Oxygen diffusion in iron-based catalyst particles in the High Temperature Fischer-Tropsch process

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Award date:
2013
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April 2012
Summary

The heterogeneously catalyzed Fischer-Tropsch (FT) process converts synthesis gas, a mixture of CO and H₂, into a range of alkenes, alkanes and oxygenated compounds. Carbon based materials like biomass, natural gas and coal, can be used to make synthesis gas. This makes the FT synthesis a possible alternative to the crude oil based process for the production of liquid fuels (gasoline and diesel) and chemicals [1].

The high temperature (300-350 °C) Fischer Tropsch (HTFT) process aims at the production of gasoline and linear low molecular mass olefins, and is studied in this work [1]. Current mechanisms in literature do not fully explain the product distribution. In order to improve efficiency of the FT process by catalyst design further details about the HTFT mechanism are desired.

The key technique used in the study was Steady State Isotopic Transient Kinetic Analysis (SSITKA). Transient data of oxygen labeled compounds leaving the reactor were obtained from SSITKA experiments in which a reactor, filled with a Fe based HTFT catalyst, was either operated under no FT reaction conditions, feeding only CO as reactant to the reactor, or under FT reaction conditions in which both CO and H₂ were fed to the reactor.

Prior SSITKA experiments showed ¹⁶O leaving the reactor long after the inlet flow was changed from C¹⁶O/H₂ to C¹⁸O/H₂. Furthermore, from XRD and SEM analysis, oxygen was found to be present in the catalyst particle. These two facts led to the hypothesis of oxygen being present inside the catalyst particle and this oxygen was able to diffuse to the catalyst surface and react.

In order to verify this assumption, and to be able to include oxygen diffusion in future FT models, a value for the oxygen diffusion coefficient in the catalyst particle, D, was determined via curve fitting of CO and CO₂ transient data. To this end, a model was proposed describing hydrocarbon, CO₂ and H₂O formation, CO and CO₂ adsorption and desorption, and oxygen diffusion from and to the catalyst bulk. Fitting the transient data to the model resulted in a value of 4.5·10⁻¹⁴ ± 7.7·10⁻¹⁵ m² s⁻¹ for D.

A realistic value for D was obtained. However, some reaction rate constants had to be fitted simultaneously to D since their values were unknown. The parameters kₜ₁₀₂,des and kₜ₂o₂,dis were correlated and kₜ₁₂₀,dis, kₜ₂o₂,dis, kₜ₂o₂,des and kₜ₃₉ had large standard deviations. Additionally H₂O transients, gas phase outlet concentrations and catalyst surface concentrations predicted by the model deviated from experimental data. The model therefore seems to be too simplified to result in an optimal fit and a more complicated model may need to be used in order to fully match the experimental results.
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Figure 1. Overview of oil price and FT related research over the last 70 years [1].
1. Introduction

1.1 Fischer-Tropsch synthesis

The heterogeneously catalyzed Fischer-Tropsch (FT) process converts synthesis gas, a mixture of CO and H₂, into a range of alkenes, alkanes and oxygenated compounds. Carbon based materials like biomass, natural gas and coal, can be used to make synthesis gas. This makes the Fischer Tropsch synthesis a possible alternative to the crude oil based process for the production of liquid fuels (gasoline and diesel) and chemicals [1].

Among the reactions taking place in the Fischer Tropsch synthesis are the following [17]:

- **Alkanes**
  \( (2n + 1) \text{H}_2 + n \text{CO} \rightarrow C_n\text{H}_{2n+2} + n \text{H}_2\text{O} \)  
- **Alkenes**
  \( 2n \text{H}_2 + n \text{CO} \rightarrow C_n\text{H}_{2n} + n \text{H}_2\text{O} \)
- **Alcohols**
  \( 2n \text{H}_2 + n \text{CO} \rightarrow C_n\text{H}_{2n+1}\text{OH} + (n-1) \text{H}_2\text{O} \)
- **Water gas shift**
  \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \)
- **Boudouard reaction**
  \( 2 \text{CO} \rightarrow \text{C} + \text{CO}_2 \)

Ruthenium, iron, nickel and cobalt are active metals for the FT synthesis. Ruthenium is an expensive metal and its activity is not high enough to compensate for this, and Nickel mainly produces methane at industrial conditions. Commercial processes are therefore either Fe or Co based [2]. The Fe catalyzed process can be operated under low and high temperature. The low temperature (200-240 °C) FT process is used for the production of diesel and high molecular mass linear waxes. The high temperature (300-350 °C) Fischer Tropsch (HTFT) process aims at the production of gasoline and linear low molecular mass olefins, and is studied in this work [1].

Research in the field of FT synthesis started in the 1920’s from the pioneering work of Franz Fischer and Hans Tropsch [2] and continues in an effort to understand the formation of hydrocarbons from synthesis gas. Figure 1.1 shows that research related to FT synthesis has a long history and that the interest in this process is correlated to the crude oil price.

As can be seen from reactions (i) to (v) many different products are formed in the FT synthesis. This especially applies to the HTFT process where the temperature is much higher allowing for reactions, kinetically limited at lower temperatures, to become feasible. Current mechanisms in literature do not fully explain the product distribution, despite the long history of FT synthesis related research. In order to improve efficiency of the FT process by catalyst design further details about the HTFT mechanism are desired.

1.2 Method

The technique used in this study is Steady State Isotopic Transient Kinetic Analysis (SSITKA). SSITKA is based on the abrupt replacement of a reactant with its isotopically labeled counterpart, without changing the operating conditions [3]. A valve realizes the abrupt replacement by switching between two feed streams. The two feed streams differ in the presence of one isotopically labeled reactant and another inert tracer (see Figure 3.1 in chapter 3). A detailed description of the SSITKA
Figure 1.2 Fractions of $^{12}$CO$_2$ and $^{13}$CO$_2$ leaving the reactor in time after a $^{12}$CO to $^{13}$CO switch.

Figure 1.3 Fractions of $^{16}$O$_2$, $^{16}$O$^{18}$O and $^{18}$O$_2$ leaving the reactor in time after a $^{16}$O to $^{18}$O switch.
technique can be found elsewhere [2, 5]. An example of a SSITKA experiment is switching the inlet flow of a reactor containing a Fe based HTFT catalyst from $^{12}$CO/H$_2$/Ar to $^{13}$CO/H$_2$/He. Following the switch from $^{12}$CO to $^{13}$CO, CO$_2$ is formed via reactions (iv) and (v). Figure 1.2 gives the mass fraction of $^{12}$CO$_2$ and $^{13}$CO$_2$ leaving the reactor. As can be observed, after a certain amount of time after the switch, all the species containing $^{12}$C in the system and leaving as CO$_2$ have been replaced by their $^{13}$C containing counterparts. Another example is an experiment in which oxygen labeled reactants were used and switch in inlet flow from C$^{16}$O/H$_2$/Ar to C$^{18}$O/H$_2$/Ne was made. Figure 1.3 gives the mass fraction C$^{16}$O$_2$, C$^{16}$O$^{18}$O and C$^{18}$O$_2$ leaving the reactor in time. This figure shows that even relatively long after the switch $^{16}$O is in the system and leaves the reactor as C$^{16}$O$^{18}$O. The results shown in Figure 1.2 and Figure 1.3 were obtained from experiments done prior to this study.

Figure 1.4 gives a SEM picture of a spent Fe based catalyst removed from the HTFT process. Via Energy-Dispersive X-ray spectroscopy (EDX) the elemental composition of the sample was determined. An EDX sample was prepared by first setting the particle in resin. Then, the sample was ground down to expose cross section surface. This surface was subsequently polished on an allegro/largo polishing mat with diamond paste. Finally this surface was sputter coated with Au/Pd to make it conductive under the electron beam of the SEM. After X-ray Diffraction (XRD) analysis, showing that the sample mainly contains Hägg carbide (Fe$_5$C$_2$) and magnetite (Fe$_3$O$_4$), these two phases can be distinguished in Figure 1.4 [4 ter Stege Sasol]. Figure 1.5 shows the changes in catalyst phases over time for a Fe based catalyst during the HTFT process. Both figures indicate that oxygen, most likely in the form of magnetite, is present inside the catalyst particle.

Figure 1.3 shows a flow of CO$_2$, which contains $^{16}$O, leaving the reactor long after a SSITKA switch was made to a C$^{18}$O inlet flow. Together with Figure 1.4 and Figure 1.5, which indicate the presence of oxygen in the catalyst particle, this strongly suggests there is oxygen in the catalyst bulk and that this oxygen is reactive. Therefore it is hypothesized that this oxygen can diffuse to the catalyst surface to participate in surface reactions and thereby leave the reactor as products of the FT synthesis. This process is schematically represented in Figure 1.6.

### 1.3 Goal of the project

Assuming that oxygen diffusion to and from the catalyst bulk takes place, the goal of the project is the determination of the oxygen diffusion coefficient in the Fe based HTFT catalyst particle.

A model describing the HTFT process will be developed. Oxygen diffusion to and from the catalyst particle is included in this model via the parameter D, the diffusion coefficient. Transient data gathered via SSITKA experiments will be used to fit the model and get a value for the oxygen diffusion coefficient.

Finding a realistic value for the oxygen diffusion coefficient will strongly support the presence of a reactive oxygen pool within the catalyst particle. The fitted value for the diffusion coefficient, can be included in FT reaction mechanisms, leading to a better mechanistic understanding and hence a better catalyst design for tailored selectivity or activity in the commercial HTFT process.
Figure 1.5 Change of phases in catalyst Fe based HTFT catalyst particle in time-on-stream, determined via XRD. [6]

Figure 1.6 Schematic representation of oxygen diffusion from and to the catalyst bulk and a surface reaction

Figure 2.1: Diffusion of oxygen to or from the catalyst bulk
2. Model formulation

2.1 Diffusion

The diffusion of oxygen into and out of the solid bulk of the catalyst particle can be described by Fick’s first (2.1) and second law (2.2) of diffusion [7]:

\[ J_O = -D \frac{\partial S_O}{\partial r} \bigg|_{r=R_{particle}} \]  
\[ \frac{\partial S_O}{\partial t} = D \frac{\partial^2 S_O}{\partial r^2} \]  

In which, \( J_O \) is the oxygen flux \([\text{mole m}_{\text{cat}}^{-2} \text{s}^{-1}]\), \( D \) the oxygen diffusion coefficient \([\text{m}_{\text{cat}}^2/\text{s}]\), \( S_O \) the oxygen concentration in the catalyst bulk \([\text{mole } \text{m}_{\text{cat}}^{-3}]\) and \( r \) the particle radius \([\text{m}_{\text{cat}}]\).

Fick’s first law relates the net flow of oxygen to or from the catalyst particle to the concentration gradient of oxygen in the solid bulk at the surface \((r=R_{particle})\), schematically represented in Figure 2.1.

The concentration of oxygen in the solid bulk at \( r=R_{particle} \) is related to the surface concentration of oxygen, via

\[ S_O \big|_{r=R_{particle}} = \rho_{cat} L_O \]  

In which \( \rho_{cat} \) is the density of the catalyst \([\text{kg}_{\text{cat}}/\text{m}_{\text{cat}}^3]\) and \( L_O \) is the oxygen surface concentration \([\text{mole/kg}_{\text{cat}}]\).

To relate oxygen surface concentrations, and thus the oxygen solid bulk concentration, to measurable gas phase concentrations a mechanism describing the reactions in the HTFT process is required.

2.2 Reaction mechanism

The reaction mechanism should describe the FT synthesis, which in general, for the synthesis of linear alkanes, is given by

\[ n \text{CO} + 2n \text{H}_2 \rightarrow -(\text{CH}_2)_n - + n \text{H}_2\text{O} \]

In the Fe catalyzed HTFT synthesis oxygenates are also produced [1]. In this study however, they are not included in the reaction mechanism because the amount of oxygenates produced under the conditions used in this study is so small, they can be neglected. A table with product yields is included in appendix 1.

In the Fe catalyzed HTFT process (reverse) water gas shift occurs [1, 8]. In this reaction \( \text{CO}_2 \) and \( \text{H}_2 \) can react to form \( \text{CO} \) and \( \text{H}_2\text{O} \),

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]
Figure 2.2: Mechanism for the reactions under FT reaction conditions

Figure 2.3: Mechanism for the reactions under no FT reaction conditions
The reaction mechanism should be able to describe CO\textsubscript{2} formation. The proposed mechanism, to be used in this work is given in Figure 2.2. This is the mechanism for the experiment under FT reaction conditions. The mass transfer by diffusion between S\textsubscript{0} and L\textsubscript{0} is described by Fick’s first law of diffusion.

This mechanism was chosen to be as simple as possible while accounting the formation of CO\textsubscript{2}, hydrocarbons and H\textsubscript{2}O, the adsorption of CO and CO\textsubscript{2}, and the diffusion of oxygen to and from the catalyst bulk.

The feed ratio H\textsubscript{2}:CO equals 10. The typical conversion of H\textsubscript{2} was 10%. This shows that a large excess of hydrogen is present throughout the reactor. Therefore the concentration of hydrogen can be considered constant over the reactor length and is not included in the reaction mechanism. Next to that, the adsorption of a component in the gas phase to the surface is usually described by [9],

\[ A(g) + * \rightleftharpoons A_{ads} \]

In describing adsorption in that way, the concentration of free surface sites, *, is included in the rate of adsorption. As is shown in appendix 2, the surface coverage is not larger than 0.17 ML in the experiments in this study, leaving a lot of free surface sites to adsorb to. It is therefore assumed that the number of free surface sites stays constant throughout the reactor and the concentration of free surface sites not is included in the reaction mechanism. It should be noted that the different surface species shown in Figure 2.2 probably occupy different kinds of surface sites. The assumption of competition between the surface species for one kind of free surface site is thus a simplification.

In the HTFT synthesis the produced hydrocarbon chains differ in length and level of saturation [6]. Furthermore, in the experiments in this study this is the case. To keep the mechanism as simple as possible, all the hydrocarbon species are lumped into one hydrocarbon gas phase concentration, \( C_{C_xH_y} \), and one (hydro)carbon surface concentration, \( L_C \). As in some other mechanisms describing the HTFT synthesis [1] it is assumed that no re-adsorption of hydrocarbon chains to the catalyst surface occurs. Figure 2.2 shows that there are 12 parameters present in the mechanism, including the diffusion constant D.

During FT synthesis CO and H\textsubscript{2} are fed to the reactor giving different products. Feeding the reactor only with CO will decrease the number of different products. Because of the absence of H\textsubscript{2} no hydrocarbon chains and no water molecules are formed, the reactor is operated under so called no FT reaction conditions. CO\textsubscript{2} is however formed. A reaction mechanism describing the formation of CO\textsubscript{2} out of CO over the iron based catalyst is shown in Figure 2.3. As can be seen, the exclusion of hydrocarbon chains and water from the mechanism reduces the number of parameters form 12 to 9.

### 2.3 Reactor model

Since SSITKA gives the transients of labeled fractions of gas phase compounds at the reactor outlet, the reactor model should describe the gas phase concentrations of labeled and non-labeled species in time.

The reactions are carried out in a fixed bed reactor, loaded with catalyst particles. The mole balances, given further on, were set up assuming:

- the absence of axial dispersion (i)
- the absence of radial concentration profiles (ii)
- no mass transfer limitations (iii)
- isothermal operation (iv)
- a constant volumetric flow rate (v)
- the absence of kinetic isotope effects (vi)
- flat plate geometry of the catalyst particles (vii)

Assumptions (i) to (v) are verified in appendix 3.

Van Dijk showed no change in conversion and selectivities for the FT synthesis over a Co based catalyst, when switching the inlet flow from C\textsubscript{16}O to C\textsubscript{18}O [2 thesis van Dijk]. This is a good indication for the absence of kinetic isotope effects for C\textsubscript{16}O to C\textsubscript{18}O switches in FT synthesis.

Based on a SEM picture of spent Fe based HTFT catalyst (Figure 2.44), the catalyst particle was modeled as a flat plate.

Since the total concentration of a certain compound will not change in time in the experiment under FT reaction conditions, only the isotopic fractions will. Steady state mole balances can be set up. The steady state concentrations are used as starting values for the balances describing the transient behavior of the labeled species. Gas phase concentrations, C [mole mg\textsuperscript{-3}], and surface concentrations, L [mole kg\textsubscript{cat}\textsuperscript{-1}], are a function of the dimensionless reactor length (x). \( F_v \) denotes the volumetric flow [m\textsuperscript{3}/s], \( V_r \) the reactor volume [m\textsuperscript{3}], \( \varepsilon_b \) the catalyst bed porosity [m\textsuperscript{3}/m\textsuperscript{3}] and \( \rho_b \) the bed density [kg cat/m\textsuperscript{3}]. The different k's express reaction rate constants. The constants \( k_{CO,ads} \), \( k_{CO2,ads} \) and \( k_{H2O,ass} \) are expressed in m\textsuperscript{3}s\textsuperscript{-1}kg\textsubscript{cat}, \( k_{CO,des} \), \( k_{CO2,des} \), \( k_{CH} \), \( k_{H2O,ass} \), \( k_{CO,dis} \) and \( k_{CO2,dis} \) in s\textsuperscript{-1}, and \( k_{CO,ass} \) and \( k_{CO2,ass} \) in kg\textsubscript{cat}mole\textsuperscript{-1}s\textsuperscript{-1}.

The subscript SS denotes steady state operation.

\[
\frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{CO,ss}}{\partial x} = \frac{\rho_b}{\varepsilon_b} \left( k_{CO,des} L_{CO,ss} - k_{CO,ads} C_{CO,ss} \right) \tag{2.4}
\]

\[
\frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{CO2,ss}}{\partial x} = \frac{\rho_b}{\varepsilon_b} \left( k_{CO2,des} L_{CO2,ss} - k_{CO2,ads} C_{CO2,ss} \right) \tag{2.5}
\]

\[
\frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{C_xH_y,ss}}{\partial x} = \frac{\rho_b}{\varepsilon_b} k_{CH} L_{C,ss} \tag{2.6}
\]

\[
\frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{H2O,ss}}{\partial x} = \frac{\rho_b}{\varepsilon_b} \left( k_{H2O,ass} L_{O,ss} - k_{H2O,dis} C_{H2O,ss} \right) \tag{2.7}
\]

0 = \(-k_{CO,des} L_{CO,ss} + k_{CO,ads} C_{CO,ss} - k_{CO,dis} L_{CO,ss} + k_{CO,ass} L_{C,ss} L_{O,ss} + k_{CO2,dis} L_{CO2,ss} - k_{CO2,ass} L_{CO2,ss} L_{O,ss} \) \tag{2.8}

0 = \(-k_{CO,dis} L_{CO,ss} + k_{CO,ass} L_{C,ss} L_{O,ss} - k_{CO,des} L_{CO,ss} + k_{CO2,ads} C_{CO2,ss} \) \tag{2.9}

0 = \(k_{CO,dis} L_{CO,ss} - k_{CO,ass} L_{C,ss} L_{O,ss} - k_{H2O,ass} L_{O,ss} + k_{H2O,dis} C_{H2O,ss} + k_{CO2,dis} L_{CO2,ss} - k_{CO2,ass} L_{CO2,ss} L_{O,ss} \) \tag{2.10}

0 = \(k_{CO,dis} L_{CO,ss} - k_{CO,ass} L_{C,ss} L_{O,ss} - k_{CH} L_{C,ss} \) \tag{2.11}

Boundary conditions for these equations are given below.

At \( x=0 \)

\[
C_{CO,ss} = C_{CO,in} \tag{2.12}
\]

\[
C_{CO2,ss} = C_{H2O,ss} = C_{C_xH_y,ss} = L_{CO,ss} = L_{CO2,ss} = L_{O,ss} = L_{C,ss} = 0 \tag{2.13}
\]
C\textsubscript{CO\_in} represents the CO inlet concentration.

With i and j expressing the isotopic label, i=16, 18, j=16, 18, i≠j, and noting that C\textsuperscript{16}O\textsuperscript{18}O is the same as C\textsuperscript{18}O\textsuperscript{16}O the model equations for the labeled species changing in time are:

\[
\frac{\partial C_{O_i}}{\partial t} + \frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{O_i}}{\partial x} = \rho_b \frac{\partial}{\partial b} \left( k_{CO,\text{des}} L_i \cdot C_{O_i} - k_{CO,\text{ads}} C_{O_i} \right) \tag{2.14}
\]

\[
\frac{\partial C_{O_2}}{\partial t} + \frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{O_2}}{\partial x} = \rho_b \frac{\partial}{\partial b} \left( k_{CO_2,\text{des}} L_i \cdot C_{O_2} - k_{CO_2,\text{ads}} C_{O_2} \right) \tag{2.15}
\]

\[
\frac{\partial C_{O_i \cdot O_j}}{\partial t} + \frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{O_i \cdot O_j}}{\partial x} = \rho_b \frac{\partial}{\partial b} \left( k_{CO_2,\text{des}} L_i \cdot C_{O_i \cdot O_j} - k_{CO,\text{ads}} C_{O_i \cdot O_j} \right) \tag{2.16}
\]

\[
\frac{\partial C_{CH}}{\partial t} + \frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{CH}}{\partial x} = \rho_b \frac{\partial}{\partial b} \left( k_{CH,L} C_i \right) \tag{2.17}
\]

\[
\frac{\partial C_{H_2O}}{\partial t} + \frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{H_2O}}{\partial x} = \rho_b \frac{\partial}{\partial b} \left( k_{H_2O,\text{ass}} L_i \cdot C_{H_2O} - k_{H_2O,\text{dis}} C_{H_2O} \right) \tag{2.18}
\]

\[
\frac{\partial L_i}{\partial t} = -k_{CO,\text{des}} L_i \cdot C_{O_i} + k_{CO,\text{ads}} L_i \cdot C_{O_i} - k_{CO,\text{dis}} L_i \cdot C_{O_i} + k_{CO,\text{ass}} C_i \cdot L_i + k_{CO_2,\text{dis}} \left( L_i \cdot C_{O_i} \cdot \frac{1}{2} L_i \cdot C_{O_i} \right) \tag{2.19}
\]

\[
\frac{\partial L_{O_2}}{\partial t} = -k_{CO_2,\text{dis}} L_i \cdot C_{O_2} + k_{CO_2,\text{ass}} L_i \cdot C_{O_2} - k_{CO_2,\text{dis}} L_i \cdot C_{O_2} + k_{CO_2,\text{ass}} C_i \cdot L_i \cdot C_{O_2} \tag{2.20}
\]

\[
\frac{\partial L_{O_2}}{\partial t} = -k_{CO_2,\text{dis}} L_i \cdot C_{O_2} + k_{CO_2,\text{ass}} L_i \cdot C_{O_2} - k_{CO_2,\text{dis}} L_i \cdot C_{O_2} + k_{CO_2,\text{ass}} C_i \cdot L_i \cdot C_{O_2} \tag{2.21}
\]

\[
\frac{\partial L_{H_2O}}{\partial t} = k_{CO,\text{dis}} L_i \cdot C_{O_i} - k_{CO,\text{ass}} L_i \cdot C_{O_i} - k_{H_2O,\text{ass}} L_i \cdot C_{H_2O} + k_{H_2O,\text{dis}} C_i \cdot L_i \cdot C_{H_2O} + k_{CO_2,\text{dis}} \left( L_i \cdot C_{O_i} \cdot \frac{1}{2} L_i \cdot C_{O_i} \right) \tag{2.22}
\]

\[
\frac{\partial L_i}{\partial t} = k_{CO,\text{dis}} \left( L_i \cdot C_{O_i} + L_i \cdot C_{O_2} \right) - k_{CO,\text{ass}} L_i \cdot C_{O_i} - k_{CH,L} C_i \tag{2.23}
\]

\[
\frac{\partial S_{L_i}}{\partial t} = D \frac{\partial^2 S_{L_i}}{\partial r^2} \tag{2.24}
\]

The surface area per mass of catalyst is represented by \(a_s [m\text{cat}^2/kg\text{cat}]\).

For these equations starting values are required.

At t=0 and for x>0

\[
L_{i,0}(x) = L_{CO,ss}(x) \tag{2.25}
\]

\[
L_{O_2,0}(x) = L_{CO_2,ss}(x) \tag{2.26}
\]

\[
L_{16O}(x) = L_{O,ss}(x) \tag{2.27}
\]

\[
L_{C}(x) = L_{C,ss}(x) \tag{2.28}
\]

\[
C_{i,0}(x) = C_{CO,ss}(x) \tag{2.29}
\]
\[ f(t) = \left( \frac{1}{1 + \exp\left(\frac{-t - a_1}{a_2}\right)} \right)^{a_3} \]

\[ a_1 = 0.025 \quad a_2 = 2.88 \quad a_3 = 1712 \quad (2.43) \]

Figure 2.5 Inlet function fitted to the inert fraction Krypton leaving the reactor
\[ C_{C}^{16}O_{2}(x) = C_{CO,ss}(x) \]  
\[ C_{H_{2}}^{16}O(x) = C_{H_{2}O,ss}(x) \]  
\[ C_{H_{2}}^{16}O(x) = C_{H_{2}O,ss}(x) \]  
\[ C_{C-xHy}(x) = C_{C-xHy,ss}(x) \]  
\[ C_{C}^{18}O(x) = C_{C}^{18}O(x) = C_{H_{2}}^{18}O(x) = L_{C}^{18}O(x) = L_{C}^{18}O_{2}(x) = L_{C}^{18}O_{16}(x) = L_{18}O(x) = 0 \]  

At t=0, for x>0 and 0>r>\( R_{\text{particle}} \)

\[ S_{16}O(x) = \rho_{\text{cat}} L_{O,ss}(x) \]  
\[ S_{18}O(x) = 0 \]  

The boundary conditions are given here.

At x=0

\[ C_{C-O,ss} = C_{CO,-in} \]  
\[ C_{C}^{16}O = C_{CO,in}(1 - f(t)) \]  
\[ C_{C}^{18}O = C_{CO,in}f(t) \]  
\[ C_{C}^{18}O = C_{C}^{18}O(x) = C_{C-xHy} = L_{C}^{18}O = L_{C}^{18}O_{2} = L_{C}^{18}O_{16} = L_{18}O = 0 \]  

At x=0 and for \( \forall \) r

\[ S_{i0} = 0 \]  

For x>0 and at r=0

\[ \frac{\partial S_{i0}}{\partial r} = 0 \]  

For x>0 and at r=\( R_{\text{particle}} \)

\[ S_{i0} = \rho_{\text{cat}} L_{i0} \]  

The function \( f(t) \) represent the inlet function. This function, going from 0 to 1 over time, describes how fast the switch is made. The outlet function of the inert tracer is equal to its inlet function under the assumption of no axial dispersion and no interaction of the inert with the reactor wall and catalyst particles. Since the piping from the switch to the top of the reactor bed is inert, the inlet function for all components is the same. Therefore the inert outlet transient is used to fit an inlet function. This is shown in Figure 2.5.

The system under no FT reaction conditions produces \( CO_{2} \) while only \( CO \) is fed to the reactor. Therefore the system is not a steady state. This means that over time carbon is deposited on the surface via the Boudouard reaction (2.44), the amount of oxygen in the catalyst particle decreases over time, or both processes happen.

\[ 2 \, CO \rightarrow C + CO_{2} \]  

(2.44)
It is assumed that in the time of the experiment no carbon species accumulate in the reactor operated under no FT reaction conditions. As the carbon balance was close to 1, which is shown in chapter 4, this assumption is valid. As a result, for the mass balances to be correct, the amount of oxygen in the catalyst bulk decreases over time. In order to get starting values for the equations describing the change in time of the labeled species a constant flow of oxygen to the surface was assumed, \( k_{O, \text{pool}} \), leading to a system at steady state. The constant \( k_{O, \text{pool}} \) was determined via the CO outlet concentrations. The steady state balances for the system under no FT reaction conditions are then as follows.

\[
\frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{CO, \text{ss}}}{\partial x} = \frac{\rho_b}{\varepsilon_b} \left( k_{CO, \text{des}} L_{CO, \text{ss}} - k_{CO, \text{ads}} C_{CO, \text{ss}} \right) \tag{2.45}
\]

\[
\frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{CO_2, \text{ss}}}{\partial x} = \frac{\rho_b}{\varepsilon_b} \left( k_{CO_2, \text{des}} L_{CO_2, \text{ss}} - k_{CO_2, \text{ads}} C_{CO_2, \text{ss}} \right) \tag{2.46}
\]

\[
0 = -k_{CO, \text{des}} L_{CO} + k_{CO, \text{ads}} C_{CO} - k_{CO, \text{dis}} L_{CO} + k_{CO, \text{ass}} L_{L_0} + k_{CO_2, \text{dis}} L_{CO_2} - k_{CO_2, \text{ass}} L_{CO} \tag{2.47}
\]

\[
0 = -k_{CO_2, \text{dis}} L_{CO_2} + k_{CO_2, \text{ass}} L_{L_0} \tag{2.48}
\]

\[
0 = k_{CO, \text{dis}} L_{CO} - k_{CO, \text{ass}} L_{L_0} + k_{CO_2, \text{dis}} L_{CO_2} - k_{CO_2, \text{ass}} L_{CO} \tag{2.49}
\]

\[
0 = k_{CO, \text{dis}} L_{CO} - k_{CO, \text{ass}} L_{L} \tag{2.50}
\]

Again, these boundary conditions apply.

At \( x=0 \)

\[
C_{CO, \text{ss}} = C_{CO, \text{in}} \tag{2.51}
\]

\[
C_{CO_2, \text{ss}} = L_{CO, \text{ss}} = L_{CO_2, \text{ss}} = L_{L_0, \text{ss}} = L_{L_{\text{ss}}} = 0 \tag{2.52}
\]

The mole balances for the system under no FT reaction conditions are given below.

\[
\frac{\partial C_{i_0}}{\partial t} + \frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{i_0}}{\partial x} = \frac{\rho_b}{\varepsilon_b} \left( k_{CO, \text{des}} L_{C} \ i_0 - k_{CO, \text{ads}} C_{C} \ i_0 \right) \tag{2.53}
\]

\[
\frac{\partial C_{i_0}}{\partial t} + \frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{i_0}}{\partial x} = \frac{\rho_b}{\varepsilon_b} \left( k_{CO_2, \text{des}} L_{C} \ i_0 - k_{CO_2, \text{ads}} C_{C} \ i_0 \right) \tag{2.54}
\]

\[
\frac{\partial C_{i_0}}{\partial t} + \frac{F_v}{V_r \varepsilon_b} \frac{\partial C_{i_0}}{\partial x} = \frac{\rho_b}{\varepsilon_b} \left( k_{CO_2, \text{des}} L_{C} \ i_0 - k_{CO_2, \text{ads}} C_{C} \ i_0 \right) \tag{2.55}
\]

\[
\frac{\partial L_{C} \ i_0}{\partial t} = -k_{CO, \text{des}} L_{C} \ i_0 + k_{CO, \text{ads}} C_{C} \ i_0 - k_{CO, \text{dis}} L_{C} \ i_0 + k_{CO, \text{ass}} L_{L} \ i_0 + k_{CO_2, \text{dis}} \left( L_{C} \ i_0 + \frac{1}{2} L_{C} \ i_0 \right) \tag{2.56}
\]

\[
\frac{\partial L_{C} \ i_0}{\partial t} = -k_{CO_2, \text{dis}} L_{C} \ i_0 + k_{CO_2, \text{ass}} L_{L} \ i_0 + k_{CO_2, \text{dis}} L_{C} \ i_0 + k_{CO_2, \text{ass}} C_{C} \ i_0 \tag{2.57}
\]

\[
\frac{\partial L_{C} \ i_0}{\partial t} = -k_{CO_2, \text{dis}} L_{C} \ i_0 + k_{CO_2, \text{ass}} \left( L_{C} \ i_0 \ i_0 + L_{C} \ i_0 \ i_0 \right) - k_{CO_2, \text{des}} L_{C} \ i_0 \ i_0 \tag{2.58}
\]
\[
\frac{\partial L_{i0}}{\partial t} = k_{CO,dis}L_{i0} - k_{CO,ass}L_{i0} + L_{i0}^2 \left( L_{i0} + \frac{1}{2} L_{i0} \right) - k_{CO,ass}(L_{i0} + L_{i0})L_{i0}
- D \left. \frac{\partial S_{i0}}{\partial r} \right|_{r=R_{particle}} a_s \quad (2.59)
\]
\[
\frac{\partial L}{\partial t} = k_{CO,dis} \left( L_{i0} + L_{i0} \right) - k_{CO,ass}L_{i0} \left( L_{i0} + L_{i0} \right) \quad (2.60)
\]
\[
\frac{\partial L_{i0}}{\partial t} = k_{CO,dis} \left( L_{i0} + L_{i0} \right) - k_{CO,ass}L_{i0} \left( L_{i0} + L_{i0} \right) \quad (2.60)
\]
\[
0 = \frac{\partial C_{160}}{\partial t} + \frac{\partial C_{180}}{\partial t} + \frac{\partial C_{16O2}}{\partial t} + \frac{\partial C_{18O2}}{\partial t} + \frac{\partial L_{160}}{\partial t} + \frac{\partial L_{180}}{\partial t} + \frac{\partial L_{16O2}}{\partial t} \quad (2.61)
\]
\[
\frac{\partial S_{i0}}{\partial t} = D \frac{\partial^2 S_{i0}}{\partial r^2} \quad (2.62)
\]

Again with the same expressions for the starting values and boundary conditions.
At \( t = 0 \) and for \( x > 0 \)

\[
L_{160}(x) = L_{CO,ss}(x) \quad (2.63)
\]
\[
L_{18O2}(x) = L_{CO,ss}(x) \quad (2.64)
\]
\[
L_{16O}(x) = L_{0,ss}(x) \quad (2.65)
\]
\[
L_{c}(x) = L_{ss}(x) \quad (2.66)
\]
\[
C_{16O}(x) = C_{CO,ss}(x) \quad (2.67)
\]
\[
C_{18O2}(x) = C_{CO,ss}(x) \quad (2.68)
\]
\[
C_{18O}(x) = C_{18O2}(x) = C_{16O}(x) = L_{16O}(x) = L_{18O2}(x) = L_{16O}^{18O}(x) = L_{18O}(x) = 0 \quad (2.69)
\]

At \( t = 0 \), for \( x > 0 \) and \( 0 > r > R_{particle} \)

\[
S_{16O}(x) = \rho_{cat} L_{0,ss}(x) \quad (2.70)
\]
\[
S_{18O}(x) = 0 \quad (2.71)
\]

At \( x = 0 \)

\[
C_{16O} = C_{CO,lin}(1 - f(t)) \quad (2.72)
\]
\[
C_{18O} = C_{CO,lin} f(t) \quad (2.73)
\]
\[
C_i = C_i + \frac{L_i}{L_i} \quad (2.74)
\]

At \( x = 0 \) and for \( \forall r \)

\[
S_{i0} = 0 \quad (2.75)
\]
For $x>0$ and at $r=0$
\[
\frac{\partial S_{i0}}{\partial r} = 0 \quad (2.76)
\]

For $x>0$ and at $r=R_{\text{particle}}$
\[
S_{i0} = \rho_{\text{cat}} L_{i0} \quad (2.77)
\]

From the concentrations of the isotopically labeled species in the gas phase mass fractions, $f [-]$, can be obtained via,

\[
f_{C_{i0}} = \frac{C_{C_{i0}}}{C_{C_{i0}} + C_{C_{i0}}} \quad (2.78)
\]
\[
f_{C_{i0}i0} = \frac{C_{C_{i0}}}{C_{C_{i0}} + C_{C_{i0}} + C_{C_{i0}} + C_{C_{i0}}} \quad (2.79)
\]
\[
f_{C_{i0}2} = \frac{C_{C_{i0}}}{C_{C_{i0}} + C_{C_{i0}} + C_{C_{i0}} + C_{C_{i0}}} \quad (2.80)
\]
\[
f_{H2_{i0}} = \frac{C_{H2_{i0}}}{C_{H2_{i0}} + C_{H2_{i0}}} \quad (2.81)
\]

## 2.4 Parameter estimation

For solving the partial differential equations given in the last section a software package called gPROMS (general PROcess Modeling System) was used. This package was also used to estimate the unknown parameters via curve fitting of the transients obtained from experiments. Parameter estimation uses the objective function [1],

\[
\Phi = \frac{N}{2} \ln(2\pi r) + \frac{1}{2} \min_\theta \left\{ \sum_{i=1}^{NE} \sum_{j=1}^{NV} \sum_{k=1}^{NM_i} \left[ \ln\left(\frac{\sigma_{ijk}^2}{\sigma_{ijk}^2}\right) + \frac{(\bar{z}_{ijk} - \bar{z}_{ijk})^2}{\sigma_{ijk}^2} \right] \right\} \quad (2.82)
\]

In which
- $\Phi$ objective function [-]
- $N$ total number of measurements taken during all experiments [-]
- $\theta$ set of model parameters to be estimated [-]
- $NE$ number of experiments performed [-]
- $NV_i$ number of variables measured in the $i$th experiment [-]
- $NM_{ij}$ number of measurements of the $j$th variable in the $i$th experiment [-]
- $\sigma_{ijk}^2$ variance of the $k$th measurement of variable $j$ in experiment $i$ [-]
- $\bar{z}_{ijk}$ $k$th measured value of variable $j$ in experiment $i$ [-]
- $z_{ijk}$ $k$th (model-)predicted value of variable $j$ in experiment $i$ [-]
The principle of parameter estimation is based upon the minimization of the difference ($\xi_i$) between the experimental value ($\tilde{z}_i$) and the value predicted by the model ($z_i(\theta)$), for all experimental values. The difference is assumed to be independent and normally distributed with zero mean and standard deviation $\sigma_i$.

$$\xi_i = \tilde{z}_i - z_i(\theta) \quad (2.83)$$

In gPROMS several variance models are available to choose from for the standard deviation of $\xi_i$ [1]. In this study the model with a constant standard deviation was used.
Figure 3.1 Schematic representation of the experimental set up. PI = Pressure Indicator, PIC = Pressure Indicator Controller, 
TC = Thermocouple, - - - = wire conducting electric current

Table 3.1 Overview of the gases fed to the reactor and their purities

<table>
<thead>
<tr>
<th>Gas</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>99.999%</td>
</tr>
<tr>
<td>Ne</td>
<td>99.999%</td>
</tr>
<tr>
<td>Kr</td>
<td>99.995%</td>
</tr>
<tr>
<td>H₂</td>
<td>99.999%</td>
</tr>
<tr>
<td>CO</td>
<td>99.997%</td>
</tr>
<tr>
<td>C¹⁸O</td>
<td>95% C¹⁸O</td>
</tr>
<tr>
<td>C¹³O</td>
<td>99% C¹³C, &lt;2% C¹⁸O</td>
</tr>
</tbody>
</table>
3. Experimental set-up and procedures

3.1 Set-up

The experimental set-up consisted of a feed section, a reactor section and an analysis section. A schematic overview is given in Figure 3.1.

Feed section
The feed section supplied the different gasses via mass flow controllers to the reactor. Two back pressure regulators (1) and (2) control the pressure to prevent a pressure drop or increase when a switch is made. Table 3.1 gives the an overview of the gasses used and their purities. A more detailed description of the feed section can be found elsewhere [1,8].

C^{18}O and ^{13}CO were purchased from Cambridge Isotope Laboratories.

Reactor section
A stainless steel, fixed bed reactor was used with a reaction zone of 5mm I.D. x 80mm. The reactor contained a catalyst bed of an alkali promoted fused iron catalyst mixed with inert SiC. The reactor was heated by an external electric heating jacket. A thermocouple placed inside the reactor wall and halfway down the catalyst bed controlled the temperature of the reactor. The catalyst bed was placed in the middle of the heating zone (± 28 cm), as such isothermal operation was assumed.

Analysis section
The analysis section consisted of a Gas Chromatograph (GC), a Mass Spectrometer (MS) and a Gas Chromatograph Mass Spectrometer (GC-MS), all three operating online. The GC measured conversion and selectivities of CO, CO_2, H_2, CH_4 and hydrocarbons (C_2 to C_4) with use of a TCD (thermal conductivity detector) and a FID (flame ionization detector). The MS was used to measure mass fractions at the inlet and the outlet of the reactor. The GCMS measured mass fractions at the outlet of the reactor. The GCMS was equipped with 16 sample loops, to store samples from a SSITKA switch for later analysis. More about GCMS and MS data analysis is given below. The GC analysis section has been described before [1,8], specifications of the GC and GCMS can be found in Table 3.2.

GC-MS
The products leaving the reactor and entering the GC-MS analysis section can be non-, partially or fully labeled. Specifications of the GC-MS are given in Table 3.2. The GC-MS analysis consists of three steps. First are the different products separated via gas chromatography (step 1). After that the fragmentation patterns of every separated product is recorded (step 2). Then, form this fragmentation pattern, the isotopic compositions are calculated (step 3). The fragmentation pattern that is recorded in step 2 is a linear combination of the individual fragmentation patterns of all isotopic variants of the product. As described by van Dijk the contribution of every isotopic variant to the fragmentation pattern, and thus its fraction, can be quantified by minimizing this objective function [2]:
<table>
<thead>
<tr>
<th></th>
<th>GC</th>
<th>GC-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Column</strong></td>
<td>TCD: CP-PoraBOND Q (I.D.=0.53 mm, L=10m)</td>
<td>PoraBOND Q (I.D.=0.32 mm, L=50m)</td>
</tr>
<tr>
<td></td>
<td>TCD: CP-PoraBOND Q (I.D.=0.53 mm, L=25m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TCD: CP-Molsieve 5a (I.D.=0.53 mm, L=25m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FID1: PoraBOND Q (I.D.=0.25 mm, L=25m)</td>
<td></td>
</tr>
<tr>
<td><strong>Carrier gas</strong></td>
<td>Argon</td>
<td>Helium</td>
</tr>
</tbody>
</table>
| **Temperature program** | For TCD and FID (same oven): 4 min at 40°C  
Ramp 10°C min\(^{-1}\) to 85°C  
5 min at 85°C  
Ramp 2°C min\(^{-1}\) to 110°C  
Ramp 15°C min\(^{-1}\) to 240°C  
20 min at 240°C | 5 min at -50°C  
Ramp 10°C min\(^{-1}\) to 130°C  
5 min at 130°C  
Ramp 15°C min\(^{-1}\) to 240 °C  
10 min at 240 °C |
| **Column flow/Pressure** | Line 1 (TCD): 2.0 ml min\(^{-1}\)  
Line 2 (FID1): 1.8 ml min\(^{-1}\) | 2.06 ml min\(^{-1}\) |
| **MS Method**       |                                                                    | Scanning range: mass 12 to 150  
Scan speed: 416 scan min\(^{-1}\)  
Ion Source Electron Impact (EI)  
Temp: 230 °C  
Interface Temp: 250 °C |
\[ S(x) = \sum_{i=1}^{m} \left( \sum_{j=1}^{n} \left( x_{i,j} \cdot f_{i,j}^{\text{ref}} \right) - f_{i}^{\text{obs}} \right)^2 \]  

In which,

- \( n \) is the number of isotopic variants of a given product.
- \( m \) is the number of m/e values of the fragmentation pattern of a given product.
- \( f_{i}^{\text{obs}} \) is the observed intensity of the fragmentation pattern of the mixture at the \( i \)th m/e value.
- \( f_{i,j}^{\text{ref}} \) is the intensity of fragmentation pattern of the \( j \)th isotopic variant at the \( i \)th m/e value.
- \( x_{i,j} \) is the fractional contribution of the \( j \)th isotopic variant to the mixture at the \( i \)th m/e value.

The fragmentation pattern of every isotopic variant of every product in the product mixture has to be known for this procedure to work. The fragmentation patterns of isotopic variants are derived from the patterns of their non-labeled counterparts assuming [2]:

- no change of peak intensities when \(^{16}\text{O} \) is replaced by \(^{18}\text{O} \), and
- secondary fragmentations can be neglected.

**MS**

The MS section measures online mass fractions of reactants entering the reactor or products and unreacted reactants leaving the reactor. Masses that were recorded, depending on the experiment, are 15.9, 17.87, 20, 22, 28, 30, 40, 44, 46, 48, 83.59 and 85.96 for \( \text{CH}_4 \), \( \text{H}_2^{16}\text{O} \), \( \text{H}_2^{18}\text{O} \), \( ^{22}\text{Ne} \), \( ^{16}\text{O} \), \( ^{18}\text{O} \), \( \text{Ar} \), \( ^{16}\text{O}_2 \), \( ^{16}\text{O}^{18}\text{O} \), \( ^{18}\text{O}_2 \), \( ^{84}\text{Kr} \), and \( ^{86}\text{Kr} \) respectively. For the inert tracers (Ne, Ar and Kr) the initial MS signal and the MS signal after full replacement of the inert tracer, the transient responses were normalized between 0 and 1, using this equation:

\[ E_I = \frac{I_{t} - I_{\text{min}}}{I_{\text{max}} - I_{\text{min}}} \]  

Where,

- \( E_I \) is the normalized transient of inert I, [-]
- \( I_{t} \) the MS intensity of I at time t [Amp]
- \( I_{\text{min}} \) the minimum MS intensity of I, and [Amp]
- \( I_{\text{max}} \) the maximum MS intensity of I [Amp]

The MS signals for the oxygen containing compounds leaving the reactor are also normalized. However, they or not normalized between 0 and 1 since no full replacement is reached. Using the same equation (3.2) as for the inert species the MS signals are normalized between 0 and their maximum fraction which is obtained from the GCMS analysis.

### 3.2 Procedures

Typically 1 g of catalyst (38-100 μm) was weighed, mixed with SiC (100-150 μm) and loaded into the reactor. SiC has good heat conducting properties and it lowers the pressure drop because its particles are larger than the catalyst particles [8]. The catalyst was then reduced with a \( \text{H}_2 \) (60 ml(n)/min) / \( \text{Ar} \) (20
Table 3.3 Overview SSITKA experiments

<table>
<thead>
<tr>
<th>Run</th>
<th>$F_v$ [ml(n)/min]</th>
<th>CO:H$_2$:Ar</th>
<th>Switch</th>
<th>$W_{cat}$ [g]</th>
<th>GHSV [ml(n)/(g$_{cat}$·h)]</th>
<th>$p$ [bar(g)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>1:0:19</td>
<td>$^{16}$O/Ar to $^{18}$O/Ne</td>
<td>1.003</td>
<td>3600</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>1:10:9</td>
<td>$^{16}$O/Ar to $^{18}$O/Kr</td>
<td>1.001</td>
<td>3600</td>
<td>5</td>
</tr>
<tr>
<td>3*</td>
<td>60</td>
<td>1:0:19</td>
<td>$^{12}$CO/Ar to $^{13}$CO/Ne</td>
<td>0.995</td>
<td>3600</td>
<td>5</td>
</tr>
</tbody>
</table>

*The catalyst bed length was 2 cm.*
mln/min) mixture at 420 °C and atmospheric pressure for 16 hours. The pressure was kept at 1 atm to avoid oxidation of the catalyst, due to the formation of water. The total gas hourly space velocity GHSV was 4800 ml(n)/gcat-h. After reduction the temperature was decreased to 330 °C under Ar. When the temperature was reached, Fischer-Tropsch synthesis was started by introducing a gas mixture of CO/H2/Ar with flows of 3, 30 and 27 ml(n)/min respectively at 5 bar(g) for approximately 24 hours to allow the reaction to reach steady state. Once steady state was reached SSITKA experiments were carried out.

Two conditions were distinguished for the SSITKA experiments, no FT reaction conditions and FT reaction conditions. Under no FT reaction conditions only CO and an inert gas were fed to the reactor. Under FT reaction conditions CO, H2 and an inert gas were fed to the reactor leading to FT synthesis. For FT reaction conditions a SSITKA switch was carried out after steady state was reached. For no FT reaction conditions the reactor was, after reaching steady state, flushed with Ar (60 ml(n)/min) for 1 hour. After this CO and Ar were introduced. When pseudo steady state was reached a SSITKA switch was carried out.
Table 4.1: Inlet and outlet flows of CO and CO₂ in the experiment under no FT reaction conditions, carbon balance \( \frac{F_{\text{CO, in}} + F_{\text{CO₂, out}}}{F_{\text{CO, in}}} \).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( F_{\text{CO, in}} ) [μmole/s]</th>
<th>( F_{\text{CO₂, in}} ) [μmole/s]</th>
<th>( F_{\text{CO₂, out}} ) [μmole/s]</th>
<th>Carbon balance [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No FT reaction conditions</td>
<td>2.23</td>
<td>2.09</td>
<td>0.15</td>
<td>1.0076</td>
</tr>
</tbody>
</table>

Figure 4.0.1 Fractions of \(^{16}\text{O}_2\), \(^{16}\text{O}^{18}\text{O}\), \(^{18}\text{O}_2\) and the inert tracer leaving the reactor for the experiment under no FT reaction conditions.

Figure 4.0.2 The fractions of \(^{12}\text{CO}_2\) and inert tracer leaving the reactor for the experiment under no FT reaction conditions.
4. Results and discussion

4.1 Experiments

Table 4. gives inlet and outlet flows of the experiment under no FT reaction conditions. CO₂ is formed and the carbon balance is close to 1, meaning that there is more oxygen leaving the reactor than entering. This supports the suggestion of an oxygen pool present in the reactor.

Observations

In Figure 4.0.1 and Figure 4.0.2 the outlet fraction of CO₂ for experiments under no FT reaction conditions are given for a switch to C¹⁸O and ¹³CO inlet flow respectively.

- In Figure 4.0.1 shows that the C¹⁸O₂ signal does not reach 1 in the time of the experiment, furthermore the signals for C¹⁶O¹⁸O and C¹⁶O₂ do not reach 0. Initially the C¹⁸O₂ signal shows a sharp increase after which it slowly increases with time to a value of 0.73 at the end of the sampling time. The signal for the C¹⁶O₂ fraction first sharply decreases and then slowly drops further to almost 0. The C¹⁶O¹⁸O fraction increases fast to a maximum value, then shows a fast decrease and subsequently a slow decrease with time. The transient for the He shows when the inert tracer leaves the reactor.
- In Figure 4.0.2, the ¹²CO₂ signal reaches 0 after 300 seconds.

Figure 4. compares the C¹⁶O transient of the oxygen labeling experiment under no FT reaction conditions to the ¹²CO transient of the carbon labeling experiment under no FT reaction conditions.

- The ¹²CO signal reaches 0 very fast, while the C¹⁶O shows a sharp decrease initially and then levels off to a value of around 0.08.

Figure 4.44 and Figure 4.55 show data from experiments done under FT reaction conditions, where both CO and H₂ were fed to the reactor. Figure 4.4 shows transients of ¹⁶O containing products after a SSITKA switch from C¹⁶O/H₂/Ar to C¹⁸O/H₂/Kr was made. Figure 4.55 gives the trends for ¹²C containing products for an experiment done under similar (FT reaction) conditions, following a SSITKA switch from ¹²CO/H₂/Ar to ¹³CO/H₂/He.

- The trends observed for the transients for ¹²CO, ¹²CO₂, C¹⁶O₂ and C¹⁶O¹⁸O are the same as for the experiments under no FT reaction conditions (Figures 4.1, 4.2 and 4.3). The transients for ¹²CO reaches 0 very fast, the transient for ¹²CO₂ after about 100 seconds. The transient for C¹⁶O₂ does not reach 0 and transient for C¹⁶O¹⁸O shows a bump and then levels off.
- The transient for C¹⁶O in the system under FT reaction conditions (Figure 4.4), drops to almost 0, while transient for C¹⁶O of the system under no FT reaction conditions (Figure 4.3) levels off to a value of around 0.08.
- In Figure 4.4 the transient for H₂¹⁶O, water being one of the products of FT synthesis, reaches, after a fast decrease, a constant value of around 0.66. The displayed data points for H₂¹⁶O were obtained by GC-MS.
Figure 4.3 Fractions of $^{12}$CO, C$_{16}$O and inert leaving the reactor for the experiment under no FT reaction conditions.

Figure 4.4 Fractions of $^{16}$O labeled compounds leaving the reactor for the experiment under FT reaction conditions.
The signal for the $^{12}$C containing hydrocarbon product $^{12}$CH$_4$ decreases to 0 after 200 s.

**Discussion**

The observations made in Figure 4.0.12 and Figure 4.3 compared to the data in Figure 4.0.22 give further evidence for the presence of an oxygen pool in the catalyst particle. Figure 4.0.22 and Figure 4.3 show that all $^{12}$C containing species present in the reactor at the moment of the switch have left the reactor 300 seconds after the $^{12}$CO to $^{13}$CO switch was made. According to the model for the system under no FT reaction conditions, presented in Chapter 2, carbon can be present in the form of CO(g), CO$_2$(g), CO$_{ads}$, CO$_{2,ads}$ and C$_{ads}$. Figure 4.0.1 and Figure 4.3 show that even after 300 seconds $^{16}$O is still leaving the reactor in the form of CO or CO$_2$. Since all the CO(g), CO$_2$(g), CO$_{ads}$, and CO$_{2,ads}$ species present before the switch have already left the reactor at 300 seconds, which can be concluded from the $^{12}$CO$_2$ and $^{12}$CO transients in Figures 4.2 and 4.3, the $^{16}$O had to be present in another form at the moment of the switch. According to the mechanism this can be either in the form of a surface species ($L_o$) or in the solid catalyst bulk ($S_o$), from which it can diffuse to the surface and react. The presence of both a surface oxygen species and a solid catalyst bulk species is supported by the shape of the $^{16}$O transients in Figure 4.0.1. The presence of a maximum can be explained by the fact that the incoming C$^{18}$O reacts with $^{16}$O on the surface to form C$^{16}$O$^{18}$O. Once all the $^{16}$O on the surface has reacted and left the surface, the solid catalyst bulk supplies the surface with $^{16}$O. This diffusion process is not infinitely fast, therefore the fraction of C$^{16}$O$^{18}$O drops to a pseudo constant value of 0.26. This offset can be viewed as a measure of the contribution by the bulk to the overall rate of exchange [10]. Presence of oxygen in the bulk of the catalyst particle, which can diffuse to the surface and react, has also been observed with different catalytic systems [3, 10].

Figure 4.4 and Figure 4.5 show that the same conclusion of the presence of oxygen in the catalyst bulk and at the surface can be drawn for the system under FT reaction conditions. All the $^{12}$C has left the reactor at 200 seconds, while after 200 seconds $^{16}$O is leaving the reactor in the form of CO (g), CO$_2$ (g) and H$_2$O (g).

The $^{16}$O transient given in Figure 4.3 also shows that the dissociation of CO$_{ads}$ to C$_{ads}$ and O$_{ads}$ is reversible,

$$CO_{ads} \rightarrow C_{ads} + O_{ads}$$

The fact that C$^{16}$O is leaving the reactor even after 300 seconds (the time at which all $^{12}$C in the reactor is replaced by $^{13}$C) shows that C$^{16}$O is formed from adsorbed oxygen and adsorbed carbon species, and that the CO dissociation thus is reversible.

The transient of the inert tracer gives the residence time of the reactor, since it does not interact with the catalyst and the reactor wall [11]. CO$_2$ is formed via reactions on the surface of the catalyst. Because surface species leading to CO$_2$ have a certain surface residence time the CO$_2$ transient comes out later than the transient of the inert tracer. As described by Shannon and Goodwin [11], the area between transient of the inert tracer and the transient of the product leaving the reactor is equal to the average surface residence time of active intermediates containing the atom which changes label at the switch, leading to the formation of that product. In general this can, for n intermediates leading to product P, be expressed as follows [12]:

35
Figure 4.5 Fractions of $^{12}$C labeled compounds leaving the reactor for the experiment under FT reaction conditions.
\[ \sum_{i=1}^{n} \tau_{i,P} = \int_{0}^{\infty} [I^p(t) - I^i(t)] \, dt \]  

(4.1)

In which
- \( \tau_{i,P} \) average surface residence time of intermediate \( i \) leading to product \( P \) [s],
- \( I^p \) the transient of the product \( P \) [-]
- \( I^i \) the transient of the inert tracer [-]

This can be converted to average surface concentrations via:

\[ \sum_{i=1}^{n} L_{i,p} = \frac{F_{P,\text{out}} \sum_{i=1}^{n} \tau_{i,p}}{w_{\text{cat}}} \]  

(4.2)

In which,
- \( L_{i,p} \) average surface concentration of intermediate \( i \) leading to product \( P \) [mole kg\( \text{cat} \)^{-1}],
- \( F_{P,\text{out}} \) the molar outlet flow of product \( P \) [mole s^{-1}]
- \( w_{\text{cat}} \) the mass of the catalyst in the reactor [kg\( \text{cat} \)]

In the absence of readsoirbing products determination of the average surface coverages of one single surface species is possible. In several FT studies on the formation of methane one is able, while having low conversions, to determine average surface coverages of adsorbed CO and the most abundant intermediate leading to the formation of methane, assuming there is one most abundant intermediate leading to the formation of methane [1, 2]. The two reaction mechanism presented in chapter 2, both include the adsorption of the product CO\(_2\) on the catalyst surface. For the reaction under no FT conditions, both the carbon present in CO and CO\(_2\) could have been present on the catalyst surface as CO\(_{\text{ads}}\), C\(_{\text{ads}}\) and CO\(_{2,\text{ads}}\). Therefore it is not possible to determine \( L_{CO}, L_c \) and \( L_{CO2} \) separately, but only the sum of the 3 surface concentrations via:

\[ L_{CO,\text{NR}} + L_{CO2,\text{NR}} + L_{C,\text{NR}} = L_{C,\text{total, NR}} = \frac{F_{CO,\text{out}} \sum_{i=1}^{n} \tau_{i,CO}}{w_{\text{cat}}} + \frac{F_{CO2,\text{out}} \sum_{j=1}^{n} \tau_{j,CO2}}{w_{\text{cat}}} \]  

(4.3)

In which
- \( L_{x,\text{NR}} \) average surface coverage of \( x \) in the experiment under No FT Reaction conditions [mole kg\( \text{cat} \)^{-1}]
- \( L_{C,\text{total, NR}} \) total average surface concentration of carbon containing species under no FT reaction conditions [mole kg\( \text{cat} \)^{-1}]

There are three intermediates CO\(_{\text{ads}}\) (1), CO\(_{2,\text{ads}}\) (2) and C\(_{\text{ads}}\) (3), resulting in \( n=3 \).

This also applies to \( L_{CO}, L_c \) and \( L_{CO2} \) for the reaction under FT reaction conditions. Here, carbon can also leave the reactor as \( C_{2,CH_4} \). Since methane is 71\% of the hydrocarbons formed, shown in appendix 1, it is assumed that the \( ^{12}\text{CH}_4 \) transient can be used for the determination of the average surface coverages of the carbon containing surface species leading to all hydrocarbon products. Therefore for the carbon containing surface species for the reaction under FT reaction conditions, the following is valid:
Figure 4.6 Total $^{16}$O leaving the reactor as CO$_2$ and $^{16}$O on the surface at the moment of the C$^{16}$O to C$^{18}$O switch leaving the reactor as CO$_2$ for the experiment under no FT reaction conditions.

Figure 4.7 CO and CO$_2$ transient under no FT reaction conditions corrected for bulk diffusion.
In which

$\bar{L}_x,FT$ average surface coverage of $x$ in the experiment under FT reaction conditions [mole kg$_{cat}^{-1}$]

$L_{C,total,FT}$ total average surface concentration of carbon containing species under FT reaction conditions [mole kg$_{cat}^{-1}$]

There are three intermediates $CO_{ads}$ (1), $CO_{2,ads}$ (2) and $C_{ads}$ (3), resulting in $n=3$.

Along the same line of reasoning the transients from the oxygen labeling experiments can be used to determine the total average surface concentration of oxygen containing intermediates. The sum of the areas between the transients of the oxygen labeling experiments and the inert tracer transients (Figure 4.0.1 and Figure 4.4) do not only represent the average residence time of total oxygen containing surface species, but also includes the bulk oxygen diffusing to the surface. For the diffusion of oxygen from the catalyst bulk to surface can be corrected. Adopted from Peil et al the transients of the oxygen labeling experiment can be corrected via [10]:

$$f_{tot,\text{16O,C}O_2}(t) = \frac{2f_{C^{16}O_2}(t) + f_{C^{16}O^{18}O}(t) - f_{b,CO_2}(t)}{2}$$  \hspace{1cm} (4.5)

$$f_{tot,\text{16O,C}O}(t) = f_{C^{16}O}(t) - f_{b,CO}(t)$$  \hspace{1cm} (4.6)

$$f_{tot,\text{16O,H}_2\text{O}}(t) = f_{H_2^{16}O}(t) - f_{b,H_2O}(t)$$  \hspace{1cm} (4.7)

$$f_{b,x}(t) = (\text{offset})_x \left( 1 - e^{-\frac{t}{t_{ss,x}}} \right)$$  \hspace{1cm} (4.8)

Where

- $f_{tot,\text{16O,x}}(t)$ fraction of $^{16}$O on the surface leaving the reactor as $x$ per oxygen atom in $x$ [-]
- $t_{ss,x}$ time at which the offset value of $x$ is reached [s]
- $f_{y}(t)$ fraction of $y$ leaving the reactor [-]
- (offset)$_x$ offset value of the transients of $x$ containing $^{16}$O, for $CO_2$ the offset value of $C^{16}O^{18}O$ is used [-]
- $f_{b,x}(t)$ is the contribution of the bulk to the transients of $x$ [-], which is assumed to be an exponential function of time [10].

Figure 4. shows the transient of the total $^{16}$O leaving the reactor as $CO_2$ for the experiment under no FT reaction conditions and compares this transient to the total $^{16}$O transient leaving the reactor as $CO_2$ corrected for diffusion. As can be expected, the corrected transient reaches 0, since all the $^{16}$O on the surface, in the form of $CO_{ads}$, $CO_{2,ads}$ or $O_{ads}$, has desorbed or reacted and no new $^{16}$O diffuses from the bulk to the surface. Figure 4.7 and Figure 4.8 give the total $^{16}$O transients corrected for bulk diffusion from the experiments under no FT reaction conditions, and FT reaction conditions respectively. The transients corrected for diffusion are used to determine the surface coverage of oxygen containing surface species.

The total surface coverage of oxygen containing intermediates can be determined in the same way as for the total surface coverage of carbon containing intermediates, however the transients corrected for diffusion should be used. When using equation (4.1) to calculate $\sum_{i=1}^{n} \tau_{i,P}$ the transient of product $P$
Figure 4.8 CO, CO₂ and H₂O transient under FT reaction conditions corrected for bulk diffusion

Table 4.2 Total average surface concentrations of carbon and oxygen containing intermediates

<table>
<thead>
<tr>
<th></th>
<th>No FT reaction conditions</th>
<th>FT reaction conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_{C,\text{total}} ) [mole kg(_{\text{cat}}^{-1})]</td>
<td>0.021</td>
<td>0.010</td>
</tr>
<tr>
<td>( L_{O,\text{total}} ) [mole kg(_{\text{cat}}^{-1})]</td>
<td>0.082</td>
<td>0.086</td>
</tr>
</tbody>
</table>
corrected for diffusion should be used. \( \text{CO}_2 \) contains two oxygen atoms. Therefore a 2 appears in front of \( \text{LCO}_2 \) and \( \text{FCO}_2 \):

\[
\text{LCO},\text{NR} + 2 \text{LCO}_2,\text{NR} + \text{LO},\text{NR} = \text{L},\text{O,total},\text{NR} = \frac{F_{\text{CO},\text{out}} \sum_{i=1}^{n} \tau_{L,\text{CO}}}{w_{\text{cat}}} + \frac{2F_{\text{CO}_2,\text{out}} \sum_{j=1}^{n} \tau_{j,\text{CO}_2}}{w_{\text{cat}}} \tag{4.9}
\]

\[
\text{LCO},\text{FT} + 2 \text{LCO}_2,\text{FT} + \text{LO},\text{FT} = \text{L},\text{O,total},\text{FT} = \frac{F_{\text{CO},\text{out}} \sum_{i=1}^{n} \tau_{L,\text{CO}}}{w_{\text{cat}}} + \frac{2F_{\text{CO}_2,\text{out}} \sum_{j=1}^{n} \tau_{j,\text{CO}_2}}{w_{\text{cat}}} + \frac{F_{\text{H}_2\text{O},\text{out}} \sum_{k=1}^{n} \tau_{k,\text{H}_2\text{O}}}{w_{\text{cat}}} \tag{4.10}
\]

In which,

\[
\text{LO,total},\text{NR} \quad \text{total average surface concentration of oxygen containing species under no FT reaction conditions}
\]

\[
\text{LO,total},\text{FT} \quad \text{total average surface concentration of oxygen containing species under FT reaction conditions}
\]

Table 4.2 shows the total average surface coverages of C containing (\( \text{L}_C,\text{total} \)) and O containing (\( \text{L}_O,\text{total} \)) intermediates for both experiments under FT and no FT reaction conditions.

As can be seen from Table 4.2, the total surface concentration of C containing intermediates is smaller under FT reaction conditions than under no FT reaction conditions. Due to the presence of hydrogen under FT reaction conditions carbon may leave the surface as a hydrocarbon product. This could explain the difference in total surface coverage of carbon containing intermediates.

### 4.2 Parameter estimation

**Results of data fitting**

Estimates for unknown parameters appearing in the reaction mechanism given in chapter 2, Figure 2.2 and Figure 2.3, were obtained via fitting. For curve fitting the CO and CO\(_2\) transients measured by the MS of the experiment under FT reaction conditions and the experiment under no FT reaction conditions were used.

The reaction mechanism describing the system under no FT reaction conditions has 9 parameters, as shown in Figure 2.3. The reaction mechanism describing the system under FT reaction conditions has 12 parameters. For curve fitting one wants to limit the amount of unknown parameters as much as possible, therefore first the model describing the reaction under no FT reaction conditions was used to fit the data. Since 9 parameters are already challenging to fit simultaneously, some parameters were set a value and excluded from the parameter estimation. The adsorption and desorption constants of CO, \( k_{\text{CO},\text{ads}} \) and \( k_{\text{CO},\text{des}} \), were taken from work on a similar Fe-based HTFT catalyst [1] and were set to 0.1 m\(^3\)kg\(_{\text{cat}}\)\(^{-1}\)s\(^{-1}\) and 38 s\(^{-1}\) respectively.

Furthermore \( k_{\text{CO},\text{ass}} \) was set, and a value for \( k_{\text{CO},\text{ass}} \) was determined from the surface coverages given in Table 2 and mole balances for \( \text{C}_\text{Culv} \) and \( \text{L}_\text{C} \) given in chapter 2. Contributions to \( \text{L},\text{O,total} \) and \( \text{L},\text{C,total} \) are described by equations (4.3), (4.4), (4.9) and (4.10). Since \( \text{L},\text{O,total} \) has a much higher value than \( \text{L},\text{C,total} \) (Table 4.2) contributions of \( \text{L},\text{C} \) and \( \text{L},\text{CO}_2 \) to \( \text{L},\text{O,total} \) can be neglected, leading to

\[
\text{LO} \approx \text{LO},\text{total} \quad \tag{4.11}
\]
Table 4.3 Results for fitting CO and CO\textsubscript{2} no FT reaction transient data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimated value</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>D [m\textsuperscript{2}s\textsuperscript{-1}]</td>
<td>4.47\times10\textsuperscript{-14}</td>
<td>7.7\times10\textsuperscript{-15}</td>
</tr>
<tr>
<td>k\textsubscript{CO,ass} [kg\textsubscript{cat} mole\textsuperscript{-1}s\textsuperscript{-1}]</td>
<td>6.4\times10\textsuperscript{-3}</td>
<td>2.6\times10\textsuperscript{-3}</td>
</tr>
<tr>
<td>k\textsubscript{CO2,dis} [s\textsuperscript{-1}]</td>
<td>3.7\times10\textsuperscript{4}</td>
<td>6.8\times10\textsuperscript{8}</td>
</tr>
<tr>
<td>k\textsubscript{CO2,ass} [kg\textsubscript{cat} mole\textsuperscript{-1}s\textsuperscript{-1}]</td>
<td>90</td>
<td>20</td>
</tr>
<tr>
<td>k\textsubscript{CO2,des} [s\textsuperscript{-1}]</td>
<td>7.0\times10\textsuperscript{3}</td>
<td>1.3\times10\textsuperscript{8}</td>
</tr>
<tr>
<td>k\textsubscript{CO2,ads} [m\textsubscript{g}\textsuperscript{-1}s\textsuperscript{-1}kg\textsubscript{cat}\textsuperscript{-1}]</td>
<td>2.1\times10\textsuperscript{-4}</td>
<td>8.8\times10\textsuperscript{-5}</td>
</tr>
</tbody>
</table>

Table 4.4 Correlation matrix for fit of CO and CO\textsubscript{2} no FT transient data

<table>
<thead>
<tr>
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<th>k\textsubscript{CO2,ads}</th>
<th>k\textsubscript{CO,ass}</th>
<th>k\textsubscript{CO2,dis}</th>
<th>k\textsubscript{CO2,ass}</th>
<th>k\textsubscript{CO2,des}</th>
</tr>
</thead>
<tbody>
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<td>D</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k\textsubscript{CO2,ads}</td>
<td>0.23</td>
<td>1</td>
<td></td>
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<tr>
<td>k\textsubscript{CO,ass}</td>
<td>-0.729</td>
<td>0.104</td>
<td>1</td>
<td></td>
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<td></td>
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<tr>
<td>k\textsubscript{CO2,dis}</td>
<td>0.224</td>
<td>0.908</td>
<td>-0.038</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k\textsubscript{CO2,ass}</td>
<td>0.9</td>
<td>0.16</td>
<td>-0.938</td>
<td>0.248</td>
<td>1</td>
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<tr>
<td>k\textsubscript{CO2,des}</td>
<td>0.224</td>
<td>0.908</td>
<td>-0.038</td>
<td>1</td>
<td>0.248</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 4.9 Experimental CO\textsubscript{2} transients versus model predicted CO\textsubscript{2} transients for the system under no FT reaction conditions. The model was fitted to CO and CO\textsubscript{2} transients under no FT reaction conditions.
The total surface concentrations of oxygen containing species in both experiments do not differ much, 0.082 mole kg\textsuperscript{-1} for the system under no FT reaction conditions versus 0.086 mole kg\textsuperscript{-1} for the system under FT reaction conditions. For the total surface concentrations of carbon containing species a significant difference is shown (Table 4.2). If it is assumed that this difference in total surface concentration of carbon containing species can be totally ascribed to a change in L\textsubscript{C} (i), and since L\textsubscript{O,total} does not differ a lot, L\textsubscript{CO}, L\textsubscript{CO2} and L\textsubscript{O} are equal for both systems (ii) a value for k\textsubscript{CO,ass} can be derived. Equations 4.12 and 4.13 express assumption (i).

\[ \Delta L_{C,total} = L_{C,total,NR} - L_{C,total,FT} \quad (4.12) \]

\[ L_{C,NR} = L_{C,FT} + \Delta L_{C,total} \quad (4.13) \]

Combining equations 4.12 and 4.13, assumption (ii) and the mole balances for L\textsubscript{C,NR}, L\textsubscript{C,FT} and C\textsubscript{C\textsubscript{a}Hy} leads to an expression for k\textsubscript{CO,ass}.

\[ \frac{\partial L_{C,NR}}{\partial t} = k_{CO,dis}L_{CO} - k_{CO,ass}L_{O}L_{C,NR} \quad (4.14) \]

\[ \frac{\partial L_{C,FT}}{\partial t} = k_{CO,dis}L_{CO} - k_{CO,ass}L_{O}L_{C,FT} - k_{CH}L_{C,NR} \quad (4.15) \]

\[ \frac{\partial L_{C,FT}}{\partial t} - \frac{\partial L_{C,NR}}{\partial t} = k_{CO,ass}L_{O}\Delta L_{C,total} - k_{CH}L_{C,FT} \quad (4.16) \]

\[ k_{CH}L_{C,FT} = \frac{F_v}{V_R\rho_b} \frac{\partial C_{C\textsubscript{a}Hy}}{\partial t} \quad (4.17) \]

\[ k_{CO,ass} = \frac{F_v}{V_R\rho_b} \frac{\partial C_{C\textsubscript{a}Hy}}{\partial x} \frac{1}{L_{O,FT}\Delta L_{C,total}} \quad (4.18) \]

When assuming a linear increase from 0 to C\textsubscript{xHY,\textsubscript{out}} for C\textsubscript{C\textsubscript{a}Hy} over the reactor length, this applies

\[ \frac{\partial C_{C\textsubscript{a}Hy}}{\partial x} = C_{C\textsubscript{a}Hy,\textsubscript{out}} \quad (4.19) \]

This results in k\textsubscript{CO,ass} = 0.155 s\textsuperscript{-1}.

Setting values for k\textsubscript{CO,ads}, k\textsubscript{CO,des} and k\textsubscript{CO,ass} leaves six parameters to estimate via curve fitting of the transient data of the experiment under no FT reaction conditions. The results are shown in Table 4.3.

The correlation matrix for these fitting results is given in Table 4.4, in which an absolute value close to 1 indicates a high correlation between two parameters.

The model prediction using the estimated values of Table 4.3 are compared to the experimentally obtained CO and CO\textsubscript{2} transients in Figures 4.9 and 4.10.

Fitting also the CO and CO\textsubscript{2} transient data of the experiment under FT reaction conditions introduces three more parameters, k\textsubscript{H\textsubscript{2}O,dis}, k\textsubscript{H\textsubscript{2}O,ass} and k\textsubscript{CH}. A value k\textsubscript{H\textsubscript{2}O,dis} can also be obtained using L\textsubscript{O,FT}.

Also assuming a linear increase from 0 to C\textsubscript{H\textsubscript{2}O,\textsubscript{out}} for C\textsubscript{H\textsubscript{2}O} in along the reactor length leads to

\[ C_{H\textsubscript{2}O}(x) = C_{H\textsubscript{2}O,\textsubscript{out}}x \quad (4.20) \]
Figure 4.10 Experimental CO transients versus model predicted CO transients for the system under no FT reaction conditions. The model was fitted to CO and CO2 transients under no FT reaction conditions.

Table 4.5 Results for fitting CO and CO2 no FT reaction transient data and CO and CO2 FT reaction transient data together

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimated value</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>D [m²s⁻¹]</td>
<td>4.53·10⁻¹⁴</td>
<td>4.1·10⁻¹⁵</td>
</tr>
<tr>
<td>k_{CO,ass} [kg_{cat} mole⁻¹ s⁻¹]</td>
<td>5.7·10⁻³</td>
<td>8.3·10⁻⁴</td>
</tr>
<tr>
<td>k_{H2O,dis} [m³ s⁻¹ kg_{cat}⁻¹]</td>
<td>2.0·10⁻⁵</td>
<td>5.2·10⁻²</td>
</tr>
<tr>
<td>k_{CO2,dis} [s⁻¹]</td>
<td>6.1·10⁻¹</td>
<td>2.1·10⁻⁴</td>
</tr>
<tr>
<td>k_{CO2,des} [s⁻¹]</td>
<td>9.4·10⁻³</td>
<td>3.2·10⁻⁴</td>
</tr>
<tr>
<td>k_{CO2,ads} [m³ s⁻¹ kg_{cat}⁻¹]</td>
<td>2.5·10⁻³</td>
<td>1.4·10⁻³</td>
</tr>
<tr>
<td>k_{CH} [s⁻¹]</td>
<td>8.0·10⁻³</td>
<td>2.3·10⁻¹</td>
</tr>
</tbody>
</table>

Table 4.6 Correlation matrix for fit of CO and CO2 no FT reaction transient data and CO and CO2 FT reaction transient data together

<table>
<thead>
<tr>
<th></th>
<th>D</th>
<th>k_{CO2,ads}</th>
<th>k_{CO,ass}</th>
<th>k_{H2O,dis}</th>
<th>k_{CO2,dis}</th>
<th>k_{CO2,des}</th>
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<td>k_{CO2,ads}</td>
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<td>k_{CO,ass}</td>
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<tr>
<td>k_{CO2,des}</td>
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<td>0.0114</td>
<td>-0.00918</td>
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</tr>
<tr>
<td>k_{CH}</td>
<td>-0.513</td>
<td>0.154</td>
<td>-0.297</td>
<td>0.701</td>
<td>0.0283</td>
<td>0.0432</td>
<td>1</td>
</tr>
</tbody>
</table>
This can be combined with the mole balances for $L_O$ and $C_{H_2O}$ presented in chapter 2 and the value for $L_{O,FT}$ estimated from Table 4.2.

\[
\frac{F_v}{V_R \rho_b} \frac{\partial C_{x,H_y}}{\partial t} = k_{H_2O,ass} L_O - k_{H_2O,dis} C_{H_2O} \tag{4.21}
\]

\[
\frac{F_v}{V_R \rho_b} C_{H_2O,\text{out}} = k_{H_2O,ass} L_O - k_{H_2O,dis} C_{H_2O} x \tag{4.22}
\]

\[
k_{H_2O,ass} = \left( \frac{F_v}{V_R \rho_b} C_{H_2O,\text{out}} + k_6 C_{H_2O,\text{out}} \cdot \frac{1}{2} \right) \frac{1}{L_O} = 8.76 \cdot 10^{-4} + 3 \cdot k_{H_2O,dis} \tag{4.23}
\]

In Table 4.5 the results of fitting the CO and CO$_2$ transients obtained from both the experiment under FT reaction and no FT reaction conditions.

Because the standard deviation for $k_{CO2,ass}$ in Table 4.3 is not too big and Table 4.4 shows no strong correlation between $k_{CO2,ass}$ and other estimated parameters, $k_{CO2,ass}$ was set to its value in Table 4.3 in this curve fit.

The correlation matrix is given in Table 4.6.

Figures 4.11, 4.12, 4.13 and 4.14 compare the model predicted transients to the experimental values.

**Discussion**

The values for D determined via curve fitting of the no FT reaction transient data, and of the no FT reaction data and the FT reaction transient data together can, based on their standard deviation, be considered equal. Both show no strong correlation with other estimated parameters and have reasonable standard deviations, which indicates that the value obtained for D close to its real value. The Figures 4.11-4.14 show that the same set of parameters is able to describe both the system under no FT reaction conditions and the system under FT reaction conditions. The parameters $k_{CO2,des}$ and $k_{CO2,dis}$ are highly correlated and have both high standard deviations. In the same fit the standard deviations for $k_{CO2,des}$ and $k_{CO2,dis}$ are in the same order of magnitude. This indicates that in the range in which the equations describing both systems are solved, one constraint is that the ratio of $k_{CO2,des}/k_{CO2,dis}$ should be equal to a constant value. This results in a high correlation between $k_{CO2,des}$ and $k_{CO2,dis}$. Furthermore this results in large standard deviations, since $k_{CO2,des}$ can vary a lot and still keeping the ratio $k_{CO2,des}/k_{CO2,dis}$ constant, as long as this change is compensated by a change in $k_{CO2,dis}$. High standard deviations are also shown for $k_{H2O}$ and $k_{C_2H_4}$. This means that more data are required for a good parameter estimates, the model should be changed or both.

Table 4.7 compares predicted values for surface concentrations and steady state outlet concentrations to experimental values.

Table 4.7 shows an underestimation of the $L_{O,\text{total}}$ by the model for both the FT reaction and no FT reaction system, while $L_{C,\text{total}}$ is overestimated. However a higher $L_{C,\text{total}}$ under no FT reaction conditions is also predicted by the model, and $L_{O,\text{total}}$ predicted by the model is also more or less equal for both systems as was concluded from experimental data.
Figure 4.11 Model prediction and experimental values for CO₂ transient under no FT reaction conditions

Figure 4.12 Model prediction and experimental values for CO transient under no FT reaction conditions

Table 4.7 Comparison between model prediction, with fitted parameters, and experimental values

<table>
<thead>
<tr>
<th></th>
<th>Model prediction</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No FT reaction con</td>
<td>FT reaction con</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No FT reaction con</td>
</tr>
<tr>
<td>L₀,total [mole kg⁻¹]</td>
<td>0.015</td>
<td>0.014</td>
</tr>
<tr>
<td>L₅,total [mole kg⁻¹]</td>
<td>1.55</td>
<td>0.023</td>
</tr>
<tr>
<td>C₃CO₂,out [mole m⁻³]</td>
<td>4.81</td>
<td></td>
</tr>
<tr>
<td>C₃CO₂,out [mole m⁻³]</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>C₃H₂O₂,out [mole m⁻³]</td>
<td>0.0030</td>
<td></td>
</tr>
<tr>
<td>C₃Hₓ,ₜ [mole m⁻³]</td>
<td>0.54</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.13 Model prediction and experimental values for CO₂ transient under FT reaction conditions

Figure 4.14 Model prediction and experimental values for CO transient under FT reaction conditions
The model predicts a lower CO conversion, a lower hydrocarbon production and a much lower water production for the system under FT reaction conditions than experimentally obtained. Also in the H$_2^{16}$O transient predicted by the model shows a large deviation from the measured values, as is shown in figure 4.15.

The lower H$_2$O production is in line with the lower L$_{O\text{total}}$. A lower L$_{O\text{total}}$ reflects a lower L$_O$, which means that there is less oxygen on the surface that can form and H$_2$O and desorb. The lower H$_2$O production and the lower L$_{O\text{total}}$ together with Figure 4.15 show that the production of H$_2$O as described by the mechanism for the FT reaction conditions is not correct. Including H$_2$O adsorption to the mechanism introducing an extra oxygen pool might increase L$_{O\text{total}}$ and describe the oxygen production better. This is however at the cost of more unknown parameters.

**Sensitivity analysis of D**

Figure 4.16 and 4.17 show model predictions for the C$_{16}$O$^{18}$O and C$_{16}$O transients under FT reaction conditions for different values of D, while the other parameters were fixed. As shifts between the lines indicate, the value of D influences the transients of C$_{16}$O$^{18}$O and C$_{16}$O$_2$. As D increases the distinction between surface oxygen and bulk oxygen becomes less clear. At the highest value for D, C$_{16}$O$^{18}$O and C$_{16}$O$_2$ decrease linearly after an instantaneously increase or drop respectively. With a slower diffusion, the transients reach a pseudo steady state value faster. First the surface $^{16}$O reacts, after which new $^{16}$O has to be supplied via diffusion, which is the rate limiting step. This shows the value of a good estimation for D.
Figure 4.015 Model prediction for H$_2^{16}$O transient versus experimental H$_2^{16}$O transients

Figure 4.016 Sensitivity analysis D for predicted C$^{16}$O$^{18}$O transient under FT reaction conditions

Figure 4.017 Sensitivity analysis D for predicted C$^{16}$O values under FT reaction conditions
5. Conclusions and recommendations

By fitting transient data of oxygen labeled CO and CO\textsubscript{2} leaving the reactor a value of \(4.5\times10^{-14}\) m\textsuperscript{2}/s for the diffusion coefficient of oxygen in a Fe based HTFT catalyst particle was obtained. A model was proposed which included the diffusion of oxygen from the catalyst bulk to the surface and the other way around.

Fitting of experimental data from both no FT and FT reaction conditions resulted in the same value for D. In both cases D was uncorrelated and had a reasonable standard deviation. The CO and CO\textsubscript{2} transients for the experiment under no FT and FT reaction conditions (two different systems), were both simulated reasonably well by the model.

The fitting results for D using both sets of data, together with the fact that the model was able to predict the CO and CO\textsubscript{2} transients for both experiments reasonably well, and the indication of oxygen inside the catalyst particle (Figures 1.4 and 1.5), verifies the presence of an oxygen pool inside the catalyst particle which can diffuse out and react at the catalyst surface. This diffusion is indicated in Figure 5.1. and shows how \(^{16}\text{O}\) decreases, and is replaced by \(^{18}\text{O}\) inside the catalyst particle over time.

Curve fitting resulted in values for other parameters (reaction rate constants). However \(k_{\text{CO}_2,\text{des}}\) and \(k_{\text{CO}_2,\text{dis}}\) were correlated and \(k_{\text{H}_2\text{O},\text{dis}}, k_{\text{CO}_2,\text{dis}}, k_{\text{CO}_2,\text{des}}\) and \(k_{\text{CH}}\) had large standard deviations. The predicted surface and outlet concentrations also deviated from experimental data. This indicates that the model may be improved since only a simple model describing hydrocarbon, water and carbon dioxide formation, together with oxygen diffusion and CO and CO\textsubscript{2} adsorption was used for this study. Further work may include the addition of more reaction steps to resemble the working system more realistically but this will also introduce more parameters. For this reason, the model was not extended in this study.

Although a very simple model was chosen, the amount of parameters was still large. In order to reduce the number of parameters that had to be estimated via curve fitting two, \(k_{\text{CO},\text{ads}}\) and \(k_{\text{CO},\text{des}}\) were taken from previous work on Fe based HTFT [1]. Expressions for two other parameters, \(k_{\text{H}_2\text{O},\text{dis}}\) and \(k_{\text{CO},\text{ass}}\) were obtained by assuming equal CO\textsubscript{ads}, CO\textsubscript{2,ads} and O\textsubscript{ads} for both the systems under no FT reaction conditions and FT reaction conditions, and linear gas phase concentration profiles along the reactor length for H\textsubscript{2}O and C\textsubscript{x}H\textsubscript{y}. The assumptions of the linear concentrations profiles could be verified by repeating the same experiments of this study but at different reactor/catalyst bed lengths. In addition to gas phase concentration profiles this will also give information on the concentration profiles of adsorbed species along the reactor axis. This information may then be used to obtain values for the adsorption and desorption constants of the different components (CO, CO\textsubscript{2}, C\textsubscript{x}H\textsubscript{y}, H\textsubscript{2}O) present in the reactor.

Furthermore, better fitting results could also be obtained by extending the model. The total amount of oxygen containing species on the catalyst surface was underestimated by the model. Introducing a H\textsubscript{2}O adsorption and desorption step to the model could increase the amount of oxygen containing species on
Figure 5.1 Predicted $^{16}$O fractions in the catalyst bulk for different times after the switch
the surface in the model. This might also result in a better estimation for the $\text{H}_2^{16}\text{O}$ transient, which was not estimated accurately in this work.

Overall the trends of the experimental data can be predicted with the current model. The model, however seems to be too simplified to result in an optimal fit and a more complicated model may need to be used in order to fully match the experimental results.
References

[4] Ter Stege G., P. Moodley, HTFT and material characterization groups Sasol Technology R&D
Appendix 1: Hydrocarbon product spectrum

The CO inlet flow for the experiment under FT reaction conditions was 2.23 μmole/s.

The total amount of C atoms leaving the reactor as oxygenates is 0.00919 μmole/s. This less than 2% of the converted amount of C atoms. Therefore it is assumed that no oxygenates are produced in the experiment under FT reaction conditions.

As can be seen in Table A1.1. Methane accounts for 71% of all the converted carbon not going to CO₂. Because of this the transient of methane was taken to represent the transients of all the hydrocarbons leaving the reactor.
Table A1.1 Outlet flows of experiment under FT reaction conditions, measured with FID

<table>
<thead>
<tr>
<th>Compound</th>
<th>Outlet flow [µmol/s]</th>
<th>Outlet flows of C atoms [µmol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.67</td>
<td>1.67</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>Methane</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>Ethene</td>
<td>0.63</td>
<td>1.27</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.0047</td>
<td>0.0095</td>
</tr>
<tr>
<td>Propene</td>
<td>0.0046</td>
<td>0.0093</td>
</tr>
<tr>
<td>Propane</td>
<td>0.00092</td>
<td>0.0028</td>
</tr>
<tr>
<td>Ethanal</td>
<td>0.00034</td>
<td>0.00067</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.000065</td>
<td>0.00013</td>
</tr>
<tr>
<td>1-Butene</td>
<td>0.0017</td>
<td>0.0069</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.00026</td>
<td>0.0011</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>0.00093</td>
<td>0.0047</td>
</tr>
</tbody>
</table>
Appendix 2: Surface coverage

In work on a similar Fe based HTFT catalyst a CO coverage of 37 μmole CO per g cat (L_{CO,0}) corresponded to 0.1 ML based on a surface area of 16 m²/g (a_{m,0}) [2]. The catalyst used in this study has a surface area of 10 m²/g (a_m). Correcting for this difference in surface area leads to,

\[ \frac{0.1}{L_{CO,0} a_{m,0}} = 1.69 \text{ ML mol}^{-1} \text{ kg}^{-1} \text{ cat} \quad (A2.1) \]

If it is assumed that CO_{ads}, CO_{2,ads}, C_{ads} and O_{ads} occupy the same area per adsorbed species, then the maximum amount of surface would be covered when only C_{ads} and O_{ads} are present on the surface, a C_{ads} and O_{ads} occupy for example twice as much surface area as CO_{ads}. This results in:

\[ L_{O,\text{max}} = L_{O,\text{total}} \quad (A2.2) \]
\[ L_{C,\text{max}} = L_{C,\text{total}} \quad (A2.3) \]
\[ L_{\text{max}} = L_{O,\text{total}} + L_{C,\text{total}} \quad (A2.4) \]

In chapter 4 values for L_{O,\text{total}} and L_{C,\text{total}} were determined. Combining (A2.1), (A2.2), (A2.3) and (A2.4) leads to a maximum of coverage of 0.17 ML for the catalyst under no FT reaction conditions and a maximum coverage of 0.16 ML for the catalyst under FT reaction conditions.
Appendix 3: Mass and heat transfer calculations

The assumptions that need to be verified are listed below.

The reactor was modeled in chapter 2 assuming:

- the absence of axial dispersion (i)
- the absence of radial concentration profiles (ii)
- no mass transfer limitations (iii)
- isothermal operation (iv)
- a constant volumetric flow rate (v)

These assumptions were verified in the graduation report of J. Riegman [8], for a similar reactor operated under at the same temperature (603 K), but a lower pressure (1.2 bar). The equations used in that report are used, and repeated below. The assumptions are verified for a reactor operated at 603 K and 6 bar, and fed with CO (3 ml(n)/min), H₂ (30 ml(n)/min) and Ar (27 ml(n)/min). The CO conversion at the outlet of the reactor was approximately 25%.

External mass transfer

External mass transfer is absent if Mears’ criterion for external mass transfer is obeyed [13]. The criterion is given by:

\[
C_{\text{Mears, mass}} = \frac{-r_A \rho_b n}{k_c a_c C_{A,b} \varepsilon_b} < 0.05
\]  

(A3.1)

In which:

- \( C_{\text{Mears}} \): Mears’ criterion
- \( r_A \): Reaction rate of disappearance for limiting reactant A \([\text{mole kg}_{\text{cat}}^{-1} s^{-1}]\)
- \( \rho_b \): Catalyst bed density \([\text{kg}_{\text{cat}}^{-1} m_r^{-1}]\)
- \( n \): Order of the reaction \([-]\)
- \( k_c \): Mass transfer coefficient \([m_p s^{-1}]\)
- \( a_c \): Specific surface area \([m_p^2 m_p^{-3}]\)
- \( C_{A,b} \): Bulk concentration of the limiting reactant A \([\text{mole m}_g^{-3}]\)
- \( \varepsilon_b \): Catalyst bed porosity \([m_g^3 m_r^{-3}]\)

The limiting reactant in this project is CO. Therefore, the reaction rate for CO can be calculated by:

\[
(-r_{CO}) = \frac{F_{CO, in} x_{CO}}{W_{cat}}
\]  

(A3.2)

In which

- \((-r_{CO})\): Rate of disappearance for the limiting reactant CO \([\text{mole kg}_{\text{cat}}^{-1} s^{-1}]\)
\( F_{\text{CO,in}} \)  
Molar flow rate of CO in the reactor feed  
[mole s\(^{-1}\)]

\( \chi_{\text{CO}} \)  
Conversion of CO  
[-]

\( W_{\text{cat}} \)  
Catalyst mass  
[kg\(_{\text{cat}}\)]

The bed density is calculated by multiplying the catalyst mass with one minus the bed porosity. The reaction order is assumed to be \( n=1 \) and the mass transfer coefficient can be obtained from Sherwood relations.

The flows used in the experiments is laminar since \( \text{Re}<2300 \). Therefore the following criterion by Thoenes and Kramers can be used [13]:

\[
Sh = \frac{k_c d_p}{D_{AB}} = 1.8 \text{Re}^{0.5} \text{Sc}^{0.33} \quad (A3.3)
\]

In which:

- \( Sh \): Sherwood number  
- \( k_c \): Mass transfer coefficient  
- \( d_p \): Catalyst particle diameter  
- \( D_{AB} \): Diffusion coefficient of component A in mixture A/B  
- \( \text{Re} \): Reynolds number  
- \( Sc \): Schmidt number

The diffusion coefficient of CO under reaction conditions cannot be found, so the diffusion coefficient of CO in hydrogen is used, since hydrogen is the most abundant species in the mixture [14].

The Reynolds number equals 0.0608 and is much smaller than 2300. The assumption for laminar flow is verified. The Reynolds number can be calculated by

\[
\text{Re} = \frac{\rho_{\text{mix}} u_s d_p}{\mu_{\text{mix}}} \quad (A3.4)
\]

In which:

- \( \text{Re} \): Reynolds number  
- \( \rho_{\text{mix}} \): Density of the gas mixture  
- \( d_p \): Catalyst particle diameter  
- \( u_s \): Superficial velocity  
- \( \mu_{\text{mix}} \): Viscosity of the gas mixture

For calculating the properties of the mixture, it is assumed that the gas mixture consist of H\(_2\) and Ar only, since these species are most abundant in the gas phase. The density of the mixture can be calculated by
\[ \rho_{\text{mix}} = \sum_i y_i C_{\text{tot}} M_i \]  

(A3.5)

With using the ideal gas law for \(C_{\text{tot}}\):

\[ C_{\text{tot}} = \frac{P_{\text{tot}}}{RT} \]  

(A3.6)

In which

\( \rho_{\text{mix}} \) Density of the gas mixture [kg m\(^{-3}\)]
\( y_i \) Mole fraction of component \(i\) in the gas phase [-]
\( C_{\text{tot}} \) The total gas phase concentration [mole m\(^{-3}\)]
\( M_i \) Molar mass of component \(i\) [kg mole\(^{-1}\)]
\( P_{\text{tot}} \) Total pressure in the reactor [Pa]
\( R \) Gas constant [J mole\(^{-1}\) K\(^{-1}\)]
\( T \) Temperature in the reactor [K]

In these calculations it is assumed that the pressure and temperature are uniform in the reactor. The assumptions for the temperature gradient and pressure drop are validated later in this appendix.

The superficial velocity, \(u_s\), can be calculated by dividing the volumetric flow rate with the cross-sectional area of the reactor. The superficial velocity is not constant in the reactor, but can be assumed constant in case the changes in volumetric flow rate can be neglected. This will be verified later in this appendix.

The viscosity of the mixture can be calculated by [15]:

\[ \mu_{\text{mix}} = \sum_i \left( \frac{y_i \mu_i}{\sum_j y_j \Phi_{ij}} \right) \]  

(A3.7)

Where \( \Phi_{ij} \) is calculated by

\[ \Phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{1/2} \left( 1 + \frac{\mu_i}{\mu_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/2} \]  

(A3.8)

In which

\( \mu_{\text{mix}} \) Viscosity of the gas mixture [Pa s]
\( y_i, y_j \) Mole fraction of component \(i,j\) in the gas phase [-]
\( \mu_{i,j} \)  Viscosity of pure component \( i,j \)  [Pa s]
\( \Phi_{ij} \)  Interaction parameter of component \( i \) with \( j \)  [-]
\( M_{i}, M_{j} \)  Molar mass of component \( i \)  [kg mole\(^{-1}\)]

The Schmidt number is calculated by

\[
Sc = \frac{\mu_{\text{mix}}}{\rho_{\text{mix}} D_{AB}}
\]

(A3.9)

In which

\( Sc \)  Schmidt number  [-]
\( \mu_{\text{mix}} \)  Viscosity of the gas mixture  [Pa s]
\( \rho_{\text{mix}} \)  Density of the gas mixture  [kg m\(^{-3}\)]
\( D_{AB} \)  Diffusion coefficient of component \( A \) in mixture \( A/B \)  [m\(^2\) s\(^{-1}\)]

The specific surface area can be calculated by dividing the surface area of the catalyst pellet by its volume. This leads to:

\[
a_{c} = \frac{6}{d_{p}}
\]

(A3.10)

\( a_{c} \)  Specific surface area  [m\(_{p}\)^2 m\(_{p}\)^{-3}]
\( d_{p} \)  Catalyst particle diameter  [m\(_{p}\)]

The bulk concentration of the limiting reactant CO is approximated by

\[
C_{CO,b} = y_{CO,in} C_{tot} \left( 1 - \frac{X_{CO}}{2} \right)
\]

(A3.11)

\( C_{CO,b} \)  Bulk concentration of CO  [mole m\(^{-3}\)]
\( y_{CO,in} \)  Mole fraction of CO in the feed  [-]
\( C_{tot} \)  The total gas phase concentration  [mole m\(^{-3}\)]
\( X_{CO} \)  Conversion of CO  [-]

In Table B.1, all the parameters are illustrated. Using the parameters equation 7.1 yields \( C_{\text{Mears}} = 0.0029 \), which is smaller than 0.05. Thus, external mass transfer can be neglected.

**Internal mass transfer**

For indicating if internal mass transfer plays an important role in this reaction, the Weisz-Prater criterion can be used. This criterion is given by:
Figure A3.1 Inert tracer measured at the top and bottom of the reactor, showing plug flow
\[ \Phi = \frac{n+1}{2} \frac{-r_A \rho_b}{D_e a_e^2 C_{A,i} \varepsilon_s} < 0.15 \]  \quad \text{(A3.12)}

In which

- \( \Phi \): Weisz-Prater criterion  [-]
- \( n \): Order of the reaction  [-]
- \( r_A \): Reaction rate of disappearance for limiting reactant A  [mole kg\(^{-1}\) cat\(^{-1}\) s\(^{-1}\)]
- \( \rho_b \): Catalyst bed density  [kg cat\(^{-1}\) m\(^{-3}\)]
- \( D_e \): Effective diffusivity  [m\(^2\) s\(^{-1}\)]
- \( C_{A,i} \): Concentration of component limiting reactant A at the catalyst surface  [mole m\(^{-3}\)]
- \( \varepsilon_s \): Solid fraction  [m\(_{\text{cat}}^3\) m\(_r^3\)]

For this calculation, the same parameters as used for the Mears criterion can be used. Only the effective diffusivity, \( D_e \), which is the diffusion coefficient corrected for the fact that pores are not straight and cylindrical and that the pellet consist of empty space and solid. This is calculated by:

\[ D_e = \frac{D_{AB} \phi_p \sigma_c}{\tau} \]  \quad \text{(A3.13)}

In which

- \( D_e \): Effective diffusivity  [m\(^2\) s\(^{-1}\)]
- \( D_{AB} \): Diffusion coefficient of component A in mixture A/B  [m\(^2\) s\(^{-1}\)]
- \( \phi_p \): Pellet porosity  [-]
- \( \sigma_c \): Constriction factor  [-]
- \( \tau \): Tortuosity  [-]

For the parameters pellet porosity, constriction factor and tortuosity, typical values are used [13].

The interface concentration of CO equals the bulk concentration, since external mass transfer is negligible. This results in \( \Phi = 3.44 \times 10^{-6} \), which is much smaller than 0.15 and thus internal mass transfer can be neglected too.

**Plug flow conditions**

Figure A3.1 shows the inert transient at the top of the reactor. The fact that the two transients overlay shows that there is plug flow in the reactor. This can be verified further when the following conditions are met:
\[ \frac{L_b}{d_p} > 50 \quad \text{(A3.14)} \]
\[ \frac{d_b}{d_p} > 10 \quad \text{(A3.15)} \]

In which
- \( L_b \): Length of the catalyst bed [m]
- \( d_p \): Catalyst particle diameter [m]
- \( d_b \): Diameter of the catalyst bed [m]

The catalyst bed has a length of 80 mm and a diameter of 5 mm. Catalyst particles between 38-100 µm are used and SiC particle sizes of 150-350 µm. For the largest particle size this leads to:

\[ \frac{L_b}{d_p} = 229 > 50 \quad \text{and} \quad \frac{d_b}{d_p} = 14 > 10 \]

This indicates that the reactor is indeed operated in ideal plug flow conditions.

**Pressure drop**

The pressure drop over a fixed bed reactor can be calculated using the Ergun equation [7].

\[ \frac{dp_{tot}}{dz} = \rho_{mix} u_s^2 \left( \frac{150 (1 - \varepsilon_b)^2}{Re \varepsilon_b^3} + 1.75 \frac{(1 - \varepsilon_b)}{\varepsilon_b^3} \right) \quad \text{(A3.16)} \]

The pressure drop over the reactor is then given by:

\[ \Delta p_{tot} = p_{tot}^{in} - p_{tot}^{out} = \frac{dp_{tot}}{dz} * L_b \quad \text{(A3.17)} \]

In which
- \( p_{tot} \): Total pressure in the reactor [Pa]
- \( z \): Axial reactor coordinate [m]
- \( \rho_{mix} \): Density of the gas mixture [kg m\(^{-3}\)]
- \( u_s \): Superficial velocity [m s\(^{-1}\)]
- \( Re \): Reynolds number [-]
- \( \varepsilon_b \): Catalyst bed porosity [m\(_g^3\) m\(_r^3\)]
- \( L_b \): Length of the catalyst bed [m]

The total pressure drop is 0.0042 bar. This is only 0.07 % of the total pressure and the pressure drop is negligible.
**Volumetric flowrate**

When using the balances under differential conditions, the volumetric flowrate is assumed to be constant. To check this assumption, the derivative of $F_v$ with respect to the dimensionless axial coordinate $\hat{z}$ can be calculated. In order to obtain this derivative, the steady state mole balance for the gas phase components is needed:

$$\frac{dF_v}{d\hat{z}} = R_i V_r \rho_b$$

(A3.18)

The derivative of the volumetric flow rate with respect to the dimensionless axial coordinate, the following relation can be applied:

$$\frac{dF_v}{d\hat{z}} = \frac{d \left( \frac{F_{tot}}{C_{tot}} \right)}{d\hat{z}} \frac{1}{C_{tot}} \frac{dF_{tot}}{d\hat{z}} = \frac{1}{C_{tot}} \sum_i \frac{dF_i}{d\hat{z}}$$

(A3.19)

At constant pressure, i.e. the pressure drop over the reactor is negligible and constant temperature, i.e. all temperature gradients are assumed to be negligible and the total concentration is constant. Combining this with both equations yields the following expression:

$$\frac{dF_v}{d\hat{z}} = \frac{V_r \rho_b}{C_{tot}} \sum_i R_i$$

(A3.20)

In which

- $F_i$: Molar flow rate of component $i$ [mole s$^{-1}$]
- $\hat{z}$: Dimensionless axial reactor coordinate [-]
- $R_i$: Reaction rate of component $i$ [mole kg$^{-1}$ cat$^{-1}$ s$^{-1}$]
- $V_r$: Reactor volume [m$^3$]
- $\rho_b$: Catalyst bed density [kg$^{-1}$ cat$^{-1}$ m$^{-3}$]
- $F_v$: Total volumetric flow rate [m$^3$ s$^{-1}$]
- $F_{tot}$: Total mole flow rate [mole s$^{-1}$]
- $C_{tot}$: The total gas phase concentration [mole m$^{-3}$]

This yields $\frac{dF_v}{d\hat{z}} = -1.18 \cdot 10^{-8}$. This means that the volumetric flow rate changes with only 3% over the length of the reactor. The volumetric flow rate is thus assumed to be uniform in the reactor.

**The axial temperature gradient**

The axial temperature gradient can be estimated by determining the maximum adiabatic temperature difference over the reactor. This criterion can be estimated by:
\[ \Delta T_{\text{max,adiabatic}} = \frac{C_{A,in}(-\Delta H_r)}{\rho C_p} \]  

(A3.21)

In which

\[ \Delta T_{\text{max,adiabatic}} \quad \text{Maximal adiabatic temperature difference} \quad [\text{K}] \]
\[ C_{A,in} \quad \text{Concentration of the rate limiting reactant in the feed} \quad [\text{mole m}^{-3}] \]
\[ \Delta H_r \quad \text{Reaction enthalpy} \quad [\text{J mole}^{-1}] \]
\[ \rho \quad \text{Catalyst density} \quad [\text{kg cat m}^{-3}] \]
\[ C_p \quad \text{Heat capacity of the catalyst (magnetite layer)} \quad [\text{J kg}^{-1} \text{ K}^{-1}] \]

Since \( \Delta T_{\text{max,adiabatic}} = 0.45 \), which is very small compared to the reactor temperature (603 K), the axial temperature gradient is negligible.

The radial temperature gradient

The radial temperature gradient can be estimated using the following Mears criterion [16]:

\[ T_{Mears} = \frac{-(1 - \varepsilon_b)r_A \rho_b (-\Delta H_r)T_a d_b^2}{4 \lambda_{b,eff} T_w^2 \left( 1 + \left( \frac{8\lambda_{b,eff}}{U d_b} \right) \right)} < 0.4 \]  

(A3.22)

In which

\[ T_{Mears} \quad \text{Mears criterion for radial temperature gradient} \quad [-] \]
\[ \varepsilon_b \quad \text{Catalyst bed porosity} \quad [\text{m}^3 \text{ m}^{-3}] \]
\[ r_A \quad \text{Reaction rate of disappearance for limiting reactant A} \quad [\text{mole kg}_{\text{cat}}^{-1} \text{ s}^{-1}] \]
\[ \rho_b \quad \text{Catalyst bed density} \quad [\text{kg}_{\text{cat}} \text{ m}^{-1}] \]
\[ \Delta H_r \quad \text{Reaction enthalpy} \quad [\text{J mole}^{-1}] \]
\[ T_a \quad \text{Adiabatic temperature} \quad [\text{K}] \]
\[ d_b \quad \text{Diameter of the catalyst bed} \quad [\text{m}] \]
\[ \lambda_{b,eff} \quad \text{Effective thermal conductivity for the catalyst bed} \quad [\text{W m}^{-1} \text{ K}^{-1}] \]
\[ T_w \quad \text{Temperature of the reactor wall} \quad [\text{K}] \]
\[ U \quad \text{Global heat exchange coefficient at the tube wall} \quad [\text{W m}^{-2} \text{ K}^{-1}] \]

The reaction rate for limiting reactant is calculated similarly as earlier in the appendix. The wall tube is assumed to be equal for the inner and outer site and is measured by a thermocouple. The global heat exchange coefficient at the tube wall is assumed to be \( U = 400 \text{ W m}^{-2} \text{ K}^{-1} \), which is a typical value under lab conditions. The adiabatic temperature and the effective thermal conductivity are calculated by these equations:

\[ T_a = \frac{E_{\text{act}}}{R} \]  

(A3.23)
\[
\lambda_{b,\text{eff}} = \lambda_{b,\text{eff}0} + \frac{0.14C_{p,g} \rho_{\text{mix}}}{1 + 46 \frac{d_p}{d_b}} \quad (A3.24)
\]

With

\[
\lambda_{b,\text{eff}0} = \varepsilon_b \lambda_g + (1 - \varepsilon_b) \lambda_{\text{inert}} \left( \frac{1}{\frac{\phi_b}{\lambda_g} + \frac{2}{\lambda_g^3}} \right) \quad (A3.25)
\]

In which

- \( T_a \) Adiabatic temperature \([K]\)
- \( E_{\text{act}} \) Activation energy for the reaction \([J \text{ mole}^{-1}]\)
- \( R \) Gas constant \([J \text{ mole}^{-1} \text{ K}^{-1}]\)
- \( \lambda_{b,\text{eff}} \) Effective thermal conductivity for the catalyst bed \([W \text{ m}^{-1} \text{ K}^{-1}]\)
- \( \lambda_{b,\text{eff}0} \) Effective stationary thermal conductivity for the catalyst bed \([W \text{ m}^{-1} \text{ K}^{-1}]\)
- \( C_{p,g} \) Heat capacity of the gas phase \([J \text{ kg}^{-1} \text{ K}^{-1}]\)
- \( \rho_{\text{mix}} \) Density of the gas mixture \([\text{kg m}^{-3}]\)
- \( d_p \) Catalyst particle diameter \([\text{m}]\)
- \( d_b \) Diameter of the catalyst bed \([\text{m}]\)
- \( \varepsilon_b \) Catalyst bed porosity \([\text{m}_g^3 \text{ m}_r^3]\)
- \( \lambda_g \) Effective thermal conductivity of the gas phase \([W \text{ m}^{-1} \text{ K}^{-1}]\)
- \( \phi_b \) Thermal effectivity parameter \([-]\)

The activation energy has been chosen as a typical value for the FT reaction of ca. 60 kJ mole\(^{-1}\). The gas phase thermal conductivity \( \lambda_g = 0.025 \text{ W m}^{-1} \text{ K}^{-1} \), which is a high value according to Handbook of Heterogeneous Catalysis [14]. The heat capacity of the gas phase is chosen such that it is a typical value for gasses at this temperature. The effectivity parameter equals 0.08 based on Kunii and Levenspiel [17].

Combining these parameters with the values calculated earlier, the radial temperature gradient equals 0.057<0.4. So it can be assumed that there is no radial gradient.

**External catalyst surface temperature gradient**

The importance of the temperature gradient at the external catalyst surface can be indicated by the Mears criterion for heat transfer [13]:

\[
\text{Mears criterion} = \frac{T_a - T_s}{T_a - T_{\text{sat}}}
\]

where
- \( T_a \) Adiabatic temperature
- \( T_s \) Surface temperature
- \( T_{\text{sat}} \) Saturation temperature
\[ C_{\text{Mears, temp}} = \frac{(-\Delta H_r)(-r_A) d_p \rho E_{act}}{(h T_r^2 R)} < 0.3 \quad (A3.26) \]

In which

- \( C_{\text{Mears}} \): Mears criterion external heat transfer, [-]
- \( \Delta H_r \): Reaction enthalpy, [J mole\(^{-1}\)]
- \( r_A \): Reaction rate of disappearance for limiting reactant A, [mole kg\(_{\text{cat}}\)\(^{-1}\) s\(^{-1}\)]
- \( d_p \): Catalyst particle diameter, [m]
- \( \rho \): Catalyst density, [kg\(_{\text{cat}}\) m\(^{-3}\)]
- \( E_{act} \): Activation energy for the reaction, [J mole\(^{-1}\)]
- \( h \): Gas solid heat transfer coefficient, [m s\(^{-2}\)]
- \( T_r \): Temperature in the reactor, [K]
- \( R \): Gas constant, [J mole\(^{-1}\) K\(^{-1}\)]

The gas solid heat transfer coefficient is determined by a Nusselt relation:

\[ N_u_{\text{loc}} = \frac{\lambda}{h d_p} = 3.66 \quad (A3.27) \]

This equation is only valid for a Greatz number larger than 0.1. The Greatz number is calculated by:

\[ Gz = \frac{a L_b}{d_p u_s} \quad (A3.28) \]

In which

- \( N_u_{\text{loc}} \): Local Nusselt number, [-]
- \( \lambda \): Thermal conductivity of the particle, [J m\(^{-1}\) K\(^{-1}\)]
- \( h \): Gas solid heat transfer coefficient, [m s\(^{-2}\)]
- \( d_p \): Catalyst particle diameter, [m]
- \( a \): Thermal diffusion coefficient, [m\(^2\) s\(^{-1}\)]
- \( L_b \): Length of the catalyst bed, [m]
- \( u_s \): Superficial velocity, [m s\(^{-1}\)]

The thermal diffusion coefficient is calculated by dividing the thermal conductivity by the density multiplied with the heat capacity of magnetite. Since \( Gz = 1.9 \), the equation is validated. The Mears criterion for external heat transfer at the particle surface, \( C_{\text{Mears, temp}} = 7.9 \cdot 10^{-4} < 0.3 \), therefore this criterion is met. There is thus no temperature gradient at the external catalyst surface.
Isothermal behavior of the reactor
Another validation has been done to determine the isothermal behaviour of the reactor. This criterion is [14]:

\[
\frac{E_{\text{act}}}{RT_w} r_{V,\text{obs}} \left(-\Delta H_r\right) \frac{d_b}{2} \left(\frac{1}{8} + \frac{d_p}{B_i_t d_b}\right) < 0.05 \quad (A3.29)
\]

In which

- \(E_{\text{act}}\): Activation energy for the reaction \([\text{J mole}^{-1}]\)
- \(R\): Gas constant \([\text{J mole}^{-1} \text{ K}^{-1}]\)
- \(T_w\): Temperature of the reactor wall \([\text{K}]\)
- \(r_{V,\text{obs}}\): Observed reaction rate per unit bed volume \([\text{mole s}^{-1} \text{ m}^{-3}]\)
- \(\Delta H_r\): Reaction enthalpy \([\text{J mole}^{-1}]\)
- \(d_p\): Catalyst particle diameter \([\text{m}]\)
- \(\lambda_{b,\text{eff}}\): Effective thermal conductivity for the catalyst bed \([\text{W m}^{-1} \text{ K}^{-1}]\)
- \(B_i_t\): Biot number for the reactor wall
- \(d_b\): Diameter of the catalyst bed

The observed reaction rate per unit bed volume is equal to the reaction rate of CO at maximum conversion multiplied by the catalyst bed density and 1 minus the inert fraction. This assumption is only valid, since the internal and external mass transfer are not present.

The Biot number for the reactor wall is calculated by

\[
B_i_t = \frac{h_w d_p}{\lambda_{b,\text{eff}}} \quad (A3.30)
\]

In which

- \(B_i_t\): Biot number for the reactor wall
- \(h_w\): The heat transfer coefficient of the wall \([\text{m s}^{-2}]\)
- \(d_p\): Catalyst particle diameter \([\text{m}]\)
- \(\lambda_{b,\text{eff}}\): Effective thermal conductivity for the catalyst bed \([\text{W m}^{-1} \text{ K}^{-1}]\)

A typical value for the heat transfer coefficient of stainless steel has been chosen for the reactor wall. This criterion is met, since its value \(0.0037 < 0.05\). Thus the reactor is running isothermally.