# Simulation Study on the Applicability and Performance of Conventional and Reverse-Selective Membranes for Upgrading of $H_2$/$CO_2$ Mixtures via Gas-Permeation

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Upgrading of a $H_2$/$CO_2$-mixture via gas-permeation process applying conventional glassy and reverse-selective rubbery membranes is systematically evaluated in Aspen Plus. The model of the gas-permeation unit is based on the solution-diffusion mechanism and considers the discretization of the membrane's surface. Calculations are based on representative pure component permeabilities from literature for both membrane types, assuming a feed concentration of 41 vol% $CO_2$ and a product gas specification of 90 vol% and 97 vol% $H_2$ at a $H_2$-recovery of 90 %, respectively.
Results for single stage separation show, that only with glassy membranes product gas specifications could be reached in case of the lower quality requirements. Applying a two stage gas-permeation process enables meeting the higher quality requirements with both membrane types. Different module and compressor configurations have been screened including configurations with and without recirculation. Interesting results are obtained combining both membrane types, resulting in a low total membrane area.

## 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 (Foglia et al., 2010). In order to finally obtain pure hydrogen, $CO_2$ has to be separated from the fermentation gas.
For separation of $CO_2$ from mixtures with $H_2$ or $CH_4$ in technical scale physical and chemical absorption, adsorption and cryogenic processes are used. However, only a few processes are suitable for the removal of $CO_2$ in smaller scale. Pressurized water scrubbing and pressure swing adsorption are used as state-of-the-art processes in biogas-upgrading at small scale.
Besides classical processes for the separation of mixtures of $H_2$/$CO_2$ and $CH_4$/$CO_2$ membrane processes represent interesting alternatives in upgrading low temperature raw gas streams in small scale facilities. Today gas-permeation is already successfully used for upgrading of $CH_4$/$CO_2$ mixtures from anaerobic digestion to feed the obtained bio-methane to the natural gas grid (Miltner et al., 2010). Furthermore, there are first attempts to use gas-permeation for upgrading hydrogen rich gases produced in biomass steam gasification processes (Makaruk et al., 2011).
However, experience and results from $CH_4$/$CO_2$ upgrading cannot be transferred directly to the separation of $H_2$/$CO_2$ mixtures, since here the fast-permeating component is $H_2$ and selectivities for the separation of $H_2$/$CO_2$-mixtures are low. As a result, it is more difficult to achieve high $H_2$-purities.

Furthermore, the stream containing enriched $H_2$ needs to be recompressed for further use in downstream devices. These disadvantages can be circumvented by the application of reverse-selective membranes. In these membranes, $CO_2$ shows a higher permeability than $H_2$, allowing a multistage separation without the needs of recompression of the feed gas.

In this work, upgrading of $H_2$/$CO_2$-mixture via gas-permeation process applying conventional glassy and reverse-selective rubbery membranes is systematically evaluated in Aspen Plus to compare the performance of different process configurations and module arrangements.

## 2. Background

A membrane is a barrier which allows a selective mass transfer between two phases. Figure 1 shows the scheme of a gas-permeation module for the separation of gas mixtures. The gaseous mixture enters the module at the feed side. Due to different permeabilities of the gas components, they are separated in a retentate and permeate stream. Optionally, on the permeate side a sweep gas stream can be foreseen.
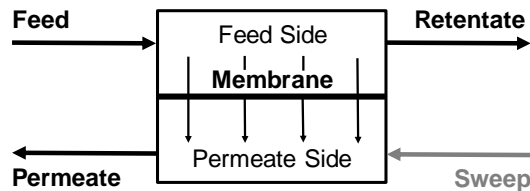


Figure 1: Scheme of gas-permeation unit

Gas transport in non-porous polymeric membranes, as used in gas-permeation, 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 differences in 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 (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 Equation 1:

$$J_i = \frac{P_i \cdot (p_{i0} - p_{il})}{l}$$  (1)

The permeability coefficient $P_i$ is a characteristic parameter available from simple permeation experiments. Furthermore, the ideal selectivity $\alpha_{i,j}$ (Equation 2) is used to describe the separation efficiency of a membrane.

$$\alpha_{i,j} = \frac{P_i}{P_j}$$  (2)

Membranes for $H_2$/$CO_2$-separation might be selective for $H_2$ (conventional/glassy membranes) or $CO_2$ (reverse-selective/rubbery membranes). In glassy polymers $H_2$, the smallest molecule among the components in the raw gas from hydrogen fermentation ($H_2$, $CO_2$, $H_2O$, traces of $H_2S$) shows the highest permeation rate. Due to the outstanding diffusivity of $H_2$ in the membrane materials a satisfying separation of $H_2$ from other components is possible although $H_2$/$CO_2$-selectivities in typical polymer materials are low. Through the application of polymer blends or by chemical cross linking selectivities can be considerably increased up to 50 (Shao et al., 2009; Low et al., 2008). However, increasing selectivity is associated with decreasing membrane permeability. An important disadvantage of use of

glassy polymers is the fact that purified $H_2$ is obtained on the permeate side at low pressure. In case of a multistage separation or for further use of $H_2$, recompression is necessary.

In rubbery polymers $CO_2$ permeates faster than $H_2$ (reverse-selective membranes). Responsible for this "inverse selectivity" is the excellent solubility of $CO_2$ in these membrane materials. This excellent solubility of $CO_2$ compensates the much faster diffusion of $H_2$ in the polymere (solubility selectivity). By applying rubbery membranes higher $H_2$-purities might be achieved with less effort and the product gas leaves the process at high pressure. However, a problem might occur from the unsatisfying separation of non-condensable gases like $N_2$ and $O_2$ which are in consequence enriched in the retentate. Membranes show high permeabilities, but the $CO_2/H_2$-selectivity hardly exceeds 10 (Bondar et al., 2000; Shao et al., 2009).

## 3. Model and settings

The performance of glassy and rubbery membranes for upgrading of $H_2/CO_2$ mixtures via gas-permeation was simulated in Aspen Plus (V7.1, Aspen Technology, Inc., Burlington, USA, 2008). The used model of the gas-permeation unit based on the solution-diffusion mechanism was developed in Aspen Custom Modeller (ACM, V7.1, Aspen Technology, Inc., Burlington, USA, 2009) and considers the discretization of the membrane's surface. Furthermore, the gas-permeation unit implies the simplifications that (1) total pressures in the retentate, permeate and feed are constant, (2) permeability and permeance are independent of pressure and (3) no plastification effects are observed in the membranes.

The model was validated using data from separation of $CH_4/CO_2$-mixtures (Rodrigues et al., 2010). Calculations are based on pure component permeabilities from literature for both membrane types. Membrane and process parameters are given in Tables 1 and 2.

*Table 1: Membrane specification (Hosseini and Chung, 2009, Lin et al., 2005); assumed membrane thickness is 1 µm*

| Membrane | Permeability (kmol m$^{-2}$ h$^{-1}$ bar$^{-1}$) | | Selectivity |
|---|---|---|---|
| | $H_2$ | $CO_2$ | |
| Glassy (conventional) | 0.00761 | 0.000228 | 33.4 |
| Rubbery (reverse-selective) | 0.0019 | 0.0166 | 8.7 |

*Table 2: Specification of feed gas*

| | |
|---|---|
| Temperature (°C) | 30 |
| Pressure (bar) | 1 |
| Total mole flow 30,6 kmol/h | 30.6 |
| Mol fraction $H_2$ (mol/mol) | 0.59 |
| Mol fraction $CO_2$ (mol/mol) | 0.41 |

## 4. Results and discussion

The following section summarizes the simulation results for single- and two-stage separation of a $H_2/CO_2$ mixture with glassy and rubbery membranes via gas-permeation. In case of two-stage separation different module and compressor arrangements have been evaluated. Calculations are performed to obtain $H_2$-purities of 90 vol% and 97 vol% (mole based) at a hydrogen recovery higher than 90%, respectively.

### 4.1 Single stage separation
Figure 2 shows the results for single stage separation. The grey shaded area represents the specifications for the product gas. In case of the glassy membrane at 90 % $H_2$-recovery a $H_2$-purity of 90 % can be reached. However, the higher purity specification cannot be met at this recovery. For glassy membranes, with increasing membrane area, the recovery of $H_2$ is increasing and the $H_2$ purity

is decreasing. With increasing membrane area more $H_2$ is passing the membrane increasing the recovery. This causes an increase of $CO_2$ concentration on the feed/retentate side and thus a higher driving force for the permeation of $CO_2$, reducing the permeate (product) purity.

With rubbery membrane separation results are far off the specifications. For a desired $H_2$-purity of 90 % the maximum recovery is approximately 75 %. In contrast to the glassy membranes, with increasing membrane area, $H_2$-recovery is decreasing, but $H_2$ purity increases. At low membrane areas only $CO_2$ is permeating through the membrane, giving low $H_2$ losses and thus high $H_2$-recoveries. Due to the small membrane area only a small $CO_2$ flux over the membrane is obtained, not considerably reducing the $CO_2$ content on the feed/retentate side, resulting in a low $H_2$-purity.
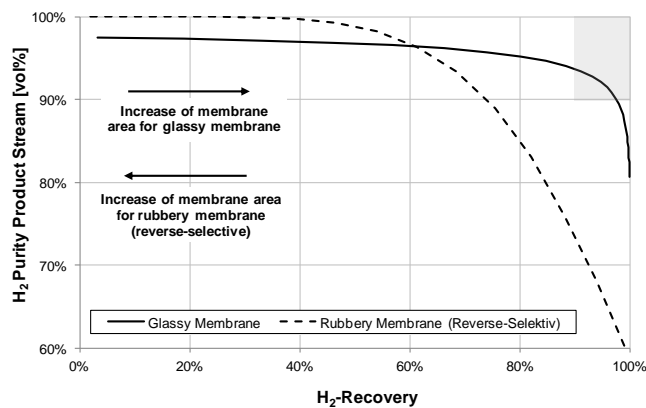


Figure 2: Results of single stage separation (Feed Pressure = 15 bar; Membrane Area = 10 – 170 m²)

### 4.2 Two stage separation

A two stage separation process allows a multitude of module arrangements. Figure 3 shows separation sequences which allow meeting the defined product specifications at a feed/intermediate pressure of 10 bar. Simulation results are presented in Figure 4. Table 3 summarizes optimization results representing the minimum membrane area necessary to reach the product gas specifications.

In module arrangement 1 (glassy membrane without recirculation) the first separation stage is responsible for the reachable overall recovery, which is increasing with increasing membrane area. An increase in the membrane area of the second separation stage increases $H_2$-concentration in the product, but reduces $H_2$-recovery. For small membrane areas in the second separation stage an increase in membrane area of first stage might decrease the purity of obtained $H_2$.

Module arrangement 2 (glassy membranes with recirculation) only gives slightly lower membrane areas, but the obtainable product purity is higher than without recirculation of retentate from the second separation stage. Both arrangements – with and without recirculation of second stage retentate – would be suitable to meet the desired specifications of the product gas.

In contrast, applying a two stage separation with rubbery (reverse-selective) membranes without recirculation the defined product specification cannot be met. Only with recirculation of permeate from the second separation stage (module arrangement 3), $H_2$-purities of 97 % can be reached at $H_2$-recoveries higher than 90 %. The necessary membrane area is slightly smaller than in arrangement 1 or 2, but at much smaller selectivities of the membrane. Furthermore, only one compressor is necessary to operate the two stage separation process and pressure level remains available for the product gas. However, the volume flow to be compressor is higher than in the first separation stage of arrangement 1 and 2.

Module arrangement 4 combines a rubbery polymer (reverse-selective) in the first stage with a glassy polymer (conventional) in the second separation step. As seen in Figure 4 the arrangement scarcely miss the desired product specification, but could be easily reached with an increase of feed pressure.
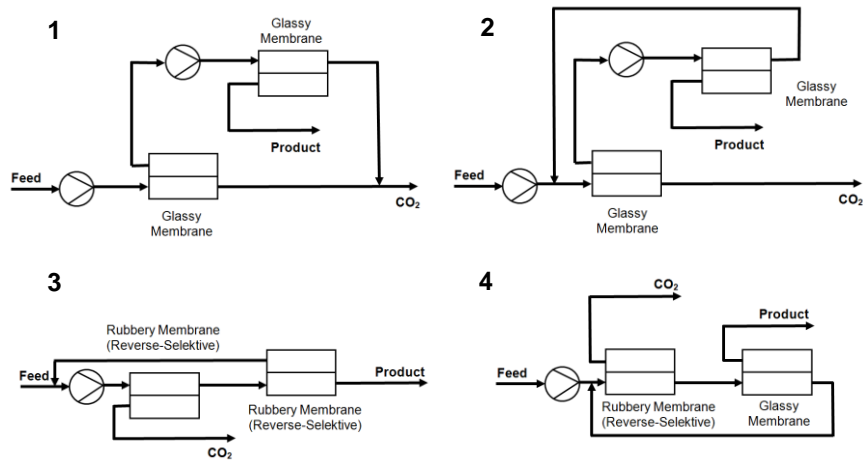
*Figure 3: Module arrangements for two stage separation: 1) glassy polymers without recirculation, 2) glassy polymers with retentate recirculation, 3) rubbery polymers with permeate recirculation, 4) combination of rubbery and glassy polymers with retentate recirculation*

The needed membrane area is considerably lower than with the other module arrangements. Just one compressor is needed to operate the separation process. However, the product gas is finally obtained at the permeate side, needing recompression for further use. Furthermore, it has to be noted that high amounts of gas has to be recirculated.
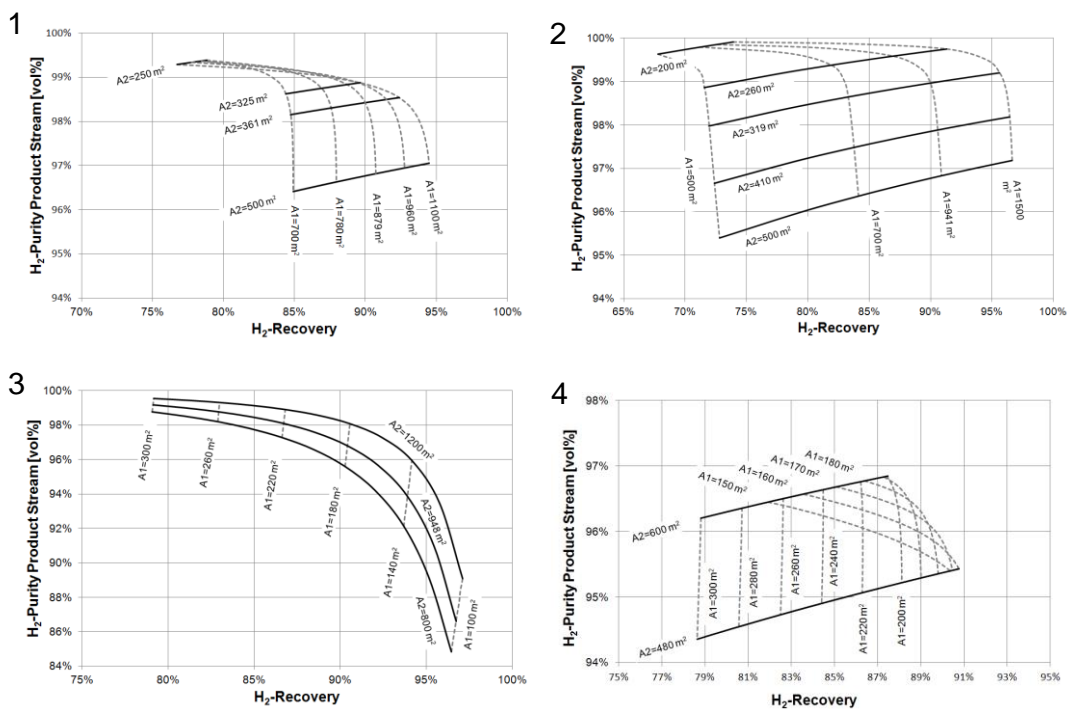


*Figure 4: Results for two stage separation arrangements: 1) glassy polymers without recirculation, 2) glassy polymers with retentate recirculation, 3) rubbery polymers with permeate recirculation, 4) combination of rubbery and glassy polymers with retentate recirculation*

*Table 3: Minimum membrane area (m²) to reach product specification*

|                       | Stage 1 | Stage 2 | Total |
|-----------------------|---------|---------|-------|
| Module arrangement 1  | 941     | 319     | 1260  |
| Module arrangement 2  | 880     | 361     | 1241  |
| Module arrangement 3  | 184     | 947     | 1131  |
| Module arrangement 4  | 164     | 589     | 753   |

## 5. Summary and outlook

In this work, upgrading of $H_2/CO_2$-mixture via gas-permeation process applying conventional glassy and reverse-selective rubbery membranes is systematically evaluated in Aspen Plus to compare the performance of different process configurations and module arrangements.

Results for single stage separation show, that only with glassy membranes product gas specifications could be reached in case of the lower quality requirements (90 vol% $H_2$, 90 % $H_2$-recovery).

Applying a two stage gas-permeation process enables meeting the higher quality requirements with both membrane types. Different module and compressor configurations have been screened. Interesting are the results combining a rubbery (reverse-selective) membrane with a glassy (conventional) membrane, resulting in low membrane areas.

At the moment the application of membranes for $H_2/CO_2$ separation is scarce. Most scientific papers focus on the characterization of membrane materials developed at small scale in laboratory. Given permeabilities and selectivities are obtained at ideal conditions based on permeation experiments with pure gases. Therefore, membrane properties and theoretical considerations presented in this paper should be proven experimentally.

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