Hollow Fiber Gas Permeation Membrane Model
USER MANUAL

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1. INTRODUCTION

This documentation introduces the Hollow Fiber Gas Permeation (HFGP) membrane steady-state model that has been developed within CCSI to simulate membrane stage units in carbon capture processes. This one-dimensional PDE process model is flexible, modular, and computationally efficient. It is suitable for process synthesis and design tasks aimed to facilitate the rapid screening of new concepts and technologies for carbon capture.

2. GENERAL INFORMATION

2.1. Overview

This multi-component, one-dimensional model is applicable for membrane materials that follow the solution-diffusion model and predicts the pressure drop in the fiber bore side according to the Hagen-Poiseuille equation for a compressible fluid. The one-dimensional permeate and retentate gas plug-flows are assumed to be counter-current to each other. The model provides profiles for component fluxes and concentrations. The equation oriented structure allows the user to perform rating or design calculations depending on the variables being specified to satisfy the degrees of freedom. The figure below shows a schematic for the model.

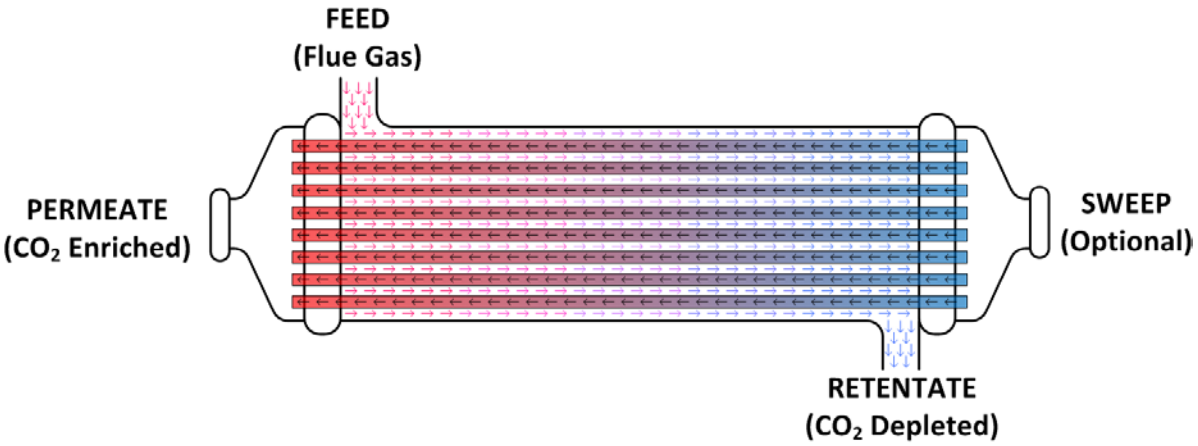

Figure 2.1.1: HFGP Membrane Device Model Schematic

2.2. Model Assumptions

The main assumptions of the HFGP membrane model are listed as follows.

- The feed gas enters the shell side of the hollow fiber membrane and permeates to the fiber's bore. The sweep gas (optional) enters the fiber bore side at the opposite end from the feed. The gases in the retentate (shell) and permeate (fiber bore) sides flow from one discretized node to the next in the direction of flow accumulating to form the retentate and permeate outlet streams (Counter-current flow).
- The fibers that make up the bundle are identical, perfectly straight, and uniform diameter, cylindrical hollow tubes. The feed gas mixture it is evenly distributed throughout a cross section of the fiber bundle. This is also the start point of the discretized length domain of

integration. The end point is at the retentate outlet stream. Radial concentration and flow gradients in the fiber bundle are neglected (Problem is reduced to one dimension).
- Under the expected operation conditions, the gas mixtures in the module are assumed to behave ideally. The driving force for gas permeation is the difference of component partial pressure across the dense skin.
- Properties and state variables are constant at each node of the discretized axial domain
- The dense skin layer of the asymmetrical hollow fiber membrane faces the shell side. The molar composition at the boundary of the dense skin layer and the porous support is equal to the bulk molar composition at the fiber bore. This assumption implies that there is no flux resistance imposed by the porous support.
- Pressure in the shell is constant. The pressure in fiber bore varies due to constrained flow and can be described by the Hagen-Poiseuille equation for a compressible fluid.
- Isothermal conditions (No energy balance required).

3. MODEL STRUCTURE

The developed model was firstly implemented in Aspen Custom Modeler® (ACM, Aspen Technology, Inc.) and all partial-differential equations are solved using method of lines. The spatial domain has been discretized using a 2nd order centered finite difference method and 20 elements are used as a default. The attached ACM file includes a newly-defined initialization parameter type, as well as the main device models. The model equations are written in the Custom Modeling library.

To find a HFGP membrane model in the Custom Modeling library:
1. In the All Items pane of the Simulation Explorer, make sure the Custom Modeling library is expanded and expand the Models folder. A list of all models in the current simulation appears.
2. Click on either HFGPnoS or HFGPw_S.
3. In the Contents panel, double-click the equal icon to view the model syntax.

3.1. IO Structure and Reactor Dimensions

There are two versions of the model. One is defined with a sweep stream port and a second one without it. Each port has associated variables that correspond to the material connection stream variables. The gas inlets and outlets are defined using the built-in ACM mole fraction port.

Given the equation oriented nature of this implementation, this model can be used to perform either rating or design calculations as long as the corresponding variables are specified as fixed to satisfy the degrees of freedom required for solution.

3.2. Membrane Transport Model

The asymmetric membrane architecture found in modern gas permeation devices was developed in order to address conflicting requirements. Membrane thickness must be sufficiently thin in order to achieve high permeation rates but sufficiently thick to be mechanically stable and endure the imposed pressure gradient. By coating a thin (0.5-1 μm) selective layer on a porous support two to three orders of magnitude thicker both requirements are fulfilled. Figure 3.2.1 shows a simplified sketch of the asymmetric membrane architecture.

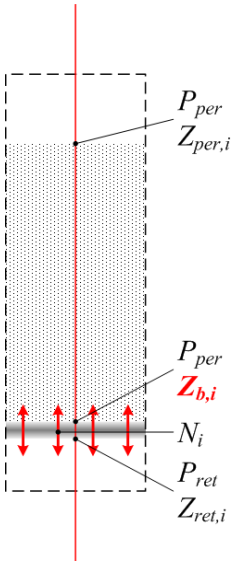

Figure 3.2.1: Asymmetric Membrane

The transport across the selective layer is assumed to follow the solution-diffusion model as described by Baker (2004). The permeance, *Q*, is the permeability divided by the layer thickness. Another important assumption of the solution-diffusion model is that the rates of adsorption and desorption are much higher than the permeation rate. Therefore, the compositions at the boundaries of the selective layer are at equilibrium with its immediate surroundings. Equations (1)-(3) describe the asymmetric membrane model.

(1) $$N_i = \frac{Q_{CO_2}}{\alpha_i}\left(P_{ret}Z_{ret,i} - P_{per}Z_{b,i}\right)$$ Component Molar Flux

(2) $$N_t = \sum_j^n N_j$$ Total Molar Flux

(3) $$\alpha_i = \frac{Q_{CO_2}}{Q_i}$$ Selectivity

The molar composition at the boundary of the porous support and the dense skin ($Z_{b,i}$) is assumed to be equal to the bulk composition at the fiber bore. This may not be a valid assumption for a system with high fluxes (high partial pressure ratio and/or component permeances) or Knudsen diffusion limited systems (porous support with relative large thickness and/or small mean pore radius).

3.3. Membrane Module Model

There are two types of industrial gas permeation modules suitable for this application: hollow fiber and spiral wound. Baker (2004) gives a complete description and comparison for these and other types of industrial membrane modules. From a modeling perspective, a hollow fiber module system is advantageous because the permeate pressure drop effects can be described from basic principles, and the flow patterns can be described in one dimension. For a spiral wound module, the permeate pressure drop is a function of the number and dimensions of the wound membrane envelopes and the spacer material. This information is typically considered proprietary and it is therefore difficult to find. The permeate flows along the spiral on a plane

perpendicular to the flow in the retentate side, which may require an additional dimension to be accurately described.

The equations that describe the hollow fiber module along the module length, *x*, under the assumptions above are:

(4) $$\frac{dF_{per}}{dx} = -J_t$$ Fiber Bore Overall Molar Balance

(5) $$\frac{dP_{per}^{\ 2}}{dx} = \frac{16RT\mu F_{per}}{\pi r_{FI}^{\ 4} n_F}$$ Fiber Bore Pressure Drop

(6) $$F_{per}\frac{dZ_{per,i}}{dx} = J_t Z_{per,i} - J_i$$ Fiber Bore Component Molar Balance

(7) $$\frac{dF_{ret}}{dx} = -J_t$$ Shell Overall Molar Balance

(8) $$\frac{dP_{ret}}{dx} = 0$$ Shell Pressure Drop

(9) $$F_{ret}\frac{dZ_{ret,i}}{dx} = J_t Z_{ret,i} - J_i$$ Shell Component Molar Balance

Where

$$J_i = 2\pi r_{FO} n_F N_i, \qquad J_t = \sum_j^n J_j$$

$r_{FO/I}$ = Fiber Outer/Inner Radius

n_F = Number of Fibers

Equations (1)-(9) are the basis for the model. Boundary conditions, physical properties procedure calls, and other equations are written in the model syntax using the same nomenclature as the equations in this document.

3.4. Hollow Fiber Module Properties

The permeation properties and dimensions of the hollow fiber membrane are treated as lumped parameters of the model.

Table 3.1 includes the values assigned to each of these model variables. Selectivity is defined as the ratio of the permeance for carbon dioxide to the permeance for a given gas species.

Table 3.1: Hollow Fiber Module Properties

Variable	Typical	Base Case
Inner fiber Diameter (μm)	100-700*	400
Outer fiber diameter (μm)	200-800*	600
Effective fiber length (m)	0.15-1.50*	1.00
CO_2 Permeance (GPU)	10-10000†	1000‡
H_2O Selectivity	<1	0.5
N_2 Selectivity	4-150†	50‡
O_2 Selectivity	N/A	50

*Chowdhury et al. (2005) , †Brunetti et al. (2010), ‡Merkel et al. (2010)

4. TUTORIAL

This section provides a detailed tutorial to simulate the performance of a two-stage membrane system in series. This tutorial was developed using v7.3 of ACM and Aspen Properties, additional modifications could be required when using different versions.

1. Open an empty ACM file from the Windows Programs folder.

2. Define the component list and property method.

   In the All Items panel of the Simulation Explorer, select “Component Lists”, select “Configure Properties” in the Components List panel. Select “Use Aspen properties system” in the dialog box and press the button “Edit using Aspen Properties”. Define CO2 (carbon dioxide), H2O (water), N2 (nitrogen), and O2 (oxygen) as components and select the Peng-Robinson (PENG-ROB) as the property method. Run the property calculation, close the window and save. A green box on the configuration window indicates that properties have been successfully configured.

   Open the Default component list dialog box by double-clicking on Default under Component Lists in the Simulation Explorer and move all available components into the list on the right side of the dialog box.

3. Change the non linear solver from standard to DMO.

   Open the solver options dialog box by pressing F10 and make the change in the Non Linear solver tab.

4. Import Custom Modeling types.

   Once the supporting files for this model have been saved in a convenient location, import the HFGP types. From the File menu, click Import Types. Browse and select HFGP.acmf. Ignore the warnings that appear in the Simulation Messages window stating that content that is not relevant to the Custom Modeling library was ignored.

5. Place an HFGPnoS block on the Process Flowsheet Window.

   Drag the HFGPnoS model from the Models folder of the Custom Modeling library in the Simulation Explorer panel onto the Process Flowsheet panel.

   Rename it M1. Renaming in ACM can be achieved by right-clicking on an item and selecting the Rename option, or with the Ctrl+M keyboard shortcut once the item has been selected. Exchange the icon by selecting the block and pressing Ctrl+K.

6. Specify M1 device variables.

   Double click on M1. On the Device Variables window enter the values in Table 4.2.

Table 4.2: M1 Device Variables

alpha("CO2")	1.0
alpha("H2O")	0.5
alpha("N2")	50
alpha("O2")	50
CCfct	0.51
Dfi	0.0004
Dfo	0.0006
L	1
Qcd	0.12047

   Note that the fiber diameters are defined in meters while the carbon dioxide permeance is defined in ACM default units (1000 GPU = 0.12047 kmol/m^2/hr/bar). CCfct is a custom variable defined as the fraction (mol basis) of carbon dioxide that leaves in the permeate outlet stream with respect to the carbon dioxide at the feed inlet.

7. Specify M1 stream variables.

   Define stream connections for the inlet and outlet streams in the device model by dragging "Connection" type streams from the Stream Types folder of the Custom Modeling Library and connecting them to M1 on the Process Flowsheet. Rename the new streams according to their block connection port (FeedM1, RetentateM1, and PermeateM1).

   Double click on the feed inlet stream and enter the values in Table 4.3. Once the value has been entered, change the variable Spec value from Free to Fixed.

Table 4.3: M1 Gas Feed Specification

FeedM1.F	100,000	kmol/hr
FeedM1.P	2.0	bar
FeedM1.T	50	°C
FeedM1.z("CO2")	0.19	
FeedM1.z("H2O")	0.04	
FeedM1.z("N2")	0.72	
FeedM1.z("O2")	0.05	

Specify the Permeate outlet stream pressure. Double click on the PermeateM1 stream and enter 0.2 for P in the PermeateM1.AllVariables Table. Finally, change its Spec from Free to Fixed.

8. Run the simulation.

   At this point the simulation is ready to be solved. This can be verified by the presence of a green square at the bottom of the ACM window. However, the ACM solver will not be capable to reach a solution from this point due to the size and non-linear nature of the problem. Verify this by running the simulation (Press F5).

   Reset the simulation (Press Ctrl+F7). This option changes the value of free variables to its default.

   A solution procedure with a custom initialization method has been defined using a VB script. The script solves the model in incremental steps of complexity by using initialization procedure selectors. The selectors are switched from an 'Initial' state that selects a set of simplified model equations to 'Rigorous' which selects a set of more accurate equations corresponding to the desired solution. In the HFGP model this script has two steps. The first one applies to the equation for the permeate side molar balance, the second one applies to the permeate side pressure drop.

   Invoke the IPsolve script. Right-click on the M1 block, select Scripts and click on IPsolve. Once the script is completed, the desired solution has been achieved.

9. Place an HFGPw_S block on the Process Flowsheet Window.

   Drag the HFGPw_S model from the Models folder of the Custom Modeling library in the Simulation Explorer panel onto the Process Flowsheet panel.

   Rename it (Ctrl+M) M2 and exchange its icon (Ctrl+K).

10. Specify M2 device variables.

    Double click on M2. On the Device Variables window enter the values in Table 4.3.

Table 4.3: M2 Device Variables

alpha(“CO2”)	1.0
alpha(“H2O”)	0.5
alpha(“N2”)	50
alpha(“O2”)	50
CCfct	0.86
Dfi	0.0004
Dfo	0.0006
L	1
Qcd	0.12047

11. Specify M2 stream variables.

    Connect M1's Retentate outlet stream to the Feed port of M2.

    Define stream connections for the remaining inlet and outlet streams in the device model by dragging "Connection" type streams from the Stream Types folder of the Custom Modeling Library and connecting them to M2 on the Process Flowsheet.

    Rename the new streams according to their block connection port (SweepM2, RetentateM2, and PermeateM2).

    Double click on the sweep inlet stream and enter the values in Table 4.4 (composition of air). Once the value has been entered, change the variable Spec value from Free to Fixed.

Table 4.4: Gas Sweep Specification

SweepM2.F	65,000	kmol/hr
SweepM2.P	1.3	bar
SweepM2.z("CO2")	0.00030	
SweepM2.z("H2O")	0.01009	
SweepM2.z("N2")	0.78223	
SweepM2.z("O2")	0.20738	

12. Run the simulation.

    Invoke the IPsolve script. Right-click on the M2 block, select Scripts and click on IPsolve. Once the script is completed, the desired solution has been achieved.

REFERENCE

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[4] T.C. Merkel, H. Lin, X. Wei and R. Baker, Power Plant Post-Combustion Carbon Dioxide Capture: An Opportunity for Membranes, *Journal of Membrane Science* **359**, pp. 126-139 (2010).