Model development of a membrane gas permeation unit for the separation of Hydrogen and Carbon Dioxide

D. F. Rodrigues Department of Chemical Engineering, Technical University of Vienna, Austria and Department of Chemical and Biological Engineering, Instituto Superior Técnico, Portugal

In this work were developed three different membrane gas permeation unit models in Aspen Custom Modeller. These models were based in the solution-diffusion mechanism and describe a single membrane module. Two of the three models built, considered a discretization of the membrane’s module whereas the other model considered the membrane as a block. The models’ results were compared against experimental data measured from the separation of carbon dioxide and methane for validation. The model that presented itself to be the most suitable one was used on sensitivity analysis calculations for the separation of hydrogen and carbon dioxide with a reverse-selective PDMS membrane. The models that provided the best results in validation were the discretized ones.

Keywords: Membranes, gas permeation, Aspen Plus, Aspen Custom modeller, bio-hydrogen, hydrogen and carbon dioxide separation.

Introduction

Hydrogen is abundant in the universe and has higher energy content per weight unit than any other available fossil fuel. Thus, the demand for this energy resource and its consumption are trends that in the past years have been increasing. Accordingly, 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. Large-scale Hydrogen production generally occurs via steam methane reforming followed by the water-gas shift reaction, partial oxidation or by the Kvaerner–process. Hydrogen can also be produced by the electrolysis of water but, to date, only for a small percentage. Other alternative ways to produce hydrogen are via biological processes such as extracting the gas from biomass through dark fermentation and/or photo-fermentation by bacteria or the production of hydrogen by algae. An up-and-coming way for the production of Hydrogen from biomass in a non-thermal way is a two-stage bioprocess. Hyvolution-project presents a bio-process consisting of a thermophilic fermentation step followed by a photo-heterotrophic fermentation, both producing Hydrogen, Carbon Dioxide and intermediates. A great deal of research at the moment is concerned with the selection of microorganisms, optimisation of yield and rate of Hydrogen production as well as reactor design. In order to obtain pure Hydrogen, Carbon Dioxide has to be separated from the product gas. Due to the pressure level of the produced gas, vacuum swing adsorption was initially selected. However, during project work it turned out that for proper operation of the thermophilic fermenter Hydrogen’s partial pressure had to be reduced. This changed significantly the gas composition up to higher percentage values of Carbon Dioxide. Additionally, the gas-upgrading system had to cope with changing gas-flow rates since the second fermentation step (photo-heterotrophic fermenter) only produces Hydrogen during day but not during night. Under these conditions, adsorption operates with high energy demand
and high Hydrogen losses. In addition to amine-scrubbing, which needs a high heat demand for regeneration of the absorption-liquid, membrane processes seem to be a good alternative for upgrading the raw product gas from Hyvolution-process. Process simulation is used to select process routes by comparing the performance of different unit operations and design options for the necessary process steps. It will help during integration and optimisation of the selected process route and provide necessary data for process engineering and cost estimation.

**Approach and workflow**

The goal of this work was to develop a membrane gas permeation unit for the separation of Hydrogen and Carbon Dioxide. In order to achieve that goal it was necessary, first of all, to define which transport mechanism should be modelled and which type of membrane system should be used. Since there were still no real systems for the separation of the bio-hydrogen because the process is still in project phase, the main concept was to find a way to build a general model that could be improved later on with the development of the project. Therefore a single module using the solution-diffusion as a transport mechanism was developed which didn’t consider the effects from temperature gradients, pressure drop or membrane’s geometry. However, three different ways of describing the membrane module were considered, giving origin to three different models based on different ways to describe the flow, with or without discretization of the membrane module. After this step came the selection of the software. The premise was that the models should run in AP and with that in mind some options like developing the model with the AP user models in connection with Excel or Fortran were studied. In the end the models were developed in ACM not only because it was already being used in the project but also because it presented itself to have the versatility needed. Since that there was no experimental data available for the Hydrogen separation, the first models were build for the Methane and Carbon Dioxide system. After validation and testing for this gaseous pair and, assuming that the successful output for this mixture could be extrapolated to the H₂/CO₂ pair, further calculation were made.

**Background**

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 that each permeant has through the membrane’s material as well as the solubility of each permeant in the membrane’s 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. This means that there is a continuous gradient in chemical potential from one side to the other side of the membrane. 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 at the high pressure value. 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 $p_r$ is removed from the downstream side of the membrane.
Model Development

Table 1. Computer characteristics

<table>
<thead>
<tr>
<th>OS</th>
<th>Microsoft Windows XP Professional Version 2002 Service Pack 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPU</td>
<td>Intel® Pentium® 4 2.66 GHz</td>
</tr>
<tr>
<td>RAM</td>
<td>512 MB</td>
</tr>
</tbody>
</table>

Table 2. Software Versions

<table>
<thead>
<tr>
<th>Software</th>
<th>Version</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net Visual</td>
<td>MS VISUAL STUDIO .NET 2003</td>
</tr>
<tr>
<td>Compaq FORTRAN</td>
<td>Compaq Visual Fortran Professional Edition 6.5.0</td>
</tr>
<tr>
<td>Aspen Custom Modeler (ACM)</td>
<td>2004.1.13.2.0.0008</td>
</tr>
<tr>
<td>Aspen Plus</td>
<td>2004.1.13.2.4.3291</td>
</tr>
</tbody>
</table>

Model 1

The first model is a simple model considering the mass balance in one block without any discretization as it is shown in Figure 1. The inputs given to the model are feed temperature, pressure and composition as well as retentate, permeate pressure, membrane area and permeances. The assumptions made in this model are that the total pressures in the retentate, permeate and feed are constant; the transport mechanism is the Solution-Diffusion mechanism; permeability and permeance are independent of pressure; the partial pressure of the component in the feed is the partial pressure before the membrane; the partial pressure of the component in the permeate is the partial pressure after the membrane; perfect mixing in the permeate side is assumed; there is no pressure drop from feed to retentate; temperature and volume are constant. The inputs given to the model are
feed temperature, pressure and composition as well as retentate, permeate pressure, membrane area and permeances.

\[
F_{\text{feed}} = F_{\text{permeate}} + F_{\text{retentate}}
\]  
Equation (4)

\[
F_{\text{feed}} \cdot y_{i,\text{feed}} = F_{\text{permeate}} \cdot y_{i,\text{permeate}} + F_{\text{retentate}} \cdot y_{i,\text{retentate}}
\]  
Equation (5)

\[
J_i = \frac{F_{\text{permeate}} \cdot y_{i,\text{permeate}}}{A_{\text{membrane}}}
\]  
Equation (6)

\[
J_i = Q_i \left[ \frac{y_{i,\text{feed}} - y_{i,\text{retentate}}}{\ln \left( \frac{y_{i,\text{feed}}}{y_{i,\text{retentate}}} \right)} \cdot P_{\text{feed}} - y_{i,\text{permeate}} \cdot P_{\text{permeate}} \right]
\]  
Equation (7)

Model 2

In this model the membrane module was broken down into \( k \) cells of equal length and each cell behaves like the simple model. Hence, for each cell the assumptions made for Model 1 apply. The number of cells is defined in the code and it is possible to change. The inputs given to the model are feed temperature, pressure and composition as well as retentate, permeate pressure, membrane area and permeances. The conditions for module \( k=0 \) were also defined. The retentate conditions of \( k=0 \) are the feed’s conditions and for the permeate they equal zero.
Model 3
In this model the discretization tools of ACM were used to create yet another discretized model. Using this discretization method on which the partition of the membrane is implemented by ACM, the user only has to write in the code the differential equations of the model. It is also possible to change the node spacing so that certain parts of the membrane are divided into smaller parts than others, i.e. the discretization method, without changing the code of the model. In this model’s case, since it is a simple model, such feature was not analyzed. However, the construction of a model on which the discretization is not implemented by the user is useful to confirm the results obtain with Model 2. The inputs given to the model are feed temperature, pressure and composition as well as permeate pressure, membrane area and the constant parameter k. The conditions for module when \( x=0 \) were also defined in the code. The retentate conditions of \( x=0 \) are the feed’s conditions and for the permeate they equal zero.

![Figure 3. Schematic drawing of Model 3](image)

\[
F_{\text{retentate}}^{k-1} + F_{\text{permeate}}^{k-1} = F_{\text{retentate}}^{k} + F_{\text{permeate}}^{k} \tag{8}
\]

\[
F_{\text{retentate}}^{k-1} \cdot y_{i,\text{retentate}}^{k-1} + F_{\text{permeate}}^{k-1} \cdot y_{i,\text{permeate}}^{k-1} = F_{\text{retentate}}^{k} \cdot y_{i,\text{retentate}}^{k} + F_{\text{permeate}}^{k} \cdot y_{i,\text{permeate}}^{k} \tag{9}
\]

\[
J_{i}^{k} = \frac{F_{\text{permeate}}^{k} \cdot y_{i,\text{permeate}}^{k}}{A_{k}} \tag{10}
\]

\[
J_{i}^{k} = Q_{i} \cdot \left[ \frac{y_{i,\text{retentate}}^{k-1} - y_{i,\text{retentate}}^{k}}{\ln \left( \frac{y_{i,\text{retentate}}^{k-1}}{y_{i,\text{retentate}}^{k}} \right)} \cdot P_{\text{feed}} - y_{i,\text{permeate}}^{k} \cdot P_{\text{permeate}} \right] \tag{11}
\]

\[
d\left( y_{i}^{R} \cdot R_{i} \right) = -Q \cdot \left( y_{i}^{R} \cdot p^{R} - y_{i}^{P} \cdot p^{P} \right) \cdot dA \tag{12}
\]

\[
d\left( y_{i}^{P} \cdot P_{i} \right) = Q \cdot \left( y_{i}^{R} \cdot p^{R} - y_{i}^{P} \cdot p^{P} \right) \cdot dA \tag{13}
\]

\[
da = H \cdot dx \tag{14}
\]

\[
d\left( y_{i}^{P} \cdot P_{i} \right) = k \cdot \left( y_{i}^{R} \cdot p^{R} - y_{i}^{P} \cdot p^{P} \right) \cdot dx \tag{15}
\]

\[
k = H \cdot Q \tag{16}
\]
Results

The experimental data used to compare the model’s results with a real system are taken from the literature and the module used to obtain the experimental data was a hollow fibre module. For each model, three sets of experimental data are compared. Firstly, permeate flow vs. feed flow, retentate flow vs. feed flow and finally retentate composition vs. feed flow. Since the membrane from the experimental set-up was a reverse-selective membrane the composition in the retentate, in terms of methane, concentration is analyzed. In order to calculate the permeances, the flow through the membrane of the experimental set-up of each pure component separately was studied. The pressure of the feed was increased and the pressure of the permeate and rate were measured. The permeances calculated can be found in Table 4 and as well as the membrane’s characteristics. The results for the discretized models were obtained using 100 modules and 100 nodes of Models 2 and 3, respectively. Concerning the permeate flow the model that has the closest results to the experimental data is Model 3, followed by Model 2 which presents similar results. The same happens with the results for the retentate flow. Model 3 presents the most approximate results to the experimental data, followed by Model 2, but in general, all 3 models give almost similar results. As far as the concentration of methane in the retentate is concerned, both discretized model present the same results and follow the same trend as the experimental results. Only Model 1 gives a different trend.

Table 3. Membrane properties and component permeances

<table>
<thead>
<tr>
<th>Number of fibers</th>
<th>800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (m)</td>
<td>0,38</td>
</tr>
<tr>
<td>Di (mm)</td>
<td>0,40</td>
</tr>
<tr>
<td>At (m²)</td>
<td>0,38</td>
</tr>
<tr>
<td>Q(CH₄) (kmol/h.bar.m²)</td>
<td>2,00x10⁻⁴</td>
</tr>
<tr>
<td>Q(CO₂) (kmol/h.bar.m²)</td>
<td>8,27x10⁻³</td>
</tr>
</tbody>
</table>

Figure 4. Experimental set-up of the membrane used in the validation
The immediate conclusion one can take from the plots above is that discretization of the models fits better to the experimental data than a simple model without discretization. Moreover, one can also notice that from Model 1 to Model 3 the error in the calculated values for the retentate flow increase but the errors on the calculated permeate flow and methane concentration decrease. The possible reason for the fact that the discretized models offer in general better results might have to do with convergence of the models. For instance, when dividing the membrane into smaller parts that means the equations described before are applied to each “slice” of the membrane taking into account that, closer to the feed side of the membrane the flux to the permeate is higher due to the bigger difference in the partial pressures of the components. This phenomenon is not accounted for when considering the membrane as a whole and even the approximation of calculating the logarithmic average of the partial pressure in the retentate side doesn’t offer as good results as the discretization of the module. Model 3 and model 2 presented similar results in the validation with experimental data and with the smallest deviations.
Sensitivity analysis

The membrane that was chosen for these sensitivity analysis calculations was a PDMS membrane with the characteristics shown in the following table. The main results analyzed are the carbon dioxide removed from the feed vs. the hydrogen lost to the permeate when the membrane’s area increases and also the pressure of the permeate. Since hydrogen is the main product it is important to study the better way to retrieve the hydrogen present in the feed using the smallest area and lower energy consumption possible. In this sensitivity analysis only calculations for a single module were performed. The reason this membrane was chosen to perform the sensitivity analysis was because it is an example of a polymeric membrane that is reverse selective at low temperatures and has been used in the separations of hydrogen and carbon dioxide. Since this membrane has a good permeability but a somewhat poor selectivity it is expected that to attain high concentrations of hydrogen in the retentate there will have to be loss to the permeate as well and vice versa. To perform the sensitivity analysis model 2 was chosen because the way it was implemented made it easier to change parameters and it is not necessary to specify the membrane’s length.

Table 4. Membrane parameters

<table>
<thead>
<tr>
<th>Permeability (Barrer)</th>
<th>3200 (CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>950 (H₂)</td>
</tr>
<tr>
<td>Thickness</td>
<td>1.3 μm</td>
</tr>
</tbody>
</table>

Table 5. Feed composition and operating conditions

<table>
<thead>
<tr>
<th>Feed (kmol/h)</th>
<th>23.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ mole fraction</td>
<td>0.3</td>
</tr>
<tr>
<td>H₂ mole fraction</td>
<td>0.7</td>
</tr>
<tr>
<td>Temperature (C)</td>
<td>35</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Figure 8. CO₂ recovery vs H₂ loss to permeate
Conclusions

The first conclusion one takes immediately is that the results of the validation can be divided in two sets, the results of the discretized models 2 and 3 and the results of model 1. In both models 2 and 3 the results are very similar and closer to the experimental data, which suggests that dividing the membrane into smaller parts describes the system more accurately. However, there seems to be a tendency of the models’ methane concentration to have smaller values than those of the experimental data. This suggests that in the real system there is a phenomenon that “blocks” the permeation of carbon dioxide or increases the permeation of methane through the membrane. Since the total flows of the retentate and permeate are almost the same in the models and in the experimental data, one is led to support a combination of both hypotheses. This additional permeation and blockage might have to do with all the factors that were disregarded such as temperature gradients or geometry. In addition to this, it is also necessary to notice that in the experimental setup, the flow was measured with standard volume units and that alone introduces an error on the reading of the flow and perhaps that is what causes such small differences between the models’ output for total retentate and permeate flows to experimental data. All in all, both models 2 and 3 seem to be able to predict quite well i.e. with a small error, the outcome of a gas permeation membrane unit and, for estimation purposes in a process, these models are suitable to be used. However, the ideal case would be that in the future corrections and alteration to this model can be made, perhaps even create a sort of a library within the model itself that allows the model user to choose which features in transport or geometry he/she wants in the system. Another upgrade that can be made is to add to the model the features necessary for dynamic simulation. Nevertheless, it is crucial that validation with experimental data of the model can be made. Setting up a model for a membrane unit for software like AP should be a compromise between experimental work and computational work in order not only to troubleshoot but also to improve the results.

Symbols

\[ D_i \] \hspace{1cm} \text{Fick's Law Diffusion Coefficient of component } i
\[ J_i \] \hspace{1cm} \text{Membrane flux of component } i
\[ \ell \] \hspace{1cm} \text{Membrane thickness}
\[ P_{io} \] \hspace{1cm} \text{Partial feed pressure of component } i
\[ P_{pi} \] \hspace{1cm} \text{Partial permeate pressure of component } i
\[ P_i, P_j \] \hspace{1cm} \text{Permeabilities of components } i \text{ and } j
\[ Q_i \] \hspace{1cm} \text{Permeance of component } i
\[ F_{feed} \] \hspace{1cm} \text{Membrane Feed Flow}
\[ F_{permeate} \] \hspace{1cm} \text{Membrane Permeate Flow}
\[ F_{retentate} \] \hspace{1cm} \text{Membrane Retentate Flow}
\[ Y_{i, feed} \] \hspace{1cm} Component } i \text{ molar fraction in the feed}
\[ Y_{i, permeate} \] \hspace{1cm} Component } i \text{ molar fraction in the permeate}
\[ y_{i, \text{retentate}} \] Component \( i \) molar fraction in the retentate

\[ A_{\text{membrane}} \] Membrane’s area

\[ P_{\text{feed}} \] Feed total pressure

\[ P_{\text{permeate}} \] Permeate total pressure

\[ k \] Membrane module number (superscript)

\[ k \] Constant

\[ R \] Retentate (superscript)

\[ P \] Permeate (superscript)

\[ R(x) \] Retentate along membrane’s length

\[ P(x) \] Permeate along membrane’s length

\[ x \] Membrane’s length axis

\[ H \] Height

\[ A \] Area

Literature


Alekssander Makaruk, Internal publication