Modeling of Porous Catalyst Pellets: Comparison of Diffusion Flux Models for Steam Methane Reforming

COMSOL Conference 2015
Boston, MA October 7 - 9

SMR Catalyst Shapes

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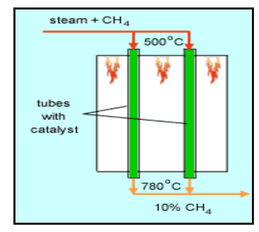
SMR Reactor



Introduction

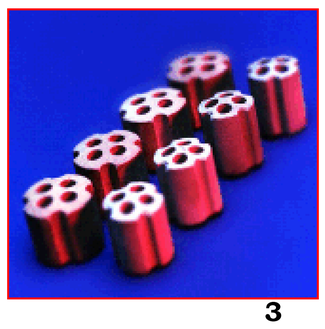
The steam methane reforming (SMR) reaction has been the most common route for producing synthesis gas (CO + H_2) for over half a century [1]. Synthesis gas is a key building block for manufacture of various organic chemicals, such as methanol, ammonia, oxo alcohols, and liquid transportation fuels. Design of chemical reactors for the SMR reaction require accurate models for the transport-kinetic interactions that occur in porous catalysts. Various diffusion flux models have been used in the literature to describe the transport-kinetic interactions on a particle-scale in which the resulting nonlinear equations have been solved using custom codes. The use of COMSOL Multiphysics to solve these equations for various flux models is demonstrated here as a first step toward developing better insight into their effect on catalyst performance.

1. Kagyrmanova, A. P., I. A. Zolotarskii, *et al.* (2006). "Modeling of Steam Reforming of Natural Gas Using Catalysts with Grains of Complex Shapes." Theoretical Foundations of Chemical Engineering **40**(2): 155-167.
2. Solsvik, J. and H. A. Jakobsen (2012). "Mathematical Modeling of Multicomponent Mass Diffusion in Porous Pellets: Mass and Molar Formulations." Energy Procedia **26**: 107-115.

Objectives

- Develop a rigorous modeling framework that accounts for diffusion and non-isothermal reaction in spherical catalysts for the SMR reaction using the Wilke and Wilke-Bosanquet flux models.
- Compare the effect of pressure on the transport and kinetics of key species in the SMR system.

Typical SMR Catalysts and Reactors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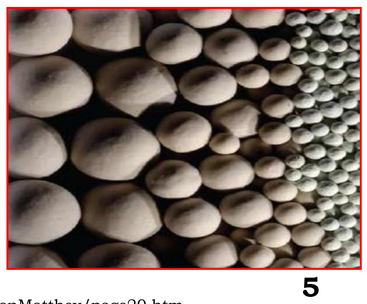
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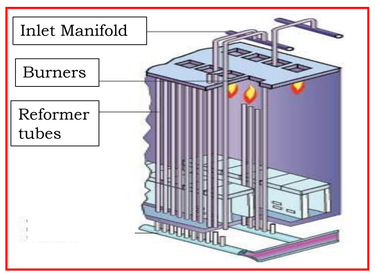

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3. http://resources.schoolscience.co.uk/JohnsonMatthey/page20.htm
4. http://www.matrostech.com/downloads/AMT-SR%20brochure.pdf
5. http://www.criterioncatalysts.com
6. http://chemeng-processing.blogspot.com/2010/05/hydrogen-production-by-steam-reforming.html

Transport-Kinetics Particle Model

Species Mass Balance: $\nabla \bullet N_i = \upsilon_i \, r \, \rho_P$

where i = CH_4, CO, CO_2, H_2, H_2O & N_2

Energy Balance: $\nabla \bullet \bar{q} = -(\Delta H_{rxn}) \, r \, \rho_p$

SMR Kinetics: $CH_4 + H_2O \leftrightarrow CO + 3H_2$

(Xu and Froment, 1989)*

$$R_1 = \frac{K_1}{P_{H_2}^{2.5}} \left[\frac{P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{e,1}}}{DEN^2} \right] \left(\frac{mol}{kg - s} \right)$$

$CO + H_2O \leftrightarrow CO_2 + H_2$ $\qquad$ $CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$

$$R_2 = \frac{K_2}{P_{H_2}} \left[\frac{P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{e,2}}}{DEN^2} \right] \qquad R_3 = \frac{K_3}{P_{H_2}^{3.5}} \left[\frac{P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_{e,3}}}{DEN^2} \right]$$

$$DEN = 1 + K_{CO} P_{CO} + K_{H2} P_{H2} + K_{CH4} P_{CH4} + K_{H2O} \frac{P_{H2O}}{P_{H2}}$$

Diffusion Flux Models

Wilke Model

$$N_i = \left(- D_{ei,m} \nabla C_i \right) \qquad \textit{where} \qquad D_{ei,m} = \frac{1}{\left(\sum_{j=1, j \neq i}^{n} \left(x_j / D_{ij}^e \right) \right)}$$

Wilke-Bosanquet Model

$$N_i = \left(- D_{i,eff} \nabla C_i \right) \qquad \textit{where} \qquad \frac{1}{D_{i,eff}} = \frac{1}{D_{ei,m}} + \frac{1}{D_{ei,k}}$$

Maxwell-Stefan Model

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

Dusty-Gas Model

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

Dimensionless Velocity

$$v^* = - \frac{\varepsilon \, d_{pore}^2}{32 \, \tau \, \mu} \nabla P$$

* Xu, J. and Froment, G.F. *AIChE J.*, **35**(1), 88 (1989)

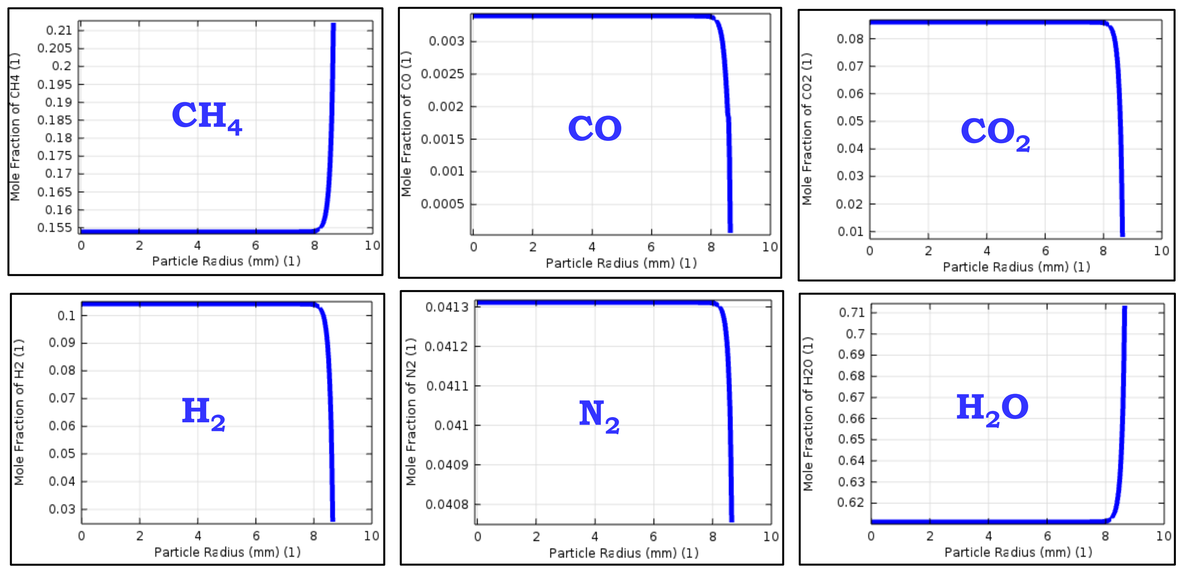
** Jannike, S., Stian, T., and Jakobsen., H. A. *Ind. Eng. Chem. Res,* **51**, 8222 (2012).

Key Results

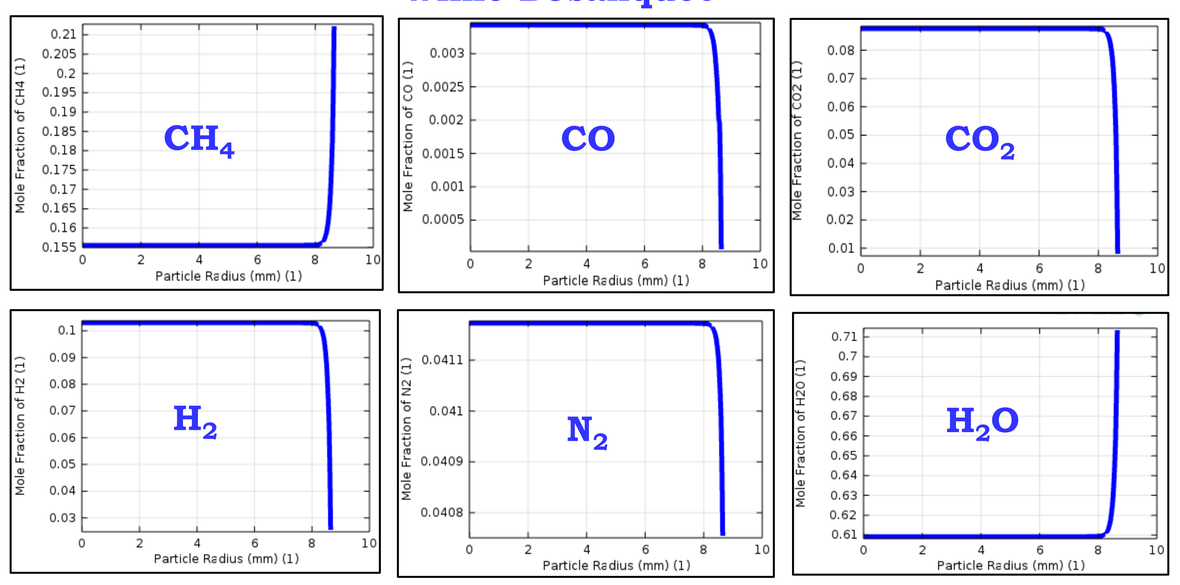
1-D Spherical Catalyst $d_p = 0.017m$ $T = 800K$ $P = 29$ bar

$y_{CH4} = 0.212$, $y_{CO} = 6.35 \times 10^{-5}$, $y_{CO2} = 0.008$, $y_{H2} = 0.025$, $y_{N2} = 0.040$, $y_{H2O} = 0.713$

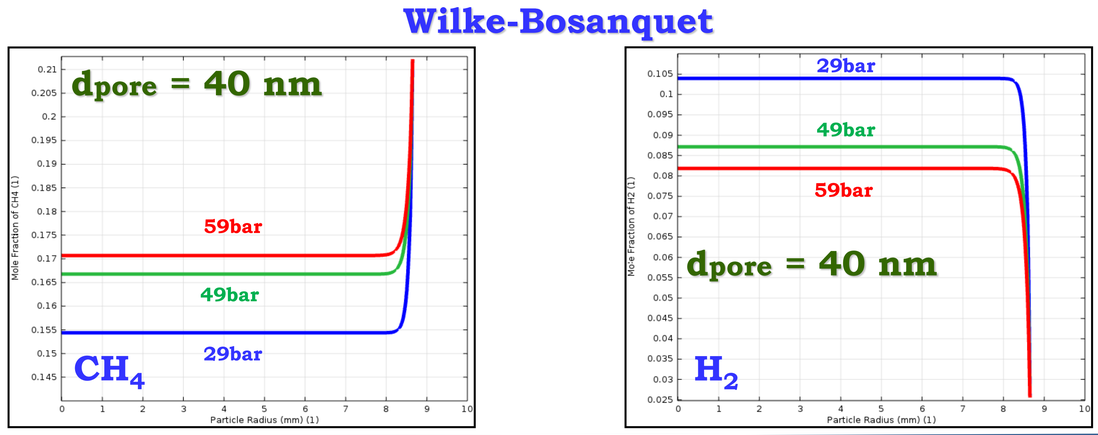
Wilke



dpore = 40 nm **Wilke-Bosanquet** **P = 29 bar**



Wilke-Bosanquet



Conclusions

- COMSOL Multiphysics framework provides a convenient numerical engine for modeling of transport-kinetics interactions for complex catalyst shapes.
- The effect of Knudsen diffusion for the cases investigated here was insignificant.
- For the conditions used here, the catalyst volume largely exists in thermodynamic equilibrium. An improved catalyst design and process conditions are needed.

Excerpt from the Proceedings of the 2015 COMSOL Conference in Boston