TEMPERATURE AND CONCENTRATION DISTRIBUTIONS IN PACKED BEDS OF CATALYST WITH EXTERNAL AND INTERNAL TRANSPORT EFFECTS

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A calculation method is presented to estimate the temperature and the concentration distribution in a catalyst packed bed by finite difference approximation and by use of the local effectiveness factor, taking into consideration the external and internal transport resistance to catalyst particles.

The method is applied to the hydrogenation of ethylene and to the oxidation of sulfur dioxide, and is compared with experimental results by us and by Schuler et al.

Introduction

Axial and radial distributions of temperature and concentration in catalyst packed beds have been analysed based on the approximate linearization of the rate expression, the model of a network of perfectly stirred tanks, and the finite difference approximations of the heat and mass balance equations. Most of those analyses do not take into consideration the effects of resistances to heat and mass transfer in fluid film and in pores of the catalyst particles. However, it has been well established for a single catalyst particle that some marked distributions in temperature and concentration can be produced through the fluid film and in pores.

In this paper, a method is presented to estimate the temperature and the concentration distribution in a catalyst packed bed by the finite difference approximation, taking into consideration the external and internal transport resistance to catalyst particles. The local effectiveness factors in the bed are calculated and stored in advance for ranges of temperature and concentration presumed for conditions in bulk fluid. A proper local effectiveness factor is evaluated for each step from the stored values and multiplied to the reaction rate in the finite difference equations. The method is applied to the hydrogenation of ethylene and to the oxidation of sulfur dioxide and is compared with experimental results by us and by Schuler et al.

Calculation Procedure

In a tubular catalyst packed bed of the external heat-exchange type, quasi-homogeneity of the bed is assumed, along with plug flow of the reactive fluid, no axial mass diffusion and heat conduction and constancy of the physical properties. At steady state, the following equations of heat and material balance are obtained for a simple reaction:

\[ \frac{\partial t}{\partial z} = \left( \frac{\partial^2 t}{\partial r^2} + \frac{1}{r} \frac{\partial t}{\partial r} \right) + aE_{ib} \frac{R}{R_i} \]  
\[ \frac{\partial X_a}{\partial z} = \left( \frac{\partial^2 X_a}{\partial r^2} + \frac{1}{r} \frac{\partial X_a}{\partial r} \right) + bE_{ib} \frac{R}{R_i} \]

The boundary conditions are:

\[ \frac{\partial t}{\partial r} = 0, \quad \frac{\partial X_a}{\partial r} = 0 \quad \text{at} \quad r = 0 \]
\[ \frac{\partial t}{\partial r} = -h_i(t-t_w), \quad \frac{\partial X_a}{\partial r} = 0 \quad \text{at} \quad r = 1 \]
\[ t = t_0(r), \quad X_a = 0 \quad \text{at} \quad z = 0 \]

The local effectiveness factor based on the conditions in bulk fluid at the location, \( E_{ib} \), was calculated in view of the external and the internal transport effect by the method published previously. Because the method is difficult to formulate as a subprogram in digital computation of Eqs. (1) and (2), values of \( E_{ib} \) are calculated in advance on the grid points \( (X_{a,i}, t_j) \) for expectable ranges of \( X_a \) and \( t \), where

\[ X_{a,i} = j \Delta X_a \quad i = 0, 1, 2, \ldots, n \]
\[ t_j = j \Delta t \quad j = 0, 1, 2, \ldots, m \]

The values of \( E_{ib} \) are converted for convenience to \( F(X_{a}, t) \) by

\[ F(X_{a}, t) = E_{ib}/E_{ib}^* \]

where, \( E_{ib}^* \) is the local effectiveness factor of the catalyst without transport effects through the fluid film. The \( E_{ib}^* \) can be calculated by standard methods such as given by Thiele for isothermal catalyst and Tinkler and Metzner or Weisz and Hicks for nonisothermal catalysts. The \( F(X_{a}, t) \) value for specified \( X_a \) and \( t \) is obtained by an interpolation of the values on grid points by the following interpolation formulas, which are stored as a subprogram.

\[ F(X_{a}, t_{j+i}) = F(X_{a}, t_j) + [F(X_{a}, t_{j+i}) - F(X_{a}, t_{j})](X_{a} - i \Delta X_{a})/\Delta X_{a} \]

and, from Eqs. (8) and (9)

\[ F(X_{a}, t) = F(X_{a}, t_j) + [F(X_{a}, t_{j+i}) - F(X_{a}, t_{j})](t - j \Delta t)/\Delta t \]

From \( F(X_{a}, t) \), \( E_{ib}^* \) can be obtained by \( E_{ib} = F(X_{a}, \).

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By the use of the numerical values of $E_{fb}$, Eqs. (1) ~ (5) are solved numerically by the published methods, and the temperature and the concentration distribution in the catalyst packed bed including the internal and the external transport effects on the catalyst particles can be evaluated. The time required for the calculation for the hydrogenation of ethylene described below was larger by 19% for the pre-calculation of the $F(X_a, t)$ on the grid points and larger by 9% for the selection of the appropriate grid points and the interpolations than the calculation neglecting the transport effects, which required about 45 mins. by the NEAC 2203 digital computer.

Hydrogenation of Ethylene

Experimental: The experimental apparatus and the procedure for the ethylene hydrogenation reaction were the same as in previous paper. Describing it briefly, granular nickel-kieselguhr catalyst prepared from a mixture of about one to ten of pulverized Harshaw nickel catalyst, Ni-0101 T, to kieselguhr as diluent was packed in a glass tubular reactor of 9.2mm I.D. with a thermocouple well of 1.5mm O.D. at the center. Particles of diameter 2.00~2.38mm were applied. No quartz particles were used as the bed diluent. The catalyst was reduced in situ in a flow of hydrogen gas and stabilized in a flow of a mixture of hydrogen and ethylene.

Reactions were performed for the conditions of thermostat temperature at 55.0°C, total pressure under atmosphere, feed composition of $C_2H_4 : H_2 = 20 : 80$, total volumetric rates of 7.50, 20.0, and 40.0cm$^3$ (18.0°C, 1 atm)/sec, and a catalyst weight of 5.00 and 10.00g, which were 8.5 and 17.0cm in height of packing.

Experimental Results: The temperature distributions along the axis of the reactor measured by an Alumel vs. Chromel thermocouple of 0.1mm dia. moving in the well and the conversions obtained at the exit of the reactor, respectively, are shown by the circular and the square points in Figs. 1, 2, and 3.

Discussion

Estimation of Local Effectiveness Factor: The reaction rate of the hydrogenation of ethylene can be expressed by the equation

$$R = 1.21 \cdot 10^{-5} \left( \frac{1 - X_A}{1 - 0.2X_A} \right)^{4.44} \exp \left( \frac{14.28t}{1 + t} \right) \left[ \text{mol-C}_2\text{H}_4/\text{sec} \cdot \text{cm}^3 \cdot \text{cat} \right] \quad (11)$$

The dimensionless terms reduce to

$$m_b = \left[ m_0 \right] \frac{z_A}{(1 + t)} \exp \left[ 7.14t/(1 + t) \right] \quad (12)$$

$$\beta_0 = \left[ \beta_0 \right] \frac{z_A}{(1 + t)} \quad (13)$$

$$3N\mu/\beta_0 = \left[ 3N\mu/\beta_0 \right] \frac{(1 + t)/z_A}{(1 - 0.2X_A)} \quad (14)$$

where, $z_A = (1 - X_A)/(1 - 0.2X_A)$

The temperature and the concentration difference through the fluid film can be obtained by

$$\theta_s = \frac{T_s - T_i}{T_i} = \frac{m_b^2E_{fb}F(X_A, t)}{3N\mu/\beta_0} = \frac{m_b^2E_{fb}^*F(X_A, t)}{3N\mu/\beta_0} \quad (15)$$

As shown in the previous paper, values of $[m_0]$ and $[\beta_0]$, respectively, were 1.94 and 1.72 for catalyst particle of $d_p = 0.219$cm. Values of $3N\mu/\beta_0$ vary with the total feed rate and are shown in Table 1, along with values of other constants. Using these numerical values, values of $E_{fb}$ and $F(X_A, t)$ were calculated by the NEAC 2203 digital computer for the ranges of
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In those figures, solid and dotted lines, respectively, calculated by the above method are shown in Figs. 1–3, it will be seen that the agreement between those distributions obtained by omitting the external transport resistances. The chain lines indicate those distributions in bulk and at the outer surface of the catalyst. The difference in these two kinds of temperature profiles reaches about 10°C at the inlet and decreases along the reactor length down to the exit. This tendency was seen also from the experimental results of Hall et al.11, although the reaction conditions were different from those of Schuler et al. Thin solid lines in Fig. 4 show the temperature profiles along the axis calculated by other investigators8.

Fig. 5 shows profiles of cross-sectional average conversion. Observed values were obtained from the volume average conversions of the exit gas. The calculated profiles obtained by the present method are shown by the thick solid lines for the bulk fluid and by the thick dotted lines for the outer surface of the catalyst. The difference is also large at the inlet and decreases along the reactor length down to the exit. Thin solid lines in Fig. 5 show conversion profiles calculated by other investigators8.

Investigations of Figs. 4 and 5 show that the calculated results obtained by the present method, in which both the internal and the external transport effects are taken into consideration, differ little from other calculations, where no consideration is taken of the local effectiveness factor. This may be attributed to the two effects compensating each other, i.e., the concentration drop through the fluid film influences the reaction rate to decrease and the temperature rise works conversely.

Table 1 Numerical values of dimensionless terms

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \tau ) [sec]</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( d )</th>
<th>( h_1 )</th>
<th>( h_2 )</th>
<th>( [\sigma^{3} \lambda^{3}]_{0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_4 + \text{H}_2 )</td>
<td>7.50</td>
<td>0.0637</td>
<td>0.0363</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 + \text{H}_2 )</td>
<td>20.0</td>
<td>0.0361</td>
<td>0.0136</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 + \text{H}_2 )</td>
<td>40.0</td>
<td>0.0176</td>
<td>0.00682</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{SO}_2 + \text{1/2O}_2 )</td>
<td>740.0</td>
<td>0.163</td>
<td>0.602</td>
<td>0.0343</td>
<td>0.131</td>
<td></td>
<td>8.31</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Temperature dependence of constants in the rate equation for the oxidation of sulfur dioxide

\[
K = \exp\left(\frac{11.178}{T} - 10.55\right)
\]

\[
T \leq 693^\circ K
B = 0.0496 \exp(4.361(1/T - 1/693))
D = 17.5 \exp(9.201(1/T - 1/693))
\]

\[
T > 693^\circ K
B = 0.499 \exp(9.064(1/T - 1/693))
D = 17.5 \exp(2.652(1/T - 1/693))
\]

\[\eta_{0} = 0.9083 \eta_{0}\]  
\[\eta_{0}^{*} = (3/\eta_{0}) \left(1/\coth \eta_{0} - 1/\dot{\eta}_{0}\right)\]

Temperature and Concentration Distribution in the Bed:

Because of the small diameter of the reactor used for the ethylene hydrogenation under discussion, a one-dimensional model was assumed and no radial gradients were considered. This assumption corresponds to the assumption that the radial heat transfer resistance exists at the wall only. Then the following equations are applicable in place of Eqs. (1) and (2):  
\[
dt/dz = aE_{fR} \alpha_{i} - h_{i}(t - t_{w}) \tag{20}\]
\[
dX_{A}/dz = bE_{fR} \alpha_{i} \tag{21}\]

Numerical solutions of Eqs. (20) and (21) were obtained from the subroutine in NEAC 2293, where the Runge-Kutta-Gill's method was applied. The increment to axial direction was taken as \( \Delta x = 0.025 \text{cm} \).

The temperature and the conversion distributions calculated by the above method are shown in Figs. 1–3. In those figures, solid and dotted lines, respectively, indicate those distributions in bulk and at the outer surface of the catalyst in view of the external and internal transport resistances. The chain lines indicate those distributions obtained by omitting the external transport effects, that is, by the use of \( E_{fR}^{*} \). From Figs. 1–3, it will be seen that the agreement between the experimental points and the calculated lines is improved by taking into consideration the external transport effects. However, the temperature distributions still show some marked discrepancies. The discrepancies may be attributed to the omission of the axial heat transfer in the calculations and the inaccuracy in the temperature measurements.

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Dioxide: Experimental results on the oxidation of sulfur dioxide obtained by Schuler et al.10 were compared with the calculations by the present method. The rate equation was given by Olson et al.9  
\[ R = \left(p_{SO}_{2}p_{O}_{2}/K\right)\left(B + Dp_{SO}_{2}\right)^{1/2} \tag{22}\]

where, the values of \( K, B, \) and \( D \) are shown in Table 2.

Values of \( F(X_{A}, t) \) were calculated for the range of \( X_{A}=0.9 \) and \( T=190-500^\circ \text{C} \) with increments of \( \Delta X_{A} = 0.1 \) and \( \Delta T=10^\circ \text{C} \). Numerical solutions to Eqs. (1) and (2) for a two-dimensional model were obtained by converting them to ordinary differential equations by the method of Kubota et al.9. Values of the dimensionless terms, \( a, b, c, d, \) and \( h_{1} \) are shown in Table 1.

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**Nomenclature**

- \( C \) = concentration of a key component \([\text{mol/cm}^3\text{-fluid}]\)
- \( C_{ps} \) = molal heat capacity of fluid \([\text{cal/mol} \cdot \text{°K}]\)
- \( D_{er} \) = radial effective diffusivity in packed bed \([\text{cm}^2\text{-fluid/sec} \cdot \text{cm-bed}]\)
- \( E_{fb} \) = local effectiveness factor based on conditions in bulk \([-]\)
- \( F(X_A, t) \) = a factor given by Eq. (7) \([-]\)
- \( G_{to} \) = total molar feed rate \([\text{mol/sec} \cdot \text{cm}^3\text{-bed}]\)
- \(-\Delta H\) = heat of reaction based on the key component \([\text{cal/mol}]\)
- \( h \) = heat-transfer coefficient \([\text{cal/sec} \cdot \text{cm}^2 \cdot \text{wall} \cdot \text{°K}]\)
- \( k_{er} \) = radial effective thermal conductivity in packed bed \([\text{cal/sec} \cdot \text{cm}^3\text{-bed} \cdot \text{°K}]\)
- \( n \) = order of reaction \([-]\)
- \( R_t \) = radius of tubular packed bed \([\text{cm-bed}]\)
- \( r' \) = radial coordinate of cylindrical packed bed \([\text{cm-bed}]\)
- \( R \) = reaction rate of the key component \([\text{mol/sec} \cdot \text{cm}^3\text{-cat}]\)
- \( T \) = temperature \([\text{°K}]\)
- \( u_{to} \) = total volumetric feed rate \([\text{cm}^3\text{-fluid/sec}]\)
- \( X_A \) = conversion of the key component \([-]\)
- \( Y_A \) = mole fraction of the key component \([-]\)
- \( z' \) = longitudinal coordinate of cylindrical packed bed \([\text{cm-bed}]\)
- \( \varepsilon_b \) = void fraction of packed bed \([\text{cm}^3\text{-void/cm}^3\text{bed}]\)

**Suffixes**

- \( b \) = values in bulk fluid
- \( o \) = values at feed conditions
- \( s \) = values at outer surface of catalyst particles
- \( w \) = values at reactor wall

**Dimensionless terms**

\[ t = \frac{T - T_o}{T_e}, \quad r = \frac{r'}{R_t}, \quad z = \frac{z'}{R_t}, \quad a = \frac{-\Delta H R_t(1 - \varepsilon_b) R_o}{C_{ps} G_{to} T_o}, \quad b = \frac{R_t(1 - \varepsilon_b) R_o}{G_{to} Y_A}, \quad c = \frac{k_{er} G_{to} R_t}{C_{pf} G_{to} R_t}, \quad d = \frac{D_w C_{oi}}{G_{to} R_t} \]
Reaction Diagram for Reversible Solid-Gas Reactions Based on Unreacted Core Model

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The $(T, x_s)$ reaction diagram is proposed for non-isothermal analyses of reversible solid-gas reactions based on the unreacted-core shrinking model. When an equilibrium curve, a reaction curve, and a tie-line are drawn on this diagram, the temperature and concentration at the reaction surface, which play an important role in solid-gas reactions but which have so far been calculated only by numerical computations, can easily be obtained. The reaction diagram can also elucidate how the three rate-determining steps of chemical reaction, mass transfer, and heat transfer are interrelated in reversible processes.

Introduction

The "unreacted-core shrinking model" has been applied not only to analyses of solid-gas reactions but also to the formation or melting of ice, the drying of porous bodies, and the thermal decomposition of solids. These moving boundary problems have always been classified into three groups by the basic equations describing their phenomena, i.e., (A) heat transfer, (B) mass transfer, and (C) simultaneous mass and heat transfer.

The formation and melting of ice have been treated as group (A), and drying in the falling-rate period as group (C). The solid-gas reaction was discussed in detail from the viewpoint of group (B) by Yagi and Kunii7). However, it is generally non-isothermal and should properly be treated also as group (C), since the heat of reaction plays a very important role in the reaction1-4).

Nissan et al.5) observed that in shell-like drying in the second-falling-rate period, the temperature at the evaporating surface was maintained almost constant (pseudo-wet-bulb temperature). On the other hand, Satterfield and Feakes6) observed a similar phenomenon in the experiment of burning carbon-cement mixture. The similarity among drying, thermal decomposition, and the solid-gas reaction suggests that the solid-gas reaction should be treated as group (C).

In the previous papers1-3), the authors reported the non-isothermal analysis of irreversible solid-gas reactions. But some reactions, e.g. the reduction of iron oxide, are reversible, and the equilibrium relation plays an important role in these reversible reactions as well as in the drying and the thermal decomposition of solids.

In this paper, in comparison with such drying and thermal decomposition, reversible solid-gas reactions are analyzed non-isothermally on the basis of the unreacted-core model. Reaction diagrams are proposed to clarify how the rate-determining processes of chemical reaction, mass transfer, and heat transfer are interrelated. They also permit easy calculation of the temperature and concentration at the reacting-core surface, which are very important in determining the reaction rate accurately. An application of such reaction diagram will be illustrated later.

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