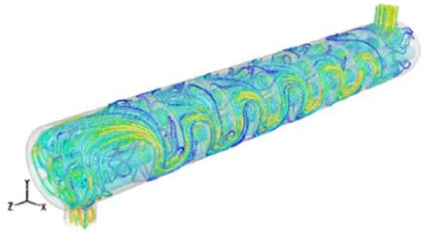
Diffusion and Reaction in Fe-Based Catalyst for Fischer-Tropsch Synthesis Using Micro Kinetic Rate Expressions

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



Ender Ozden and Ilker Tari (2010)

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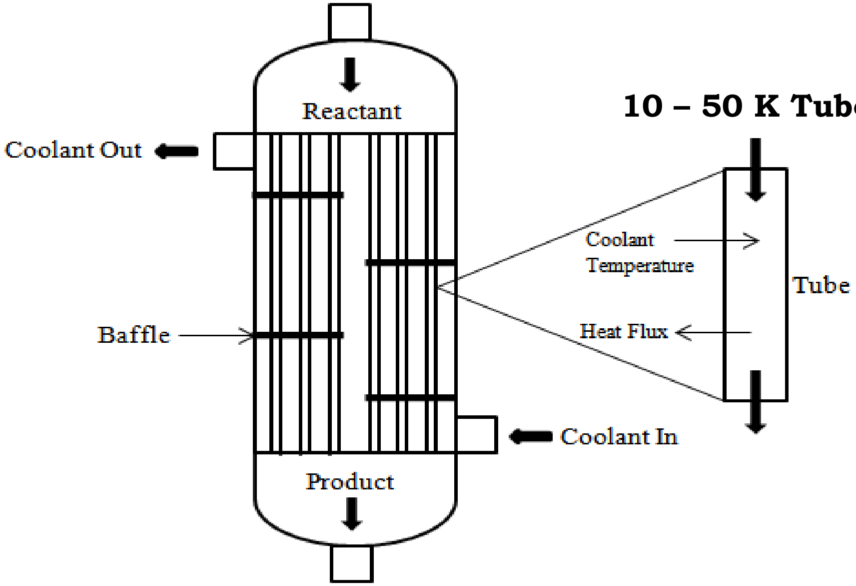
Kingsville, TX 78363-8202 USA

***Patrick.Mills@tamuk.edu**

Multitubular Reactor Design for Low Temperature Fischer-Tropsch



COMSOL CONFERENCE 2014 BOSTON

Session: Transport Phenomena

October 9, 2014

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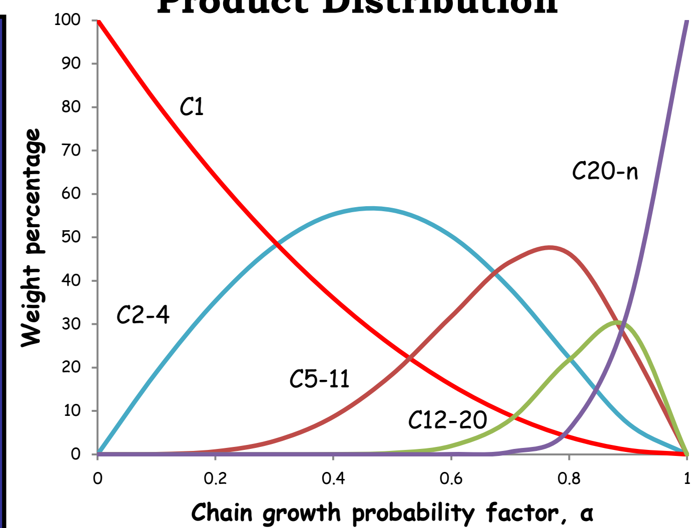
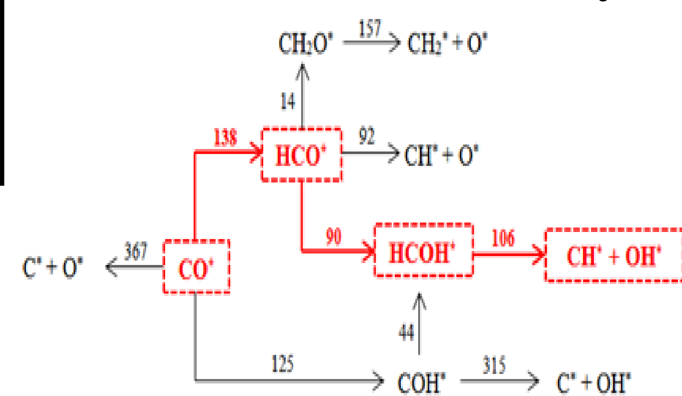
Presentation Outline

- Introduction
- Objectives
- F-T Chemistry, Kinetics & Thermo
- Multiphysics Model Equations
- Key Results
  - Catalyst Performance
  - Concentration Profiles
  - Computational Difficulties
- Conclusions

Anderson-Schulz-Flory (ASF) Product Distribution



CO Dissociation Pathway



M. Ojeda *et al.* (2008)

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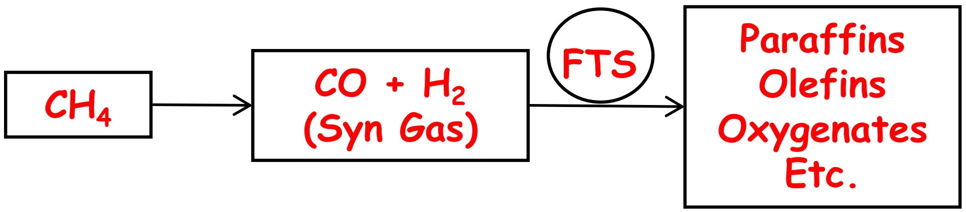
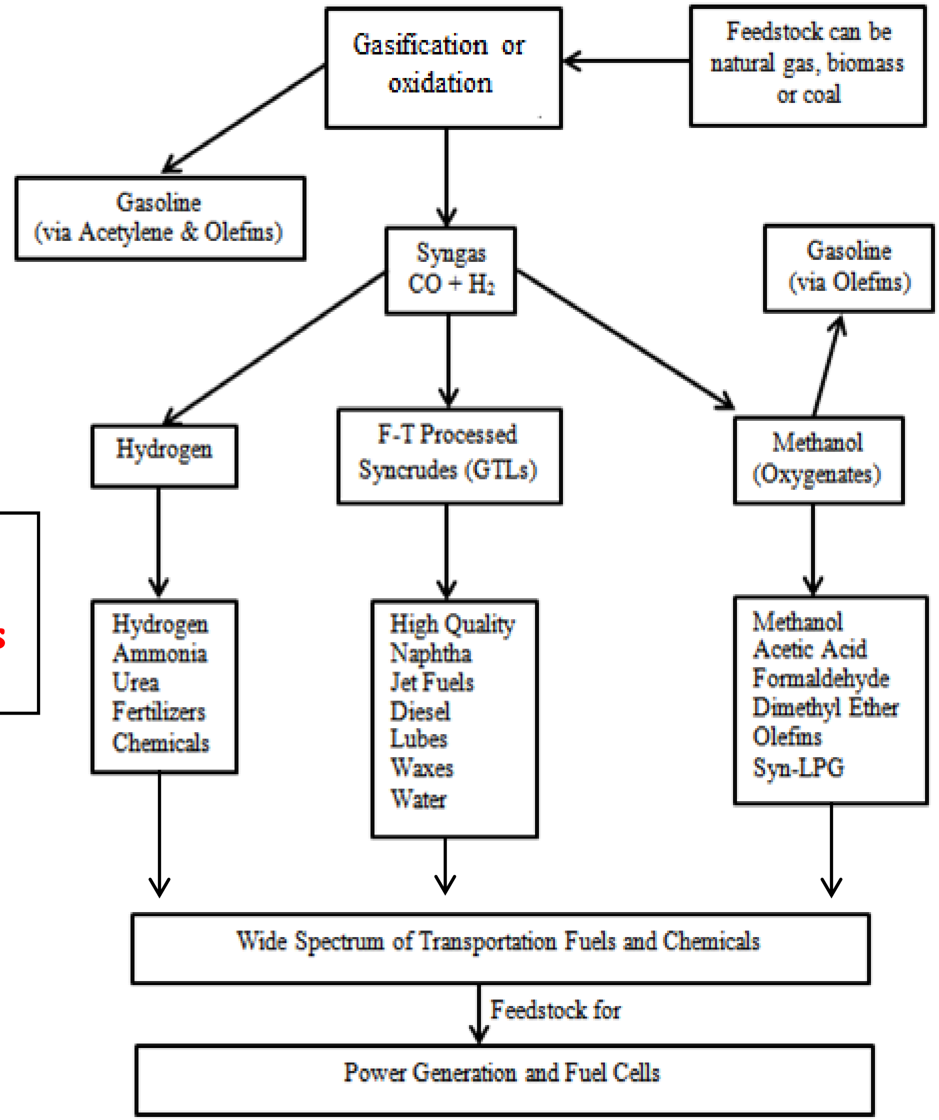
Introduction

- 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*



  - Standard large-scale gas conversion
  - Isolated "Stranded gas" conversion

$$n\,CO + 2n\,H_2 \longrightarrow -(CH_2)_n- + n\,H_2O$$



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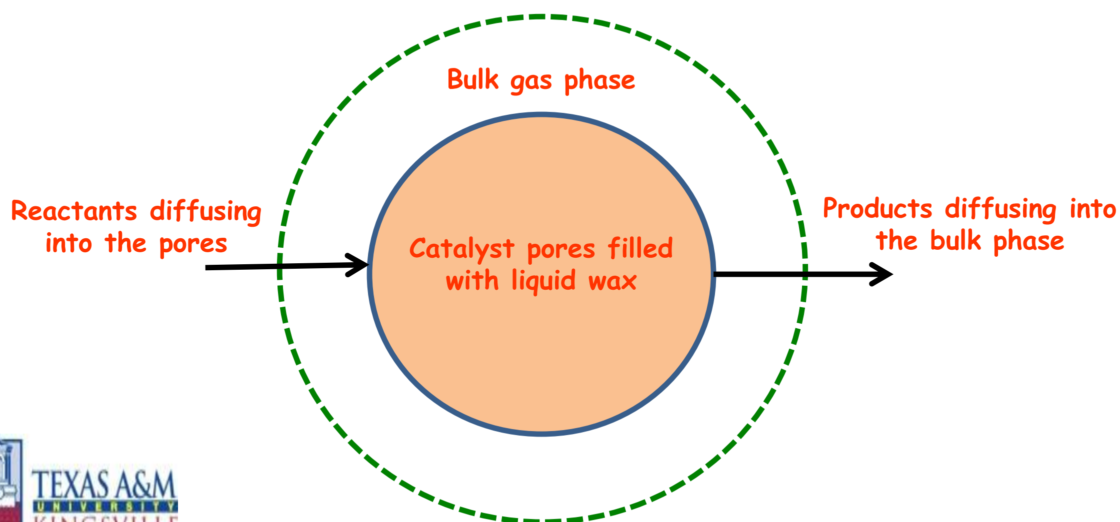
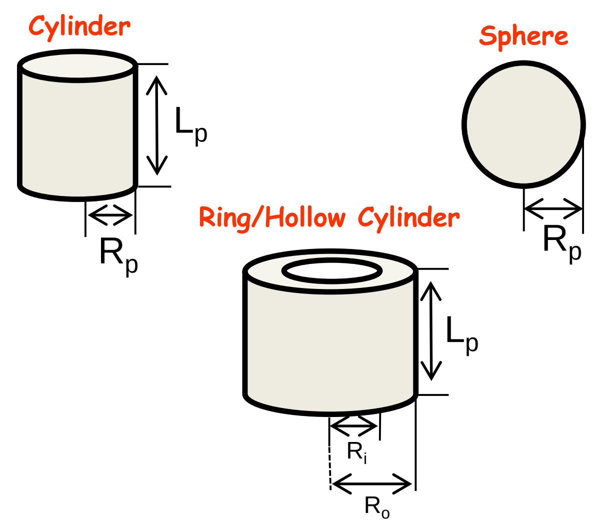
David A. Wood, Chikezie Nwaoha, & Brian F. Towler, *Journal of Natural Gas Science and Engineering* (2012)

Objectives

- Model the Fischer-Tropsch (FT) reaction network
  - Implement micro-kinetic rate expressions
  - Assess the effect of process parameters on the FT product distribution
    i. Catalyst particle shape
    ii. Operating conditions (T, P)

- Incorporate Soave-Redlich-Kwong (SRK) 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.





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Key F-T Catalytic Reactions

	Main Reactions	
1	Methane	$CO + 3H_2 \rightarrow CH_4 + H_2O$
2	Paraffins	$(2n+2)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$
3	Olefins	$2n\ H_2 + n\ CO \rightarrow C_nH_{2n} + n\ H_2O$
4	WGS (only on Fe catalyst)	$CO + H_2O \leftrightarrow CO_2 + H_2$
	Side Reactions	
5	Alcohols	$2n\ H_2 + n\ CO \rightarrow C_nH_{2n+1}\ O + n\ H_2O$
6	Boudouard Reaction	$2CO \rightarrow C + CO_2$
	Catalyst Modifications	
7	Catalyst Oxidation/Reduction	(a) $M_xO_y + y\ H_2 \rightarrow y\ H_2O + x\ M$ (b) $M_xO_y + y\ CO \rightarrow y\ CO_2 + x\ M$
8	Bulk Carbide Formation	$y\ C + x\ M \rightarrow M_xC_y$

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+}

David A. Wood, Chikezie Nwaoha, & Brian F. Towler, *Journal of Natural Gas Science and Engineering* (2012)

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Fischer-Tropsch Micro-kinetic Rates

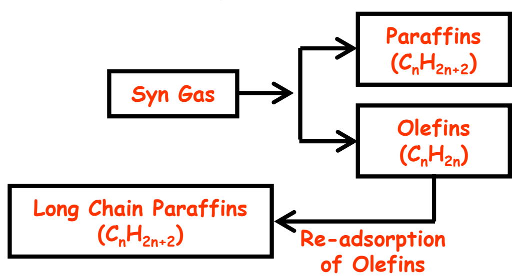
Fe-Based Olefin Readsorption Microkinetic Model

$$R_{CH_4} = \frac{k_{5M} P_{H_2} \alpha_1}{1 + \left(1 + \frac{1}{K_2 K_3 K_4} \frac{P_{H_2O}}{P_{H_2}{}^2} + \frac{1}{K_3 K_4} \frac{1}{P_{H_2}} + \frac{1}{K_4}\right) \sum_{\mathrm{i}=1}^{N} \left(\prod_{\mathrm{j}=1}^{i} \alpha_j\right)}$$

$$R_{C_n H_{2n+2}} = \frac{k_5 P_{H_2} \prod_{\mathrm{j}=1}^{n} \alpha_j}{1 + \left(1 + \frac{1}{K_2 K_3 K_4} \frac{P_{H_2O}}{P_{H_2}{}^2} + \frac{1}{K_3 K_4} \frac{1}{P_{H_2}} + \frac{1}{K_4}\right) \sum_{\mathrm{i}=1}^{N} \left(\prod_{\mathrm{j}=1}^{i} \alpha_j\right)}$$

$$R_{C_n H_{2n}} = \frac{k_6 (1 - \beta_n) \prod_{\mathrm{j}=1}^{n} \alpha_j}{1 + \left(1 + \frac{1}{K_2 K_3 K_4} \frac{P_{H_2O}}{P_{H_2}{}^2} + \frac{1}{K_3 K_4} \frac{1}{P_{H_2}} + \frac{1}{K_4}\right) \sum_{\mathrm{i}=1}^{N} \left(\prod_{\mathrm{j}=1}^{i} \alpha_j\right)}$$

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



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

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

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

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

n = 2 to 20

Wang *et al.*, *Fuels* (2003)

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Thermodynamics of F-T Reaction Mixtures

Soave-Redlich-Kwong (SRK) EOS

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

$$Z_i^3 - Z_i^2 + Z_i(A_i - B_i - B_i^2) - A_i B_i$$

$$A_i = \frac{a_i P_i}{R^2 T^2} \qquad a_i = 0.42747 \frac{R^2 T_{ic}^2}{P_{ic}}$$

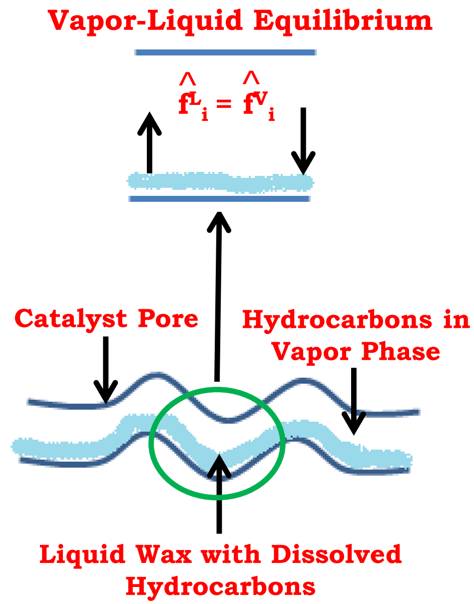
$$B_i = \frac{b_i P_i}{RT} \qquad b_i = 0.08664 \frac{R T_{ic}}{P_{ic}}$$

$$\alpha_i = \left(1 + m_i\left(1 - \sqrt{T_{ir}}\right)\right)^2$$

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

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

$$a_m = \sum_i \sum_j y_i y_j (a_i a_j)^{1/2}(1 - k_{ij}) \qquad b_m = \sum_i y_i b_i$$



Flash Calculations

Rachford-Rice Objective Function

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

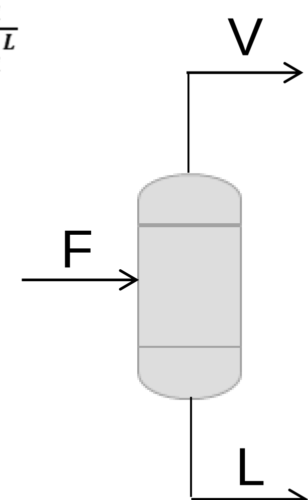
i = 1 to 43 with 43 distinct roots

> **Only the positive roots less than 1 are used for VLE calculations**

Wilson's Correlation

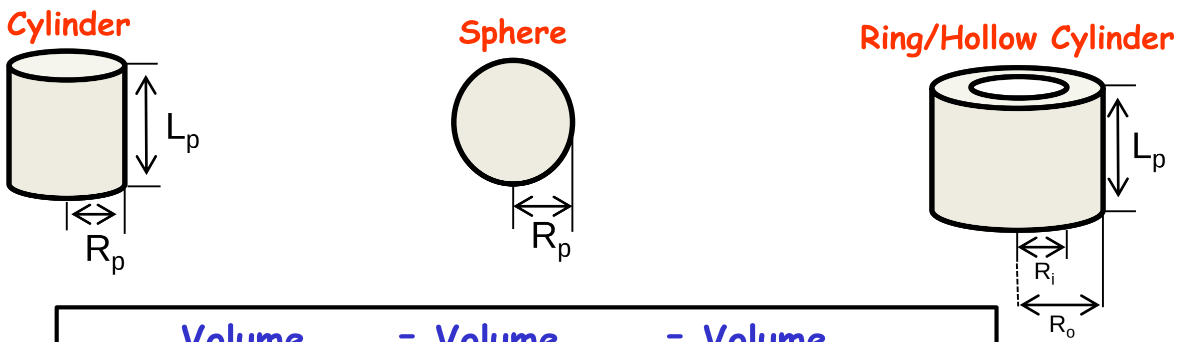
$$K_i^{guess\ value} = \frac{P_{ic}}{P}\exp\left(5.37(1 + \omega_i)\left(1 - \frac{T_{ic}}{T}\right)\right)$$

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



Wang *et al.*, *Fuels* (1999)

Catalyst Properties & Process Conditions



$$Volume_{sphere} = Volume_{cylinder} = Volume_{ring}$$

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

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

Catalyst Properties

Density of pellet, ρ_p	1.95×10^6 (gm/m^3)
Porosity of pellet, ε	0.51
Tortuosity, τ	2.6

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

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

Operating Conditions

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

Governing Multiphysics Model Equations

43 species and 43 reactions

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

Species Balance for Spherical Catalyst Particle:

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

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, $\xi = (r-R_i)/(R_o-R_i)$ & $\delta = R_o-R_i$

Effective Diffusivity: $D_{ei} = \frac{\varepsilon D_{iB}}{\tau}$ (ε = porosity and τ = 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 Hydrocarbons in Wax

$$D_{i,B} = D_{CO,B}\left(\frac{V_{CO}}{V_i}\right)^{0.6}$$

V = molar volume

Model Assumptions & Boundary Conditions

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Boundary Conditions

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

Species Flux

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

COMSOL Modules

- Transport of Diluted Species
- Coefficient Form PDE Solver

Key Assumptions

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

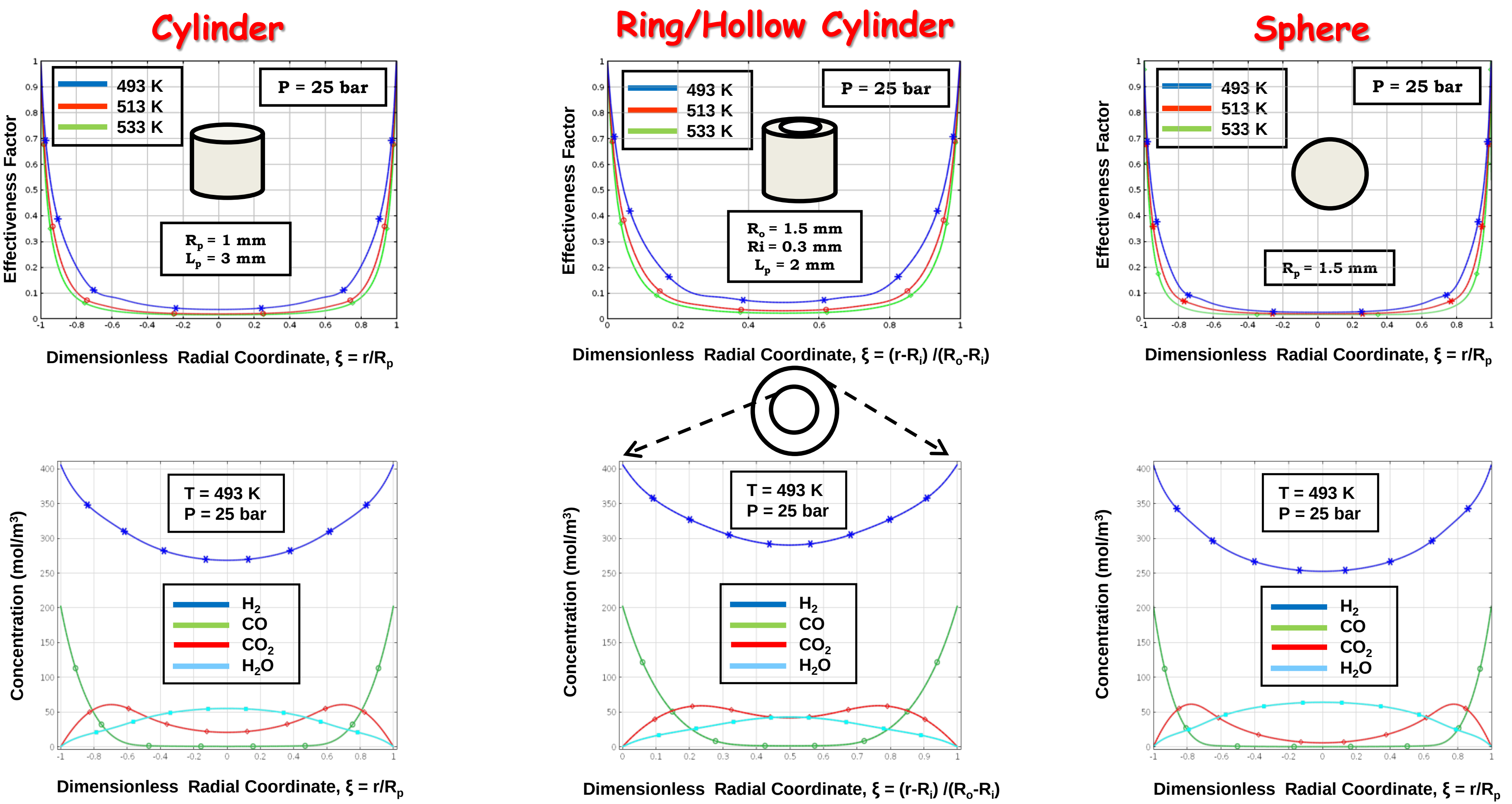
ii. Steady-state

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)

Various Catalyst Shapes: η & C_i Profiles



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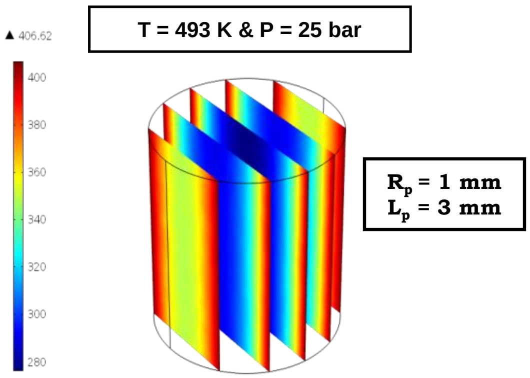
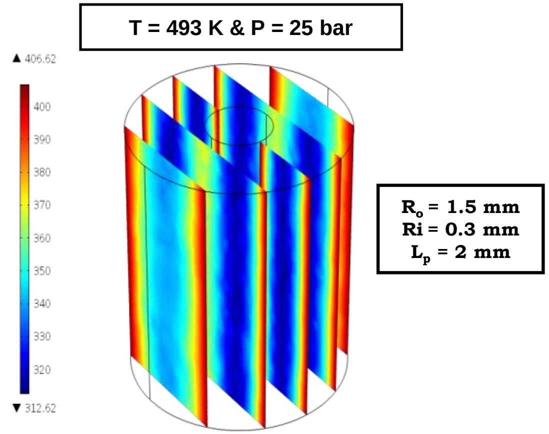
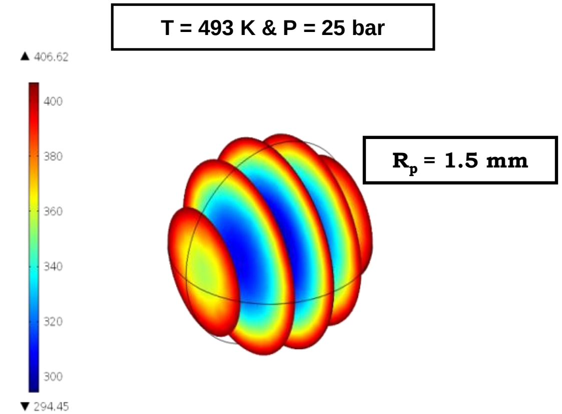


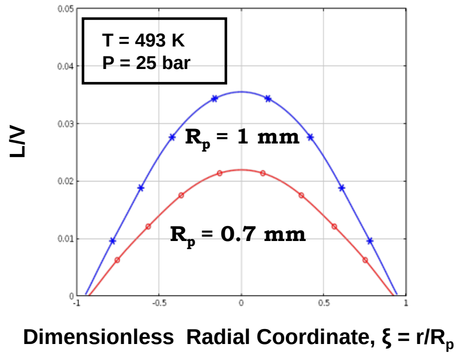
H_2 Concentration Profile

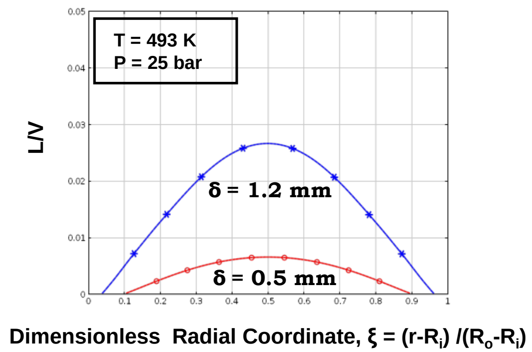


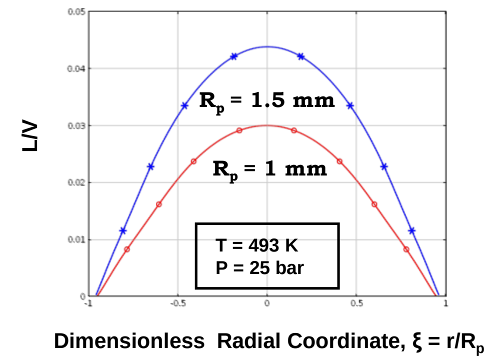
H_2 Concentration Profile

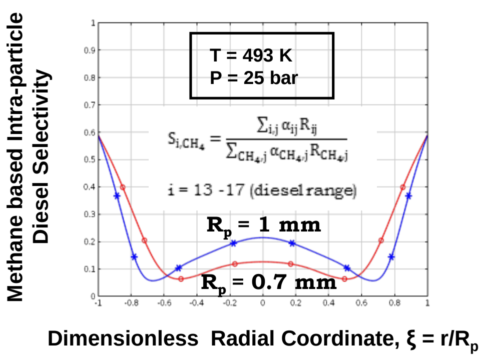


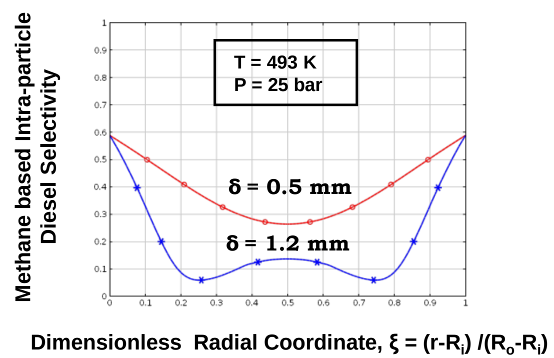
H_2 Concentration Profile

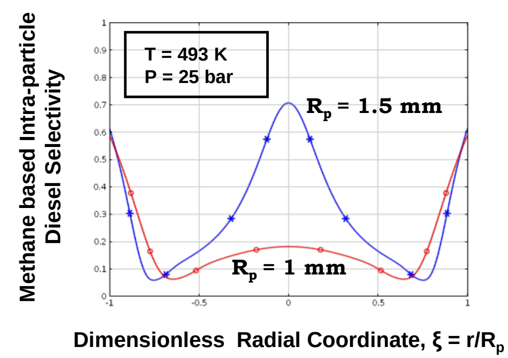




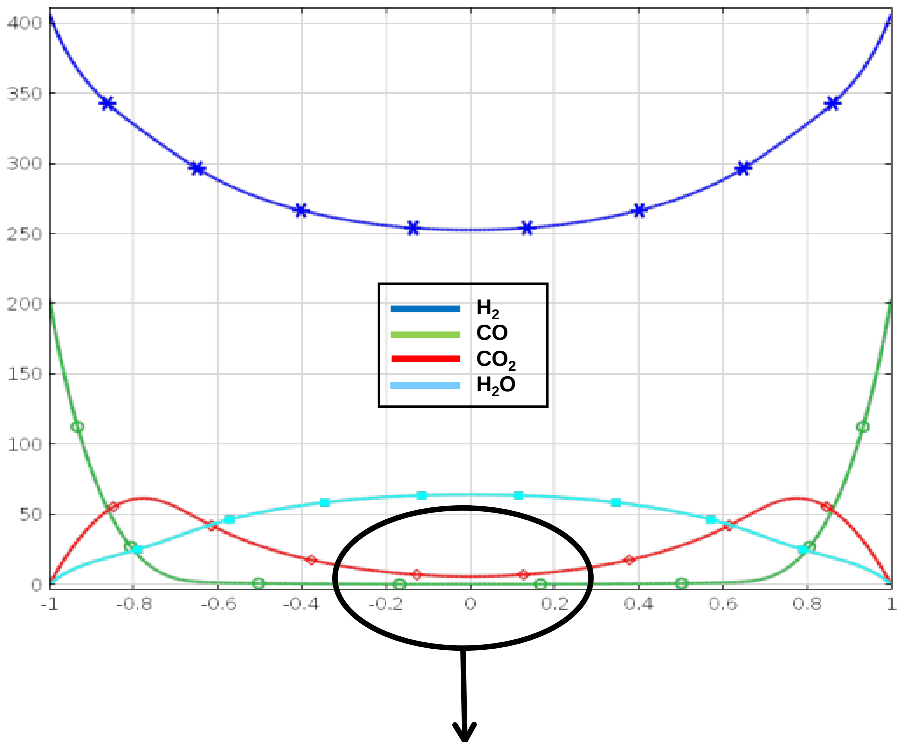








Computational Issues



Region with numerical instabilities

Once the convergence issue was solved the mesh was refined to get smooth curves.

- To avoid convergence issues, the radius of the particle was set to a very small number and the subsequent solution was stored to be used as initial conditions for higher radius.
- Numerical instabilities were encountered in the region where CO and CO_2 concentrations approached zero leading to convergence issues and unrealistic values.
- The convergence issues were solved by not letting CO and CO_2 concentrations approach zero by using $CO=if(CO\leq 0,eps,CO)$ and $CO_2=if(CO_2\leq 0,eps,CO)$.

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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, catalyst strength 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.

Thank You

References

[1] D. A. Wood, C. Nwaoha and B. F. Towler, "Gas-to-Liquids (GTL): A Review of an Industry Offering Several Routes for monitizing Natural Gas," vol. 9, 2012.

[2] O. O. James, B. Chowdhury, M. Adediran Mesubi and S. Maity, "Reflections on the Chemistry of the Fischer-Tropsch Synthesis," vol. 2, no. 19, 2012.

[3] A. Lecarpentier and D. Favreau, "Natural Gas in the World," CEDIGAZ, 2011.

[4] IEA, "Golden Rules for a Golden Age of Gas," International Energy Agency, 2012.

[5] D. A. Wood, S. Mokhatab and M. J. Economides, "Technology Options for Securing Markets for Remote Gas," in Proceedings of 87th Annual Convention of the Gas Processors Association, Grapevine, 2008.

[6] P. Samuel, "GTL Technology - Challenges and Opportunities in Catalysis," Catalysis Society of India 2, pp. 82-99, 2003.

[7] R. Tillerson, "Leading the Way," Fyndamentals of Gas to Liquids, p. 53, June 2005.

[8] A. Buchanan, "Reaching New Energy Frontiers Through Competitive GTL Technology," in SASOL Synfuels International, 2006.

[9] OPEC, "World Oil Outlook," Organization of Petroleum Exporting Countries, 2012.

[10] B. C. Enger, R. Lodeng and A. Holmen, "A Review of Catalytic Partial Oxidation of Methane to Synthesis Gas with Emphasis on Reaction Mechanisms Over Transition Metal Catalyst," vol. 346, 2008.

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References (cont'd)

[11] H. A. J. v. Dijk, "The Fischer-Tropsch Synthesis: A Mechanistic Study Using Transient Isotopic Tracing (PhD dissertation)," Eindhoven University of Technology, 2001.

[12] A. A. Adesoji, "Hydrocarbon Synthesis via Fischer-Tropsch Reaction: Travails and Triumphs," Applied Catalysis A: General, pp. 345-367, 1996.

[13] R. B. Anderson, The Fischer-Tropsch Synthesis, Orlando, Florida: Academic Press Inc, 1984.

[14] H. Schulz, "Short History and present trends of Fischer-Tropsch Synthesis," Applied Catalysis A: General, pp. 3-12, 1999.

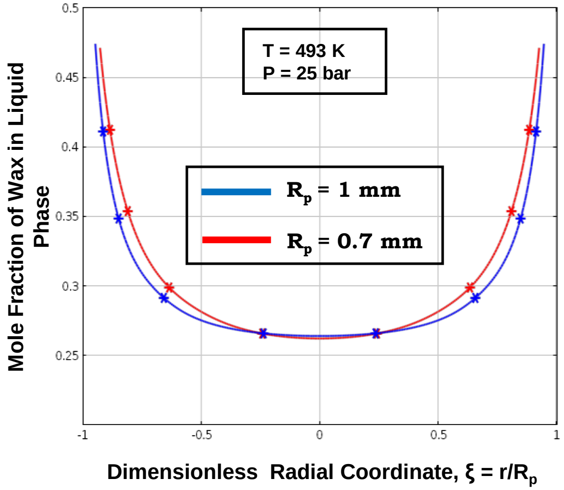
[15] J. M. Bucher, "The Effect of Interference Techniques on Fischer-Tropsch Product Distribution (PhD dissertation)," University of Michigan, 2010.

[16] M. E. Dry, "The Fischer-Tropsch Process - Commercial Aspects," Catalysis Today, pp. 183-206, 1990.

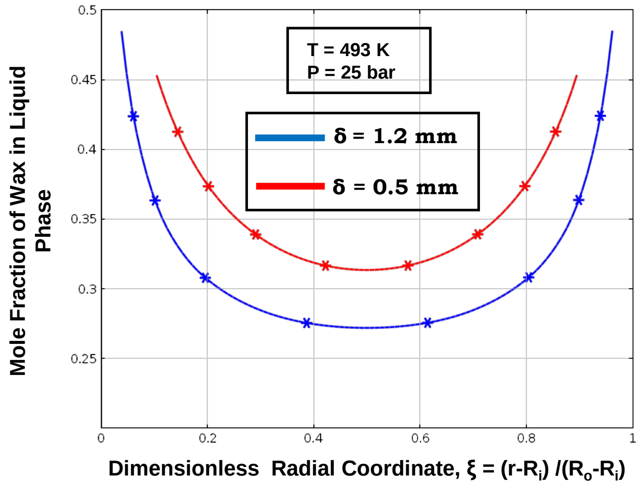
[17] J. Eilers, S. A. Posthuma and S. T. Sie, "The SHELL Middle Distillate Synthesis Process (SMDS),"

Mole Fraction of Wax & Diesel in Liquid Phase

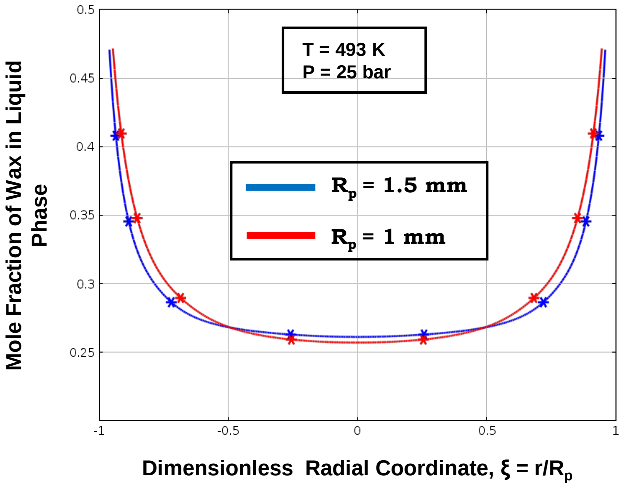
Cylinder

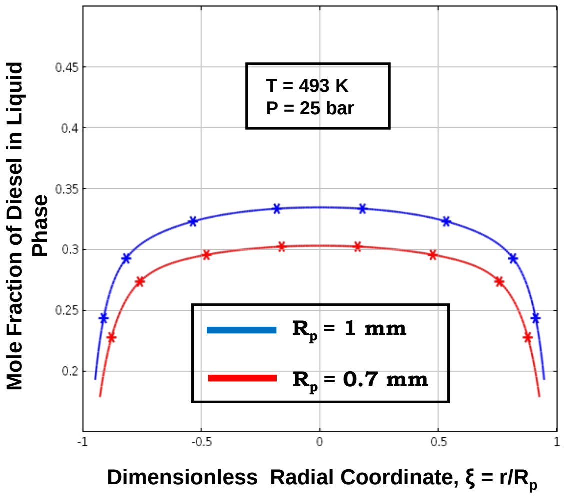


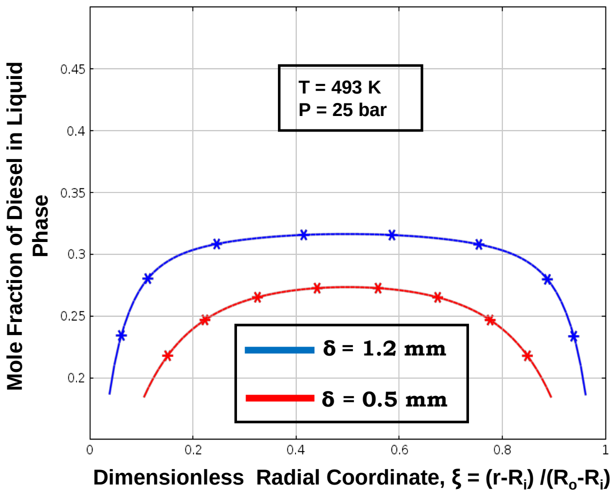
Ring/Hollow Cylinder

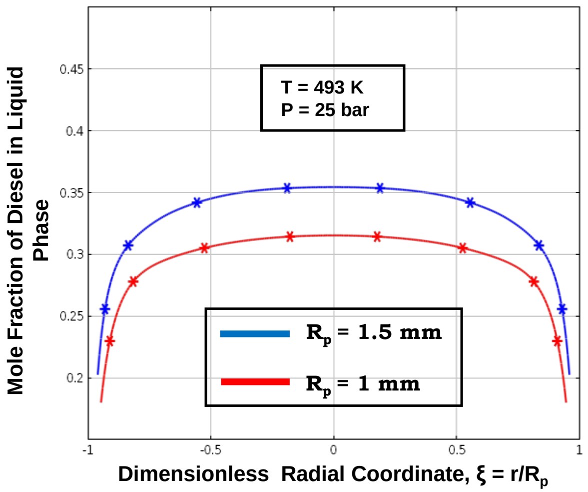


Sphere



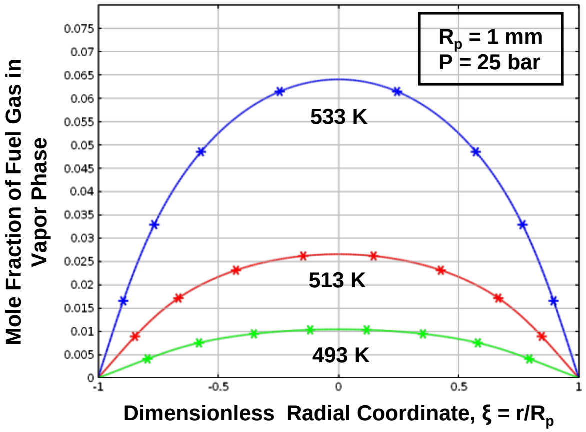




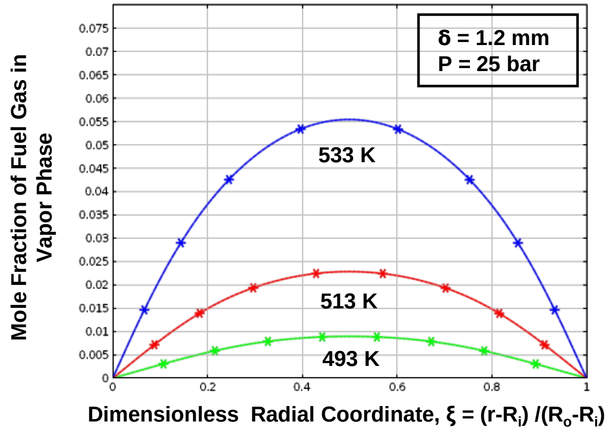


Mole Fraction of Fuel Gas in Vapor Phase

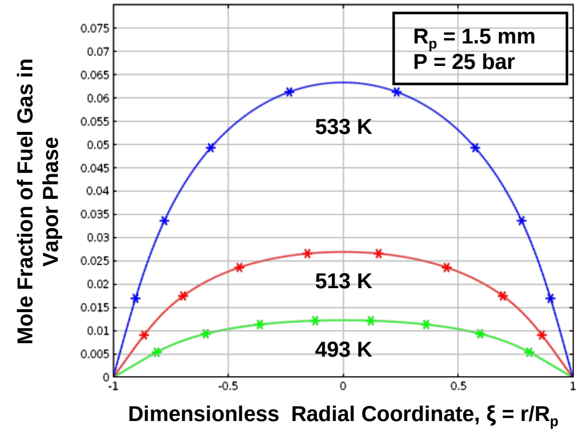
Cylinder



Ring/Hollow Cylinder



Sphere



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