

Model Development of a Membrane Gas Permeation Unit for the Separation of Hydrogen and Carbon Dioxide

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This work describes co- and counter-current gas permeation unit models developed in Aspen Custom Modeler. The models are based on the solution-diffusion mechanism and describe a single membrane module considering discretization of membrane area. After evaluation against data measured from the separation of carbon dioxide and methane the models have been used to calculate the performance of a reverse selective membrane for the separation of hydrogen and carbon dioxide.

1. Introduction

The employment of renewable sources rather than fossil fuels in the production of hydrogen is an important step in the process of achieving a sustainable Hydrogen Economy in the future.

Besides biomass gasification, production of hydrogen from renewable sources is also possible in a fermentative way through thermophilic (dark) fermentation and/or photo-heterotrophic fermentation.

Research on fermentative hydrogen production at the moment is mainly concerned with the selection of micro-organisms, optimization of yield and rate of hydrogen production as well as reactor design. In order to finally obtain pure hydrogen, carbon dioxide has to be separated from the product gas of the fermentation steps. Besides classical processes for the separation of mixtures of hydrogen and carbon dioxide like amine absorption or pressure swing adsorption, membrane processes might give advantages in upgrading low temperature raw gas streams in small scale facilities.

Goal of this work was to develop a membrane gas permeation unit model for the separation of hydrogen and carbon dioxide to be used with the commercial process simulation tool Aspen Plus (V7.1, Aspen Technology, Inc., Burlington, USA, 2008), to compare the performance of different process configurations for separation of hydrogen/carbon dioxide mixtures.

2. Background

In gas permeation, a gas mixture at a pressure p_0 is applied to the feed side of the membrane, while the permeate gas at a lower pressure p_1 is removed from the downstream side of the membrane. Depending on the properties of the gases as well as the morphology, material and functionality of the various membrane types a

combination of different mechanisms fits to explain the gas-transport mechanism of a given separation. Generally, gas transport in dense membranes occurs via the solution-diffusion mechanism.

In the solution-diffusion model, permeants dissolve in the membrane material and then diffuse through the membrane along a concentration gradient. The separation occurs due to the difference in rates of diffusion of the different permeants through the membrane material as well as the solubility of each permeant in the membrane material. The first assumption regarding the transport through membranes is that the fluids on both sides of the membrane are in equilibrium with the membrane material at the interface. It is implicit that the rates of absorption and desorption at the interface are much higher than the rate of diffusion through the membrane. The pressure applied across a dense membrane is also considered to be constant (Wijmans and Baker, 1995). The component flow rate across a membrane is proportional to the difference in partial pressure and inversely proportional to the membrane thickness as shown in Equations 1-3:

$$J_i = \frac{P_i \cdot (p_{io} - p_{il})}{\ell} \quad (1)$$

$$J_i = Q_i \cdot (p_{io} - p_{il}) \quad (2)$$

$$Q_i = \frac{P_i}{\ell} \quad (3)$$

The permeability coefficient P_i is a characteristic parameter that is often described as an intrinsic parameter easily available from simple permeation experiments.

3. Model Development

Aspen Custom Modeler (ACM, V7.1, Aspen Technology, Inc., Burlington, USA, 2009) was used to develop the gas permeation models. Models then have been imported to the Aspen Plus model library. During the development of the gas permeation model the discretization tools of ACM were used to break down the membrane area into k cells of equal dimensions.

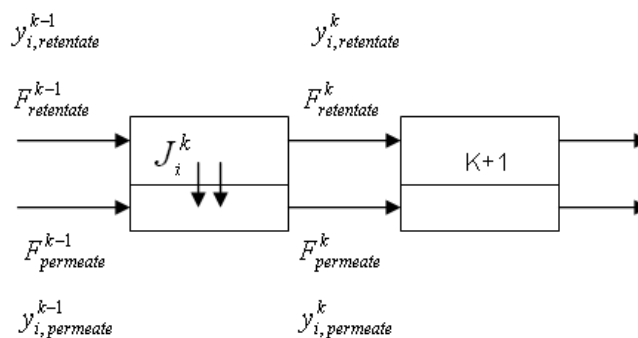


Figure 1: Schematic drawing of the co-current model

Component transport was modeled using the solution-diffusion mechanism without consideration of effects from temperature gradients or membrane's geometry. However, two different flow arrangements were considered: co-current and counter-current.

The following assumptions are valid for both flow arrangements:

- total pressures in the retentate, permeate and feed are constant
- permeability and permeance are independent of pressure
- no pressure drop from feed to retentate

The model inputs are feed temperature, pressure and composition as well as retentate and permeate pressure, membrane area and permeances. The number of cells is defined in the code but can be changed (Rodrigues, 2009).

As an example scheme and balance equations for the co-current model are given in Figure 1 and Equations 4-7, respectively.

$$F_{retentate}^{k-1} + F_{permeate}^{k-1} = F_{retentate}^k + F_{permeate}^k \quad (4)$$

$$\begin{aligned} F_{retentate}^{k-1} \cdot y_{i,retentate}^{k-1} + F_{permeate}^{k-1} \cdot y_{i,permeate}^{k-1} &= \\ = F_{retentate}^k \cdot y_{i,retentate}^k + F_{permeate}^k \cdot y_{i,permeate}^k & \end{aligned} \quad (5)$$

$$J_i^k = \frac{F_{permeate}^k \cdot y_{i,permeate}^k}{A_k} \quad (6)$$

$$J_i^k = Q_i \cdot \left[\frac{y_{i,retentate}^{k-1} - y_{i,retentate}^k}{\ln \left(\frac{y_{i,retentate}^{k-1}}{y_{i,retentate}^k} \right)} \cdot P_{feed} - y_{i,permeate}^k \cdot P_{permeate} \right] \quad (7)$$

4. Validation And Results

Since no experimental data were available for the hydrogen/carbon dioxide separation, the developed models were validated against data for the separation of methane/carbon dioxide taken from Makaruk et al. (2009).

Table 1 Membrane properties and component permeances for separation of methane/carbon dioxide

Number of fibers	800
Length (m)	0.38
Inner diameter (mm)	0.40
Total area (m ²)	0.38
Q CH ₄ (kmol h ⁻¹ bar ⁻¹ m ⁻²)	2.00 10 ⁻⁴
Q CO ₂ (kmol h ⁻¹ bar ⁻¹ m ⁻²)	8.27 10 ⁻³

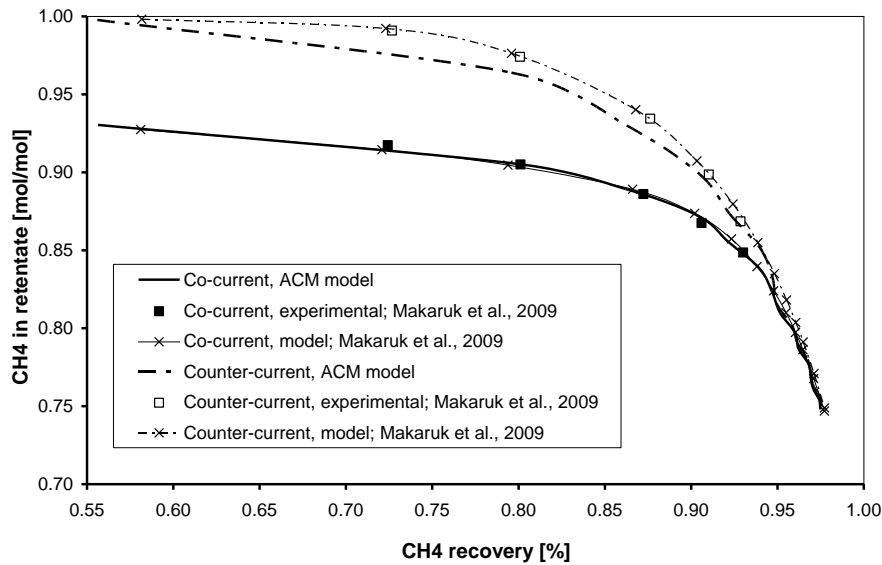


Figure 2: Validation of model results against literature based on separation of methane and carbon dioxide

The experimental data are obtained with a hollow fiber module. Module and membrane data are given in Table 1. The permeances, are obtained from studies of pure component flow. Figure 2 compares the methane concentration in retentate as a function of methane recovery obtained from Aspen Plus simulations using the ACM model against experimental and modeled results from literature for co- and counter-current arrangement.

For both flow configurations the models installed in Aspen Plus can predict the behavior of gas permeation module with a relatively small deviation to the experimental data. However, the results for the co-current are more consistent than the ones obtained for the counter-current model.

Separation of hydrogen/carbon dioxide mixtures is possible using H_2 - and CO_2 -selective membranes. H_2 -selective membranes generally are made of glassy polymers showing higher thermal stability than rubbery polymers, used for CO_2 -selective membranes.

Table 2 Process conditions and component permeabilities for separation of hydrogen and carbon dioxide

Feed flow (kmol/h)	23.3
CO_2 content feed (mol/mol)	0.3
H_2 content feed (mol/mol)	0.7
Temperature ($^{\circ}C$)	35
Pressure (bar)	7.7
Membrane thickness (μm)	1.3
P_{H_2} (barrer)	950
P_{CO_2} (barrer)	3200

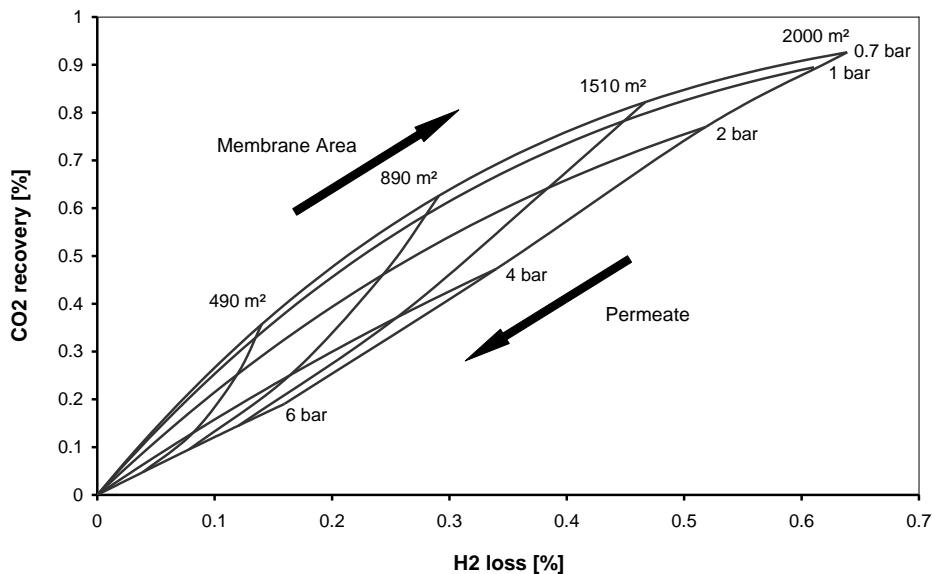


Figure 3: CO_2 recovery versus H_2 loss to permeate for reverse selective membrane

H_2 -selective membranes are able to handle higher compression in feed streams and work predominantly on the principle of diffusivity selectivity; were the higher diffusivity of H_2 (compared to the other gases) ensures the exclusion of other gases. A serious drawback of H_2 -selective membranes for hydrogen purification is the need to recompress the permeate stream after separation which is highly energy demanding.

For a first analysis of hydrogen/carbon dioxide separation a PDMS membrane was selected. Process conditions and membrane parameters are given in Table 2. It is an example for a membrane, which is reverse selective at low temperatures. A distinct economic advantage of CO_2 -selective membranes is the elimination of the recompression of H_2 since it remains in the high-pressure retentate stream. However, a drawback of these reverse selective membranes is that impurities such as N_2 and O_2 in the feed stream may remain in the retentate stream with H_2 .

A sensitivity study was performed based on process conditions and membrane parameters summarized in Table 2 varying the membrane area from 20 to 2000 m^2 and the permeate pressure from 0.7 to 6 bar. Results are shown in Figure 3 presenting lines of constant pressure and constant area in one plot.

With increasing membrane area a higher concentration of hydrogen was calculated in the permeate. However with this increase in the concentration an increase in hydrogen loss to the permeate was also obtained. The same was observed when the permeate pressure was decreased, increasing the partial pressure difference between retentate and permeate.

Since the membrane has a good permeability but a somewhat poor selectivity it was expected that to attain high concentrations of hydrogen in the retentate considerable loss of hydrogen to the permeate has to be accepted. To obtain a concentration higher than

0.8 a membrane area higher than 1500 m² has to be foreseen and the loss of hydrogen to the permeate will always be higher than 0.45.

5. Summary And Outlook

Aspen Custom Modeler (ACM) was used to develop a user gas permeation model for the commercial process simulation software Aspen Plus 7.1. The obtained co- and counter-current membrane models were evaluated against experimental data for the separation of a mixture of methane and carbon dioxide. As an example of application the performance of a reverse selective membrane for separation of hydrogen and carbon dioxide was calculated, showing that to attain high concentrations of hydrogen in the retentate considerable loss of hydrogen to the permeate has to be accepted.

A way to overcome the loss of hydrogen to the permeate would be to recycle the permeate and/or add additional modules to the separation scheme. Both membrane models will be used to evaluate different separation sequences and compare scenarios based on H₂- and CO₂-selective membranes.

Acknowledgement

We gratefully acknowledge the use of experimental data on the separation of methane and carbon dioxide of Aleksander Makaruk for evaluation of ACM models.

List Of Symbols

A	membrane area
F	flow rate
J	membrane flux
L	membrane thickness
P	permeability
Q	permeance
p	pressure
y	molar fraction gas component
Subscripts / Superscripts	
i	component i
0	feed
l	permeate
k	cell number discretization

References

- Makaruk A. and Harasek M., 2009, Numerical algorithm for modeling multicomponent multipermeator systems, *J. Membrane Sci.* 344, 258-265.
- Rodrigues D., 2009, Model development of a membrane gas permeation unit for the separation of Hydrogen and Carbon Dioxide, Master Thesis, Universidade Tecnica de Lisboa, Lisbon, Portugal.
- Wijmans J. G. and Baker R. W., 1995, The solution-diffusion model: A review, *J. Membrane Sci.* 107, 1-21.