NOTE

REACTOR SIMULATION USING A NEW ANALYTICAL EFFECTIVENESS FACTOR ESTIMATION, COMPARISON WITH THE RIGOROUS NUMERICAL RESULTS

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Abstract

A new analytical method based upon a perturbation and matching technique was used to estimate effectiveness factors during the simulation of a fixed bed reactor for methanol synthesis. The results are in close agreement with those obtained by the rigorous numerical solution over a wide range of operating conditions.

Introduction

Recently Xu and Froment (1989a) used a global spline collocation to obtain the rigorous solution of the second order differential equation arising from a mass balance on the key component in a catalyst particle. They also applied this approach to methanol synthesis and simulated a methanol synthesis reactor based upon the heterogeneous model with intraparticle gradients (Xu and Froment, 1990). The rigorous solution was compared with that obtained on the basis of the generalized modulus approach, introduced by Bischoff (1965), Petersen (1965) and Aris (1965), for the effectiveness factor calculation.

In this work, a perturbation and matching technique previously developed (Gottifredi and Gonzo, 1987), in order to obtain the approximate analytical expression for the effectiveness factor estimation is used (Gonzo and Gottifredi, 1983, Gottifredi et al., 1986). Results of the reactor simulation using this procedure are compared with those presented by Xu and Froment (1990).

Analysis

The dimensionless mass balance for the key component, in this case carbon monoxide, in an isothermal spherical catalyst pellet in which methanol synthesis reaction take place is:

$$\frac{1}{\xi^2}\frac{d}{d\xi}\xi^2\frac{dC}{d\xi} = h^2 r^* \tag{1}$$

with

$$C=\frac{P_{CO}}{P_{CO^s}} \qquad H=\frac{P_{H_2}}{P_{CO^s}} \qquad M=\frac{P_{Me}}{P_{CO^s}} \tag{2a}$$

$$r^* = \frac{r}{r^s} \qquad h^2 = \frac{R_p^2 r^s}{D_{e,CO}(P_{CO}/RT)^s} \tag{2b}$$

and where ξ is the dimensionless radius.

The superscript s denotes properties evaluated at the external pellet surface. The Eq. (1) must be solved subject to the boundary conditions:

$$\frac{dC}{d\xi}=0 \quad \text{at} \quad \xi=0 \quad \text{and} \quad C=1 \quad \text{at} \quad \xi=i \tag{3}$$

The dimensionless concentrations of the other reactants and products involved in the reaction are related in a simple way with the dimensionless concentration of key component C, provided the effective diffusivities are constant through out the catalyst pellet:

$$H=\gamma_H (C-1)+\beta_H \tag{4a}$$

$$M=\gamma_M (C-1)+\beta_M \tag{4b}$$

with

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$$\gamma_H = 2\frac{D_{e,\,CO}}{D_{e,\,H_2}} \qquad \gamma_M = -\frac{D_{e,\,CO}}{D_{e,\,Me}} \tag{5a}$$

$$\beta_H = \frac{P_{H_2}{}^2}{P_{CO}{}^2} \qquad \beta_M = \frac{P_{Me}{}^2}{P_{CO}{}^2} \tag{5b}$$

assuming the reaction stoichiometry

$$CO + 2\,H_2 \rightarrow CH_3OH \tag{6}$$

Using a perturbation technique the asymptotic solutions of Eq. (1) for small and large values of the normalized Thiele modulus ϕ is found and therefrom the asymptotic behaviour of the effectiveness factor (Gonzo and Gottifredi, 1983);

$$\eta = 3\int_0^1 r^*\,\xi^2\,d\xi \tag{7}$$

$$\eta = 1 - \sigma_1\,\phi^2 + \sigma_2\,\phi^4 + 0(\phi^6) \qquad \text{for } \phi \rightarrow 0 \tag{8a}$$

$$\eta = \frac{1}{\phi} + \frac{\rho_2}{\phi^2} + 0\,(\phi^{-3}) \qquad \text{for } \phi \rightarrow \infty \tag{8b}$$

where:

$$\phi = \frac{h}{\rho_1} \tag{9a}$$

$$\rho_1 = 3\left[2\int_{C_{eq}}^{1} r^*\,dC\right]^{1/2} \tag{9b}$$

$$\rho_2 = -(18/\rho_1{}^3)\int_{C_{eq}}^{1}\left(2\int_{C_{eq}}^{C} r^*\,dC\right)^{1/2} dC \tag{9c}$$

$$\sigma_1 = r^{*\prime}(1)\;\rho_1{}^2/15 \tag{9d}$$

$$\sigma_2 = (2/315)\,[r^{*\prime}(1)^2 + 05\;r^{*\prime\prime}(1)]\,\rho_1{}^4 \tag{9e}$$

Here $r^{*\prime}(i)$ denotes the first derivative and $r^{*\prime\prime}(i)$ the second derivative with respect to concentration, all evaluated at $C = i$.

The following analytical expression for the effectiveness factor estimation was used, which fits the asymtotic behavior for η (Eqs. (8a) y (8b)) (Gottifredi et al. 1986).

$$\eta = (\phi^2 + \exp(-a\,\phi^2))^{-1/2} + \rho_2\,\phi^2(\phi^2 + \exp(-b\,\phi^2))^{-2} \tag{10}$$

where

$$a = 1 - 2(\sigma_1 + \rho_2) \tag{11a}$$

$$b = 1 + \left(\sigma_2 - \frac{3}{8} + \frac{3}{4}a - \frac{1}{8}a^2\right)/2\rho_2 \tag{11b}$$

The rate equation, the kinetic parameters and the equation for the equilibrium constant are those of Xu and Froment (1989b).

The effective difusivities were obtained from

$$D_{e,i} = \frac{\epsilon_s}{\tau}\left[\frac{1}{D_{k,i}} + \frac{1}{D_{i,m}}\right]^{-1} \tag{12}$$

The molecular binary diffusion coefficient D_{ij} was calculated from the correlation of Fuller et al. (Reid et al. 1987). The mean binary diffusion coefficient $D_{i,m}$ of component i in the multicomponent mixture was calculated according to the equation proposed by Xu and Froment (1990).

The heterogeneous model used assumes plug flow and does not include neither interfacial temperature and concentration gradients nor an intraparticle temperature gradient; since generally in industrial reactors flow velocity is high, while the particle effective thermal conductivity is also high.

The model equations and the conditions for simulation are also taken from Xu and Froment (1990).

The fourth order Runge-Kutta method was used for integration through the reactor coordinate z.

To obtain parameters ρ_1 and ρ_2 the calculation of the equilibrium concentration C_{eq} is required. Therefore the method of Euler was used to solve:

$$r^*(C) = 0 \tag{13}$$

The results of the reactor simulation are shown in Figs. 1 and 2, in which results obtained with the rigurous approach and Bischoff method are also shown.

The effectiveness factors estimated via analytical expression are about 0.5% lower than those calculated by the rigorous numerical method. The reactor exit conversion calculated by the Bischoff method is 0.1561, whereas the method proposed here yields 0.1385 in very close agreement with the rigorous result of 0.1392.

Following the procedure of Xu and Froment, an unrealistic case with strong internal diffusion limitation was simulated. A particle diameter of 6 cm was used, instead of 0.787 cm for the commercial catalyst. The relative difference between the values of the effectiveness factors calculated by Bischoff or the approximated method and the rigurous method are about 3%. But Bischoff method predicts effectiveness factors values higher than those calculated by the

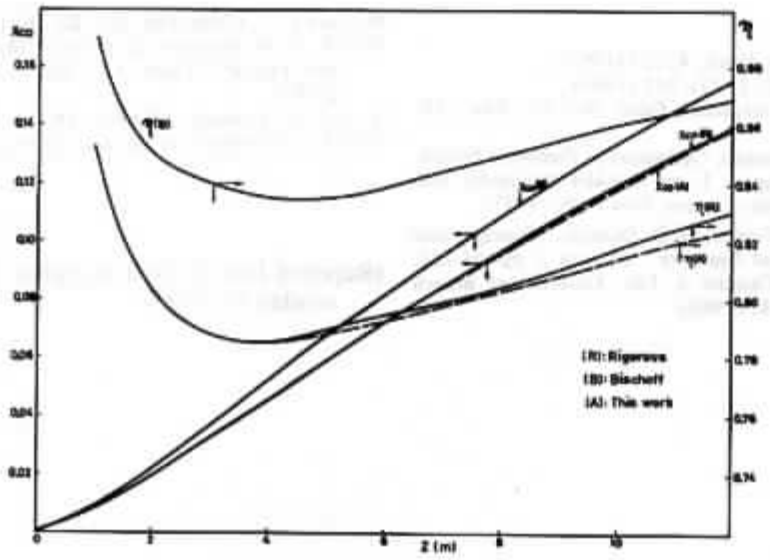

Fig. 1.– Effectiveness factors and CO conversion along the reactor.

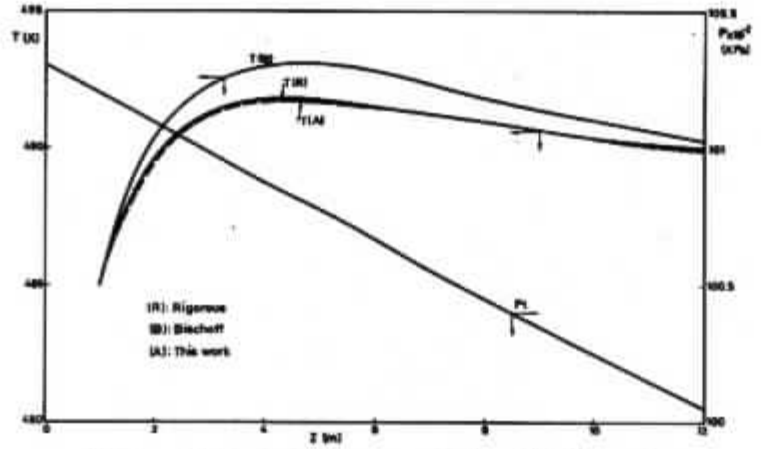

Fig. 2.– Temperature and pressure profiles within the reactor.

rigorous method, while the analytical approximate method gives values lower than those of the rigorous calculation.

As it can be seen, especially in the actual case, the effectiveness factor estimations as well as the conversion at the exit of the reactor predicted using Eq. (10) are in very close agreement with those obtained with the rigorous numerical method.

The main advantage of the method presented hereby is that effectiveness factors are analytically predicted, avoiding the computational effort for solving the particle mass balance differential equation; solution which is cumbersome even with novel numerical methods.

The method applied in this paper substantially reduces the computational effort involved in the simulation of fixed bed reactors with internal diffusional limitations. This opens new perspectives for on-line simulations, as required for advanced control algorithms, for instance.

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Notation

The nomenclature cited here is that of Xu and Froment (1990). (In this same issue).

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