko Skiborowski (RWTH Aachen University-Process Systems Engineering) for his helpful insights about modeling and optimization in General Algebraic Modeling System. Matthias Wessling appreciates the financial support through the Alexander-von-Humboldt Foundation.

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Structural optimization of membrane-based biogas upgrading processes

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ARTICLE INFO

Article history:

Received 17 February 2014

Received in revised form

8 August 2014

Accepted 14 August 2014

Available online 28 September 2014

Keywords:

Process modeling

Structural optimization

Gas permeation

Biogas upgrading

ABSTRACT

Gas permeation membranes are well known for separating CO₂ and CH₄. Single stage processes cannot provide both, high product gas purity and high recovery at the same time, but multistage processes do. Commonly, the design of multistage gas permeation processes relies on heuristics and experience, so that often sub-optimal separation processes are designed. We apply a structural optimization approach to biogas upgrading processes. This systematic method determines the most profitable process layout including membrane areas and pressures required for two commercial membranes. Furthermore, we determine the optimal selectivity and CO₂ permeance following the upper bound of the Robeson plot. The process model is implemented using General Algebraic Modeling System (GAMS). For commercial membranes a three stage gas permeation process is the most profitable process which operates with only a single compressor. Optimizing the process layout together with the membrane properties a two stage process is the best process configuration. CO₂/CH₄ selectivities of approximately 120 are optimal. The impact of changed feed conditions and required product purity was investigated. The results highlight that for biogas upgrading commercial gas permeation membranes already provide powerful separation characteristics. The optimal membrane processes are capable to economically compete with conventional biogas upgrading techniques.

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1. Introduction

The depletion of fossil resources triggers the transition to renewable energies. Biogas upgrading will contribute to future energy supply. Contrary to solar and wind power, biogas is produced continuously. Biogas will considerably contribute to future energy supply as it is a renewable resource. Biogas upgrading refers to the separation of CH₄ and CO₂, where a CH₄ rich gas is polished so that it can be used as natural gas substitute [1]. Gas permeation membranes are well known for separating CO₂ and CH₄ [2–4]. Their application in biogas upgrading offers several advantages over conventional gas separation techniques. First the gas permeation operates with the upgraded product gas being at elevated pressure so that it can directly be injected into the natural gas grid [1]. Secondly gas permeation modules are robust and the process is simple, which is particularly suitable for on-farm application [5].

The objective of the study at hand is to design a membrane based biogas upgrading process based on structural process optimization. Here, (i) the optimal process configuration, (ii) the required membrane areas in the various stages and (iii) the

pressure to drive the gas permeation process for a commercial membrane material are determined simultaneously. In a further step selectivity of the membrane material is optimized together with the process layout and the process conditions.

Process design often relies on heuristics and experience [6] which may result in suboptimal process configurations. The application of systematic methods for process design ensures the identification of the most profitable process configuration. Although superstructure optimization provides a systematic framework for the design of membrane based separation processes only limited work has been published. Sargent and Gaminibandara were the first who introduced the concept of structural optimization in designing distillation sequences. This concept has been adapted by El-Hawagi and Manousiouthakis who optimized mass exchange networks [7].

In the optimization of gas permeation processes Uppaluri et al. [8] studied the enriched oxygen production, hydrogen recovery from synthesis gas, and hydrogen recovery from refinery streams. They obtained new process designs which reduces the costs by 20% compared to process designs previously reported in the literature. They applied stochastic optimization using a simulated annealing algorithm.

Qi and Henson [9,10] report on CO₂/CH₄ separation in natural gas treatment and enhanced oil recovery. Here, only recycle compressors are investigated as the raw gas is already pressurized.

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They used GAMS along with the DICOPT++ algorithm to solve the MINLP. They even introduced discrete variables to account for a more realistic process design as membrane modules are available with fixed active membrane areas. They identified a four stage gas permeation process as the process configuration with the lowest gas treatment costs for natural gas polishing. For enhance oil recovery they also determined a four stage process as optimal process configuration as it has the lowest costs. In an additional publication [10] they extend the binary model to multicomponent model. The separation of CH₄, CO₂, H₂S and heavier hydrocarbons in natural gas treatment as well as the separation of CH₄, CO₂, H₂S, C₂H₆ and heavier hydrocarbons in enhanced oil recovery were investigated.

Kookos [11] does not only optimize the process layout and process conditions, but he also determines the best selectivity along with the best permeance for the production of nitrogen and oxygen from air. The upper bound correlation published by Robeson is applied to account for the membrane material performance. For the production of oxygen the comparison of an optimized membrane material and a commercial membrane material leads to the conclusion that impressive cost reductions are obtained.

We adapt the structural optimization approach to identify the most profitable membrane based biogas upgrading system. The process model is implemented in the General Algebraic Modeling System (GAMS). In a first step commercial gas permeation membranes are applied to the process optimization. The best process layout together with the optimal membrane areas and process conditions were calculated. In a second step the membrane's selectivity is an additional optimization parameter. The relation between selectivity and CO₂ permeance is determined according to the upper bound published by Robeson [12]. In contrast to Kookos [11] we applied the updated data for the upper bound correlation published in 2008. A three stage process is the optimal process configuration for the commercial membrane materials while a two stage process is the best layout for optimal membrane materials. An optimal CO₂/CH₄ selectivity in the order of 120 was most profitable for a process in which a single selectivity is applied to all membrane stages. When calculating the optimal selectivity for each membrane stage individually, a first highly selective stage is combined with highly permeable stage cleaning the permeate of the first stage.

The process model can easily be adapted to other gas separation problems such as helium production from natural gas, natural gas upgrading or air separation to determine the most profitable process configurations.

2. Process model

Commonly gas permeation processes include multiple membrane stages to achieve high gas purities and recoveries simultaneously. Favre [13] reported that more than three stages are usually not installed in industrial applications since these processes seem to be less efficient and cost demanding. In biogas upgrading it is rather unsuitable to use more than three stages as the complexity of the system increases rapidly and the application of such a system at a biogas site seems to be less robust. The process model implemented here is not limited to any number of membrane stages, but for the optimization of the biogas upgrading process a maximum number of three membrane stages is defined.

The gas permeation modules considered in the simulations are equipped with polymeric membrane materials to separate CO₂ and CH₄. CO₂ will permeate faster through the membrane so that the permeate is enriched in CO₂. Thus, CH₄ is enriched on the retentate side of the membrane which is particularly advantageous in biogas

upgrading as the product gas is pressurized and can thereby directly be injected into the natural gas grid. Table 1 lists the raw gas conditions and the product gas requirements. A membrane CO₂/CH₄ selectivity of 60 is assumed based on a current patent [14] for a polyimide membrane material.

However, no information is given on the permeances of such a membrane material and we assume a CO₂ permeance of 60 GPU. In addition, a membrane material with selectivities reflecting the characteristics of a cellulose acetate membrane is investigated. The permeances are also listed in Table 1.

In general, feed gas conditions, product gas requirements and economic parameters such product gas pressure and energy costs considerably determine the optimal process configuration. Consequently, the optimal process configuration presented here, is identified by applying the boundary conditions set here. This process configuration is most likely not optimal for the entire range of parameters to be applied in biogas upgrading and boundary conditions have to be reviewed carefully. The objective of the optimization is to maximize the profit of the biogas upgrading plant. Four different types of unit operations are implemented and could be used in the process model. These are a gas permeation module to perform the separation and equipment to generate the driving force of permeation such as compressors, vacuum pumps, and pressure control valves. Fig. 1 shows the respective unit operations and illustrates the potential connections of the individual unit operation with other unit operations. Here only selected connections are presented. For the gas permeation model it is also possible to use a sweep gas on the permeate

Table 1

Feed and product gas conditions of a common biogas upgrading process. The permeances of the polymeric membrane materials are also listed. PI – polyimide; CA – cellulose acetate; 1 GPU = $2.7 \times 10^{-3} \text{ m}^3/\text{m}^2\text{h bar}$.

	Unit	Value
Raw gas mole fraction CH ₄	–	0.6
Raw gas mole fraction CO ₂	–	0.4
Raw gas flow rate	$\text{m}^3(\text{STP})/\text{h}$	150
Raw gas temperature	°C	20
Raw gas pressure	bar	1
Product pressure	bar	16
Product mole fraction CH ₄	–	0.96
CH ₄ permeance PI	GPU	1
CO ₂ permeance PI	GPU	60
CH ₄ permeance CA	GPU	3
CO ₂ permeance CA	GPU	60

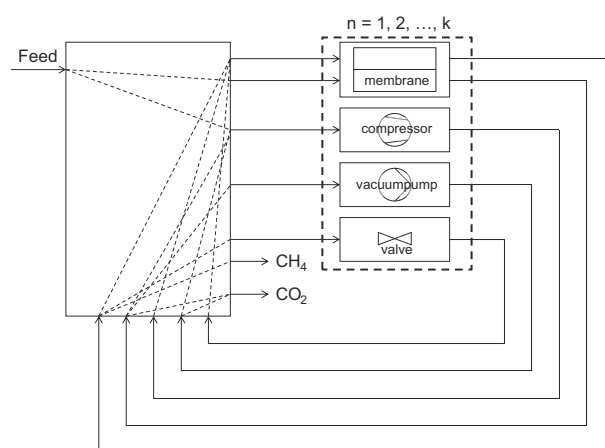


Fig. 1. Superstructure approach to optimize a membrane based biogas upgrading plant. Note that not all possible connections between the various unit operations are presented.

side. At the inlet (bottom) of the so called distribution box each stream can be split and connected to all available outlet ports of the distribution box. The inlets are splitters while the various outlet ports on the right side of the distribution box are mixers. Each unit operation can be selected several times, so that multi-stage processes can be optimized with the process model.

The gas permeation module itself is the most important piece of process equipment as it performs the separation. The driving force can either be generated by compressing the feed gas, by applying sub-ambient pressure on the permeate side or by diluting the permeate with a sweep gas. The solver selects the compression equipment based on the operational and investment costs since the driving force method determines the pressure levels as well as the recycle flow rates.

The superstructure model including the models for the unit operations and their connections were programmed in the General Algebraic Modeling System (GAMS). GAMS is a modelling system for mathematical programs that are occasionally used in process optimization [15]. In GAMS the mathematical problem is programmed independently of the solver. Various algorithms are available to solve linear programs (LP), nonlinear programs (NLP) and mixed integer nonlinear programs (MINLP). Optimizing the biogas upgrading process is a MINLP as the connections between the unit operations are of integer type and nonlinear equations (e.g. capital cost calculation) are solved.

The Branch-And-Reduce Optimization Navigator (BARON) is used which is a branch and bound type global optimization solver. With this kind of solver, identification of the global optimum is guaranteed even if fairly general assumptions are made [16].

2.1. Unit operation models

The gas permeation module is built as a short cut model based on the fundamental equations for conservation of mass and a simple mass transfer equation. The gas permeation module is discretized in 100 elements j and solved together with the superstructure equations by BARON. The mole balances for counter current flow for each gas species i of the feed side and the permeate side are solved for each element j :

$$\dot{n}_{R,i,j} = \dot{n}_{i,j} + \dot{n}_{R,i,j+1} \quad (1)$$

$$\dot{n}_{P,i,j} = \dot{n}_{i,j} + \dot{n}_{P,i,j+1} \quad (2)$$

Here, $\dot{n}_{R,i,j}$ refers to the flow rate on the feed side and $\dot{n}_{P,i,j}$ is the flow rate on the permeate side, respectively. The mass transfer through the membrane $\dot{n}$ is determined by the partial pressure difference, the permeance of the gas species Q_i , the active membrane area A and it is determined for each discretized element:

$$\dot{n}_{i,j} = Q_i \cdot (x_{i,j} p_F - y_{i,j} p_P) A \quad (3)$$

Mole fractions are determined by

$$x_{i,j} = \frac{\dot{n}_{r,i,j}}{\sum_i \dot{n}_{r,i,j}} \quad (4)$$

$$y_{i,j} = \frac{\dot{n}_{p,i,j}}{\sum_i \dot{n}_{p,i,j}} \quad (5)$$

Simplifying assumptions have been made: (i) no pressure losses are considered, (ii) isothermal operation, (iii) concentration polarization is neglected, (iv) constant permeances and (v) ideal gas behavior are assumed.

The compressors and the vacuum pumps are modeled as single stage isentropic compression units without interstage cooling. The

isentropic outlet temperature T_{out} is determined by

$$T_{out} = T_{in} \cdot \left(\frac{p_{out}}{p_{in}} \right)^{(\kappa-1)/\kappa} \quad (6)$$

The isentropic exponent κ is 1.3. T_{in} and p_{in} delineate the inlet temperature and pressure, and p_{out} is the compressor's discharge pressure. The real outlet temperature T_{real} is calculated by

$$\eta_{isent} = \frac{T_{out} - T_{in}}{T_{real} - T_{in}} \quad (7)$$

The isentropic efficiency η_{isent} of the compressor is 0.72. Vacuum equipment has isentropic efficiencies of far less than 0.5, in case of a jet pump it is only 0.1 [17]. Thus, we assume an isentropic efficiency of 0.5 for the vacuum equipment. The net power e , which is the energy supplied to the gas stream, is determined by

$$e = \dot{m} \cdot c_p \cdot (T_{real} - T_{in}) \quad (8)$$

whereby, $\dot{m}$ is the mass flow rate through the compression equipment and c_p is the specific heat capacity of the gas (34.77 J/mol K). A simple constraint for the pressure control valve was implemented. Here, the upstream pressure has to be higher than the pressure on the downstream side:

$$p_{in} \geq p_{out} \quad (9)$$

Compared to the costs for compressors and vacuum pumps the costs for a pressure valve can be neglected. Since a pressure valve has to be installed anyway.

Generally any outlet of an unit operation can be connected to any inlet of all available unit operations. Therefore it is possible to optimize membrane cascades including recycle streams. Fig. 1 illustrates a set of connections between the different unit operations. To mix two different process streams the pressure of the streams have to be equal. In case of different stream pressures these are either increased by a compressor or reduced by a pressure control valve.

To reduce the number of process configurations and the calculation effort some connections can be precluded which do not contribute to the separation process or even have a negative impact on process performance. Fig. 2 illustrates these respective connections which are not considered in the optimization. These connections are for instance:

- recycling of a retentate stream and mixing with the feed stream of a membrane module;
- direct connection of the feed and the product stream;
- mixing of permeate streams with the product stream;
- connection of a retentate outlet stream and a vacuum pump inlet.

2.2. Economics

To optimize the process it is more appropriate to determine the economic optimum rather than the energetic optimum, since the membrane based biogas upgrading process has to compete economically with well established gas separation techniques. The energetic optimum can be fairly different from the economic

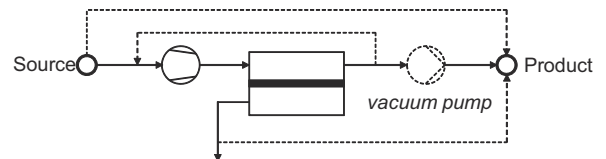


Fig. 2. Connections which are excluded from the optimization. Excluded connections are labelled with dashed lines.

Table 2

Parameters to estimate the investment costs for the compression equipment with Guthrie's method [18].

Parameter	Unit	Value
Update factor 2011		4.91
Material and pressure factor		2.9
Module factor		5.11
Conversion bhp* in kW	kW/bhp	0.746
Reference costs for compressor in 1968	US Dollar	23,000
Reference compressor size	bhp	100
Cost function exponent		0.77
Conversion US Dollar in Euro	US Dollar/Euro	1.2719

* bhp – brake horse power.

Table 3

Economic parameters used for optimization of a membrane based biogas upgrading plant.

Costs	Unit	Value
Membrane module costs	$\frac{\text{Euro}}{\text{m}^2}$	55
Electrical costs	$\frac{\text{Euro}}{\text{kWh}}$	0.08
Commission of purified gas	$\frac{\text{Euro}}{\text{m}^3}$	0.2
Membrane lifetime	year	4
Annual operation	h	8,000
Interest rate	–	0.09
Amortization period	years	8

optimum. In this study we determine the most profitable process configuration by taking both, operational cost, mainly caused by electrical energy consumption, and investment costs for the compression equipment and the membrane modules into account.

The membranes lifetime is 4 years and the membranes have to be exchanged after this operation period. Table 3 summarizes the economic parameters chosen for the optimization simulation.

Investment costs for the compressor and the vacuum pump can be estimated with Guthrie's method [18,19]. This method enables the calculation of capital costs based on the size of the compression equipment and the process conditions. The method roughly estimates investment cost with an $\pm 25\%$ error [18].

In a first step the bare module costs (BC) are determined:

$$BC = C_0 \cdot \left(\frac{S}{S_0} \right)^\alpha \quad (10)$$

where C_0 are reference costs for the equipment, S is a variable taking the size of the respective equipment into account and S_0 is a reference size of the equipment. In case of compression S is the required compression duty and S_0 is the reference compression duty. The parameter α considers the cost increase with increasing equipment size. Here, the economy of scale is taken into account since α is generally lower than 1. The required values for C_0 and S_0 are tabulated in Biegler et al. [18].

To determine the capital costs the reference costs have to be updated as the values were determined for the reference year 1969. In addition, the capital costs of the equipment depend on the operating conditions and the materials used. Thus, the capital costs CC are calculated by

$$CC = UF \cdot BC \cdot (MPF + MF - 1) \quad (11)$$

Here UF delineates the update factor which takes the current price level into account. MPF is the material and pressure factor accounting for the material of the equipment. The module factor MF additionally considers the size of the equipment. Hirschberg [20] suggests that 2 should be added to this factor to realistically

reflect today's investment costs. The Guthrie parameters used here are listed in Table 2.

2.3. Robeson plot

Many efforts are made to develop new membrane materials which have improved selectivities and permeances. From an operational point of view the application of these membranes in gas permeation processes is limited. High selectivities together with high permeances induce concentration polarization significantly limiting the separation performance of the gas permeation modules. Thus the driving force for the retained gas species increases while the driving force for the fast permeating species reduces [21,22]. However, the effect of concentration polarization is not accounted for in the model but it is remarkable for membranes with selectivities and permeances as high as 100 and 1000 GPU, respectively [22].

Furthermore, for gas permeation processes high pressure ratios have to be provided to take advantage of high membrane selectivities [23]. The trade-off between permeability and selectivity is well known [12]. In terms of process design low selectivities increase the amount of the retained gas species which permeates through the membrane resulting in increased compression duty. For high selectivity, permeance drops which increases the required membrane area remarkably. As a consequence higher investment costs and membrane replacement costs reduce the profitability of the upgrading process.

Robeson [12] introduced a correlation to determine the permeability as a function of the selectivity for upper bound materials. We implemented the upper bound correlation into the superstructure model, to determine the most profitable selectivity simultaneously with the optimal process layout, the membrane areas and pressures. For CO_2 and CH_4 Robeson published the following correlation:

$$P_{\text{CO}_2} = 5369140 (\alpha_{\text{CO}_2/\text{CH}_4})^{-2.636} \text{ Barrer} \quad (12)$$

Assuming a membrane thickness of 30 nm transforms permeability into permeance.

$$Q_{\text{CO}_2} = 33.77 \cdot 5369140 (\alpha_{\text{CO}_2/\text{CH}_4})^{-2.636} \text{ GPU} \quad (13)$$

where, $\alpha_{\text{CO}_2/\text{CH}_4}$ is the selectivity:

$$\alpha_{\text{CO}_2/\text{CH}_4} = \frac{Q_{\text{CO}_2}}{Q_{\text{CH}_4}} \quad (14)$$

3. Results and discussion

3.1. Model validation

Pan [24] reported experimental data on the separation of CO_2 , N_2 , H_2S and CH_4 , and for the separation of CO_2 , CH_4 , C_2H_6 and C_3H_8 . We compared this data to the simulation results of the gas permeation model. Fig. 3 shows the mole fractions of CO_2 , N_2 , H_2S and CH_4 as a function of the stage cut. For a wide range of stage cuts the model applied here reflects the experimental data. Analogously, Fig. 4 shows the mole fraction of CO_2 , CH_4 , C_2H_6 and C_3H_8 as a function of stage cut. Here, the model results agree with the published data.

Fig. 6 depicts the investment costs for a compressor as a function of the compression demand. The line refers to the data obtained by Guthrie's method, while the squares represent data provided by a compressor manufacturer, who does not want to be mentioned here. The difference between the estimated costs and the real compressor costs are less than 20%. In general, Biegler et al. [18] report an error of $\pm 25\%$ for Guthrie's method. It has to

be noted that for low compression duties the investment costs for compressors might fluctuate significantly. Compressors with a low discharge pressure can be single stage, while a slight increase in the discharge pressure results in an additional compression stage which increases the costs for the compressor. However, we apply Guthrie's investment cost estimation method to determine investment costs in the superstructure optimization model.

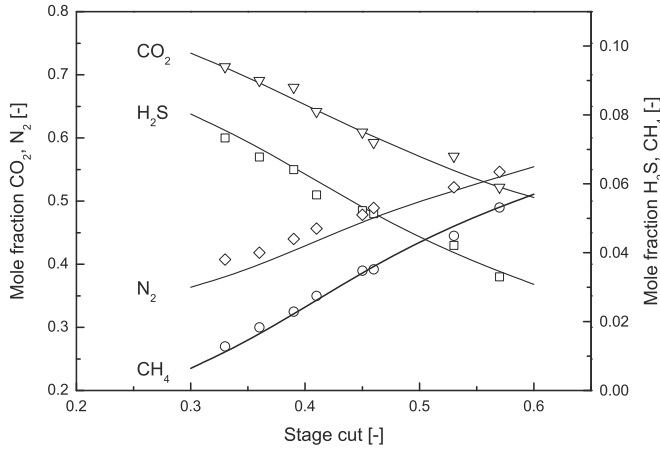


Fig. 3. Permeate mole fractions as a function of stage cut. The model data (lines) is compared to data reported by Pan (symbols) [24].

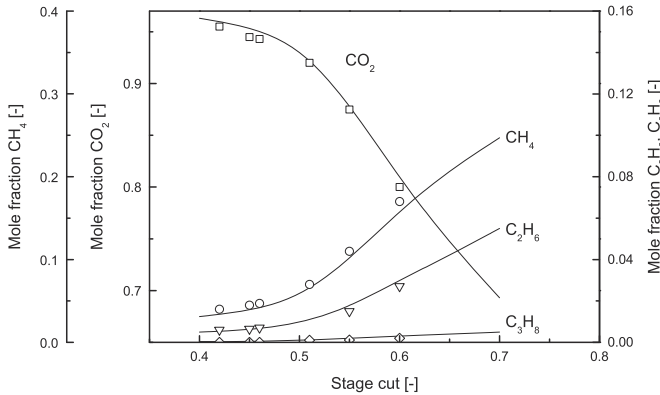


Fig. 4. Permeate mole fractions as a function of stage cut. The model data (lines) is compared to data reported by Pan (symbols) [24].

3.2. Superstructure optimization with commercial membranes

In this section two commercial membrane materials are compared. One with a CO_2/CH_4 selectivity of 60 which is typical for polyimide type of materials and a second materials reflecting the properties of cellulose acetate membranes with a selectivity of 20. While the cellulose acetate membrane is well established in the gas permeation applications [25], the polyimide membranes considered have recently be launched. Both types of membranes are considered to investigate the impact of selectivity on the process performance. In the optimization a product gas purity of at least 96% together with a CH_4 recovery of more than 95% and 99.5%, respectively, have to be met.

Fig. 5 shows the optimal process layout together with the process parameters for a membrane material with a CO_2/CH_4 selectivity of 60 and a CO_2 permeance of 60 GPU. A three stage membrane process using a single compressor is identified to be the best process configuration. The raw gas is compressed to pipeline pressure of 16 bar and fed to the first membrane stage. The first stage performs a bulk separation of CO_2 and CH_4 and significant amounts of CH_4 also permeate through the gas permeation membrane. The retentate of the first stage is fed to a second stage in which the final product purity is obtained. The permeate

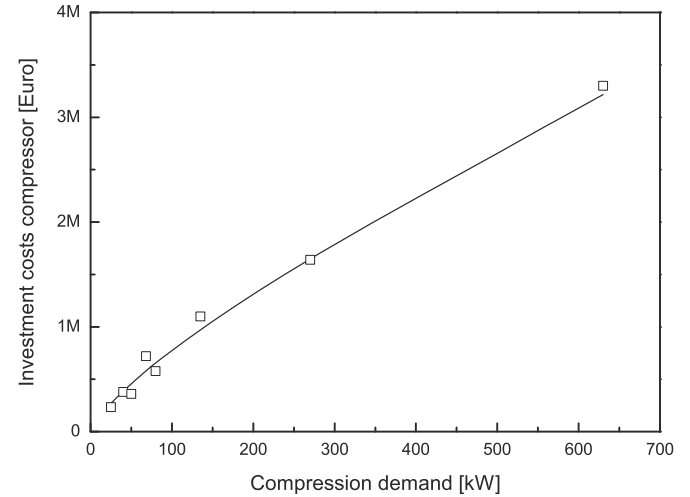


Fig. 6. Comparison of real investment costs for compressor (symbols) and investment costs estimated by Guthrie's method as a function of the compression demand.

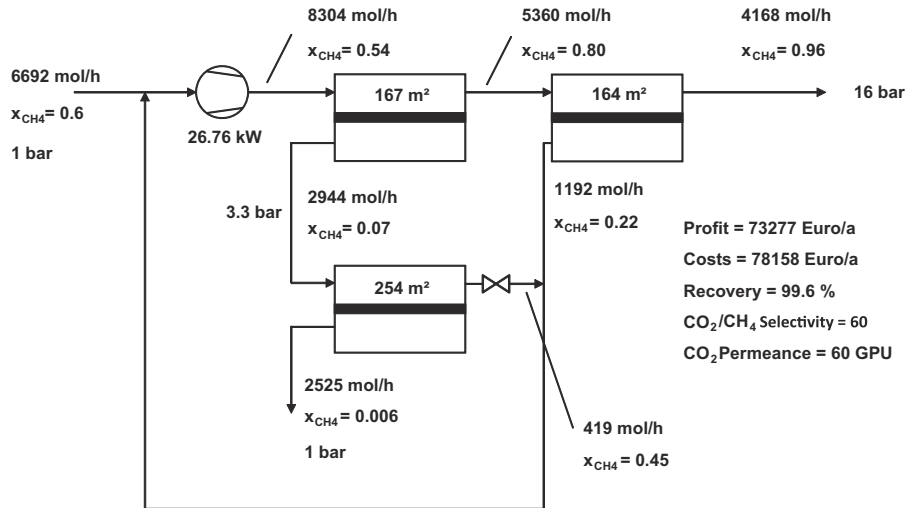


Fig. 5. Optimal process design and process conditions for gas permeation membranes with a CO_2/CH_4 selectivity of 60 and a CO_2 permeance of 60 GPU.

of the second stage is recycled and mixed with the raw gas stream to enhance the CH₄ recovery. The third stage polishes the permeate of the first stage and the retentate of the third stage is also recycled to further increase the CH₄ recovery of the process. The pressure valve on the retentate outlet of the third stage controls the feed pressure in the third stage, hence, it provides the driving force for permeation. Accordingly, the elevated pressure on the permeate side of the first stage reduces the driving force in the first stage. The optimal feed pressure in the third membrane stage is 3.3 bar.

By using this process a CH₄ recovery of 99.6% can be obtained, which is slightly higher than the required recovery of 99.5%. Unsurprisingly, the same process layout as well as the process conditions are chosen for the case in which the lower bound of CH₄ recovery is set to 95%. An annual profit of approximately 73,300 Euro can be realized along with annual upgrading costs of approximately 78,158 Euro. A compressor with a compression duty of 26.76 kW is required to drive the process, which translates to a specific electrical energy demand of 0.178 kWh/m³(STP) with respect to the raw gas flow rate. A total membrane area of 585 m² has to be installed. This results in a specific area demand of 3.9 m²h/m³(STP). Assuming a gas permeation module size of 25 m² per module, 24 modules have to be installed.

For a membrane reflecting the characteristics of a cellulose acetate membrane with a CO₂/CH₄ selectivity of 20 the results are depicted in Fig. 7. In Fig. 7(a) the lower bound for CH₄ recovery is set to 95%. However, a higher CH₄ recovery of 98.7% is identified to be optimal for this constraint. The process layout does not change compared to the case in which more selective membrane materials are applied. An annual profit of approximately 62,000 Euro is obtained and annual costs of approximately 90,000 Euro have to be paid. While the total membrane area (524 m²) is almost constant compared to the process using more selective membranes, the compression demand increases significantly due to the increased recycle flow rate. A specific electrical compression demand of 0.22 kWh/m³(STP) together with a specific area demand of 3.5 m²h/m³(STP) are required. 21 gas permeation modules have to be installed in case that a single module contains 25 m² membrane area.

By demanding a CH₄ recovery of at least 99.5%, the profit for a process using membranes with selectivities of 20 drops significantly. The optimal process is still the three stage process describe for the better selective material, while the areas to be installed in the three stages differ remarkably. However, the high recovery can only be obtained on cost of an increased recycle flow rate. The recycle flow rate (9,024 mol/h) is even higher than the raw gas flow rate (6,692 mol/h). This translates to a high compression demand and a high specific energy demand of 0.34 kWh/m³(STP). Since large amounts of gas are recycled, large membrane area is also required to obtain the required product gas purity. The total membrane area of 1,739 m² results in a specific area demand of 11.6 m²h/m³(STP) with respect to the raw gas. Assuming a module size of 25 m² per module, 70 modules have to be installed. This poor performance results in low profitability ($\approx$ 5,800 Euro/a) and high annual upgrading cost ($\approx$ 145,000 Euro/a).

Although the solver can select a vacuum pump to generate the driving force for permeation, for each set of parameters considered here, the compression of the feed side is preferred. In any case the gas has to meet the natural gas grid pressure of 16 bar, so that at least a single compressor is needed to provide the natural gas grid pressure.

In general, the investment costs for the membranes are 10% of the total investment costs. This agrees well with the data published by Baker [23].

Comparing these results to conventional upgrading techniques such as amine absorption (e_{elec} =0.15 kWh/m³(STP), e_{therm} =0.3–0.8 kWh/m³(STP)) and pressurized water scrubbing (e_{elec} =0.25 kWh/m³(STP))

clearly shows that the gas permeation process can compete with these established technologies [1,26]. Note that the energy demands for the conventional techniques are obtained at a gas grid pressure of 7 bar while the energy demand determined here refers to a grid pressure of 16 bar. In addition, the application of a multistage compressor would further reduce the energy demand for the gas permeation processes.

3.3. Identifying the optimal selectivity and permeance

As material development aims for higher selectivities and permeances, we used both parameters in process optimization. Hence, not only the process layout, the membrane area and the pressures are optimized, but also the optimal selectivity is determined. The optimal CO₂ permeance is calculated with the characteristic of the upper bound correlation of Robeson. For the processes considered here, the CH₄ recovery should be at least 99.5% to minimize the environmental impact caused by extensive CH₄ losses. Two cases are investigated. In the first case a single selectivity is determined for all membrane stages while in the second case an optimal selectivity is calculated for each individual membrane stage.

Fig. 8(a) shows the optimal process flowsheet for the first case in which only a single selectivity is applied to all membrane stages. Here, an optimal CO₂/CH₄ selectivity of 123 together with a CO₂ permeance of 555 GPU is determined. Compared to the processes in which a commercial gas permeation material is applied, the optimal process only consists of two membrane stages. This process design is similar to the three stage process presented in Section 3.2. However, the stage for final purification is not required as the first stage already polishes the raw gas to product grade without generating large CH₄ losses in the permeate. Due to the Robeson's upper bound characteristic the required membrane area reduces significantly compared to the commercial membranes (585 m² $\rightarrow$ 127 m²). Hence, only 5 gas permeation modules are required, assuming a module size of 25 m². Interestingly, the energy demand to drive the process is similar to the case in which commercial materials are applied. Here, a specific energy demand of 0.161 kWh/m³(STP) is required. Hence, the optimization of the membrane material has the strongest impact on the membrane area rather than on the energy demand. In terms of energy demand the commercial membrane with a CO₂/CH₄ selectivity requires similar energies to drive the gas permeation process (compare Section 3.2). An annual profit of approximately 86,000 Euro with annual cost of approximately 65,000 Euro can be obtained.

Fig. 8(b) illustrates the process layout for the process optimization in which the membrane properties for each stage are determined individually. Although the selectivities and permeances differ significantly from the case in which only a single selectivity is optimized, the annual profit as well as the annual upgrading costs are almost constant. A small reduction in the energy demand is compensated by providing more membrane area.

3.3.1. Changing the CH₄ feed mole fraction

In this section the impact of the CH₄ feed mole fraction on the process layout and selectivity is analyzed. Here, two effects have to be accounted for. On one hand the CO₂ driving force increases with increasing CO₂ level in the feed gas. On the other hand, the higher the CH₄ mole fraction in the feed gas the less CO₂ has to be removed to meet the gas grid standard.

Fig. 9 shows the optimal selectivity and the permeance of CO₂ as a function of the CH₄ mole fraction in the feed gas. Here, selectivity and CO₂ permeance follow the correlation of Robeson's upper bound. Although the feed mole fraction of CH₄ changes considerably from 50% to 70% the optimal selectivity is in the range between 118 and 123. The resulting CO₂ permeance ranges between 560 and

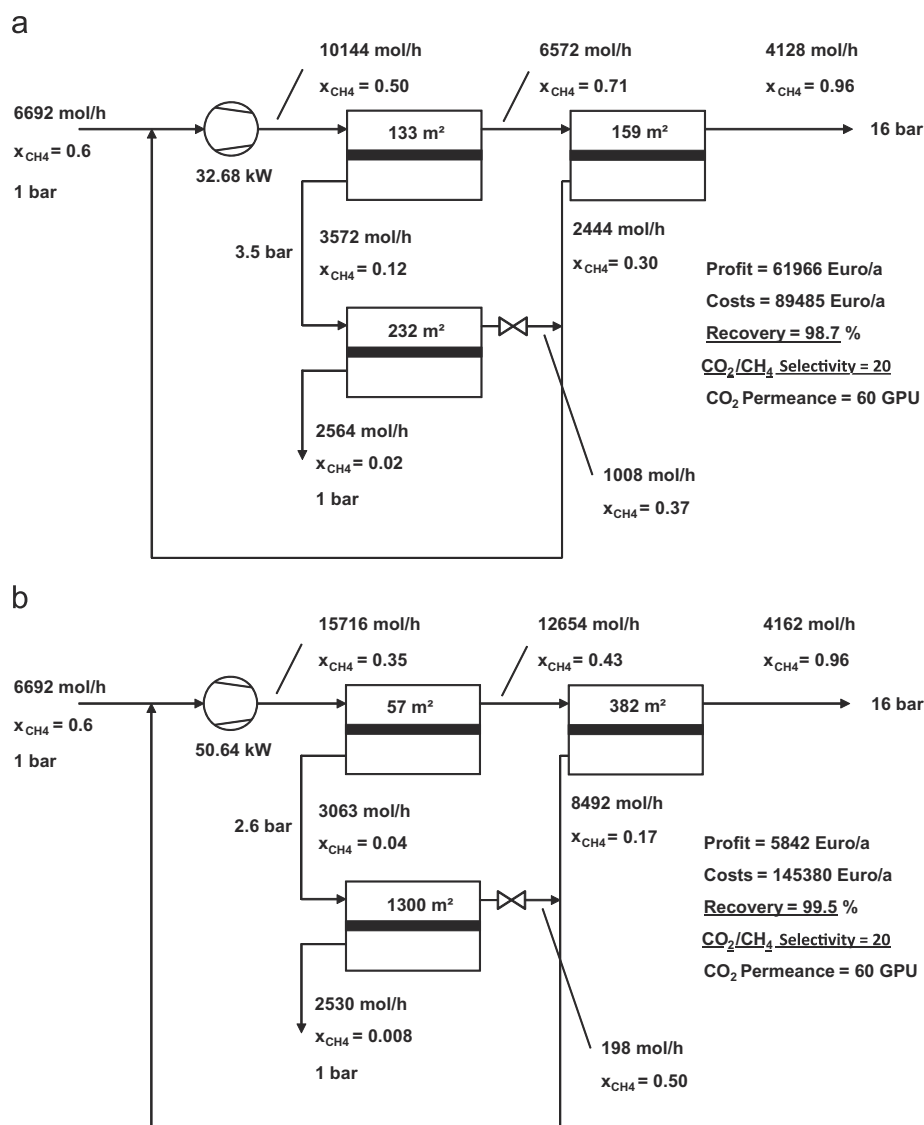


Fig. 7. Optimal process design and process conditions for gas permeation membranes with a CO_2/CH_4 selectivity of 20 and a CO_2 permeance of 60 GPU. (a) The required CH_4 recovery is higher than 95%. (b) The required CH_4 recovery is higher than 99.5%.

600 GPU. Regarding their selectivity polypyrrolones might be an adequate polymer of choice with a selectivity of 130 [27,12].

The maximum in selectivity and as a consequence the minimum in permeance are caused by a trade-off between recycle ratio and driving force. The recycle ratio, which is the ratio of the recycle flow rate to the feed flow rate, increases with increasing CH_4 feed mole fraction. Increasing the selectivity steers against the increase in recycle ratio. On the other hand driving force decreases with increasing CH_4 feed mole fraction. Thus, larger membrane areas are required to compensate the loss in driving force. To reduce the required membrane area higher permeances have to be applied resulting in reduced selectivities.

The impact of the CH_4 feed mole fraction on annual profit is depicted in Fig. 10. Since the product gas flow rate increases with an increased CH_4 feed mole fraction at a fixed CH_4 recovery, the profit also increases linearly with increasing CH_4 feed mole fraction.

3.3.2. Changing the required CH_4 product purity

Fig. 11 shows the optimal CO_2/CH_4 selectivity as a function of the required CH_4 mole fraction in the product gas for a CH_4 feed mole fraction of 0.6 for the case in which only a single selectivity is optimized for all membrane stages. Selectivity increases with

increasing product purity. Increasing the CH_4 level in the product gas results in increased permeation of CH_4 in the first gas permeation stage which increases the recycle flow rate. As a consequence the energy demand to drive the compressor increases. To reduce the recycle flow rate selectivity increases which also translates to lower permeances.

Compared to the change in the feed mole fraction of CH_4 the change in the required CH_4 mole fraction of the product gas is more pronounced. The impact of the required product purity on optimal selectivity is more pronounced than the impact of the CH_4 feed mole fraction since the selectivity drops by more than 8% while only increasing the CH_4 mole fraction of the product gas by 3.5% (compare to Fig. 9). This typically reflects the characteristic of gas permeation processes which are good in performing a bulk separation but need a strong effort for providing high purities. Consequently, the required product purity has to be chosen carefully, since it has a tremendous impact on the process performance and only the required natural gas standard should be met.

Fig. 12 illustrates the annual profit as a function of CH_4 mole fraction of the product gas. Due to an increase in the recycle flow rate and required membrane area the annual profit decreases by 3.2%.

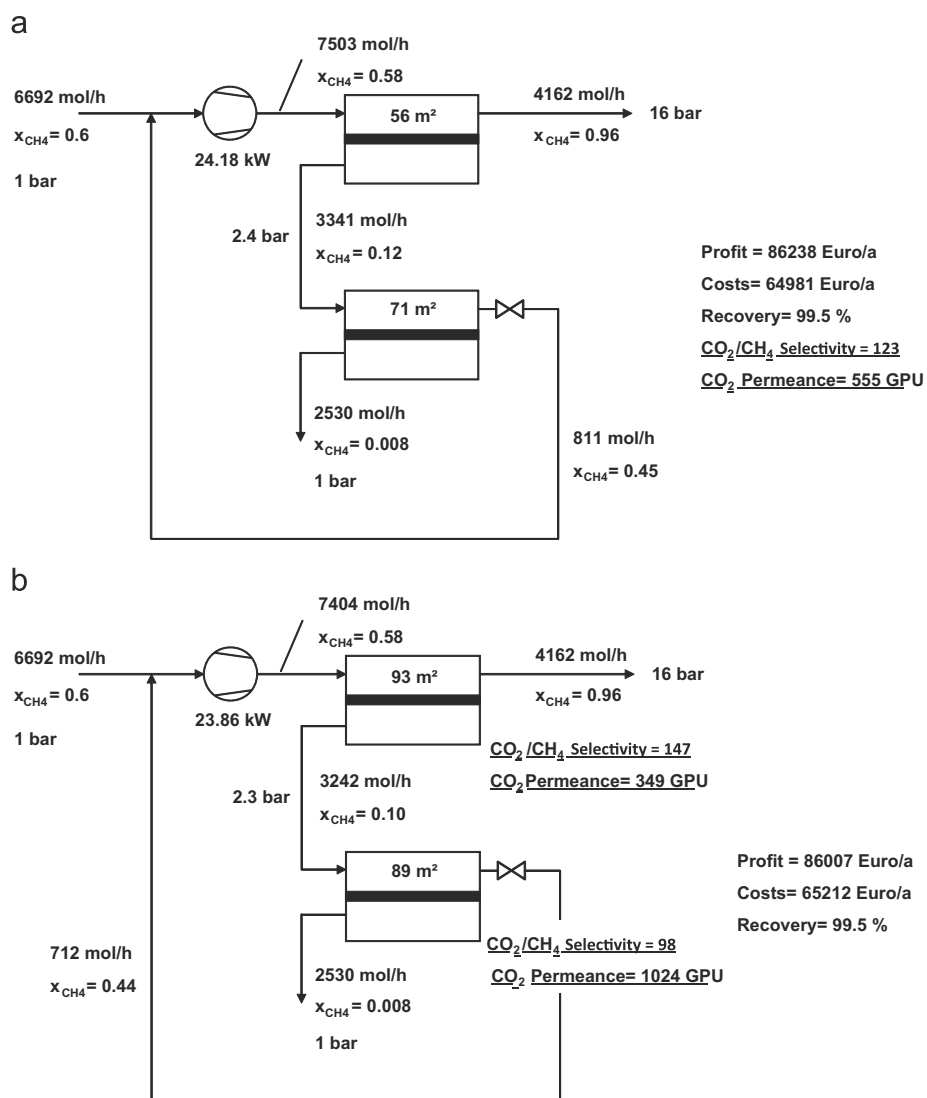


Fig. 8. Optimal process design and process conditions for a gas permeation material inherent Robeson's upper bound characteristics. (a) A single optimal selectivity is determined for all membrane stages. (b) Individual optimal selectivities are calculated for each stage.

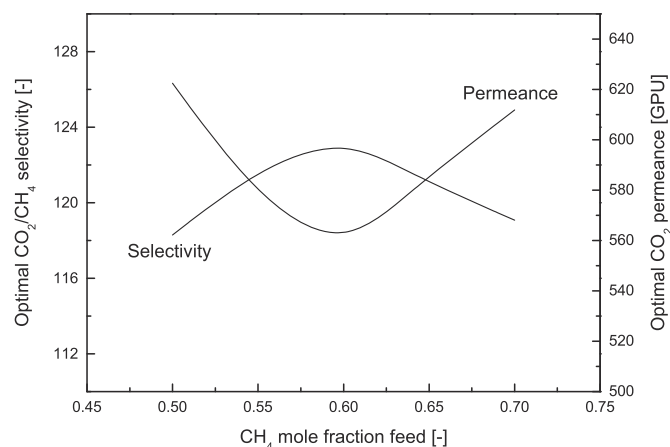


Fig. 9. Optimal selectivity and CO_2 permeance as a function of the CH_4 mole fraction in the feed gas.

3.3.3. Does the process benefit from higher selectivity and permeance?

From a technical point of view the process benefits from a better membrane material inherent upper bound characteristics. However,

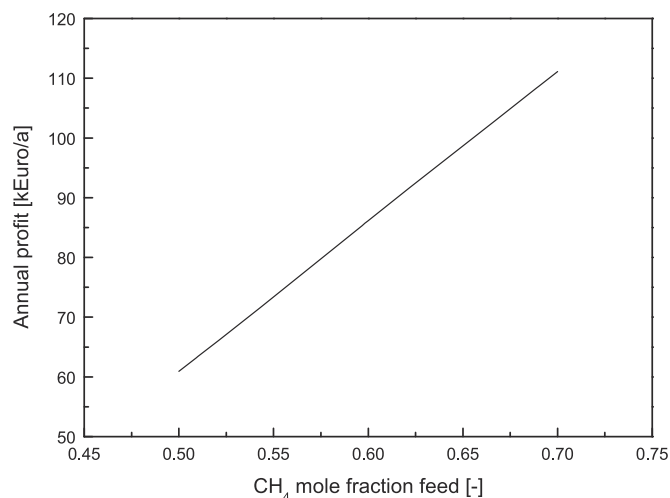


Fig. 10. Profit as a function of the CH_4 mole fraction in the feed gas for an optimal selectivity and CO_2 permeance following the Robeson upper bound.

the profit for a process in which the CH_4 product mole fraction of 96% and a CH_4 recovery of 99.5% are achieved is 73,000 Euro for a commercial membrane material ($Q_{\text{CO}_2} = 60$ GPU, $\alpha_{\text{CO}_2/\text{CH}_4} = 60$) and

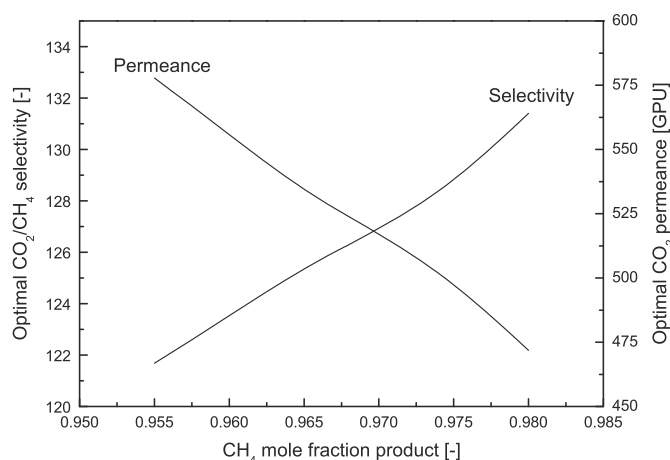


Fig. 11. Optimal selectivity and CO₂ permeance as a function of CH₄ mole fraction of the product gas. The feed mole fraction of CH₄ is 60%.

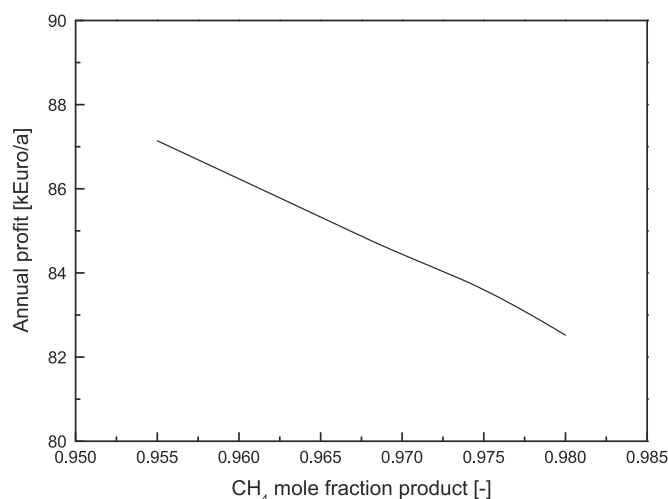


Fig. 12. Profit for an optimal gas permeation process as a function of CH₄ mole fraction of the product gas. The feed mole fraction of CH₄ is 60%.

86,000 Euro for a material of the upper bound ($Q_{\text{CO}_2}=580$ GPU, $\alpha_{\text{CO}_2/\text{CH}_4}=120$), respectively. The annual upgrading costs can be reduced from 78,000 Euro for a current membrane material to 65,000 Euro for an optimal material. Thus, the annual costs decrease by approximately 16%. Taking the material development costs into account and considering that this material has to be manufactured in large quantities it is unlikely that the increase in profitability justifies the effort for material development for this particular separation process. In addition, Baker [23] reported that only nine polymeric membrane materials play a role in large scale application of gas permeation membranes. Furthermore, for selectivities as high as 100 and permeances exceeding 1,000 GPU concentration polarization will have an impact on the module performance. Most likely the increase in profitability will be diminished by concentration polarization.

4. Conclusions

A process model for structural optimization of gas permeation processes is presented and applied to the separation of CH₄ and CO₂ in biogas upgrading. Short cut models for a gas permeation module, a compressor, a vacuum pump and a pressure valve have

been implemented in GAMS. Both, commercial membrane materials as well as optimal membrane materials have been investigated. For the commercial gas permeation membranes and for the boundary conditions set here a three stage gas permeation process using only a single compressor is most profitable. Comparing two types of membrane materials the process equipped with membrane materials with CO₂/CH₄ selectivity of 60 has a higher profit and lower costs than the process with low selective materials. Regarding the specific energy demand, the optimized gas permeation processes can compete with established gas separation techniques for biogas upgrading. The simple process layout and the robustness of the process would even favor the application of gas permeation technology in biogas upgrading.

Moreover, we investigated the impact of optimal selectivity on the process performance where the membrane material follows the correlation for Robeson's upper bound. Two cases have been investigated in which a two stage process is identified to be most profitable. First a single optimal selectivity for all gas permeation stages have been determined ($\alpha_{\text{CO}_2/\text{CH}_4}=120$). Subsequently, the selectivity is optimized for each individual membrane stage. Here, a high selective stage ($\alpha_{\text{CO}_2/\text{CH}_4}=147$) is combined with a stage in which high permeances (CO₂ = 1,024 GPU) are required.

However, the impact of optimized membrane materials on profitability is low, as the CH₄ recovery of the three stage process using commercial membrane modules is already high. Hence, the product gas flow rate cannot be increased significantly. The choice of the membrane material has an impact on the upgrading costs. For the optimal membrane material it is questionable if development and product launching costs justify the application of such a material.

Ultimately, the application of a three stage gas permeation process with current commercial membranes already shows good performance.

Acknowledgments

We are grateful to Mirko Skiborowski (RWTH Aachen University-Process Systems Engineering) for his helpful insights about modeling and optimization in General Algebraic Modeling System. Matthias Wessling appreciates the financial support through the Alexander-von-Humboldt Foundation.

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