Comparison of Diffusion Flux Models for Fischer-Tropsch Synthesis

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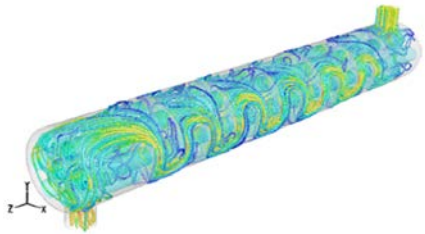
3-D CFD Model for Shell & Tube Exchanger with 7 Tubes



Ender Ozden and Ilker Tari (2010)

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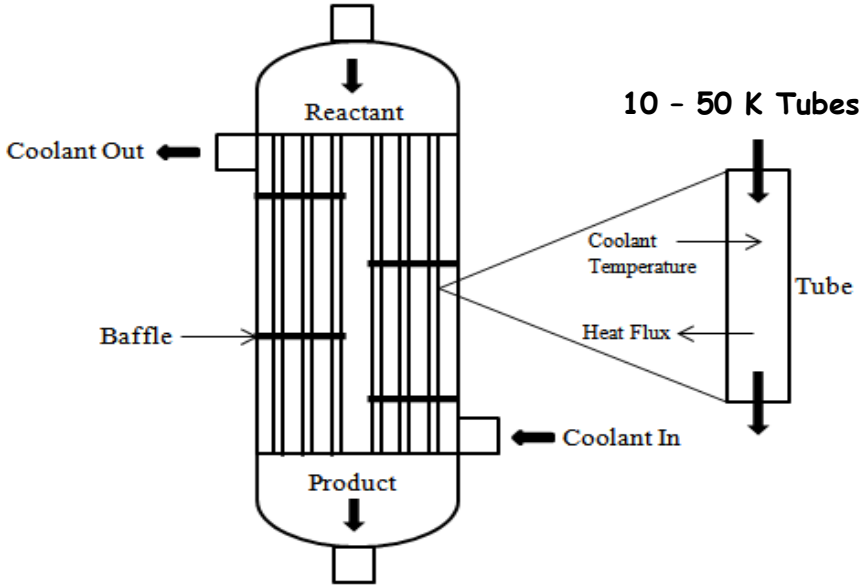
Multitubular Reactor Design for Low Temperature Fischer-Tropsch



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Session: Multiphysics Modeling for Reactor Engineering

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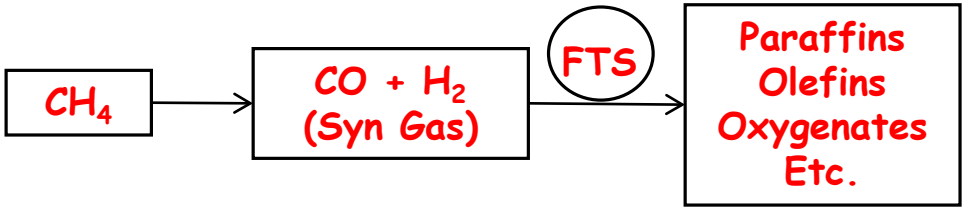
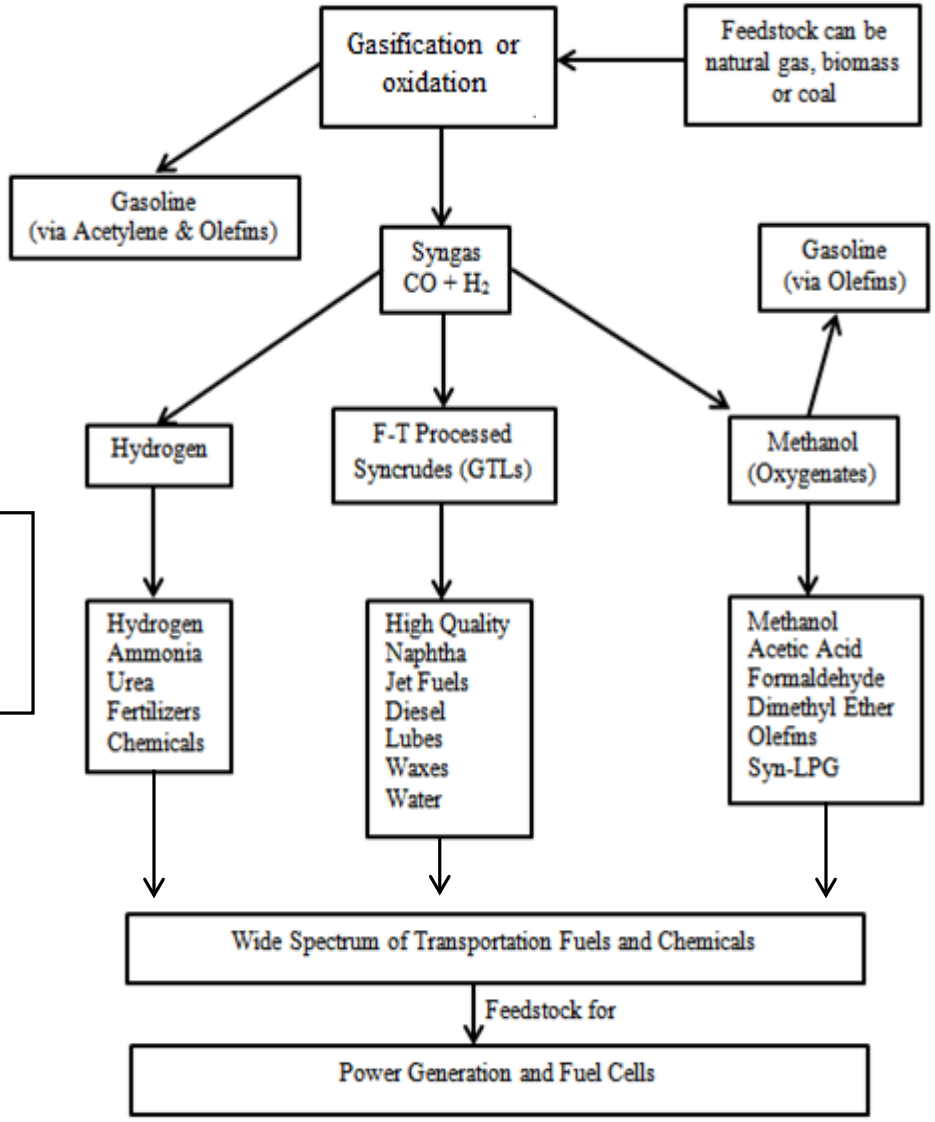
Introduction

- 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

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



David A. Wood, Chikezie Nwaoha, Brian F. Towler (2012)

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 (2012)

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F-T Kinetics Expressions

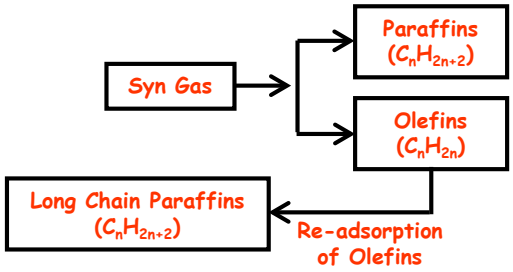
Fe-Based Olefin Re-adsorption Microkinetic Model

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

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

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

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



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

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

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

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

n = 2 to 20

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

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F-T Thermodynamic Expressions

Soave-Redlich-Kwong (SRK) EOS

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

$$Z_i{}^3 - Z_i{}^2 + Z_i\left(A_i - B_i - B_i{}^2\right) - A_i B_i$$

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

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

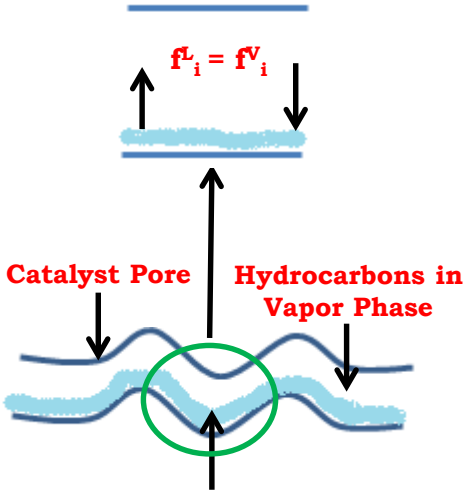
$$\alpha_i = \left(1 + m_i\left(1 - \sqrt{T_{ir}}\right)\right)^2$$

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

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

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

Vapor-Liquid Equilibrium



Flash Calculations

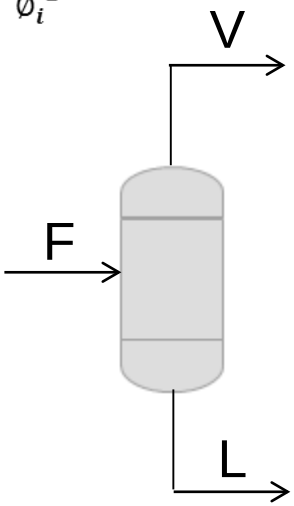
Rachford-Rice Objective Function

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

Wilson's Correlation

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

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



Wang *et al.* (2008)

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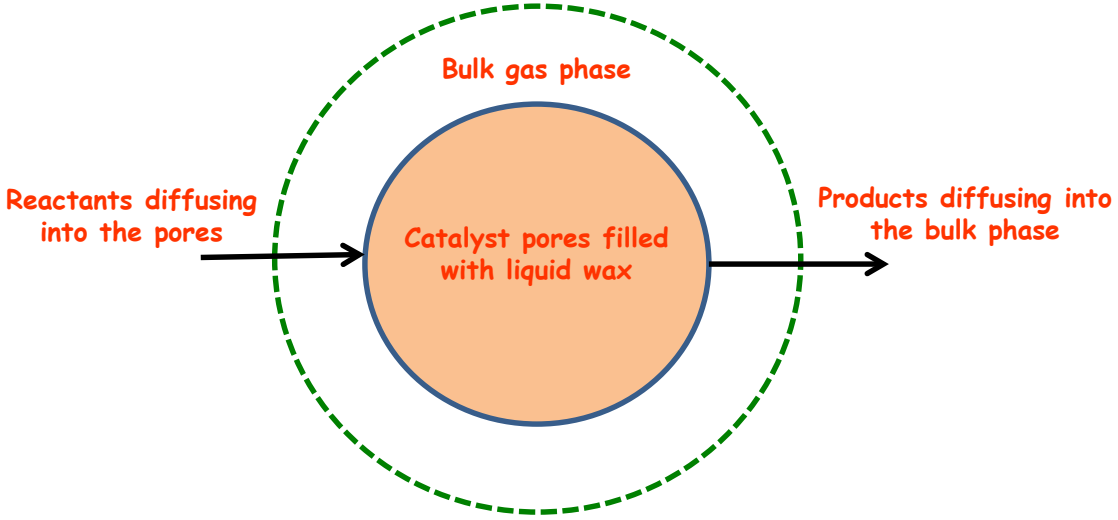
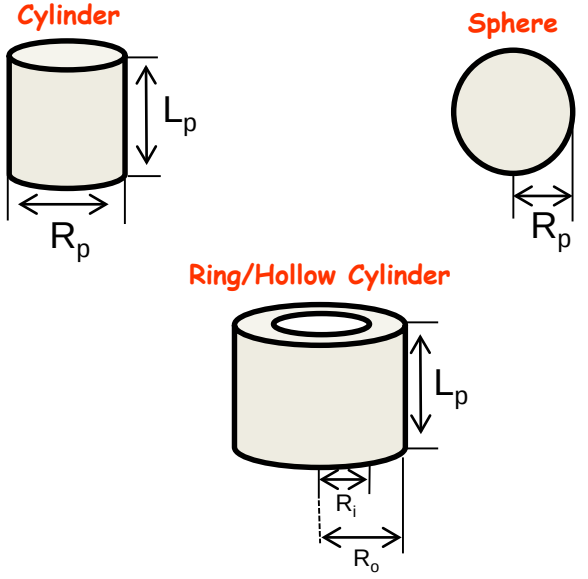
Objectives

- Compare the effect of various flux models on the FT hydrocarbon product distribution for a spherical catalyst shape under isothermal conditions.
- Assess the role of mean pore diameter on the FT hydrocarbon product distribution when both Knudsen and molecular diffusion are included





Governing Equations, Catalyst Properties & Operating Conditions

Dimensionless Specie Balance for Spherical Pellet:

$$\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(D_{ei}\xi^2\frac{\partial C_i}{\partial \xi}\right) = -\rho_p {R_p}^2 \sum_{j}^{44}\sum_{i}^{43}\alpha_{ij}R_{ij}$$

Wang Diffusion Flux (temperature based correlations):

$$N_i = -D_{ei}\nabla C_i \qquad D_{ei} = \frac{\varepsilon D_{i,B}}{\tau} \qquad D_{i,B} = D_{CO,B}\left(\frac{V_{CO}}{V_i}\right)^{0.6} \qquad D_{CO,B} = 5.584 * 10^{-7} e^{-\frac{1786.29}{T}}$$

$$D_{H_2,B} = 1.085 * 10^{-6} e^{-\frac{1624.63}{T}} \qquad D_{CO_2,B} = 3.449 * 10^{-7} e^{-\frac{1613.65}{T}}$$

Wilke Model:

$$N_i = -D_{im}\nabla C_i \qquad D_{im} = \frac{1 - x_i}{\sum_{j=1,j\neq i}^{n}\frac{x_j}{\widetilde{D_{ij}}}} \qquad \widetilde{D_{ij}} = \frac{0.00266T^{\frac{3}{2}}}{PM_{ij}^{\frac{1}{2}}\sigma_{ij}^{2}\Omega_{D,ij}}$$

Wilke-Bosanquet Model:

$$N_i = -D_{i,eff}\nabla C_i \qquad \frac{1}{D_{i,eff}} = \frac{1}{D_{im}} + \frac{1}{D_{ik}}$$

Maxwell-Stefan Model:

$$N_i = \frac{-\nabla C_i + \sum_{j=1,j\neq i}^{n}\frac{x_i N_j}{\widetilde{D_{ij}}}}{\sum_{j=1,j\neq i}^{n}\frac{x_j}{\widetilde{D_{ij}}}}$$

Dusty-Gas Model:

$$N_i = \frac{-\nabla C_i + \sum_{j=1,j\neq i}^{n}\frac{x_i N_j}{\widetilde{D_{ij}}}}{\sum_{j=1,j\neq i}^{n}\frac{x_j}{\widetilde{D_{ij}}} + \frac{1}{D_{ik}}} \qquad D_{ik} = \frac{2\varepsilon a}{3\tau}\sqrt{\frac{8RT}{\pi M_i}}$$

a = mean pore diameter = 25 nm

Catalyst Properties

Density of pellet, ρ_p	1.95 x 10^6 (gm/m^3)
Porosity of pellet, ε	0.51
Tortuosity, τ	2.6
Sphere radius, r_p	1.5 mm

Operating Conditions

Temperature, °K	493
Pressure, bar	25
H_2/CO	2

Wang *et al.* (2003)

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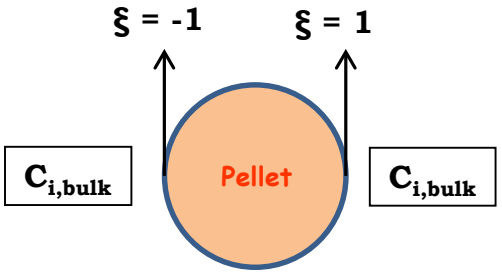
Boundary Conditions and Model Assumptions

Boundary Conditions (Dirichlet Conditions)

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



Key Assumptions

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

ii. Steady-state

iii. Isothermal conditions (since ΔT is small)

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

COMSOL Modules

- Transport of Diluted Species
- Coefficient Form PDE Solver

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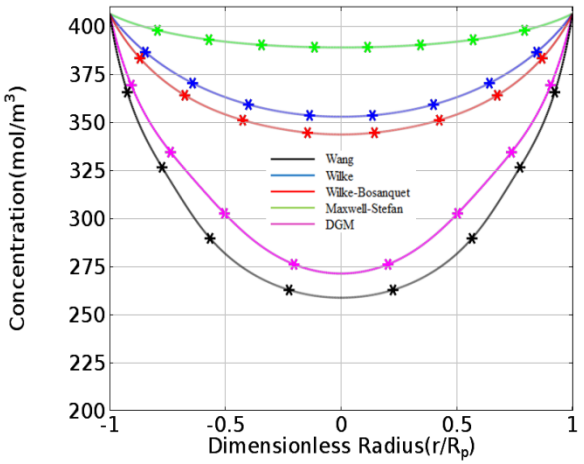
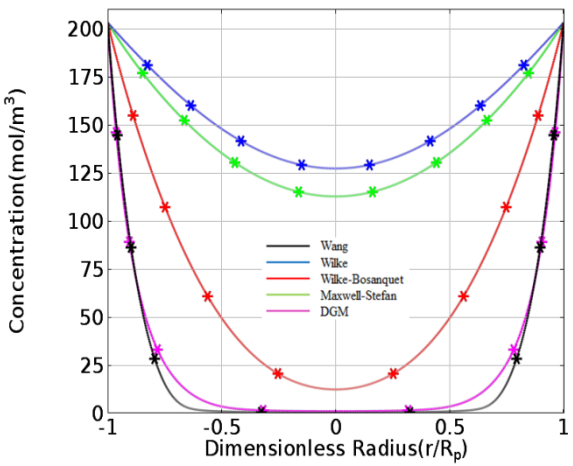
Concentration Profiles for the Key Reactants & Diesel Range

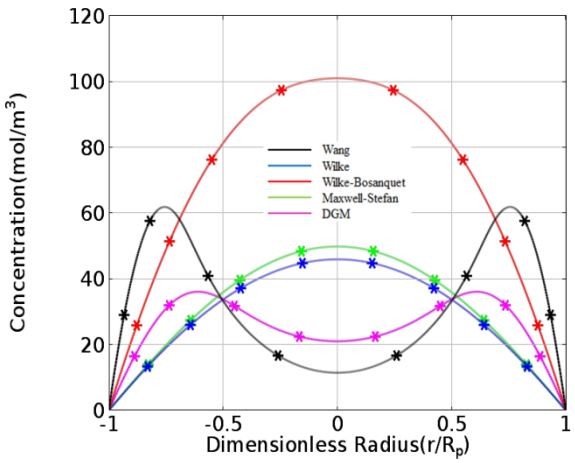
H_2



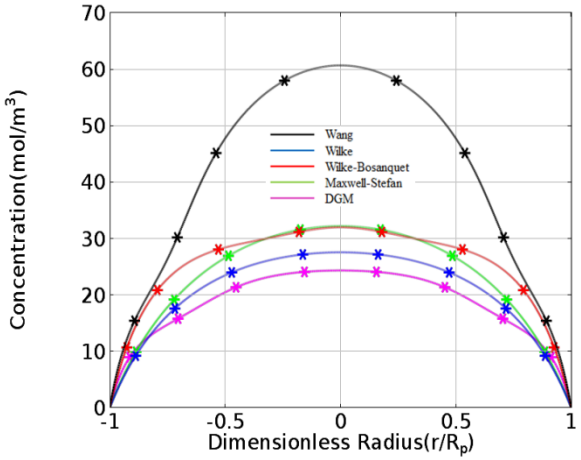
CO

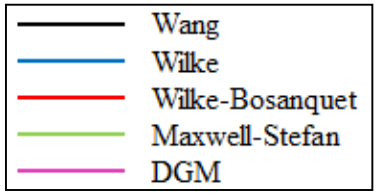


CO_2



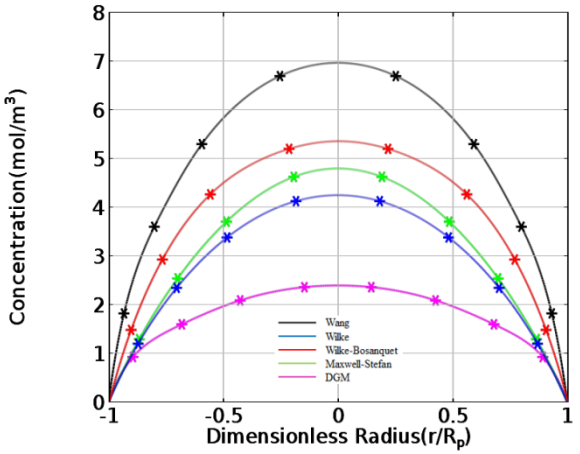
H_2O





Diesel Range
C_{13}-C_{17}

Diesel



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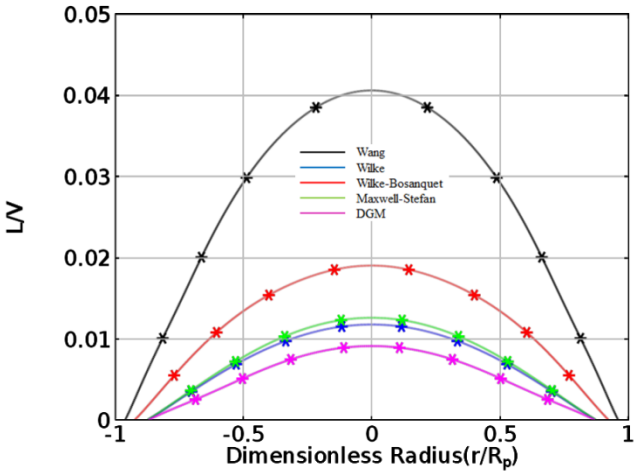
Intra-Particle Liquid-To-Vapor Ratio and Methane-Based Diesel Selectivity

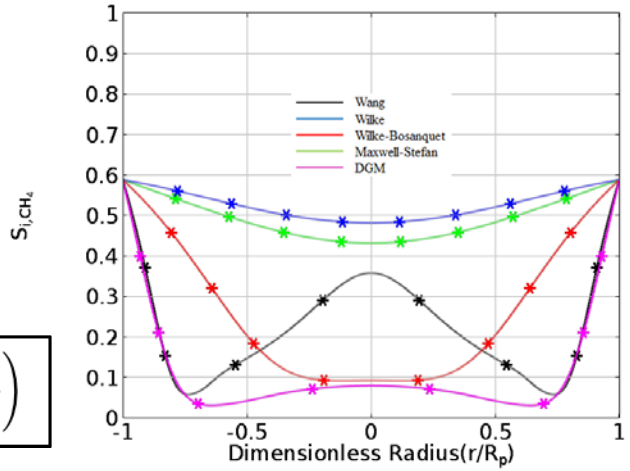
Liquid-to-Vapor Ratio



Wang
Wilke
Wilke-Bosanquet
Maxwell-Stefan
DGM

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

Methane-based Diesel Selectivity

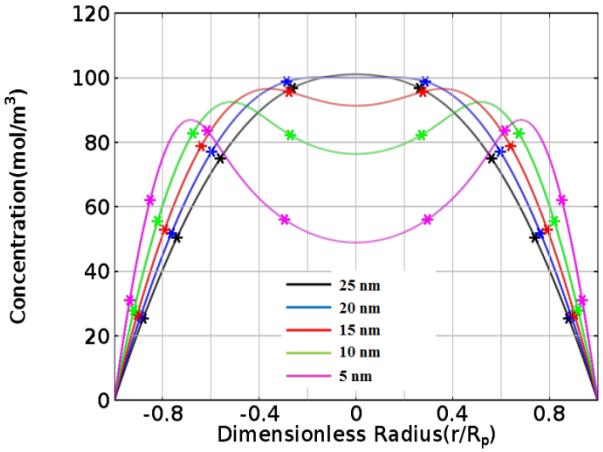


- The temperature based flux model (Wang Model) predicts a high L/V ratio when compared to Wilke, Wilke-Bosanquet, Maxwell-Stefan and DGM models.
- The methane-based diesel selectivity rapidly decreases till the reverse WGS happens, and after this point, olefin-readsorption converts long chain olefins to respective paraffins leading to an increase in diesel selectivity.

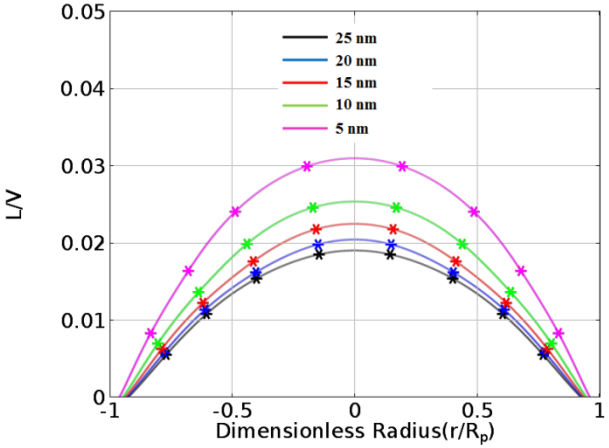
Effect of Catalyst Mean Pore Diameter on CO_2 Concentration Profile and Liquid-To-Vapor Ratio

Wilke-Bosanquet Model

CO_2



L/V



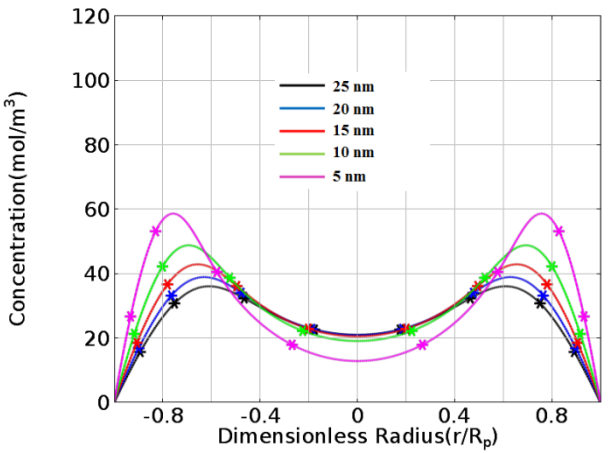
$$D_{ik} = \frac{2\varepsilon a}{3\tau}\sqrt{\frac{8RT}{\pi M_i}}$$

a = mean pore diameter

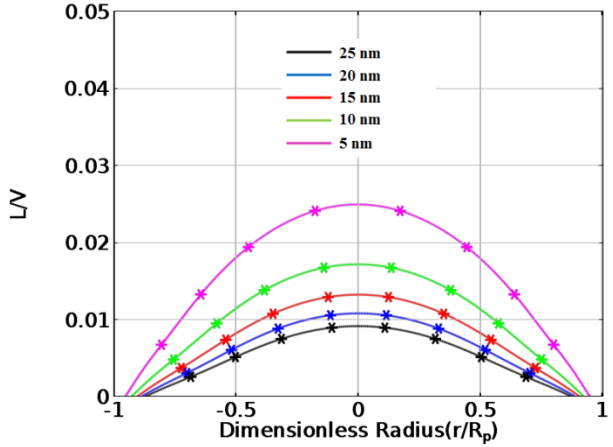
25 nm
20 nm
15 nm
10 nm
5 nm

Dusty-Gas Model

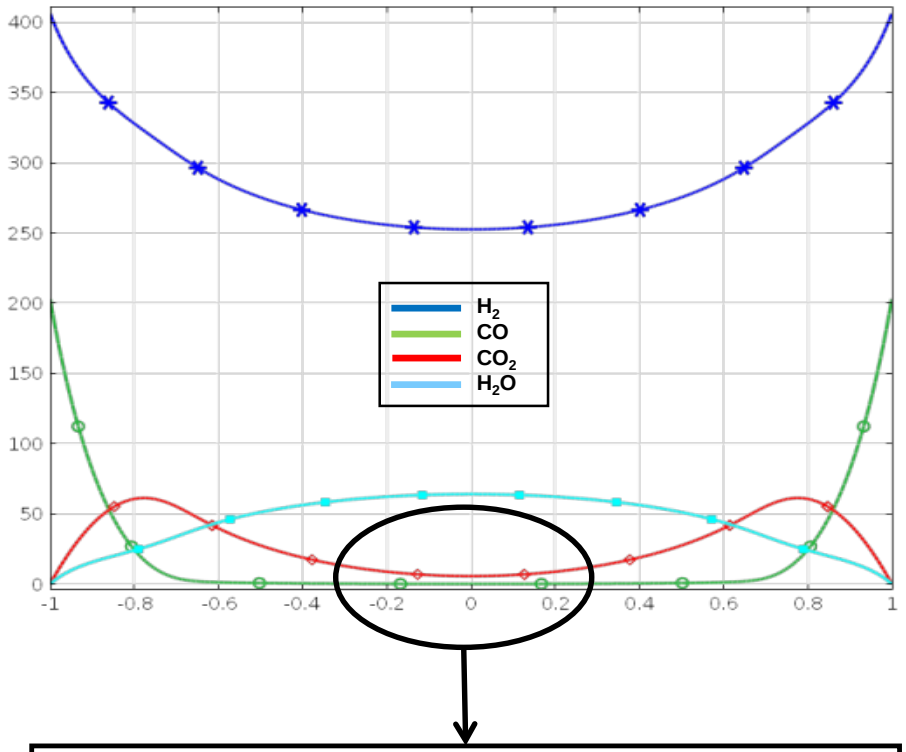
CO_2



L/V



Computational Difficulties



Region with numerical instabilities

Once the convergence issue was solved, the mesh was refined to produce smooth solutions.

- To avoid convergence issues, the radius of the particle was set to a very small number (*ca.* 10^{-3} mm) 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

- The temperature-based diffusivity correlations do not take into consideration the *change in the effective diffusivities* of species in a reaction-diffusion system.
- This work demonstrates that COMSOL can be a powerful numerical engine in solving complex multicomponent diffusion flux models to study the intra-particle transport-kinetic interactions.
- Catalyst properties, such as *pore size distribution*, play a major role in understanding the intraparticle FT product distribution.
- The inclusion of *Knudsen diffusion* in the Wilke-Bosanquet and Dusty-Gas Models produce results that closely approximate the FT product distribution of the Wang model due to the formation of CO through *reverse WGS reaction* which, in-turn, participates in the FT reaction network producing hydrocarbons.
- Including the various *multi-component flux models* as an option in the COMSOL species transport modules is suggested as a future add-on feature.