MASTER

Fluidized bed membrane reactor model including concentration polarization

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Fluidized bed membrane reactor model including concentration polarization

A.J. Raijmakers

July 2015
Abstract

Extended 1D models for a binary case of H₂/N₂ were made for an empty- and a fluidized bed membrane reactor in which the effect of concentration polarization has been taken into account. This was done by assuming a stagnant film layer around the membrane in which concentration polarization takes place and which behaves as a mass transfer resistance. The models were compared with experiments and with a regular 1D model (which does not take concentration polarization into account). From the experiments a large effect of concentration polarization of around 80% for both an empty reactor and a fluidized bed was observed. From the experiments it also looked like external mass transfer is the rate limiting step.

By comparing the extended 1D model from this work with the regular 1D model a large effect of concentration polarization could be seen. The regular 1D model over predicts a lot while the extended model predicts the experiment within an accuracy of in between 0% and 50%. From the results of the extended 1D model it can also be concluded that external mass transfer is rate limiting.
# Nomenclature

## Greek Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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</thead>
<tbody>
<tr>
<td>δ</td>
<td>Film layer thickness</td>
<td>m</td>
</tr>
<tr>
<td>&lt; ϵ &gt; A</td>
<td>Average particle holdup at cross section</td>
<td>-</td>
</tr>
<tr>
<td>ϵ</td>
<td>Holdup</td>
<td>-</td>
</tr>
<tr>
<td>μ</td>
<td>Viscosity</td>
<td>Pa·s</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
<td>kg/m³</td>
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</table>

## Roman Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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</thead>
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<tr>
<td>α</td>
<td>Polarization</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
<td>m²</td>
</tr>
<tr>
<td>A_c</td>
<td>Area distributor plate per opening</td>
<td>m²</td>
</tr>
<tr>
<td>Ar</td>
<td>Archimedes number = gρₙ(ρₑρₚ)dₚ³/μ²</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>Concentration</td>
<td>mol/m³</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
<td>m²/s</td>
</tr>
<tr>
<td>d</td>
<td>Diameter</td>
<td>m</td>
</tr>
<tr>
<td>d_H</td>
<td>Hydraulic diameter = dₑ - d_m</td>
<td>m</td>
</tr>
<tr>
<td>D_m</td>
<td>Molecular diffusion coefficient</td>
<td>m²/s</td>
</tr>
<tr>
<td>D_r</td>
<td>Radial dispersion coefficient</td>
<td>m²/s</td>
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<tr>
<td>E_a</td>
<td>Activation energy</td>
<td>J/mol</td>
</tr>
<tr>
<td>f</td>
<td>Fraction</td>
<td>-</td>
</tr>
<tr>
<td>G_s</td>
<td>Solid net circulation rate</td>
<td>kg/m²/s</td>
</tr>
<tr>
<td>H</td>
<td>Height of bed</td>
<td>m</td>
</tr>
<tr>
<td>J</td>
<td>Diffusive flux</td>
<td>mol/m²/s</td>
</tr>
<tr>
<td>K</td>
<td>Bubble-emulsion mass transfer coefficient</td>
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<tr>
<td>k_d</td>
<td>External mass transfer coefficient</td>
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<tr>
<td>M</td>
<td>Molecular weight</td>
<td>kg/mol</td>
</tr>
<tr>
<td>N</td>
<td>Diffusive flux + convective flux</td>
<td>mol/m²/s</td>
</tr>
</tbody>
</table>
Nomenclature

\[ n \quad \text{Number} \]
\[ P \quad \text{Pressure} \quad \text{Pa} \]
\[ P_{m} \quad \text{Membrane permeance} \quad \text{mol/msPa}^{0.5} \]
\[ g \quad \text{Gravitational constant}=9.81 \quad \text{m/s}^{2} \]
\[ N_{or} \quad \text{Number of orifices in distributor plate} \quad \text{-} \]
\[ R \quad \text{Gas constant}=8.314 \quad \text{J/molK} \]
\[ r \quad \text{Radial position} \quad \text{m} \]
\[ Re \quad \text{Reynolds number}=\rho ud/\mu \quad \text{-} \]
\[ S \quad \text{Surface renewal rate} \quad \text{s}^{-1} \]
\[ Sh \quad \text{Sherwood number}=k_{d}d_{H}/D \quad \text{-} \]
\[ T \quad \text{Temperature} \quad \text{K} \]
\[ t_{c} \quad \text{Contact time} \quad \text{s} \]
\[ t_{m} \quad \text{Membrane thickness} \quad \text{m} \]
\[ u \quad \text{Superficial gas velocity} \quad \text{m/s} \]
\[ V \quad \text{Volume} \quad \text{m}^{3} \]
\[ V_{t} \quad \text{Diffusion volume} \quad \text{m}^{3}/\text{mol} \]
\[ v_{x} \quad \text{Cross sectional average particle velocity} \quad \text{m/s} \]
\[ X \quad \text{Mol fraction} \quad \text{-} \]
\[ z \quad \text{Axial position} \quad \text{m} \]

Subscripts

\[ 0 \quad \text{Inlet} \]
\[ avg \quad \text{Average} \]
\[ b \quad \text{Bubble} \]
\[ b_{r} \quad \text{Bubble rise} \]
\[ bulk \quad \text{Bulk} \]
\[ c \quad \text{Cloud} \]
\[ c \quad \text{Critical} \]
\[ dpc \quad \text{Dilute pneumatic conveying} \]
\[ e \quad \text{Emulsion} \]
\[ g \quad \text{Gas} \]
\[ H_{2} \quad \text{Hydrogen} \]
\[ m \quad \text{Membrane} \]
\[ mf \quad \text{Minimum fluidization} \]
\[ ms \quad \text{Minimum slugging} \]
Nomenclature

\begin{itemize}
  \item \textit{p} \quad \text{Particles}
  \item \textit{per} \quad \text{Permeate}
  \item \textit{r} \quad \text{Reactor}
  \item \textit{sc} \quad \text{Fast fluidization}
  \item \textit{tot} \quad \text{Total}
\end{itemize}

**Superscripts**

<table>
<thead>
<tr>
<th>Superscript</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Inlet</td>
</tr>
<tr>
<td>\textit{avg}</td>
<td>Average</td>
</tr>
<tr>
<td>\textit{max}</td>
<td>Maximum</td>
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<tr>
<td>\textit{n}</td>
<td>Coefficient between 0.5-1.0 in Sievert’s law</td>
</tr>
</tbody>
</table>
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Chapter 1

Introduction

With the worldwide oil supply becoming more scarce, hydrogen is becoming an increasingly more important substance. For example, it is required in the refining of petroleum as well as other chemical processes such as hydrogenation of fats and oils and the production of methanol and ammonia. Hydrogen is also required for proton exchange membrane (PEM) fuel cells. These fuel cells convert chemical energy from hydrogen to electricity. A fuel cell is different from a battery in that it requires a continuous source of hydrogen to generate electricity. Fuel cells can be used for small scale electricity generation and for example to power electric motors in vehicles. Currently there is a lot of research concerning the small scale production of ultra pure hydrogen for the use in fuel cells.

Currently the dominating technology to produce hydrogen is via the steam methane reforming (SMR) reaction followed by the water gas shift (WGS) reaction. The SMR reaction is an endothermic reaction ($\Delta H_r = 206 \text{ kJ/mol}$) which takes place at high temperatures of around $700-1100^\circ \text{C}$ and in the presence of a nickel catalyst. In the second stage additional hydrogen is produced by the slightly exothermic WGS reaction ($\Delta H_r = -41 \text{ kJ/mol}$). This reaction requires temperatures of around $360^\circ \text{C}$.

Steam methane reforming reaction (SMR):

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (1.1)$$

Water gas shift reaction (WGS):

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (1.2)$$

SMR has an efficiency of approximately 65-75% because the SMR and WGS reactions are limited by their thermodynamic equilibrium. The equilibrium can be shifted in favorable direction by using a membrane reactor (in either a packed bed or a fluidized bed) which selectively extracts hydrogen from the reaction mixture. This results in ultrapure hydrogen ($<10 \text{ ppm CO}$) with a high conversion and lower energy costs [19]. The hydrogen is immediately usable in for example a PEM fuel cell. Another advantage of integrating membranes inside the reactor is that they become inherently smaller because of process integration.

A fluidized bed reactor is an excellent choice to use as a membrane reactor because of its good heat- and mass transfer characteristics and ease of inserting membranes. The quality of the membranes is increasing a lot over the last years resulting in very high flux membranes. However, this high flux induces concentration polarization [3]. At higher fluxes a concentration gradient arises near the membrane wall. The mass transfer from the bulk to the membrane starts playing a more important role. The concentration at the membrane surface becomes lower than in the bulk. Because the concentration gradient over the membrane becomes smaller, the flux is negatively influenced by concentration polarization. This research focuses on making a model for both an empty- and a fluidized bed membrane reactor (FBMR) incorporating the effect of concentration polarization.
1.1 Literature review

Much research has been done dedicated to the effect of concentration polarization near a membrane wall. Hara et al [11] did research concerning the decline of hydrogen permeation in a packed bed membrane reactor. In his research mixtures of H₂-Ar and H₂-CO were used. It was found that the reduction in hydrogen permeation compared to the model where due to CO poisoning and concentration polarization. It was concluded that in order to make the model fit, concentration polarization needs to be taken into account.

Mori et al [16] investigated the influence of concentration polarization on the hydrogen production in the SMR reforming reaction in a packed bed membrane reactor with a highly permeable membrane. He did experiments and compared them with a simple model that did not take into account the effect of concentration polarization. With increasing reactor pressure he found that the experimental methane conversion became lower than the simulated results. This implies concentration polarization. The presence of concentration polarization was confirmed with experiments with a binary mixture of hydrogen and nitrogen. Mori then successfully tried to reduce this effect by making the reactor more narrow and by adding baffles.

It is clear at this point that concentration polarization should be taken into account when making a membrane reactor model. Ludtke et al [15] made a simple two resistance model (resistance in a boundary layer and over the membrane) for the case of a gas-vapor mixture in an empty membrane reactor. He compared the results of his model with his experiments. He found that his model predicted the permeation well and that the effect of concentration polarization leads to a significant decrease in separation properties. The polarization can be decreased by increasing the Reynolds number, using thicker membranes or by lowering the feed pressure.

Caravella et al [3] made a more complex model predicting the permeance of hydrogen in a hydrogen nitrogen mixture including the effect of concentration polarization in an empty tube annulus. He compared his simulations with the permeance when no concentration polarization was taken into account. He made so called "polarization maps" by plotting variables like: mole fraction, pressure difference and temperature, against the concentration polarization coefficient. In his research he found that the effect of polarization is relevant not only for the very thin membranes (1-5 μm) but also for the thicker ones (100 μm). He also compared his findings with experimental data found in literature and found a good agreement.

A CFD study of gas mixtures in an empty reactor with (i) the membrane at the wall and (ii) an annular cylinder with the membrane as the inner tube was done by Nekhamkina et al [18]. A model was made predicting the membrane permeance well. A parameter Γ was identified which represents the ratio of diffusive to permeating flux. When Γ>6 the effect of concentration polarization is negligible.

1.2 Research goal

From previous research it can clearly be seen that concentration polarization has a significant influence on the membrane permeation. Multiple models have been made to predict this effect successfully in both empty- and packed bed membrane reactors. However, there is no research done concerning the effect of concentration polarization in a fluidized bed membrane reactor. This work focusses on making a model of a fluidized bed membrane reactor Incorporating polarization. A model will also be made for an empty membrane reactor to see the difference between the two. Finally experiments will be done in order to validate the models.
Chapter 2

Theory

In this project a model will be made for both an empty reactor and a fluidized bed reactor which include
the effect of concentration polarization. A fluidized bed is a complex system. In this chapter the theory
behind a fluidized bed is given.

2.1 Bubble- and Emulsion phase

In this project the Kunii and Levenspiel bubbling bed model \[14\] will be used to describe the fluidized
bed. The Kunii and Levenspiel model is valid for fluidized beds without internals (membranes). However,
this model will still be used as a starting point. According the Kunii and Levenspiel model the bed is
divided into different phases: the bubble-, the cloud-, the emulsion phase and the wake of the bubble.
The bubble phase behaves as a PFR. The cloud phase behaves as a CSTR. The emulsion phase can be
modelled as a single- or multiple CSTR's. The more CSTR's the closer the emulsion phase comes to a
PFR. Each bubble contains a cloud that contains a significant amount of solids. In this project only the
bubble and emulsion phase will be taken into account. The bubbles contain very small amounts of solids.
It will be assumed that no solids are present in the bubbles. Although the bubbles are not spherical,
they are modelled as if they are. A schematic picture of a bubble is shown in figure 2.1.

![Figure 2.1: Schematic picture of a bubble in a fluidized bed](image)

Because the bubbles pull the wake of solids up with them, the net particle flow in the emulsion phase
must be downward. The gas within a bubble stays for the most part in the bubble. It only penetrates
a short distance into the surrounding emulsion phase, the cloud. The model assumptions by Kunii and
Levenspiel are presented below:

1. The bubbles are all the same size.
2. The solids in the emulsion phase flow smoothly downward, essentially in plug flow.
3. The emulsion phase exists at minimum fluidization conditions \(u_{mf}\). The gas occupies the same
   void fraction in this phase as it had in the entire bed at the minimum fluidization point \(\varepsilon_{mf}\).
4. In the wakes, the concentration of solids is equal to the concentration of solids in the emulsion phase, and therefore the gaseous void fraction in the wake is also the same as in the emulsion phase. Because the emulsion phase is at the minimum fluidization condition, the void fraction in the wake is equal to $\varepsilon_{mf}$.

2.2 Fluidization regimes

Fluidization occurs when the drag force of the gas flowing through the bed is equal or bigger than the gravitational force on the particles. If the gas flow is increased, the bed starts to expand more. At a certain point, bubbles start to form. The fluidized bed is then comparable to a bubbling liquid. If the gas flow is increased even more, the bubbles become bigger until the bubbles start to slug. After the slugging regime, the bed comes into the turbulent regime. In the figure below 2.2 the regimes are shown.

![Fluidization regimes](image)

Figure 2.2: Fluidization regimes.

The fluidization behavior is also dependent on the type of particles in the bed. One way to classify the particles is with the Geldart classification [14]. Geldart classified the particles into four clearly recognizable kinds. These classification are as follows (from smallest to largest):

**Group C:** These are extremely fine and cohesive particles. The size is between 20 and 30 $\mu$m. The particles fluidize under very difficult to achieve conditions.

**Group A:** The particles in this group are in between 20 and 100 $\mu$m and the density is typically lower than 1.4 g/cm$^3$. Before beds with this type of particles start to fluidize, they will expand by a factor of 2 to 3. Most powder type beds are in this group.

**Group B:** The particle size is between 40 and 500 $\mu$m and the particle density is between 1 and 4 g/cm$^3$. Bubbles typically form immediately when the bed starts to fluidize. The particles are sand like. This is the preferred regime for this project.

**Group D:** The particles in this regime are large (above 600 $\mu$m) and typically have a high density. Fluidization requires a very high fluid velocity. This kind of particles are usually processed in shallow beds or in spouting mode.

In figure 2.3 the Geldart classification are shown in a graph.
A more complete diagram of the fluidization behavior can be obtained with the dimensionless parameters $u^*(=\text{Re}/\text{Ar}^{1/3})$ and $d_p^*(=\text{Ar}^{1/3})$ as suggested by Grace [10]. Where the Reynolds number is:

$$\text{Re} = \frac{\rho_p u d_p}{\mu_g}$$  \hspace{1cm} (2.1)

And the Archimedes number is:

$$Ar = \frac{9 \rho_g (\rho_p - \rho_g)}{\rho_g^2 \mu_g^2} d_p^3$$ \hspace{1cm} (2.2)

The boundary between particles of type A-B and B-D can be calculated via the Archimedes number $2.2$.

**AB Boundary:** The AB boundary separates the systems where interparticle forces are important (A) between systems where interparticle forces do not play a role (B). A correlation has been made by Grace [10] from data of various gases at different temperatures and pressures:

$$Ar_{AB} = 1.0 \times 10^6 \left[ \frac{(\rho_p - \rho_g)}{\rho_g} \right]^{-1.275}$$ \hspace{1cm} (2.3)

**BD Boundary:** This boundary separates systems where the flow through the particles is dominated by viscous forces from those where inertial effects are dominant. According to Grace [10] this boundary is at:

$$Ar_{BD} = 1.45 \times 10^6$$ \hspace{1cm} (2.4)

In figure 2.4 the diagram can be seen where $u^*$ is plotted against $d_p^*$. 

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Fluidized bed membrane reactor model including concentration polarization
2.2.1 Minimum fluidization velocity

For particles in the Geldart classifications B and D, bubbling starts as soon as \( u \) exceeds \( u_{mf} \). So the minimum bubbling velocity \( u_{mb} \) is equal to \( u_{mf} \). For powders of type A however, there is a considerable gap between these two (as can be seen in figure 2.4). As mentioned in the previous paragraph, the bed will first expand (sometimes by a factor of 2 to 3) before it starts to bubble. In this project the focus will be on Geldart type B particles. The minimum fluidization velocity can be determined with the Reynolds correlation derived by Grace [12] from the Wen and Yu correlation [22]:

\[
\text{Re}_{mf} = \sqrt{27.2^2 + 0.0408Ar - 27.2}
\]  

(2.5)

2.2.2 Minimum slugging velocity

Slugging starts to occur when the bubble diameter is 50 % of the total reactor diameter. For the fluidized bed to be in the slugging regime, two conditions need to be satisfied:

- The ratio of the expanded bed height to the column diameter (\( H/d_r \)) must be large enough, so the bubbles have time to coalesce into bubbles that are considered to be slugs. For this to happen it requires that:

\[
H/d_r \geq 3.5 \left( 1 - N_{or}^{-0.5} \right) [6]
\]  

(2.6)

In which \( N_{or} \) is the number of orifices in the distributor plate.

- The maximum bubble diameter must be of the same order as \( d_r \) or greater.
If these conditions are met, the minimum slugging velocity according to Steward and Davidson is [20]:

\[ u_{ms} = u_{mf} + 0.711\sqrt{gd_r} \tag{2.7} \]

### 2.2.3 Critical fluidization velocity

If the superficial gas velocity \( u \) is increased even more, turbulent fluidization occurs. Instead of continuing to increase, the bubbles or slugs begin to break down. Usually the critical velocity \( (u_c) \) at which this occurs is determined experimentally. There are still correlations describing the critical velocity. They are usually of the form:

\[ Re_c = \frac{\rho g d_p u_c}{\mu_g} = BA r^\eta \tag{2.8} \]

Values of \( B = 0.565 \) and \( \eta = 0.461 \) are recommended based on a wide range of data [4]. However this kind of correlation does not take the ratio \( H/d_r \) into account. A correlation made by Ellis [8] does take this into account and is valid for columns up to 1.6 m. This correlation can be seen below:

\[ Re_c = \frac{(H/d_r)^{0.43}Ar^{0.74}}{\sqrt{4.2(H/d_r)^{0.86} + 3.1Ar^{0.33}}} \tag{2.9} \]

### 2.2.4 Transition to fast fluidization

With a further increase of the superficial velocity the "bed" ceases to exist. There is so much turbulence that there is no distinct upper bed surface. Massive recycling of solids is needed to keep the particles in suspension. Particles are pushed upward in the core of the column and then descend on the edges of the reactor. The transition to fast fluidization can be determined with equation 2.10, according to Bi [2]:

\[ Re_{sc} = 1.53\sqrt{Ar} \tag{2.10} \]

### 2.2.5 Transition to dilute pneumatic conveying

The last stage of fluidization (at a very high gas velocity) is dilute pneumatic conveying. At this point the stage of fast fluidization is exceeded. The transition from fast fluidization to dilute pneumatic conveying has been correlated by Kim [13]:

\[ \frac{u_{dpc}}{\langle \varepsilon \rangle_A v_s} = 1160 \left( \frac{G_s}{\rho_p (1 - \langle \varepsilon \rangle_A v_s)} \right)^{0.59} Ar^{-0.20} \tag{2.11} \]

Since the average voidage can change over the height of the reactor, the transition velocity may also change over the length of the reactor.

### 2.3 Bubbling fluidization

In this project the focus will be on the bubbling regime. The experiments are being done in this regime. The bubbling regime ranges from the minimum fluidization velocity \( (u_{mf}) \) till the minimum slugging velocity \( (u_{ms}) \).

There are a number of correlations for predicting the bubble diameter as a function of the height in the bed. The correlation made by Darton [6] usually works well for cylindrical columns without internals:

\[ d_b = \frac{0.54(u - u_{mf})^{0.4}(z + 4.0\sqrt{\varepsilon_c})^{0.8}}{\rho^{0.2}} \tag{2.12} \]

Here \( A_c \) is the area of distributor plate per opening in the distributor. However, in this project there are internals inside the reactor. The membrane influences the bubble behaviour. In this project, the correlation for the bubble diameter determined by Mori and Wen will be used [17]:

\[ d_b = d_b^{\text{max}} - \left( d_b^{\text{max}} - d_b^0 \right) \exp \left( -0.3z \right) d_r \tag{2.13} \]
The average bubble diameter will be determined with the following correlation which is derived from equation 2.13:

\[
d_{b}^{avg} = d_{b}^{max} - (d_{b}^{max} - d_{0}^{b}) \exp \left( -\frac{0.15z}{d_{r}} \right)
\] (2.14)

The initial bubble diameter for a porous plate distributor has been determined by Kunii and Levenspiel [14]. The correlation can be seen in equation 2.15:

\[
d_{0}^{b} = 0.376(u_{0} - u_{mf})^{2}
\] (2.15)

Finally the maximum bubble diameter, following from the correlation by Kunii and Levenspiel, can be calculated with the following equation:

\[
d_{b}^{max} = \min \left\{ d_{r}, 0.65 \left( \frac{\pi}{4} d_{r}^{2} (u_{0} - u_{mf}) \right)^{0.4} \right\}
\] (2.16)

The total superficial velocity in a fluidized bed reactor is the sum of the minimum fluidization velocity, which is present in the emulsion phase and the superficial bubble velocity. The superficial bubble velocity is the bubble fraction multiplied by the bubble rise velocity. The bubble rise velocity is:

\[
u_{b,r} = u_{0} - u_{mf} + 0.711 \sqrt{g d_{b}}
\] (2.17)

So the equation for the total superficial velocity is:

\[
u_{tot} = u_{mf} + f_{b} u_{b,r}
\] (2.18)
2.4 Bubble to emulsion mass transfer

It will be assumed that the bubbles in the fluidized bed behave as a PFR. In this project the cloudphase and the wake of the bubbles will not be taken into account. The mass transfer coefficient between the bubble and the emulsion phase consists of the mass transfer coefficients between the bubble and the cloud:

\[ K_{bc} = 4.5 \left( \frac{u_m f}{d_{b,avg}} \right) + 5.85 \left( \frac{\sqrt{D_g^{1/4}}}{d_{b,avg}^{3/4}} \right) \]  

(2.19)

And between the cloud and the emulsion:

\[ K_{ce} = 6.77 \left( \frac{\varepsilon_m f D_{ub,avg}}{d_{b,avg}^3} \right)^{1/2} \]  

(2.20)

And thus the total mass transfer resistance between the bubble and the emulsion phase is:

\[ \frac{1}{K_{be}} = \frac{1}{K_{bc}} + \frac{1}{K_{ce}} \]  

(2.21)

These mass transfer coefficients were determined by Davidson and Harrison [7]. The unit of the mass transfer coefficients is s$^{-1}$. The mass transfer coefficient has to be multiplied by the concentration difference between the bubble and the emulsion phase and by the bubble volume. So for the total mass transfer between the bubble and the emulsion phase, the following equation is obtained:

\[ K_{be} V_b (C_b - C_e) \text{[mol/s]} \]  

(2.22)

2.5 Bulk to wall mass transfer

There are several models describing the mass transfer from the bulk of a fluid to the membrane wall. Examples of some of these models are the film layer model, the penetration model and the surface renewal model.

2.5.1 Film layer model

The simplest of these models is the film layer model. In this model it is assumed that the mass transfer from the bulk to the membrane wall occurs entirely in a thin stagnant film of thickness $\delta$ around the membrane. In other words, concentration polarization occurs only in a stagnant film layer around the membrane. A picture of this model can be seen in figure 2.5. Furthermore it is assumed that:

- The flux is independent of the radial distance from the membrane.
- There is steady state.
- The concentration in the bulk in the radial direction is constant.
- There is no axial convection in the film layer.
- There is no axial dispersion, only radial dispersion.
From Fick’s law it follows that:

\[ N_{H_2} = J_{H_2} = D \frac{dC_{H_2}}{dr} \]  

(2.23)

Solving gives:

\[ N_{H_2} = \frac{D}{\delta} (C_b - C_m) \]  

(2.24)

So in this case the mass transfer coefficient from the bulk to the membrane wall becomes:

\[ k_d = \frac{D}{\delta} \]  

(2.25)

The assumptions that are made here are physically not very accurate. However they are widely used nonetheless. Because of the induced flux of the membrane, a radial convective flow is expected. When the film theory takes into account this radial convection the following equation is obtained:

\[ N_{H_2} = \frac{J_{H_2}}{1 - X_{H_2}} = \frac{D}{1 - X_{H_2}} \frac{dC_{H_2}}{dr} \]  

(2.26)

Solving gives:

\[ N_{H_2} = \frac{k_d}{1 - X_{H_2}} (C_b - C_m) \]  

(2.27)

The mass transfer coefficient to the membrane wall \( (k_d) \) can be determined via a Sherwood correlation. The definition of the Sherwood number is:

\[ Sh = \frac{k_d d_H}{D} \]  

(2.28)

Combining equation 2.26 and 2.29 gives the following expression for the thickness of the film layer:

\[ \delta = \frac{d_H}{Sh} \]  

(2.29)

A Sherwood correlation from the bulk to the membrane wall in a fluidized bed is not available. In this project the film layer theory will be used to model the mass transfer from the bulk to the membrane wall for both the empty- and the fluidized bed reactor models.

In a fluidized bed membrane reactor, a densified zone will form around the membrane where the particle density \( (\epsilon_s) \) is higher than in the bulk of the reactor [3]. This is caused by the high suction of the membrane. In the densified zone the mixing is worse than in the bulk because the particles are more stagnant. It is expected that there is no concentration gradient in the radial direction in the bulk...
because of the good mixing. There is only concentration polarization in the densified zone around the membrane. However, this needs to be validated.

Important parameters in the mass transfer from the bulk to the membrane wall are the molecular diffusion \(D_m\) and the radial dispersion coefficient \(D_r\) in a fluidized bed. A well known correlation for the molecular diffusion coefficient of a binary gas mixture is the Fuller equation [9]:

\[
D_m = 0.001 \frac{T^{1.75} \sqrt{M_g}}{P (V_A^{1/3} + V_B^{1/3})} \tag{2.30}
\]

The molecular weight of the gasphase is represented by \(M_g\). The parameters \(V_A\) and \(V_B\) are the diffusion volumes of component A and B. For hydrogen \(V_a = 7.07\ [m^3\ mol^{-1}]\) and for nitrogen \(V_b = 17.9\ [m^3\ mol^{-1}]\). In an empty reactor the radial diffusion coefficient is equal to the molecular diffusion coefficient. In a fluidized bed the gas disperses through the bed because of the particles. For this case a dispersion coefficient needs to be used. Unfortunately no correlation for the radial gas dispersion in a fluidized bed is available. In this project the dispersion coefficient of Tsotsas and Schlunder [21] for a packed bed will be used:

\[
D_r = \left(1 - \sqrt{1 - \epsilon_{mf}}\right)D_m + \frac{u_0 d_p}{8} \tag{2.31}
\]

The dispersion is a packed bed is lower than in a fluidized bed. This needs to be taken into account while interpreting the results of the model. The model could under predict the experiments for this reason.

2.5.2 Penetration model and surface renewal model

There are also other models about the mass transfer from the bulk to the membrane wall. In Higby’s penetration model it is assumed that pockets of fluid travel from the bulk to the membrane wall where they stay for a period of time \(t_c\). After that time the pockets are replaced with new pockets of fluid. During the time \(t_c\) there is mass transfer between the pockets and the membrane wall. For this model the mass transfer coefficient becomes:

\[
k_d = 2 \sqrt{\frac{D}{\pi t_c}} \tag{2.32}
\]

In the surface renewal model it is taken into account that fluid pockets that are longer at the surface are more likely to be replaced then pockets that are at the surface for a short time. The mass transfer coefficient becomes:

\[
k_d = \sqrt{D s} \tag{2.33}
\]

In which \(s\) is the rate of surface renewal \((1/s)\). It is the fraction of the membrane surface area that is replaced with new fluid pockets in per unit of time. It is very hard to determine \(s\).

2.6 Membrane permeation

The membrane consists of a ceramic support layer on which a thin palladium-silver layer is present which only lets hydrogen through. The membrane only works at temperatures higher than 300 °C. The mass transfer of hydrogen through the membrane is described as a solution diffusion mechanism. The hydrogen molecules interact with the palladium surface. The molecules dissociate and the separate hydrogen atoms diffuse through the membrane and recombine at the other side of the membrane. The diffusion through the membrane is induced by the gradient between the concentration at the membrane wall and the concentration in the permeate side. It will be assumed that there is no concentration gradient in the ceramic support layer. A schematic picture of the situation is shown in figure 2.6.
The membrane flux is described by Sievert's law:

\[ J_{H_2} = \frac{P_m}{t_m} \sqrt{RT} \left( C_{in}^m - C_{per}^m \right) \text{[mol/m}^2\text{s]} \]  

(2.34)

In which \( P_m \) is the membrane permeance and \( t_m \) is the membrane thickness. The parameter \( n \) depends on whether the mass transfer is limited by the solution of the hydrogen to the palladium surface \((n=1)\) or by the diffusion of hydrogen through the membrane \((n=0.5)\). In the work of K.T. Coenen [4] it is determined that for the membrane used in this project the atomic diffusion through the membrane is rate limiting and thus \( n=0.5 \). The equation for the permeance \((P_m)\) is:

\[ P_m = P_{m,0} \exp \left( -\frac{E_a}{RT} \right) \]  

(2.35)

The parameters \( P_{m,0} \) and \( E_a \) will be determined experimentally. Equation 2.28 can be written as follows:

\[ \ln \left( P_m \right) = \ln \left( P_{m,0} \right) - \frac{E_a}{RT} \]  

(2.36)

The flux at different temperatures needs to be determined. With equation 2.27 the permeance \((P_m)\) can then be determined. By determining the permeance at different temperatures a straight line will form with an intersect of \( P_{m,0} \) and a slope of \( E_a \). This is shown in figure 2.7.

Figure 2.7: Plot of \( \ln(P_m) \) vs \( 1/RT \). The intercept at \( T = \) infinite is \( P_{m,0} \) and the slope of the graph is \( E_a \).
2.7 Model equations

A model will be made for both an empty reactor and a fluidized bed reactor both with a membrane tube in the center of the reactor. Since this project is mainly about incorporating mass transfer from the bulk to the membrane wall in the model, reactions are not taken into account. Only a binary mixture of nitrogen and hydrogen will be looked at to see if the concentration polarization can be predicted well. The model is an extended 1D model in which the membrane concentration is predicted by assuming a film layer $\delta$ around the membrane in which concentration polarization occurs. The film layer has an external mass transfer coefficient $k_d$. The model will be called: 1D/$k_d$ model.

2.7.1 Empty membrane reactor

For the empty reactor model two phases are considered the bulk phase and the film layer. The film layer model is applied. The bulk phase behaves as a PFR and the film layer is a stagnant layer in which only diffusion takes place. The reactor is divided into multiple CSTR’s to simulate PFR behavior.

Bulk phase

In the bulk phase the hydrogen in transported to the film layer.

$$A_r \frac{d(nC_{bulk})}{dz} = A_r u \frac{dC_{bulk}}{dz} + A_r C_{bulk} \frac{du}{dz} = -n_mC_d\pi d_m \frac{(C_{bulk} - C_m)}{1 - X_{bulk}}$$  \hspace{1cm} (2.37)

From this equation it follows that:

$$\frac{dC_{bulk}}{dz} = -\frac{1}{A_r u} \left[ A_r C_{bulk} \frac{du}{dz} + n_mC_d\pi d_m \frac{(C_{bulk} - C_m)}{1 - X_{bulk}} \right]$$  \hspace{1cm} (2.38)

The equation is solved by discretizing:

$$C_{bulk,n} = C_{bulk,n-1} + \frac{dC_{bulk}}{dz} \bigg|_{n-1} \Delta z$$  \hspace{1cm} (2.39)

The total superficial velocity in CSTR $n$ is calculated as follows:

$$u_n = u_{n-1} - \frac{\text{flux} \times A_m}{A_r C_{tot}}$$  \hspace{1cm} (2.40)

Film layer

The flux coming into the film layer is equal to the flux going out through the membrane:

$$J_{H_2} = \frac{P_m}{t_m} \sqrt{RT} \left( \sqrt{C_m} - \sqrt{C_{per}} \right) = k_d \frac{(C_{bulk} - C_m)}{1 - X_{bulk}}$$  \hspace{1cm} (2.41)

The membrane permeance $P_m$ is calculated with equation 2.35 in which $E_a$ and $P_{m,0}$ are determined experimentally.

2.7.2 Fluidized bed membrane reactor

In the fluidized bed membrane reactor (FBMR) there are 3 phases: the bubble phase, the emulsion phase and the film layer. The bubble and emulsion phase behave as PFR’s and the film layer is stagnant. From the bubble phase there is only mass transfer to the emulsion phase, not directly to the membrane. From the emulsion phase the hydrogen transfers to the film layer and from there it fluxes through the membrane. The reactor will be divided into multiple CSTR’s. In figure 2.8 a schematic of the FBMR model is shown.
**Figure 2.8:** Schematic for fluidized bed membrane reactor model.

**Bubble phase**

There is only mass transfer between the bubbles and the emulsion phase. There is no direct mass transfer from the bubble to the membrane.

\[
\frac{d(u_{b,r} f_b C_b)}{dz} = u_{b,r} f_b \frac{dC_b}{dz} + f_b C_b \frac{d u_{b,r}}{dz} + u_{b,r} C_b \frac{df_b}{dz} = -K_{be} f_b (C_b - C_e) \tag{2.42}
\]

The equation is solved by discretizing:

\[
C_{b,n} = C_{b,n-1} + \left. \frac{dC_b}{dz} \right|_{n-1} \Delta z \tag{2.43}
\]

With:

\[
\frac{dC_b}{dz} = -\frac{1}{f_b u_{b,r}} \left[ u_{b,r} C_b \frac{df_b}{dz} + f_b C_b \frac{d u_{b,r}}{dz} + K_{be} f_b (C_b - C_e) \right] \tag{2.44}
\]

The bubble rise velocity \(u_{\text{bub},r}\) and the bubble fraction \(f_{\text{bub}}\) can be calculated from equation 2.17 and 2.18 respectively. The bubble to emulsion mass transfer coefficient \(K_{be}\) will be determined with equations 2.19, 2.20 and 2.21. The total superficial velocity in CSTR n \(u_{\text{tot},n}\), needed to calculate \(f_b\), is calculated by subtracting the flow through the membrane from the axial flow in CSTR \(n-1\):

\[
u_{\text{tot},n} = u_{\text{tot},n-1} - \frac{\text{flux} \times A_m}{A_r C_{\text{tot}}} \tag{2.45}
\]
Emulsion phase

The emulsion phase receives hydrogen from the bubbles and transports it via the film layer to the membrane wall.

\[
\frac{dC_e}{dz} = \frac{1}{u_{mf}A_r} \left[ f_b K_{be} A_r (C_b - C_e) - \frac{k_d \pi d_m (C_e - C_m)}{1 - X_e} \right]
\]  

(2.46)

Discretizing gives:

\[
C_{e,n} = C_{e,n-1} + \left. \frac{dC_e}{dz} \right|_{n-1} \Delta z
\]  

(2.47)

The minimum fluidization velocity \(u_{mf}\) is constant and will be determined experimentally in this project.

Film layer

The flux coming into the film layer is equal to the flux going through the membrane.

\[
J_{Hz} = \frac{P_m}{t_m} \sqrt{RT} \left( \sqrt{C_m} - \sqrt{C_{per}} \right) = \frac{k_d (C_e - C_m)}{1 - X_e}
\]  

(2.48)
Chapter 3

Experimental

Experiments were done measuring the hydrogen permeance through the membrane for binary cases ($H_2 + N_2$) and for pure $H_2$ cases. The experiments were done in both an empty reactor and a fluidized bed. The results were used to validate the models and to see the effect of concentration polarization.

Before experiments could be done, the particle size distribution needs to be determined. Furthermore, the $u_{mf}$ and the membrane permeance parameters ($P_{m0}$ and $E_a$) need to be determined. During the experiments the $N_2$ leakage will be constantly measured. Finally, the flux at different compositions and at different $u/u_{mf}$ will be measured to validate the model.

3.1 Particle size distribution

The particles that are used for the experiments are Pt/Al$_2$O$_3$ particles. The density is 1400 [kg m$^{-3}$]. They do not interact with the Pd membrane surface so that reductions in flux is not because of the particles. The distribution of the particle size was measured 5 times with a Wet Dispersion Unit ANALYSETTE 22 NanoTec plus. The size is needed for example to determine the Geldart classification.

3.2 Minimum fluidization velocity

When the flowrate in a bed of particles is increased, at first the pressure drop will increase. When the flowrate reaches $u_{mf}$ the pressure drop will become constant. Plotting $\Delta P$ versus the flowrate ($u$) using a log scale will obtain the following graph.

![Figure 3.1: Pressure drop over a bed as a function of the flowrate. The solid line is when increasing the flowrate, the dashed line is when decreasing the flowrate.](image)

To get to fluidizing behavior, the bed has to get over a certain point (B). The pressure drop here is bigger than during fluidization because it takes more energy to initiate fluidization. When decreasing the flowrate, the bed will reach point E which is $u_{mf}$. This point will be determined experimentally in this project. The setup used to determine $u_{mf}$ is shown in figure 3.2.
The minimum fluidization velocity was measured from 20 to 400 °C and air was used. Al 5 and 6 are the pressure sensors. The sensors are at the inlet of the bed and at 6 cm above the distributor. The pressure sensor is relatively low so that the pressure measurements are more accurate. Higher in the bed the pressure fluctuates more because of the bubbles.

### 3.3 Experimental setup

The reactor used for the flux experiments is cylindrical, 45 mm in diameter and 365 mm long. The distributor is a porous plate. In the center of the reactor the membrane with a diameter of 10.3 mm and a length of 113 mm is placed. The membrane is 30 mm above the distributor. The reactor is placed inside an oven which regulates the temperature. Thermocouples are placed inside the membrane and just outside the membrane in the reactor. In case of the fluidized bed experiments, 180.6 gr of Pt/Al₂O₃ particles are used. This fills the reactor for 205 mm. In figure 3.3 a schematic of the reactor is shown.
CHAPTER 3. EXPERIMENTAL

Figure 3.3: Schematic of the reactor setup.

The $\text{H}_2$ and $\text{N}_2$ is fed via mass flow controllers. It is possible to put an air or nitrogen flow through the membrane. At the membrane side there is a pump. When this pump is on a pressure inside the membrane of around 10 mbar can be reached. There is a pressure sensor inside the reactor and at the permeate side. The pressure inside the reactor is regulated by a valve at the retentate side. The gas leaving the reactor via the retentate side is let to an exhaust. The gas coming through the permeate side can be let directly to the exhaust or it can pass through a flow meter. To measure the flow coming through the permeate side a Horiba liquid film flow meter was used. For the complete P&ID of the setup see figure A.1 in appendix A.

3.4 Hydrogen permeation experiments

Membrane activation

Before the membrane can be used it needs to be activated. This is done by putting the membrane under hydrogen at a flowrate of 3 [L min$^{-1}$] in an empty reactor. The pressure difference was set small. The activation could take up to several days.

Membrane permeance

First the membrane permeance parameters ($P_{m,0}$ and $E_a$) of the membrane were determined. This was done as described in paragraph 2.6. Experiments were done at 350°C, 400°C and 450°C with pure hydrogen so that there is no concentration polarization. The pressure was varied between 1.2 and 1.6 bar in the reactor and 1 bar in the permeate side. The flowrate was 3 [L min$^{-1}$] and an empty reactor was used.
Nitrogen leakage

At the start of every day and at every new temperature the nitrogen leakage was measured. This was done to be sure that during the hydrogen experiments the measured flow is almost only hydrogen. The reactor pressure during the experiments was between 3 and 5 bar and the permeate pressure was 1 bar. The flowrate was set at 2 [L min⁻¹].

Binary case

To measure the concentration polarization experiments were done with binary mixtures of N₂ and H₂. Also pure hydrogen experiments were done as a base case to validate the permeance. Experiments were done in both an empty reactor and a fluidized bed to see if there is a difference in flux (and thus concentration polarization). The temperature used was 400°C because this would be the reaction temperature of the Steam Methane Reforming reaction.

The experiments with pure hydrogen (X=1,0) were done between 1.1 and 1.5 bar in the reactor and 1 bar in the permeate side. In a fluidized bed it is important to keep the u/umf constant to stay in the same fluidization regime. Since the volumetric flowrate becomes lower at higher pressures, this needs to be accounted for. The u/umf was set around 3.3 for all the experiments. For this reactor this comes down to a total flowrate between 2 and 3.5 [L min⁻¹].

The mole fraction of hydrogen for the binary experiments was set to 0.1, 0.25 and 0.45. The pressure in the reactor was set between 1.3 and 1.9 bar and the pressure in the permeate side was 10 mbar. The u/umf was again kept around 3.3.

Varying u/umf

To see if the flowrate has an influence on the concentration polarization, experiments were done at varying u/umf. The ratio was varied between 1.3 and 3.3. It needs to be made sure that the bed does not defluidize at lower flowrates. Experiments were done at the same conditions as mentioned above. Instead of varying the reactor pressure, the flowrate was varied. The pressure was kept constant at approximately 1.3 bar.
Chapter 4

Results and discussion

4.1 Particle size distribution

In order to use the model, the particle size needs to be determined. The particle size is needed in the calculation of the minimum fluidization velocity for example. The density of the particles is \( \rho_p = 1400 \text{ kg m}^{-3} \). The experiment was done five times. In figure 4.1 the results can be seen.

![Figure 4.1: Particle size distribution.](image)

It can be seen that experiments 2, 3 and 5 have a wide peak between 800 and 1600 \( \mu \text{m} \). This is because either the smaller particles are clumped together or dirt got into the measuring device. This wide peak will be ignored. It can further be seen that all the experiments show a narrow peak between 90 and 290 \( \mu \text{m} \). As 190 \( \mu \text{m} \) is the average value, this will be used as the particle diameter in the model calculations.

4.2 Minimum fluidization velocity

The bed starts to fluidize when the superficial gas velocity exceeds the minimum fluidization velocity \( (u_{mf}) \). It is assumed that in the emulsion phase the gas velocity is equal to \( u_{mf} \). The minimum fluidization velocity of air was determined experimentally at temperatures ranging from 20 to 400°C as described in section 3.2. In figure 4.2 the results of these experiments can be observed.
Figure 4.2: The pressure drop expressed in the amplitude of the pressure sensors plotted versus the flowrate in the bed at different temperatures. The gas used is air and the average particle diameter is 190 µm.

It can be seen that the minimum fluidization velocity decreases at higher temperature. The flowrates are converted to superficial velocities and are plotted against the temperature. These experimental results are compared with the $u_{mf}$ correlation of Wen and Yu in equation 2.5. The result can be seen in figure 4.3.
CHAPTER 4. RESULTS AND DISCUSSION

4.3 Membrane permeance

The membrane permeance constants (\(P_m,0\) and \(E_\alpha\)) of the membrane used during the experiments needs to be determined. The theory behind this is described in section 2.6 and the experimental procedure in section 3.4. The experimentally determined permeance \(P_m\) is plotted against \(1/RT\). The permeance constant determined in this project will be compared with the constants of the membrane used by K.T. Coenen [4]. The comparison is made because the membranes come from the same batch. The results can be observed in figure 4.4.

Figure 4.3: Comparison of experimentally determined \(u_{mf}\) of air with \(u_{mf}\) of air, hydrogen and nitrogen from correlation Wen and Yu. The experimental data is fitted with function \(y\). The average particle diameter is 190\(\mu\)m.

For air the correlation of Wen and Yu under predicts the actual minimum fluidization velocity. This is because Wen and Yu used a different particle size resulting in a different \(\epsilon_{mf}\). The experiments are under predicted with an approximately constant value of 0.43 \([\text{cm s}^{-1}]\).

The minimum fluidization velocity of a hydrogen-nitrogen mixture lies in between the minimum fluidization velocity of pure hydrogen and pure nitrogen and can be determined by a linear dependency of the mol fraction. From the correlation of Wen and Yu it can be seen that the values are higher than for air. At 400\(\degree\)C it follows from Wen and Yu that the minimum fluidization velocity lies in between 1.2 and 2.45 \([\text{cm s}^{-1}]\). Assuming that for hydrogen and nitrogen the under prediction is also approximately 0.43 \([\text{cm s}^{-1}]\), the \(u_{mf}\) range of a mixture is 1.63-2.88 \([\text{cm s}^{-1}]\).
CHAPTER 4. RESULTS AND DISCUSSION

Figure 4.4: \( \ln(P_m) \) plotted versus \( 1/RT \). The intercept represents \( P_{m,0} \) and the slope is \( E_a \).

From equation 2.36 and this experimental the membrane permeance constant and the activation energy can be determined. They are shown in the table below:

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( P_{m,0} \times 10^{-8} ) [mol m(^{-1}) s(^{-1}) Pa(^{-0.5})]</th>
<th>( E_a ) [J mol(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Team</td>
<td>6.19</td>
<td>7079</td>
</tr>
<tr>
<td>Kai</td>
<td>5.06</td>
<td>7799</td>
</tr>
</tbody>
</table>

Even though the membranes of K.T. Coenen and this work come from the same batch, a difference can be seen in the permeance constants. The activation energy of the membrane of K.T. Coenen is a little bit higher, which means that his membrane is affected more by changing the temperature. So increasing the temperature would increase the permeance of his membrane more. However, the activation energies are close and are probably in the variance regime. The pre exponential factor of the membrane of this work is higher which means a higher membrane permeance.

The difference can be explained by the activation time both membranes had. The membrane performance is very sensitive to the activation period, the longer it is activated with hydrogen the better the performance. The membrane performance can also be increased by burning the surface with oxygen. This is done to remove dirt from the membrane surface. So either the membrane used in this work is activated longer or is oxidized more than the membrane used in the work of K.T. Coenen.

4.4 Nitrogen leakage

To be sure that the membrane removes mostly hydrogen, the nitrogen leakage will be monitored during the experiments. In order for the flux measurements to be valid, the selectivity towards hydrogen should be much higher than towards nitrogen. Nitrogen leakages can occur when the membrane sealing is not good enough and there is also some nitrogen that passes through the membrane. To detect the nitrogen leakage, a high pressure drop needs to be used. The hydrogen permeation experiments are done at a maximum pressure drop of 1 bar, however to detect nitrogen a pressure drop between 2 and 4 bar is used. The measurements are done at 400°C. Pure nitrogen and pure hydrogen are used. The flowrate of the nitrogen experiments is 2 L [min\(^{-1}\)] and the flowrate of hydrogen is 3 L [min\(^{-1}\)]. In figure 4.5 the permeance is plotted against the square root of the pressure difference.
The permeation should be independent of the pressure drop. It can be seen that that is the case for the hydrogen permeance. The nitrogen leakage is increasing with an increasing pressure drop. This is the case when the leakage is caused by nitrogen passing by the sealing. It can clearly be seen that the nitrogen leakage is much lower than the hydrogen permeance. The nitrogen leakages is approximately $9 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-0.5}$ and the hydrogen permeance is around $4,65 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-0.5}$. This leads to a selectivity $(P_{m,N_2}/P_{m,H_2})$ of $1.93 \times 10^{-4}$ towards nitrogen. This small nitrogen leakage will not influence the results of the hydrogen permeation experiments.

4.5 Hydrogen permeation and concentration polarization, experiments vs model

In this section the results of the hydrogen permeation experiments, of both an empty reactor and a fluidized bed, are shown and the effect of concentration polarization will be determined. Experiments were done at mol fractions of: $X=0.1$, $X=0.25$, $X=0.45$ and $X=1.0$. At every mol fraction experiments were done at different pressure drops. The experimental results will be compared with the model. In order for the model to work, a parameter $\delta$ needs to be assumed. This parameter represents the thickness of the concentration polarization layer. The $\delta$ will be validated with the results of a 2D CFD two fluid model (TFM). The effect of the mol fraction of $\text{H}_2$ and the reactor pressure on $\delta$ will also be determined with this model. Finally it will be determined whether the bubble-emulsion, emulsion-membrane or the mass transfer over the membrane is the rate limiting step.
4.5.1 Effect of concentration polarization from experiments

Empty reactor

Concentration polarization can obviously only take place when there is a mixture of gasses. By comparing the flux of a mixture with the flux of pure H\textsubscript{2} at comparable pressure drops, the effect of concentration polarization can be seen. In figure 4.6 the fluxes of the pure hydrogen case and the case for X=0.45 are plotted versus the pressure drop for the experiments done in this work. In figure 4.7 the fluxes of pure hydrogen and for the X=0.5 case coming from the work of K.T. Coenen [4] are plotted. The difference between the experiments are the superficial gas velocity and the membrane permeance. Both the gas velocity and the membrane permeance are higher in this work.

![Diagram of concentration polarization](image)

Figure 4.6: Effect of concentration polarization in an empty reactor from this work. $u_0=0.074$ [m s\textsuperscript{-1}], $P_m=1.76\times10^{-8}$ [mol m\textsuperscript{-2} s\textsuperscript{-1} Pa\textsuperscript{-0.5}].
Figure 4.7: Effect of concentration polarization in an empty reactor from the work of K.T. Coenen [4]. $u_0=0.02 \text{ m s}^{-1}$, $P_m=1.01e-8 \text{ m}^3 \text{ s}^{-1} \text{ Pa}^{-0.5}$.

It can be seen that at the same partial pressure difference over the membrane, the flux of the case of pure $H_2$ is much bigger than the flux of the binary case. The only reason for this reduction in flux is concentration polarization. The polarization will be defined as:

$$\alpha = 1 - \frac{\text{Flux}_{\text{binary\_case}}}{\text{Flux}_{\text{pure\_H}_2}}$$

(4.1)

The concentration polarization of the $X=0.45$ case of this work is around $\alpha \approx 0.8$. For the experiments of K.T. Coenen at a mol fraction of $X=0.5$ it follows that $\alpha \approx 0.75$. The polarization of the work of K.T. Coenen is slightly lower. It is hard to say anything about this difference because the hydrogen mol fraction, the superficial gas velocity and the membrane permeance are different.

It is expected that a higher membrane permeance results in higher concentration polarization. The higher the flux the more external mass transfer to the membrane starts playing a role and thus the higher the concentration polarization becomes. Furthermore it is assumed that the higher the gas velocity, the higher the Reynolds number and the higher the surface renewal rate which would results in lower polarization.
Fluidized bed reactor

In this work no suitable experiments with a fluidized bed where done to compare a pure H₂ case with a binary case. K.T. Coen did do that kind of experiments. The result is shown in figure 4.8.

![Concentration polarization K.T. Coen Fluidized bed](image)

Figure 4.8: Effect of concentration polarization in a fluidized bed reactor from the work of K.T. Coen [4]. \( u_0=0.02 \text{ [m s}^{-1}] \), \( P_{m}=1.01\times10^{-8} \text{ [mol m}^{-1} \text{s}^{-1} \text{Pa}^{-0.5}] \).

Again a large effect of the concentration polarization can be observed. The concentration polarization has a value of \( \alpha\approx0.78 \). This is a little bit higher than the polarization observed in the empty reactor of the experiments of K.T. Coen. The difference is small so it is hard to say anything about these results other than that the concentration polarization has to be reckoned with.

Concentration polarization is induced because mass transfer from the bulk to the membrane wall is not sufficient compared to the flux that can go through the membrane. Because the effect of concentration polarization is so large during the experiments, it will be assumed that mass transfer from the bulk to the membrane wall (external mass transfer) is the rate limiting step. For the fluidized bed in principle the rate limiting step could also be the mass transfer from the bubble to the emulsion phase, but since a large reduction in flux can also be observed in the empty reactor experiments, it will be assumed that the external mass transfer is rate limiting.

4.5.2 Comparison empty reactor and fluidized bed experiments

It is expected that the concentration polarization in a fluidized bed is smaller than in an empty reactor because of the better mixing properties. In figures 4.9, 4.10 and 4.11 the results of the experiments in an empty reactor and in a fluidized bed reactor are compared. This is done for both the experiments done in this work and in the work of K.T. Coen [1].
Comparing FB with empty reactor
this work

![Graph comparing FB with empty reactor](image)

**Figure 4.9:** Comparison between fluidized bed and empty reactor experiments done in this work. $u_0=0.05$ m s$^{-1}$, $X=0.1-0.45$, $P_{\text{reactor}}=1.4-2.1$ bar.

Comparing FB with empty reactor
work K.T. Coenen

![Graph comparing FB with empty reactor](image)

**Figure 4.10:** Comparison between fluidized bed and empty reactor experiments done in the work of K.T. Coenen [4]. $u_0=0.02$ m s$^{-1}$, $X=0.4-0.73$, $P_{\text{reactor}}=2-5$ bar.

Looking at figures 4.9 and 4.10 it can be observed that there is hardly any difference between the flux in an empty reactor and a fluidized bed. In the experiments done by K.T. Coenen a slightly higher flux can be seen in the fluidized bed. However, this difference is too small to draw any conclusion from.
So opposed to what was expected, the concentration polarization in an empty reactor is approximately the same as in a fluidized bed under these conditions. This is the same thing that could be concluded from section 4.5.1. Interesting to see in figure 4.9 is that the membrane permeance \((P_{m})\) is higher for the empty reactor case because these where done in another set of experiments. Despite the permeance being different, the membrane flux is still equal. From this fact it can be concluded that the membrane permeance is not the rate limiting step.

From figure 4.9 it looks like the flux is not completely linear dependent on the pressure difference. At every mol fraction (especially at \(X=0.1\) and \(X=0.25\)) the relative flux seems to decrease at higher pressure drop. This is because the pressure drop was increased by increasing the absolute reactor pressure at a certain mol fraction. Increasing the pressure decreases the diffusion coefficient, as can be seen in equation 2.30. Decreasing the diffusion coefficient decreases the external mass transfer coefficient \((k_d)\), so at higher pressure the external mass transfer becomes lower.

![Comparison this work with work K.T. Coenen](image)

**Figure 4.11:** Comparison between the experiments done in this work with the experiments done by K.T. Coenen [4].

A comparison between the experiments done in this work and the experiments done by K.T. Coenen is shown in figure 4.11. The experiments done in this work show a higher flux. This can be explained by the fact that the superficial inlet velocity of the experiments done in this work is higher. A higher gas velocity results in more turbulence and a higher surface renewal rate resulting in a higher concentration in the reactor. This increases the flux because the concentration gradient is increased. It is also expected that a higher flowrate decreases \(\delta\), which increases \(k_d\). Also the membrane permeance in this work is higher, however as can be concluded from figure 4.9, this does not have a big influence on the flux. Another thing that contributes to a lower flux in the work of K.T. Coenen is that he used a higher absolute reactor pressure because his permeate pressure was 1 bar instead of 0 bar. This results in a lower diffusion coefficient (lowering \(k_d\)) and thus decreasing the flux. Finally the mol fraction used by K.T. Coenen is higher. It is unclear whether this increases the polarization or not.

### 4.5.3 Results 1D and 1D/\(k_d\) model compared with experiments

In this section the results of both the 1D- and the 1D/\(k_d\) model will be compared to the experiments. The 1D/\(k_d\) model is described in chapter 2. This model accounts for the mass transfer limitation from the bulk to the membrane by adding an extra resistance compared to the 1D model. In the 1D model it is assumed that the concentration of hydrogen is constant in the radial direction. The concentration at the membrane surface is the same as in the bulk. Before this work, a 1D model was already available in Delphi. However, this model over predicted the flux by quite a lot as can be seen further on in this section. The reason for this is that concentration polarization is not taken into account. Because of
polarization the hydrogen concentration at the membrane surface is a lot lower than in the bulk of the reactor. In this work the 1D model will be expanded to a 1D/$k_d$ model. As described in chapter two, in this work concentration polarization is modelled by assuming a film layer ($\delta$) around the membrane with an external mass transfer coefficient ($k_d$). Over this film layer, concentration polarization will take place. In case of the fluidized bed, the film layer is not necessarily the same thickness as the densified zone around the membrane.

**Determine film layer thickness**

In order to use the 1D/$k_d$ model which is developed in this work, the thickness of the film layer ($\delta$) needs to be estimated. It will be assumed that $\delta$ is constant in the axial direction. To help estimate the magnitude of $\delta$ the two fluid model (TFM) developed by R.J.W. Voncken will be used. Voncken developed a complete 2D CFD model which describes the fluidized bed membrane reactor. The experiments done is this work where simulated. The results can be seen in figure 4.12.

![Experiments vs TFM](image)

**Figure 4.12:** Experiments done in this work simulated with the TFM developed by R.J.W. Voncken. $X=0.1$ $X=0.25$ and $X=0.45$; $P_{\text{reactor}}=1.5-1.8$ bar; $u_0=0.05$ m s$^{-1}$; $D_r=5e-5$ m$^2$ s$^{-1}$.

It can be observed that the TFM under predicts by approximately 25%. This can be explained by the fact that the used dispersion coefficient during the simulations is derived from the correlation of Tsotsas and Schlünder as can be seen in chapter two. This correlation describes the dispersion in packed beds instead of fluidized beds but is used nonetheless because correlations for fluidized beds are not available. The under prediction can easily be explained by this fact because the dispersion in a packed bed is always lower than in a fluidized bed. For future work accurate correlations for the dispersion coefficient in fluidized beds need to be determined. It should also be noted that for these simulations a constant $D_r$ of $5e-5$ m$^2$ s$^{-1}$ was used while the dispersion coefficient is actually a function of the pressure in the reactor. The predictions of this model are reasonable and will be used to determine the film layer thickness. It should be noted that this model is for a fluidized bed but the resulting film layer thickness will also be used for the empty reactor.

In figures 4.13, 4.14 and 4.15 the radial concentration profiles at different axial positions are plotted for the simulations at $X=0.1$, $X=0.25$ and $X=0.45$. The reactor pressure is 1.5 bar for all the cases. The concentration profiles at different reactor pressures where not added because they where the same for the cases 1.5-1.8 bar.
Figure 4.13: Concentration profile from the TFM model for the case: $X=0.1$, $P_{\text{reactor}}=1.5$, $u_0=0.05$ m s$^{-1}$.

Figure 4.14: Concentration profile from the TFM model for the case: $X=0.25$, $P_{\text{reactor}}=1.5$, $u_0=0.05$ m s$^{-1}$. 
Figure 4.15: Concentration profile from the TFM model for the case: X=0.45, P_{reactor}=1.5, u_0=0.05 m s^{-1}.

In the graphs it can be seen that for all the cases the concentration polarization (film layer) starts at approximately the same position. There is only a small difference between the different mol fractions. A trend seems that at lower axial positions, the film layer is thinner. This is because the hydrogen is injected at the bottom causing a higher refresh rate at the bottom of the membrane. The change of the film layer thickness in the axial direction is visualized in figure 4.17. This shows that the assumption of the film layer having a constant thickness is a simplification. In figure 4.16 the thickness of the film layer is shown as a function of the mol fraction and the partial pressure in the reactor. Here the slight differences between the different conditions can be seen.

Figure 4.16: Film layer thickness.
The film layer thickness is decreasing slightly at higher mol fractions and the pressure indeed seems to have no influence. For the 1D/\(k_d\) model a film layer thickness of 0.01 m will be assumed.

**Model versus experiments, empty reactor**

The 1D/\(k_d\) model of the empty reactor with the film layer thickness \(\delta\) set at 0.01 m is compared with the experimental results. The results will also be compared with the 1D model in which the parameter \(\delta\) is set to zero. Two sets of experiments were done in this work. The first set had a membrane permeance (\(P_m\)) of 1.76e-8 [mol m\(^{-1}\) s\(^{-1}\) Pa\(^{0.5}\)] and an inlet superficial velocity of 0.074 [m s\(^{-1}\)], the second set had a membrane permeance of 2.08e-8 [mol m\(^{-1}\) s\(^{-1}\) Pa\(^{0.5}\)] and an inlet superficial velocity of 0.05 [m s\(^{-1}\)]. The experiments of the work of K.T. Coenen were also simulated. He had a membrane permeance of 1.01e-8 [mol m\(^{-1}\) s\(^{-1}\) Pa\(^{0.5}\)] and a superficial velocity of 0.02 [m s\(^{-1}\)]. In the figures 4.18, 4.19, 4.20, 4.21, 4.22 and 4.23 the results are plotted.
Figure 4.18: 1D and 2D model predictions versus experiments of an empty reactor $X=0.1$ and $X=0.25$. $P_{\text{reactor}}=1.96-2.34$ [bar]; $P_m=1.76e-8$ [mol m$^{-1}$ s$^{-1}$ Pa$^{-0.5}$]; $u_0=0.074$ [m s$^{-1}$].
Figure 4.19: 1D and 2D model predictions versus experiments of an empty reactor $X=0.45$ and $X=1.0$. $P_{\text{reactor}}=1.43\text{-}2.12$ [bar]; $P_m=2.08e-8$ [mol m$^{-1}$ s$^{-1}$ Pa$^{-0.5}$]; $u_0=0.05$ [m s$^{-1}$].
Figure 4.20: 1D and 2D model predictions versus experiments of an empty reactor $X=0.1$ and $X=0.25$. 
$P_{\text{reactor}}=1.96-2.34$ [bar]; $P_m=1.766-8$ [mol m$^{-1}$ s$^{-1}$ Pa$^{-0}$5]; $u_0=0.074$ [m s$^{-1}$].
Figure 4.21: 1D and 2D model predictions versus experiments of an empty reactor X = 0.45 and X = 1.0. 

For the first case the 1D/k₂ model under predicts the experiments by a small amount. However, for the second case the model over predicts the results. The reason for this is probably that the actual value for δ is lower for the first set of experiments due to the higher flow rate. The higher flow rate induces better mixing and thus the thickness of the polarization layer decreases. A smaller value of δ increases the external mass transfer coefficient (k₂) as can be seen by the definition of k₂:

\[ k₂ = \frac{D}{\delta} \]  

(4.2)

It should be validated with the TFM if the thickness of δ decreases at higher flow rates. It should also be noted that δ is determined for a fluidized bed. For an empty reactor the film layer thickness could be different. This should also be validated with the TFM be setting \( \epsilon_a = 0 \). The δ was determined for a flow rate of 0.05 [m s⁻¹] which is the same as used in case 2. However, case 2 has the worse fit compared to case 1 so it seems that the δ is actually different than 0.01 m. It could also be that the diffusion coefficient is actually different from the molecular diffusion coefficient.

Another thing that should be noted is that the membrane permeance in the second set of experiments is higher, however as could be seen in figure 4.9 the membrane permeance is not the rate limiting step so this should have only a small influence. As can be seen from the results of the pure hydrogen cases,
the used membrane permeances in the model are correct.

It can also be seen that the model predicts a high polarization for both cases by comparing the 1D model with the 2D model. The polarization by the definition of equation 4.1 for all cases is in between 0.5 and 0.7. On the next page the results of the work of K.T. Coenen are shown.
Figure 4.22: 1D and 2D model predictions versus experiments of K.T. Coenen [4] of an empty reactor $X=0.4$, $X=0.5$ and $X=0.6$. $P_{\text{reactor}}=2.5$ [bar]; $P_m=1.08e-8$ [mol m$^{-1}$ s$^{-1}$ Pa$^{-0.5}$]; $u_0=0.02$ [m s$^{-1}$].
Figure 4.23: 1D and 2D model predictions versus experiments of K.T. Coenen [4] of an empty reactor $X=0.73$ and $X=1.0$. $P_{\text{reactor}}=2.5$ [bar]; $P_m=1.08\times10^{-8}$ [mol m$^{-1}$ s$^{-1}$ Pa$^{-0.5}$]; $u_0=0.02$ [m s$^{-1}$].

The model predicts the experiments of K.T. Coenen very well. Apparently the film layer thickness of 0.01 m is correct for these experiments. The polarization calculated by the model is lower than for the experiments done in this work. The modelled polarization is approximately 0.35. The superficial gas velocity is lower in these experiments which should result in a higher external mass transfer resistance and thus would increase the polarization. However, the membrane permeance is lower and the mol fractions are higher. A higher mol fraction results in a lower $\delta$, thus increasing the external mass transfer coefficient ($k_d$) and decreasing the polarization. The membrane permeance is lower which also reduces the polarization. In the model it can also be seen that the flux (especially at higher $X$) shows a square root dependence of the partial pressure difference. This is a sign that the membrane permeance following Sievert’s law is becoming more important. This behaviour cannot clearly be derived from the experimental results because the accuracy is not high enough.

A complete plot of the flux versus the partial pressure difference at all the molfractions of case 1 and 2 is shown in figures 4.24 and 4.25.
CHAPTER 4  RESULTS AND DISCUSSION

Case 1

![Graph](image1)

Figure 4.24: Plot of case 1 for the mol fractions X=0.1, X=0.25 and X=0.45.

Case 2

![Graph](image2)

Figure 4.25: Plot of case 2 for the mol fractions X=0.1, X=0.25 and X=0.45.

In these plots it can be seen that the experimental data and the 1D/k_d model results are not perfectly on a one line. Especially the 1D/k_d model results have a less steep slope. The reason for this is that at each mol fraction (each of the 3 sets of points is a certain mol fraction, X=0.1, X=0.25 and X=0.45) the higher pressure drops where at higher absolute reactor pressures. As can be seen in the Fuller equation, the diffusion coefficient becomes lower at higher pressure drops. Since k_d=D/δ the external mass transfer coefficient becomes lower at higher pressure drops resulting in a relatively lower flux. The 1D model does show a straight line because the external mass transfer is not taken into account. The line should actually behave as a square root dependence on ΔP because of Sievert’s law. This is probably the case but it cannot be seen because only a small part of the beginning of the line is plotted.

In figure 4.26 the experiments of case 1 and 2 are plotted in the same graph. It can be seen that the experiments of case 1 show roughly a higher flux at the same partial pressure drop even though the membrane permeance is higher in case 2. The reason for this is that the flowrate of case 1 is higher. A
higher flowrate causes a higher refreshment rate, resulting in higher bulk concentration which increases the concentration gradient between the bulk and the membrane wall. A higher flowrate also results in better mixing and thus decreasing the thickness of $\delta$.

![Comparison case 1 and case 2](image)

Figure 4.26: Experiments of case 1 and 2. Case 1: $P_m=1.76e^{-8}$, $u_0=0.074$. Case 2: $P_m=2.08e^{-8}$, $u_0=0.05$.

From the results shown in this section it can be concluded that the external mass transfer to the membrane wall is rate limiting compared to the mass transfer over the membrane. This can also be seen when the mol fraction in the axial direction of one of the experiments is plotted. In figure 4.27 the mol fraction at the membrane surface and in the bulk are plotted for an experiment of case 1 at a mol fraction of 0.25, the permeate pressure is 10 mbar.

![H2 mol fraction](image)

Figure 4.27: Hydrogen mol fraction at the membrane surface and in the bulk in the axial direction. Experiment case 1: $X=0.25$, $u=0.074$ [m s$^{-1}$], $P_{\text{reactor}}=1.95$ [bar], $P_m=1.76e^{-8}$ [mol m$^{-1}$ s$^{-1}$ Pa$^{-0.5}$].
Since the gradient between the bulk and the membrane wall is much higher than between the membrane wall and the permeate side, it can be concluded that the external mass transfer resistance is much higher than the membrane resistance.

In order to quantify the magnitude of the external mass transfer coefficient \(k_d\), a Sherwood correlation should be developed. In equation 2.29 it can be seen that the Sherwood number is only a function of the hydraulic diameter and \(\delta\). Since delta was kept constant in this work at 0.01 m, the Sherwood numbers are also constant. For the experiments done in this work \(Sh=3.47\) and for the experiments done by K.T. Coen Sh=1.97. The actual Sherwood number is not constant, it is a function of the superficial velocity for example. The dependence of Sherwood on other parameters should be investigated in future work.

Models versus experiments, fluidized bed reactor

In this section the models for the fluidized bed will be compared with the experiments. As in the case for the empty reactor, the film layer thickness \(\delta\) is set at 0.01 m. The experiments in the fluidized bed were done at an inlet superficial gas velocity of \(u_0=0.05\) m s\(^{-1}\), the membrane permeance was \(P_m=1.76\times10^{-8}\) [mol m\(^{-1}\) s\(^{-1}\) Pa\(^{-0.7}\)], the temperature was 400\(^\circ\)C, the reactor pressure was varied between \(P=1.44\) and \(P=1.8\) bar and the mol fractions where \(X=0.1\), \(X=0.25\), \(X=0.45\) and \(X=1.0\). The experiments will be compared with the 1D model of both this work and the one that was developed in Delphi before this project. The 1D/\(k_d\) model developed in this work will also be compared. In the 1D/\(k_d\) model the correlation of Tsotsas and Schlunder [21] for packed beds is used to determine the dispersion coefficient. No correlation for a fluidized bed is available. Because this is a correlation for a packed bed, the dispersion coefficient is underpredicted and is approximately \(D_r=4e-5\) m\(^2\) s\(^{-1}\). By fitting the dispersion coefficient at a constant value of \(D_r=9e-5\) m\(^2\) s\(^{-1}\) the 1D/\(k_d\) model shows a very good fit, these results are also plotted. Finally the model was plotted with the mass transfer resistance between the bubble- and emulsion phase neglected (by setting \(K_{bd}\) very high) to see what the influence on the flux is. In figures 4.28 and 4.29 the results are plotted.
Figure 4.28: Model predictions versus experiments X=0.1 and X=0.25. $P_{\text{reactor}}=1.44-1.8$ [bar]; $P_m=1.76e-8$ [mol m$^{-1}$ s$^{-1}$ Pa$^{0.5}$]; $u_0=0.05$ [m s$^{-1}$].
The under prediction of the 1D/ kd model because of the use of the packed bed dispersion correlation is approximately 50%. By doubling the dispersion coefficient (and thus $k_d$) the 1D/ kd model predicts the experiments very well. Thus it can clearly be seen that the dispersion coefficient (and thus $k_d$) have a major influence on the flux. When taking a close look it can be seen that at higher pressure the model with $D=9e-5$ starts to over predict more. This is because $D$ is kept constant while in reality is decreases at higher pressure. The TFM uses a dispersion coefficient of $D=5e-5$ which is of the same order as from the correlation of Tsotsas and Schlunder. The prediction of the TFM is almost the same as the 1D/ kd model developed in this work so the simple 1D/ kd model is able to make the same predictions as the
The predictions of the Delphi model and the 1D model from this work are almost equal. The Delphi model predictions are a little bit higher. This is because in the Delphi model mass transfer directly from the bubble to the membrane is taken into account while that has not been done in the 1D model of this work. Since both models are close to each other, it can be concluded that the mass transfer from the bubble to the membrane is negligible. Both of the 1D models predict a much higher flux than the experiments which is again proof of a large concentration polarization. The higher the pressure drop the more the 1D model under predicts the experiments in the pure hydrogen case. However, the under prediction is small. The reason for this is that the membrane permeance used in the model was not completely correct. Furthermore it can be seen that the model results of the case without bubble-emulsion mass transfer give almost the same results as the 1D/k_d model with bubble-emulsion mass transfer taken into account. This means that the bubble-emulsion resistance is negligible compared to the external mass transfer resistance to the membrane wall.

The 1D and 1D/k_d model of this work will also be compared with the experiments done by Patil [19]. He did experiments at 400°C, the superficial gas velocity was between u_0=3 and u_0=5 m s⁻¹, the partial pressure drop was between ∆P=0.5 and ∆P=3 bar. The membrane he used is much worse than the membrane used in this work. Therefore the diffusion of hydrogen through the membrane is rate limiting and in Sievert's law the exponent n=1 instead of 0.5. This means that the permeance has a different unit and is P_m=1.35e-12 [mol m⁻² s⁻¹ Pa]. In his work Patil found almost no influence of concentration polarization. In figure 4.30 the model and experimental results are plotted.

As Patil found in his work, the model predicts no effect of concentration polarization. The 1D model with no concentration polarization modelled predicts the experimental results perfectly. The 1D/k_d model underpredicts slightly because of the external mass transfer resistance that has been taken into account while it is not there. However, since the underprediction is only small, it can be seen that the external mass transfer resistance in the 1D/k_d model is small.

In figure 4.31 all the results of the experiments done in this work are plotted in one graph.
As is the case for the empty reactor, the dispersion coefficient becomes lower at higher reactor pressure. Therefore, the results at different mol fractions are not on the same line. However, the results of the 1D/$k_d$ model seem to deviate more from the straight line than the experimental results. This could mean that the actual dispersion coefficient does not change as much with the reactor pressure than the correlation predicts. The 1D model results do show a straight line because there is no dependence of the dispersion on the external mass transfer. The TFM and the 1D/$k_d$ with $D=9e-5$ [m$^2$ s$^{-1}$] are on the same line because the dispersion coefficients are kept constant. The straight line, as for the empty reactor, should actually be a square root function because $n=0.5$ in Sievert’s law.

In figure 4.32 the different mol fractions are plotted over the length of the membrane. This has been done for one experiment, but all the other showed the same trend. Since the gradients between the bubble-emulsion and over the membrane are small compared to the gradient between the emulsion and the membrane wall it can be concluded that again the external mass transfer is rate limiting.
Figure 4.32: Hydrogen mol fraction at the membrane surface, in the emulsion-, and in the bubble phase. Experiment: \( X = 0.25, \ u = 0.05 \ \text{m s}^{-1}, \ P_{\text{reactor}} = 1.44 \ \text{bar}, \ P_m = 1.76 \times 10^{-8} \ \text{mol m}^{-2} \ \text{s}^{-1} \ \text{Pa}^{-0.5} \).

In general for the fluidized bed model it should be noted that a lot more research needs to be done. The influence of the membrane on bed parameters like the bubble diameter and the porosity needs to be investigated. Now correlations are used for a regular fluidized bed but the membrane has big influence. The 1D/\( k_d \) model only gives a rough estimate because of the assumptions that are made. When \( D \) is fitted a good agreement with the experiments is found. However, an accurate correlation determining this should be made. Other complications are that the film layer thickness is quite large compared to the annular space between the membrane and the reactor wall \( (\delta = 0.01 \ \text{m and} \ d_r = 0.045 \ \text{m}) \). The model assumes no axial convection in the film layer, since this is such a large part of the reactor this assumption is very inaccurate.
Chapter 5

Conclusions

Models were made to predict the flux for an empty membrane- and a fluidized bed membrane reactor incorporating concentration polarization. The membranes used were high flux membranes. The concentration polarization was modeled by extending a 1D model to correct for the hydrogen concentration at the membrane wall. This was done by assuming a stagnant film layer around the membrane in which concentration polarization takes place. The film layer has a thickness $\delta$ and acts as an extra mass transfer resistance with an external mass transfer coefficient $k_d$. Depending on the magnitude of $k_d$ the bulk concentration was converted to the concentration at the membrane wall to correct for concentration polarization. The extended 1D model was also compared with a regular 1D model. Finally experiments were done to determine the concentration polarization and to validate the model.

From experiments it could be seen that the high flux membranes used in this work suffer a lot from concentration polarization. The flux in both an empty- and a fluidized bed reactor are reduced by approximately a factor 0.8 compared to the case with no concentration polarization. It was expected that a fluidized bed suffers less from concentration polarization because of its better mixing properties. From experiments it appeared that this was not the case for the conditions used in this work. The effect of concentration polarization was equal to that of an empty reactor. It also appeared that the membrane permeance had almost no influence on the flux at the higher membrane permeances. From this it can be concluded that external mass transfer from the bed to the membrane wall is rate limiting. On the other hand, the flowrate did have a large influence on the flux. This is because a higher flowrate causes a higher renewal rate and thus increasing the concentration gradient. It is also expected that a higher flowrate reduces the thickness of the film layer $\delta$ and thus increasing the external mass transfer coefficient. From this fact it can also be concluded that external mass transfer to the membrane wall is rate limiting.

In order to use the extended 1D/$k_d$ model, the thickness of $\delta$ was determined. This was done by looking at the concentration profiles of a two fluid model (TFM) of a fluidized bed membrane reactor. From the TFM it could be seen that $\delta$ was increasing over the length of the membrane. Furthermore the value of $\delta$ slightly decreased as the mol fraction increased. Looking at all the TFM simulations an average value of approximately 0.01m was observed. It was expected that the partial pressure drop had a bigger influence on $\delta$. Even though $\delta$ increases over the length of the membrane, in the model the value of 0.01m was assumed for all the cases.

The regular 1D model over predicts the experiments by a lot for both the empty- and the fluidized bed reactor. The 1D/$k_d$ model developed in this work had much better predictions. The deviation of this model compared to the experiments for an empty bed ranged between 0% and 50% depending on the experiments (both over- and under predictions). The fluidized bed model under predicts by approximately 50%. The reason for this is that the exact value of $\delta$ is unknown. For all cases it was kept constant while this is not the reality. Also the dispersion coefficient for a fluidized bed is unknown. A correlation for the dispersion coefficient in a packed bed was used [21]. Since the dispersion in a packed bed is lower, this is expected to cause the under prediction of the fluidized bed model. By fitting the dispersion coefficient in the fluidized bed model to $D=9\times10^{-5}$ m$^2$ s$^{-1}$ a very good fit to the experiments was found. For the fluidized bed the complex 2D TFM predicted almost the same results as the 1D/$k_d$ model. The under prediction is also caused by the use of the correlation of Tsvatsas and Schlunder for the dispersion coefficient. Other reasons for the deviation of the fluidized bed model from the experi-
ments is that the parameters used (like \( d_b, \epsilon_s \) etc) are for a regular fluidized bed and not a membrane assisted fluidized bed. The membrane is expected to have a big influence on the hydrodynamics. Also the minimum fluidization velocity has not been accurately determined for the case of a \( \text{H}_2/\text{N}_2 \) mixture at 400°C. The assumption that there is no axial convection in the film layer is also critical since the film layer occupies approximately 50% of the reactor.

From the concentration profiles produced by the extended 1D model a large partial pressure gradient can be seen between the bulk and the membrane wall. This gradient is much bigger than the partial pressure gradient over the membrane, and for the fluidized bed the gradient between the bubble and the emulsion phase. From this it can also be concluded that the external mass transfer to the membrane wall is the rate limiting step.
Chapter 6

Recommendations

A basis has been made for a simple model which is reasonably capable of predicting the membrane flux incorporating the effect of concentration polarization. However, there are still a lot of things that need to be researched in order to improve the model. In this project it can be concluded from the model (and a little bit from experiments) that external mass transfer is rate limiting. In the future this should also be determined more clearly from experiments. A way to do this is by changing the membrane permeance while keeping all other parameters constant. This should first be done in an empty reactor so that bubble to emulsion mass transfer does not have to be taken into account. When the flux does not change anymore when increasing the membrane permeance, external mass transfer has become rate limiting.

The external mass transfer resistance $k_d$ needs to be determined more accurately. This can be done by developing a Sherwood correlation for mass transfer from the bulk to the membrane wall in an empty- and fluidized bed reactor. This can also be done by developing a correlation for $\delta$. A promising way of observing $\delta$ from experiments is with infrared technique which is being developed at the moment.

Furthermore correlations for the hydraulic parameters in a fluidized bed membrane reactor need to be determined. Experiments need to be done to monitor e.a. the bubble diameter, the solid holdup and the minimum fluidization velocity. Also a correlation to determine the dispersion to the membrane wall in a fluidized bed needs to be made.

To increase the accuracy of the model, axial convection in the film layer needs to be taken into account. In the future the model developed in this work should be extended to a 2D model. In order to use the model for multicomponent systems maxwell stefan diffusion should be incorporated.
Chapter 7

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Bibliography


Appendix A

P&ID of the reactor setup

Figure A.1