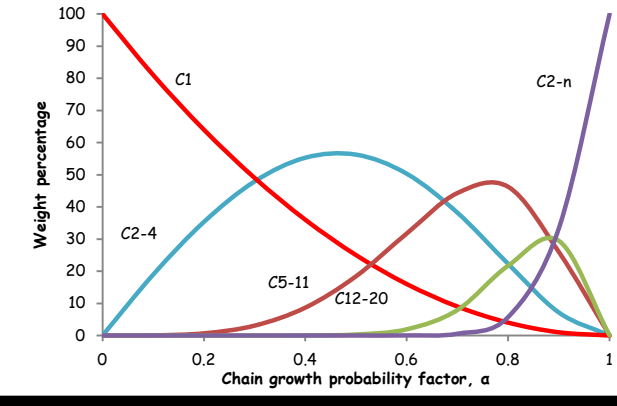


Comparison Of Diffusion Flux Models For Fischer-Tropsch Synthesis

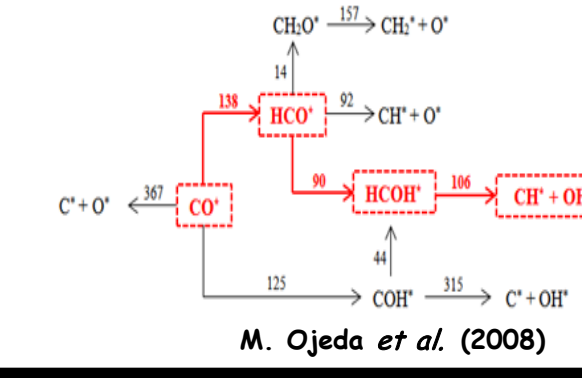
COMSOL
CONFERENCE
2015

Anderson-Schulz-Flory (ASF) Product Distribution



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CO Dissociation Pathway

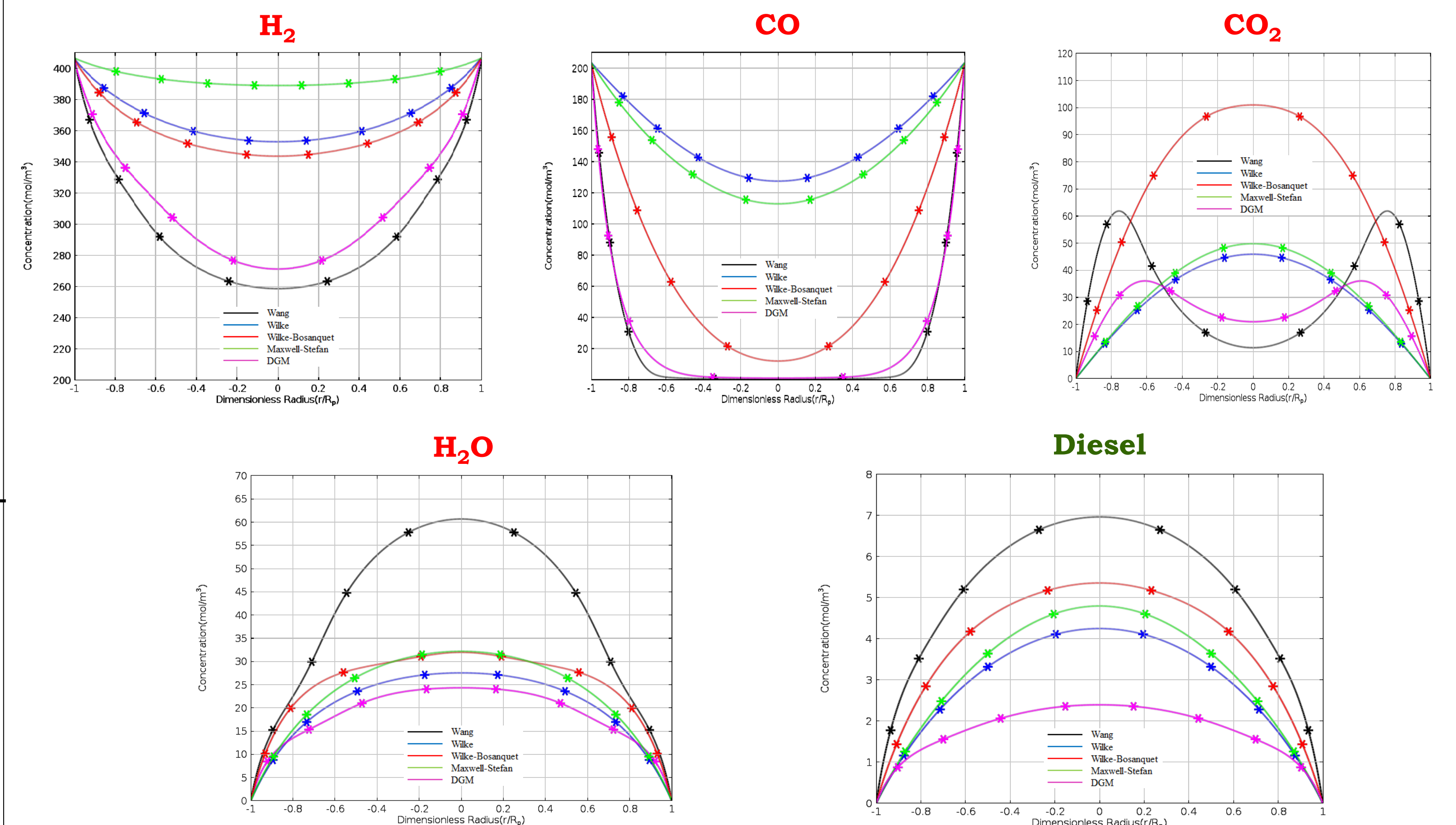


Introduction

Fischer-Tropsch synthesis (FTS) is a highly exothermic polymerization reaction of syngas (CO+H₂) in the presence of Fe/Co/Ru-based catalysts to produce a wide range of paraffins, olefins and oxygenates, often known as *syncrude*. The FTS reaction network produces hydrocarbons with carbon numbers typically ranging from 1 to 100 so the catalyst pores in this process can be potentially filled with liquid wax (C20+) leading to high diffusional limitations. To model such a reaction network and account for all species, micro-kinetic rate expressions for each individual species must be coupled with the intraparticle solubility of gases in liquid wax and transport equations for the various reaction species in the porous catalyst. Temperature based correlations for diffusivities of FT products in wax are widely used and a comparison of diffusion flux models (Wilke, Wilke-Bosanquet, Maxwell-Stefan, and Dusty Gas) to describe species transport-kinetic interactions for FTS has not been reported in literature. This poster describes the initial results of comparing various diffusion flux models for a spherical catalyst shape using COMSOL Multiphysics as the numerical engine for solving the model equations.

Results

Concentration Profiles for the Key Reactants & Diesel Range



Kinetic and Thermodynamic Expressions

Fe-Based Olefin Re-adsorption Kinetics

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

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

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

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

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

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

$$\beta_n = \frac{\frac{k_{-6}}{K_6} P_{C_n H_{2n}}}{\left[\alpha_A^{-1-2} \frac{k_1 P_{CO}}{k_1 P_{CO} + k_5 P_{H_2}} + \frac{k_{-6}}{k_1 P_{CO} + k_5 P_{H_2} + k_6} \sum_{i=2}^n (\alpha_A^{-1-2} P_{C_{(n-i+2)} H_{2(n-i+2)}}) \right]}$$

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

where n = 2 to 20

Wang et al. (2008)

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 ₅ -C ₁₂
Kerosene	C ₁₁ -C ₁₃
Diesel/Gasoil	C ₁₃ -C ₁₇
F-T Wax	C ₂₀₊

D. A. Wood et al. (2012)

Modified Soave-Redlich-Kwong EOS

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

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

Cubic equation valid for FT product distribution
Wang et al. (2008)

$$a_i = 0.42747 \frac{R^2 T_{ic}^2}{P_{ic}} \quad b_i = 0.08664 \frac{RT_{ic}}{P_{ic}} \quad \alpha_i = (1 + m_i(1 - \sqrt{T_{ir}}))^2$$

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

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

$$a_m = \sum_j y_j (\alpha_j a_j)^{1/2} (1 - k_{ij}) \quad b_m = \sum_j y_j b_j$$

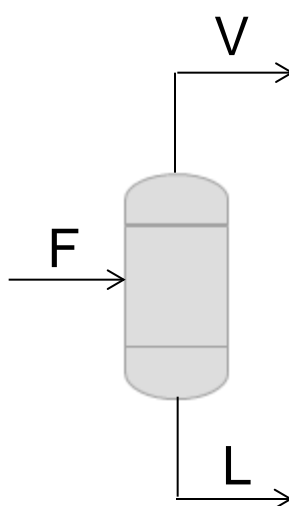
VLE Flash Calculations

Rachford-Rice Objective Function

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

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

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



Governing Equations and Boundary Conditions

General Specie Balance: $\nabla \cdot (-D_{ei} \nabla C_i) = \rho_p \sum_{j=1}^{44} \sum_{l=1}^{43} \alpha_{ij} R_{lj}$

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

Wang Diffusion Flux: $N_i = -D_{ei} \nabla C_i$ where $D_{ei} = \frac{\epsilon D_{iB}}{\tau}$ $D_{iB} = D_{CO_2,B} \left(\frac{V_{CO}}{V_i} \right)^{0.6}$ Wang et al. (2008)

Wilke Model: $N_i = -D_{im} \nabla C_i$ where $D_{im} = \frac{1 - x_i}{\sum_{j=1}^n \frac{x_j}{D_{ij}}} = \frac{C_t - C_i}{\sum_{j=1}^n \frac{C_j}{D_{ij}}}$ $\bar{D}_{ij} = \frac{0.00266 T^{3/2}}{PM_{ij}^{1/2} \sigma_{ij}^2 \Omega_{D,ij}}$

Wilke-Bosanquet Model: $N_i = -D_{i,eff} \nabla C_i$ where $\frac{1}{D_{i,eff}} = \frac{1}{D_{im}} + \frac{1}{D_{ik}}$ $D_{ik} = \frac{2\epsilon a}{3\tau} \sqrt{\frac{8RT}{\pi M_i}}$ a = mean pore diameter (Å)

Maxwell-Stefan Model: $N_i = \frac{-\nabla C_i + \sum_{j=1}^n \frac{x_j N_j}{D_{ij}}}{\sum_{j=1}^n \frac{x_j}{D_{ij}}}$

Dusty-Gas Model: $N_i = \frac{-\nabla C_i + \sum_{j=1}^n \frac{x_j N_j}{D_{ij}}}{\sum_{j=1}^n \frac{x_j}{D_{ij}} + \frac{1}{D_{ik}}}$ At $\xi = -1$ and $\xi = 1$, $C_i = C_{i,bulk}$ ($CO_2,bulk = \text{eps}$ for convergence)

Boundary Conditions

Catalyst Properties and Process Conditions

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

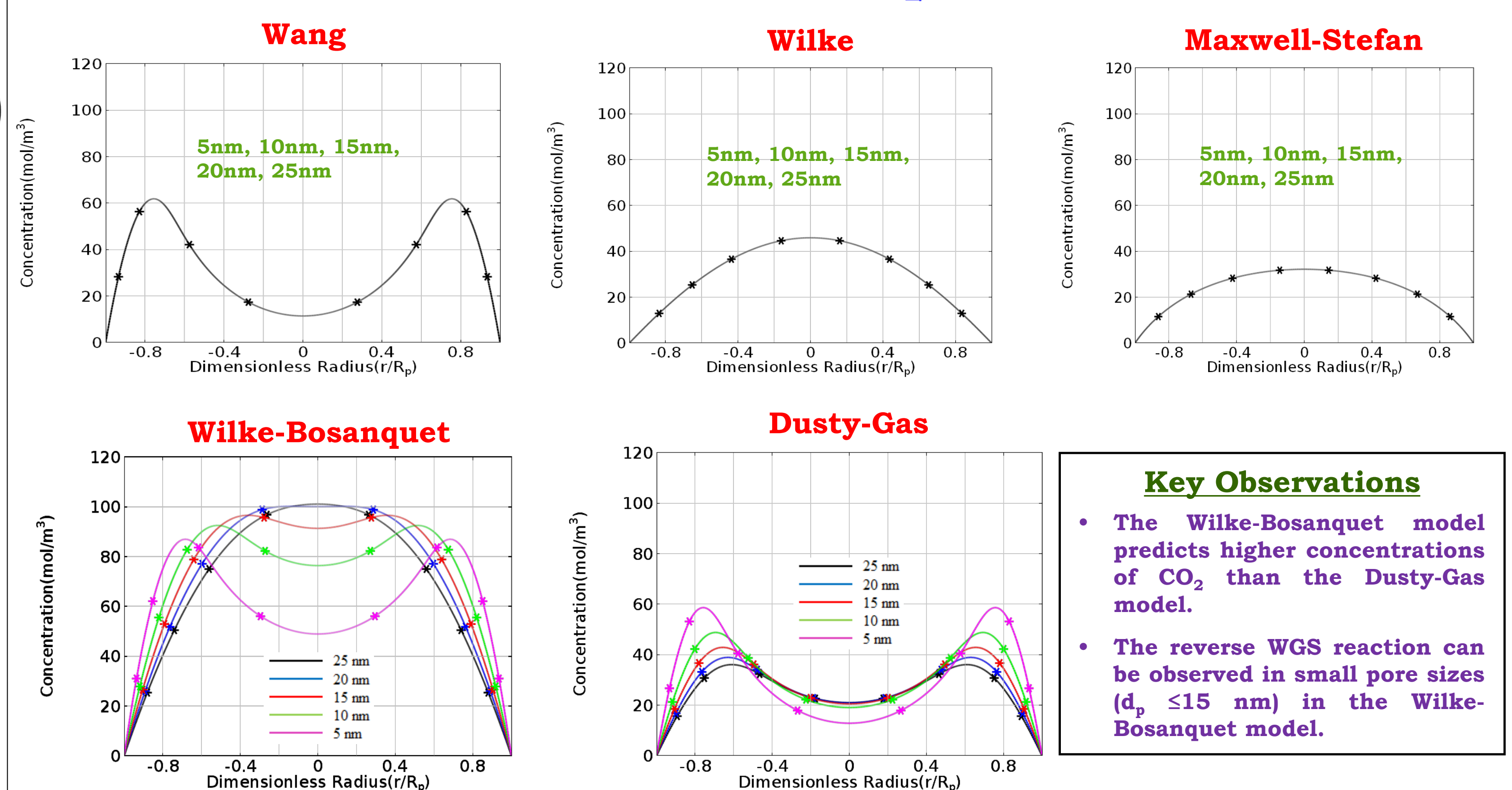
Operating Conditions

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

Objectives

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

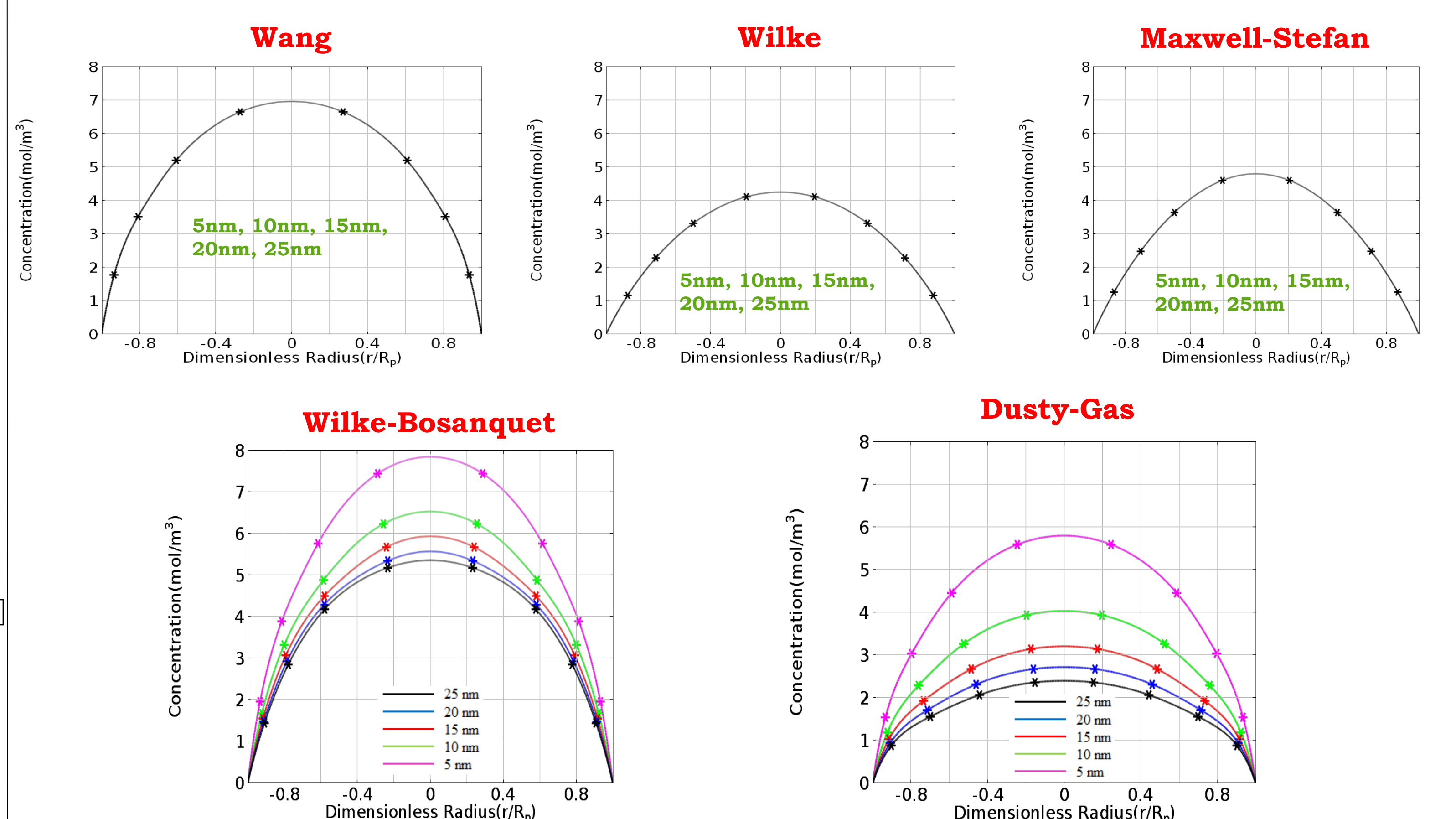
Effect of Mean Pore Diameter on CO₂ Concentration Profiles



Key Observations

- The Wilke-Bosanquet model predicts higher concentrations of CO₂ than the Dusty-Gas model.
- The reverse WGS reaction can be observed in small pore sizes ($d_p \leq 15$ nm) in the Wilke-Bosanquet model.

Effect of Mean Pore Diameter on Diesel Concentration Profiles



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.