

A CFD Simulation Study of the Effect of Thermal Conductivity of the Catalyst Bed on Fischer-Tropsch Synthesis

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One of the most challenging technical barriers for fixed bed Fischer-Tropsch (FT) reactors is the formation of a hot spot in the catalyst bed because of the tremendous release of reaction heat. Increasing the thermal conductivity of the catalyst bed is a direct and efficient solution to solve this problem. In this work, Computational Fluid Dynamics (CFD) simulations were carried out to study the effect of the thermal conductivity of a catalyst bed on the Fischer-Tropsch synthesis (FTS) fixed bed reactor. A reasonable constraint was defined for the temperature rise in the catalyst bed, in order to ensure system safety and stability of the catalyst for long-term operation. The catalyst activity and space velocity (SV) were modified in each simulation experiment to ensure the maximum temperature in the catalyst bed did not exceed the temperature rise constraint. The potential maximum productivity of the specific catalyst bed was then predicted and the optimized catalyst activity and SV were obtained, which provided valuable guidance for practical FTS applications. The results showed that by applying a catalyst bed with higher thermal conductivity, better temperature control of the system was achieved, and a higher FTS reaction rate in the catalyst was ensured, which resulted in higher heavier hydrocarbon productivity.

1. Introduction

Fischer-Tropsch synthesis (FTS) is a chemical process whereby syngas is catalytically converted into a mixture of hydrocarbons, including ultra-clean fuel and bulk chemicals. The process allows for renewable and sustainable energy and provides an environmentally-friendly solution to solid waste treatment when using biomass and solid municipal waste to generate syngas by gasification. The FTS process is strongly exothermic and the theoretical adiabatic temperature rise may be as high as 1750 K. Many types of FTS reactors have been developed since the discovery of FTS in the 1920s, including tubular fixed bed reactor, circulating fluidized bed reactor, fixed fluidized bed reactor, slurry phase reactor and the microchannel reactor. However, each type of reactor suffers from certain drawbacks, thus there is no "optimal" FTS reactor; therefore, the type of reactor chosen depends on the application and the situation. Currently, the fixed bed reactor (FBR) is still a significant option for practical FTS applications. The FBR, which comprises a tube bundle in a cooling system, is widely considered to have the following advantages: 1) simple installation and robust operation; 2) high catalyst loading volume; 3) high potential productivity.

The major challenge when using the fixed bed FT reactor is that a hot spot can easily form on the catalyst bed. Enhancing the thermal conductivity of the catalyst bed is an efficient strategy to improve the heat removal capacity of the reactor. A number of studies have been done on this strategy. Zhu et al. (2014) tested three catalyst beds in FTS, which were formed by catalysts with different thermal conductivity support materials, namely SiO₂, TiO₂ and SiC. The effective thermal conductivity coefficients were calculated using a specially-designed experimental set-up. The researchers concluded that the effective thermal conductivity of the catalyst bed will increase with an increase in the thermal conductivity of the support material, but not linearly, as expected. In the Liu et al. (2014) study, high thermal conductivity material SiC was used as the promoter to improve the catalyst support thermal properties. The experimental results indicated that doping SiC had a positive effect on reducing the temperature gradient and enhancing selectivity for long-chain hydrocarbons (Liu et al., 2014). Another method to improve the overall catalyst bed thermal conductivity is to mix the metal wire or mesh with the catalyst particles.

The intensified heat removal capability of a catalyst bed can be transferred into economic advantage for the whole FTS applications. A catalyst bed with better temperature control allows a higher FTS reaction rate without concerns about system safety and catalyst stability for long-term operation, which ensures higher hydrocarbon productivity. The maximum temperature in the catalyst bed can be used to characterize the hot spot, and to prevent temperature runaway and catalyst deactivation. It has been reported that the performance of FTS catalysts measured in a laboratory is often much higher than what can be safely achieved in industrial reactors. Even in many laboratory experiments, the catalysts are diluted with inert materials, so that the hot spot that forms in the catalyst bed does not affect the catalyst bed negatively.

In this study, the effect of the thermal conductivity of a catalyst bed on the FTS process was investigated by varying the average thermal conductivity of the catalyst bed in a sufficiently-validated FBR model. Furthermore, an approach is proposed to increase the productivity of heavier hydrocarbons in a catalyst bed with improved thermal conductivity by optimizing the catalyst activity and space velocity (SV) by CFD simulation under a suggested temperature rise constraint.

2. Simulation

2.1 Modelling and validation

The 2D pseudo-homogeneous FBR model used in this study was based on a previous CFD simulation study done (Shen et al., 2021), which was developed against an actual bench-scale FBR. The FBR was 0.05 m in diameter and 1 m in length. The base case (E_{BC}) was operated with a syngas (the ratio of CO/H₂ was 1/2) at 458 K, 2 MPa and 300 h⁻¹. Two protective layers of ceramic balls were loaded at both ends of the catalyst bed, which included 300 ml Co-SiO₂ catalyst and ceramic balls for dilution. According to the modelling approach, the main assumptions were: the species in process were incompressible ideal gas; the catalyst bed was considered a porous region and the porosity was uniform; thermal equilibrium was achieved between the gaseous bulk and solid catalyst bed; the gaseous flow pattern was laminar. The average thermal conductivity was set as a constant 1.4 W/m/K.

In the low temperature FTS process, when using a cobalt catalyst, the predominant product is linear paraffins. To simplify the FTS reaction scheme, the FTS products were only paraffins, while olefin and oxygenated products were ignored. The water gas shift reaction was not taken into consideration, because of the weak activity on Co catalysts. The FTS reaction scheme was represented by following three reactions - see Table 1. A widely-accepted semi-empirical kinetic model was used to predict the FTS reaction results, including: FTS reaction rate (Eq(1)); CO consumption rate (Eq(2)); formation rate of the products C₁-C₃ (Eq(3) to Eq(5)). The hydrocarbon products with a carbon number 3 or higher were lumped together as C₃₊ products and represented by pentane.

$$r_{FTS} = k_1 \cdot \exp(-E_1/RT) \cdot C_{CO} \cdot C_{H_2} / (1 + k_2 \cdot \exp(-E_2/RT) \cdot C_{CO})^2 \quad (1)$$

$$r_{CO} = -r_{FTS} \quad (2)$$

$$r_{C_1} = k_3 \cdot \exp(-E_3/RT) \cdot r_{FTS} \quad (3)$$

$$r_{C_2} = k_4 \cdot \exp(-E_4/RT) \cdot r_{FTS} \quad (4)$$

$$r_{C_{3+}} = [1 - k_3 \cdot \exp(-E_3/RT) - 2 \times k_4 \cdot \exp(-E_4/RT)] \cdot r_{FTS} / 5 \quad (5)$$

Table 1: FTS reaction scheme

	Reaction
Reaction 1	CO + 3H ₂ ↔ CH ₄ + H ₂ O
Reaction 2	2CO + 5H ₂ ↔ C ₂ H ₆ + 2H ₂ O
Reaction 3	5CO + 11H ₂ ↔ C ₅ H ₁₂ + 5H ₂ O

The model was successfully validated by comparing both the predicted FTS reaction results (CO conversion, methane selectivity and S_{C₃₊} selectivity) and the predicted temperature distribution in the catalyst bed against the results obtained in experiments. In this study, the model geometry and the modelling approach were kept constant. Therefore, the simulation results (both the FTS reaction results and the temperature distributions) can be considered reliable and accurate enough for use in extrapolations and to draw conclusions in the current study.

2.2 Simulation strategy

It is clear that the higher average thermal conductivity of the catalyst bed contributes to the better heat removal capability of FBR. From the stand-point of practical FTS applications, a higher reaction rate is expected in order to obtain a higher productivity, under the condition that it can be operated in FBR safely and stably. In this study, a constraint was set for temperature rise in the catalyst bed (T_{max}), in order to ensure system safety and stability. The activity of the catalyst and the SV were adjusted so that the predicted maximum temperature would not exceed the set temperature rise constraint. This allowed the effect of average thermal conductivity of catalyst bed on potential maximum productivity to be studied.

Temperature rise constraint

It is believed that the formation of a hot spot in the catalyst bed significantly affects system safety and stable catalyst activity. However, studying a suitable temperature rise limit to guarantee system safety and stable long-term operation is insufficient. Thus, it is difficult to set a credible temperature rise constraint for catalyst bed.

According to the experiment using the reported bench-scale FBR for the low temperature FTS process, the critical temperature rise before temperature runaway is 14 K. However, this critical value for temperature rise may vary, depending on reactor specifications, catalyst used and operating conditions. Jess and Kern (2012) reported that the “safe temperature rise” for a 40 mm diameter reactor used in their study was 35 K. Mazidi et al. (2013) claimed that the reactor simulated in their study could be operated safely when the maximum temperature rise was below 50 K.

It is widely accepted that an excessively high temperature can result in sintering of cobalt crystallites and bulk carbide formation, which leads to a loss of catalyst activity. Bertole et al. (2002) reported that catalyst sintering at a temperature of 483 K may result in permanent deactivation of a cobalt catalyst. Steen et al. (2005) claimed that catalyst sintering happened even with cobalt crystallites with a diameter of less than 4.3 nm with an FTS condition of 523 K. It was also reported that carbide was detected on the catalyst at a temperature of 493 K (Tavasoli et al., 2008). FTS product distribution is sensitive to temperature, and higher temperatures favour the production of undesired methane. Therefore, the maximum temperature increase allowed in the catalyst bed in this study was set at 10 K, i.e. the temperature rise constraint in the catalyst bed was 468 K and the feed temperature 458 K.

Catalyst activity coefficient

Changing the average thermal conductivity of the catalyst bed can allow the reaction rate to be intensified, in order to maximize productivity, while the temperature peak does not exceed 468 K. To realize this, the catalyst was considered ideal and its activity was considered adjustable, but only the reaction rate was changed, while product selectivity was not influenced. A constant parameter (MA) that indicated the modified activity was defined for the proportion of FTS reaction rate in simulation case (r_{FTS}) to that in base case ($r_{FTS,0}$). The r_{FTS} was thus expressed as Eq(6).

$$r_{FTS} = MA \cdot r_{FTS,0} \quad (6)$$

Combining Eq(1) and Eq(6), the modified r_{FTS} described by Eq(7).

$$r_{FTS} = MA \cdot k_1 \cdot \exp(-E_1/RT) \cdot C_{CO} \cdot C_{H_2} / (1 + k_2 \cdot \exp(-E_2/RT) \cdot C_{CO})^2 \quad (7)$$

The CO consumption rate in the base case, when using the experimental data, was as low as 0.023 mmol/(g cat·min) (Shen et al., 2021). Compared to the reported CO consumption rates, there is a wide reachable space for the modified FTS reaction rate. For example, Atashi et al. (2010) reported that the CO consumption rate was as high as 1.419 mmol/(g cat·min), which means that the MA in Eq(7) can potentially be increased up to 6170%.

Simulation experiments

The simulation results for the base case (E_{BC}), cited from Shen et al. (2021), were obtained at at 458 K, 2 MPa and 300 h⁻¹. In this study, the effect of thermal conductivity on FTS was first studied by increasing the average thermal conductivity of the catalyst bed, while keeping the other parameters as constant. Secondly, the potential maximum productivity was predicted in different simulation experiments. The conditions used for these simulation experiments in this study are summarized in Table 2.

Table 2: Summary of conditions adopted for simulation experiments

	E _{BC}	E _{5TC}	E _{25TC}	E ₁	E ₂	E ₃	E ₄
SV/h ⁻¹	300	300	300	300	300	1000	1500
Average thermal conductivity/W/m/K	1.4	7 (5 times that in E _{BC})	35 (25 times that in E _{BC})	7 (5 times that in E _{BC})	35 (25 times that in E _{BC})	35 (25 times that in E _{BC})	35 (25 times that in E _{BC})
Modify catalyst activity	theNo	No	No	Yes	Yes	Yes	Yes

3. Results and discussion

3.1 Effect of thermal conductivity of catalyst bed

Based on the validated FBR model, simulations were performed by enhancing the average thermal conductivity of the catalyst bed to 5 times and 25 times that of the base case. The simulation results from E_{BC}, E_{5TC} and E_{25TC} were compared - see Table 3. Pro was defined as the productivity of heavier products and calculated by following Eq(8).

$$\text{Pro} = V_{bed} * SV * \frac{1}{3} * \frac{1}{22.4} * X_{CO}\% * S_{C3+}\% * \frac{1}{5} * M_{pentane} \quad (8)$$

Table 3: Simulation results for catalyst beds with different thermal conductivity

	E _{BC}	E _{5TC}	E _{25TC}
T _{MAX} /K	476.1	462.6	461.1
Δ T	18.1	4.6	3.1
T _{AVE} /K	463.6	460.3	459.7
X _{CO}	52.0	46.0	45.0
S _{C1}	7.1	5.6	5.4
S _{C3+}	93.6	93.8	94.2
Pro/(g/min)	0.1566	0.1390	0.1365

As shown in Table 3, both the T_{MAX} and T_{AVE} decreased when the average thermal conductivity of the catalyst bed (E_{BC} to E_{25TC}) was increased. Enhancing the thermal conductivity of the catalyst bed can significantly improve heat removal of FBR in the FTS process, which is consistent with the conclusions reported in the study done by Zhu et al. (2014). The temperature rise in the catalyst bed in the base case was 18.1 K, while in cases of E_{5TC} and E_{25TC} it was as low as 4.6 K and 3.1 K, respectively. It was also observed that, when increasing the average thermal conductivity of the catalyst bed, the CO conversion and methane selectivity showed a downward trend, while the selectivity for heavier products (C₃₊) showed an upward trend. These reaction results were considered to be closely affected by the actual temperature in the catalyst bed. As an overall consequence of X_{CO} and S_{C3+}, Pro decreased from the case of E_{BC} to the case of E_{25TC}.

3.2 Approach to intensify productivity

Since temperature control in the catalyst bed can be effectively improved by enhancing the average thermal conductivity of the catalyst bed, there is significant potential to boost productivity under the temperature rise constraint. The simulations (named E₁ and E₂) with enhanced average thermal conductivity of the catalyst bed were performed with modified catalyst activity, in order to maximize the productivity, while the temperature peak in the catalyst bed will reach but not exceed the temperature rise constraint. That is to say, under the system safety requirement for temperature rise, the potential maximum productivity in the catalyst beds with improved average thermal conductivity was predicted. The results are listed in Table 4 and compared with those from the base case.

Table 4 shows that the temperature peak was controlled to meet the safety restriction in the simulation cases of E₁ and E₂, while the required catalyst activity coefficients were 114.0% and 348.0% of that in base case, respectively. The actual local FTS reaction rate was influenced by both the catalyst activity coefficient and the concentration of syngas. The concentration of syngas decreased faster along the axial direction in the case of E₂ than in E₁, because of its higher catalyst activity coefficient. It can also be seen that X_{CO} increased from 52.0% in E_{BC} to 83.9% in E₂. Although the temperature peak was the same, the average temperature of the catalyst bed in E₂ was slightly lower than that in E₁, because of its steeper temperature distribution. This may

be due to the quick decrease in the FTS reaction rate in the axial direction of the catalyst bed and the higher thermal conductivity. Compared to E_{BC} , Pro increased significantly from 0.1566 g/min in E_{BC} to 0.2515 g/min in E_2 . Furthermore, the results from E_2 to E_4 show that when increasing the SV, the potential maximum productivity showed a parabolic trend: it first increased, then decreased. The optimization of Pro was 0.4185 g/min at SV condition of 1000 h^{-1} . X_{CO} declined from 83.9% to 29.4% with an increase in SV, which is considered inefficient.

Table 4: Simulation results for catalyst beds with different thermal conductivity and modified catalyst activity

	E_1	E_2	E_3	E_4
T_{MAX}/K	467.9	468.0	468.0	468.0
ΔT	9.9	10.0	10.0	10.0
T_{AVE}/K	461.0	460.1	463.3	463.8
MA/%	214.0	448.0	247.0	232.0
X_{CO}	71.5	83.9	42.0	29.4
S_{C_1}	6.2	6.4	6.6	6.7
$S_{C_{3+}}$	93.2	93.0	92.7	92.7
Pro/(g/min)	0.2146	0.2515	0.4185	0.2921

3.3 Feasibility

The average thermal conductivity studied is the superficial thermal conductivity of the catalyst bed. It has been reported that average thermal conductivity can be improved using various methods, including: using catalyst supports with high thermal conductivity; using a monolith catalyst bed; mixing the catalyst bed with the conductor. The catalyst bed used in the base case was a common random packed catalyst bed with SiO_2 as the support. Zhu et al. (2014) suggested using SiC as the catalyst support, which has thermal conductivity 75 times that of SiO_2 . Liu et al. (2014) claimed that the thermal conductivity was approximately 48 W/m/K, which is about 34 times that of SiO_2 . Thus, the studied range of average thermal conductivity for catalyst bed was achievable.

Table 4 shows that the modified catalyst activity varied from 214.0% to 448.0% that in E_{BC} . The CO consumption rate was 0.023 mmol/(g cat•min) in E_{BC} , thus, the expected CO consumption rate in this study was in the range of 0.049 to 0.103 mmol/(g cat•min). This catalyst activity is achievable according to current FTS catalyst research. For example, the CO consumption rate when using a Co/SiC catalyst reported by Liu et al. (2013) was 0.8333 mmol/(g cat•min), while the Co/N-CSs catalyst used by Xiong et al. (2010) reached 2.3333 mmol/(g cat•min).

4. Conclusion

The effect of average thermal conductivity of the catalyst bed on the FTS process was studied using simulations performed in a sufficiently-validated FBR model. When increasing the thermal conductivity and keeping the other conditions the same, unexpected temperature rise in catalyst bed was efficiently prohibited. The catalyst activity was then modified in order to boost the productivity potential. The simulation results showed that the potential maximum productivity under the temperature rise constraint increased with an increase in the average thermal conductivity of the catalyst bed. Furthermore, the potential maximum productivity showed an optimization value when increasing the SV, and the optimized maximum productivity was 0.4185 g/min at the SV condition of 1000 h^{-1} with the average thermal conductivity of 35 W/m/K. Both the recommended thermal conductivity of the catalyst bed and the modified catalyst activity were considered achievable.

Nomenclature

C - molar concentration, kmol/m³

E_i - activation energy, kJ/mol

k_i - pre-exponential factor

MA – modified catalyst activity coefficient

Pro - productivity of C_{3+} product

R - gas constant, 8.314 J/mol/K

r_{C_1} - C_1 product formation rate, kmol/m³/h

r_{C_2} - C_2 product formation rate, kmol/m³/h

$r_{C_{3+}}$ - C_{3+} product formation rate, kmol/m³/h

r_{CO} - CO consumption rate, kmol/m³/h

r_{FTS} - FTS reaction rate, kmol/m³/h

T - temperature, K

T_{AVE} - average temperature of catalyst bed, K

T_{MAX} - maximum temperature in catalyst bed, K

S_i - selectivity for component i, %

X_{CO} - CO conversion, %

V_{bed} - volume of catalyst bed, m³

$M_{pentane}$ - molecular weight of pentane, g/mol

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References

- Atashi, H., Siami, F., Mirzaei, A.A., Sarkari, M., 2010. Kinetic study of Fischer–Tropsch process on titania-supported cobalt-manganese catalyst. *J. Ind. Eng. Chem.* 16, 952–961.
- Bertole, C.J., Mims, C.A., Kiss, G., 2002. The effect of water on the cobalt-catalyzed Fischer-Tropsch synthesis. *J. Catal.* 96, 84–96.
- Jess, A., Kern, C., 2012. Influence of particle size and single-tube diameter on thermal behavior of Fischer-Tropsch reactors. *Chem. Eng. Technol* 35, 369–378.
- Liu, Y., Edouard, D., Nguyen, L.D., Begin, D., Nguyen, P., Pham, C., Pham-huu, C., 2013. High performance structured platelet milli-reactor filled with supported cobalt open cell SiC foam catalyst for the Fischer-Tropsch synthesis. *Chem. Eng. J.* 222, 265–273.
- Liu, Y., Ersen, O., Meny, C., Luck, F., Pham-Huu, C., 2014. Fischer-Tropsch reaction on a thermally conductive and reusable silicon carbide support. *ChemSusChem* 7, 1218–1239.
- Mazidi, S.K., Sadeghi, M.T., Marvast, M.A., 2013. Optimization of Fischer-Tropsch process in a fixed-bed reactor using non-uniform catalysts. *Chem. Eng. Technol* 36, 62–72.
- Shen, J., Li, Y.-C., Ho, W.H., Liu, X., Hildebrandt, D., 2021. Experimental and simulation study of the temperature distribution in a bench-scale fixed bed Fischer-Tropsch reactor. *AIChE J. Early View*.
- Steen, E., Claeys, M., Dry, M.E., Loosdrecht, J., Viljoen, E.L., Visagie, J.L., 2005. Stability of nanocrystals: Thermodynamic analysis of oxidation and re-reduction of cobalt in water/hydrogen mixtures. *J. Phys. Chem.* 109, 3575–3577.
- Tavasoli, A., Malek, R.M., Dalai, A.K., 2008. Deactivation behavior of ruthenium promoted Co/g-Al₂O₃ catalysts in Fischer–Tropsch synthesis. *Appl. Catal. A Gen.* 346, 58–64.
- Xiong, H., Moyo, M., Rayner, M.K., Jewell, L.L., Billing, D.G., 2010. Autoreduction and catalytic performance of a cobalt Fischer-Tropsch synthesis catalyst supported on nitrogen-doped carbon spheres. *ChemCatChem* 2, 514–518.
- Zhu, X., Lu, X., Liu, X., Hildebrandt, D., Glasser, D., 2014. Heat transfer study with and without Fischer-Tropsch reaction in a fixed bed reactor with TiO₂, SiO₂, and SiC supported cobalt catalysts. *Chem. Eng. J.* 247, 75–84.