Modelling of a packed bed membrane reactor for Fischer Tropsch synthesis

van Wijk, F.L.

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2015

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Modelling of a packed bed membrane reactor for Fischer Tropsch synthesis

F.L. van Wijk
August 2014 - confidential
Abstract

In this project a numerical model is used to perform a feasibility study on the effects of the usage of membranes in a Fischer Tropsch reactor. A 1D packed bed membrane reactor (PBMR) model has been used to solve the kinetic model of the Fischer Tropsch synthesis (FTS) over a Co/Al₂O₃ and a Ru-B/TiO₂ catalyst. With this model a numerical feasibility study has been performed and compared to experimental results from the reactor at CSIC, Spain. A membrane has been implemented in the packed bed reactor to improve the reactor performance. Two different set-ups have been considered: the feeding of H₂ via a Pd-Ag membrane to optimize the H₂/CO ratio, and the subtraction of H₂O via different membranes to optimize the reactor performance. In this project the main focus lies with the H₂ addition along the reactor axis. Validation has been performed on the kinetic model used to simulate the FTS, on the reactor model for an isothermal and non-isothermal first order reaction and specifically for the membrane section of the reactor model. The used kinetic model has been improved for the Ru-B/TiO₂ catalyst and this model has been validated with an experimental dataset obtained by CSIC. Finally a feasibility study on the reactor performance with the selective feeding of H₂ has been performed over a wide range of operating conditions. Feeding H₂ via the membrane has shown an increase in the production of higher hydrocarbons and a decrease in the formation of methane, while a same conversion has been obtained.
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Chapter 1

Introduction

The worldwide energy demand has been increasing rapidly the last few decades. With this rising energy demand new, more energy efficient ways to fossil or renewable fuels have to be investigated. The International Energy Agency (IEA) predicts in their World Energy Outlook of 2013\cite{12} a huge increase in the supply of unconventional oil, such as oil shales, GTLs or coal-based liquids\cite{11}, between now and 2035. One of the processes to produce unconventional oils is the Fischer Tropsch Synthesis (FTS). This process can convert the syngas, obtained from coal, biomass or natural gas, via the hydrogenation of CO to a wide range of mainly paraffins and olefins. The general reaction can be written as:

$$nCO + 2nH_2 \rightarrow -(CH_2)_n + nH_2O$$ \hspace{1cm} (1.1)

The Fischer Tropsch process was discovered in 1926 by the German scientists Franz Fischer and Hans Tropsch\cite{10} and has been used in times of scarcity of fossil fuels\cite{5}. Although the process is known for almost a century, little is known about the mechanism and a lot of research is taking place on this subject.

Common catalysts used in the FTS are based on the metals Ru, Fe or Co. Fe and Co based catalyst are currently the only feasible option for large industry plants, due to the high price of Ru. In this project an alumina supported Co based catalyst and a titania supported Ru-B based catalyst have been used for the FTS. The cobalt catalyst is used to investigate the cheap catalysts, used in industry and the ruthenium catalyst is used to investigate the more active and stable catalyst.

To perform the FTS different types of reactors are used in industry, such as the Packed Bed Reactor (PBR), the Multitubular Packed Bed Reactor and the Slurry Bubble Column. A way to possibly improve the FTS is to use a membrane reactor to obtain optimal reactor conditions by the addition or subtraction of certain reactants or products. This is also one of the four main goals of the DEMCAMER project, an European project on the Design and Manufacturing of Catalytic Membranes Reactors.

The DEMCAMER project has as aim to develop innovative multifunctional catalytic membrane reactors based on new nano-architectured catalysts and selective membranes materials to improve their performance, durability, cost effectiveness and sustainability over four selected chemical processes for pure hydrogen, liquid hydrocarbons and ethylene production.

Modelling of a packed bed membrane reactor for Fischer Tropsch synthesis
Within the DEMCAMER project the FTS will be investigated in a Chemical Membrane Reactor with the following configurations:

- The addition of hydrogen along the reactor axis for an optimum $\text{H}_2/\text{CO}$ ratio;
- The subtraction of water to prevent negative side reactions or catalytic poisoning.

An experimental Packed Bed Membrane Reactor (PBMR) setup has been constructed at the Consejo Superior de Investigaciones Científicas (CSIC) in Madrid, Spain, to investigate the FTS with different catalysts in a membrane reactor.

In this project a computational study will be performed on the PBMR at CSIC with the following configuration: the addition of hydrogen along the reactor axis for an optimum $\text{H}_2/\text{CO}$ ratio.
Chapter 2

Project description

This Master project is a collaboration between the University of Technology Eindhoven (TU/e) and the Consejo Superior de Investigaciones Cientificas (CSIC) in Madrid within the DEMCAMER project. At CSIC an experimental setup will be used to perform experiments on the FTS reaction in a PBR and a PBMR setting. This experimental setup consists of two compartments, an outer shell and an inner tube, that is placed in an oven. The wall between these two compartments can be used as a membrane wall to perform the addition or subtraction of certain reactants or products. The PBR experiments function as a base case, to determine the behavior of the FTS in the experimental reactor. Furthermore, in this setup different catalysts will be tested in order to obtain a full dataset to validate the kinetic model and fit certain parameters.

Two types of catalyst are used in this project: a cobalt catalyst on a alumina support and a ruthenium-boron catalyst on a titania support. The first catalyst is a regular FTS catalyst with a cheap active metal, while the second catalyst is a catalyst that is developed within the DEMCAMER project, based on the more expensive ruthenium as active metal. A literature study has been performed on the regular Co-catalyst, due to the fact that this catalyst is widely used in industry and research.

In the FTS the two reactants, H\textsubscript{2} and CO, need to adsorb to the catalytic surface and dissociate to obtain the building blocks for the hydrocarbon chains. For H\textsubscript{2} this happens via the dissociative adsorption on two free catalytic sites to two adsorbed hydrogen atoms. The CO dissociation is more complicated and a lot of research is done in this area. Currently two pathways for the CO dissociation are considered: the unassisted CO dissociation (also known as the carbide theory) and the hydrogen assisted CO dissociation, see Table 2.1.

Several researchers have considered the carbide theory, as the common accepted theory for their kinetic model\cite{24,25,15}. However, detailed research into the activation pathways on iron and cobalt catalysts by Ojeda\cite{16} has shed new light on the proposed pathway. Ojeda shows that for a cobalt catalyst the hydrogen assisted CO dissociation is favored over the unassisted CO dissociation and that therefore the oxygen rejection only takes places as H\textsubscript{2}O and not as CO\textsubscript{2}. The same conclusion is drawn by Shetty and van Santen\cite{20}. Their theoretical study into the CO activation on the Co and Ru surface resulted in the findings that for the Co surface the formation of HCO intermediate has a lower energy barrier in comparison with the direct dissociation. This resulted in a shift in understanding and a rephrasing of the kinetic
CHAPTER 2. PROJECT DESCRIPTION

<table>
<thead>
<tr>
<th>Step</th>
<th>Carbide theory</th>
<th>H-assisted CO dissociation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$H_2 + 2* \rightarrow 2H*$</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>$CO + * \rightarrow CO*$</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>$CO * + * \rightarrow C * + O*$</td>
<td>$CO * + H* \rightarrow HCO * + *$</td>
</tr>
<tr>
<td>4.</td>
<td>$C * + H* \rightarrow CH * + *$</td>
<td>$HCO * + H* \rightarrow HCOH * + *$</td>
</tr>
<tr>
<td>5.</td>
<td>$O * + H* \rightarrow OH * + *$</td>
<td>$HCOH * + * \rightarrow CH * + OH*$</td>
</tr>
<tr>
<td>6.</td>
<td>$CO * + O* \rightarrow CO_2 + 2*$</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>$CH * + H* \rightarrow CH_2* + *$</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>$OH * + H* \rightarrow H_2O + 2*$</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: The carbide theory versus the hydrogen assisted CO dissociation.

models for Co catalysts. Since 2010 the hydrogen assisted CO dissociation is used in most papers\cite{26,8} on Co catalysts. However, Shetty and van Santen also show that the carbide pathway has a lower energy barrier on the investigated Ru surface. It is therefore assumed that the unassisted CO dissociation is the correct pathway for the Ru catalyst.

In this project both a Co and a Ru catalyst are used and thus both pathways have to be considered. A detailed kinetic model is required to be able to describe all the reactions inside the reactor. However, in literature most models use only a reaction rate for CO and a fitted product spectrum\cite{1,2,6,8,14} and do not offer a full kinetic model. The most detailed kinetic model that is fully available, including values for the kinetic parameters, is the 2007 model by Visconti\cite{24}. This model is based on the carbide theory, but also considers the O-rejection only via the $H_2O$ pathway as used in the H-assisted CO dissociation.

The detail in the model by Visconti\cite{24} and the availability of the necessary values for the kinetic parameters are in this project of more importance than the pathway of the CO dissociation and the formation of the CH$_2$ radicals. Therefore, the kinetic model as proposed by Visconti in his 2007 paper will be used as model in this project.

Using a membrane in the PBR setup enables the possibility to influence the reaction by adding or subtracting molecules from the reactor. In detail the addition of $H_2$ along the reactor axis or the subtraction of $H_2O$ have been considered. The reasons will be discussed in the following paragraphs.

CO strongly adsorbs on the surface of the cobalt catalyst, impeding the adsorption of hydrogen\cite{26}. The adsorption of $H_2$ on the surface is driven by the partial pressure of $H_2$. This adsorption can thus be improved by a high concentration of $H_2$ in the gas feed. A high concentration of $H_2$ also lessens the amount of cokes formed, because the stoichiometry of the general FTS reaction, see Equation 1.1, indicates that a $H_2/CO$ ratio of two is favored for the formation of paraffins. Therefore, it is good to investigate the behavior if the $H_2/CO$ ratio is kept constant, by adding $H_2$ along the reactor axis. However, the formation of methane is also increased with a higher concentration of $H_2$, this has to be kept in mind while optimizing the reactor, and a too high $H_2$ concentration should be avoided.

Three reasons for the removal of $H_2O$ from the reactor will be discussed. Since it is the main byproduct of the reaction, it is one of the most abundant components in the reactor. This
can have a negative effect on the partial pressure and thus the reaction rate, it can have a poisonous effect on the catalyst and it can perform the water gas shift (WGS) reaction, which can distort the syngas composition and produce CO\textsubscript{2} as byproduct.

Due to the presence of H\textsubscript{2}O in the gas mixture it decreases the partial pressures of H\textsubscript{2} and CO. Since the adsorption rates of H\textsubscript{2} and CO are functions of their partial pressures, lowering the partial pressures of these components lowers these adsorption rates. This has a negative effect on the overall reactor performance. If water could be removed alongside the reactor axis, just after formation, there will be a positive effect on the overall reaction rate, because the partial pressures of H\textsubscript{2} and CO will remain higher. Therefore, it is advised to investigate the reactor performance if water is removed from the reactor during the reaction.

The influence of water on the CO conversion by a cobalt catalyst depends on the support used. It can be either negative, positive and small or negligible\textsuperscript{[6]}. An alumina supported cobalt catalyst seems to be less sensitive to the negative effect if the Co loading is higher\textsuperscript{[13]}. However, other research shows a strong positive effect of water on the CO conversion\textsuperscript{[14]}. This influence is still under investigation and it seems to be really depending on a lot of different parameters. Because of this disagreement in the literature it is good to monitor the effect of H\textsubscript{2}O on the specific catalyst and if needed subtract H\textsubscript{2}O to improve the catalytic function of the catalyst.

Lastly, for catalysts that have a high activity for the WGS reaction, removing water can also help the overall reaction\textsuperscript{[19]}. At the low temperatures used in the FTS, the WGS equilibrium shifts to the CO\textsubscript{2} side of the reaction. This uses the CO from the reactants and forms more H\textsubscript{2}, which results in high H\textsubscript{2}/CO ratios inside the reactor. This in turn can lead to a higher formation of CH\textsubscript{4} and lower hydrocarbons. Removing H\textsubscript{2}O from the system shifts the equilibrium to the CO side, using formed CO\textsubscript{2} from the FTS and some of the H\textsubscript{2} to form more CO. This means that the undesired side product CO\textsubscript{2} can be used to form hydrocarbons and increase the overall conversion. However, the Co and Ru catalyst show no activity for the WGS reaction, so this effect can be neglected for this particular project.

Summarizing, this project aims for a dynamic reactor model that in detail describes the production of synthetic hydrocarbons in catalytic FTS in a PBMR. The model includes a full kinetic scheme of the different reactions towards paraffins and olefins, as well as a membrane unit that serves to distribute hydrogen into or remove water out of the reactor.

The main goal of this project is to perform a numerical study with this model on the influence of the addition of H\textsubscript{2} to, or the subtraction of H\textsubscript{2}O from a FTS reactor, and to compare this with an experimental study performed by CSIC. With the model different reaction conditions will be simulated to obtain a full dataset.
Chapter 3

Theory

3.1 Reactor model

A dynamic 1D reactor model, based on the work due to Smit\cite{21}, has been used to account for all relevant transport phenomena in the reactor, such as a per-component description for convection, diffusion, axial dispersion, chemical reactions and addition/extraction through membrane walls. Additionally, the model includes an energy balance. The mass and energy balance for the gas phase are given in Equation 3.1-3.5, following the description by Tiemersma\cite{22}. To solve the equations, the Danckwerts boundary condition has been used for the inlet and a gradient-free condition is provided at the outlet (see Eq. 3.2 and Eq. 3.4). Additionally, an overall balance was used to secure mass conservation (see Eq. 3.5).

\[
\varepsilon_g \rho_g \frac{\partial \omega_i}{\partial t} = -\frac{\partial \rho_g u_g \omega_i}{\partial z} + \frac{\partial}{\partial z} \left( \rho_g D_{ax} \frac{\partial \omega_i}{\partial z} \right) + n_i a_s + \phi''_{m,i} a_m 
\]  (3.1)

\[
- D_{ax} \rho_g \frac{\partial \omega_i}{\partial z} \bigg|_{z=0} + \rho_g u_g \omega_i \bigg|_{z=0} = \phi''_{inlet,i} \frac{\partial \omega_i}{\partial z} \bigg|_{z=L} = 0 
\]  (3.2)

\[
\varepsilon_g \rho_g C_{p,g} \frac{\partial T}{\partial t} = -C_{p,g} \rho_g u_g \frac{\partial T}{\partial z} + \frac{\partial}{\partial z} \left( \lambda_g \frac{\partial T}{\partial z} \right) + \sum_{i=1}^{N} n_i a_s H_i + \sum_{i=1}^{N} \phi''_{m,i} a_m H_i + \alpha_{b\rightarrow w} a_w (T - T_w) 
\]  (3.3)

\[
- \lambda_g \frac{\partial T}{\partial z} \bigg|_{z=0} + \rho_g u_g C_{p,g} T \bigg|_{z=0} = \sum_{i=1}^{N} H_i \phi''_{inlet,i} \frac{\partial T}{\partial z} \bigg|_{z=L} = 0 
\]  (3.4)

\[
\varepsilon_g \frac{\partial \rho_g}{\partial t} = -\frac{\partial \rho_g u_g}{\partial z} - \phi''_{m,\text{tot}} a_m \quad \text{with} \quad a_m = \frac{4d_i}{d_o^2 - d_i^2} 
\]  (3.5)

The model incorporates dynamic grid size and time step adaptation to reduce calculation time while maintaining the desired accuracy.

3.2 Kinetic model

The kinetic model for the FTS over the Co/Al\(_2\)O\(_3\) catalyst has been implemented according to Visconti\cite{24}. The reaction scheme is given in Table 3.1, with the reaction rates and supplementary notes. The two main assumptions for this model are:
CHAPTER 3. THEORY

<table>
<thead>
<tr>
<th>Step</th>
<th>Elementary reaction</th>
<th>Kinetic expression</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \text{H}_2 + 2* \rightarrow 2\text{H}^* )</td>
<td>( r_{\text{H}<em>2} = k</em>{\text{H}<em>2}P</em>{\text{H}<em>2}\frac{\partial}{\partial P</em>{\text{H}_2}} )</td>
<td></td>
</tr>
<tr>
<td>2a.</td>
<td>( \text{CO} + * \rightarrow \text{CO}^* )</td>
<td>( r_{\text{M}} = k_{\text{M}}P_{\text{CO}}\frac{\partial}{\partial P_{\text{CO}}} )</td>
<td>Step 2a is rate</td>
</tr>
<tr>
<td>2b.</td>
<td>( \text{CO}^* + * \rightarrow \text{C}^* + \text{O}^* )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2c.</td>
<td>( \text{C}^* + \text{H}^* \rightarrow \text{CH}^* + * )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2d.</td>
<td>( \text{CH}^* + \text{H}^* \rightarrow \text{CH}_2^* + * )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2e.</td>
<td>( \text{O}^* + \text{H}^* \rightarrow \text{OH}^* + * )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2f.</td>
<td>( \text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O} + 2* )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>( \text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3^* + * )</td>
<td>( r_{\text{IN}} = k_{\text{IN}}\frac{\partial}{\partial P_{\text{CH}_2}} )</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>( \text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4^* + 2* )</td>
<td>( r_{\text{CH}<em>4} = k</em>{\text{CH}<em>4}\frac{\partial}{\partial P</em>{\text{CH}_3}} )</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>( \text{R}_n^* + \text{CH}<em>2^* \rightarrow \text{R}</em>{n+1}^* + \text{CH}_2^* )</td>
<td>( r_{\text{G,n}} = k_{\text{G}}\frac{\partial}{\partial P_{\text{R}_n}} )</td>
<td>( n : 1 \rightarrow 49 )</td>
</tr>
<tr>
<td>6.</td>
<td>( \text{R}<em>n^* + \text{H}^* \rightarrow \text{P}</em>{n} + 2* )</td>
<td>( r_{\text{P,n}} = k_{\text{P}}\frac{\partial}{\partial P_{\text{R}_n}} )</td>
<td>( n : 2 \rightarrow 50 )</td>
</tr>
<tr>
<td>7.</td>
<td>( \text{R}_n^* \leftrightarrow \text{Q}_n^* + \text{H}^* )</td>
<td>( r_{\text{Q,n}} = k_{\text{Q}<em>{n, dx}}\frac{\partial}{\partial P</em>{\text{R}<em>n}} - k</em>{\text{Q}<em>{n, sx}}x</em>{\text{Q}<em>n}\frac{\partial}{\partial P</em>{\text{H}}} )</td>
<td>( n : 3 \rightarrow 50 )</td>
</tr>
<tr>
<td>8.</td>
<td>( \text{R}_2^* \leftrightarrow \text{C}_2\text{H}_4^* + \text{H}^* )</td>
<td>( r_{\text{Q,2}} = k_{\text{Q}<em>{2, dx}}\frac{\partial}{\partial P</em>{\text{R}<em>2}} - k</em>{\text{Q}<em>{2, sx}}x</em>{\text{Q}<em>2}\frac{\partial}{\partial P</em>{\text{H}}} )</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Reaction scheme of the FTS over a Co/Al\(_2\)O\(_3\) catalyst\([24]\).

- The adsorption of CO on the catalytic surface is assumed to be rate determining for reaction 2a to 2f.
- The reactions for the formation of the intermediates, the paraffins and the olefins are assumed to be independent of the length of the chain.

The free sites in Table 3.1 are given by the symbol *, furthermore the symbol \( P_n \) and \( Q_n \) are used for the corresponding paraffin and olefin of length \( n \) up to \( C_{50} \). The reaction rates are all in mmol per second per gram catalyst. Reaction 7 and 8 are in equilibrium with the liquid surrounding the catalyst pellet. The subscript \( Q_n \) represents the \( \alpha \)-olefin with length \( n \), in the liquid surrounding the catalyst and is obtained via the combination of the vapor pressure, calculated by Yaws’ handbook\([27]\) of the component and Raoult’s law, see Equation 3.6.

\[
x_{i}P_{\text{vap},i} = y_{i}P_{\text{tot}} = P_{i} \quad \rightarrow \quad x_{i} = \frac{P_{i}}{P_{\text{vap},i}} \quad (3.6)
\]

The kinetic model follows the carbide theory: hydrogen adsorbs irreversibly as dissociated hydrogen to the catalytic surface, while CO first adsors as molecule and then dissociates on the surface (see reaction 2b). Oxygen elimination takes only place via reaction 2e and 2f and thus all the reacted oxygen leaves the reactor as water. Different rates are assumed for the first paraffin and first olefin product, methane and ethylene, see reaction 4 and reaction 8.

The kinetic parameters are also taken as suggested by Visconti\([24]\), see Table 3.2. For the first two reactions an activation energy is introduced, to account for the temperature dependency of these reactions.

The first two kinetic constants, \( k_{\text{H}_2} \) and \( k_{\text{M}} \), are calculated using an Arrhenius equation. However, the exact equation has not been given in the paper by Visconti in 2007 and calculating the kinetic constants using the regular Arrhenius equation at 503K yields kinetic
### Table 3.2: Kinetic parameters of the FTS over a Co/Al₂O₃ catalyst

<table>
<thead>
<tr>
<th>Parameter, Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{H_2,0}$</td>
<td>$3.77 \cdot 10^{-5}$ mmol s⁻¹g⁻¹bar⁻¹</td>
</tr>
<tr>
<td>$E_{H_2}$</td>
<td>$267.30$ kJ mol⁻¹</td>
</tr>
<tr>
<td>$k_{M,0}$</td>
<td>$1.36 \cdot 10^{-3}$ mmol s⁻¹g⁻¹bar⁻¹</td>
</tr>
<tr>
<td>$E_M$</td>
<td>$177.44$ kJ mol⁻¹</td>
</tr>
<tr>
<td>$k_{IN}$</td>
<td>$3.34 \cdot 10^{-1}$ mmol s⁻¹g⁻¹</td>
</tr>
<tr>
<td>$k_{CH_4}$</td>
<td>$1.61$ mmol s⁻¹g⁻¹</td>
</tr>
<tr>
<td>$k_G$</td>
<td>$2.26 \cdot 10^{-1}$ mmol s⁻¹g⁻¹</td>
</tr>
<tr>
<td>$k_{P_n}$</td>
<td>$1.32 \cdot 10^{-1}$ mmol s⁻¹g⁻¹</td>
</tr>
<tr>
<td>$k_{Q_n,dx}$</td>
<td>$5.54 \cdot 10^{-3}$ mmol s⁻¹g⁻¹</td>
</tr>
<tr>
<td>$k_{Q_n,sx}$</td>
<td>$3.63$ mmol s⁻¹g⁻¹bar⁻¹</td>
</tr>
<tr>
<td>$k_{Q_2,sx}$</td>
<td>$1.64 \cdot 10^2$ mmol s⁻¹g⁻¹bar⁻¹</td>
</tr>
</tbody>
</table>

This adjusted equation is an Arrhenius equation evaluated around a reference temperature, in this case 503K. Assumed is that both kinetic constants, $k_{H_2}$ and $k_M$, are calculated using this equation. Therefore, Equation 3.7 is used in the model to calculate the first two kinetic constants at a different temperature. Assumed is that this equation is valid between 200°C and 230°C.

The kinetic model is solved for an isothermal packed bed reactor, using a set of ordinary differential equations, combined with a set of algebraic equations and the catalytic site balance. These equations are shown in Equation 3.8-3.11. In these reactions $i$ describes all general reactants and products, $j$ describes all the catalytic adsorbed species, $k$ specifies all the reactions and $\alpha$ describes all the stoichiometric coefficients for species $i$ or $j$ in the $k^{th}$ reaction.

\[
\frac{dF_i}{dW_{cat}} = \sum_{k=1}^{NR} (\alpha_{i,k}r_k) \quad (3.8)
\]

\[
W_{cat} = 0, F_i = F_{i,0} \quad (3.9)
\]

\[
0 = \sum_{k=1}^{NR} (\alpha_{j,k}r_k) \quad (3.10)
\]

\[
1 = \theta_s + \theta_H + \theta_{CH_2} + \sum_{n=1}^{NP} \theta_{R_n} \quad (3.11)
\]

To obtain a solution for the different catalytic sites ($H^*, CH_2^*, n R_n^*$ and the free sites) the two algebraic equations (Equation 3.10 and 3.11) are used. The (pseudo) steady state
approximation is assumed for all the catalytic adsorbed species, see Equation 3.10, and Equation 3.11 is the site balance. This is the balance that all fractions should add up to unity.

To solve the algebraic equations of the kinetic model a Newton-Raphson non-linear equation (NLE) solver is used. This solver solves the combination of $n+2$ equations following from Equation 3.10 to obtain the solutions for $H^*$, $\text{CH}_2^*$ and $n\text{ R}_n^*$. The solution for the free sites fraction is obtained from a rewritten version of Equation 3.11. The tolerance in the Newton-Raphson solver is set to $10^{-12}$.

Using only the NLE solver, an instantaneous solution for the catalytic site fractions and thus for all the reaction rates can be found. This enables the possibility of an easy and fast comparison between a preliminary solution and literature. The solution, obtained from only the NLE solver, has been tested in the two reaction rates for the consumption of $\text{H}_2$ and CO. When compared to literature, reaction rates in the same order of magnitude have been found.

### 3.3 Physical properties

The database of physical properties, based on the work by Daubert and Danner\cite{7}, that already has been present in the model is insufficient to describe all the properties of all the reaction products in the FTS. Therefore, this database has been complemented with the use of the online edition of Yaws’ handbook\cite{27} up to the C$_{40}$ components. The relevant physical properties are the gas viscosity, the gas conductivity, the gas heat capacity and the vapor pressure. For the first three properties a general polynomial has been used as function of the temperature, see Equation 3.12.

$$\text{Physical Property} = A + BT + CT^2 + DT^3 + ET^4$$ (3.12)

The vapor pressure has been calculated using the Antoine equation, see Equation 3.13.

$$P_{vap} = 10^{[A - \frac{B}{T + C}]}$$ (3.13)

All paraffins and olefins have been calculated using Yaws’ handbook, while the properties of the components CO, $\text{H}_2$, $\text{H}_2\text{O}$ and $\text{N}_2$ have been calculated using Daubert and Danner. For the gas viscosity and gas conductivity Equation 3.14 has been used and for the gas heat capacity Equation 3.15 has been used.

$$\text{Physical Property} = \frac{AT^B}{1 + \frac{C}{T} + \frac{D}{T^2}}$$ (3.14)

$$C_p = A + B \left( \frac{C}{T} \right)^2 + D \left( \frac{E}{\sinh \left( \frac{C}{T} \right)} \right)^2$$ (3.15)

Using two sources for the physical properties could bring an extra error in the model. This error has been minimized by using as much data as possible from one source. In this case, all the hydrocarbons are calculated using Yaws’ handbook and only four components are calculated using Daubert and Danner. With great care has been ensured that all components
have been calculated in the same units throughout the whole model. A simple conditional statement has been incorporated in the model that lets the model select the proper equation to calculate the physical properties for the component. This way all the physical properties could be calculated correctly for all the relevant hydrocarbons up to n=40.

3.4 Membranes

The reactor consists of two compartments: an inner tube in an outer shell, as shown in Figure 3.1. The inner tube can be placed within the reactor shell and a sealing can be placed to prevent leakage between the two compartments. Rubber O-rings are used as sealing rings.

![Figure 3.1: Sketch of the reactor: an inner tube in an outer shell; the wall between the tube and the shell can be used as membrane wall.](image)

The reactor can be used in three configurations:

- A stainless tube as inner part;
- A Pd-Ag membrane as inner part to provide the reactor with hydrogen;
- A membrane as inner part to subtract water from the reactor (different types).

The membrane flux is calculated in the model first as the molar flux in mol/m$^2$/s and then for that component transcribed to a mass flux in kg/m$^2$/s. In the source term, after the total mass flux is corrected per component for the reacted molecules, the membrane mass flux, multiplied with the specific area of the membrane wall, is added (or subtracted).

The theory of the different membrane fluxes will be discussed in the following two paragraphs.

3.4.1 Hydrogen Membranes

To optimize the H$_2$/CO ratio in the reactor a Pd-Ag membrane, manufactured by TECNALIA, is used to selectively feed hydrogen along the reactor axis. The membrane flux can be calculated using Sieverts law, see Equation 3.16

$$J_{H_2} = \frac{Q_{Pd}}{d_{mem}} \left( p_{H_2,tube}^{n_{mem}} - p_{H_2,shell}^{n_{mem}} \right)$$

(3.16)

In which $Q_{Pd}$ is defined by the following equation:

$$Q_{Pd} = Q_{Pd,0} \exp \left[ -\frac{E_{act,Pd}}{RT} \right]$$

(3.17)
CHAPTER 3. THEORY

Table 3.3: Membrane parameters for a Pd-Ag membrane.

<table>
<thead>
<tr>
<th>Membrane parameters</th>
<th>Value by Patil\textsuperscript{[18]}</th>
<th>Value by Coenen\textsuperscript{[4]}</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{Pd,0}$</td>
<td>$1.7 \cdot 10^{-10}$</td>
<td>$6.135 \cdot 10^{-8}$</td>
<td>mol m$^{-1}$ s$^{-1}$ Pa$^{-n_{mem}}$</td>
</tr>
<tr>
<td>$E_{act,Pd}$</td>
<td>6.17</td>
<td>7.799</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$d_{mem}$</td>
<td>$4.5 \cdot 10^{-6}$</td>
<td>$4.8 \cdot 10^{-6}$</td>
<td>m</td>
</tr>
<tr>
<td>$n_{mem}$</td>
<td>0.72</td>
<td>0.50</td>
<td>-</td>
</tr>
</tbody>
</table>

For validation the same values were used as given in the thesis of Patil\textsuperscript{[18]}, see Table 3.3. In the DEMCAMER project new values were obtained by Coenen\textsuperscript{[4]}. Coenen has performed activation energy experiments on the new Pd-Ag membranes and found a deviation of the values used by Patil ten years ago. Since the PBMR reactor is equipped with the same type of Pd-Ag membranes, the values of Coenen will be used in further modeling. However, the range of temperatures investigated by Coenen is 300° C - 500° C, while the operation temperature of the FTS is between 200° C and 280° C.

At this lower temperature, hydrogen embrittlement starts to play a role. This phenomenon occurs at temperatures below 300° C and high pressures of hydrogen\textsuperscript{[9,17]}. To avoid this problem the operating pressure for the FTS has been reduced to 10 bar for the PBMR experiments. Furthermore, TECNALIA tries to solve this problem by improving the membranes, by increasing the Ag content in the Pd-Ag alloy.

3.4.2 Water Membranes

To remove water from the reactor different types of membranes can be used. In the DEMCAMER project several different membranes have been produced to remove H$_2$O from the reactor, such as different zeolite membranes and carbon membranes. A NaA zeolite membrane and a carbon membrane have been used within the setup, but without success. The first membrane consists of a NaA zeolite deposited over the inner part of an Al$_2$O$_3$ tube. This membrane has yielded no data, since leaks have been observed between the outer and inner sides due to a heterogeneous zeolite layer. The carbon membrane has yielded a conversion of 3% and thus the main focus of this model has shifted towards the H$_2$ addition to the reactor.

12 Modelling of a packed bed membrane reactor for Fischer Tropsch synthesis
Chapter 4

Experimental

The experimental part of this thesis is divided in two parts:

- The synthesis of the Ru-catalyst;
- The experiments with the PBMR setup.

During this project a Ru-B/TiO₂ catalyst has been synthesized and used in the packed bed reactor. Furthermore experiments have been performed with the PBMR setup present at CSIC. These experiments vary from membrane flow experiments to Fischer Tropsch synthesis in the membrane setup.

4.1 Catalyst synthesis

Both the Co/Al₂O₃ and the Ru-B/TiO₂ catalyst have been investigated for the FTS in a PBR. For the PBMR experiments only the Ru catalyst has been used. The Co catalyst has to be activated at 450°C, while the Ru catalyst has to be activated at 250°C. This activation is a reducing under H₂ and cannot be performed ex situ, since the transport to the reactor through the air would oxidize the catalyst. As described in paragraph 3.4 the membranes are sealed with rubber O-rings. With a melting temperature of 325°C this sealing cannot withstand the high temperature at which the Co catalyst has to be activated. However, it can withstand the temperature at which the Ru catalyst has to be activated and thus only the Ru catalyst has been used in the PBMR experiments.

The Ru-B/TiO₂ catalyst has been synthesized during this project. This catalyst has been developed within CSIC to produce a stable, active catalyst for the FTS. The catalyst is based on a Ru/TiO₂ catalyst, with an active content of 3 wt% of Ru. This catalyst however deactivates over time[3] and B is added, in a 1:1 mole ratio with Ru, to stabilize the catalyst.

The following procedure has been followed to synthesize 10g of Ru-B/TiO₂ catalyst:

1. Preparation of the TiO₂

   (a) Calcinate 10g TiO₂ at 450°C (10°C/min) for 3h.
2. Preparation of the Ru-Solution
   (a) 3 wt% of Ru equals 0.30g.
   (b) Weigh 0.9400g of RuNO(NO\textsubscript{3})\textsubscript{3} (precursor).
   (c) Dissolve the precursor in 33.3 mL water (general rule: use 10 mL water per 3g TiO\textsubscript{2}).
3. Preparation of the Ru/TiO\textsubscript{2}
   (a) Impregnate the TiO\textsubscript{2} with the Ru-solution, via addition of the solution to the solids by Pasteur pipet.
   (b) Dry the solution for 12h (overnight) on ambient temperature (25°C).
   (c) Calcinate the product at 450°C (10°C/min) for 3h.
4. Preparation of the B-solution
   (a) Ru/B molar ratio is 1:1.
   (b) 0.1883g B(OH)\textsubscript{3} is needed (precursor).
   (c) 1.5 mL water per 1g of solid Ru/TiO\textsubscript{2} (calculate the water needed from solid weight).
   (d) Dissolve the B-precursor in the water.
5. Preparation of the Ru-B/TiO\textsubscript{2}
   (a) Impregnate the Ru/TiO\textsubscript{2} with the B-solution, via addition of the solution to the solids by Pasteur pipet.
   (b) Dry the solution for 12h (overnight) on ambient temperature (25°C).
6. Sieving of the catalyst
   (a) Sieve the solid product (catalyst) with 0.250mm and 0.300mm sieves.
   (b) Press the remaining solids to a tablet, using a hydraulic press set for 7 ton pressure and leave for 10 minutes.
   (c) Crush the solids with a mortar and pestle and repeat the sieving.

The obtained catalyst has been characterized by CSIC with X-ray diffraction for verification and the catalyst has been used in the PBMR setup. The results will be discussed in paragraph 5.3.

4.2 Reactor experiments

The reactor experiments have been performed with a packed bed membrane reactor, situated at CSIC in Spain. This reactor consists of an outer tube of 25cm length and with a diameter of 2cm. The inner tube, which can either be a membrane tube or a stainless steel tube, has a diameter of 0.8cm and a wall thickness of 0.2cm. This tube can be inserted in the outer shell and in this configuration has been sealed with rubber O-rings. The catalytic bed inside the inner tube has a bedheight of 6cm. This is correlated with the length of the membrane part.
of the Pd-Ag membranes. The dismantled reactor is shown in Figure 4.1.

Once assembled, the reactor is connected to the setup and hung inside the oven inside a hotbox. The PFD of the setup is given in Figure 4.2. The full setup is equipped with five PID controllers: three for the temperature control and two for the pressure control. The temperature of the oven, of the hotbox and of the outlet flow can be controlled as well as the pressure inside the tube and inside the shell. With simple two-way valves the flow is distributed from the lines to either the shell or the tube. The flow through the lines is controlled by a touch-screen display on which the flow in mL/min can be adjusted. To measure the flow of the outlets an Optiflow 570, a digital flowmeter, has been used to measure the flow in mL/min. Via a two-way valve the outlet flows could be sent to either the GC or the vent.

The experiments have been performed with four variables: pressure, temperature, $\text{H}_2/\text{CO}$ ratio and GHSV. With these four variables a complete dataset for the behaviour of the Ru-B/TiO$_2$ catalyst in the reactor has been constructed. Experiments have been performed with the reactor in the two settings:

- A stainless tube present as inner tube;
- A membrane tube present as inner tube.

With the stainless tube present the same configuration has been kept and thus the results of these experiments are comparable with the membrane experiments. First a base case has been established and a base dataset has been obtained with the stainless tube present in the reactor. After the base dataset the membrane tube has been implemented in the reactor and
CHAPTER 4. EXPERIMENTAL

Figure 4.2: The PFD of the packed bed reactor setup.

experiments with the membrane have been performed. All experiments were started using the following procedure, after which the experiments would commence:

- Connect the reactor to the setup.
- Put 25 mL/min N\textsubscript{2} over the reactor (shell) to test for leakages.
- Increase the flow to 100 mL/min N\textsubscript{2}.
- Test the membrane side for leakages.
- Increase the temperature for the reactor to the setpoint (200-280\degree C) and the hotbox to 160\degree C.

The outlet flow of the reactor has been measured by a GC Varian CP3800, with two columns: a packed Hayesep Q column, connected to a thermal conductivity detector and a capillary Rtx-1 column, connected to a flame ionization detector. The first column is used to detect and analyze H\textsubscript{2}, CO and CO\textsubscript{2} and the second column is used to detect and analyze the hydrocarbons (C\textsubscript{1} to C\textsubscript{13}). The results of the experiments are grouped in selectivities to certain hydrocarbon fractions, olefin over paraffin ratios and the conversion.

The experiments have been performed by the people from CSIC. In order to obtain a good dataset several variables have been varied to describe the FTS within process conditions in industry. The experimental conditions have been varied in the following ranges: T = 200-280\degree C, P = 5-30 bar, GHSV = 5,000-20,000 m\textsubscript{L}\textsubscript{H\textsubscript{2}+CO (STP)}/g\textsubscript{cat} / h and H\textsubscript{2}/CO ratio = 2-4. For the different catalysts different settings have been used, the full set is shown in Appendix A.
Chapter 5

Results

5.1 Validation

The implementation of the transport equations and the kinetic model by Visconti\textsuperscript{[24]} has
been validated. Every part was successfully validated and the procedures and results will be
discussed in the following paragraphs.

5.1.1 Reactor model

The PBMR model has been validated by simulating a simple first order kinetic reaction and
comparing the result to the exact solution, as proposed by Tiemersma\textsuperscript{[22]} in his thesis. The
full model is used in the simulations, thus apart from the reaction also all relevant transport
phenomena (as described in paragraph 3.1) are solved over the full length of the reactor.
First an isothermal, irreversible first order reaction has been used with constant properties,
see Table 5.1. All other relevant physical properties were given by Daubert and Danner\textsuperscript{[7]}.
After the successful validation of the reaction part of the model a non-isothermal reaction, with
the same properties, has been used for validation so that also the heat transport equation
could be verified.

The following cases have been investigated and validated:

- An isothermal case, with a fixed rate constant;
- An isothermal case, with an Arrhenius type dependent rate constant;

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_{in}$</td>
<td>1.5 bar</td>
<td>$x_{A, in}$</td>
<td>0.15</td>
</tr>
<tr>
<td>$T_{in}$</td>
<td>800°C</td>
<td>$x_{N_2, in}$</td>
<td>0.85</td>
</tr>
<tr>
<td>$\rho_{ug}$</td>
<td>1 kg/m(^2)/s</td>
<td>$M_{av}$</td>
<td>0.015 kg/mol</td>
</tr>
<tr>
<td>L</td>
<td>0.25 m</td>
<td>$\varepsilon_s/\tau_s$</td>
<td>0.3</td>
</tr>
<tr>
<td>$d_p$</td>
<td>0.003 m</td>
<td>D</td>
<td>$1\cdot10^{-3}$ m(^2)/s</td>
</tr>
<tr>
<td>$E_{act}$</td>
<td>100 kJ/mol</td>
<td>$\Delta H$</td>
<td>10 kJ/mol</td>
</tr>
<tr>
<td>$\lambda_{eff}$</td>
<td>10 W/m/K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1: Model settings for the validation of the reactor model.
A non-isothermal case, with an Arrhenius type dependent rate constant.

The isothermal case has been validated with the following reaction rate, see Equation 5.1. The isothermal case with the Arrhenius type dependent rate constant and the non-isothermal case have been validated with the reaction rate given in Equation 5.2. The validations have been performed with different kinetic constants to describe both fast and slow reactions, the used constants are also given in the equations.

\[ r_A = k_0 c_A \text{ with } k_0 = [10, 75, 150, 300, 600, 1200, 2400, 4800] \text{ s}^{-1} \] (5.1)

\[ r_A = k_0 \exp \left[ -\frac{E_{\text{act}}}{RT} \right] c_A \text{ with } k_0 = [150, 300, 600, 1200, 2400, 4800] \cdot 10^4 \text{ s}^{-1} \] (5.2)

The effectiveness factor has been taken into account for all cases using the same correlations used by Tiemersma \[^{[22]}\] in his thesis. The Thiele modulus has been calculated using Equation 5.3.

\[ \phi = \frac{d_p}{6} \sqrt{\frac{k}{D}} \] (5.3)

The effectiveness factor for the isothermal case has been calculated using Equation 5.4 and the effectiveness factor for the non-isothermal case has been calculated using an empirical equation that takes into account the reaction heat, see Equation 5.5.

\[ \eta = \frac{3\phi - \tanh(3\phi)}{3\phi^2 \tanh(3\phi)} \] (5.4)

\[ \eta = \exp \left[ 0.14\phi \left( -\frac{\Delta H_{\text{eff}} c_A E_{\text{act}}}{\lambda_{\text{eff}} T} \right)^{1.6} \right] - 1 + \frac{\tanh(\phi)}{\phi} \] (5.5)

The validation has been successful for all the investigated cases. For the first two cases only the development of the molar fraction of component A along the reactor axis is relevant. These figures are shown in Figure 5.1a and Figure 5.1b. The analytical solution is plotted as line versus the results from the model, which are given as the squares. Only one in five squares is shown for layout reasons.

As can be seen in Figure 5.1, the model is in good agreement with the analytical solution. A root mean square deviation (RMSD) has been calculated for all different kinetic constants. The RMSD varies between 5.0·10^{-4} and 1.5·10^{-3}, with an average of 9.5·10^{-4} for the isothermal case. For the isothermal case with the Arrhenius dependency the RMSD varies between 5.1·10^{-4} and 1.7·10^{-3}, with an average of 1.0·10^{-3}. The average RMSDs are less than 1.0% of the maximum mole fractions calculated and the conclusion can be drawn that the model is in good agreement with the analytical solution. Therefore, the reactor model is suitable to solve first order isothermal reactions.

As for the non-isothermal case a \( \Delta H \) of 10 kJ/mole has been used, to describe the non-isothermal reaction. For this reaction both the temperature profile and the concentration profile along the reactor axis are relevant. These figures are shown in Figure 5.2.
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Figure 5.1: Validation of the reactor model for the isothermal cases.

(a) Isothermal case.  
(b) Isothermal case with Arrhenius dependency.

Figure 5.2: Validation of the reactor model for the non-isothermal cases.

(a) Mole fraction along the reactor axis.  
(b) Temperature profile along the reactor axis.
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As can be seen in Figure 5.2, the model can predict both the behavior of the chemical species and the temperature development alongside the reactor axis. The RMSD for the mole fraction varies between $1.7 \times 10^{-4}$ and $1.1 \times 10^{-3}$, with an average of $5.8 \times 10^{-4}$. For the temperature the RMSD varies between $2.3 \times 10^{-2}$ and $1.9 \times 10^{-1}$, with an average of $1.0 \times 10^{-1}$. Although the RMSD for the temperature is higher, the calculated values in this case are also higher. Both average RMSDs are less than 1.0% of the range of observed values. The results from the numerical model match the outcome of the analytical solutions very well.

It can be concluded that the model is correctly validated for both the isothermal as the non-isothermal case and that the model can be used in the further modeling of the FTS in this PBMR model.

5.1.2 Kinetic sites

The results of the kinetic model (using only the NLE solver, as discussed in paragraph 3.3) have been compared with results obtained from the literature [8,14,15,23]. The reaction rate given by the model is in the same order of magnitude as reaction rates observed in literature [8,14,15,23], see Figure 5.3, and a similar trend for the paraffin formation has been observed, see Figure 5.4.

Since the obtained results are only the results of the kinetic sites, obtained with the Newton-Raphson solver, and not the results of a full reactor model a less accurate result should be obtained. Figure 5.4 shows the same trend for the paraffin formation with different H$_2$/CO ratios.
The reactor initially contains a mix of 50% H₂ and 50% N₂, the flow in the shell is pure hydrogen and the flow through the membrane is 100% selective towards hydrogen. For the

5.1.3 Membranes

The membrane section of the model has been validated in a two-step procedure. First a constant molar flow through the membrane has been taken to check if the implementation of the membrane fluxes has been done correctly. After this, Sieverts law has been implemented, as discussed in section 3.3.1, and it has been checked if this function of the temperature and pressures has also correctly been implemented.

The reactor initially contains a mix of 50% H₂ and 50% N₂, the flow in the shell is pure hydrogen and the flow through the membrane is 100% selective towards hydrogen. For the

(a) Product distribution plot by Visconti[26].

(b) Product distribution plot by the model.

Figure 5.4: Comparison of poduct distribution plots for the paraffin formation.

(a) Product distribution plot by Visconti[24].

(b) Product distribution plot by the model.

Figure 5.5: Comparison of the full poduct distribution plots.

ratios. Thus the formation of the paraffins in the kinetic model is in good accordance with the results Visconti[24,26] got with his (full) model. When looking to both the olefin and paraffin formation, see Figure 5.5, it can be seen that the characteristic olefin peak at n=3 is not visible in the model plot. This is due to the fact that the olefin reactions can not be properly simulated using only the kinetic model, since the liquid fraction of the olefins surrounding the catalytic particles has to be taken into account, in contrast to the full model results obtained by Visconti.
fixed flux test cases, different fluxes have been taken to check for large and small membrane fluxes. For the Sieverts law different pressures for the membrane side have been taken to change the membrane flux. The results to both validation methods are shown in Figure 5.6, in which the analytical solution is plotted as lines versus the result from the model as squares.

As can be seen in Figure 5.6 the molar fraction of hydrogen in the reactor is following precisely the analytical solution. The calculated RMSD for the fixed flux varies between $1.9 \times 10^{-5}$ and $7.8 \times 10^{-4}$, with an average of $3.2 \times 10^{-4}$. For the flux calculated using Sieverts law, the RMSD varies between $9.9 \times 10^{-5}$ and $2.6 \times 10^{-4}$, with an average of $2.1 \times 10^{-4}$. With a deviation of less than 0.1% of the range of observed values, it can be concluded that the model is following the analytical solution almost perfectly and that the membrane section of the model has been implemented correctly in the full reactor model.

5.2 Co/Al$_2$O$_3$ catalyst

After the validation of the different parts of the model, the full 1D reactor model first has been used with the Co/Al$_2$O$_3$ kinetics. The results from the model have been compared with the experiments by Visconti$^{[26]}$ and with the full dataset obtained at CSIC with the experimental setup (see Appendix A for the experimental conditions).

5.2.1 Kinetics

The kinetic parameters, as described in paragraph 3.3, have been used to see if the model is able to describe the experiments without any alternative optimization. To reduce computational time the model has been limited to calculate the products up to the C$_{25}$ fraction.

The paper by Visconty from 2007 does not contain data that allows for a detailed comparison between the experimental results obtained by him and the experimental results obtained by CSIC. Therefore the CO conversion figures from his 2011 paper are used. The experimental data obtained from these figures, together with the experimental conversions obtained at CSIC are shown in Figure 5.7.

Figure 5.6: Validation of the membrane section of the reactor model.
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At different GHSVs.

At different pressures.

At different ratios.

At different temperatures.

Figure 5.7: Comparison of the experimental conversion by Visconti\cite{26} and by CSIC vs the model.

As can be seen in Figure 5.7a, Figure 5.7b and Figure 5.7d the conversion obtained in the experiments by Visconti and by CSIC are in good agreement at different GHSVs, pressures and temperatures. For the temperature, this means that Equation 3.7 is also valid for the range of 200°C to 220°C.

At different ratios Visconti obtains a much higher conversion than CSIC, as can be seen in Figure 5.7c. The exact composition, specifically the fraction of N$_2$, used by Visconti at the different H$_2$/CO ratios are not given in his papers and therefore his results cannot be reproduced. This could be the reason for the difference with the experiments with CSIC. A quick simulation with 25% N$_2$ instead of 7% already showed an increase in the conversion from 26% to 44%. Assumed is that relatively the same amount of inert is used in the base case by Visconti and by CSIC. However, it is furthermore assumed that with the other cases, in which the ratios have been changed, a different amount of inert has been used and that the deviation between the two experiments is due to this fact. The results of the 1D model are in good agreement with the experimental results by CSIC. Only at different pressures the model tends to overestimate the effect of the pressure on the conversion. At lower pressure a much lower conversion is predicted than found in the experiments.

The products from the FTS have been divided into four groups of hydrocarbons: the methane-
fraction \( (C_1) \), the light, gaseous fraction \( (C_2-C_5) \), the gasoline fraction \( (C_6-C_{10}) \) and the higher hydrocarbons \( (C_{10+}) \). The selectivities to the different products obtained at CSIC have been compared to those obtained from the 1D model and are shown in Figure 5.8.

For the different GHSVs the results of the model are a reasonable match for the results with the experiments. With the other variables, temperature, pressure and \( \text{H}_2/\text{CO} \) ratio, this is not the case. The model predicts a much lower \( C_{10+} \) fraction, but predicts the \( C_6-C_{10} \) fraction reasonably well. At higher pressures the model fits the experiments better than at the lower pressures. This can also be due to the fact that the conversion predicted by the model is much lower than in the experiments. At increasing ratios the model predicts a same trend as the experiments, however the model predicts a much higher selectivity to the \( C_1 \) fraction at higher ratios than is obtained in the experiments.

The results from the experiments performed by Visconti and by CSIC are comparable and therefore no problems are expected when using the model by Visconti to predict the behavior of the FTS in the PBR at CSIC. For the conversion a good agreement between the model and the experiments is found. For the selectivities there is a good agreement at different GHSVs. With changing other variables the difference between the model and the experiments is high, certainly at the points where also the conversion is not predicted well by the model.
5.3 Ru-B/TiO₂ catalyst

For the PBMR case only the Ru-B/TiO₂ catalyst can be used and therefore the model has to be optimized for this catalyst. This catalyst has been synthesized as described in paragraph 4.1. The synthesized catalyst has been analyzed by the people from CSIC to validate that the synthesis has been succesfull. The implemented kinetics for the Co/Al₂O₃ catalyst have to be improved for the Ru-B/TiO₂ catalyst.

5.3.1 Catalyst

The catalyst has been succesfully synthesized following the synthesis procedure described in paragraph 4.1. 9.9997g of TiO₂ has been impregnated using a solution of 0.9400g of RuNO(NO₃)₃ in 3.5 mL H₂O. Drying took more than 12 hours and the product has been calcined during the weekend. After the calcination 10.1523g of solid product has been obtained. This product has been impregnated using a solution of 0.1883g of H₃BO₃ in 15.2 mL H₂O and this has been dried over the weekend. The final product has not been weighed, but stored. A few grams of the product has been sieved using a 0.250mm sieve and a 0.300mm sieve and this final product has been used as catalyst in the reactor.

The product has been characterized by CSIC using XRD to check for the presence of boron in the final product, see Figure 5.9. It can be seen that there is a very small peak for the TiB₂ phase present in the XRD spectrum of the synthesized catalyst and that the addition of boron to the catalyst has been succesful.

5.3.2 Kinetics

The kinetic parameters, as decribed in paragraph 3.3 have been varied to match the outcome of the base case experiment as closely as possible. A full dataset has been used to validate
CHAPTER 5. RESULTS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental results</th>
<th>Model results</th>
<th>RMSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{C_1}$</td>
<td>0.16</td>
<td>0.0772</td>
<td>0.0828</td>
</tr>
<tr>
<td>$S_{C_2-C_5}$</td>
<td>0.21</td>
<td>0.1764</td>
<td>0.0336</td>
</tr>
<tr>
<td>$S_{C_6^+}$</td>
<td>0.64</td>
<td>0.7464</td>
<td>0.1065</td>
</tr>
<tr>
<td>$Q/P_{C_2-C_5}$</td>
<td>0.90</td>
<td>2.0431</td>
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<tr>
<td>$Q/P_{C_6-C_{10}}$</td>
<td>0.60</td>
<td>1.5824</td>
<td>0.9824</td>
</tr>
<tr>
<td>$X$</td>
<td>0.37</td>
<td>0.1369</td>
<td>0.2331</td>
</tr>
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Table 5.2: Experimental results of the base case versus the preliminary results of the model. $S$ is the selectivity towards the different hydrocarbon fractions, $Q/P$ the olefin over paraffin ratio of the specified hydrocarbon fractions and $X$ the conversion of CO.

these new kinetic parameters. To reduce computational time the model has been limited again to calculate the olefins and paraffins up to the C$_{25}$ fraction.

The base case used in the Ru-B/TiO$_2$ experiments is at $P=20$ bar, $T=250^\circ$C, GHSV=10,000 cm$^3$/g$_{cat}$/h and a H$_2$/CO ratio of 2.0. The results of the experiments and the results of the model, with the kinetics by Visconti$^{[24]}$, are shown in Table 5.2. The selectivities to the C$_5$-C$_{10}$ and the C$_{10^+}$ fractions have been lumped together for the fitting, because it has been difficult to make a clear separation between these two groups with the GC used at CSIC.

As can be seen in Table 5.2 the first results of the model are deviating a lot from the experimental results. The RMSD varies between 0.03 and 1.14, with an average of 0.43. This is high in comparison with the range of the calculated values, with an average deviation of 73%. This can be easily explained by the fact that the kinetics in the model are based on a Co catalyst and the experiments have been performed with a Ru catalyst. The Ru catalyst has a higher activity than the Co catalyst, which also is clearly visible in the difference in conversion, which is lower by a factor 2.7.

A fitting has been performed on the nine kinetic parameters suggested by Visconti$^{[24]}$. All the parameters have been increased by a factor, to account for the higher activity. Once the conversion was within the experimental conversion, specific parameters have been changed individually and simultaneously to find the right fit for the data. The parameters for the formation of paraffins and methane have been changed the most. This is also due to a very high Q/P ratio as is shown in Table 5.2. Also the formation of methane is much lower than obtained in the experiments. Since this fit has been performed for the base case, the activation energies of reaction 1 and 2a have not been taken into account and Equation 3.7 has been modified for the 250$^\circ$C setpoint. In the end a good fit for the experimental data of the base case has been found, as can be seen in Table 5.3. The fitted parameters are given in Table 5.4.

The data from the model is in good accordance with the experiments. The RMSD is much lower than in the first scenario, and varies between 0.0131 and 0.0621, with an average value of 0.03. With respect to the range of calculated values, the average deviation is around 7.5%. The kinetic parameters are not increased with one single factor, but a difference between the different reactions has been made. To fit the data correctly certain parameters had to
CHAPTER 5. RESULTS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental results</th>
<th>Model results</th>
<th>RMSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{C_1}$</td>
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<td>0.1469</td>
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<td>$S_{C_5}$</td>
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</tr>
<tr>
<td>$X$</td>
<td>0.37</td>
<td>0.3486</td>
<td>0.0214</td>
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</table>

Table 5.3: Experimental results of the base case versus the fitted results of the model. $S$ is the selectivity towards the different hydrocarbon fractions, $Q/P$ the olefin over paraffin ratio of the specified hydrocarbon fractions and $X$ the conversion of CO.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value $^{[24]}$</th>
<th>Fitted value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{H_2,0}$</td>
<td>$3.77 \cdot 10^{-5}$</td>
<td>$1.14 \cdot 10^{-4}$</td>
<td>$\text{mmol s}^{-1} \text{g}^{-1} \text{bar}^{-1}$</td>
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<td>$k_{M,0}$</td>
<td>$1.36 \cdot 10^{-3}$</td>
<td>$4.11 \cdot 10^{-3}$</td>
<td>$\text{mmol s}^{-1} \text{g}^{-1} \text{bar}^{-1}$</td>
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<td>$k_{IN}$</td>
<td>$3.34 \cdot 10^{-1}$</td>
<td>$1.01$</td>
<td>$\text{mmol s}^{-1} \text{g}^{-1}$</td>
</tr>
<tr>
<td>$k_{CH_4}$</td>
<td>1.61</td>
<td>9.74</td>
<td>$\text{mmol s}^{-1} \text{g}^{-1}$</td>
</tr>
<tr>
<td>$k_G$</td>
<td>$2.26 \cdot 10^{-1}$</td>
<td>$5.13 \cdot 10^{-1}$</td>
<td>$\text{mmol s}^{-1} \text{g}^{-1}$</td>
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<tr>
<td>$k_{P_n}$</td>
<td>$1.32 \cdot 10^{-1}$</td>
<td>$9.48 \cdot 10^{-1}$</td>
<td>$\text{mmol s}^{-1} \text{g}^{-1}$</td>
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<tr>
<td>$k_{Q_n,dx}$</td>
<td>$5.54 \cdot 10^{-3}$</td>
<td>$1.82 \cdot 10^{-2}$</td>
<td>$\text{mmol s}^{-1} \text{g}^{-1}$</td>
</tr>
<tr>
<td>$k_{Q_n,sx}$</td>
<td>3.63</td>
<td>8.24</td>
<td>$\text{mmol s}^{-1} \text{g}^{-1} \text{bar}^{-1}$</td>
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<td>$k_{Q_2,sx}$</td>
<td>$1.64 \cdot 10^{2}$</td>
<td>$4.02 \cdot 10^{2}$</td>
<td>$\text{mmol s}^{-1} \text{g}^{-1} \text{bar}^{-1}$</td>
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</tbody>
</table>

Table 5.4: The kinetic parameters of the FTS over a Co/Al$_2$O$_3$ catalyst and the fitted parameters for the Ru-B/TiO$_2$ catalyst of CSIC.
be increased more than others. The first three parameters, the adsorption reactions and the
initiation of the chain, have been increased with a factor 3.0, while the termination reactions
to CH$_4$ and to the paraffins have been increased with respectively a factor 6 and 7.2. As
discussed before, the paraffin formation, and the formation of CH$_4$ in particular, have been
too low in comparison with the experiments and increasing these kinetic parameters solved
this problem.

To check the validity of this fit the full data set of the experiments with the Ru-B/TiO$_2$
catalyst has been modelled and the outcome has been plotted versus the experimental output. The different graphs are given in Figure 5.10. For the ratio case the model has been limited up to the C$_{15}$ fraction. This limitation has been performed due to the fact that in the simulation up to the C$_{25}$ fraction an accumulation has been found in the weight fraction of the C$_{25}$ paraffin and olefin. Due to this accumulation the summation of the weight fractions yielded a value above 1.0 which caused the results of these simulations to be unreliable. A limitation to the lower hydrocarbons solved this problem. With the base case this action has been checked and the results of two simulations, with a limitation up to respectively the C$_{15}$, and the C$_{25}$ fraction, have been compared with eachother, see Table 5.5.

As can be seen, both cases are almost identical and thus the limitation to the C$_{15}$ fraction has no significant influence on the output of the model. Therefore, limiting the model to the C$_{15}$ fraction can be done without risk of wrong data.

As can be seen in Figure 5.10a and Figure 5.10b the model follows the same trends as the experiments and has an accurate prediction of the real behaviour. The model predicts a higher production of methane, in case of increasing the H$_2$/CO ratio, than found in experiments. Where the experiments show a peak at a ratio of three, the model does not have an optimum, but increases with the higher H$_2$ concentration. This is a direct consequence of the used model by Visconti$^{[24]}$, see also Figure 5.5a. His model predicts a decrease of the higher hydrocarbons on increasing the H$_2$/CO ratio, which is also visible with the Co-catalyst, see Figure 5.8c. For the temperature case there is a big deviation between the model and the experiments. This is due to the fact that activation energies have not been optimized. Figure 5.10d show clearly that this has to be done in order to predict the behaviour of the Ru-catalyst at different temperatures.

Table 5.5: Comparison between the two simulations. $S$ is the selectivity towards the different hydrocarbon fractions, $Q/P$ the olefin over paraffin ratio of the specified hydrocarbon fractions and $X$ the conversion of CO.
(a) At different GHSVs. 
(b) At different pressures. 
(c) At different ratios. 
(d) At different temperatures.

Figure 5.10: Comparison plot of the experiments vs the model.
Table 5.6: The activation energies of the FTS over a Co/Al₂O₃ catalyst and the fitted parameters for the Ru-B/TiO₂ catalyst of CSIC.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Literature value[24]</th>
<th>Fitted value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_H₂</td>
<td>267.30</td>
<td>71.510</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>E_M</td>
<td>177.44</td>
<td>37.986</td>
<td>kJ mol⁻¹</td>
</tr>
</tbody>
</table>

A quick fitting of the activation temperatures has been attempted. The main reason to fit the activation energies is the fact that the membrane experiments have been performed at 280°C, because the permeation of H₂ through the Pd-Ag membrane is very low at 250°C or lower. The first results showed a too large effect with increasing temperature and thus the activation energies are too large. Therefore, lower values have been tried and fitted for the experimental data. The final fitted values are given in Table 5.6.

As can be seen in Figure 5.11 the fitting of the activation energies of the first two reactions improved the model alot. The model is now capable of predicting the trends that occur with the different selectivities. At 280°C the methane fraction is under estimated and the higher fraction (C₅+) is over estimated. This is something that has to be kept in mind when modelling the PBMR.

The kinetic model in the 1D reactor model has been succesfully fitted to predict the behaviour of the Ru-B/TiO₂ catalyst in the PBR setup. At different GHSV and pressures the model has a good agreement with the experiments. At different ratios the model still predicts a Co-based trend for the products formation. A first fit has been atempted for the activation energies to predict the behaviour at different temperatures. The predicted trends are the same as in the experiments, but the overall value could be improved.

5.4 Membrane reactor

After careful validation of the model, simulations with the membranes incorporated in the reactor have been performed. For the membrane case the model has also been limited to the
fraction, for computational reasons and in a few cases an accumulation of mass occurred, as described in the previous paragraph. While limiting the model to the C\textsubscript{15} fraction the mass balance was closed all the time.

For the PBMR a fixed flux has been used over the membrane, to see what the direct effect was of the added hydrogen. Simulations have been performed at 250\textdegree C, the temperature of the base case of the PBR and at 280\textdegree C, the temperature at which the experiments at CSIC have been performed. The effect of the other parameters, the GHSV, the H\textsubscript{2}/CO ratio and the pressure, has been investigated. A comparison between the experiments and the model has been made at 280\textdegree C, a H\textsubscript{2}/CO ratio of 2 (of which half the H\textsubscript{2} has been fed via the membrane and the other half via the reactor entrance), a GHSV of 7,300 cm\textsuperscript{3}/g\textsubscript{cat}/h and a pressure of 10 bar. This is the only experimental result obtained at CSIC and thus the only data point for comparing the model with the experiments.

The comparison between the PBR and the PBMR has been made using the following steps. First a simulation has been performed for the PBR, using the CSIC experimental conditions for a H\textsubscript{2}/CO ratio of 2 (31% CO, 62% H\textsubscript{2} and 7% N\textsubscript{2}). Then a calculation has been performed on the actual molar flows flowing through the reactor in the PBR case. The molar flow of H\textsubscript{2} has been divided over the tube and the shell and the total molar flow and composition of the flow through the tube has been calculated. This value has been used in the simulation in order to be able to make a proper comparison between the PBR case and the PBMR case.

### 5.4.1 Comparison with CSIC

At CSIC the experimental setup has been used to obtain results in the PBMR setup. The E100 and E101 Pd/Ag membrane, supplied by TECNALIA, have successfully been used in the setup and experimental results with the PBMR have been obtained by the people there. A feed of 46% H\textsubscript{2}, 46% CO and 8% N\textsubscript{2} has been used as feed to the reactor, while over the membrane the H\textsubscript{2} feed was diluted with an equal amount of He. The pressure in the tube has been kept constant at 10 bar, while the pressure in the shell has been kept constant at 12 bar. The experiments have been performed at 280\textdegree C to obtain enough H\textsubscript{2} permeation through the membrane and the GHSV was varied between 7,200 and 7,500 cm\textsuperscript{3}/g\textsubscript{cat}/h.

With the E100 membrane they obtained results and proved the concept that H\textsubscript{2} would flow through the membrane to the reactor. However, the conversion was still low in comparison with the PBR case. With the E101 membrane finally a higher conversion was obtained. This conversion is similar to the conversion obtained with the PBR setup, using a H\textsubscript{2}/CO ratio of 2. A lower selectivity to CH\textsubscript{4} and a higher selectivity to the higher hydrocarbons has been obtained. However, during operation the H\textsubscript{2} permeation via the membrane decreases, probably due to the formation of waxes, see Figure 5.12.

A successful regeneration of the membrane has been performed overnight at 300\textdegree C with pure He inside the tube at atmospheric pressure and pure H\textsubscript{2} at 2 bar inside the shell. After this regeneration step, the membrane could be used again in the reactor setup.

A comparison has been made between the results of the experiments with the PBR and PBMR setup and the results from the model, see Figure 5.13. The results of the PBR experiments are an average of 3h measuring time (three datapoints) and the results of the PBMR experiments
an average of 19.4h measuring (seven datapoints). The GHSV for the PBR is 7,500 and for the PBMR is 7,200. For both experiments the pressure has been kept at 10 bar, the H$_2$/CO ratio at 2 and the temperature at 280°C.

As can be seen in the bar plot the membrane has a large effect on the products formation. Using the membrane decreases the formation of CH$_4$ alot and the higher hydrocarbons are favored. The experiments show that the conversion has been decreased by 40%. This decrease could be the result by the deactivation of the membrane by the waxes and thus a decrease in the H$_2$ addition to the reactor. The model has almost a constant conversion, due the fact that the permeation of the H$_2$ through the membrane has been calculated beforehand. The same trends in the selectivites are observed. There is a decrease in the formation of the lower hydrocarbons (C$_1$-C$_5$) and an increase in the higher hydrocarbons. The C$_5$-C$_{10}$ fraction stays almost the same and the C$_{10+}$ fraction increases. However, the differences between the PBR and PBMR are not as large as in the experiments.

To validate the experimental results with the model also an experiment at 250°C has been attempted. At this temperature the kinetic model has been fitted and the error in the model is lower than at 280°C. However, the permeation of H$_2$ through the membrane at the lower temperature is troublesome and so far no successful experiments have been performed.

### 5.4.2 Pressure

Apart from the comparison with the two experiments by CSIC a larger range of the used variables have been investigated using only the model. A comparison between the PBR and the PBMR results has been made. The same strategy as described in first part of this paragraph has been applied to calculate the flows through the shell and tube.

To investigate the effect of the pressure in combination with the membrane a comparison is
made at 250°C, a GHSV of 10,000 cm³/gcat/h in a range of 5-30 bar. To analyse the difference at a higher temperature a small range of 10-20 bar is also simulated at 280°C. The results are shown in Figure 5.14.

As can be seen in both the figures the conversion in the PBR and the PBMR model are almost identical, the PBMR model has a slightly higher conversion. Also at both temperatures the formation of lower hydrocarbons is lower for the membrane configuration and higher for the higher hydrocarbons (C_{10+}). The formation of the C_6-C_{10} fraction is at lower pressure a bit higher in the membrane configuration, but at higher pressures it is lower. This tipping point is at 250°C around 7.5 bar and at 280°C around 12.5 bar. However, the effect is very low.

Figure 5.13: Comparison between the experiments and the model. S is the selectivity towards the different hydrocarbon fractions, and X the conversion of CO.

Figure 5.14: Comparison plot of the PBR model vs the PBMR model at different pressures.
and at lower pressures the formation of CH₄ is still very high in comparison to the other hydrocarbons. The best results are obtained at higher pressures, since the CH₄ formation decreases with increasing pressure. However, the current state of the Pd-Ag membranes does not allow the PBMR to operate at a higher pressure than 10 bar. At 10 bar also detailed comparison has been made between the PBR and the PBMR model along the length of the reactor and with increasing time. The axial profiles of the conversion and the partial pressure of H₂ are given in Figure 5.15 during the reaction time.

As can be seen in Figure 5.15a., with increasing time and over the length of the catalyst bed, the conversion increases for both the PBR and the PBMR case. However, the increase in conversion for the PBR case is limited due to the fact of the decreasing amount of H₂ in this reactor, as can be seen in Figure 5.15b. The conversion in the PBMR profits from the continuous feeding of H₂ via the membrane to increase the conversion. Therefore, the conversion of the PBMR is in the end a bit higher than for the the PBR.

Furthermore a detailed comparison of the different selectivities has been investigated. These four plots of the axial profiles during the reaction time are given in Figure 5.16.

Figure 5.16a immediately shows a remarkable effect: the selectivity to the C₁ fraction remains constant at 24% during reaction time for the PBR case. For the PBMR case it is clear that with increasing time and thus increasing H₂ feeding to the reactor the C₁ fraction drastically increases, from 7.5% to 20%. This effect of hydrogen decreases with the increasing carbon atom number. In Figure 5.16b still an increase in the selectivity is visible, but in Figure 5.16c and 5.16d a decrease in selectivity is visible over time. The reverse effect is shown for the PBR reactor. The selectivities to lower hydrocarbons decrease over time and the selectivity to the highest hydrocarbons increases.

It is clear that adding hydrogen to the reactor increases the termination to the products; an increase in selectivity to C₁-C₅ is visible. However, if the reactor is fed with a mixture with a low hydrogen content, such as a H₂/CO ratio of 1, the selectivities of the C₁-C₅ fractions is still lower than in the conventional case. For the PBR the H₂ content in the reactor decreases over time and this effect is also visible in the selectivities, although the effect is lower than
(a) Selectivity to C$_1$.

(b) Selectivity to C$_2$-C$_5$.

(c) Selectivity to C$_6$-C$_{10}$.

(d) Selectivity to C$_{10+}$.

Figure 5.16: Axial profiles of the selectivities over time for the PBR and PBMR.
5.4.3 GHSV

To investigate the effect of the GHSV in combination with the membrane a comparison is made at 10 and 20 bar in a range of 5,000-25,000 cm$^3$/g$_{cat}$/h, while keeping the temperature constant at 250°C. The results are shown in Figure 5.17. As with the pressures, the conversion of the PBR and the PBMR model are almost identical, with a slightly higher conversion in the membrane case. With increasing GHSV the conversion decreases, due to the decrease in the residence time inside the catalyst bed. The effect of the membrane is similar as with the pressure case: a decrease is seen in the formation of the C$_1$ and C$_2$-C$_5$ fractions, and there is an increase in the formation of the higher hydrocarbons. The C$_6$-C$_{10}$ fraction has a tipping point at the 10 bar case (as Figure 5.14 showed that the tipping point lies around that pressure). At 10 bar the tipping point can be found around 15,000 cm$^3$/g$_{cat}$/h and at higher GHSVs there is a small increase in the formation of the C$_6$-C$_{10}$ fraction.

At 20 bar, around 45% of the products are higher hydrocarbons and only 10% of the products is methane. At 10 bar the product fractions are closer to each other, around 20-30%. It is therefore advisable to work at higher pressures, however the effect of the higher pressure on the membrane and membrane performance should be investigated.

5.4.4 Ratio

To investigate the effect of the H$_2$/CO ratio in combination with the membrane a comparison is made at 20 bar and 10,000 cm$^3$/g$_{cat}$/h, while keeping the temperature constant at 250°C. The ratio has been varied between 2 and 4. Two different feeding techniques have been investigated: feeding a H$_2$/CO ratio of 1 to the reactor and adding the rest of the H$_2$ via the membrane to raise the ratio, and dividing the H$_2$ feed in two equal molar flows, one through the entrance together with the CO and N$_2$ and the other through the membrane to obtain the desired ratio. The results are shown in Figure 5.18.
While varying the $\text{H}_2/\text{CO}$ ratio the conversion of the PBMR is again slightly higher than the conversion of the PBR. At the beginning the selectivity to $\text{C}_6-\text{C}_{10}$ is higher for the PBR, but around the $\text{H}_2/\text{CO}$ ratio of 3 the PBMR has a higher selectivity for this fraction. The higher hydrocarbons gradually decrease with increasing ratio, as is expected with an increasing concentration of $\text{H}_2$ in the reactor. The $\text{C}_1$ fraction is hugely favored and increases to a selectivity of above 50% for the PBR and above 40% for the PBMR case at a $\text{H}_2/\text{CO}$ ratio of 4.

The difference between the two investigated feeding techniques (either feeding a $\text{H}_2/\text{CO}$ ratio of 1 and adding more $\text{H}_2$ via the membrane, or splitting the $\text{H}_2$ flow in two equal flows through the tube and through the membrane) is clearly visible. Feeding a $\text{H}_2/\text{CO}$ ratio of 1 has as result that the overall $\text{H}_2$ concentration is lower in the reactor than if the $\text{H}_2$ is equally divided over the reactor and the membrane. Due to this lower concentration, the performance of the 1:1 feed is better than the equal feed: the amount of $\text{CH}_4$ is lower, and the amount of higher hydrocarbons is higher.

5.4.5 Comparison fixed flux with Sieverts law

All simulations have been performed with a fixed flux through the membrane. The Pd-Ag membranes follow Sieverts law, as discussed in paragraph 3.4.1. The driving force of this law is the pressure difference of $\text{H}_2$ over the membrane. During the experiments by CSIC this pressure difference has been kept to 2 bar difference over the membrane. In the numerical simulation a maximum of $4.51 \cdot 10^{-3}$ and a minimum of $9.01 \cdot 10^{-4}$ mol/m²/s have been used as molar flow through the membrane.

With the values given in paragraph 3.4.1, a maximum pressure difference of 2 bars, the
maximum pressure of 10 bar and a temperature of 280°C Sieverts law yields a flow through the membrane of $3.18 \cdot 10^{-1}$ mol/m²/s. This is a factor 70 higher than the maximum flow through the membrane needed for the numerical simulations. Therefore, the Pd-Ag membranes should be able to supply the reactor with enough H₂ to perform the FTS as simulated. However, Coenen only investigated the performance of the Pd-Ag membranes between 300°C and 500°C. Therefore, the performance of the membrane outside this temperature range could deviate.
Chapter 6

Conclusions and discussion

The Fischer Tropsch synthesis has been investigated in both a packed bed reactor as a packed bed membrane reactor. Using a membrane in the reactor setup enables the possibility to co-feed \( \text{H}_2 \) along the reactor axis. A literature research showed that the different adsorption rates for CO and \( \text{H}_2 \) on the catalytic surface can have a negative effect on the overall reactor performance. The higher adsorption rate of CO can impede the adsorption of \( \text{H}_2 \). Since the adsorption of \( \text{H}_2 \) is mainly driven by the partial pressure of \( \text{H}_2 \) a higher concentration of \( \text{H}_2 \) would be advisable. However, a higher concentration of \( \text{H}_2 \) also favors the formation of methane. Therefore, it is advisable to co-feed \( \text{H}_2 \) alongside the reactor axis, by means of a membrane, to optimize the \( \text{H}_2/\text{CO} \) ratio in the whole reactor. This way less \( \text{H}_2 \) can be fed at the entrance, favoring the formation of longer hydrocarbons.

A 1D reactor model, developed by Smit and Tiemersma, has been used and set up with the relevant FTS kinetics. This model has been successfully validated for an isothermal and a non-isothermal case, as proposed by Tiemersma. The model could predict the behavior of the chemical species and the temperature in the axial direction of the reactor with deviations less than 1.0% of the analytical solution. The membrane section in the model has also been validated successfully and this model can be used to simulate both a PBR as a PBMR.

The kinetic model has been validated using experimental results and equations obtained from literature. The reaction rate of CO is in the same order of magnitude as found in literature. The kinetic model has been validated with the experimental results of CSIC for the Co-catalyst within the experimental conditions. Only a small deviation of the conversion at different pressures has been found. The assumed adjusted Arrhenius equation has been successfully used to account for the temperature effect of the FTS reaction. The product spectrum of the model has been following the same trends as the experiments, investigating the behaviour under changing GHSV, temperature, pressure and \( \text{H}_2/\text{CO} \) ratio. The best predictions of the selectivities have been found with changing GHSV.

Ten grams of the Ru-B/TiO\(_2\) catalyst have been successfully synthesized, sieved and used in the PBR and PBMR. A characterization has been performed by CSIC and has proven the addition of the boron to the Ru-TiO\(_2\) catalyst.

The kinetic parameters have been successfully fitted to match the outcome of the experiments with the Ru-B/TiO\(_2\) catalyst. A full data set has been modelled and the model follows the experiments very well at different superficial gas velocities and pressures. With different ratios
the model still follows the cobalt catalyst kinetics as described by Visconti. A first attempt to fitting the activation energies has been made and the conversion and selectivities follow the same trend as the experiments at different temperatures. At 280°C the deviation of the model is small and the model can be used at this temperature for the simulation of the PBMR experiments.

The full reactor model, including the membrane section, has been successfully used in modelling the FTS in a PBMR. A comparison of the model and the experiments done by CSIC has been made and this shows that the model is predicting the same trends as the experiments at CSIC. Adding H\textsubscript{2} via the membrane results in a lower selectivity to the undesired C\textsubscript{1} fraction and a higher selectivity to the C\textsubscript{10} fraction. If enough H\textsubscript{2} is added via the membrane and a same H\textsubscript{2}/CO ratio is reached as without the membrane, a similar conversion is observed.

A more detailed investigation has been made into the effects of the membrane on the conversion and selectivities at different operating conditions. At different temperatures, pressures, GHSVs and ratios the conversion of the PBMR is slightly higher than for the PBR. At all operating conditions the effect on the C\textsubscript{1}, C\textsubscript{2}-C\textsubscript{5} and the C\textsubscript{10+} fraction has been the same. The C\textsubscript{1} and the C\textsubscript{2}-C\textsubscript{5} fractions decrease and the C\textsubscript{10+} fraction increases. The C\textsubscript{6}-C\textsubscript{10} fraction shows a tipping point at different pressures, GHSVs and ratios.

Two different feeding techniques have been investigated: feeding a H\textsubscript{2}/CO ratio of 1 to the reactor and the rest of the H\textsubscript{2} via the membrane, and dividing the total H\textsubscript{2} molar flow equally over the flow at the reactor inlet and the flow through the membrane. Over a range of H\textsubscript{2}/CO ratio, feeding as little H\textsubscript{2} at the entrance and the rest via the membrane showed the best results. This technique resulted in the lowest selectivity towards CH\textsubscript{4} and the highest selectivity towards the higher hydrocarbons.

The conversion along the reactor axis has been investigated. The conversion of the PBMR increases a bit more over time due to the addition of H\textsubscript{2} along the reactor axis. The axial profile of the partial pressure of H\textsubscript{2} shows that over time this partial pressure increases due to the addition of H\textsubscript{2} via the membrane. Due to the addition of H\textsubscript{2} the final conversion in the PBMR case is a bit higher than for the PBR case. The selectivities also show an effect over time, due to the addition of H\textsubscript{2}. With increasing time and increasing H\textsubscript{2} concentration in the reactor the higher hydrocarbons decrease and the C\textsubscript{1} fraction is favored, however due to the low H\textsubscript{2}/CO ratio that the reactor starts with, the effect is lower than adding all the H\textsubscript{2} at the reactor entrance.

When decreasing the amount of CH\textsubscript{4} produced in the FTS is the main goal and with the assumption that all higher hydrocarbons can be used in a cracker to be reduced to desired fractions it is advised to work at higher pressure and high temperature. The GHSV does not have an influence on the selectivity to the C\textsubscript{1} fraction, but due to the reducing residence time with higher GHSV the conversion also decreases. It is therefore advised to work at a low GHSV of around 5,000 - 10,000 cm\textsuperscript{3}/g\textsubscript{cat}/h. Increasing the H\textsubscript{2}/CO ratio increases the conversion a bit, but hugely favors the formation of the C\textsubscript{1} fraction and it is therefore advised to work at a low (overall) H\textsubscript{2}/CO ratio of around 2. At this ratio the best result is obtained when feeding as little H\textsubscript{2} as possible at the entrance and co-feed the rest of the H\textsubscript{2} via the membrane. A quick calculation showed that the Pd-Ag membranes should be able to deliver the desired flow of H\textsubscript{2} through the membrane with a partial pressure difference of 2 bar.
Chapter 7

Recommendations

The model has been limited to the C_{25} fraction and later to the C_{15} fraction due to computational time and due to an accumulation of weight. It is recommended to investigate the possibility to rewrite or transcribe the code to be able to simulate on a cluster instead of a desktop computer. Furthermore, the accumulation of weight should be investigated. This has now been solved with a reduced model to the C_{15} hydrocarbons. It occurred only in the case of changing ratios or at the membrane simulations. Since the model has been changed for the FTS and a NLE solver has been incorporated to calculate the site balance the results of the site fractions could be a starting point to investigate.

It is further recommended to perform a thorough kinetic study on the Ru-B/TiO_{2} catalyst, since still little is known about this specific, newly developed, catalyst. This kinetic study can use the estimated kinetic parameters in this thesis as starting point. Also a more precise study of the catalyst at higher temperatures is recommended. This study can properly investigate the activation energies for the CO and the H_{2} adsorption.

Literature research showed the possibility of negative effect of H_{2}O on the performance of the catalyst. Furthermore, the formation of H_{2}O will have an influence on the partial pressures of the other components, by lowering the mole fractions of the main reactants, and therefore lowering the reaction rates. Therefore, it is advised to investigate the usage of membranes to subtract H_{2}O alongside the reactor axis.

The formation of carbon as a solid is not taken into account with the kinetic model used. However, during the experiments carbon formation has always been detected. This solid carbon can have a deactivating effect on the catalyst. An improvement to the model can be made by incorporating the formation of solid carbon. A way to do this is incorporating the Boudouard reaction in the kinetic model.

This model does only take the paraffin and \( \alpha \)-olefin formation into account. To properly model the FTS experiments also the formation of oxygenates and other products should be taken into account. The WGS can also influence the reaction. However, this has not been taken into account for the Co and Ru catalyst, but should be taken into account if the model is used for a Fe catalyst.

The FTS has been performed isothermal in this thesis. However, the reaction is exothermic and in large industrial plants this can lead to hot spots in the reactor. A non-isothermal
version of the model could be build, by incorporating the heat of reaction and assuming a non-isothermal reaction. The model can then be used to scale up the reactor from lab scale to (pilot) plant scale and predict the temperature profile inside the reactor. Tuning the temperature of the H\textsubscript{2} fed through the membrane could be a way to keep the temperature in the reactor at a steady level.

Finally, an investigation into the behaviour of the Pd-Ag membrane at temperatures lower than 300\textdegree C should be made. This investigation can shed more light on the behaviour of the membrane at FTS temperatures and prove if the parameters found by Coenen for the Sieverts law are valid at this temperature. Furthermore, it is recommended to perform more experimental studies with other membranes to supply H\textsubscript{2} to the reactor. The limitation of the Pd-Ag membrane lies in the pressure that the membrane can withstand, without the chance on embrittlement. If a membrane can be used that can perform at higher pressures, then the FTS can be performed at pressures higher than 10 bar. As shown in the conclusion, this will have a great effect on the formation of higher hydrocarbons and a decrease in the formation of methane.
Chapter 8

Acknowledgements

I would like to thank Prof. dr. ir. M. van Sint Annaland for giving me the chance to do this final project in his group and for helping me with the 1D model.

I would like to thank Dr. F. Gallucci for his advise and discussions during the project meetings.

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I would like to thank Dr. H. Friedrich for accepting the position as external committee member.

I would like to thank the people from CSIC, especially Dr. S. Rojas, Dr. J. Perez Alonso and D. Liuzzi for helping me during the project, giving answers on all my questions and providing the insight from the experimental point of view in this project. I also would like to thank them for the nice time I had at CSIC during my time there.

I want to thank all the people from the SMR group for the very nice time I had the last year. There is a great atmosphere in the group and all the coffee breaks and PhD-lectures (with the drinks afterwards) were a pleasant distraction during and after the workday.

Finally, I would like to thank my family and especially my girlfriend, who always have supported me during my project. The final two months have been hectic with a lot of change and I could not have done this without you.
List of symbols

Roman letters

- **a** \( \frac{m^2}{m^3} \): Specific surface
- **c** \( \text{mol/m}^3 \): Concentration
- **C_p** \( \text{kJ/kg/K} \): Heat capacity
- **D** \( m^2/s \): Diffusion coefficient
- **D_{ax}** \( m^2/s \): Axial dispersion coefficient
- **d** \( m \): Diameter
- **d_{mem}** \( m \): Membrane thickness
- **E_k** \( \text{J/mol} \): Activation energy of the \( k^{th} \) elementary step
- **F_i** \( \text{mol/s} \): Molar flow of component \( i \)
- **FTS** Fischer Tropsch synthesis
- **GHSV** \( \text{cm}^3(\text{STP})/\text{h/g}_{\text{cat}} \): Gas hourly space velocity
- **H_i** \( \text{J/kg} \): Enthalpy of component \( i \)
- **J_{H_2}** \( \text{kg/m}^2/s \): Hydrogen flux
- **k_k** \( \text{mmol/s/g}_{\text{cat}} \): Rate constant of the \( k^{th} \) elementary step
- **L** \( m \): Length
- **M_{av}** \( \text{kg/mol} \): Average mole mass
- **n** - Number of carbon atoms
- **n_i** \( \text{kg/m}^2/s \): Mass flux of component \( i \)
- **n_{mem}** - Pressure exponent for the Pd-Ag membrane
- **NLE** Non linear equation
- **P, p** \( \text{bar} \): Pressure
- **P_i** \( \text{bar} \): Partial pressure of component \( i \)
- **P_n** \( \text{bar} \): Paraffin with \( n \) carbon atoms
- **PBMR** Packed bed membrane reactor
- **PBR** Packed bed reactor
- **PFD** Process flow diagram
- **PID** Proportional integral derivative
- **PL** Power law
- **Q_{n}** \( \text{mol/m/Pa}^{n_{mem}} \): Olefin with \( n \) carbon atoms
- **Q_{Pd}** \( \text{mol/m/Pa}^{n_{mem}} \): Permeability of the Pd-Ag membrane
- **R** \( \text{J/mol/K} \): Gas constant
- **r_k** \( \text{mmol/s/g}_{\text{cat}} \): Reaction rate of the \( k^{th} \) elementary step
- **RMSD** Root mean square deviation
- **R_n** Intermediate component \((\text{CH}_2)_n-\text{CH}_3\)
- **S_i** - Selectivity to component \( i \)
- **STP** Standard temperature and pressure
- **SW** Sarup and Wojcieckowski
- **t** \( s \): Time

Modelling of a packed bed membrane reactor for Fischer Tropsch synthesis
CHAPTER 8. ACKNOWLEDGEMENTS

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Modelling of a packed bed membrane reactor for Fischer Tropsch synthesis
Bibliography


Appendix A

Experimental settings used by CSIC
### APPENDIX A. EXPERIMENTAL SETTINGS USED BY CSIC

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<th>Temperature (°C)</th>
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Table A.1: Experimental settings used by CSIC with the Co/Al\(_2\)O\(_3\) catalyst.

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Table A.2: Experimental settings used by CSIC with the Ru-B/TiO\(_2\) catalyst.