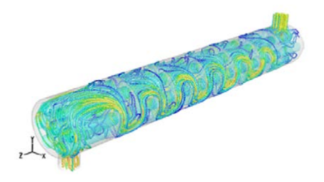
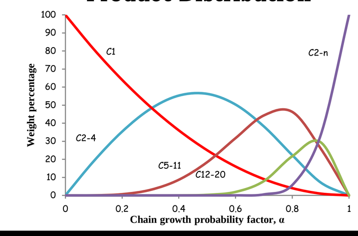
3-D CFD Model for Shell & Tube Exchanger with 7 Tubes



Ender Ozden and Ilker Tari (2010)

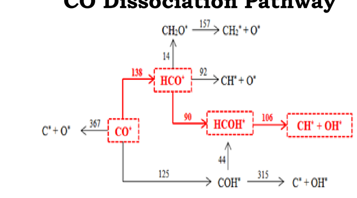
Anderson-Schulz-Flory (ASF) Product Distribution



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

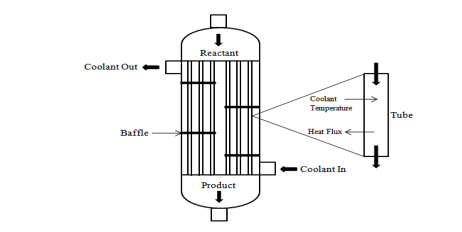
A. Nanduri and P. L. Mills
Department of Chemical and Natural Gas Engineering
Texas A&M-Kingsville, Kingsville, TX, USA

CO Dissociation Pathway



M. Ojeda *et al.* (2008)

Multi-tubular Reactor Design for Low Temperature Fischer-Tropsch



Introduction

Fischer-Tropsch synthesis (FTS) is a highly exothermic polymerization reaction of syngas ($CO+H_2$) in the presence of Fe/Co/Ru-based catalysts to produce a wide range of paraffins, olefins and oxygenates, often known as *syncrude*. Multi-Tubular Fixed Bed Reactors (MTFBR) and Slurry Bubble Column Reactors (SBCR) are widely employed for FTS processes. The scale-up of MTFBR is complicated by the occurrence of hot spots in both the tube and shell coolant regions. The emphasis of this research is to model a wall-cooled fixed-bed reactor using COMSOL Multiphysics. This poster focuses on comparing the performance of a fixed-bed reactor with cylindrical, spherical and hollow cylindrical catalyst particle shapes by accounting for transport-kinetic interactions and thermodynamic phenomena using micro kinetic rate expressions.

Kinetic and Thermodynamic Expressions

Fe-Based Olefin Re-adsorption Kinetics

$$R_{CH_4} = \frac{k_{5M} P_{H_2} \alpha_1}{1 + \left(1 + \frac{1}{K_2K_3K_4}\frac{P_{H_2O}}{P_{H_2}{}^2} + \frac{1}{K_3K_4}\frac{1}{P_{H_2}} + \frac{1}{K_4}\right)\sum_{i=1}^{N}\left(\prod_{j=1}^{i}\alpha_j\right)}$$

$$R_{C_nH_{2n+2}} = \frac{k_5 P_{H_2} \prod_{j=1}^{n}\alpha_j}{1 + \left(1 + \frac{1}{K_2K_3K_4}\frac{P_{H_2O}}{P_{H_2}{}^2} + \frac{1}{K_3K_4}\frac{1}{P_{H_2}} + \frac{1}{K_4}\right)\sum_{i=1}^{N}\left(\prod_{j=1}^{i}\alpha_j\right)}$$

$$R_{C_nH_{2n}} = \frac{k_6 (1-\beta_n) \prod_{j=1}^{n}\alpha_j}{1 + \left(1 + \frac{1}{K_2K_3K_4}\frac{P_{H_2O}}{P_{H_2}{}^2} + \frac{1}{K_3K_4}\frac{1}{P_{H_2}} + \frac{1}{K_4}\right)\sum_{i=1}^{N}\left(\prod_{j=1}^{i}\alpha_j\right)}$$

$$R_{CO_2} = \frac{k_v\left(\frac{P_{CO}P_{H_2O}}{P_{H_2}^{0.5}} - \frac{P_{CO_2}P_{H_2}^{0.5}}{K_p}\right)}{1 + \frac{K_v P_{CO} P_{H_2O}}{P_{H_2}^{0.5}}}$$

$$\alpha_n = \frac{k_1 P_{CO}}{k_1 P_{CO} + k_5 P_{H_2} + k_6(1-\beta_n)}$$

$$\alpha_A = \frac{k_1 P_{CO}}{k_1 P_{CO} + k_5 P_{H_2} + k_6}$$

$$\beta_n = \frac{\frac{k_{-6}}{k_6} P_{C_nH_{2n}}}{\left[\alpha_A^{i-2}\frac{k_1 P_{CO}}{k_1 P_{CO} + k_5 P_{H_2}} + \frac{k_{-6}}{k_1 P_{CO} + k_5 P_{H_2} + k_6}\sum_{i=2}^{n}\left(\alpha_A^{i-2} P_{C_{(n-i+2)}H_{2(n-i+2)}}\right)\right]}$$

$$K_p = \exp\left[\frac{5078.0045}{T} - 5.8972089 + 13.958689 * 10^{-4}\,T - 27.592844 * 10^{-8} T^2\right]$$

where n = 2 to 20

Conventional Names of F-T Products

Name	Composition
Fuel Gas	C_1-C_2
LPG	C_3-C_4
Gasoline	C_5-C_{12}
Naphtha	C_8-C_{12}
Kerosene	C_{11}-C_{13}
Diesel/Gasoil	C_{13}-C_{17}
F-T Wax	C_{20+}

D. A. Wood *et al.* (2012)

Wang *et al.* "Kinetics Modelling of Fischer-Tropsch Synthesis over an Industrial Fe-Cu-K Catalst", Fuel, Vol 82, Pg 195-213, 2003

Modified Soave-Redlich-Kwong EOS

$$P_i = \frac{RT}{(V_i - b_i)} - \frac{\alpha_i a_i}{V_i(V_i + b_i)} \qquad Z_i{}^3 - Z_i{}^2 + Z_i\left(A_i - B_i - B_i{}^2\right) - A_iB_i$$

$$A_i = \frac{a_i P_i}{R^2T^2} \qquad B_i = \frac{b_i P_i}{RT}$$

Cubic equation valid for FT product distribution

Wang *et al.* (2008)

$$a_i = 0.42747\frac{R^2 T_{ic}{}^2}{P_{ic}} \qquad b_i = 0.08664\frac{RT_{ic}}{P_{ic}}$$

$$m_i = 0.48508 + 1.55171\omega_i - 0.1561\omega_i{}^2 \qquad b_m = \sum_i y_i b_i$$

$$\alpha_i = \left(1 + m_i\left(1 - \sqrt{T_{ir}}\right)\right)^2 \qquad a_m = \sum_i\sum_j y_i y_j \left(a_i a_j\right)^{1/2}\left(1 - k_{ij}\right)$$

$$\ln\emptyset_i{}^P = \frac{b_i}{b_m}(Z_i - 1) - \ln(Z_i - B_i) + \frac{A_i}{B_i}\left(\frac{b_i}{b_m} - \frac{2}{\alpha_i a_i}\sum_j y_i(\alpha_i a_i)_{ij}\right)\ln\left(1 + \frac{B_i}{Z_i}\right)$$

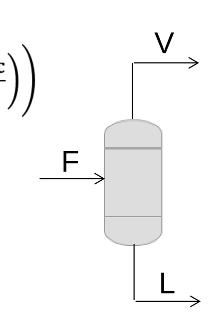
VLE Flash Calculations

Rachford-Rice Objective Function

$$F(\alpha_g) = \sum_i \frac{z_i(K_i - 1)}{\left(1 + \alpha_g(K_i - 1)\right)} = 0$$

$$K_i{}^{\text{guess value}} = \frac{P_{ic}}{P}\exp\left(5.37(1 + \omega_i)\left(1 - \frac{T_{ic}}{T}\right)\right)$$

$$K_i = \frac{\emptyset_i{}^V}{\emptyset_i{}^L}$$



Governing Equations and Boundary Conditions

Specie Balance for Spherical Pellet: $\frac{1}{\xi^2}\frac{\partial}{\partial\xi}\left(D_{ei}\xi^2\frac{\partial C_i}{\partial\xi}\right) = -\rho_p R_p{}^2\sum_{j=1}^{44}\sum_{i=1}^{43}\alpha_{ij}R_{ij}$ *where* $\xi = \frac{r}{R_p}$

Specie Balance for Cylindrical Pellet: $\frac{1}{\xi}\frac{\partial}{\partial\xi}\left(D_{ei}\xi\frac{\partial C_i}{\partial\xi}\right) = -\rho_p R_p{}^2\sum_{j=1}^{44}\sum_{i=1}^{43}\alpha_{ij}R_{ij}$ *where* $\xi = \frac{r}{R_p}$

Specie Balance for Ring Catalyst Pellet: $\frac{1}{(\xi\delta + R_i)}\frac{\partial}{\partial\xi}\left((\xi\delta + R_i)D_{ei}\frac{\partial C_i}{\partial\xi}\right) = -\rho_p\delta^2\sum_{j=1}^{44}\sum_{i=1}^{43}\alpha_{ij}R_{ij}$ *where* $\xi = \frac{r - R_i}{R_o - R_i}$ & $\delta = R_o - R_i$

Reactor-Scale Specie Balance : $\frac{1}{L_r{}^2}\frac{d}{d\xi}\left(D_{a,i}\frac{dC_i}{d\xi}\right) + \frac{u}{L_r}\frac{dC_i}{d\xi} = \rho_p\eta_i\sum_{j=1}^{44}\sum_{i=1}^{43}\alpha_{ij}R_{ij}$ *where* $\xi = \frac{x}{L_r}$

Reactor-Scale Energy Balance : $\frac{\rho_{gas}C_{p,gas}u_s}{L_r}\frac{dT}{d\xi} = \frac{U_{overall}4(T - T_{cool})}{D_r} - \rho_b\sum_i\eta_i\sum_j(-\Delta H_{ij})R_{ij}$ *where* $\xi = \frac{x}{L_r}$

$$D_{a,i} = \frac{u^{int}D_p}{Pe_i} \qquad Pe_i = \left(\frac{1}{\frac{0.72}{ReSc_i} + \frac{0.52}{1 + \frac{9}{ReSc_i}}}\right) \qquad Sc_i = \frac{\mu_{gas}}{\rho_{gas}D_{i,B}} \qquad u^{int} = \frac{u_s}{\varepsilon_{bed}} \qquad Re = \frac{D_p u_s \rho_{gas}}{\mu_{gas}} \qquad \eta_i = \frac{\int\sum_{ij}\alpha_{ij}R_{ij}{}^{pellet}dv}{\left(\sum_{ij}\alpha_{ij}R_{ij}{}^{pellet}V_p\right)_{surface}}$$

Boundary Conditions

1-D Reactor Domain	At x = 0 (entrance), $C_{i,tube} = C_{i,inlet}$ and at x = 1, $dC_{i,tube}/dx = 0$ (zero flux)
2-D Pellet Domain	Sphere & Cylinder: At r = 0 (center of pellet), $dC_i/dx = 0$ and at r=1, $C_i = C_{i,tube}$ Hollow cylinder : At r = 0 (inner surface) and at r=1 (outer surface), $C_i = C_{i,tube}$

Process Variables and Catalyst Properties*

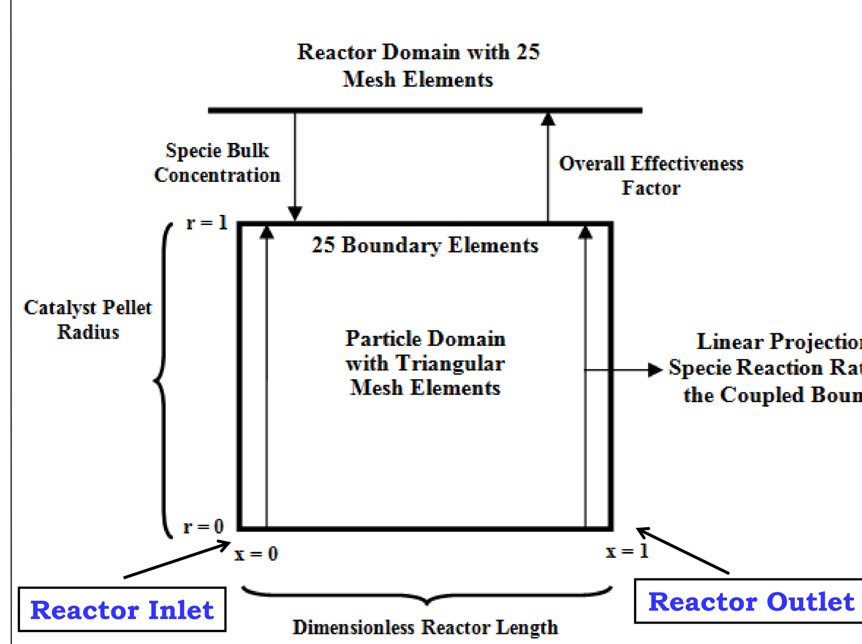
Reactor Length, L_r	12 m
Tube Diameter, D_r	5 cm
Pressure, P_{inlet}	25 bar & 30 bar
Superficial Velocity, u_s	0.55 m/s
Overall Heat Transfer Coefficient, $U_{overall}$	364 W/m^2K
T_{cool}	493 K
T_{inlet}	493 K
Dimensions of cylindrical pellet	L = 3 mm and R = 1 mm
Dimensions of spherical pellet	R = 1.5 mm
Dimensions of hollow cylindrical pellet	L = 3 mm, R_o = 2 mm & R_i = 1 mm
Density of pellet, ρ_p	1.95 x 10^6 (gm/m^3)
Porosity of pellet, ε	0.51
Tortuosity, τ	2.6

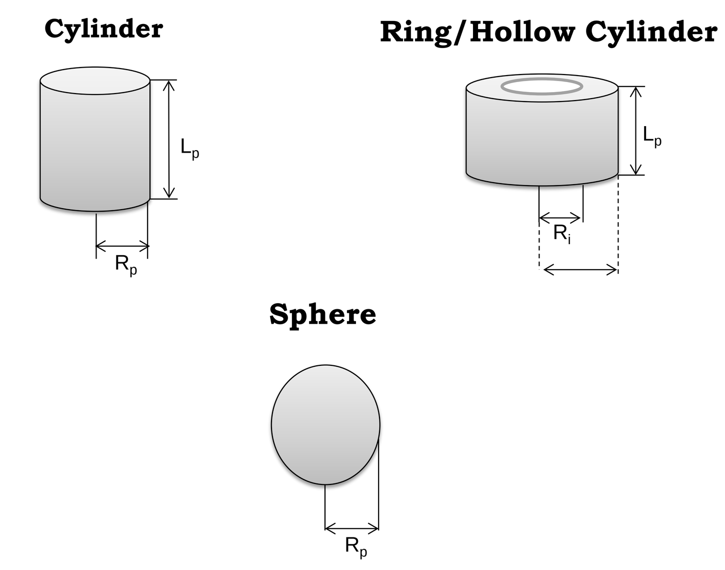
*Andreas Jess *et al.* " Modeling of Multi-Tubular Reactors for Fischer-Tropsch Synthesis", Chem. Eng. Technol, Vol 32, No. 8, Pg 1164-1175, 2009

Objectives

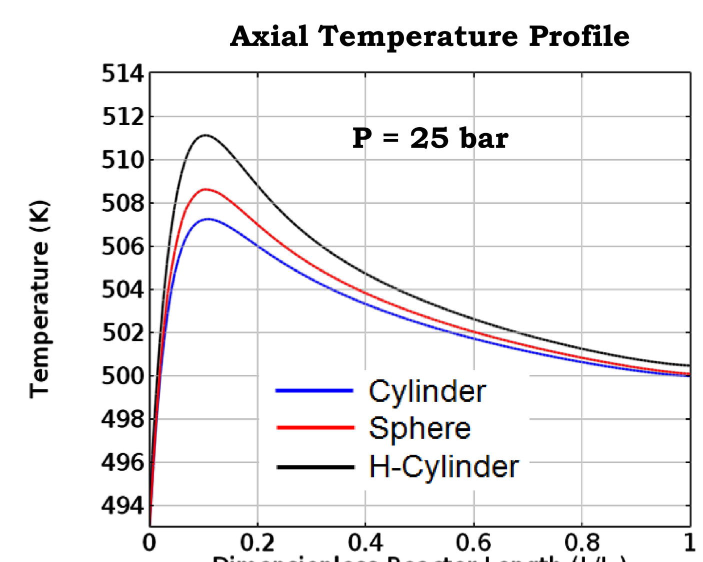
- Employ a 1-D heterogeneous axial dispersion model to describe the specie and energy balances in a wall-cooled fixed-bed reactor for the Fischer-Tropsch (FT) reaction network using micro-kinetic rate expressions.
- Assess the role of catalyst particle shape on the reactor scale FT product distribution.
- 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.

Numerical Extrusion Coupling and Linear Projection Strategy

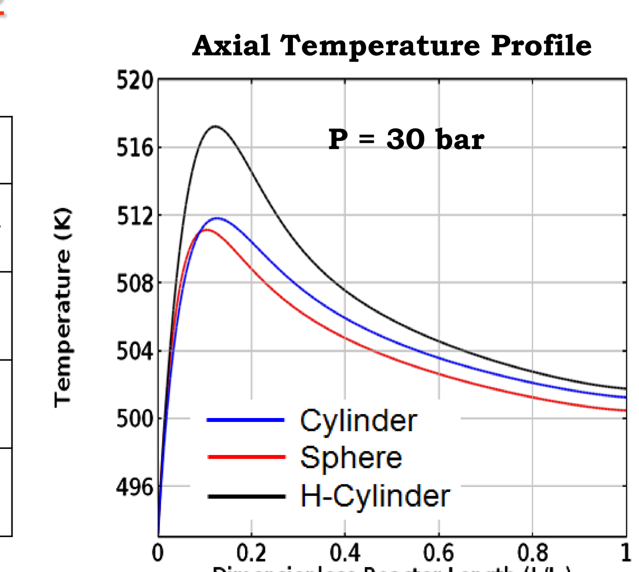




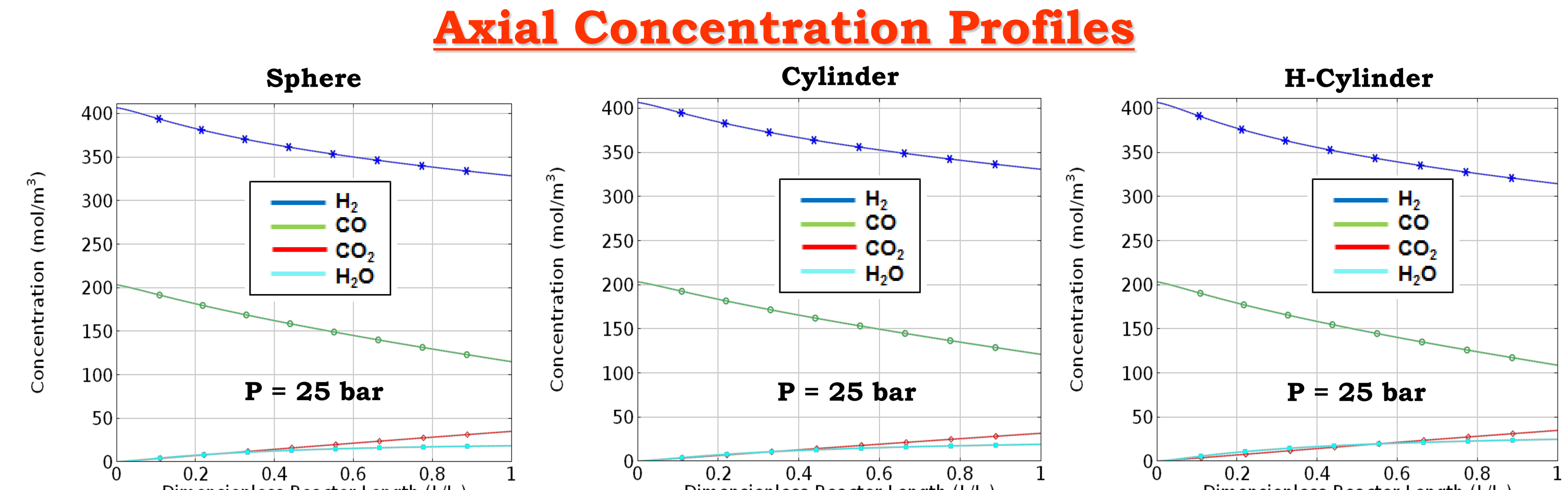
Key Results

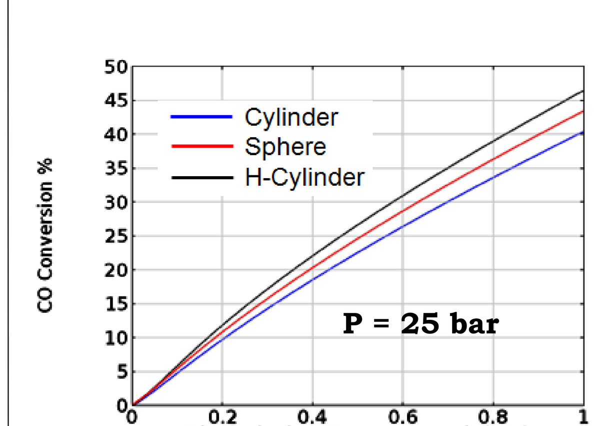


Shape	T_{max}	
	25 bar	30 bar
Cylinder	507 K	512 K
H-Cylinder	511 K	517 K
Sphere	509 K	511 K

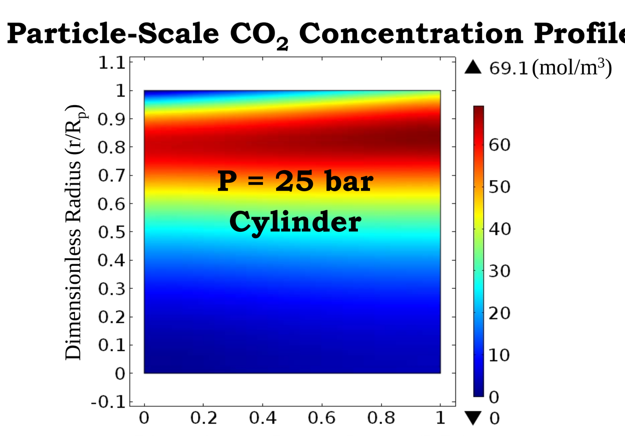


Axial Concentration Profiles

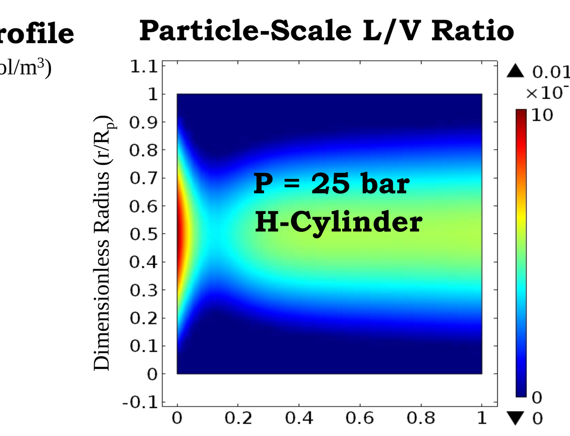




Particle-Scale CO_2 Concentration Profile



Particle-Scale L/V Ratio



- Specie concentration in the catalyst is a function of only the radial coordinate, *i.e.*, $C_i = C_i(r)$
- Steady-state
- All catalyst particle shapes have the same material properties (ε, τ, r, k_{eff})

- The porosity of the catalyst bed is constant
- The radial heat, and mass transfer is neglected
- The bulk concentration of species is a function of only the axial coordinate

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 and intra-particle liquid to vapor (L/V) fraction results suggest that hollow rings are preferred over spherical and cylindrical particle shapes, but the magnitude of the hot spot is greater for this shape. This may lead to a higher rate of catalyst deactivation, reduce the catalyst mechanical strength and generate unsafe reactor operating conditions.