Modeling of Packed Bed Reactors: Hydrogen Production By the Steam Reforming of Methane and Glycerol

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Abstract

The production of hydrogen is important in the chemical industry, including hydrotreating and energy conversion by fuel cells. The conventional route is by the endothermic steam reforming of methane ($CH_4 + H_2O \rightarrow 3H_2 + CO$, MSR) in a multitubular packed bed, at > 20 bar and 700-800 °C and using high flow rates. With the increasing use of biodiesel as a renewable fuel, interest has grown in steam reforming of the excess glycerol ($C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2$, GSR) produced as a side product. This endothermic reaction also takes place at high temperature but at lower pressures and flow rates.

The aim of our research is to use COMSOL Multiphysics® software to model a tubular packed bed reactor where the tube is an effective continuum, with the reaction rates obtained by solving a single pellet model at each point [1]. The reforming reactions studied involve changes in moles, and a rigorous treatment of the effects of this on velocity and conversion is sought. In the present paper we present the impact of the mole changes in the absence of heat effects, so the simulations reported here are isothermal. We illustrate the use of a one-dimensional heterogeneous reaction engineering model with a coupled single particle model [2] in COMSOL.

Our approach follows that of the Packed Bed Reactor example in the COMSOL User Guide [3], but we have modified the treatment of mole changes. We formulate the equations in mole fractions, and then include equations for the evolution of the mean molar mass [4]. Two model domains are used, a 1-D tube model and a 2-D spherical particle model, connected by coupling variables (Figure 1). Tube pressure drop is calculated by the Ergun equation using the Coefficient PDE interface of COMSOL. The equations for diffusion and reaction in the pellet and convective dispersion in the tube are handled by use of COMSOL Multiphysics and the Chemical Reaction Engineering Module.

Literature kinetics were available for both the MSR [5] and GSR [6,7] reactions. The MSR system comprises a set of three reversible reactions, and in Figure (2) pressure decrease and conversion increase along the tube are illustrated; velocity increased and mean molar mass decreased by only 1.5 % in this case due to the low conversion. Methane profiles down the tube and through the pellet are shown in the insert where most of the pellet is at equilibrium. The single GSR

reaction is irreversible, and in Figure (3) we see the strong decrease in glycerol in the pellet for this case where there is 25% conversion but pressure decreases by only 1%, while in Figure (4) the effects of the much higher mole change on reaction are shown on mean molar mass and velocity in the tube.

The effects of mole increases on the gas velocity and conversion for MSR and GSR were simulated rigorously using the variable mean molar mass. Results are reported for isothermal 1-D calculations; future papers will present results for 2-D non-isothermal cases.

Reference

1. Allain, F.; Dixon, A. G., Modeling of transport and reaction in a catalytic bed using a catalyst particle model, Proceedings of the COMSOL Conference, Boston (2010).

2. Petera, J.; Nowicki, L.; Ledakowicz, S., New numerical algorithm for solving multidimensional heterogeneous model of the fixed bed reactor, Chem. Eng. J. 214, 237-246 (2013).

3. COMSOL Multiphysics Model Library, Chemical Reaction Engineering Module, Packed bed reactor, Version 4.3b, COMSOL AB (2013).

4. Cropley, J. B.; Burgess, L. M.; Loke, R. A., The optimal design of a reactor for the hydrogenation of butyraldehyde to butanol, ACS Symp. Ser., 237, 255-270 (1984).

5. Hou, K.; Hughes, R., The kinetics of methane steam reforming over a Ni/α-Al2O3 catalyst, Chem. Eng. J., 82, 311-328 (2001).

6. Cheng, C. K.; Foo, S. Y.; Adesina, A. A., Glycerol steam reforming over bimetallic Co-Ni/Al2O3, Ind. Eng. Chem. Res., 49, 10804-10817 (2010).

7. Iliuta, I.; Iliuta, M.; Radfarnia, H., Hydrogen production by sorption-enhanced steam glycerol reforming: sorption kinetics and reactor simulation, AIChE J., 59, 2105-2118 (2013).
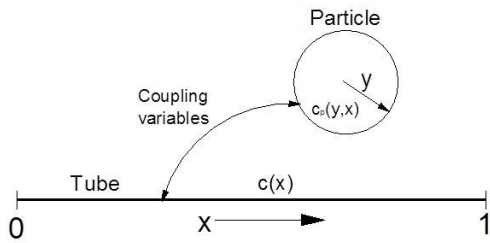
Figures used in the abstract

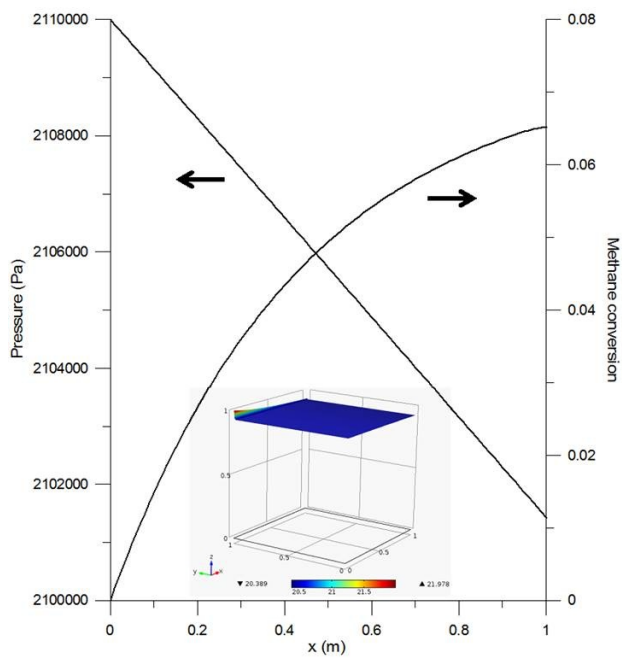**Figure 1**: Schematic of computational domains.

Figure 2: Axial conversion and pressure profiles for MSR; inset shows methane concentration inside pellet (y-coordinate) and along tube (x-coordinate).
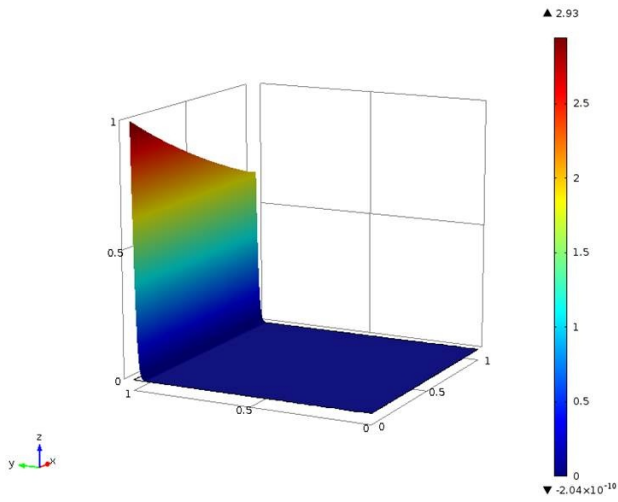
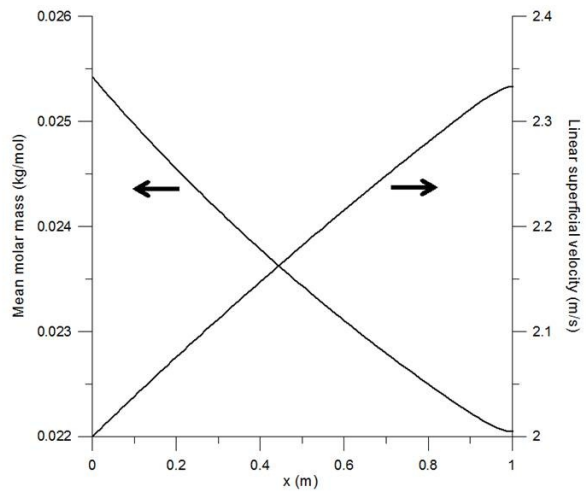**Figure 3**: Glycerol concentration inside pellet (y-coordinate) and along tube (x-coordinate) for GSR.

Figure 4: Axial mean molar mass and velocity profiles for GSR.