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

Introduction

Fischer-Tropsch synthesis (FTS) is a highly exothermic polymerization reaction of syngas (CO+H₂) in the presence of Fe/Ca/Ru-based catalysts to produce a wide range of paraffins, olefins and oxygenates, often known as Fischer-Tropsch wax. The emphasis of this research is to model a MTFBR using COMSOL Multiphysics. This paper focuses on comparing the performance of various catalyst particle shapes by accounting for transport interactions and thermodynamic phenomena using micro kinetic rate expressions.

Kinetic and Thermodynamic Expressions

**Fe-Based Olefin Re-adsorption Kinetics**

\[
R = \frac{1}{1 + \frac{1}{B} + \frac{1}{B^2} + \frac{1}{B^3} + \frac{1}{B^4} + \frac{1}{B^5}} \times \left( k_{\text{ads}} \times \left( \frac{H_2}{CO} \right)^{-n} \right)
\]

**Modified Soave-Redlich-Kwong EOS**

\[
K = \frac{1}{1 + \frac{1}{B} + \frac{1}{B^2} + \frac{1}{B^3} + \frac{1}{B^4} + \frac{1}{B^5}} \times \left( k_{\text{ads}} \times \left( \frac{H_2}{CO} \right)^{-n} \right)
\]

**Boundary Conditions**

- **General species balance:** \( \sum (i=1,N) \frac{\partial C_i}{\partial t} = \sum (i=1,N) \left( \frac{\partial (C_i D_i) \delta}{\partial x} \right) \)
- **Effective diffusivity:** \( D_{\text{eff}} = \frac{1}{C} \sum (i=1,N) \left( \frac{\partial C_i}{\partial x} \right) \)

**Key Assumptions**

- *Independent of composition C*,
- *Dependent on local temperature T*,
- *Future work: Use multi-component flux transport model*

**Catalyst Particle Shapes, Catalyst Properties and Process Conditions**

**Objectives**

- Model the Fischer-Tropsch (FT) reaction network using micro-kinetic rate expressions and assess the role of catalyst particle shape and operating conditions (\( P, T \), 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.

**Results**

**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 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.