Simulation of Commercial Plant Fischer-Tropsch Reactor in Gas to Liquid Process

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Introduction

Gas to liquid (GTL) technology can convert methane from natural gas to liquid fuel and other valuable hydrocarbons that can then be quickly and efficiently transported. The catalytic Fischer-Tropsch (FT) synthesis is the most critical step of the GTL process, as it is in this step that high-value products are produced. The syngas (H_2+CO) undergoes a polymerization reaction in the presence of a catalyst (Fe/Co/Ru-based) to produce a wide range of products, like paraffins, olefins and oxygenates, often known as Syncrude. The reaction conditions play a crucial role in defining the product distribution. It is desirable to have heavier hydrocarbons (C_{5+}) as a significant fraction in the products due to their commercial value. A low temperature (220-250 ℃), high pressure, and a low H_2/CO ratio are the process conditions favorable to heavy hydrocarbon production. Design and operation of FT pilot-scale is presented in a GTL plant [1,2].

COMSOL Multiphysics 5.3, which has built-in mass, energy, and momentum modules in the simulation package, was used for CFD modeling. The primary aims of this study are 1) increasing the efficiency of jet fuel and 2) defining the kinetic model most suitable to predict improved behavior of the FT reactor. The main challenge in designing the FT reactor is choosing the proper kinetic model with specific attention to the complexity of the reaction mechanism.

The FTS reactor is described by the following main reactions:

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \quad (1)$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

Where $-(CH_2)_n-$ is the methylene group polymerizing into a hydrocarbon chain [3]. Table 1 shows the lumped kinetic model over cobalt catalyst in the FT reactor [4].

Many studies have been done using a lumped kinetic model; however, there are some problems with this approach. One of these problems is that this type of kinetic model cannot estimate the exact amount of heat released by exothermic reactions through the FT reactor. It is well known that the heat released from producing one mole of decane is different from the heat released by producing ten moles of methane. 156 kJ and 206 kJ of heat are released per CO mole consumed in each case. As shown in Table 1, the consumption rate of syngas in the lumped kinetic model is not defined for each species of hydrocarbon fractions. This is why the complicated FT reactions (1) to (3) cannot be estimated by one single equation like the lumped kinetic model.

Table 1: Lumped kinetic rate equations [4]

No.	Kinetic Expression
a	$-r_{CO} = kP_{H_2}$
b	$-r_{CO} = kP_{H_2}^{a}P_{CO}^{b}$
c	$-r_{CO} = \frac{kP_{H_2}P_{CO}}{P_{CO} + 2P_{H_2O}}$
d	$-r_{CO} = \frac{kP_{H_2}^2P_{CO}}{P_{CO}P_{H_2} + aP_{H_2O}}$
e	$-r_{CO} = \frac{kP_{H_2}^2P_{CO}}{1 + aP_{CO}P_{H_2}^2}$

Pilot Plant Set-up

As shown in Figure 1, the FTR commercial plant consists of two stages of multi tubular reactors. In the first stage it is assumed to get the 50% conversion of syngas. In addition, in this stage, each tube has dimensions of 1 inch in diameter and 30 feet in length. The 20 wt% cobalt catalyst was loaded on the SiO_2 support filled in each tube.

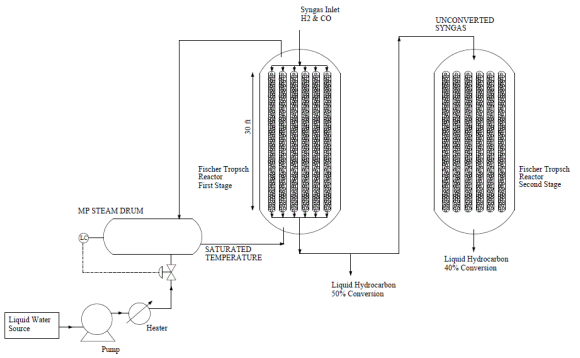

Figure 1. Schematic design of two-step FT reactors

The syngas molar ratio of H2/CO=2 was fed through the top of the first stage with a temperature of 235 ℃, was kept at the operating conditions of 300 psig, and was finally passed through the packed bed. The FT product from the first stage (unconverted syngas) was removed from the end of the reactor tube and fed to the top of the second stage of the reactor. The synthesis temperature was maintained by circulation of pressurized water in the shell. To control the inside temperature of the reactor according to the exothermic reactions therein, saturated water was used to adjust the profile temperature inside the reactor to prevent coking of the catalysts. Water was heated to create saturated liquid water and was then pumped into the reactor.

Numerical Model

A computational axisymmetric 2-D model coupled with mass and heat transport and hydrodynamic equations was used to predict the FT reaction performance. The hot-spot formation and the performance of the FT reactor were investigated in regard to parameters such as feed space velocity, feed temperature, and coolant temperature.

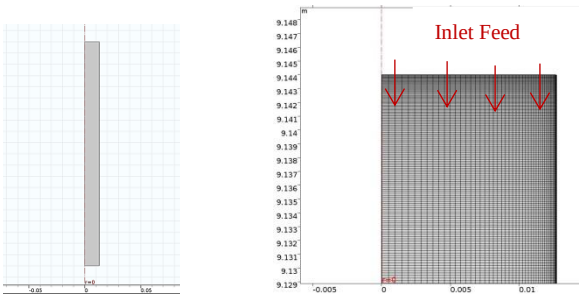

Figure 2. 2-D axisymetric and generated mesh used in this study

In this model, it was assumed that saturated liquid water keeps the multi tubular reactor under isothermal conditions. As shown in Figure 2, a symmetric tube was chosen for the simulation in this study. Also, 250,000 structured mesh was applied in this model. The assumptions were based on steady state conditions. Moreover, the detailed stationary equations examined in this study are described in Table 3, and the related boundary conditions are illustrated in Equations (4) through (11).

Kinetics of Fischer–Tropsch synthesis

The major challenge in designing the FT reactor is choosing proper kinetic modeling with special attention to the complexity of the reaction mechanism. Some models are based on CO and/or H_2 conversion and do not pay attention to the selectivity. Iron and cobalt on various oxide supports are used for FT synthesis. Cobalt catalysts are more expensive compared to iron ones, but cobalt catalysts have much higher resistance and also less sensitivity to water [4]. The catalyst properties, 20%Co/SiO_3, associated with the chosen kinetic model and used in this model, are illustrated in Table 2.

Table 2: Characteristics of the catalyst Co/SiO_2

ρ_{bulk}	510 [kg/m^3]
ε	0.5 [-]
d_p	3 [mm]
Cobalt content	20 [%wt]

Only paraffin production is considered in this study (reaction 1). For more simplicity, reaction (2) and (3) are neglected because of weak activity of the cobalt catalyst over water gas shift (WGS) reaction. Here, Arrhenius law is applied to the kinetic model, the parameters of which are described in Table 4. The monoxide carbon consumption rate and other species involved in the FT reactor are listed from Equations (12) through (19) [3, 5]:

Table 3: Detailed stationary equations for each module

Module Name	Balance Equation	Remarks
Transport of diluted species	$\nabla.(-D_i\nabla c_i) + u.\nabla c_i = r_i$ $N_i = -D_i\nabla c_i + uc_i$	Mass balance for the reactant flow
Porous media flow (Darcy's Law)	$\nabla.(\rho u) = Q_m$ $u = -\frac{K_{pr}}{\mu}\nabla \mathrm{P}$	Momentum balance for the reactant flow
Heat transfer in porous media	$\rho C_p \mathrm{u}.\nabla T = \nabla.(K_{eff}\nabla T) + Q$	Energy balance for the reactant and coolant flow

At $r = 0$

$$\vec{u}(r,0) = \overrightarrow{u_0} \quad (4)$$

$$T(r,0) = T_0 \quad (5)$$

$$C_i(r,0) = C_{i,0} \quad (6)$$

$$P(r,L) = P_{out} \quad (7)$$

$$\forall z, \quad r = 0: \frac{\partial C_i}{\partial r} = \frac{\partial T}{\partial r} = 0 \quad (8)$$

$$\forall z, \quad r = R: \vec{u}(R,z) = 0 \quad (9)$$

$$\frac{\partial C_i}{\partial r} = 0 \quad (10)$$

$$\forall z, r = R: K_{eff}\frac{\partial T}{\partial r} = h_c(T - T_c) \quad (11)$$

$$r_{CO} = -r_{FT} \quad (12)$$

With

$$r_{FT} = \frac{a.exp^{\left(\frac{-E_a}{RT}\right)}.c_{CO}c_{H_2}}{\left(1 + b.exp^{\left(\frac{-E_b}{RT}\right)}.c_{CO}\right)^2} \quad (13)$$

According to the stoichiometry of reaction (1), the water formation rate is calculated by:

$$r_{H_2O} = -r_{CO} = r_{FT} \quad (14)$$

The production rates of methane (rC_1) and ethane (rC_2) are listed by Arrhenius law:

$$r_{C_1} = d.exp^{\left(\frac{-E_d}{RT}\right)}.r_{FT} \quad (15)$$

$$r_{C_2} = e.exp^{\left(\frac{-E_e}{RT}\right)}.r_{FT} \quad (16)$$

For higher linear hydrocarbons (n>2), each hydrocarbon production rate is determined using a recursive kinetic model based on Anderson–Schultz–Flory theory. The constant chain growth probability (α) is assumed to be 0.9. Therefore, the rate of hydrocarbons production is given by:

$$r_{C_n} = \alpha.r_{C_{n-1}} \quad (17)$$

Also, according to Equation 1, the consumption rate of hydrogen is given by:

$$-r_{H_2} = \sum_i^N (2i+1).r_{C_i} \quad (18)$$

And

$$-r_{CO} = 1.r_{C_1} + 2.r_{C_2} + 3.r_{C_3} + \cdots + N.r_{C_n} = \sum_i^N i.r_{C_i} \quad (19)$$

For the first step, a simple model was made using chemical reaction rate equations, and a system of differential equations was developed. For each chemical reaction included in the system, the chemical equilibrium equation that incorporates reaction rate was defined. One goal of this study was to find the optimum values for the reaction rates in the developed model. For the simple model, strong agreement with the lab experiments was difficult to achieve. The solution of the system provided a concentration of all of the chemical species as a function of time. The final values of the concentrations were converted into the appropriate quantities that were measured in the experiment.

Next, an objective function on errors between measured and simulated values was defined. The Low objective function value close to zero indicated a good fit. An optimization problem with the defined objective function to find an optimum set of values for the uncertain reaction rates was set up. Two reaction rates for CH_4 and all of the other hydrocarbons were modified such that a new temperature dependency was created that could be manipulated. Specifically, two extreme experimental results in the lower and higher bounds of the temperature window where the simulation and experiment differed from the modified equations were chosen to compensate for the difference and fit the model to the data.

Table 4: List of kinetic models used in this model

Parameter	Value	Unit
a	31.79	$m^{6}\cdot kg_{cat}^{-1}\cdot mol^{-1}s^{-1}$
b	3.187	$m^{3}mol^{-1}$
d	2.0147×10^{8}	-
e	8004.9	-
E_a	100	$kJ.mol^{-1}$
E_b	20	$kJ.mol^{-1}$
E_d	81	$kJ.mol^{-1}$
E_e	49	$kJ.mol^{-1}$

Results and Discussion

The simulation of the FT reactor is presented in this study. The developed kinetic FT model was illustrated using a cobalt catalyst in the GTL process. Temperature and syngas conversion distributions along the packed bed is presented in Figures 3a and 3b under inlet temperature of 235 ℃.

Drastically increasing temperatures were experienced throughout the FT reactor because of the high exothermic reactions that took place at the entrance region of the reactors. As shown in Figure 3a, there is a hot spot in the inlet of the reactor that should be removed by coolant to keep the reactor under isothermal condition. As shown in Fig. 3b, the temperature of the catalytic bed increased at the inlet and was kept steady through the outlet of the bed. The increase in temperature was less than 1 ℃, which is near isothermal conditions.

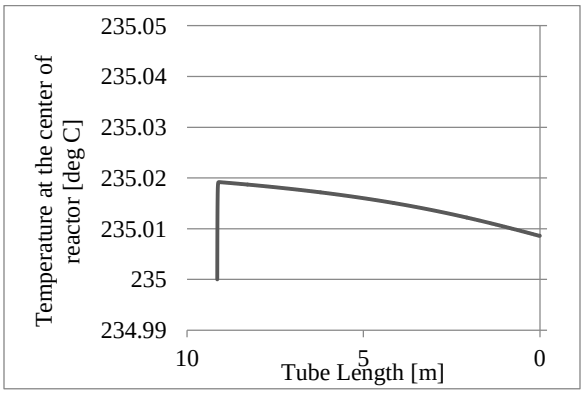

Figure 3a. Temperature profile, feed temperature: 235 °C

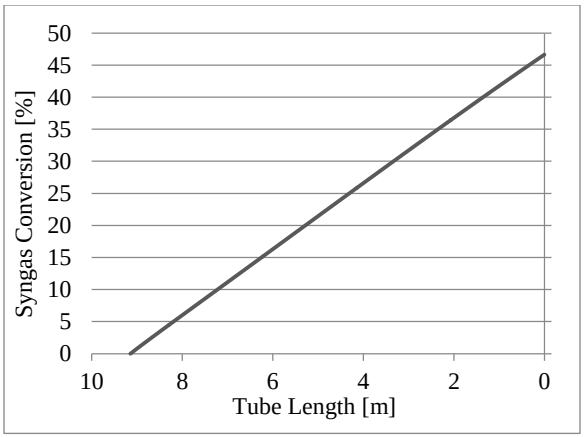

Figure 3b. Syngas conversion profile, Feed temperature:235 °C

Carbon monoxide concentration, hydrogen concentration, Syngas conversion, and bulk temperature in the first step of the FT reactor, under feed temperature of 235 ℃., are illustrated in Figures 4a through 4d.

In this study, required syngas space velocity and coolant temperature were investigated to get the 50% syngas conversion and higher productivity.

As shown in Figures 5a and 5b, increases in feed temperature caused improved syngas conversion. Also, the effect of syngas space velocity was investigated. Higher space velocity leads to lower syngas conversion.

As shown in Figures 5c and 5d, as the coolant temperature increased, slight increases and decreases were observed in syngas conversion and oil selectivity, respectively.

At the different inlet temperature (220-240 $°C$), as the inlet temperature changes in the constant space velocity, increases in conversion can be seen because of sufficient reaction time for the syngas and catalyst bed. When comparing Figure 5a and 5b, it can be observed that increases in space velocity of syngas causes less conversion through the packed bed reactor.

As the temperatures at the center of the catalytic bed were close to the feed temperature, temperature differences were less than 1 ℃, and it can be assumed that the bed was under isothermal conditions due to high heat transfer rates. In addition, the coolant temperature in lower feed temperature could be kept near feed temperature, which causes a high rate of heat transfer. The syngas conversion and the temperature at the center increase while the feed temperature goes up.

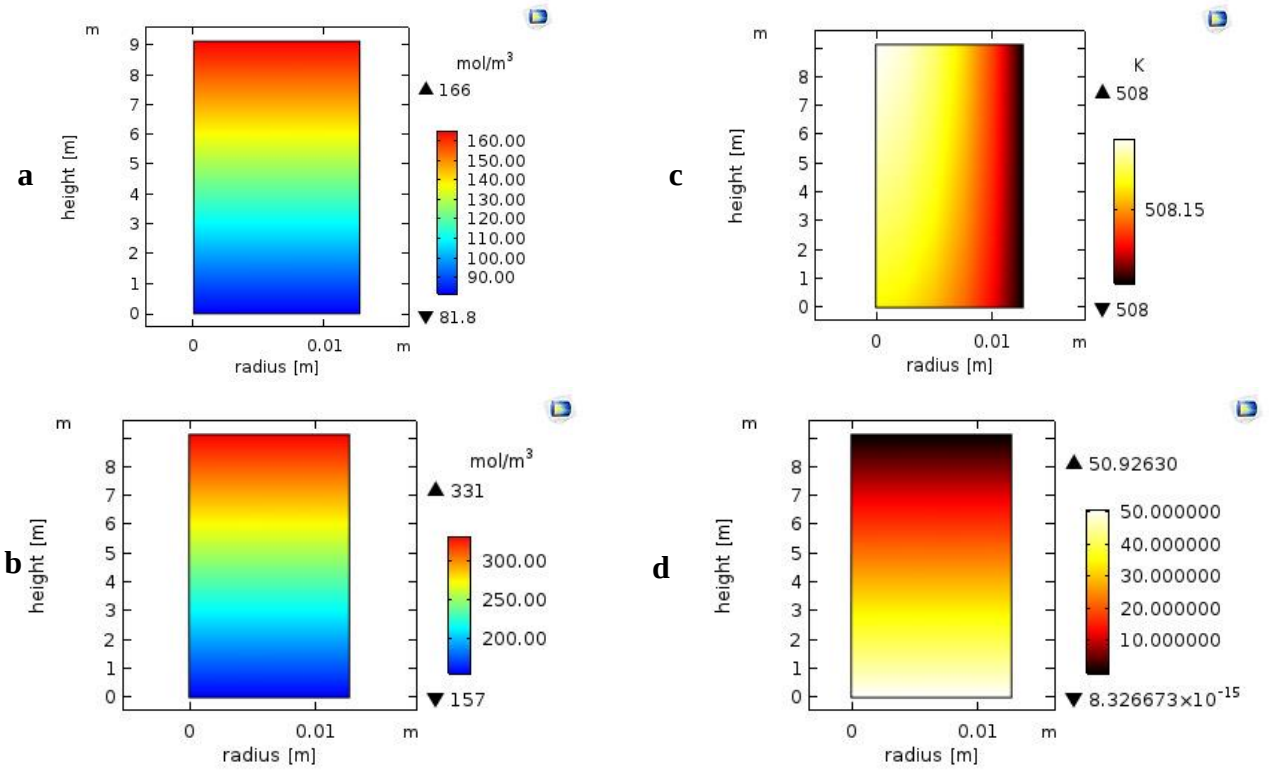

Figure 4. Two-dimensional profiles of (a) CO concentration, (b) H2 concentration, (c) temperature of syngas flow, (d) syngas conversion

Conclusions

Simulation studies were conducted to predict the effect of operating conditions on syngas conversion and temperature profiles of the cobalt-based FTS reaction in the FT reactor. The kinetic model proposed in the present study was shown to be effective for application to a commercial software package (COMSOL Multiphysics).

A fixed bed reactor model for FTS using a cobalt catalyst was developed. This kinetic model has two series of multi-tubular FT reactors over a cobalt catalyst, and the COMSOL Multiphysics was applied to simulate and predict the profiles of syngas conversion, feed concentration, oil selectivity, and temperature in the reactor under a variety of conditions including: feed temperature, syngas space velocity, and coolant temperature.

Results show overall CO conversion of 50% and controlled temperature applied in operating temperatures of 220 °C to 240 °C in the first step of the multi tubular reactor.

Moreover, the effect of coolant temperature was evaluated to determine optimum operating conditions to achieve more conversion and higher heat flux to keep the FT tubes near isothermal conditions.

Non-isothermal reactor was investigated in this study for different feed temperature to get higher selectivity of jet fuel (this sentence does not make sense. Are you trying to say “at different temperatures to find the highest selectivity of jet fuel”?s. Further simulation shows higher productivity and selectivity to control the FT packed bed rector near isothermal conditions, which started at a temperature of 235 °C.

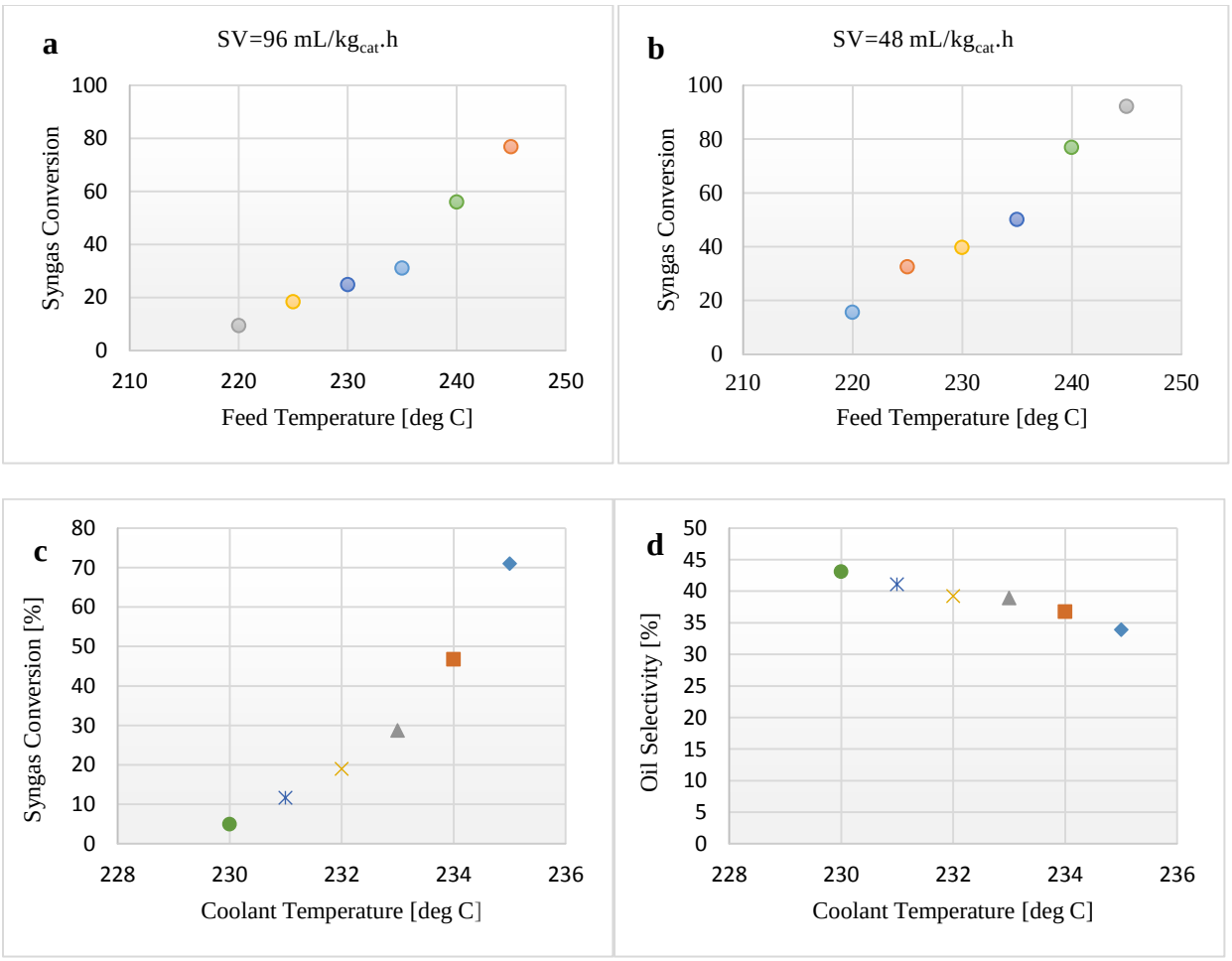

Figure 5. (a,b) CO conversion in different syngas space velocity, (c) CO conversion for various coolant temperatures, SV=48 mL/kg$_{cat}$.h (d) Oil selectivity different for various coolant temperatures, SV=48 mL/kg$_{cat}$.h

Appendix: Correlations used in this study [6,3]

Parameters	Equations
Syngas conversion	$\frac{\dot{m}_{oil} + \dot{m}_{H_2O} + \dot{m}_{CH_4}}{\dot{m}_{syngas} + \dot{m}_{oil} + \dot{m}_{H_2O} + \dot{m}_{CH_4}} \times 100$
Oil selectivity	$\frac{\dot{m}_{oil}}{\dot{m}_{oil} + \dot{m}_{H_2O} + \dot{m}_{CH_4}} \times 100$
Mixture heat capacity	$\sum_i x_i . C_{p,i}$
Space velocity	$\frac{\dot{Q}_{syngas}}{m_{cat}}$
Permeability of the porous medium	$\frac{\varepsilon^3 . d_p^2}{180.(1-\varepsilon)}$
Effective thermal conductivity	$K_{cat} \times (1 - \varepsilon) + K_f \times \varepsilon$
Mixture thermal conductivity	$\sum K_i x_i M_i^{1/3} / x_i M_i^{1/3}$

Nomenclature

Latin Letters

$\dot{Q}_{syngas}$	Syngas volume flow rate [mL/h]
T	Temperature [K]
C_i	Concentration of "i" specie [mol/m^3]
D_i	Diffusion coefficient [m^2/s]
r_i	Rate of Consumption or production of "i" specie [mol/(kg.s)]
K_{br}	Permeability of the porous medium [m^2]
$\dot{m}_i$	Mass flow rate of "i" specie [kg/s]
h_c	Heat transfer coefficient [W/m^2.K]
P	Pressure [Pa]
Q	Heat source [W/m^3]
m_{cat}	Mass of catalyst [kg]
x_i	Molar fraction of " i" specie
ρ	Mixture density [kg/m^3]
ρ_b	Bulk density [kg/m^3]
d_p	Particle diameter [mm]
k_f	Mixture thermal conductivity [W/(m^2.K)]

$C_{p,i}$	Heat capacity of "i" specie, at constant pressure [J/(Kg.K)]
u	Superficial velocity of the fluid [m/s]
SV	Space velocity [$mL_{syngas}/(kg_{cat}.h)$]
d_p	Particle diameter [mm]
k_{eff}	Effective Thermal conductivity [$W/(m^2.K)$]
k_{cat}	Catalyst thermal conductivity [$W/(m^2.K)$]
P_i	Partial pressure of specie i [Pa]
M_i	Molecular weight [kg/mol]
Greek Letters	
ε	Void fraction of the catalyst bed
α	Growth probability factor
Subscripts	
i	Specie i
c	coolant
eff	effective

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