A DYNAMIC TWO-DIMENSIONAL HETEROGENEOUS MODEL FOR QUASI-ISOTHERMAL METHANOL SYNTHESIS REACTORS

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Abstract

A dynamic two-dimensional heterogeneous model for methanol synthesis reactor of quasi-isothermal type is presented. The model is aimed at predicting reactor performance during catalyst deactivation. The model is also useful in finding concentration gradients inside the catalyst pellet. The effects of feedstock properties and operating conditions on deactivation rates and catalyst lifetime are demonstrated. The sensitivities of these effects in the model were analyzed to avoid operating the reactor in runaway or parametrically sensitive region. The latter has been implemented in Aspen Custom Modeler for accurate representation of thermodynamic and physical properties over the range of conditions in the system. Optimal operating conditions were determined to maximize methanol production.

Keywords

Heterogeneous, quasi-isothermal, Aspen Custom Modeler, runaway, thermodynamic properties.

Introduction

Methanol is widely used as feedstock for a variety of industrial chemicals such as Formaldehyde, Acetic acid, Dimethyl Ether (DME), and Methyl Tert-Butyl Ether (MTBE). More recently, Methanol is considered to be promising fuel for fuel cells (DMFC), in which methanol is directly oxidized with air to water and carbon dioxide while producing electricity. Methanol can be an alternative clean fuel for future, replacing fossil fuel as a means of energy storage, ground transportation fuel. Consequently, growing attentions have been paid to the synthesis of methanol.

Many of today's technologies licensors are offering methanol plant capacities at 5,000 tons per day or more, aiming at energy saving and process intensification. Along with this trend, Mitsubishi Heavy Industry (MHI) developed new methanol production technology, which has high efficiency in the reaction and energy saving for the methanol synthesis. A new isothermal reactor so called SUPERCONVERTER has been used to increase the rate of one-pass reaction, hence the required power for unreacted gas recycle is reduced as well as a large-scale methanol production is delivered. The reactor design employs an inner tube that is disposed in the reactor and the catalyst is charged into a circular space surrounded by the reaction tube on one side and inner tube on the other side. Our previous studies indicate that this design allows the temperature to increase gradually and delays the equilibrium to be reached at the end of the reactor. The production of methanol is improved by 3%, compared to the conventional converter.

In this article, a dynamic two-dimensional heterogeneous model for methanol synthesis reactor of quasi-isothermal type is proposed to evaluate the benefits of this type of reactor over the conventional type. This model also considers catalyst deactivation and is able to show the effect of operating the reactor under milder temperature on the catalyst lifetime and to determine the optimal operating conditions to maximize methanol production.

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Model Development

A two-dimensional model with axial and radial gradients developed by DeWasch and Froment, (1971) is used to simulate a multitubular methanol reactor and has been extended to include catalyst deactivation. The continuity and energy equations are written as:

Fluid phase:

$$\varepsilon_b \frac{\partial C_i}{\partial t} = -\frac{\partial}{\partial z}(v_z C_i) + \frac{\partial}{\partial z}\left(\varepsilon_b D_z \frac{\partial C_i}{\partial z}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(\varepsilon_b D_r r \frac{\partial C_i}{\partial r}\right) + k_{g,i} a_v (C_i^s - C_i) \quad (1)$$

$$\frac{\partial}{\partial t}(\rho_f C_{pf} T) = -\frac{\partial}{\partial z}(v_z\, \rho_f C_{pf} T) + \frac{\partial}{\partial z}\left(k_z \frac{\partial T}{\partial z}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(k_r r \frac{\partial T}{\partial r}\right) + h_f\, a_v (T^s - T) \quad \forall\, z \in (0, L_a),\ r \in (0, L_r) \quad (2)$$

Initial conditions:

$$C_i = C_{i0}\,, T = T_0 @\, t = 0, z \in (0, L_a), r \in (0, L_r) \quad (3)$$

Boundary conditions:

$$-\varepsilon_b D_z \frac{\partial C_i}{\partial z} = v_z (C_{i0} - C_i) \quad @ t \neq 0, z = 0, r \in [0, L_r] \quad (4)$$

$$\frac{\partial C_i}{\partial z} = 0 \ @\ t \neq 0, z = L_a, r \in [0, L_r] \quad (5)$$

$$\frac{\partial C_i}{\partial r} = 0 \ @\ t \neq 0, r = 0, z \in (0, L_a) \quad (6)$$

$$\frac{\partial C_i}{\partial r} = 0 \ @\ t \neq 0, r =, z \in (0, L_a) \quad (7)$$

$$-k_z \frac{\partial T}{\partial z} = \rho_f C_{pf} v_z (T_R - T) \ @\ t \neq 0, z = 0, r \in [0, L_r] \quad (8)$$

$$\frac{\partial T}{\partial z} = 0 \quad @\ t \neq 0, z = L_a, r \in [0, L_r] \quad (9)$$

$$\frac{\partial T}{\partial r} = 0 \quad @\ t \neq 0, r = 0, z \in (0, L_a) \quad (10)$$

$$-k_r \frac{\partial T}{\partial r} = h_w (T - T_w) \quad @\ t \neq 0, r = L_r, z \in (0, L_a) \quad (11)$$

Solid phase:

$$\varepsilon_s \frac{\partial C_i^s}{\partial t} = \rho_b\, \tilde{a} \sum_{j=1}^{N_{rxn}} v_{ij}\, \eta_j\, r_j(C_i^s, T^s) + k_{g,i} a_v (C_i^s - C_i) \quad (12)$$

$$\frac{\partial}{\partial t}(\rho_s c_{p,s} T^s) = \rho_b\, \tilde{a} \sum_{j=1}^{N_{rxn}} \eta_j\, r_j(C_i^s, T^s)\left(-\Delta H_{r,j}(T^s)\right) - h_f a_v (T^s - T_2) \quad (13)$$

Initial conditions:

$$C_i^s = C_{i0}^s, T^s = T_0^s \ @\ t = 0, z \in (0, L_a), r \in (0, L_r) \quad (14)$$

Catalyst deactivation model given by Hanken, L. (1995).

$$\frac{da}{dt} = -K_d\, exp\left(\frac{-E_d}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right) a^5 \quad (15)$$

$$\tilde{a} = 1 - \frac{a_0 - a}{a_0} \quad (16)$$

Conclusions

Aspen custom modeler has been successfully used for discretization of the space, using orthogonal collocation on finite elements 3rd-order to solve the differential model equations. Following the steady state solutions, the method of lines is employed to convert the system of PDEs to ordinary differential equations. The results are presented graphically in Figure 1 and Figure 2.

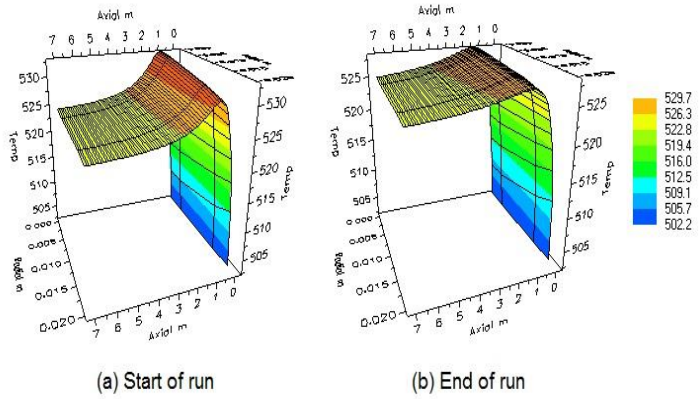

Figure 1. 2D Temperature profiles at the start and end of run.

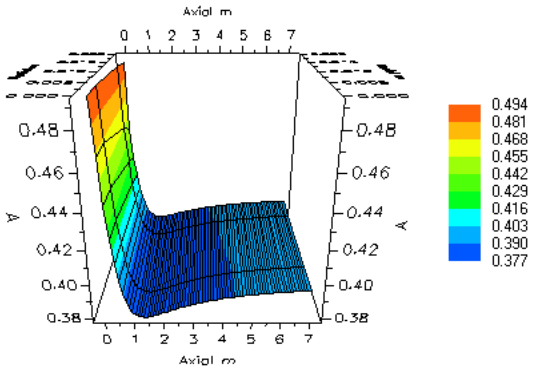

Figure 2. Catalyst activity at the end of run.

References

Alarifi, A., Alsobhi, S., Elkamel, A., Croiset, E. (2015). Multiobjective Optimization of Methanol Synthesis Loop from Synthesis Gas via a Multibed Adiabatic Reactor with Additional Interstage CO2 Quenching. *Energy & Fuels,29,530.*

Alarifi, A., Elkamel, A., Croiset, E. (2013). Steady-State Simulation of a Novel Annular Multitubular Reactor for Enhanced Methanol Production. *Ind. Eng. Chem. Res.,52,15387.*

De Wasch, A. P., and Froment, G. F. (1971). A two-dimensional heterogeneous model for fixed bed catalytic reactor, *Chem. Eng. Sci., 26, 629.*

Hanken, L. (1995), Optimization of Methanol Reactor. *Master's thesis, Nor. Univ. Sci. Technol.*