A Wall-Cooled Fixed-Bed Reactor for Gas-Phase Fischer-Tropsch Synthesis

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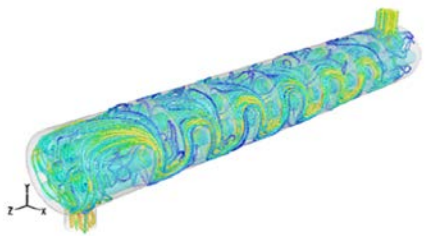
3-D CFD Model for Shell & Tube Exchanger with 7 Tubes

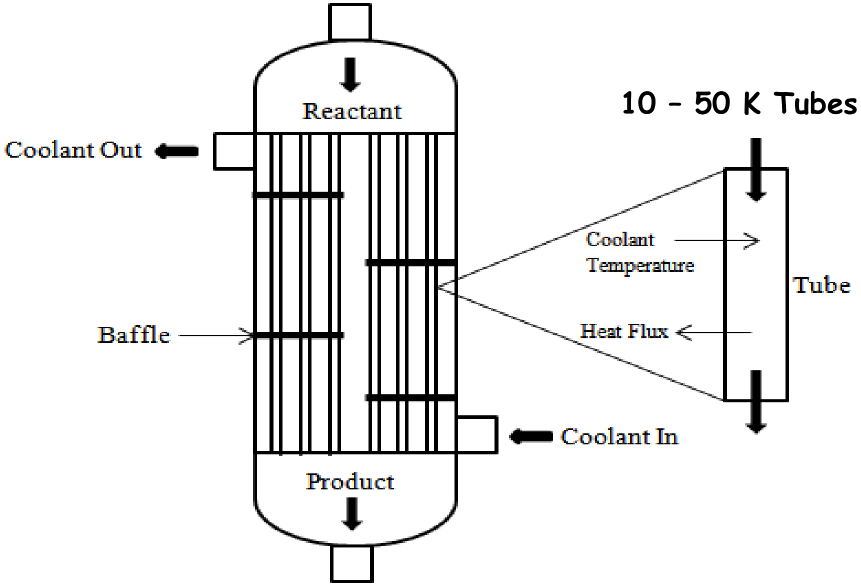


Ender Ozden and Ilker Tari (2010)

Arvind Nanduri
Department of Sustainable Energy & Systems Engineering
Patrick L. Mills*
Department of Chemical & Natural Gas Engineering
Texas A&M University-Kingsville
Kingsville, TX 78363-8202 USA

*Patrick.Mills@tamuk.edu

Multitubular Reactor Design for Low Temperature Fischer-Tropsch



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Session: Multiphysics Modeling for Reactor Engineering

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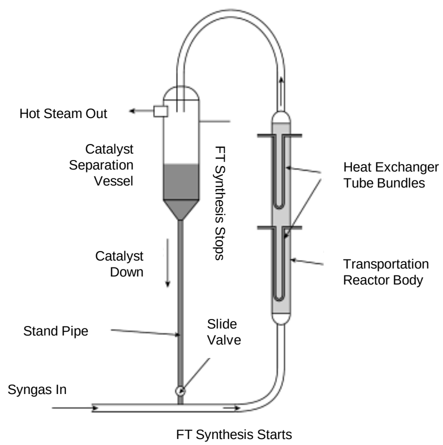
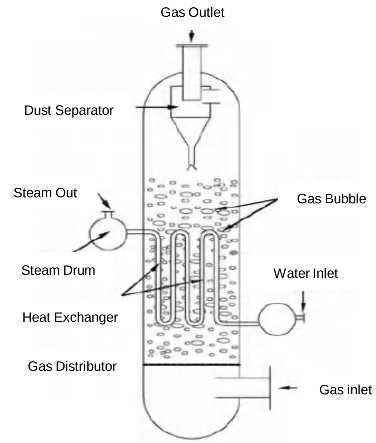
Fischer-Tropsch Reactor Technologies

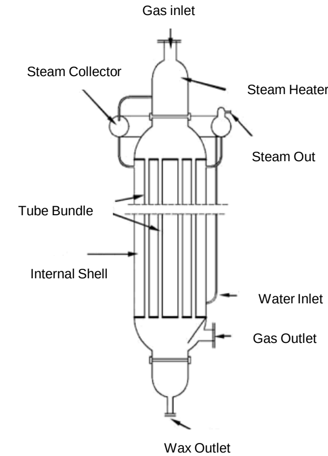
Circulating Fluidized Bed Reactor[1]



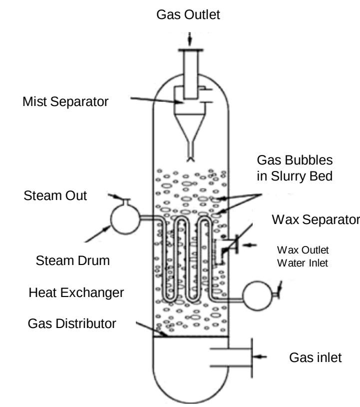
Fixed Fluidized Bed Reactor[1]



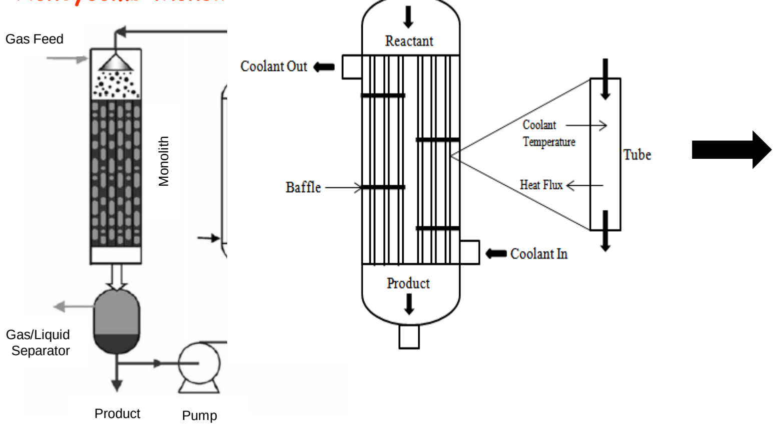
Multi-Tubular Fixed Bed Reactor[1]



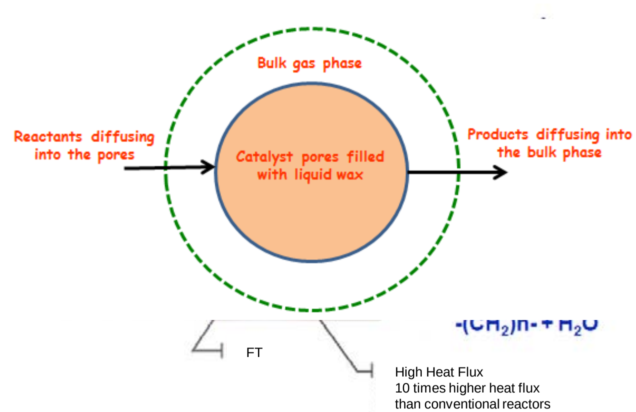
Slurry Bubble Column Reactor[1]



Honeycomb Monoli



F-T Micro-reactor[3]



1. M. Maitlis & A. de Klerk, Greener Fischer-Tropsch processes for Fuels and Feedstocks, *Wiley- VCH* (2013)
2. J. A. Moulijn, R. M. de Deugd & F. Kapteijn, *Catalysis Today* (2003)
3. S. LeViness, A. Tonkovich, K. Jarosch, S. Fitzgerald, B. Yang & J. McDaniel, *Velocys* (2011)

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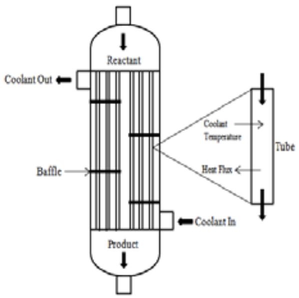
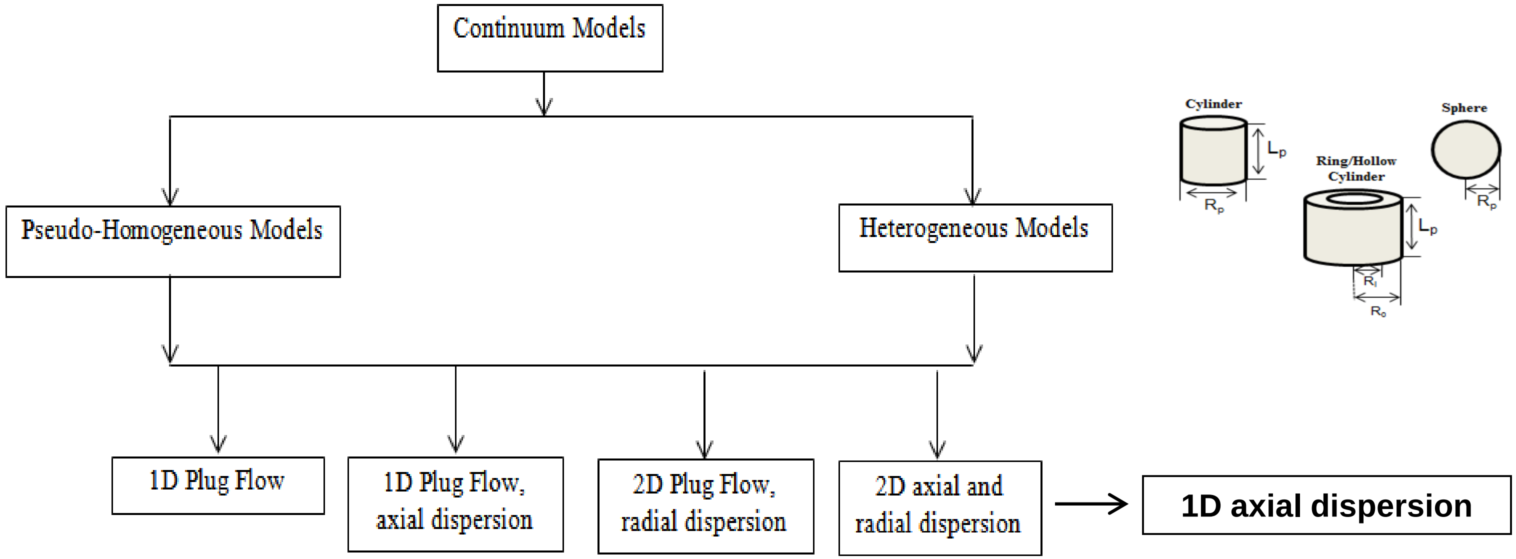
Fixed-Bed Reactor Models





- **Pseudo-homogeneous model**: The solid-to-fluid heat and mass transfer resistances are neglected *i,e.* the catalyst surface is assumed to be exposed to bulk fluid conditions, and the intra-particle diffusion effects are not accounted.

- **Heterogeneous model**: The transport equations for both liquid and solid phase are taken into account *i,e.* intra-particle diffusion limitations are captured.

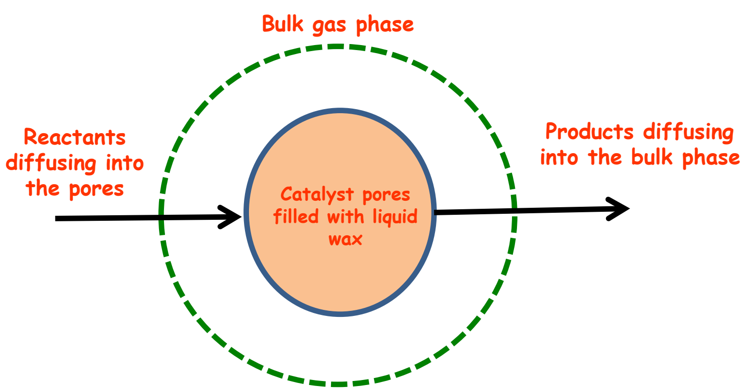
- A majority of the F-T fixed-bed reactor models are either based on a pseudo-homogeneous reactor model with traditional lumped kinetics or a fixed-bed consisting of spherical catalyst particles. Hence, other complicated features are not accounted for.

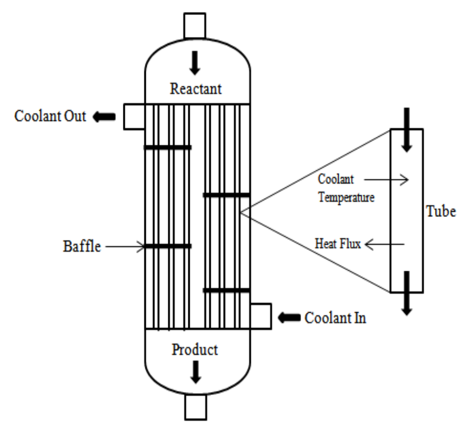
Objectives

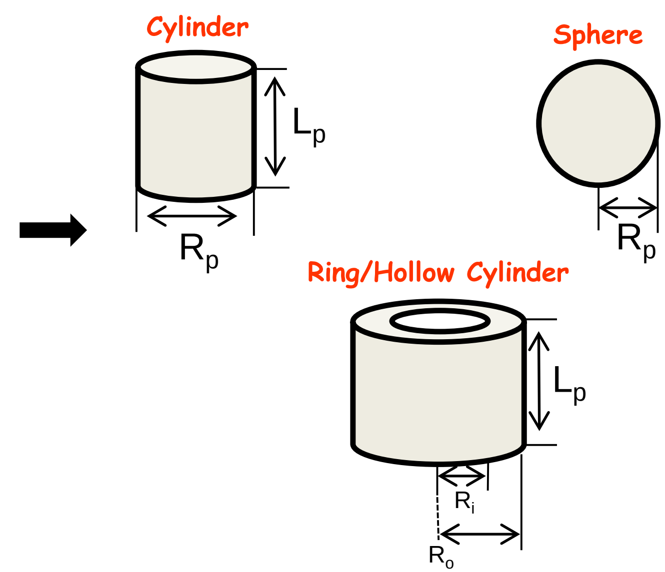
- Employ a 1-D heterogeneous axial dispersion model to describe the species and energy balances in a wall-cooled fixed-bed reactor for the Fischer-Tropsch (FT) reaction network using micro-kinetic rate expressions.

- Incorporate a Modified Soave-Redlich-Kwong (MSRK) equation of state (EOS) into the particle-scale and reactor-scale transport-kinetics model to more accurately describe the vapor-liquid-equilibrium (VLE) behavior of the FT product distribution.

- Assess the role of catalyst particle shape on the reactor scale FT product distribution.







Particle-Scale & Reactor-Scale Governing Equations

Specie Balance for Spherical Pellet:

$$\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(D_{ei}\xi^2\frac{\partial C_i}{\partial \xi}\right) = -\rho_p R_p^{\,2}\sum_j^{44}\sum_i^{43}\alpha_{ij}R_{ij} \qquad \xi = \frac{r}{R_p}$$

Specie Balance for Cylindrical Pellet:

$$\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(D_{ei}\xi\frac{\partial C_i}{\partial \xi}\right) = -\rho_p R_p^{\,2}\sum_j^{44}\sum_i^{43}\alpha_{ij}R_{ij} \qquad \xi = \frac{r}{R_p}$$

Specie Balance for Hollow Cylindrical Pellet:

$$\frac{1}{(\xi\delta + R_i)}\frac{\partial}{\partial \xi}\left((\xi\delta + R_i)D_{ei}\frac{\partial C_i}{\partial \xi}\right) = -\rho_p \delta^2\sum_j^{44}\sum_i^{43}\alpha_{ij}R_{ij} \qquad \xi = \frac{r - R_i}{R_o - R_i} \qquad \delta = R_o - R_i$$

Reactor-Scale Specie Balance:

$$\frac{1}{L_r^{\,2}}\frac{d}{d\xi}\left(D_{a,i}\frac{dC_i^{\,tube}}{d\xi}\right) + \frac{u}{L_r}\frac{dC_i^{\,tube}}{d\xi} = \rho_b \eta_i \sum_j^{44}\sum_i^{43}\alpha_{ij}R_{ij} \qquad \xi = \frac{x}{L_r}$$

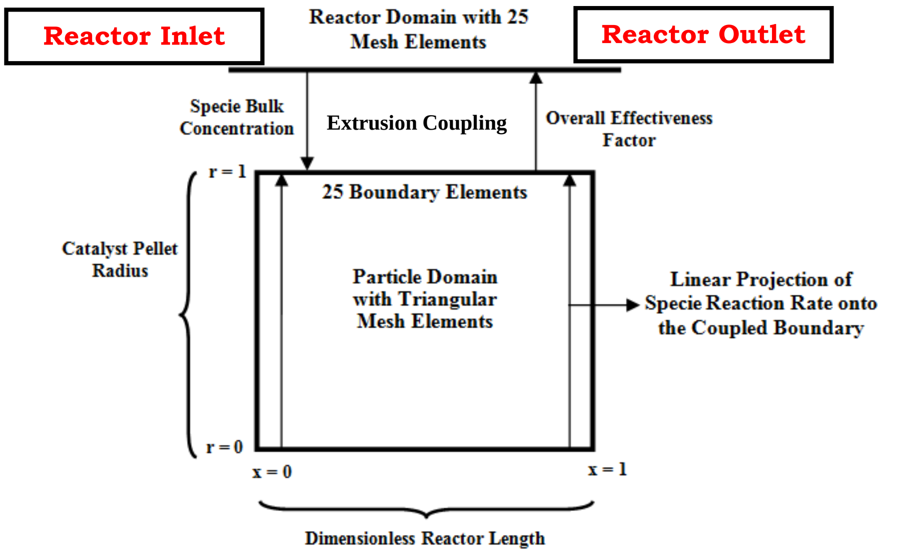
$$D_{a,i} = \frac{u^{int}D_p}{Pe_i} \qquad Pe_i = \left(\frac{1}{\frac{0.72}{ReSc_i} + \frac{0.52}{1 + \frac{9}{ReSc_i}}}\right) \qquad Sc_i = \frac{\mu_{gas}}{\rho_{gas}D_{i,B}} \qquad Re = \frac{D_p u_s \rho_{gas}}{\mu_{gas}}$$

Reactor-Scale Energy Balance:

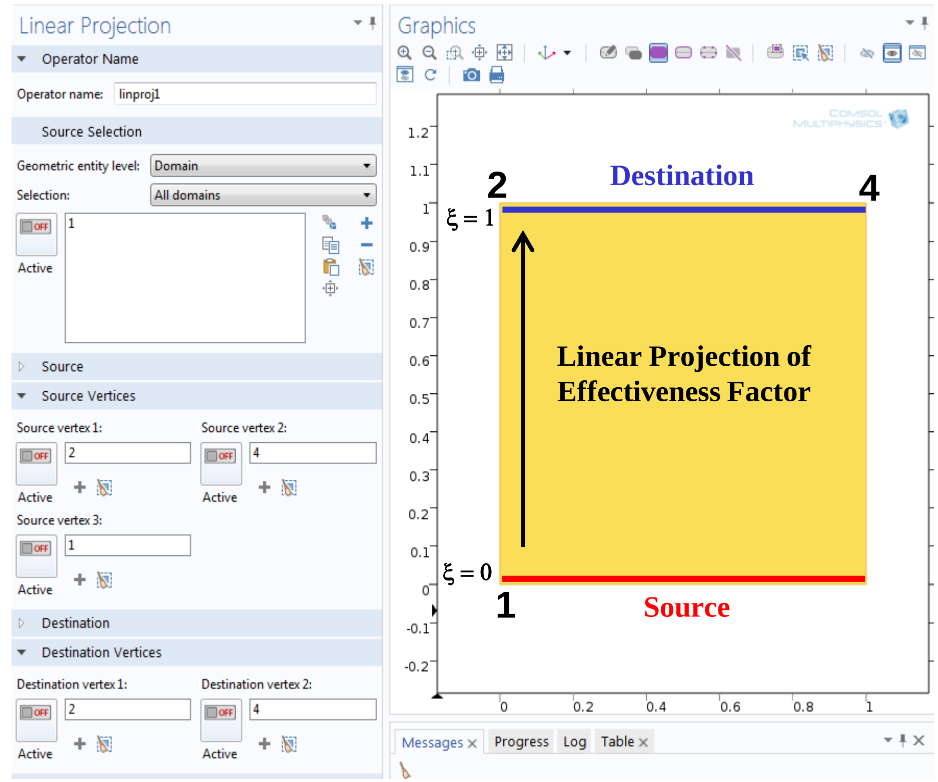
$$\frac{\rho_{gas}C_{p,gas}u_s}{L_r}\frac{dT_{tube}}{d\xi} = \frac{U_{overall}4(T_{tube} - T_{cool})}{D_r} - \rho_b\sum_i \eta_i \sum_j (-\Delta H_{ij})(R_{ij})^{surface}$$

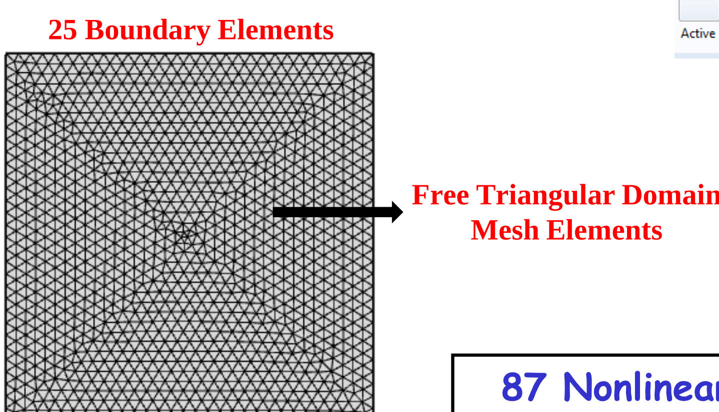
$T_{tube} = T_{bulk\ gas}$

Numerical Extrusion Coupling and Linear Projection Strategy



The extrusion coupling variables are tube-side bulk specie concentration ($C_{i,tube}$), catalyst-scale specie effectiveness factor (η_i) and axial temperature (T_{tube})





87 Nonlinear, Coupled Boundary-Value ODEs

Effectiveness Factor of Component 'i' in the F-T Reaction Network

$$\eta_i = \left(\frac{\int \sum_{ij} \alpha_{ij} R_{ij}^{pellet} dv}{\left(\sum_{ij} \alpha_{ij} R_{ij}^{pellet} V_p\right)_{surface}} \right)$$

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Boundary Conditions and Model Assumptions

Particle Domain Boundary Conditions (Dirichlet & Neumann Conditions)

Spherical Particle	At $\xi = 1$, $C_i = C_{i,tube}$ and At $\xi = 0$, $dC_i/d\xi = 0$
Cylindrical Particle	At $\xi = 1$, $C_i = C_{i,tube}$ and At $\xi = 0$, $dC_i/d\xi = 0$
Hollow Cylindrical Particle	At $\xi = 0$ and $\xi = 1$, $C_i = C_{i,tube}$

Reactor Domain Boundary Conditions (Dirichlet & Neumann Conditions)

Specie Balance	At $\xi = 0$, $C_{i,tube} = C_{i,inlet}$ and At $\xi = 0$, $dC_{i,tube}/d\xi = 0$
Energy Balance	At $\xi = 0$, $T_{tube} = T_{tube}$ and At $\xi = 0$, $dT_{tube}/d\xi = 0$

Particle Domain Assumptions

i. Concentration is a function of only the radial coordinate, *i.e.*, $C_i = C_i(r)$

ii. Steady-state conditions

iii. Particle surface exists at bulk temperature

Reactor Domain Assumptions

i. The porosity of the catalyst bed is constant

ii. The radial heat and mass transfer is neglected

iii. The bulk concentration of species and temperature are a function of only the axial coordinate, *i.e.*, $C_i = C_i(x)$ and $T_{tube} = T(x)$

Process Variables and Catalyst Properties

Reactor Length, L_r	12 m
Tube Diameter, D_r	5 cm
Pressure, P_{inlet}	25 bar & 30 bar
Superficial Velocity, u_s	0.55 m/s
Overall Heat Transfer Coefficient, $U_{overall}$	364 W/m^2K
T_{cool}	493 K
T_{inlet}	493 K
Dimensions of cylindrical pellet	L = 3 mm, R = 1 mm and D_r/d_s = 19.08
Dimensions of spherical pellet	R = 1.5 mm and D_r/d_s = 16.67
Dimensions of hollow cylindrical pellet	L = 3 mm, R_o = 2 mm, R_i = 1 mm and D_r/d_s = 13.23
Density of pellet, ρ_p	1.95×10^6 (gm/m^3)
Porosity of pellet, ε_p	0.51
Tortuosity, τ	2.6
Bed porosity, ε_b	Sphere: 0.58[1] Cylinder: 0.36[2] Ring: 0.48[2]

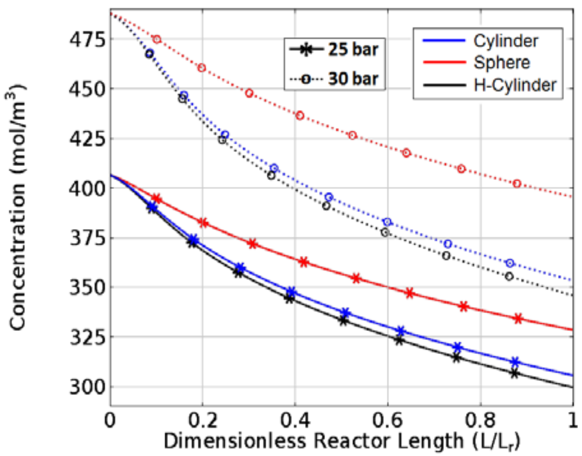
Equivalent volume sphere diameter

$d_s = (6 * V_p/\pi)^{1/3}$

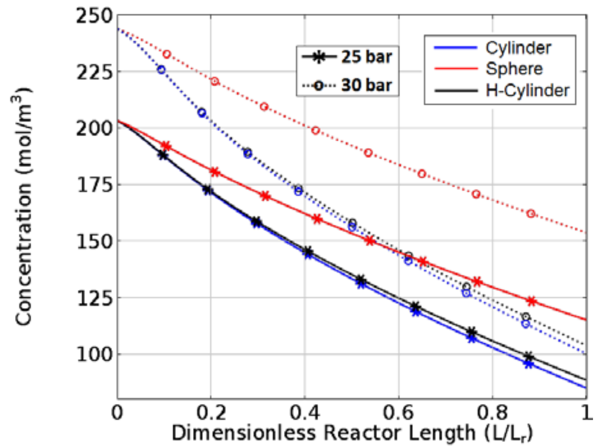
1. A. Jess, and C. Kern, *Chemical Engineering* Technology (2012)
2. Damjan Nemec, and Janez Levec, *Chemical Engineering Science* (2005)

Axial Concentrations of the Key Reactants & CO Conversion Profiles

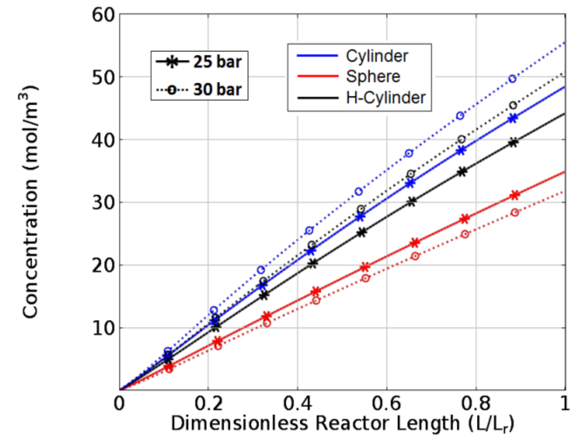
H_2



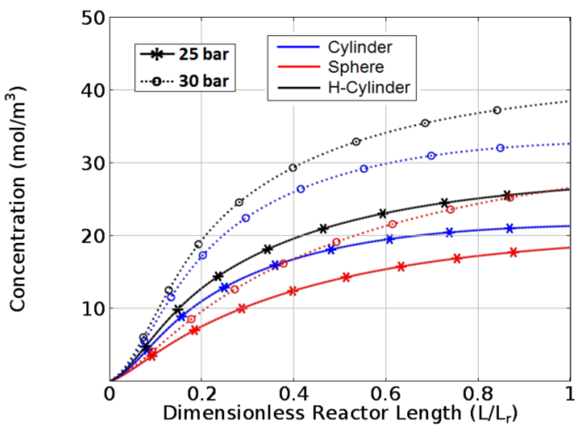
CO



CO_2



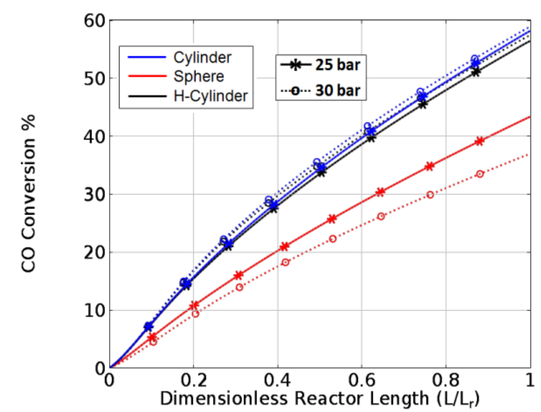
H_2O



Key Observations

- The cylinder and the ring catalyst particle shapes predict higher conversion of CO on a reactor-scale when compared to the spherical catalyst shape.
- It is important to study the intra-particle concentration profiles of CO_2 on a reactor-scale, as the Water-Gas-Shift (WGS) reaction controls the availability of CO for the F-T synthesis.

CO Conversion



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Particle-Scale Concentration Profiles of CO_2

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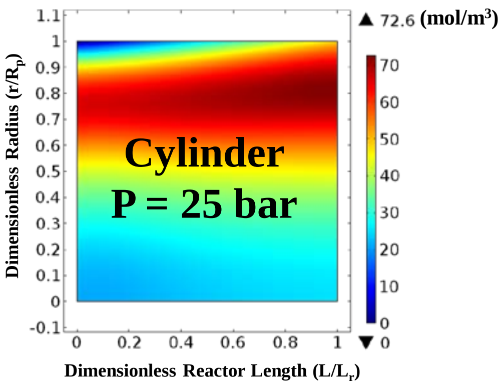
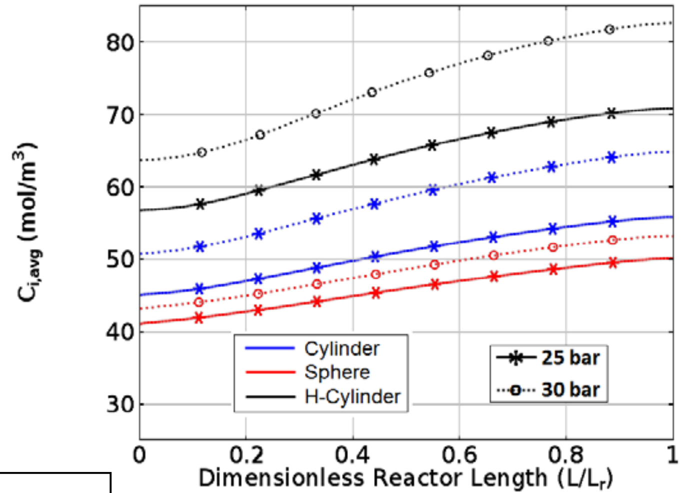
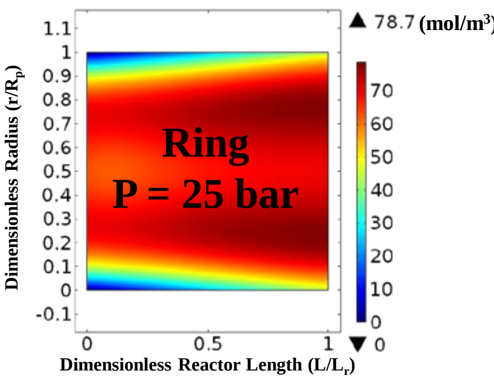
$$\text{Intra}-\text{Particle Volume Average Concentration, } C_{i,avg} = \frac{\int C_i\, dv}{V_p}$$

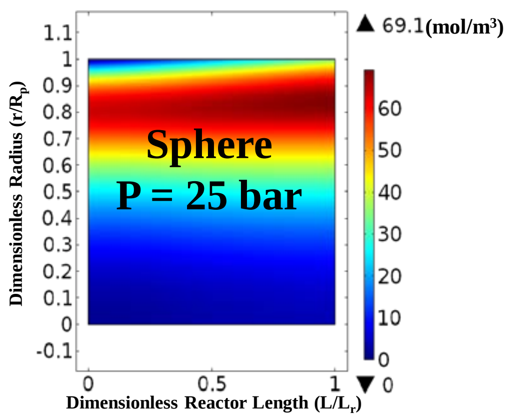






Key Observations

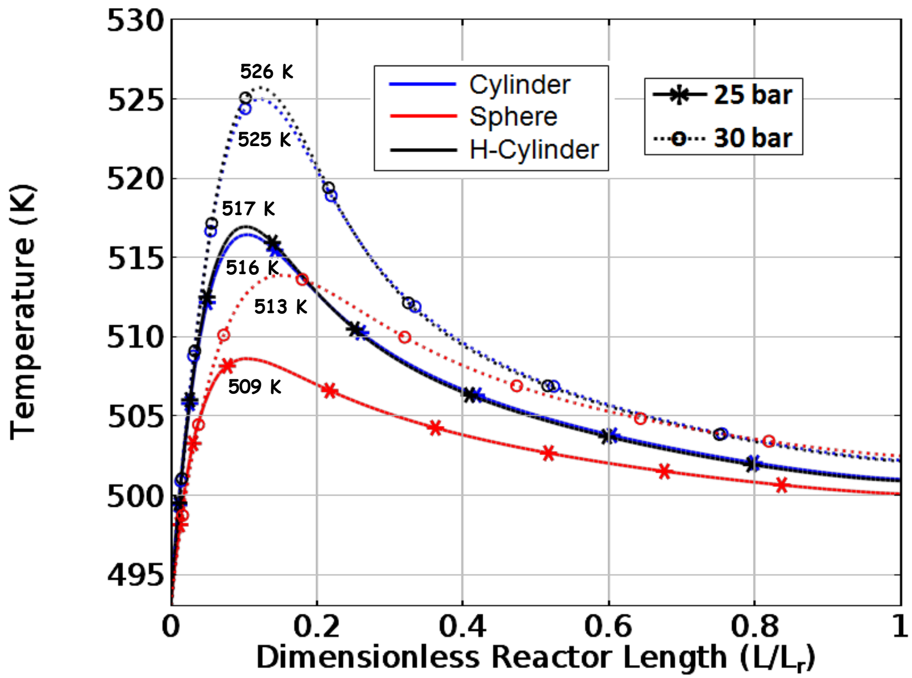
- The average CO_2 concentration increases not only along the length of the fixed-bed, but also with an increase in operating pressure.
- The magnitude of difference between the average CO_2 concentration for the spherical catalyst, for 25 and 30 bar, is less when compared to the other particle shapes.
- The WGS reaction rate becomes limited in the spherical catalyst with increase in pressure .



Key Observations

- The magnitude of difference between the average CO_2 concentration for cylinder and ring catalyst shapes increases with increase in operating pressure.
- WGS reaction is not limited in these shapes
- It is important to understand the F-T reaction chemistry in a fixed-bed with non-spherical catalyst particle shapes.

Fixed-Bed Axial Temperature Profiles



Hot-spot temperature magnitudes for different catalyst particle shapes

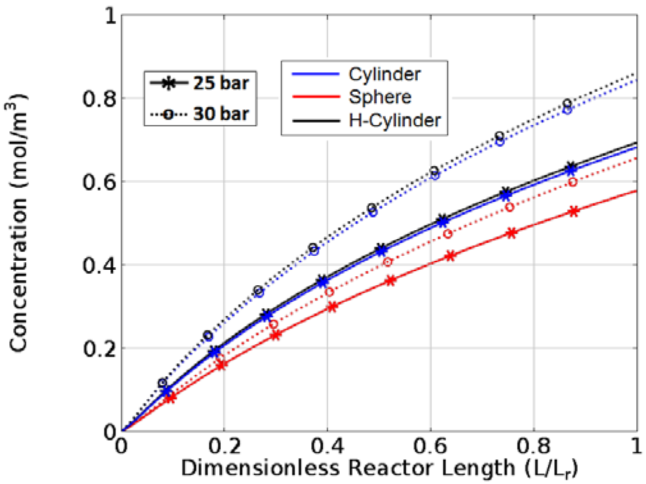
Shape	T_{max}	
	25 bar	30 bar
Cylinder	516 K	525 K
H-Cylinder	517 K	526 K
Sphere	509 K	513 K

Key Observations

- Cylinder and ring catalyst particle shapes predict hot spots of similar magnitude, but higher than that corresponding to the spherical catalyst shape.
- Hot spot occurs at the reactor inlet, and the magnitude increases with an increase in operating pressure.
- A high temperature in the reactor facilitates the methanation reaction and also breaks down diesel range hydrocarbons to small chain paraffins.
- It is important to study the axial temperature profiles of the fixed-bed, as it dictates the F-T product selectivity.

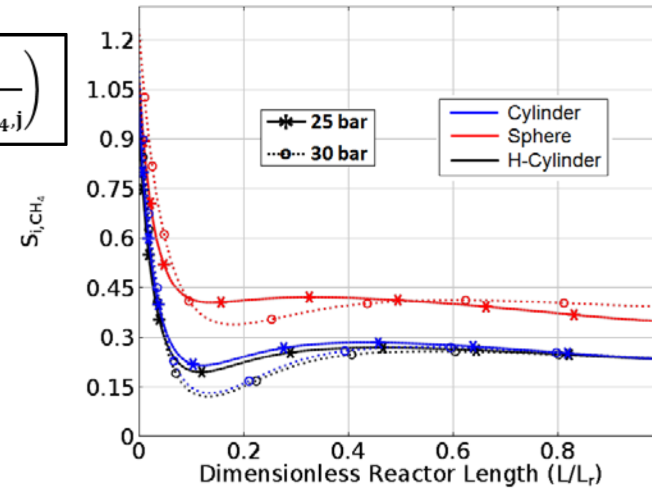
Reactor-Scale Diesel Range Concentration and Methane-Based Diesel Selectivity Profiles

Diesel Range



$$S_{i,CH_4} = \left(\frac{\sum_{i,j} \alpha_{ij} R_{ij}}{\sum_{CH_4,j} \alpha_{CH_4,j} R_{CH_4,j}} \right)$$

Methane-Based Diesel Selectivity

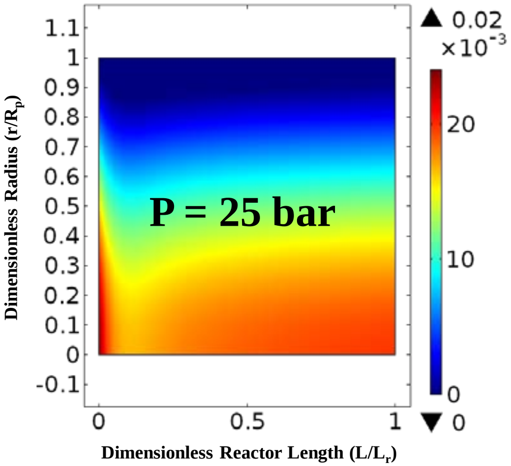


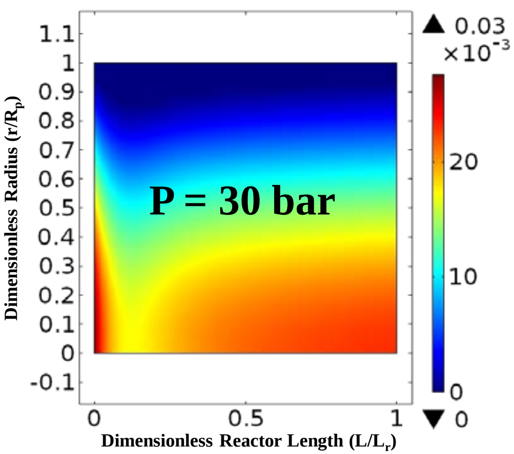
Key Observations

- Cylinder and ring catalyst particle shapes predict a higher concentration of diesel range hydrocarbons than the spherical catalyst shape.
- The diesel range concentration increases with an increase in operating pressure for all the catalyst particle shapes.
- The methane-based diesel selectivity profiles follow a decreasing trend at the reactor inlet due to the occurrence of hot spots
- The diesel range concentration profiles suggest that cylinder and ring particle shapes are preferred over the spherical catalyst shape.

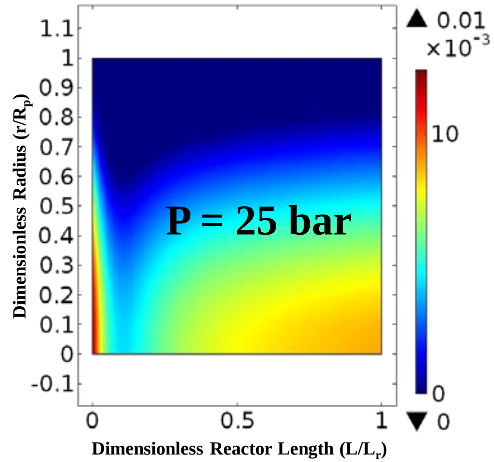
Intra-Particle Liquid-to-Vapor Ratio

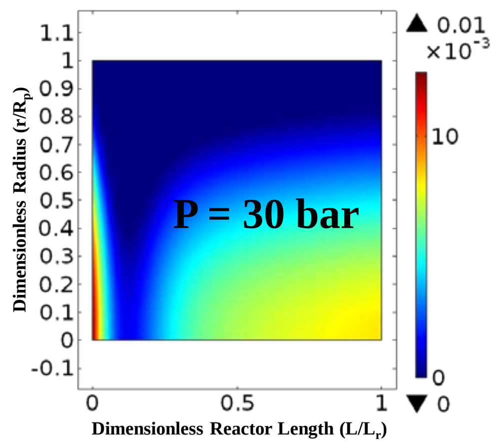
Sphere



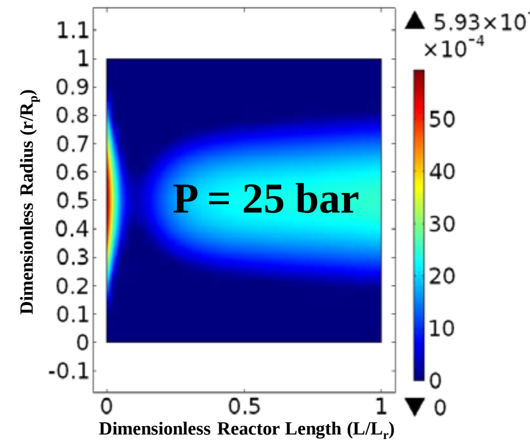


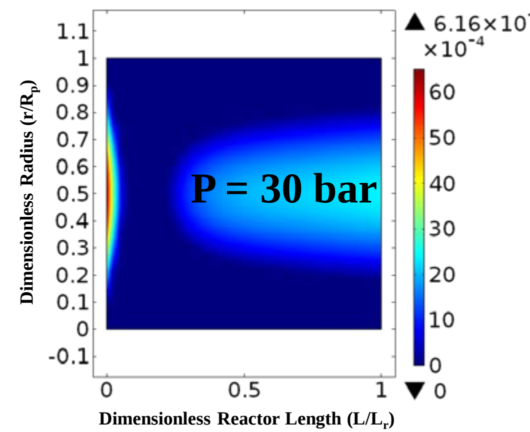
Cylinder





Ring





Ring < Cylinder < Sphere

Computational Techniques for Error-Free Convergence

- The 2-D particle domain is first simulated without coupling to the reactor domain to get an initial solution, which is then used as an initial guess.

- The coupling variables are activated with a small reactor length (about 0.1 m), and then the length is slowly increased.

- To avoid convergence issues in the heat balance equation, due to the high exothermic nature of the reaction, the net heat of the reaction is multiplied with a perturbation factor of 10^{-10}, and then this factor is slowly increased to 1 (by a factor of 10^2 for each step; *ca.* 1.5 hours for convergence on a Dell computer with Intel(R) Core(TM) i5-3570 CPU @ 3.4 GHz and 16 GB RAM).

- Negative specie concentrations, in both reactor and particle domains, can be avoided by not letting CO and CO_2 concentrations approach zero by using $CO=if(CO\leq 0,eps,CO)$ and $CO_2=if(CO_2\leq 0,eps,CO)$.

- Mesh refinement was manually performed until the concentration profiles were relatively constant and satisfied the convergence criterion.

Conclusions

- A 2-D catalyst pellet model coupled with a 1-D **heterogeneous axial dispersion reactor model** can be used to analyze both particle-level and reactor-level performance of different catalyst particle shapes.

- Micro kinetic rate equations, when coupled with intraparticle transport effects and vapor-liquid equilibrium phenomena, captures the **transport-kinetic interactions and phase behavior** for gas-phase FT catalysts on both the particle-scale and reactor-scale.

- The CO conversion, intra-particle liquid-to-vapor ratio, and the reactor-scale diesel range concentration profiles results suggest that *cylinder and hollow ring shapes are preferred* over spherical particle shapes, but the magnitude of the hot spot is greater for those shapes. This may lead to a higher rate of catalyst deactivation, reduce the catalyst mechanical strength and generate unsafe reactor operating conditions.

- The results in the current work show the importance of *understanding the axial temperature profile* of a single fixed-bed in order to efficiently design a MTFBR.