Comparison of Fischer-Tropsch Fixed and Monolith Bed Reactors Using Pseudo-homogeneous 2D Model

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Abstract

The purpose of this work is to study the performance of fixed and monolith bed reactors in Fischer-Tropsch (FT) synthesis by modeling these reactors. A pseudo-homogeneous 2D model was proposed for FT fixed and monolith bed reactors. The model results show good agreement with experimental data reported in the literature. The performance of the FT reactors was investigated in industrial scale under low temperature FT conditions (pressure = 2 MPa and temperature = 230 °C). The modeling results were organized in three sections, (1) effect of operating condition parameters, which have similar effects on both reactors, (2) effect of structure parameters, which have different effects such as pellet diameter on FT fixed bed reactors, and thermal support property, the number of channels per cross section area (CPSI) and wash coated catalyst thickness on FT monolith bed reactors, and (3) comparison of FT fixed and monolith bed reactors.

Keywords

Fischer-Tropsch, Modeling, Fixed bed reactor, Monolith bed reactor, Hot spot

1. Introduction

Fischer-Tropsch (FT) synthesis is a catalytic process, which converts CO and H₂ obtained from coal (CTL process), natural gas (GTL process) or biomass (BTL process) into a mixture of linear gaseous, liquid and solid hydrocarbons 1). Fischer-Tropsch process has received considerable attention by both the industrial and the academic worlds in the last decade due to some of its advantages such as (1) an easy way of exploiting coal, biomasses or the huge and cheap natural gas reservoirs located in remote areas and (2) producing high-grade synthetic lubricating oils, and high added value 2)–4).

In FT synthesis, the reaction of H₂ and CO can be regarded as a surface polymerization reaction on the surface of the catalyst in-situ. The steps in this reaction are respectively, first, monomer units are formed from the reagents. Then, a wide product spectrum of HCs (mainly paraffins) is formed by the successive addition of C1 units to the growing chains on the catalyst surface 5).

For high exothermic FT synthesis, the exothermicity and the moderate range of catalytic activity are important parameters dictating the choice of the reactor. Nowadays, two types of reactors, namely fixed bed reactor (FBR) and slurry bubble column reactor (SBCR), are used in industrial scale 6)–7). Fine catalyst particles are suspended in liquid FT products in slurry reactors and the synthesis gas enters from bottom of the reactor. In these reactors, temperature control is easy. However, separation of catalysts from the product, back mixing phenomenon and scale up of the reactor are disadvantages 7)–9). The other type of FT reactors, multitubular fixed bed reactors consist of tubes, which are loaded fixedly by catalysts in the form of spherical pellets with diameters of a few millimeters or less. The tubes also transfer heat to the cool fluid surrounding them (similar to shell and tube heat exchangers). Fixed bed reactors can be easily scaled up to industrial size. However, separation of products from catalyst is not necessary. Mass and heat limitations, hot spots and high pressure drop are disadvantages of these reactors 9)–10). Some limitations of FT fixed bed reactors like high pressure drop and low mass and heat transfer in pellets may be overcome by the application of reactors with microstructures. The structures used mostly in microstructure reactors are honeycomb monoliths 11)–12), foams 13), knitted wires 14) and micro-channel reactors 15)–16). The catalyst in microstructure reactors is usually either deposited as a thin layer over a structured support or is used itself as the support. Some advantages of structure supports such as high void fraction and high geometric surface area result in less pressure drops and intra porous mass transfer resistances.
Microstructures allow more heat transfer between catalyst and reaction component. Another important advantage of these reactors is that they do not have products/catalyst separators. The structures used mostly for FT synthesis are usually honeycomb microchannels\(^{(16)–(18)}\), monoliths\(^{(12,19)–(21)}\) and foams\(^{(13)}\). Microstructure reactors have received scarce attention by the industrial world due to capital and operating costs, but they have been successfully used in experimental studies in lab scale in FT synthesis\(^{(12,19)–(23)}\). Many studies were done on mesoporous ceramic honeycomb monoliths, whose channels are coated with layers of a microporous ceramic membrane and a FT synthesis catalyst\(^{(12,13)}\). These structures enable high pressure gas synthesis to permeate throughout the monolith and react with FT catalyst.

However, most of available researches on FT fixed and monolith bed reactors are in lab scale, and industrial scale studies on these reactors are limited. Moreover, modeling is necessary for selecting the type of FT reactors, design, cost optimization and industrial scale up. Limited numbers of literature reports, which have modeled FT fixed and monolith bed reactors, are available. A heterogeneous 1D plug flow model was proposed by Atwood and Bennett\(^{(25)}\) in order to investigate parameter effects on commercial reactors. Bub and Baerns\(^{(26)}\) developed a pseudo-homogeneous 2D plug flow model, but they neglected intra-particle diffusion limitations. Marvast et al.\(^{(27)}\) studied the performance of FT reactors using a bifunctional Fe-based catalyst. They considered both 1D and 2D, pseudo-homogeneous models to study the performance of these reactors. Guttel and Turek\(^{(28)}\) compared different reactor types including fixed bed, slurry, monolithic, and microreactors. They proposed a 1D approach, including all mass transfer resistances for cobalt catalyst, and discussed that new material properties applied in monolith reactors on heat transfer.

Considering above reports, it can be concluded that limited data exist, which compare the performances of both fixed and monolith bed reactors in FT synthesis. In this article, a homogeneous 2D model was developed for both FT fixed and FT monolith bed reactors in the industrial scale was developed and evaluated using experimental data reported in the literature by Rafiq et al.\(^{(30)}\) and Kapteijn et al.\(^{(31)}\) for FT fixed and FT monolith bed reactors, respectively. Also the effects of several parameters such as operating parameters, reactor structure and their thermal properties on the performance of the reactors were investigated.

### 2. Reactor Model

As mentioned above, a homogeneous 2D model is proposed for modeling both FT fixed and FT monolith bed reactors in the industrial scale. As shown in Fig. 1, reactor structure is similar to shell and tube heat exchanger, in which each tube is filled by a pellet catalyst in the fixed bed reactor or wash coated monolith in the monolith bed reactor. Before modeling the reactors, the existence of thermal gradient in the radial direction of FT fixed and monolith bed reactors should be checked. Mears criteria\(^{(31)}\) in Eq. (1) are used for this purpose. The Mears criterion shows that radial thermal gradient exists.

\[
(1 - e_{\text{cat}}) R_{\text{FT}} \Delta H \left( \frac{T_c - D_{\text{in}}}{4 \lambda_{\text{c}} T_{\text{w}}} \left( 1 + \frac{8 \lambda_{\text{c}}}{U D_{\text{v}}} \right) < 0.4 \right.
\]

Where, \( T \) (°C), \( \lambda_{\text{c}} \) (W m\(^{-1}\) K\(^{-1}\)), \( R \) (kmol kg\(-1\) cat\(^{-1}\)), \( U \) (W m\(^{-2}\) K\(^{-1}\)) and \( \Delta H \) (kJ/mol) are temperature, thermal conductivity, reaction rate of jth reaction, overall heat transfer coefficient and reaction heat, respectively.

The equations governing reaction inside tubes are determined with the following assumptions:
- Steady state, plug flow, ideal gas behavior.
- The size of pellet catalyst in FT fixed bed reactor or thickness wash coated catalyst on support in FT monolith bed reactor is small enough to ignore the mass transfer limitations in catalyst.

![Fig. 1 Structure of FT Fixed Bed and Monolith Bed Reactors](image_url)
• Due to thermodynamic conditions, low temperature FT conditions (2 MPa and 230°C), almost 99% of the reactants are in the gas phase, and thus the reaction medium is considered a gas-solid medium.

• Since FT reaction produces a wide range of hydrocarbon such as paraffins and olefins, paraffin is used for calculating the properties of hydrocarbons because the properties of paraffin and olein are very similar.

• For hydrocarbons with more than five carbons, C_s^+ is used as a pseudo-hydrocarbon.

• Effect of axial mass dispersion on both reactors is very low and negligible.

According to these assumptions, governing equations will be as follows:

2. 1. Mass Balance

\[ \rho_i \frac{\partial \hat{\rho}_i}{\partial z} = \rho_j D_{ij} \frac{\partial \hat{\rho}_j}{\partial r} \left( \frac{\partial Z_i}{\partial r} + \frac{\partial \hat{\rho}_j}{\partial r} \right) + M_{ij} \rho_e c_{eff} \frac{\partial \hat{\eta}_j}{\partial r} \]

Where, \( \rho_i \) (kg m\(^{-3}\)), \( \hat{\rho}_i \) (m\(^{-3}\) s\(^{-1}\)), \( u_i \), \( \hat{\rho}_j \) (m\(^{-3}\) s\(^{-1}\)), and \( c_{eff} \) are density of mixed gases, gas velocity in \( r \) direction, effective axial thermal conductivity, effective axial thermal conductivity, respectively.

2. 2. Energy Balance

\[ \rho_i u_i c_{py} \frac{\partial T_i}{\partial z} = \lambda_{eff} \frac{\partial^2 T_i}{\partial z^2} + \rho_i \frac{\partial}{\partial r} \left( \lambda_{eff} \frac{\partial T_i}{\partial r} \right) + \rho_i c_{eff} \sum_{j=1}^{n} \rho_j \left( \Delta H_f \right) \]

Where, \( T_i \) (°C), \( c_{py} \) (J kg\(^{-1}\) K\(^{-1}\)), \( \lambda_{eff} \) (W m\(^{-1}\) K\(^{-1}\)), \( \Delta H_f \) (kJ/mol) are density of mixed gases, effective axial thermal conductivity, effective axial thermal conductivity, respectively.

2. 3. Momentum Balance

\[ \frac{dP_j}{dz} = -f \rho_i u_i^2 \frac{\partial u_i}{\partial z} \]

In this equation, \( f \) is friction coefficient. This parameter is determined from Ergun and Moody friction factor equations for FT fixed and FT monolith bed reactors, respectively. In addition, \( u_i \) is characteristic length. This parameter is equivalent to diameter of pellet catalyst in FT fixed bed reactors and hydrodynamic diameter of a channel in FT monolith bed reactors.

2. 4. Continuity

\[ \frac{\partial \hat{\rho}_i}{\partial z} = - \hat{u}_i \frac{\partial \hat{\rho}_i}{\partial z} \]

Equation (5) shows the continuity of mixed gas. Ideal gas relation was applied to calculate gas density in fixed and monolith bed reactors. Thus, the term \( \frac{\partial \hat{\rho}_i}{\partial z} \) in Eq. (5) is converted to following form.

\[ \frac{\partial \hat{\rho}_i}{\partial z} = \frac{\hat{p}_i}{\hat{T}_i} \left( \sum_{j=1}^{n} \hat{w}_j \right) \frac{1}{\hat{M}_i} \frac{1}{\hat{M}_j} \frac{\partial \hat{T}_j}{\partial z} \]

2. 5. Boundary Conditions

\[ @z = 0; \frac{\partial \hat{w}_i}{\partial r} = 0 \]

\[ @z = L; \frac{\partial \hat{w}_i}{\partial z} = 0 \]

Where, \( U \) (W m\(^{-2}\) K\(^{-1}\)) is overall heat transfer coefficient between reactor and cooling fluid and \( T_c \) is defined as cooling fluid temperature. For convenient study, governing equations from Eqs. (2) to (10) have been dimensionless by using the following dimensionless parameters.

\[ \xi = \frac{z}{L}, \eta = \frac{r}{L}, \hat{u}_i = \frac{u_i}{\hat{u}_0}, \rho_i = \frac{\rho_i}{\rho_0}, \hat{T}_i = \frac{T_i}{\hat{T}_0}, \frac{\partial \hat{T}_i}{\partial z} = \frac{\hat{M}_i}{\hat{M}_0} \]

By replacing dimensionless parameters in Eqs. (2) to (10), the dimensionless equations and their boundary conditions will be as follows:

\[ \frac{\partial \hat{T}_i}{\partial z} = \frac{1}{\hat{\rho}_0 \hat{M}_0} \left( \hat{\beta}_0 \hat{\rho}_0 \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( \hat{\rho}_0 \frac{\partial \hat{T}_i}{\partial \eta} \right) \right) + \hat{\beta}_M \hat{M}_0 \hat{n}_0 \]

\[ \frac{\partial \hat{T}_i}{\partial \eta} = \frac{1}{\hat{\rho}_0 \hat{M}_0 \hat{C}_r} \left( \hat{\beta}_0 \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( \hat{\rho}_0 \frac{\partial \hat{T}_i}{\partial \eta} \right) \right) + \hat{\beta}_H \frac{\partial^2 \hat{T}_i}{\partial \eta^2} + \hat{\beta}_H \sum_{j=1}^{n} \hat{f}_{ij} (-\Delta \hat{H}_{ij}) \]

\[ \frac{d \hat{P}_j}{\partial \zeta} = -\hat{f} \hat{P}_j \hat{u}_j^2 \frac{\partial \hat{u}_j}{\partial \zeta} \]

\[ \frac{d \hat{M}_j}{\partial \zeta} = -\hat{f} \hat{P}_j \hat{u}_j^2 \frac{\partial \hat{M}_j}{\partial \zeta} \]

\[ \frac{d \hat{P}_j}{\partial \zeta} = \frac{\hat{P}_j \hat{M}_j \left( \sum_{i=1}^{n} \hat{w}_i \right)^{\frac{1}{2}}}{\hat{T}_j} \frac{1}{\hat{M}_j} \frac{1}{\hat{M}_j} \frac{\partial \hat{T}_j}{\partial \zeta} + \left( \sum_{i=1}^{n} \hat{w}_i \right) \frac{1}{\hat{M}_j} \frac{\partial \hat{M}_j}{\partial \zeta} \]

\[ \frac{\partial \hat{w}_i}{\partial \eta} = \frac{\partial \hat{T}_i}{\partial \eta} = 0 \]
heat transfer, transfer through wall tubes, and reaction rate, (\(\beta_{\text{cat}}\)) is dimensionless parameter of the radial heat transfer, \(\beta_{\text{HRT}}\) is dimensionless parameter of the axial heat transfer, \(\beta_{\text{U}}\) is dimensionless parameter of heat transfer through wall tubes, and \(\beta_{\text{P}}\) is dimensionless parameter of pressure drop.

By considering Fig. 2, structure parameters of monolith such as open, catalyst, and support fractions are calculated by the following equations.

\[
e_{\text{open}} = \frac{(d_c - 2t_{\text{cat}} - t_{\text{sup}})^2}{d_c^2}
\]

\[
e_{\text{cat}} = \frac{(d_c - t_{\text{sup}})^2 - (d_c - 2t_{\text{cat}} - t_{\text{sup}})^2}{d_c^2}
\]

\[
e_{\text{sup}} = 1 - e_{\text{cat}} - e_{\text{open}}
\]

\[
d_c = \left(\text{CPSI} \times 39.72^2\right)^{0.5}
\]

Where, \(d_c\) (m) is the distance between two centers of adjacent channels, \(t_{\text{sup}}\) (m) is support thickness, \(t_{\text{cat}}\) (m) is wash coated catalyst thickness, and CPSI is the number of channels per cross section area (in\(^2\)).

In Table 1, ceramic monolith structure characteristics\(^{35}\) (wall thickness, catalyst fraction and support fraction) and the rest of the properties and correlations used in governing equations are shown.

### 2.6. Kinetic Model

The reaction mechanism of FT synthesis is complex and has been studied in many papers. The kinetic model used in this work is proposed by Philippe et al.\(^{36}\). The model proposes a simple semi-empirical kinetic model, which well predicts the trend of chemical reactions by concentration of reactant component and reaction temperature. The model was combined by two expressions of rate law to describe the CO conversion: the Yates and Satterfield\(^{40}\) expression used for FT synthesis and the Keyser et al.\(^{37}\) expression used for the water gas shift reaction (WGS). The model does not take into account olefins and oxygenates for simplicity. In addition, the model considers two specific law expressions for methane and ethane formation, whereas for high hydrocarbon products, the recursive ASF theory of Anderson et al.\(^{38}\) was applied. Chain growth probability (\(\alpha\)) is obtained from analyzing experimental data. In this model, ten kinetic parameters exist in the Arrhenius law terms, which are determined by fitting experimental data. The values of the parameters used in this work are presented in Philippe et al.\(^{1}\) and are presented in Table 2.

The kinetic model is presented as follows:

\[
n_{\text{FT}} = a \cdot \exp\left(\frac{-E_a}{RT_f}\right)\left(\frac{C_{\text{CO}}C_{\text{H}_2}}{1 + b \cdot \exp\left(\frac{-E_b}{RT_f}\right)C_{\text{CO}}^2}\right)
\]

\[
r_{\text{WGS}} = c \cdot \exp\left(\frac{-E_c}{RT_f}\right)\left(\frac{C_{\text{CO}} - C_{\text{CO}_2}C_{\text{H}_2}}{K_{\text{WGS}}C_{\text{H}_2}O}\right)
\]

\[
\ln(K_{\text{WGS}}) = \frac{2073}{T_f(K)} - 2.2029
\]

\[
r_{\text{CO}} = -n_{\text{FT}} - r_{\text{WGS}}
\]

\[
r_{\text{H}_2O} = n_{\text{FT}} - r_{\text{WGS}}
\]

\[
r_{\text{CO}_2} = r_{\text{WGS}}
\]

\[
r_{\text{H}_2} = -2n_{\text{FT}} + r_{\text{WGS}} - r_{\text{CH}_4} - \frac{n_{\text{CH}_4}}{1 - \alpha}
\]

\[
r_{\text{CH}_4} = d \cdot \exp\left(\frac{-E_d}{RT_f}\right)n_{\text{FT}}
\]

\[
r_{\text{C}_2H}_4 = e \cdot \exp\left(\frac{-E_e}{RT_f}\right)n_{\text{FT}}
\]

\[
r_{\text{C}_3H}_8 = \alpha n_{\text{C}_2H}_4
\]
Table 1  Ceramic Monolith Structure Characteristics and Correlations of Physical Properties

| Ceramic monolith structure characteristics | 35) |
|--------------------------------------------|-----|
| Component heat capacity                    |     |
| $C_P = C_{i0} + C_{i1}T + C_{i2}T^2 + C_{i3}T^3$ | (39) |
| Mixture heat capacity                      |     |
| $C_n = \sum_{i=1}^{n} x_i C_i$            |     |
| Component conductivity                     |     |
| $\lambda_i = C_{i0} + C_{i1}T + C_{i2}T^2 + C_{i3}T^3$ | (39) |
| Mixture gas conductivity                   |     |
| $\lambda_m = \sum_{i=1}^{n} x_i \lambda_i$ |     |
| Component viscosity                        |     |
| $\mu_i = \frac{C_{i0}T^{1.5}}{T_i + C_{i3}}$ | (40) |
| Mixture viscosity                          |     |
| $\mu_m = \sum_{i=1}^{n} x_i \mu_i$        |     |

Correlations of physical properties

| (Parameters) | (Equation) | (Reference) |
|--------------|-----------|-------------|
| Overall heat coefficient (fixed bed) | $1 - \frac{1}{\alpha_w} + \frac{D_r}{2\lambda_w} | D_r, D_w$ | (41a) |
| $\alpha_w = \alpha_W^0 + 0.444 Re \cdot Pr \cdot \frac{\lambda_w}{D_w}$ | $\alpha_W^0 = 8.694 \frac{D_w}{\rho_w \mu_w} \lambda_w^0$ | $(41b, 42)$ |
| $\lambda^0 = \lambda_{es} \left[ 1 + \beta(1 - \epsilon_{es}) \right] + \frac{\beta(1 - \epsilon_{es})}{1 + \beta(1 - \epsilon_{es}) \lambda_{es}}$ | $(41a)$ |
| $\alpha_n = \frac{0.227 \times 10^{-3}}{1 + \epsilon_{es} P_T^2} \left( \frac{T}{100} \right)^3$ | $\alpha_n = 0.227 \times 10^{-3} \frac{P_T}{P_T^2 - 2} \left( \frac{T}{100} \right)^3$ |
| $\gamma = \frac{2}{3}, \beta = 0.85; \phi = 0.3$ | $\gamma = 0.3, \beta = 0.85; \phi = 0.3$ |

Radial diffusivity (fixed bed) | $D_{er} = \frac{1}{1.1Pr} \left[ \frac{1}{\mu_d d_p} - \frac{\rho_l \left( 1 - \sqrt{1 - \epsilon_{es}} \right)}{Re \mu_s} \right]$ | (43) |
| $Pe_r = 8 \left[ 2 - \frac{1}{2} \left( \frac{D_{er}}{D_p} \right)^2 \right]$ | $Re = \frac{\rho_d \mu_d d_p}{\mu_s}$ |

Effective radial conductivity (fixed bed) | $\lambda_{er} = \lambda_{es}^0 + 0.144 \lambda_{es} Re Pr$ | (41b) |
| $Pr = \frac{C_{es} \mu_{es} d_p}{\lambda_{es}}$ | $\lambda_{es} = \lambda_{er}$ | (41b) |

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3. Numerical Method and Validation

The governing equations of this research are formed as a set of partial differential equations coupled with the non-linear algebraic equations of kinetic model. The numerical method used for solving the equations is the Method of Line. By this method, the radial direction terms in partial equations were discretized and the set of PDEs converted to the set of ODEs in axial direction. Then, the set of ODEs was solved by fourth-order Runge-Kutta method. Radial direction terms were discretized by orthogonal collocation technique based on symmetric Legendre polynomials. The feasibility of this kind of model is verified using the experimental data obtained by the works of Rafiq et al.30 and Kapteijn et al.33 on FT fixed bed and wash coated monolith bed reactors at low temperatures, respectively. As shown in Fig. 3, the model results well predict experimental data. Relative error is 10.3 % for FT fixed bed reactors and 15.6 % for FT monolith bed reactors.

4. Base Point Study

When there are too many parameters to study, base point study is necessary for conveniently investigating the effect of each parameter on the performance of the FT fixed and monolith bed reactors. Indeed, by varying a parameter and fixing other parameters in base point study, we can investigate the effect of the parameter on performance of reactors.

In this research, the parameter values of base point study were chosen around the values of industrial FT reactors at low temperature condition. Material properties assumed for the structure of the reactors are presented in Table 3, and the values of base point study and their range of parameters are presented in Table 4. The parameters in Table 4 are divided into two groups, operating and structure parameters. Operating parameters include parameters, which have similar effects on performances of FT fixed and monolith bed reactors. Structure parameters include bed structure parameters such as pellet diameter for FT fixed bed reactors, and CPSI, wash coated catalyst thickness, and thermal properties of support for FT monolith bed reactors.

All parameters in Table 4 are scaled between zero to one and the obtained figures are shown by using the scaled values. The relation between scale value and actual value of each parameter is linear, as follows:

Continued from previous page
\[ P_{\text{actual}} = (P_{\text{max}} - P_{\text{min}})P_{\text{scaled}} + P_{\text{min}} \]  

(39)

Where, \( P_{\text{min}} \) and \( P_{\text{max}} \) are minimum and maximum values of a parameter, respectively, and \( P_{\text{actual}} \) and \( P_{\text{scaled}} \) are actual value in Table 4 and scaled value of a parameter, respectively.

5. **Results and Discussion**

The trends of pressure, temperature, density, and mass fraction of component profiles with reactor length for FT fixed bed are similar to those for FT monolith bed reactors. Therefore, for investigating the perfor-
formance of both reactors, the trends of pressure, temperature, density, and component mass fractions profiles are first investigated on one of the reactors in base point study, followed by the investigation of the effect of each parameter in Table 4 on the performance of the reactors.

Temperature, pressure, mass fraction, density, and velocity profiles are presented in Fig. 4. More of the reactants (H₂ and CO) are converted to water and hydrocarbon products in the FT reactions by increasing length of reactor. Therefore, in Fig. 4-a, mass fractions of H₂ and CO components decrease versus reactor length, while hydrocarbon and water mass fractions increase with reactor length.

Dimensionless velocity, density, and pressure profiles are shown in Fig. 4-b. The trend of density profile is opposite that of velocity profile. Therefore, when light reactants are converted to heavy hydrocarbons by FT reactions, density of mixed gas increases, and hence velocity of gas decreases.

Pressure drop exists in both FT monolith and fixed beds because of friction force. Friction force or pressure drop in FT monolith bed is generally smaller than that in FT fixed bed with random channels because of higher void fraction in FT monolith bed.

Figures 4-c and 4-d show temperature profiles versus length and reactor radius in FT monolith and fixed bed reactors, respectively. By considering these figures, temperature increases at around entrance of the reactors due to heat released by FT reactions, although temperature decreases with length of tubes; especially at around reactor outlet due to heat transfer from tube inside to surrounding cool fluid.

The performance of FT reactors depends highly on operating conditions and reactor structure parameters. Therefore, for convenient study: (1) the operating condition parameters, which have similar effects on the performance of the reactors have been separately investigated on one of the reactors in section 5.1. (2) The effect of other parameters including structure parameters of monolith bed and fixed bed are discussed separately on FT monolith and FT fixed bed reactors in section 5.2., (3) and finally, the differences between two reactors are discussed in section 5.3.

5.1 Effect of Operating Condition Parameters

Figures 5 and 6 present the effect of operating conditions on outlet reactant conversions, hot spot and its position, and average dimensionless heat transfer
parameters ($\beta_U$, $\beta_{\lambda\text{er}}$) in FT monolith bed reactors. By considering these figures, the effect of each parameter on FT monolith bed reactors is investigated as follows:

5.1.1 Effect of Feed Pressure

The rates of FT synthesis are high at higher concentration of reactants. When feed pressure increases, concentration of components increases in gas feed, and rate of FT synthesis, conversion of reactants (H$_2$ and CO), and heat generation by FT reactions increase. As shown in Figs. 5 and 6, if feed pressure changes from

![Figure 5: Reactant Conversions in FT Monolith Bed Reactor vs. Scaled Parameters Defined in Eq. (37) and Table 4](image1)

![Figure 6: Hot Spot (a) and Its Position (b), Dimensionless Heat Transfer Parameter through Wall Tube (c) and Radial Direction (d) vs. Scaled Operating Parameters Defined in Eq. (37) and Table 4](image2)
1.5 to 2.5 MPa, the conversion of CO and H\textsubscript{2} in outlet changes from 19 to 43 % and from 21.5 to 47.5 % in FT monolith bed, respectively. Moreover, effective radial conductivity and gas density increase under high pressure condition. Under this condition, dimensionless heat transfer parameters (β\textsubscript{U} and β\textsubscript{L}) decrease and the decreasing rate of β\textsubscript{U} is higher than that of β\textsubscript{L}. Consequently, the heat transfer from reactor wall to cooling fluid (β\textsubscript{U}) decreases highly, although heat transfer by conduction in radial direction (β\textsubscript{L}) decreases slightly. Therefore, temperature of hot spot and its lengths from inlet reactor increase because of more heat released from reactions. As shown in Figs. 6-a, b, when feed pressure increases from 1.5 to 2.5 MPa, dimensionless temperature of hot spot increases from 1 to 1.035 and its position is relocated from inlet of tubes to 38 % of tube length (4.56 m).

5.1.2 Effect of Feed Temperature

As shown in Fig. 5, conversion of reactants at high temperatures is greater than that at low temperatures. Moreover, position of hot spot moves to entrance tube with increasing temperature, and dimensionless hot spot temperature is initially decreased and then increased, as shown in Fig. 6. It should be noted that with increasing feed temperature, rate of reactions and the released heat increase. Therefore, although the heat transfer through wall tube is high at higher feed temperatures, dimensionless hot spot temperature increases due to higher released heat by FT reactions. As a result, when feed temperature is changed from 200 to 210 °C, conversion of CO changes from 27 to 33 %, hot spot temperature changes from 203 to 212.63 °C, and its distance from inlet of tubes changes from 3.9 to 0.3 m.

5.1.3 Effect of H\textsubscript{2}/CO Ratio in Feed

As shown in Fig. 5, when H\textsubscript{2}/CO ratio in feed of FT reactor increases from 1 to 3, conversion of CO component initially increases rapidly and then slowly from 22.5 to 30 %, although H\textsubscript{2} conversion decreases from 47.5 to 22 %. Indeed, when H\textsubscript{2} concentration in the feed is fixed at fixed CO concentration, the probability of reaction or collision of reactants (CO and H\textsubscript{2}) with each other and the catalyst is greater. Therefore, conversion of CO increases, but H\textsubscript{2} conversion decreases due to approximately fixed consumption of H\textsubscript{2} for fixed CO concentration. As shown in Fig. 6, with increasing H\textsubscript{2}/CO ratio in feed, the heat transfer from wall tube to cooling fluid (β\textsubscript{U}) increases, but the heat transfer in radial direction (β\textsubscript{L}) decreases. Therefore, heat transfer from reactor to cooling fluid overcomes heat generation by FT reactions in the reactor, and dimensionless temperature of hot spot and its position moves to entrance of tube.

5.1.4 Effect of GHSV

As shown in Figs. 5 and 6, with decreasing residence time or increasing GHSV, conversion of reactants (CO, H\textsubscript{2}) decreases, although dimensionless temperature of hot spot and its distance from entrance of tube increase. The reason is that heat transfers through wall (β\textsubscript{U}) and in radial direction (β\textsubscript{L}) decrease faster than heat generated by FT reactions. Consequently, these trends cause increased dimensionless temperature hot spot and its position in the reactor. As shown in Fig. 6, when GHSV changes from 600 to 1400 N mL kg-cat\textsuperscript{-1} h\textsuperscript{-1}, hot spot temperature changes from 205.5 to 207.6 °C. This occurs in 1.2 m and 3.9 m of reactor length, respectively.

5.1.5 Effect of Temperature of Cooling Fluid (T\textsubscript{c})

Effect of cooling fluid temperature on the performance of both FT fixed and monolith bed reactors can be explained by the last right hand term of Eq. (20). Heat transfer through wall is decreased by increasing T\textsubscript{c}, and FT synthesis is reacted in higher temperatures. Therefore, conversion of reactants increases at higher temperatures of surrounding cooling fluid, as shown in Fig. 5.

Rate of heat generation by FT reactions is higher than heat transfer through wall (β\textsubscript{U}) and conductive heat transfer in radial direction (β\textsubscript{L}). Therefore, dimensionless temperature hot spot and its length form inlet tube increase at high temperatures of surrounding cooling fluid. As shown in Fig. 6, hot spot temperature changes from 205.5 to 212.7 °C and its length form inlet tube is 0.24 m and 3.84 m, respectively, when T\textsubscript{c} changes from 185 to 205 °C.

5.1.6 Effect of Inert Component in Feed

Rate of FT reactions depends directly on concentration of reactants (H\textsubscript{2} and CO). Therefore, rate of FT reactions, conversion of reactants, and heat generation by reactions decrease with increasing concentration of the inert component in feed. Since the rate of heat production by FT reactions is lower than heat transfer by wall tube (β\textsubscript{U}) and heat transfer conduction in radial direction (β\textsubscript{L}), dimensionless temperature hot spot decreases, as shown in Fig. 6. For example, when mole fraction of inert component in feed changes from 0 to 0.5, hot spot temperature and its length change from 206.4 °C and 2.64 m to 205.2 °C and 0.24 m, respectively.

5.2 Effect of Reactor Structure Parameters

Structure of monolith bed reactors is more complex than that of fixed bed reactors. For monolith bed reactors, structure parameters include the number of channels per area (CPSI), thermal conductivity of support material (λ\textsubscript{sup}), and thickness of catalyst (t\textsubscript{cat}). For fixed bed reactors, structure parameters only include the diameter of pellet (d\textsubscript{p}). Range of structure parameters for both reactors is presented in Table 4 and effect of each parameter on the performance of the reactor is explained in the following sections.

5.2.1 Effect of Pellet Diameter on FT Fixed Bed Reactor

With decreasing pellet diameter and hence pressure,
low concentration of reactants is available for FT reactions and rate of FT reactions and conversion of reactants (CO and H₂) decrease, as shown in Fig. 7. As shown in Fig. 8-d, when pellet catalyst used in FT fixed bed resizes from 3 to 5 mm, hot spot temperature decreases from 207.2 to 206.4 °C. Indeed, when pellet diameter decreases, pressure drop increases due to more force fraction working opposite of flow direction, as illustrated by a decline in pressure with $\beta_P$ parameter in Fig. 8-c. In addition, conductive heat transfer in radial direction ($\beta_{\lambda_r}$) increases, and its influence causes temperature profile to be flat in radial direction, although released heat from FT reactions and heat transfer through wall tube ($\beta_U$) decrease. Thus, dimensionless temperature of hot spot decreases delicately with increasing pellet diameter.

5.2.2. Effect of CPSI on FT Monolith Bed Reactor

When the number of channels per area (CPSI) increases with constant thickness of wash coated catalyst, open fraction of monolith bed and hydrodynamic diameter of each channel decrease. Therefore, pressure drop increases as much as CPSI and conversion of reactants also decreases due to reduction of reactant concentration, as shown in Fig. 7.

The effect of increasing CPSI on heat transfer of FT monolith bed can be explained by considering Fig. 8. When CPSI increases from 200 to 1200 in⁻² (1 in² ≈ 6.4516 × 10⁻⁴ m²), heat transfer through wall tube ($\beta_U$) increases in FT monolith bed, but conductive heat transfer in radial direction ($\beta_{\lambda_r}$) and heat generation by FT reactions decrease. The result of these trends is that dimensionless temperature of hot spot increases slightly as shown in Fig. 8-d.

5.2.3. Effect of Thermal Conductivity of Support ($\lambda_{\text{sup}}$) on FT Monolith Bed

One of the flexibilities of monolith bed is the application of different materials as supports with special properties such as high thermal conductivity, permeability for special component, etc. In this work, effect of thermal conductivity of different supports on the performance of FT monolith bed is investigated.

As shown in Fig. 8, when a high thermal conductivity material is used as the support, only conductive heat transfer in radial direction ($\beta_{\lambda_r}$) increases, but heat transfer through wall tube ($\beta_U$) remains approximately constant. Therefore, when conductive heat transfer is the controlling parameter for heat transfer in monolith beds, temperature in reaction side decreases with using high thermal conductivity materials as supports. By decreasing temperature in reaction side, conversion of reactants and dimensionless temperature of hot spot decrease, as shown in Figs. 7 and 8. Indeed, when thermal conductivity of materials used as support in FT monolith bed changes from 1.4 to 400 W m⁻¹ K⁻¹, hot spot temperature changes from 205.6 to 205 °C.

5.2.4. Effect of Thickness of Coated Catalyst ($t_{\text{cat}}$) on FT Monolith Bed

As shown in Fig. 8, pressure drop ($\beta_P$) increases with enlarging thickness of wash coated catalyst because less open fraction is available. In addition, because of using more thickness of cobalt catalyst whose thermal conductivity is low and works like an insulating material ($\lambda_{\text{cat}}$ = 1.2 W m⁻¹ K⁻¹) in monolith, radial conductive heat transfer ($\beta_{\lambda_r}$) and heat transfer through wall ($\beta_U$) decrease. In this situation, temperature increases in FT monolith beds with using more thickness of catalyst, and hence conversion of reactants, shown in Fig. 7, and dimensionless temperature of hot...
spot, shown in Fig. 8, increase. As demonstrated in Fig. 8-d, when the thickness of catalyst enlarges from 20 to 80 μm, hot spot temperature increases from 205.2 to 207.6 °C, respectively.

5.3 Difference between FT Fixed and FT Monolith Bed Reactors

The difference between performance of FT fixed and monolith beds results from different structure of the reactors. The effect of each structure parameter on the reactor is investigated in section (5.2). Different structures of the reactors mainly affect on pressure drop and heat transfer of the reactors, the influences of which will be explained in following section.

5.3.1 Pressure Drop Factor

The amount of pressure drop for fluid flow depends on friction force working in the opposite direction of flow. Because fluid flow has erratic pattern through pellets in fixed bed rather than regular pattern in monolith bed, friction force for fixed bed is usually higher than that for monolith bed.

Pressure drop in fixed bed is reversely related to diameter pellet and void fraction, and in monolith bed, pressure drop is related to hydrodynamic diameter of channels. By considering Fig. 8-c, pressure drop in FT fixed bed is generally higher than in FT monolith bed; especially in low CPSI. However, for FT monolith bed with high CPSI, pressure drop in this reactor can be higher than FT fixed bed due to more decreased hydrodynamic diameter of channels of monolith bed.

5.3.2 Heat Transfer Factor

As shown in Fig. 8, with variations in pellet diameter, heat transfer resistances (β_U, β_L) do not change significantly. In monolith beds, these heat transfer resistances change more with variations in structure parameters (λ_sup, CPSI, t_cat). Therefore, FT monolith bed reactors have more flexibility than FT fixed bed reactors for heat transfer, and more options are available for designing FT monolith bed reactors.

Figure 9 shows temperature profiles for monolith beds in various thermal conductivity supports and CPSI, showing that FT monolith bed reactors have more flexibility for heat transfer. As shown in this figure, temperature profile is sharp and it can have hot spot in monolith beds, which have supports with low thermal conductivity and high CPSI. Moreover, temperature profile is flat and has no hot spot in monolith beds, whose supports have high thermal conductivity and low CPSI.
6. Conclusion

The performance of fixed and monolith beds in FT synthesis has been investigated by a modeling study. A pseudo-homogeneous 2D model was developed for both of these reactors in this study and this model was evaluated by experimental data reported in the literature by Rafiq et al.\textsuperscript{30} and Kapteijn et al.\textsuperscript{33} for FT fixed bed and monolith beds, respectively. Equation of model is solved by the method of line and orthogonal collocation technique. Accuracy of model is fair and results of proposed model are in good agreement with experimental data for FT fixed and monolith beds. Modeling results have been presented in three parts. First, the effect of operating condition parameters, which have the similar effects on both reactors, second, the effect of structure parameters, which are special for each reactor, and finally difference between FT fixed and FT monolith beds. The findings of this work can be summarized as follows:

- Conversion of reactants, H\textsubscript{2} and CO, are increased in both reactors at high feed temperatures and pressures, temperatures of cooling fluid, and low mass fractions of inert component and GHSV. Maximum temperature point in reactor (temperature of hot spot) and its distance from entrance reactor increase at high feed pressures, GHSV, and temperatures of cooling fluid. The maximum temperature and its distance decrease at low mass fractions of inert component and H\textsubscript{2}/CO ratio of feed.
- With increasing H\textsubscript{2} concentration in the feed, conversion of H\textsubscript{2} decreases, but CO conversion increases.
- Conversion of reactants (H\textsubscript{2} and CO), pressure drop and temperature of hot spot increase with decreasing pellet diameter in FT fixed bed reactors.
- In FT monolith bed reactors, using a support with high thermal conductivity causes radial heat transfer to increase, and hence reactant conversions and temperature hot spot decrease due to more removal of heat from the reactor. In FT monolith bed reactor, when monolith with high CPSI is used or thickness of wash coated catalyst is increased, pressure drop and temperature of hot spot will increase. Because monolith beds have more structure parameters such as thermal conductivity of support and CPSI than fixed bed, FT monolith bed reactors are flexible for design and control of temperature profile.
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