HYGRID

FLEXIBLE HYBRID SEPARATION SYSTEM FOR H2 RECOVERY FROM NG GRIDS

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D.8.1
Report on modelling of membrane separation

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Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	
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Content

1. EXECUTIVE SUMMARY

1.1. Description of the deliverable content and purpose

The permeation through the membrane in the different membrane separation modules is being simulated with a dynamic 1D model. This document aims to model the membrane behaviour in different operating conditions also taking into account mass transfer limitation in the retentate side.

1.2. Brief description of the state of the art and the innovation brought

A 1D modelling on membrane permeation has been validated and used for simulation of the HyGrid system. Different membrane types were considered for the modelling. A comparison between sweep gas and vacuum pump has been considered in the work.

1.3. Deviation from objectives

The deliverable was delayed one month.

1.4. If relevant: corrective actions

There are no deviations.

1.5. If relevant: Intellectual property rights

N/A

2. Introduction

In recent years, palladium membranes received increasing interest due to their extremely high selectivity and permeability and for the possibility to integrate in membrane reactors for hydrogen purification and production [1]. Most of the commercially available Pd alloy membranes have a thickness above 20-30 µm (up to 150 µm) and are self-supported. Therefore, they have low hydrogen permeation flux and therefore higher costs. The hydrogen permeable membranes can mathematically be described by the Sieverts' law if the diffusion through the dense layer is the rate limiting step, as stated in Equation (1). The flux through the membrane has a permeability, which is dependent on the membrane thickness. Additionally, the flux is dependent on the partial pressure on the retentate side as well as the permeate side. The hydrogen flux scales with a factor n, which is a number between 0 and 1. Generally, n is chosen as 0.5, which represents that diffusion through the dense layer is the rate limiting step. In other cases, a value not equal to 0.5 can be found that indicates that an other phenomena is rate limiting.

3. Model description

The 1-D PBMR model described in this work is the update version of the PBMR model developed by TU/e taking into account the concentration polarization [2]. The model solves the momentum, mass and energy conservation balances simultaneously to determine the parameters on axial position in the reactor, thus it has no radial coordinate.

The main equations are described below:

Mass conservation equation:

$$\varepsilon_g \frac{\partial \rho_g}{\partial t} = -\frac{\partial \rho_g u_g}{\partial z} - \phi_{m,i}^{mass} a_m$$

Mass balance for the gas phase:

$$\varepsilon_{g\rho_g} \frac{\partial \omega_i}{\partial t} = -\frac{\partial \rho_g u_g \omega_i}{\partial z} + \frac{\partial}{\partial z}\left(\rho_g D_{ax} \frac{\partial \omega_i}{\partial z}\right) + n_i a_s + \phi_{m,i}^{mass} a_m$$

Energy balance for the gas phase:

$$\varepsilon_g \rho_g C_{p,g} \frac{\partial T}{\partial t} = -C_{p,g} \rho_g u_g \frac{\partial T}{\partial z} + \frac{\partial}{\partial z}\left(\lambda_g \frac{\partial T}{\partial z}\right) + \sum_{i=1}^{N} n_i a_s H_i + \sum_{i=1}^{N} \phi_{m,i}^{mass} a_m H_i + \alpha_{b\to w} \alpha_w (T - T_w)$$

In which ε_g is the gas fraction, ρ_g the gas density, u_g gas velocity, $\phi_{m,i}^{mass}$ the mass flow, a_m the specific surface membrane, ω_i the mass fraction of component i, D_{ax} the axial dispersion, a_s the specific surface solid phase, $C_{p,g}$ heat capacity at constant pressure, T the temperature and λ_g the gas thermal conductivity.

The reactor consists of two cylindrical compartments. The inner compartment is considered the permeate side, operating with a sweep gas or vacuum. The outer compartment is packed with inert and catalytic particles and fed with the reaction mixture. The inner and outer compartment are separated by the perm-selective membrane. For membrane modelling the inner compartment is the permeate side of the membrane while the outer compartment is the retentate of the membrane. For visualization purposes, a schematic of the reactor is represented in Figure 1. The main assumptions of the model are:

- Gas transport in the axial direction can be described as convective flow with superimposed axial dispersion
- Pseudo-homogeneous reaction, thus no external mass and heat transfer limitation of the catalyst.

The numerical model uses a finite difference technique with higher order discretization schemes,

adaptive time-stepping, and automatic local grid refinement. The isothermal model only solves the mass balances, while the non-isothermal model also solves the energy balances.

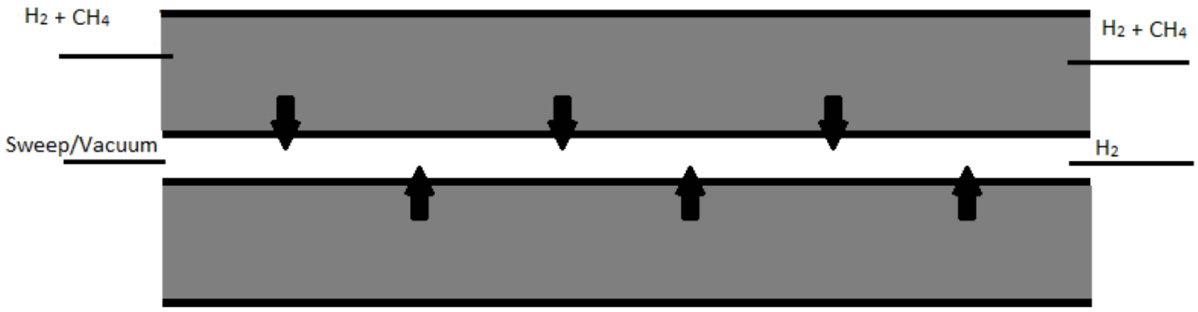

Figure 1. Schematic representation of the membrane module in the model

The hydrogen permeances is described by the Sieverts' law and is proportional to the permeability, the thickness of the membrane and the difference between the hydrogen partial pressure of retentate and permeate as it is stated in equation (1). Usually for palladium membrane the exponent n is equal to 0.5.

$$J_{H_2}=\frac{Q}{\delta}\exp\left(-\frac{E_a}{RT}\right)*\left(p_{ret}^{n}-p_{perm}^{n}\right) \qquad (1)$$

Normally, the Sieverts' law is considered for modelling the hydrogen permeance through dense Pd alloy membranes, meaning the diffusion through the membrane bulk is limiting the flux. However, the pressure exponent can vary depending on the limiting step. To find the limiting step, it is important to know were it might be. Ward et al. (1999) consideres the following steps from retentate to permeate side [3]:

1. Molecular transport from the bulk to the gas layer adjacent to the surface,

2. Dissociative adsorption onto the surface,

3. Transition of atomic H from the surface into the bulk material,

4. Atomic diffusion through the bulk metal,

5. Transition from the bulk metal to the surface on the permeate side,

6. Recombinative desorption from the surface, and

7. Gas transport away from the surface to the bulk gas.

Normally, the atomic diffusion through the membrane bulk is limiting. However, as membranes become thinner, at some "critical" thickness the diffusion through the membrane becomes rapid enough that another step might limit the permeation rate. At that point, the Sieverts' law will no longer be sufficient and other forms of the flux equation are better suited [4]. Ward et al (1999) found a shift of rate limiting step towards recombinative desorption on the permeate side at lower temperatures, and adsorption can be rate limiting at very low hydrogen partial pressures on the retentate side or substantial surface contamination. These shifts in the rate limiting step can alternate the pressure exponent within the Sieverts' law lower exponents are observed when the recombinative surface reaction on the permeate side is limiting, while higher exponents are observed when the gas phase resistance or dissociative adsorption are limiting.

The 1D-PBMR is extended with a correction factor on the partial pressure of hydrogen at the wall to correct the mass transfer rates in radial direction. The mass transfer are corrected to simulate the potential concentration polarization so the pressure of hydrogen at the wall can be estimated. To achieve this polarization the stagnant-film model was used. The stagnant-film model is described by the sum of molecular and convective contributions to the mass flux as it is possible to see in equation (2).

$$N_{H_2} = J_{H_2} + x_{H_2} \sum_{i=1}^{N} N_i \quad (2)$$

To achieve a better estimation of the partial pressure of hydrogen at wall, the zero rate mass transfer coefficient, is adjusted for a non-zero flux. The correction is based on the stagnant-film model. With the stagnant-film model and the Fick's law, the partial pressure of hydrogen at the membrane surface was estimated based on the bulk phase pressure and zero mass transfer coefficient. The flux computation is divided into two parts as it is possible to see in figure 2. First, the concentration, flux and mass transfer coefficient at the interface between the bulk and the boundary layer are calculated. Then, the same method has been used for calculating the concentration at the membrane wall and the correction factor for the permeation through the membrane wall. When only the hydrogen flux is considered, as stated in equation (3) and the Fick's law (4) is considered, it is possible to derive equation (5). The continuity equation states the flux does not change at steady state according to equation (6). While equation (7) is obtained integrating twice equation (6).

$$\sum_{i=1}^{N} N_i = N_{H_2} \qquad (3)$$

$$J_{H_2 =} - cD_{H_2B} \frac{\partial x_{H_2}}{\partial y} \qquad (4)$$

$$N_{H_2} = \frac{-cD_{H_2B}}{1 - x_{H_2}} \frac{\partial x_{H_2}}{\partial y} \qquad (5)$$

$$\frac{\partial N_{H_2}}{\partial y} = \frac{\partial}{\partial y}\left(\frac{-cD_{H_2B}}{1 - x_{H_2}} \frac{\partial x_{H_2}}{\partial y}\right) = 0 \qquad (6)$$

$$cD_{H_2B} \ln\left(1 - x_{H_2}\right) = k_1 y + k_2 \qquad (7)$$

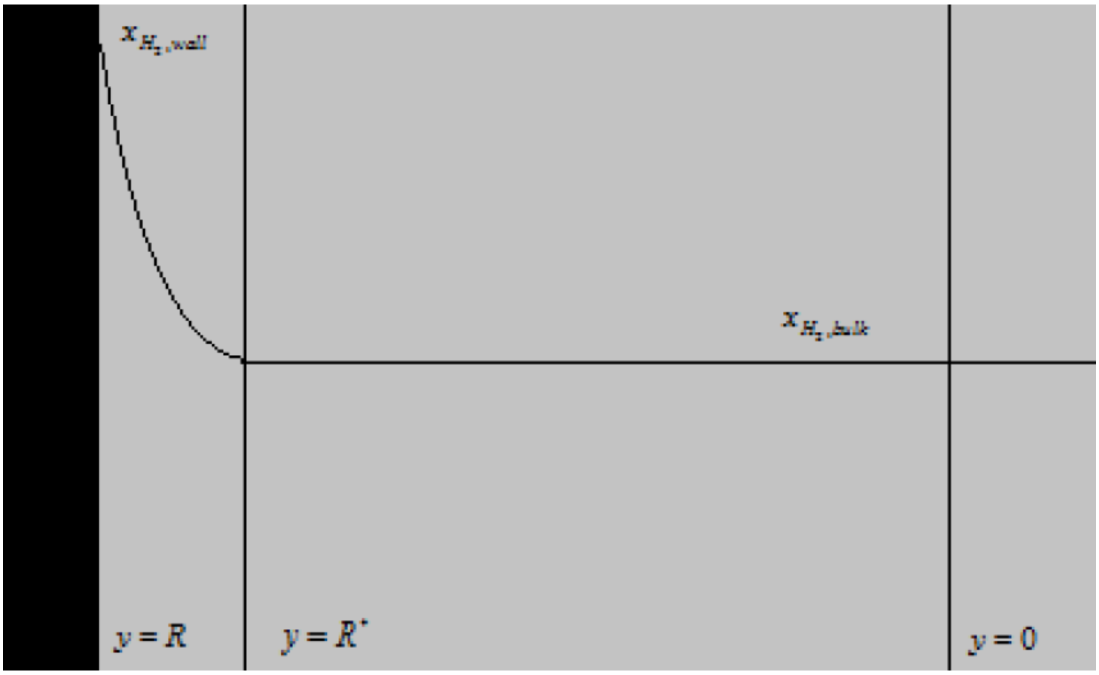

Figure 2. A visualization of the two step of the hydrogen concentration

k1 and k2 can be calculated from the following boundary conditions:

$$y = 0 \quad x_{H_2} = x_{H_{2,bulk}}; \;\; k_2 = cD_{H_2B}\ln\left(1 - x_{H_{2,bulk}}\right)$$

$$y = R^* \quad x_{H_2} = x^*_{H_2}; \;\; k_1 = \frac{cD_{H_2B}}{R^*}\ln\left(\frac{1 - x^*_{H_2}}{1 - x_{H_{2,bulk}}}\right)$$

Both constants are substituted in equation (7) and the equation can be rewritten in order to obtain x_{H_2} equation (8) is the differential form of equation (7). Equation (8) can be combined with in order to obtain (9).

$$x_{H_2} = 1 - \left(1 - x_{H_{2,bulk}}\right)\left[\frac{1 - x^*_{H_2}}{1 - x_{H_{2,bulk}}}\right]^{\frac{y}{R^*}} \qquad (7)$$

$$\frac{\partial x_{H_2}}{\partial y} = -\frac{1 - x_{H_{2,bulk}}}{R^*}\left[\frac{1 - x^*_{H_2}}{1 - x_{H_{2,bulk}}}\right]^{\frac{y}{R^*}}\ln\left[\frac{1 - x^*_{H_2}}{1 - x_{H_{2,bulk}}}\right] \qquad (8)$$

$$N_{H_2} = \frac{cD_{H_2B}}{R^*}\frac{1 - x_{H_{2,bulk}}}{1 - x_{H_2}}\left[\frac{1 - x^*_{H_2}}{1 - x_{H_{2,bulk}}}\right]^{\frac{y}{R^*}}\ln\left[\frac{1 - x^*_{H_2}}{1 - x_{H_{2,bulk}}}\right] \qquad (9)$$

When the molar fractions are rewritten into partial pressure and the mass transfer coefficient, $k_g$is considered $\frac{D_{H_2B}}{R^*}$, equation (10) is found. Then equation (10) is rewritten in equation (11).

$$N_{H_2}|_{y=R^*} = k_g c ln\left[\frac{P-P^*_{H_2}}{P-P_{H_{2,bulk}}}\right] = Q\left(P^{*0.5}_{H_2} - P_{H_{2,perm}}\right) \quad (10)$$

$$\frac{P-P^*_{H_2}}{P-P_{H_{2,bulk}}} = \frac{Q}{k_g c}\left(P^{*0.5}_{H_2} - P^*_{H_{2,perm}}\right) \quad (11)$$

Equation (11) can be rewritten by the series Taylor expansion to solve it as a polynomial equation in the form of $aP^*_{H_2} + b\sqrt{P^*_{H_2}} + c = 0$

The quadratic form of the roots of the system will provide the value of $P^*_{H_2}$, constants a, b and c can be derived and are defined as follows:

$$a = \frac{1}{2!}\left(\frac{Q}{k_g c}\right)^2 + \frac{1}{P - P_{H_{2,bulk}}}$$

$$b = \frac{Q}{k_g c} - \left(\frac{Q}{k_g c}\right)^2 P^{0.5}_{H_{2,perm}}$$

$$c = 1 - \frac{Q}{k_g c}P^{0.5}_{H_{2,perm}} + \frac{1}{2}\left(\frac{Q}{k_g c}\right)^2 P^{0.5}_{H_{2,perm}} - \frac{P}{P - P_{H_{2,bulk}}}$$

k_g can be derived using the Sherwood number that is based on the Schmidt and Reynolds number. The set of the equation is solved algebraically in the model.

4. Validation of the model

The model has been validated with experimental results. A palladium membrane with ceramic support has been used as reference. The length of the membrane is equal to 112.79 mm, while the diameter is 10.36 mm. The permeability and the activation energy were equal respectively to $4*10^{-6}$ mol/s/m^2/Pa and 8.058 kJ/mol.

The system has been tested in co-current mode as the model is defined. A mixture of H_2/N_2 has been fed in the membrane while CO was used as sweep gas. The pressure of the retentate side was changed from 5 to 1.5 bar while the pressure of the permeate was equal to 1 bar. In the picture 2 it is possible to see the comparison between experiments and modelling. From the results it is possible to see that the model is able to predict well the experimental results.

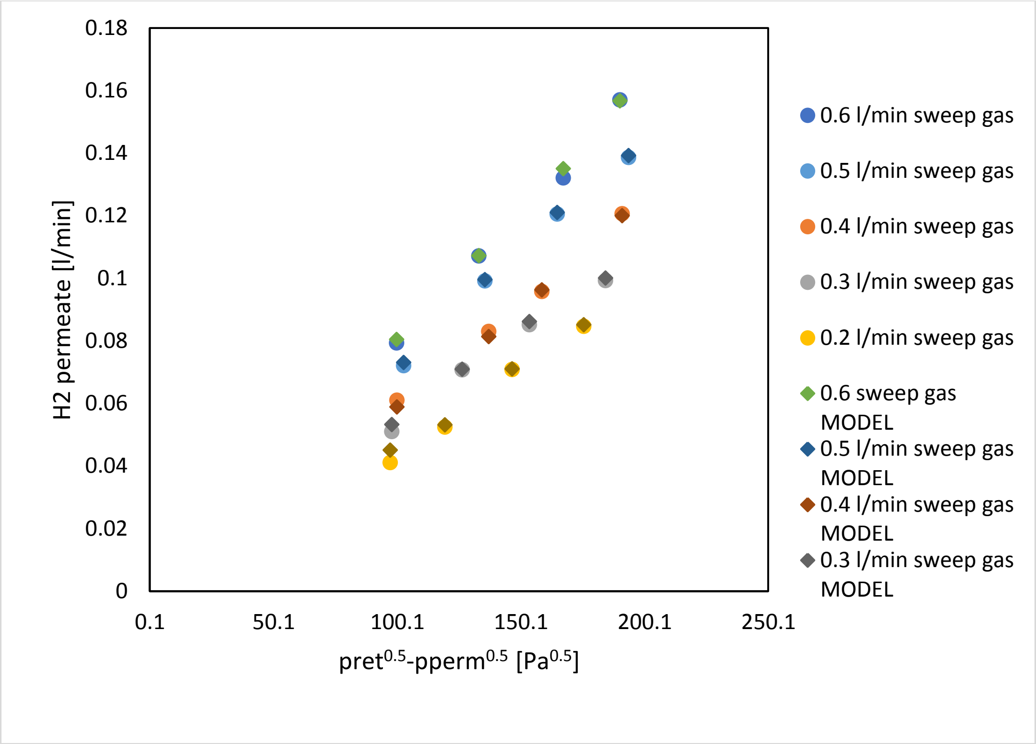

Figure 3. Comparison between experimental and modelling results

4. Results

The simulation of the membrane has been carried out considering a co-current system for the sweep gas. The first case consists on an initial feed equal to 624.61 mol/h of hydrogen, 5621.49 mol/h of methane and the amount of steam as sweep gas has been increased taking into account the area of membrane required. The aim of the simulation is to evaluate the area of membrane required in order to reach a HRF of 80%. The pressure has been changed from 5 bar until 10 bar in order to study the influence of the pressure on the hydrogen recovery. The simulation has been done to compare Pd-Ag membranes with metallic support and Pd-Ag membranes with ceramic support. The characteristics considered in the simulation for membranes with metallic support are a permeability equal to $10^{-6}\frac{mol}{s*Pa*m^2}$ and $4.5*10^{-6}\frac{mol}{s*Pa*m^2}$ for ceramic support. The activation energy was considered equal to 7.779 kJ/mol for metallic support and to 8 kJ/mol for ceramic support. The value of thickness considered in the modelling is equal to 5 µm. In the figure 4 and in figure 5 it is possible to see the comparison between palladium membrane with metallic and ceramic support in terms of area required changing the pressure. The main advantage of ceramic support is related to a lower area of membrane in order to reach the same HRF but since the selectivity is less compare to metallic support membranes, the purity decreases. In figure 6 it is possible to see the comparison between metallic and ceramic support in terms of purity obtained.

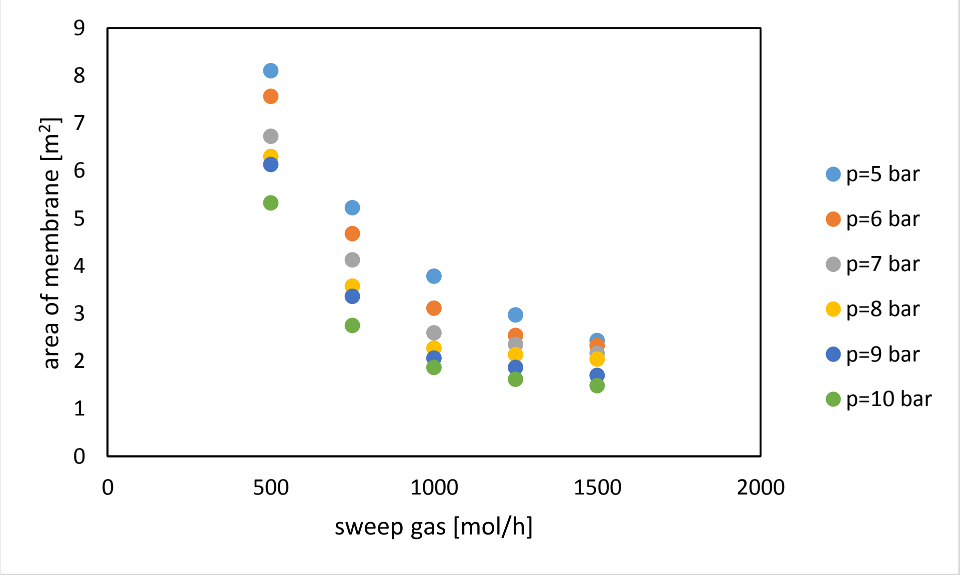

Figure 4. Area of membrane required with sweep gas for Pd-Ag membranes with metallic support

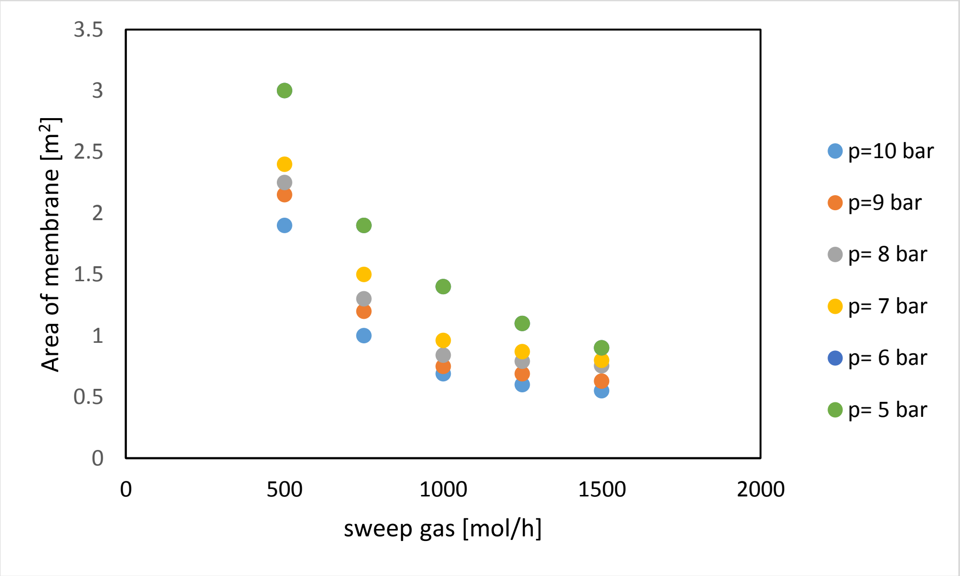

Figure 5. Area of membrane required with sweep gas for Pd-Ag membranes with ceramic support

Metallic membranes seem to be promising for obtaining higher purity even if the area required is higher. Theoretically increasing the sweep gas it is possible to reduce the area of membrane required for reaching the hydrogen recovery but in the simulation since the mass transfer limitation is taken into account, over a certain amount of sweep gas the area of membrane decreases with a smaller contribution. According to figure 4 increasing the sweep gas lead to lower area of membrane required but on the other hand the heat consumption related to the evaporation of the steam is higher.

Moreover the sweep gas decreases the partial pressure of hydrogen in the permeate side but at the same time decreases the partial pressure of methane and it means the impurities will increase. The methane passing through the membrane follows a linear trend with the pressure while the hydrogen permeates with an exponent equal to 0.58 with the pressure. For this reason increasing the sweep gas over a certain value, lead to a lower purity as it is possible to see in figure 5. In order to reach the target of purity required it is better to work at lower pressure in the HyGrid system.

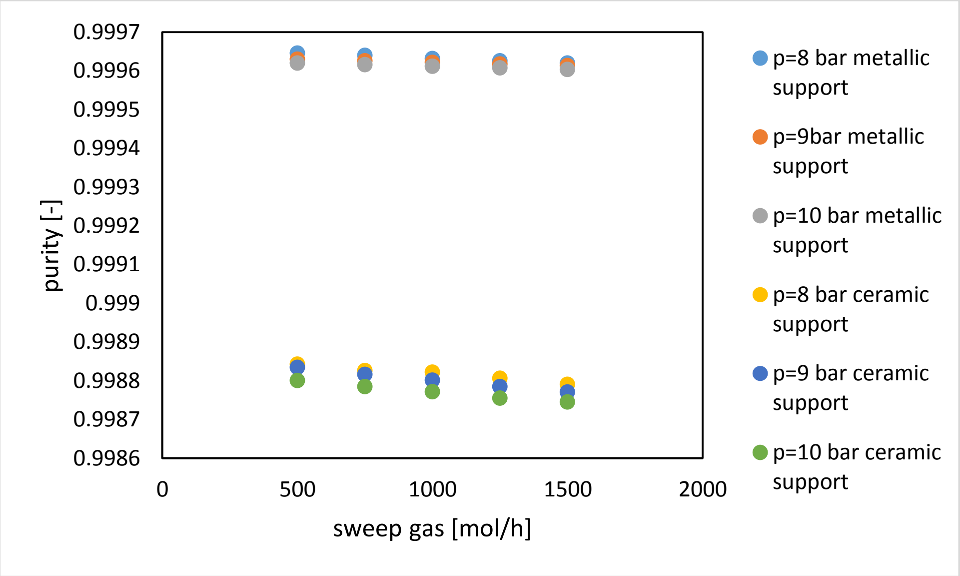

Figure 6. Purity obtained with ceramic support and metallic support at different amount of sweep gas

target of purity in the HyGrid system is equal to 99.97%. Only using a palladium membrane with metallic support, it seems possible to reach the aim otherwise the possible solution is to use two membrane modules or to split the hydrogen recovery into EHP and membrane.

A second possible scenario has been considered in order to evaluate the area of membrane required for recovering 250 kg/day of hydrogen in the system. The pressure has been changed from 5 bar until 10 bar studying the influence of the sweep gas on the area required. The feed has been considered equal to 5800 mol/h of hydrogen and 52200 mol/h of methane. The trend obtained is the same described in the previous case. For membranes with ceramic support at 8 bar an area of membrane equal to 18 m^2 with 5 kmol/h of sweep gas while for metallic support with the same conditions an area of 72.9 m^2 is required as it is possible to see in figure 7 and 8.

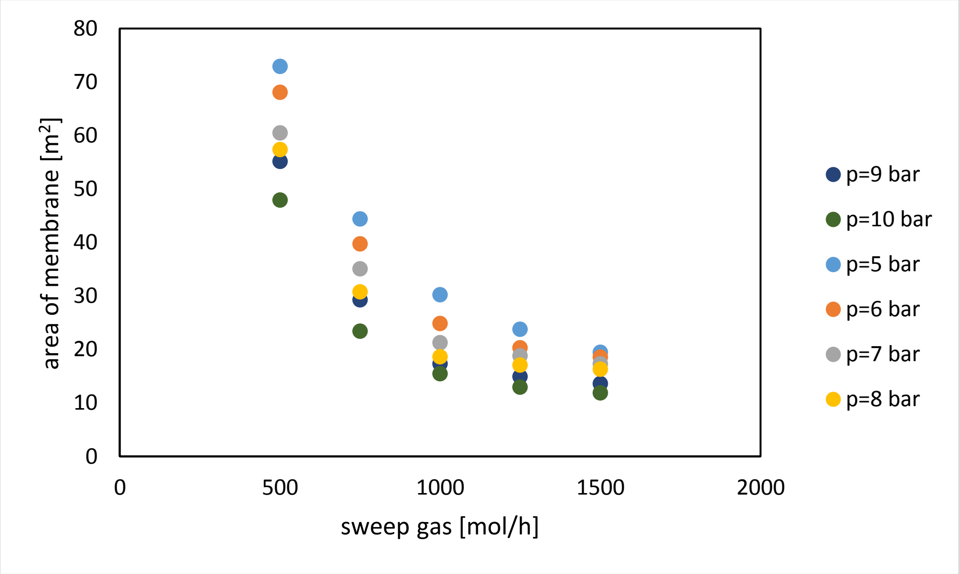

Figure 7. Area of membrane required with sweep gas for Pd-Ag membranes with metallic support for separating 250 kg/day of hydrogen

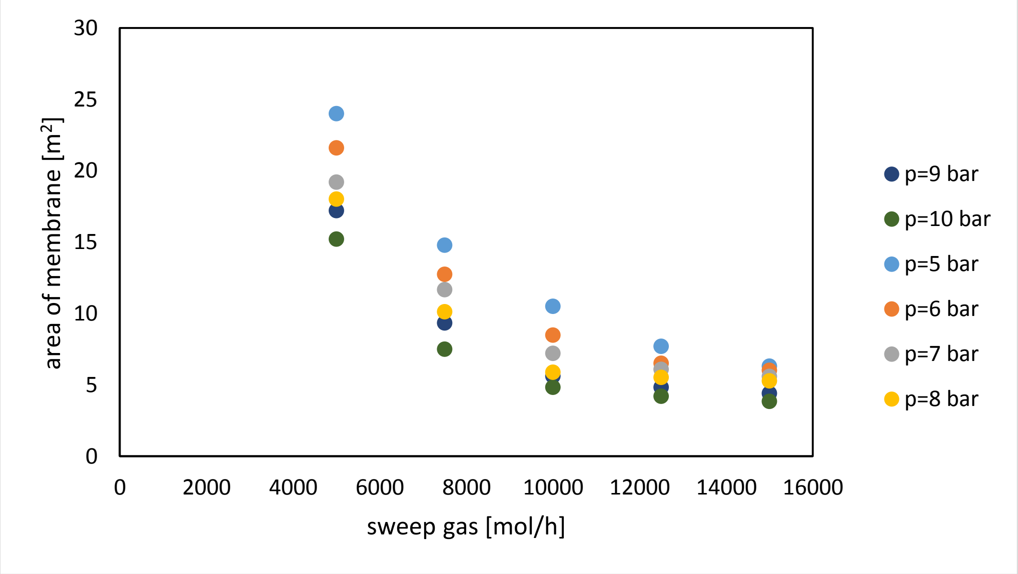

Figure 8. Area of membrane required with sweep gas for Pd-Ag membranes with ceramic support for separating 250 kg/day of hydrogen

6. Conclusions

The Delphi model is able to predict in a proper way the possible experimental results taking into account the mass transfer limitation in the retentate side. From the modelling in order to decrease the area of membrane it is necessary to increase the amount of sweep gas even if it requires higher heat consumption. For a case in which 25 kg/day of hydrogen are separated, it is necessary an area of 8.6 m^2 with a retentate pressure of 8 bar.

If Pd-Ag with metallic support are used in order to reach a HRF of 80% and a purity of 99.96%. While ceramic support asks lower membrane but does not allow to reach the purity request. For this reason in the HyGrid system it is important to consider two membrane modules or to decrease the HFR in the membrane increasing the recovery in the EHP.

The model has been used for describing hydrogen permeation in ultra-thin palladium membrane. A difference between modelling and experiments has been found. It could be explained considering that at some critical thickness the diffusion through the membrane becomes rapid enough that another step might limit the permeation rate. The model need to be developed considering mass transfer limitation in the permeate side.

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