Multicomponent Reaction Engineering Model for Fischer-Tropsch Synthesis in Commercial Scale Slurry Bubble Column Reactors

Abstract

A multicomponent mathematical model is presented for a large scale slurry bubble column reactor operating in the heterogeneous or churn-turbulent flow regime. The model accounts for both the Fischer-Tropsch reaction as well as the water gas shift reaction and the individual paraffin and olefin formation rates. It provides all the data necessary for reliable scale up, process optimization, and prediction of the performance of industrial scale Fischer-Tropsch bubble column reactors.
7.1 Introduction

Synthesis gas (CO and H\textsubscript{2}) from coal or natural gas can be converted in the Fischer-Tropsch (FT) process to a multicomponent mixture of predominantly linear hydrocarbons. The FT synthesis in slurry bubble column reactors (SBCR) is very attractive relative to fixed bed reactors \cite{1}. The advantages are: 1) Low pressure drop over the reactor. 2) Excellent heat transfer characteristics resulting in stable reactor temperatures. 3) No diffusion limitations. 4) Possibility of continuous refreshment of catalyst particles. 5) Relatively simple construction and low investment costs. Mathematical modeling of a FT SBCR was reviewed by Saxena et al. \cite{1} and more recently by Saxena \cite{2}. The bottleneck appears to be the lack of reliable kinetic equations for all products and reactants based on realistic reaction mechanisms.

A summary of previous slurry bubble column reactor models for the Fischer-Tropsch synthesis is given in Table 7.1. Most models are only applicable in small scale slurry bubble columns operating in the homogeneous regime. However, the churn-turbulent or heterogeneous regime is the most optimal one for the FT synthesis \cite{13}. In this regime, there is a range of bubble sizes. The gas bubbles can be divided into two classes: 1) the small bubbles with a constant bubble diameter less than 0.01 m, and 2) the large bubbles: bubbles larger than 0.01 m with irregular shape and varying size. The mixing behavior of both classes is completely different due to the difference in rise velocity. Krishna and co-workers modeled a slurry bubble column containing cobalt catalyst particles with the use of flow patterns for the large and small bubbles \cite{13, 16, 17}.

Appropriate rate equations for both the Fischer-Tropsch and the water gas shift reaction are needed for modeling of bubble columns operated with iron catalysts. Kuo \cite{9}, Stenger and Satterfield \cite{10}, Prakash and Bendale \cite{11}, Prakash \cite{12}, and Inga and Morsi \cite{15} included rate expressions for the FT and WGS reactions to obtain accurate hydrogen and carbon monoxide axial concentration profiles. Until now, none of the available literature models can describe the complete product distribution of the FT synthesis at industrial conditions (high temperature and pressure) as a function of overall consumption of synthesis gas components and operating conditions.

This study will investigate an iron-based Fischer-Tropsch SBCR operating in the heterogeneous flow regime. The model takes into account both the water gas shift and the FT reactions, as well as individual hydrocarbon product formation rates. Here, multicomponent vapor-liquid equilibria (VLE) with detailed kinetic expressions for all reactants and hydrocarbon products are combined with SBCR hydrodynamics and...
Table 7.1 Comparison of reaction engineering models for the Fischer-Tropsch synthesis in slurry bubble column reactors.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Gas phase</th>
<th>Liquid phase</th>
<th>Catalyst distribution</th>
<th>Energy balance</th>
<th>Components</th>
<th>FT</th>
<th>WGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calderbank et al. [3]</td>
<td>PF</td>
<td>PF</td>
<td>uniform</td>
<td>isothermal</td>
<td>H₂</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Satterfield and Huff [4]</td>
<td>PF</td>
<td>PM</td>
<td>uniform</td>
<td>isothermal</td>
<td>H₂</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Deckwer et al. [5]</td>
<td>PF</td>
<td>PM</td>
<td>uniform</td>
<td>isothermal</td>
<td>H₂</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Deckwer et al. [6]</td>
<td>AD</td>
<td>AD</td>
<td>non-uniform</td>
<td>non-isothermal</td>
<td>H₂</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Bukur [7]</td>
<td>PF</td>
<td>PF, PM</td>
<td>uniform</td>
<td>isothermal</td>
<td>H₂</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Stern et al. [8]</td>
<td>PF</td>
<td>PM</td>
<td>uniform</td>
<td>isothermal</td>
<td>H₂, CO, CO₂, H₂O, CH₄, C₅H₁₀</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Kuo [9]</td>
<td>PF</td>
<td>PM, PF, AD</td>
<td>non-uniform</td>
<td>isothermal</td>
<td>H₂</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Kuo [9]</td>
<td>PF</td>
<td>PF</td>
<td>non-uniform</td>
<td>isothermal</td>
<td>H₂, CO, CO₂, H₂O</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Stenger and Satterfield [10]</td>
<td>AD</td>
<td>AD</td>
<td>non-uniform</td>
<td>isothermal</td>
<td>H₂, CO, CO₂, H₂O, C₃H₁₀</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Prakash and Bendale [11]</td>
<td>AD</td>
<td>AD</td>
<td>non-uniform</td>
<td>isothermal</td>
<td>H₂, CO, CO₂, H₂O, C₁₋₃</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Prakash [12]</td>
<td>AD</td>
<td>AD</td>
<td>non-uniform</td>
<td>isothermal</td>
<td>H₂, CO, CO₂, H₂O, C₁₋₃</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>De Swart [13]¹</td>
<td>AD</td>
<td>AD</td>
<td>non-uniform</td>
<td>non-isothermal</td>
<td>H₂</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>De Swart [13]²</td>
<td>PF</td>
<td>PM</td>
<td>uniform</td>
<td>isothermal</td>
<td>H₂</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Mills et al. [14]</td>
<td>AD</td>
<td>AD</td>
<td>non-uniform</td>
<td>non-isothermal</td>
<td>H₂</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Inga and Morsi [15]</td>
<td>PF</td>
<td>MC</td>
<td>uniform</td>
<td>isothermal</td>
<td>H₂, CO, H₂O</td>
<td>1,3</td>
<td>2</td>
</tr>
<tr>
<td>Krishna and Maretto [16]²</td>
<td>PF</td>
<td>PM</td>
<td>uniform</td>
<td>isothermal</td>
<td>H₂, CO</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Our model²</td>
<td>PF</td>
<td>PM</td>
<td>uniform</td>
<td>isothermal</td>
<td>H₂, CO, CO₂, H₂O, N₂, C₁₋₁₀</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PF: plug flow, PM: perfectly mixed, MC: mixing cells, AD: axial dispersion

¹ Heterogeneous flow regime: Large bubbles: PF, Small bubbles and liquid: AD

² Heterogeneous flow regime: Large bubbles: PF, Small bubbles and liquid: PM
mass transfer characteristics to predict the detailed product composition of both gas and liquid phase as a function of operating conditions.

**Table 7.2** Kinetic models for Table 7.1.

<table>
<thead>
<tr>
<th>FT kinetic expressions</th>
<th>WGS kinetic expressions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( kC_{\text{H}_2,\text{L}} )</td>
<td>( k \left( C_{\text{CO,L}}C_{\text{H}<em>2\text{O,L}} - C</em>{\text{CO}<em>2,L}C</em>{\text{H}_2,L}/K_P \right) )</td>
</tr>
<tr>
<td>( \frac{kC_{\text{H}<em>2,L}C</em>{\text{CO,L}}}{C_{\text{CO,L}} + aC_{\text{H}_2\text{O}}} )</td>
<td>( \frac{k \left( C_{\text{CO,L}}C_{\text{H}<em>2\text{O,L}} - C</em>{\text{CO}<em>2,L}C</em>{\text{H}<em>2,L}/K_P \right)}{P</em>{\text{CO}} + aP_{\text{H}_2\text{O}}} )</td>
</tr>
<tr>
<td>( \frac{kC_{\text{H}<em>2,L}C</em>{\text{CO,L}}}{(1 + aC_{\text{CO,L}})^2} )</td>
<td></td>
</tr>
</tbody>
</table>

### 7.2 Kinetics and Hydrocarbon Selectivity

The rate expression for the FT reaction on a precipitated iron catalyst in the slurry phase proposed in Chapter 6 was used (Table 7.3):

\[
R_{\text{FT}} = \frac{kP_{\text{CO}}P_{\text{H}_2}^{1/2}}{(1 + aP_{\text{CO}} + bP_{\text{CO}_2})^2} \tag{7.1}
\]

The water gas shift reaction is an exothermic and reversible reaction proceeding simultaneously with the Fischer-Tropsch reaction. Due to the WGS reaction, synthesis gas with a \( \text{H}_2/\text{CO} \) ratio below 2 can be used because excess of carbon monoxide is converted with water to carbon dioxide and hydrogen. The equilibrium constant \( K_P \) was obtained from Graaf et al. [18] and the following rate expression was used for the kinetics of the WGS (see Table 7.3 and Chapter 6):

\[
R_{\text{WGS}} = \frac{k_{\text{WGS}} \left( P_{\text{CO}}P_{\text{H}_2\text{O}} - P_{\text{CO}_2}P_{\text{H}_2}/K_P \right)}{(P_{\text{CO}} + K_PP_{\text{H}_2\text{O}})^2} \tag{7.2}
\]

The product selectivity to \( \alpha \)-olefins and paraffins was calculated using a recently developed selectivity model for iron catalysts, called \( \alpha \)-Olefin Readsoption Product Distribution Model (ORPDM) (see Chapters 4 and 6). This model allows for a chain-length dependent chain growth factor due to readsoption of \( \alpha \)-olefins. The appropriate model parameters are shown in Table 7.3 as a function of process variables \( (P_{\text{CO}}, P_{\text{H}_2}, \Phi_{e,0}/W) \) at a constant temperature of 523 K.
Table 7.3  Kinetic and selectivity model parameters at 523 K (Chapter 6).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_P^1 )</td>
<td>6.5 (mol kg(^{-1}) s(^{-1}) MPa(^{-1}))</td>
<td>( k )</td>
<td>0.0339</td>
</tr>
<tr>
<td>( t_P^2 )</td>
<td>1.7 MPa(^{-1})</td>
<td>( a )</td>
<td>1.185</td>
</tr>
<tr>
<td>( c )</td>
<td>0.35 MPa(^{-1})</td>
<td>( b )</td>
<td>0.656</td>
</tr>
<tr>
<td>( k_R^2 )</td>
<td>17.6 ( k_Re^2 )</td>
<td>( k_{WGS} ) (mol kg(^{-1}) s(^{-1}))</td>
<td>0.0292</td>
</tr>
<tr>
<td>( p )</td>
<td>14.0 ( P_{H_2} ) ( P_{CO}^{0.40} )</td>
<td>( K ) (-)</td>
<td>3.07</td>
</tr>
<tr>
<td>( t_O )</td>
<td>3.71 ( P_{H_2}^{0.5} )</td>
<td>( K_P )</td>
<td>85.81</td>
</tr>
<tr>
<td>( k_R )</td>
<td>8.00 ( 10^{-5} P_{H_2}^{1.2} P_{CO}^{0.47} ) ( \Phi_{v,0}/W )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Pressures in MPa, space velocity \( \Phi_{v,0}/W \) in Nm\(^3\) kg\(_{cat}\) s\(^{-1}\).

7.3  Model Equations

A mathematical description for the simulation of an industrial Fischer-Tropsch SBCR is presented. The reactor model can be applied in the heterogeneous or churn-turbulent regime (see Figure 7.1). The large bubbles are assumed to be in plug flow with a superficial gas velocity of \( U_G = U_{DF} \). The superficial velocity of the gas present in the well mixed small bubbles is \( U_{DF} \), which is equal to the total superficial gas ve-
locity at regime transition. The mathematical model for the Fischer-Tropsch synthesis is based on the following assumptions: 1) Gas-liquid mass transfer resistance is located in the liquid phase. 2) Large gas bubbles are in plug flow due to high rise velocities, typically 1-2 m s\(^{-1}\). 3) The gas phase in the small gas bubbles, and the liquid phase are each completely mixed, due to the large reactor diameter of 8 m [6]. Catalyst distribution is uniform due to upflow of the slurry phase, the large reactor diameter and the turbulence created by the fast-rising large bubbles. 4) Hydrocarbon products, paraffins and olefins only, in the gas and liquid phase of the reactor outlet are assumed to be in equilibrium at the reactor outlet. 5) The reactor operates isothermally due to the completely mixed liquid phase. 6) The slurry velocity is constant. 7) The reactor operates at steady state conditions. 8) The effectiveness factor of the catalyst particles is equal to unity and mass and heat transfer resistances between catalyst and liquid are negligible due to the small particle size applied (50 µm).

The gas phase mass balance for component \(i\) in the large bubbles, rising in plug flow is:

\[
\frac{d (U_G - U_{DF}) C_{i,G}^{\text{large}}}{dh} + (k_{L,G})_{i}^{\text{large}} \left( \frac{C_{i,G}^{\text{large}}}{m_{i,G}^{GL}} - C_{i,L} \right) = 0 \quad (7.3)
\]

with concentrations in mol m\(^{-3}\) subject to the boundary conditions at the reactor entrance: \(h=0\): \(C_{i,G}^{\text{large}} = C_{i,G}^{\text{in}}\). The gas phase mass balance for component \(i\) in the small bubbles (completely mixed) is:

\[
\frac{U_{DF}}{H} \left( C_{i,G}^{\text{in}} - C_{i,G}^{\text{small}} \right) = (k_{L,G})_{i}^{\text{small}} \left( \frac{C_{i,G}^{\text{small}}}{m_{i,G}^{GL}} - C_{i,L} \right) \quad (7.4)
\]

The mass balance for component \(i\) in the completely mixed liquid phase can be written as:

\[
\frac{1}{H} \int_{0}^{H} (k_{L,L})_{i}^{\text{large}} \left( \frac{C_{i,G}^{\text{large}}}{m_{i,G}^{GL}} - C_{i,L} \right) dh + (k_{L,L})_{i}^{\text{small}} \left( \frac{C_{i,G}^{\text{small}}}{m_{i,G}^{GL}} - C_{i,L} \right) +
\]

\[
+ \varepsilon_{L,F} \rho \sum_{j=1}^{n} v_{ij} R_{j} - \frac{U_{S}}{H} C_{i,L} = 0 \quad (7.5)
\]

where \(\varepsilon_{L}\) is the liquid holdup (m\(^{3}\) m\(^{-3}\)), \(\varepsilon_{F}\) is the solids holdup (m\(^{3}\) m\(^{-3}\)), \(\rho\) is the catalyst density, \(R_{j}\) is the FT \((j=1)\) or WGS \((j=2)\) reaction rate (mol kg\(^{-1}\) cat s\(^{-1}\)), \(v_{ij}\) is the stoichiometric coefficient for component \(i\) in the \(j\)-th reaction. The reaction heat
is removed with vertical cooling tubes of 1.5 inch diameter at a constant steam temperature $T_c$ of 495 K. The overall heat transfer coefficient $\alpha_{\text{eff}}$ from slurry to coolant is estimated from the correlation of Deckwer et al. [19]:

$$\alpha_{\text{eff}} = 0.1 U_G^{0.25} \rho_S^{-0.75} C_{p,S}^{0.25} \eta_S^{0.25} \delta_S^{0.5}$$  \hfill (7.6)

At gas velocities higher than 0.10 m s$^{-1}$ the heat transfer coefficient does not increase any more and is calculated from $U_G$ equal to 0.10 m s$^{-1}$.

The energy balance for the slurry phase reads, assuming the catalyst and the liquid temperature to be equal:

$$\varepsilon_L \rho_p \rho_p \sum_j \left( -\Delta H_{R,j} \right) R_j - \alpha_{\text{eff}} a_c (T - T_c) +$$

$$+ \frac{U_S}{H} \left( (\rho_S C_p ST)_{in} - (\rho_S C_p ST)_{out} \right) = 0$$  \hfill (7.7)

where $a_c$ is the specific heat transfer area (m$^{-1}$), $C_{p,S}$ is the heat capacity of the slurry phase, $\rho_S$ is the slurry density and $-\Delta H_{R,j}$ is the reaction heat of reaction $j$ (J mol$^{-1}$).

The molar flow rate of the gas phase will change due to reaction. The superficial velocity is assumed to be a linear function of the overall synthesis gas conversion, $X_{CO+H_2}$ [14]:

$$U_G = (1 + \alpha_c X_{CO+H_2}) U_G^{in} = \left( 1 + \alpha_c (1 + U) / (1 + F) X_{H_2} \right) U_G^{in},$$  \hfill (7.8)

where $\alpha_c$ is the contraction factor, defined as:

$$\alpha_c = \frac{U_G(X_{CO+H_2} = 1) - U_G(X_{CO+H_2} = 0)}{U_G(X_{CO+H_2} = 0)}$$  \hfill (7.9)

$U$ is the usage ratio of hydrogen to carbon monoxide ($-R_{H_2}/-R_{CO}$) and $F$ is the feed ratio of H$_2$ to CO. The reported values of $\alpha$ are between -0.5 and -0.65 [6]. The contraction factor $\alpha_c$ is determined by the product selectivity ($m$ and $n$).

### 7.4 Hydrodynamic Parameters

The most important hydrodynamic parameters are the gas holdup of the large and small bubbles in presence of solids under Fischer-Tropsch reaction conditions. The rise velocity of the small bubbles will increase with increasing solids holdup due to enhanced coalescence according to:

$$V_{\text{small}} = V_{\text{small}}^{ref} \left( 1 + 0.8 \varepsilon_p / V_{\text{small}}^{ref} \right)$$  \hfill (7.10)
with $V_{\text{small}}^{\text{ref}} = 0.095 \text{ m}^{-1}$ [20]. The gas holdup at the transition from homogeneous to churn turbulent regime in the presence of a high solids loading follows from Krishna et al. [20]:

$$
\varepsilon_{DF} = \varepsilon_{DF}^{\text{ref}} \left( \frac{\rho_G}{\rho_G^{\text{ref}}} \right)^{0.48} \left( 1 - 0.7 \varepsilon_P / \varepsilon_{DF}^{\text{ref}} \right) \quad (7.11)
$$

where the small bubble holdup in solids-free liquid is $\varepsilon_{DF}^{\text{ref}} = 0.27$ and the atmospheric density is $\rho_G^{\text{ref}} = 1.3 \text{ kg m}^{-3}$. The corresponding superficial gas velocity at regime transition is calculated from $U_{DF} = V_{\text{small}}^{\text{ref}}$. The model of Krishna and Ellenberger [21] is used to predict the gas holdup of the large bubbles. This model is corrected for the influence of gas density according to a recent study of Letzel et al. [22]. For large bubble columns ($D > 1 \text{ m}$) and high slurry concentrations ($\varepsilon_P > 0.16$), the large bubble holdup can be estimated from a combination of the correlations given by Letzel et al. [22] and Krishna et al. [20]:

$$
\varepsilon_B = 0.3 \left( U_G - U_{DF} \right)^{0.58} \left( \frac{\rho_G}{\rho_G^{\text{ref}}} \right)^{0.5} \quad (7.12)
$$

The total gas holdup in the heterogeneous regime is calculated from:

$$
\varepsilon_G = \varepsilon_B + \varepsilon_{DF} (1 - \varepsilon_B) \quad (7.13)
$$

The volumetric mass transfer coefficient of large bubbles is obtained from the relation proposed by Vermeer and Krishna [23] and more recently by Letzel et al. [22]:

$$
k_{L, \text{large}}^{\text{ref}} / \varepsilon_B = 0.5 \quad (7.14)
$$

which is corrected for the mass transfer coefficient of component $i$ by the factor:

$$
k_{L, i}^{\text{large}} / k_{L, \text{ref}}^{\text{large}} = \left( D_i / D_{\text{ref}} \right)^{0.5} \quad (7.15)
$$

where $D_{\text{ref}} = 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. In the same way, the volumetric mass transfer coefficient for component $i$ of the small bubbles is defined as [16]:

$$
k_{L, i}^{\text{small}} / \varepsilon_{DF}^{\text{ref}} = 1.0 \quad (7.16)
$$

### 7.5 Physical Properties and Flash Calculations

For calculating the physical properties of the liquid, it was assumed that the FT wax consisted of n-paraffins with a carbon number of 28 ($\text{C}_{28}\text{H}_{58}$). The physical properties at 523 K were estimated with the asymptotical behavior correlations developed by
### Table 7.4 Operation conditions and physical properties.

<table>
<thead>
<tr>
<th>Reactor configuration</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>reactor diameter</td>
<td>( D = 8 ) m</td>
</tr>
<tr>
<td>reactor height</td>
<td>( H = 30 ) (20% disengagement zone) m</td>
</tr>
<tr>
<td>dispersion height</td>
<td>( H = 24 ) m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pressure</td>
<td>( P = 3 \times 10^5 ) Pa</td>
</tr>
<tr>
<td>temperature</td>
<td>( T = 523 ) K</td>
</tr>
<tr>
<td>catalyst concentration</td>
<td>( \varepsilon_p = 0.20 - 0.35 ) m (^3) m (^{-3})</td>
</tr>
<tr>
<td>superficial gas velocity</td>
<td>( U_G = 0.15 - 0.40 ) m s (^{-1})</td>
</tr>
<tr>
<td>superficial slurry velocity</td>
<td>( U_s = 0.01 ) m s (^{-1})</td>
</tr>
<tr>
<td>cooling tube diameter</td>
<td>( d_c = 0.0381 ) m</td>
</tr>
<tr>
<td>coolant temperature</td>
<td>( T_c = 495 ) K</td>
</tr>
<tr>
<td>feed composition</td>
<td>( F = 0.5 - 2.0, \ y_{CO_2} = 0.05, \ y_{inert} = 0.05 ) -</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Liquid phase (L)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>liquid viscosity</td>
<td>( \eta_L = 5.95 \times 10^{-4} ) Pa s</td>
</tr>
<tr>
<td>liquid density</td>
<td>( \rho_L = 656.7 ) kg m (^{-3})</td>
</tr>
<tr>
<td>surface tension</td>
<td>( \sigma = 0.017 ) N m (^{-1})</td>
</tr>
<tr>
<td>liquid heat capacity</td>
<td>( C_{p,L} = 2721 ) J kg (^{-1}) K (^{-1})</td>
</tr>
<tr>
<td>liquid heat conductivity</td>
<td>( \lambda_L = 0.181 ) W m (^{-1}) K (^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalyst phase (P)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>catalyst diameter</td>
<td>( d_p = 50 \times 10^{-6} ) m</td>
</tr>
<tr>
<td>catalyst density</td>
<td>( \rho_p = 1957 ) (Lox et al. [24]) kg m (^{-3})</td>
</tr>
<tr>
<td>catalyst heat capacity</td>
<td>( C_{p,p} = 993 ) J kg (^{-1}) K (^{-1})</td>
</tr>
<tr>
<td>catalyst heat conductivity</td>
<td>( \lambda_p = 1.7 ) W m (^{-1}) K (^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Slurry phase (S)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>catalyst weight fraction</td>
<td>( w_p = \frac{\varepsilon_p \rho_p}{\varepsilon_p (\rho_p - \rho_L) + \rho_L} ) [6] -</td>
</tr>
<tr>
<td>slurry density</td>
<td>( \rho_S = \varepsilon_p \rho_p + (1 - \varepsilon_p) \rho_L ) [6] kg m (^{-3})</td>
</tr>
<tr>
<td>slurry viscosity</td>
<td>( \eta_S = \eta_L (1 + 4.5 \varepsilon_p) ) [19] Pa s</td>
</tr>
<tr>
<td>slurry heat capacity</td>
<td>( C_{p,S} = w_p C_{p,p} + (1 - w_p) C_{p,L} ) [6] J kg (^{-1}) K (^{-1})</td>
</tr>
<tr>
<td>slurry heat conductivity</td>
<td>( \lambda_S = \frac{\lambda_L - \lambda_p}{2 \lambda_L + \lambda_p - 2 \varepsilon_p (\lambda_L - \lambda_p)} ) [25] W m (^{-1}) K (^{-1})</td>
</tr>
</tbody>
</table>
Marano and Holder [26, 27] (see Table 7.4). Henry constants for CO, CO₂, H₂, H₂O, N₂ and light hydrocarbons (C₁ - C₃) were obtained from Marano and Holder [28]. Diffusivities at high temperatures and pressures, necessary for calculating mass transfer coefficients, were estimated using correlations of Erkey et al. [29] based on the rough hard sphere theory. The multicomponent VLE model of Marano and Holder [28] was applied. However, we assumed ideal gas behavior of the gas phase because under the reaction conditions applied, the fugacity coefficients (upto C₃₀) as calculated with the Peng-Robinson equation of state are between 0.95 and 1.01. The equilibrium constants between vapor and liquid for non-hydrocarbons and C₁₋₃ hydrocarbons were calculated from:

\[ K_i \equiv \frac{y_i}{x_i} = H_i^\infty \Phi_i / P \]  
(7.17)

where \( K_i \) is the \( K \)-value for component \( i \), \( H_i^\infty \) is the Henry constant for component \( i \) at infinite dilution, and \( \Phi_i \) is the Poynting-factor. For the other hydrocarbons, the \( K \)-value is given by:

\[ K_i = \gamma_i^\infty P_{i,sat} \Phi_i / P \]  
(7.18)

where \( \gamma_i^\infty \) is an activity coefficient, and \( P_{i,sat} \) is the vapor pressure of pure component \( i \). The appropriate parameter values were obtained from Marano and Holder [28]. A flash calculation using these \( K \)-values gives the final composition of the liquid and gas phase outlet of the SBCR:

\[ \rho_p \bar{V}_{le} \bar{p} V R_{FT} \sum_{i} \frac{m_i}{n_i m_i} = U_G^H A y_i C_G + U_S A x_i C_L \]  
(7.19)

where \( m_i \) is the molar selectivity to product \( i \) with carbon number \( n \), and \( C_G \) and \( C_L \) are the total gas and liquid concentration, respectively.

### 7.6 Results and Discussion

A commercial scale SBCR with diameter \( D = 8 \text{ m} \), dispersion height \( H = 24 \text{ m} \), pressure \( P = 3.0 \text{ MPa} \) and temperature \( T = 523 \text{ K} \) is used in our simulations. The superficial slurry velocity \( U_s \) is 0.01 \text{ m s}^{-1}. The slurry enters the reactor with an inlet temperature of 423 K. The properties of the catalyst applied (Ruhrchemie LP 33/81 Fe/Cu/K on SiO₂) are: catalyst particle diameter 50 \text{ 10}^{-6} \text{ m}, catalyst density \( \rho_p = 1957 \text{ kg m}^{-3} \). The properties of the slurry were determined using the relations of Deckwer et
Table 7.5  Physical properties and concentrations of the components in the SBCR mentioned in Figure 7.2. Operating conditions: $F=1$, $U_{in}^G=0.20$ m s$^{-1}$, $\varepsilon_P=0.25$, $D=8$ m, $H=24$ m, $T=523$ K.

<table>
<thead>
<tr>
<th>Component</th>
<th>$m_i^{GL}$ $(C_G/C_L)$</th>
<th>$D_i$ $(10^{-8}$ m$^2$ s$^{-1}$)</th>
<th>$C_{i,G}^{in}$</th>
<th>$C_{i,G,out}^{large}$</th>
<th>$C_{i,G}^{small}$</th>
<th>$C_{i,L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>5.83</td>
<td>3.85</td>
<td>310.5</td>
<td>152.6</td>
<td>155.1</td>
<td>26.2</td>
</tr>
<tr>
<td>CO</td>
<td>4.86</td>
<td>1.53</td>
<td>310.5</td>
<td>125.2</td>
<td>129.2</td>
<td>25.8</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2.32</td>
<td>1.26</td>
<td>34.5</td>
<td>150.3</td>
<td>149.0</td>
<td>64.9</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.85</td>
<td>1.89</td>
<td>0</td>
<td>53.5</td>
<td>53.3</td>
<td>62.9</td>
</tr>
<tr>
<td>N$_2$</td>
<td>5.65</td>
<td>1.54</td>
<td>34.5</td>
<td>44.5</td>
<td>44.3</td>
<td>7.9</td>
</tr>
</tbody>
</table>

al. [6, 19] (see Table 7.4). The complete reactor model consists of a system of ordinary differential equations and algebraic equations, with the corresponding boundary conditions. The set of equations was solved numerically using a backward differentiation scheme with 60 grid points using the gPROMS software package (Version 1.6a, Process Systems Enterprise, London).

The concentration gradients of CO, H$_2$, CO$_2$, H$_2$O and N$_2$ are large in the bottom of the slurry reactor. Particularly at the top of the reactor, the liquid phase is in equilibrium with the gas phase ($C_{i,L} = C_{i,G}^{large}/m_i^{GL}$, see Table 7.5). Resulting from the difference in solubility, the H$_2$/CO ratio in the liquid phase is larger than that in the gas feed. The liquid phase concentrations of H$_2$ and CO influence the chain length and olefin content of the products formed. The axial concentration profiles of CO, H$_2$, CO$_2$, H$_2$O and N$_2$ in the large gas bubbles are plotted in Figure 7.2.

Figure 7.3 shows the corresponding productivity of each individual paraffin and olefin, both in the gas and liquid phase. The model predicts the FT product distribution between the vapor and liquid phases. The lighter products with a high olefin yield are in the gas phase, and the heavier products, mainly paraffins, leave the reactor in the liquid or wax phase. Our model predicts the effect of the process conditions on the selectivity and composition of the individual phases.

The major results of our simulations on the reactor performance are shown in Figure 7.4a-b for a range of catalyst concentrations $\varepsilon_P$ between 0.2 and 0.35, feed ratios of H$_2$ to CO ($F$) in the synthesis gas between 0.67 and 2, with a constant mole fraction of CO$_2$ and N$_2$ in the feed of 0.05 and superficial inlet gas velocity $U_{in}^G$ from 0.15 to 0.4 m s$^{-1}$ (see Table 7.4). Increase of the inlet gas velocity causes a decrease of the synthesis gas conversion, as expected. At low gas velocities, $U_{in}^G < 0.15$ m s$^{-1}$,
Figure 7.2  Axial concentration profiles for CO, H₂, CO₂, H₂O and N₂. Operating conditions: \( F=1, U_G^{in} = 0.20 \text{ m s}^{-1}, \epsilon_p=0.25, D=8 \text{ m}, H=24 \text{ m}, T=523 \text{ K}. \) See also Table 7.5.

Figure 7.3  Paraffin (\( P_n \)) and olefin (\( O_n \)) production rates in the gas and liquid outlet streams \( (p=12.6, t_O=4.6, k_R=0.27) \). Operating conditions: \( F=1, U_G^{in} = 0.20 \text{ m s}^{-1}, \epsilon_p=0.25, D=8 \text{ m}, H=24 \text{ m}, T=523 \text{ K}. \)
the synthesis gas conversion reaches a constant level of about 80% as a consequence of the kinetic expressions with product (CO₂) inhibition. Higher conversions can be obtained when the operating conditions (P, T) or catalyst are changed or when the dispersion height is increased to, for example, H= 30 m. The reactor productivity, expressed as total hydrocarbon production in kg h⁻¹ m⁻³, shows an increase with increasing gas velocity. The effect of catalyst concentration on the reactor performance at F=1 is shown in Figure 7.4a. Increasing the catalyst concentration (ε_P) shows an

Figure 7.4  a. Effect of catalyst concentration and gas velocity on the synthesis gas conversion and productivity (F=1, T= 523 K). b. Effect of the H₂/CO feed ratio F and gas velocity on the same (ε_P=0.25, T= 523 K).
increase of the conversion and productivity. The catalyst concentration influences the concentration levels as well as $e_{DF}$ according to eq 7.11. The highest productivity is obtained at high catalyst concentrations ($e_p=0.35$) and gas velocities up to 0.4 m s$^{-1}$. The effect of the feed ratio $F$ at a constant catalyst concentration of $e_p=0.25$ is given in Figure 7.4b. The decrease of the synthesis gas conversion with increasing $F$ is mainly caused by the kinetics. At low feed ratios, conversions of CO are large due to the high water gas shift reaction rate. The optimal productivity is obtained at a feed ratio of $F=1.5$. The feed ratio influences the gas holdup due to changing gas density. Significantly lower gas holdup values were observed with increasing $F$. The number of cooling tubes required strongly depends on the productivity and varies between 600 and 1700 cooling tubes. The corresponding pitch distance varies from 0.33 to 0.20 m, which is large enough not to influence the hydrodynamics of the SBCR [16].

The effect of the feed ratio on the selectivity to several product classes is shown in Table 7.6. The total hydrocarbon (paraffin and olefin) selectivities in mass percentages were lumped in four groups: methane ($w_1$), light gases C$_{2-4}$ ($w_{2-4}$), gasoline C$_{5-10}$ ($w_{5-10}$), and a diesel/wax fraction C$_{10-100}$ ($w_{10+}$). The olefin content is shown for the C$_2$ products ($w_{O,2}$), C$_{3-4}$ products ($w_{O,3-4}$) and the total olefin yield of all products ($w_O$). The selectivities in Table 7.6 were calculated with the model parameters in Table 7.3. Increasing $F$ has a pronounced effect on the increasing selectivity to methane and a decreasing olefin content of the product spectrum. The hydrogen concentration in the liquid bulk increases, which causes an increase of the termination to paraffins relative to olefins and a decrease of the chain growth parameter.

<table>
<thead>
<tr>
<th>$F$</th>
<th>$p$</th>
<th>$t_0$</th>
<th>$k_R$</th>
<th>$w_1$</th>
<th>$w_{2-4}$</th>
<th>$w_{5-10}$</th>
<th>$w_{10+}$</th>
<th>$w_{O,2}$</th>
<th>$w_{O,3-4}$</th>
<th>$w_O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.67</td>
<td>17.4</td>
<td>5.6</td>
<td>0.17</td>
<td>3.7</td>
<td>17.5</td>
<td>26.5</td>
<td>52.3</td>
<td>43.0</td>
<td>85.3</td>
<td>37.7</td>
</tr>
<tr>
<td>1.0</td>
<td>12.6</td>
<td>4.6</td>
<td>0.27</td>
<td>5.7</td>
<td>18.9</td>
<td>27.2</td>
<td>48.2</td>
<td>28.5</td>
<td>79.3</td>
<td>33.5</td>
</tr>
<tr>
<td>1.5</td>
<td>9.6</td>
<td>3.9</td>
<td>0.41</td>
<td>8.2</td>
<td>20.5</td>
<td>28.4</td>
<td>43.0</td>
<td>19.0</td>
<td>72.7</td>
<td>29.6</td>
</tr>
<tr>
<td>2.0</td>
<td>7.9</td>
<td>3.6</td>
<td>0.56</td>
<td>10.6</td>
<td>21.8</td>
<td>29.3</td>
<td>38.3</td>
<td>13.9</td>
<td>66.8</td>
<td>26.5</td>
</tr>
</tbody>
</table>
7.7 Conclusions

A mathematical design model for a large scale Fischer-Tropsch SBCR is developed. The model takes into account the water gas shift and Fischer-Tropsch reactions as well as individual hydrocarbon product formation rates. Under the operating conditions investigated the FT SBCR is mainly reaction controlled. This is caused by the limited activity of Fe catalysts on the one hand and the large value of the volumetric mass transfer coefficient of the large bubbles due to frequent bubble coalescence and breakup on the other hand. The model predicts the composition of the gaseous and liquid streams of a large scale bubble column operating in the churn-turbulent regime as a function of the operating parameters. It provides all the data necessary for reliable scale up, process optimization and prediction of the performance of industrial scale FT bubble column reactors.

List of Symbols

\[
\begin{align*}
A & \quad \text{reactor area, m}^2 \\
ac & \quad \text{specific cooling area, m}^{-1} \\
C & \quad \text{concentration, mol m}^{-3} \\
CP & \quad \text{heat capacity, J kg}^{-1} \text{K}^{-1} \\
D & \quad \text{reactor diameter, m} \\
D & \quad \text{diffusion coefficient, m}^2 \text{s}^{-1} \\
F & \quad \text{H}_2/\text{CO feed ratio} \\
g & \quad \text{gravity acceleration factor, 9.81 m s}^{-2} \\
h & \quad \text{axial position, m} \\
H & \quad \text{dispersion height, m} \\
HI^{\infty} & \quad \text{Henry constant, Pa} \\
Ki & \quad \text{equilibrium constant (y}_i/x_i) \\
kLa & \quad \text{volumetric mass transfer coefficient, s}^{-1} \\
m_{GL}^i & \quad \text{solubility coefficient C}_G/C_L \\
m_i & \quad \text{molar selectivity} \\
n & \quad \text{carbon number} \\
P & \quad \text{pressure, Pa} \\
P_{i}^{\text{sat}} & \quad \text{vapor pressure, Pa} \\
R & \quad \text{gas constant, 8.314 J mol}^{-1} \text{K}^{-1} \\
Rj & \quad \text{reaction rate, mol kg}_{\text{cat}}^{-1} \text{s}^{-1}
\end{align*}
\]
temperature, K
H$_2$/CO consumption ratio ($-R_{H_2}/-R_{CO}$)
superficial velocity, m s$^{-1}$
reactor volume, m$^3$
rise velocity small bubbles, m s$^{-1}$
weight fraction of product $i$
synthesis gas conversion
hydrogen conversion
mole fraction in liquid phase
mole fraction in gas phase

Greek Letters
effective heat transfer coefficient, W m$^{-2}$ K$^{-1}$
contraction factor
liquid phase activity coefficient
reaction enthalpy, J mol$^{-1}$
holdup
liquid viscosity, Pa s
heat conductivity, W m$^{-1}$ K$^{-1}$
stoichiometric coefficient
density, kg m$^{-3}$
surface tension, N m$^{-1}$
Poynting factor
space velocity, Nm$^3$ kg$^{-1}$ s$^{-1}$

Sub- and Superscripts
large
out
ref
in
small
liquid phase
Kinetic and selectivity parameters (see List of Symbols for Chapters 2-6):
$a$, $b$, $k$, $K_P$, $k_{WGS}$, $K$, $t_p$, $t_p^1$, $t_p^2$, $p$, $t_O$, $k_R$, $c$, $\alpha_n$, $\theta_n$
References


[27] Marano, J.J.; Holder, G.D., General equation for correlating the thermophysical properties of n-paraffins, n-olefins, and other homologous series. 3. Asymptotic

