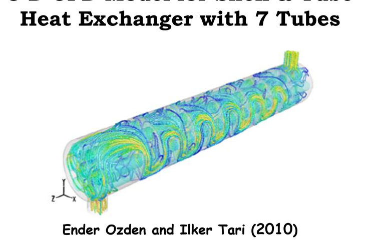
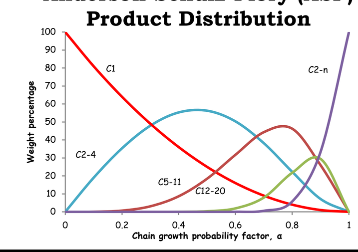
Diffusion and Reaction in Fe-Based Catalyst for Fischer-Tropsch Synthesis Using Micro Kinetic Rate Expressions

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



Ender Ozden and Ilker Tari (2010)

Anderson-Schulz-Flory (ASF) Product Distribution



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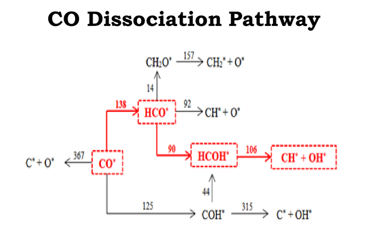
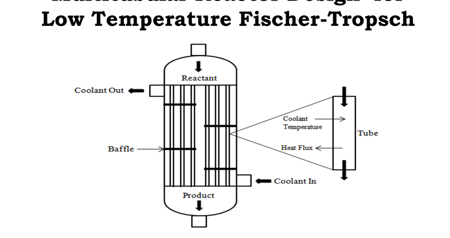
CO Dissociation Pathway



M. Ojeda et al. (2008)

Multitubular 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 MTFBR using COMSOL Multiphysics. This poster focuses on comparing the performance of various catalyst particle shapes by accounting for transport-kinetic interactions and thermodynamic phenomena using micro kinetic rate expressions.

Objectives

- Model the Fischer-Tropsch (FT) reaction network using micro-kinetic rate expressions and assess the role of catalyst particle shape and operating conditions (T, P, bulk gas composition) on the FT product distribution.
- Incorporate a Modified Soave-Redlich-Kwong (MSRK) equation of state (EOS) into the particle-scale transport-kinetics model to more accurately describe the vapor-liquid-equilibrium (VLE) behavior of the FT product distribution within the porous catalyst particle.

Kinetic and Thermodynamic Expressions

Fe-Based Olefin Re-adsorption Kinetics

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

$$R_{C_nH_{2n+2}} = \frac{k_5P_{H_2}\prod_{j=1}^{n}\alpha_j}{1+\left(1+\frac{1}{K_2K_3K_4}\frac{P_{H_2O}}{{P_{H_2}}^2}+\frac{1}{K_3K_4}\frac{1}{P_{H_2}}+\frac{1}{K_4}\right)\sum_{i=1}^{N}\left(\prod_{j=1}^{i}\alpha_J\right)}$$

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

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+}

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

$$\alpha_n = \frac{k_1P_{CO}}{k_1P_{CO}+k_5P_{H_2}+k_6(1-\beta_n)}$$

$$\beta_n = \frac{\frac{k_{-6}}{k_6}P_{C_nH_{2n}}}{\left[\alpha_A^{i-2}\frac{k_1P_{CO}}{k_1P_{CO}+k_5P_{H_2}}+\frac{k_{-6}}{k_1P_{CO}+k_5P_{H_2}+k_6}\sum_{i=2}^{n}\left(\alpha_A^{i-2}P_{C_{(n-i+2)}H_{2(n-i+2)}}\right)\right]}$$

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

where $n = 2$ to 20

Wang *et al.* (2008) D. A. Wood *et al.* (2012)

Modified Soave-Redlich-Kwong EOS

$$P_i = \frac{RT}{(V_i-b_i)}-\frac{\alpha_i a_i}{V_i(V_i+b_i)}$$

Cubic equation valid for FT product distribution

$${Z_i}^3-{Z_i}^2+Z_i(A_i-B_i-{B_i}^2)-A_iB_i$$

Wang *et al.* (2008)

$$A_i = \frac{a_iP_i}{R^2T^2} \qquad B_i = \frac{b_iP_i}{RT} \qquad a_i = 0.42747\frac{R^2{T_{ic}}^2}{P_{ic}}$$

$$b_i = 0.08664\frac{RT_{ic}}{P_{ic}} \qquad \alpha_i = \left(1+m_i\left(1-\sqrt{T_{ir}}\right)\right)^2$$

$$m_i = 0.48508+1.55171\omega_i-0.1561{\omega_i}^2$$

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

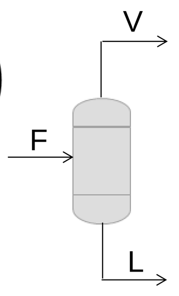
$$a_m = \sum_i\sum_j y_iy_j(a_ia_j)^{1/2}(1-k_{ij}) \qquad b_m = \sum_i y_ib_i$$

VLE Flash Calculations

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

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

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



Governing Equations and Boundary Conditions

General species balance: $\nabla.(-D_{ei}\nabla C_i) = \rho_p\sum_j\alpha_{ij}R_{ij}$

Species balance for spherical catalyst particle: $\frac{1}{\xi}\frac{\partial}{\partial\xi}\left(D_{ei}\xi\frac{\partial C_i}{\partial\xi}\right) = -\rho_p{R_p}^2\sum_j\alpha_{ij}R_{ij}$, where $\xi = r/R_p$

Species balance for cylindrical catalyst particle: $\frac{1}{\xi}\frac{\partial}{\partial\xi}\left(D_{ei}\xi\frac{\partial C_i}{\partial\xi}\right) = -\rho_p{R_p}^2\sum_j\alpha_{ij}R_{ij}$, where $\xi = r/R_p$

Species balance for ring catalyst particle: $\frac{1}{(\xi\delta+R_i)}\frac{\partial}{\partial\xi}\left((\xi\delta+R_i)D_{ei}\frac{\partial C_i}{\partial\xi}\right) = -\rho_p\delta^2\sum_j\alpha_{ij}R_{ij}$, where $\xi = (r-R_i)/(R_o-R_i)$ and $\delta = R_o-R_i$

Effective diffusivity, $D_{ei} = \frac{\varepsilon D_{iB}}{\tau}$ (ε = catalyst porosity and τ = catalyst tortuosity)

$$D_{CO,B} = 5.584*10^{-7}e^{\left(\frac{-1786.29}{T}\right)}$$

$$D_{H_2,B} = 1.085*10^{-6}e^{\left(\frac{-1624.63}{T}\right)}$$

$$D_{CO_2,B} = 3.449*10^{-7}e^{\left(\frac{-1613.65}{T}\right)}$$

Molecular Diffusivities of the hydrocarbons in wax, $D_{i,B} = D_{CO,B}\left(\frac{V_{CO}}{V_i}\right)^{0.6}$

Species Flux

- Independent of composition C_i
- Dependent on local temperature T
- Future work: Use multicomponent flux transport models

Key Assumptions

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

ii. Steady-state

iii. All catalyst particle shapes have the same material properties (ε, τ, ρ, k_{eff})

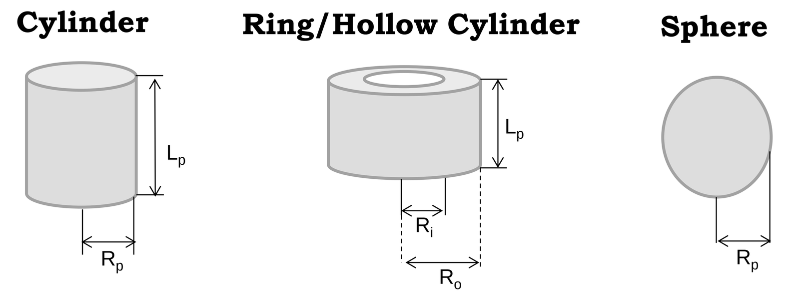
iv. Isothermal conditions (since ΔT is small)

v. Bulk gas phase contains only H_2 and CO (Reactor entrance conditions)

Boundary Conditions

Spherical Particle	At ξ = -1 and ξ = 1, $C_i = C_{i,bulk}$ ($CO_{2,bulk}$ = eps for convergence)
Cylindrical Particle	At ξ = -1 and ξ = 1, $C_i = C_{i,bulk}$ ($CO_{2,bulk}$ = eps for convergence)
Ring Particle	At ξ = 0 and ξ = 1, $C_i = C_{i,bulk}$ ($CO_{2,bulk}$ = eps for convergence)

Catalyst Particle Shapes, Catalyst Properties and Process Conditions



$$\text{Volume}_{sphere} = \text{Volume}_{cylinder} = \text{Volume}_{ring}$$

$$(4/3)\,R^3_{sphere} = L_{cylinder}R^2_{cylinder} = L_{ring}(R^2_o-R^2_i)$$

Dimensions of Cylinder and Ring for R_{sphere} = 1.5 mm

Cylinder	L = 3 mm & R = 1 mm
Ring	L = 2 mm, R_o=1.5 mm & R_i=0.3 mm

Dimensions of Cylinder and Ring for R_{sphere} = 1 mm

Cylinder	L = 3 mm & R = 0.7mm
Ring	L = 2 mm, R_o=1.5 mm & R_i=1 mm

Catalyst Properties

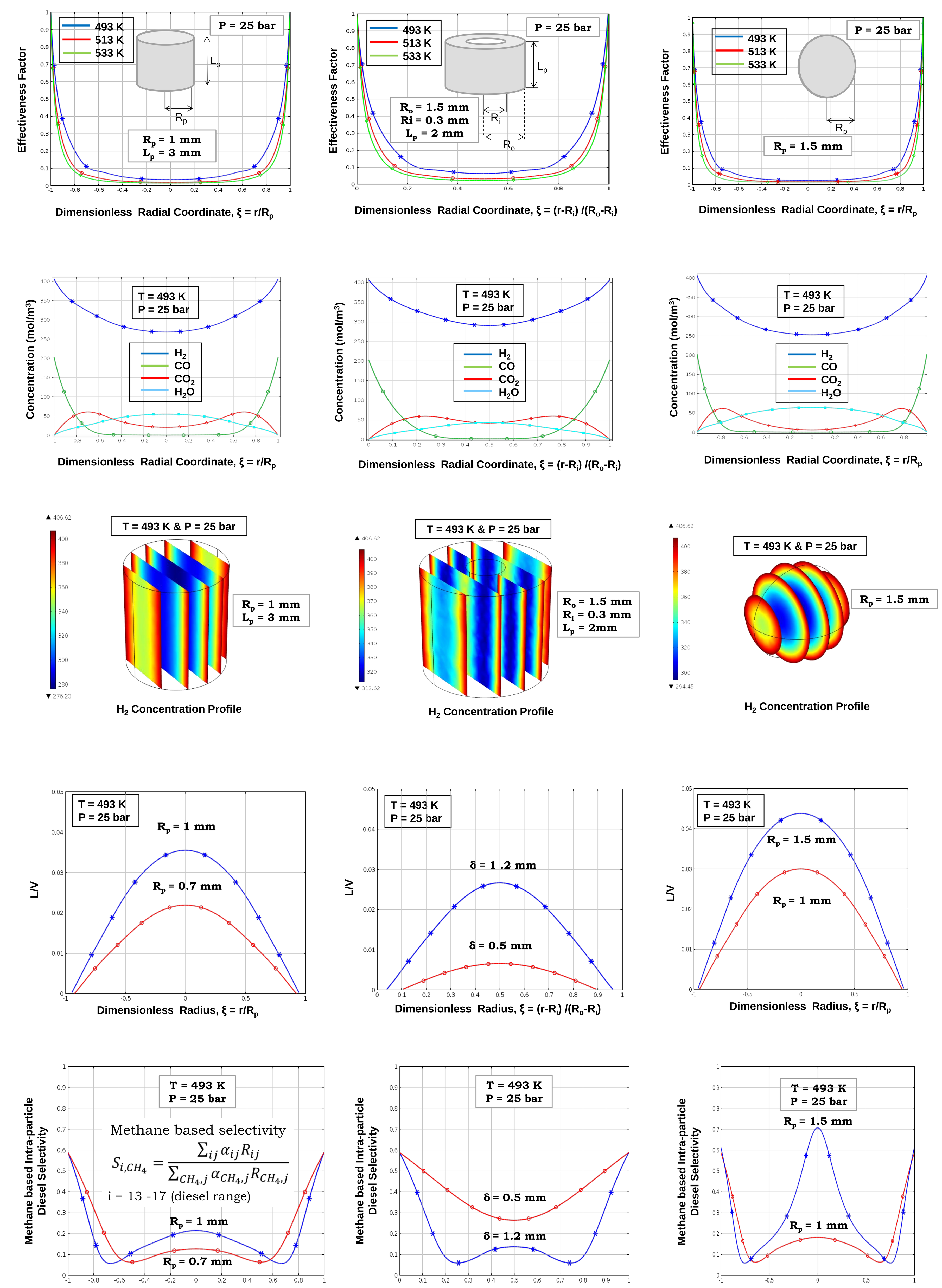
Density of pellet, ρ_p	1.95 x 10⁶ (gm/m³)
Porosity of pellet, ε	0.51
Tortuosity, τ	2.6

Operating Conditions

Temperature, °K	493, 523 & 533
Pressure, bar	20, 25 & 30
H_2/CO	2

Results

Solid Cylinder | Ring/Hollow Cylinder | Sphere



Conclusions

- A 1-D catalyst pellet model can be used to analyze particle-level performance. Catalyst performance on a reactor-scale can be studied by coupling the pellet model to the tube & shell-side models for the MTFBR.
- The CO conversion, effectiveness factor, intra-particle liquid to vapor (L/V) fraction and the diesel selectivity results suggest that the cylindrical and spherical catalyst particle shapes are preferred over hollow rings. The presence of more liquid in the spherical particle creates an advantage for the cylindrical catalyst shape due to diffusional limitations in the wax.
- 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.
- Convergence can be a major issue in fast reaction-diffusion systems. This can sometimes be easily resolved by using simple built-in operators, such as '*if* ()' and '*eps*', to avoid negative and other unrealistic values of dependent variables at the boundaries or interior and then refining the mesh in accordance with computational time.

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