CATAYST-SCALE MODELING OF NON-SPHERICAL PARTICLE SHAPES FOR THE GAS-PHASE FISCHER-TROPSCH SYNTHESIS

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Abstract

A 2-D catalyst particle model for different shapes (solid cylinder, hollow cylinder, 4-hole cylinder, modified 4-hole cylinder and 7-hole cylinder) was numerically simulated to compare the particle-level performance for the Fischer-Tropsch Synthesis (FTS). A Fe-based micro-kinetic olefin re-adsorption model developed by Wang *et al*. (2003) was coupled with the Soave-Redlich-Kwong (SRK) equation of state to describe the particle-scale transport-kinetic interactions and phase behavior for the gas-phase FTS (Wang *et al*. 1999). The intra-particle effectiveness factor, liquid-to-vapor ratio, CO conversion and intra-particle volume-averaged concentration of diesel were analyzed at different process conditions to compare the performance of the different catalyst particle shapes.

Keywords

Fischer-Tropsch Synthesis, Catalyst particle shapes, Gas-phase micro-kinetics

Introduction

The 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, which is often called *syncrude*. Multi-Tubular Fixed Bed Reactors (MTFBR) and Slurry Bubble Column reactors (SBCR) are widely employed for FTS processes (Davis, 2005). To understand the reactor-scale catalyst performance, it is important to first quantify the particle-scale transport-kinetic interactions.

The FTS is a polymerization reaction producing hydrocarbons with carbon numbers typically ranging from 1 to 100 so the catalyst pores in this process can be potentially filled with liquid wax (C_{20}+) 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 transport equations for the various reaction species in the porous catalyst along with an accounting of the solubility of gases in the liquid wax. A total number of 20 paraffins (C_1 to C_{20}), 19 olefins (C_2 to C_{20}) and 4 key components (H_2, CO, CO_2, and H_2O) are considered in the reaction network, which leads to 43 nonlinear differential equations for the specie mass balances. The micro-kinetic and thermodynamic expressions used in the model can be found elsewhere (Wang *et al*., 1999; Wang *et al*., 2003). Five different particle shapes based on a solid cylinder, sphere, and hollow cylinders of equal effective diffusion length ($L_e = V_p/S_p$) are simulated in this study. The catalyst shapes are illustrated in Figure 1.

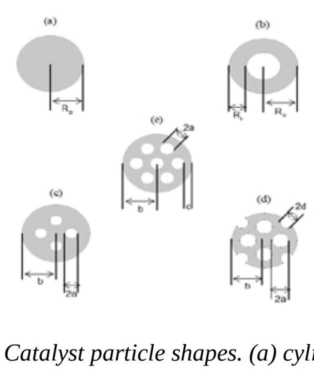

Figure 1. Catalyst particle shapes. (a) cylinder, (b) hollow cylinder (H-Cylinder), (c) 4-hole cylinder (4-H Ring), (d) modified 4-hole cylinder (M-4-H Ring), and (e) 7-hole cylinder (7-H Ring).

Key Results

Concentration Profiles of CO and CO_2

The 2-D isothermal intra-particle concentration profiles and the volume average concentration profiles of CO and CO_2 for different catalyst particle shapes are shown in Figure 2 - 5. The profiles show that the CO concentration approaches zero for all shapes due to the presence significant diffusional limitations. The CO_2 concentration reaches a maximum and then decreases due to the reverse Water-Gas-Shift (WGS) reaction. The reverse WGS reaction produces CO, which is then consumed in the subsequent hydrocarbon-producing FT reactions. Figure 4 and 5 show that the reverse WGS reaction does not occur in the M-4-H ring.

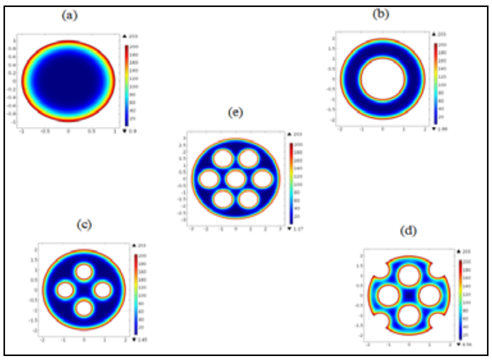

Figure 2. Intra-particle Concentration Profile of CO (mol/m^3) at T = 493 K and P = 25 bar. (a) cylinder, (b) hollow cylinder (H-Cylinder), (c) 4-hole cylinder (4-H Ring), (d) modified 4-hole cylinder (M-4-H Ring), and (e) 7-hole cylinder (7-H Ring).

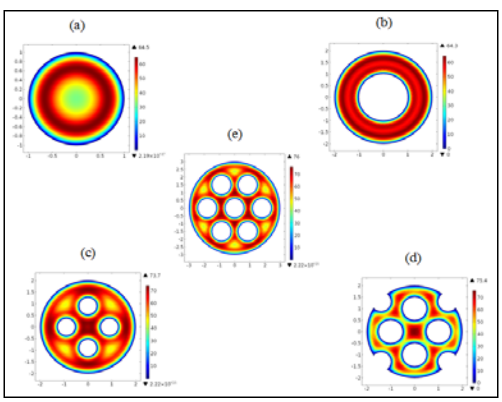

Figure 3. Intra-particle Concentration Profile of CO_2 (mol/m^3) at T = 493 K and P = 25 bar. (a) cylinder, (b) hollow cylinder (H-Cylinder), (c) 4-hole cylinder (4-H Ring), (d) modified 4-hole cylinder (M-4-H Ring), and (e) 7-hole cylinder (7-H Ring).

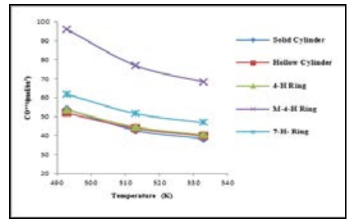

Figure 4. Average Concentration of CO (mol/m^3) for Temperature range of 493 K, 513 K & 533 K and P = 25 bar.

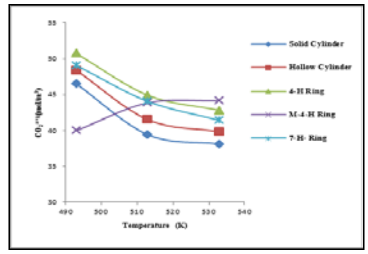

Figure 5. Average Concentration of CO_2 (mol/m^3) for Temperature range of 493 K, 513 K & 533 K and P = 25 bar.

Conclusions

The transport-kinetic interactions for FTS in 2-D catalyst pellet models for various shapes using a detailed micro-kinetic model were successfully analyzed for the first time using COMSOL Multiphysics™. This study is an important extension to the previous work by Wang *et al.* (2001) who used the same micro-kinetic model to study the F-T reaction-diffusion mechanism in a spherical catalyst, but did not study the effect of catalyst shape nor report the interparticle average diesel concentration. Also, the numerical technique was based upon a custom computer code that implemented the orthogonal collocation method for the two-point boundary value system of ODEs. The results in the current work provide the basis for modeling a packed-bed reactor model where intraparticle gradients are coupled to interparticle gradients in terms of concentration, temperature and total reactor pressure.

References

Davis, B. H. (2005). Fischer-Tropsch Synthesis: Overview of Reactor Development and Future Potentialities, *Topics in Catalysis*, 32, 143-168.

Wang, Y. N., Li, Y. W., Bai, L., Zhao, Y. L., Zhang, B. J. (1999). Correlation for Gas-Liquid Equilibrium Prediction in Fischer-Tropsch Synthesis, *Fuel*, 78, 911-917.

Wang, Y. N., Xu, Y. Y., Xiang, H. W., Li, Y. W., Zhang, B. J. (2001). Modeling of Catalyst Pellets for Fischer-Tropsch Synthesis, *Industrial & Engineering Chemistry Research*, 40, 4324-4335.

Wang, Y. N., Ma, W. P., Lu, Y. J., Yang, J., Xu, Y. Y., Xiang, H. W., Li, Y. W., Zhao, Y. L., Zhang, B. J. (2003). Kinetic Modelling of Fischer-Tropsch Synthesis over an Industrial Fe-Cu-K Catalyst, *Fuel*, 82, 195-213.