Thermoflow Multiplicity in a Packed-Bed Reactor. II: Impact of Volume Change

Steady states with different flow rates and temperature profiles may exist in a monolith or multitube packed-bed reactor operating under a prescribed pressure drop, due to the coupling among the species, energy, and momentum balances, and the change of physical properties with temperature and pressure. Criteria are derived predicting the conditions under which thermoflow multiplicity can occur for a gaseous reaction involving a change in the number of moles. In general, a reaction-induced volume increase enables thermoflow multiplicity to occur for reactions with a lower adiabatic temperature rise. A surprising finding is that thermoflow multiplicity may be found for an isothermal reaction involving a volume decrease. This point emphasizes the difference in the feedback mechanism leading to thermoflow and thermokinetic multiplicity.

J. P. Lee, V. Balakotaiah, Dan Luss
Department of Chemical Engineering
University of Houston
Houston, TX 77004

Introduction

When heat is generated or transferred to a system, several different flow rates may be obtained under the same pressure drop. This thermoflow multiplicity is caused by the interaction between the momentum and energy balances and a sensitive dependence of the physical properties on the state of the fluid (temperature, composition, etc.). This behavior is known to exist for flow in heated pipes (Pearson et al., 1973; Merzhanov and Stolin, 1974; Davis et al., 1983), evaporators (Ledinegg, 1938; Dogan et al., 1983), heated granular bed (Goldshtik, 1979), and tubular reactors (Gupalo and Ryazantsev, 1968; Bostandzhiyan et al., 1979; Zhirkov et al., 1980).

Matros and Chumakova (1980) pointed out that thermoflow multiplicity may occur in an adiabatic packed-bed reactor in which the reactant was incompressible. In the first part of this work (Lee et al., 1987) we found that the same multiplicity can occur if the fluid is compressible. That analysis showed that the pseudohomogeneous plug flow model with no axial dispersion predicts that thermoflow multiplicity can exist in an adiabatic reactor only for extremely exothermic single reactions.

The possible existence of different flow rates and temperature profiles in different tubes in a multitube or monolith reactor may create highly undesired thermal stresses, which can damage the reactor. Thus, it is of practical importance to know if thermoflow multiplicity will exist under practical conditions.

Correspondence concerning this paper should be addressed to V. Balakotaiah and D. Luss.

The goal of this study is to examine the impact of the change in the volume of a gaseous reaction mixture on the parameters for which thermoflow multiplicity occurs. This will be accomplished by deriving criteria predicting the conditions under which thermoflow multiplicity occurs for several limiting models and comparing these with those found by Lee et al. (1987) for the case of no volume change.

Development of a Mathematical Model

Consider a single, irreversible, exothermic reaction $A \longrightarrow \upsilon B$ that occurs in an adiabatic packed-bed reactor, operating under a prescribed pressure drop. The steady-state continuity, species, energy, and momentum balances for a one-dimensional plug-flow model, which ignores any axial dispersion, are

$$\frac{d}{dz}(\rho u) = 0 \tag{1}$$

$$\frac{d}{dz}(uC_A) = -r \tag{2}$$

$$\frac{d}{dz}(uC_B) = \upsilon r \tag{3}$$

$$\frac{d}{dz}(uC_i) = 0 \quad (4)$$

$$\rho u c_p \frac{dT}{dz} = (-\Delta H) r \quad (5)$$

$$\frac{dP}{dz} + \rho u \frac{du}{dz} = -f_p \quad (6)$$

The frictional pressure drop f_p is computed by the Ergun equation

$$f_p = A\mu u + B\rho u^2 \quad (7)$$

where the constants A and B depend on the properties of the packing. The corresponding boundary conditions are

$$P = P_o, C_A = C_{Ao}, C_B = C_{Bo}, T = T_o \quad \text{at } z = 0 \quad (8)$$

$$P = P_1 \quad \text{at } z = L \quad (9)$$

Multiplying Eq. 2 by $-\Delta H$, adding it to Eq. 5 and integrating gives

$$y = 1 + \beta x \quad (10)$$

where

$$y = \frac{T}{T_o} \quad \beta = \frac{(-\Delta H) C_{A_o}}{\rho_o c_p T_o} \quad (11)$$

and the conversion

$$x = \frac{u_o C_{A_o} - u C_A}{u_o C_{A_o}} \quad (12)$$

Assuming that the gaseous reactant satisfies the ideal gas law, Eqs. 1–4 give

$$C_{T0} = \frac{P_o}{RT_o} = \frac{u}{u_o}\frac{P}{RT} - (v - 1) C_{A_o} x \quad (13)$$

which may be brought to the form

$$\frac{u}{u_o} = \frac{y}{\Pi}\left(1 + \sigma \frac{y - 1}{\beta}\right) \quad (14)$$

where

$$\Pi = \frac{P}{P_o} \quad \sigma = (v - 1)\frac{C_{A_o}}{C_{T0}} \quad (15)$$

σ is the maximal possible change in the number of moles by the reaction.

Differentiation of Eq. 14 with respect to z and substitution into Eq. 6 gives

$$\left[1 - \frac{\rho_o u_o^2}{P_o}\frac{y}{\Pi^2}\left(1 + \sigma\frac{y-1}{\beta}\right)\right]\frac{d\Pi}{dz} + \frac{\rho_o u_o^2}{P_o}\frac{1}{\Pi} \cdot \left(1 + \sigma\frac{2y - 1}{\beta}\right)\frac{dy}{dz} = -\frac{1}{P_o}(A\mu u + B\rho u^2) \quad (16)$$

Under practical conditions the term $\rho_o u_o^2$ is significantly smaller than P_o. Thus, to simplify the analysis we omit the second term in the brackets multiplying $d\Pi/dz$. We assume that the reaction is of zero order, so that

$$r(C, T) = k(T)H(C) = k(T_o)X(y)H(C) \quad (17)$$

where H is the Heaviside function and

$$X(y) = k(T)/k(T_o) = \exp\left[\frac{E}{RT_o}\left(1 - \frac{1}{y}\right)\right] \quad (18)$$

We assume that the viscosity is independent of conversion and pressure and is an increasing function of the temperature, namely

$$\mu = \mu(T_o)\left(\frac{T}{T_o}\right)^\delta \quad (19)$$

where the positive constant δ is usually between 0.5 and 1. Introducing the dimensionless variables

$$s = \frac{z}{L} \quad \gamma = \frac{E}{RT_o}$$

$$Da = \frac{k(T_o)L}{u_o C_{Ao}} \quad E_1 = \frac{A\mu(T_o)k(T_o)L^2}{P_o C_{Ao}}$$

$$E_2 = \frac{B\rho_o k(T_o)^2 L^3}{P_o C_{Ao}^2} \quad E_3 = \frac{\rho_o k(T_o)^2 L^2}{P_o C_{Ao}^2} \quad (20)$$

the energy and momentum balances can be written in the dimensionless form

$$\frac{dy}{ds} = \beta Da X(y) H(1 + \beta - y) \quad (21)$$

$$\frac{1}{2}\frac{d\Pi^2}{ds} = -\left(\frac{E_1 y^{1+\delta}}{Da} + \frac{E_2 y}{Da^2}\right)\left(1 + \sigma\frac{y-1}{\beta}\right) - \frac{E_3}{Da^2}\left(1 + \sigma\frac{2y-1}{\beta}\right)\frac{dy}{ds} \quad (22)$$

subject to the boundary conditions

$$y(0) = \Pi(0) = 1 \quad \Pi(1) = \Pi_1 \quad (23)$$

To derive the steady state equation, we treat separately two cases. First, we consider cases in which the conversion is not complete, that is, $y_1 < 1 + \beta$. Integrating Eq. 21 we get

$$G(y_1, Da, p^*) = \beta Da - J(y_1, 0) = 0 \quad (24)$$

where we define

$$J(y_1, \alpha) = \int_1^{y_1} y^\alpha X^{-1}(y)\, dy \quad (25)$$

and the parameter vector

$$p^* = (\gamma, \beta, \sigma, \delta, E_1, E_2, E_3) \quad (26)$$

Dividing Eq. 22 by Eq. 21 and integrating gives

$$F_1(Da, \Lambda_j, p) = \frac{1}{\Lambda_j} - \frac{2E_1/E_j}{\beta Da^2}\left[\left(1 - \frac{\sigma}{\beta}\right) J(y_1, 1+\delta) + \frac{\sigma}{\beta} J(y_1, 2+\delta)\right] - \frac{2E_2/E_j}{\beta Da^3}\left[\left(1 - \frac{\sigma}{\beta}\right) J(y_1, 1) + \frac{\sigma}{\beta} J(y_1, 2)\right] - \frac{2E_3/E_j}{Da^2}(y_1 - 1) \cdot \left(1 + \frac{\sigma}{\beta} y_1\right) = 0 \tag{27}$$

where we define

$$\Lambda_j = \frac{E_j}{1 - \Pi_1^2} \quad j = 1, 2, 3 \tag{28}$$

and $p = (\gamma, \beta, \sigma, \delta$ and two $E_i/E_j\ i \neq j)$.

In solving Eq. 27 one needs to use Eq. 24 to determine the monotonic dependence of y_1 on Da. Equation 27 is valid for all $y_1 < 1 + \beta$, or equivalently for all $Da < Da^*$, where Da^* is the smallest Da for which the conversion is complete. It satisfies the relation

$$\beta Da^* = J(1 + \beta, 0) \tag{29}$$

For $Da > Da^*$, the reactant is completely consumed within the bed at $s_c = Da^*/Da$ and $y = 1 + \beta$ for $s_c < s < 1$. The value of Π_c^2 can be found by substitution of $y_1 = 1 + \beta$ into Eq. 27, and $\Pi_c^2 - \Pi_1^2$ can be found by integration of Eq. 22 from s_c to $s = 1$. Eliminating Π_c^2 between these two relations we get the steady state equation

$$F_2(Da, \Lambda_j, p) = \frac{1}{\Lambda_j} - \frac{2E_1/E_j}{\beta Da^2}\left[\left(1 - \frac{\sigma}{\beta}\right) \cdot J(1+\beta, 1+\delta) + \frac{\sigma}{\beta} \cdot J(1+\beta, 2+\delta)\right] - \frac{2E_2/E_j}{\beta Da^3} \cdot \left[\left(1 - \frac{\sigma}{\beta}\right) J(1+\beta, 1) + \frac{\sigma}{\beta} \cdot J(1+\beta, 2)\right] - \left[\frac{2E_1/E_j}{Da}(1+\beta)^{1+\delta} + \frac{2E_2/E_j}{Da^2}(1+\beta)\right](1+\sigma) \cdot \left(1 - \frac{J(1+\beta, 0)}{\beta Da}\right) - \frac{2E_3/E_j}{Da^2} \cdot [\beta + \sigma(1+\beta)] = 0 \tag{30}$$

Thus, the steady state equation is of the form

$$F(Da, \Pi_1, p) = \begin{cases} F_1 = 0 & Da < Da^* \\ F_2 = 0 & Da > Da^* \end{cases} \tag{31}$$

Analysis of F indicates that it has the following properties:

1. F is continuous for all $Da > 0$
2. dF/dDa is not continuous at $Da = Da^*$ unless $E_3 = 0$
3. d^mF/dD_a^m $(m \geq 2)$ is discontinuous at $Da = Da^*$

Analysis of Limiting Cases

The influence of a change in the number of moles on the multiplicity features will be determined by dividing the global parameter space into regions with qualitatively different bifurcation diagrams of Da vs. Π_1, using the mathematical tools presented by Lee et al., (1987). The emphasis here will be on the results; details of the algebraic manipulations can be found elsewhere (Lee, 1987).

The parameter vector p contains six elements. Thus, to simplify the analysis and presentation of results we consider here only three limiting cases, in each of which we assume that two of the E_i vanish.

Limiting case a, laminar pressure loss

This limiting case is based on the assumption that the turbulent pressure loss term in the Ergun equation is negligible in comparison to the laminar one, and that the momentum change due to the thermal expansion of the fluid is also very small. This assumption is equivalent to setting $E_2 = E_3 = 0$.

Similar to the case of no volume change, it can be shown that thermoflow multiplicity may exist for some feasible Λ_1 only if the (γ, β) values are to the right of the g_1^* curve. This sufficient uniqueness boundary is the set of all (γ, β) values satisfying the conditions

$$\frac{dF_1}{dDa}(Da^*) = 0 \tag{32a}$$

and

$$F(Da^* - \epsilon)F(Da^* + \epsilon) < 0 \tag{32b}$$

Simplification of Eq. 32a gives the sufficient uniqueness boundary

$$\sigma = \frac{2\beta J(1+\beta, 1+\delta) - \beta(1+\beta)^{1+\delta}J(1+\beta, 0)}{\beta(1+\beta)^{1+\delta}J(1+\beta, 0) + 2J(1+\beta, 1+\delta) - 2J(1+\beta, 2+\delta)} \tag{33}$$

The impact of the viscosity parameter δ on the multiplicity features has been examined by Lee et al. (1987). In the following analysis δ is set to be 0.5.

Figure 1 shows a plot of Eq. 33 for various σ values. It is seen that increasing σ shifts the g_1^* to the left. Thus, an increase in the number of moles $(\sigma > 0)$ decreases the minimum β value for which multiplicity exists for some γ and Λ_1 values, while a decrease in the volume with reaction $(\sigma < 0)$ increases the minimum β for which thermoflow multiplicity occurs for some γ and Λ_1.

The g_1^* graphs intersect the β axis $(\gamma = 0)$ at β values that satisfy the relation

$$\sigma = \frac{+0.8\beta(1+\beta)^{2.5} - \beta^2(1+\beta)^{1.5} - 0.8\beta}{-\frac{4}{7}(1+\beta)^{3.5} + \frac{4}{5}(1+\beta)^{2.5} + \beta^2(1+\beta)^{1.5} - \frac{8}{35}} \tag{34}$$

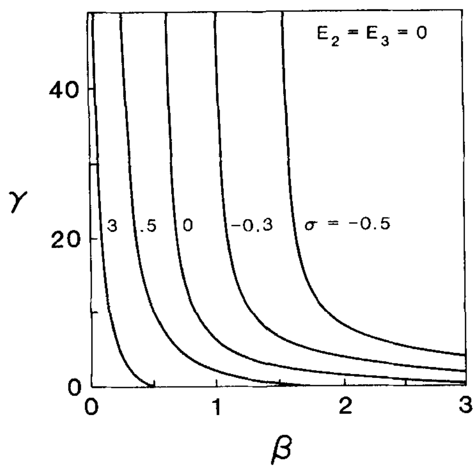

Figure 1. Dependence of uniqueness region on volume expansion parameter σ.
A unique solution always exists to the left of the curve

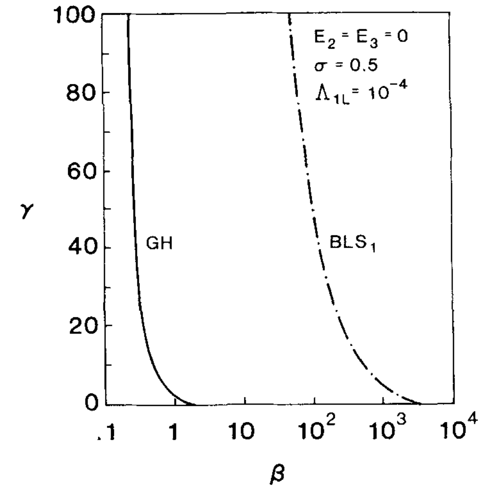

Figure 2. A typical multiplicity region in the (γ, β) plane.
Boundaries formed by g_1^* curve and boundary limit set 1, BLS_1

For any $\sigma \leq 1$ the g_1^* graph approaches for large γ values an asymptotic β value denoted by β_m, which satisfies the relation

$$\beta_m = \left(\frac{2}{\sigma + 1}\right)^{1/(1+\delta)} - 1 = \left(\frac{2}{\sigma + 1}\right)^{2/3} - 1 \quad \sigma \leq 1 \quad (35)$$

Numerical calculations show that β_m is a conservative lower bound on β, and that thermoflow multiplicity cannot occur for any

$$\beta < \beta_m \quad (36)$$

When $\sigma \geq 1$, multiplicity exists for arbitrarily small values of β for some γ and Λ_1. In this case, the g_1^* graph approaches asymptotically for large γ values the graph of

$$\beta\gamma = c(\sigma) \quad (37)$$

This value of c may be estimated from the relation

$$\sigma = \frac{1}{1 - \frac{2}{c}\left[1 - \frac{c \exp(-c)}{1 - \exp(-c)}\right]} \quad (38)$$

The approximation of c improves as σ increases.

In this case thermoflow multiplicity does not occur for an isothermal reaction as the g_1^* curve is always to the right of the γ axis. The region of (γ, β) for which thermoflow multiplicity occurs for some exit pressure larger than a limiting value Π_L, or equivalently for some $\Lambda_1 > \Lambda_{1L}$, is bounded between the g_1^* and the BLS_1 (boundary limit set 1) graphs. The BLS_1 consists of the (γ, β) values for which ignition occurs for $\Pi_1 = \Pi_L$, or equivalently $\Lambda_1 = \Lambda_{1L}$. At these points

$$F_1 = \frac{dF_1}{dDa} = 0 \quad \text{at } \Lambda_1 = \Lambda_{1L} \quad (39)$$

Figure 2 shows a typical multiplicity region for $\sigma = 0.5$ and $\Lambda_{1L} = 10^{-4}$. A comparison of this figure with Figure 8 presented by Lee et al. (1987) for the case of no volume change ($\sigma = 0$) clearly shows that the multiplicity region has been shifted to lower (and more realistic) parameter values.

Limiting case b, turbulent pressure loss

This limiting case is based on the assumption that both the laminar pressure term in the Ergun equation and the momentum change due to thermal expansion of the gas are negligible in comparison to the turbulent pressure drop. This is equivalent to setting $E_1 = E_3 = 0$ in the steady state equation. This model predicts the observed pressure drop under industrial conditions better than other limiting models (Lee et al., 1987). For realistic values of the parameters $(0 < \beta < 5)$ a sufficient uniqueness boundary in the (γ, β) space is the g_2^* curve, defined by Eq. 32. Simplifying Eq. 32a we find that this sufficient uniqueness boundary must satisfy the relation

$$\sigma = \frac{3\beta J(1+\beta, 1) - \beta(1+\beta)J(1+\beta, 0)}{\beta(1+\beta)J(1+\beta, 0) + 3J(1+\beta, 1) - 3J(1+\beta, 2)} \quad (40)$$

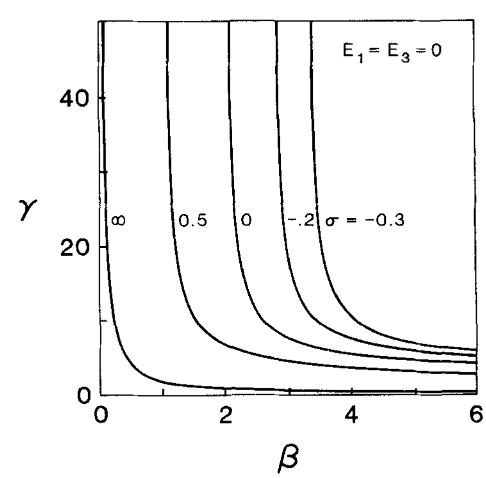

Figure 3. Dependence of uniqueness region on volume expansion parameter σ.
A unique solution always exists to the left of g_2^*

A plot of Eq. 40 for several σ values, Figure 3, shows that the uniqueness boundary is shifted to the left as σ is increased. This implies that the higher the volume expansion caused by the reaction, the smaller is the minimal β for which multiplicity occurs for some γ and Λ_2 values.

For all σ in $(2 - \sqrt{6}, 2)$ each g_2^* graph approaches for large γ an asymptotic β value, denoted by β_m. It can be shown that

$$\beta_m = \frac{2 - \sigma}{1 + \sigma} \tag{41}$$

Thus, a sufficient condition for uniqueness for σ in $(2 - \sqrt{6}, 2)$ is

$$\beta < \beta_m \tag{42}$$

For $\sigma \geq 2$ the g_2^* graph approaches asymptotically the hyperbola defined by Eq. 37 with

$$\sigma = \frac{2}{1 + 3\dfrac{(c+1)\exp(-c) - 1}{c[1 - \exp(-c)]}} \tag{43}$$

This approximation of the value of c improves as σ increases. Numerical calculations show that for any $\sigma > 2$ each g_2^* curve is to the right of the hyperbola $\gamma\beta = 2.07$.

The computations show that there always exists a minimal γ value below which uniqueness exists for all β. This minimal value is a monotonic decreasing function of σ, being 2.34 for $\sigma = 1$ and 3.65 for $\sigma \leq 0$. In practice γ is usually much larger than these limiting values.

The multiplicity region in the (γ, β) plane is shown in Figure 4 for $\sigma = 1$ and $\Lambda_{2L} = 10^{-4}$. The reaction-induced volume change shifts the multiplicity region to parameter values attainable in applications such as $\gamma = 20$ $\beta = 0.7$. This is a very important conclusion, because in practice the turbulent pressure drop is much larger than the laminar one or that due to gas expansion. Moreover, it was shown by Lee et al. (1987) that when the reaction does not cause a change in moles ($\sigma = 0$), this limiting model predicts that thermoflow multiplicity will occur only for unrealistic parameter values for an adiabatic reactor in which a zero-order reaction occurs.

Limiting case c, momentum change by gas expansion

This limiting model is based on the assumption that the frictional pressure drop is negligible in comparison to that due to the change in temperature and reaction-induced volume change. This is equivalent to assuming that $E_1 = E_2 = 0$. We consider separately the case in which the volume increases ($\sigma > 0$) and that in which it decreases ($\sigma < 0$), as there are major differences between the two.

Reaction Causing a Volume Increase ($\sigma > 0$). It can be proven that in this case no singular point can exist if the conversion is complete, that is, $Da > Da^*$. Thus, when multiplicity exists, the conversion is not complete at both ignition and extinction states.

It is found that for all σ in (0, 2.84), a sufficient uniqueness boundary in the (γ, β) space is given by the g_3^* curve, which satisfies Eqs. 32. It can be proven that the graphs of g_3^* (for any σ) approach asymptotically for small β and large γ the curve

$$\gamma\beta = 1.256 \tag{44}$$

Figure 5 describes the g_3^* graphs for the two limiting values of $\sigma = 0$ and $\sigma = \infty$. It is seen that g_3^* is shifted to slightly lower (γ, β) value with increasing σ values and that the sufficient uniqueness boundary is rather insensitive to changes in volume expansion parameter σ.

The value of Λ_3 decreases monotonically with increasing β along the g_3^* curves shown in Figure 5. Thus, the BLS_1 can intersect this curve at most once, and the region of multiplicity has the shape of a cusp that extends to unbounded γ values. A comparison of the (γ, β) region in which multiplicity can occur for several σ values, Figure 6, shows that both the g_3^* and the BLS_1 are shifted to the left (lower β values) with increasing σ. This causes a reduction in the size of the multiplicity region with increasing values of the volume expansion parameter.

Reaction Involving a Volume Decrease ($\sigma < 0$). A reaction-induced reduction in the volume and thus velocity may lead to a

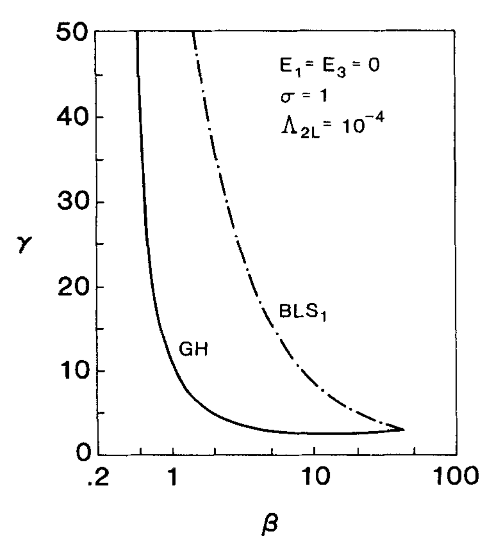

Figure 4. A typical multiplicity region in the (γ, β) plane.

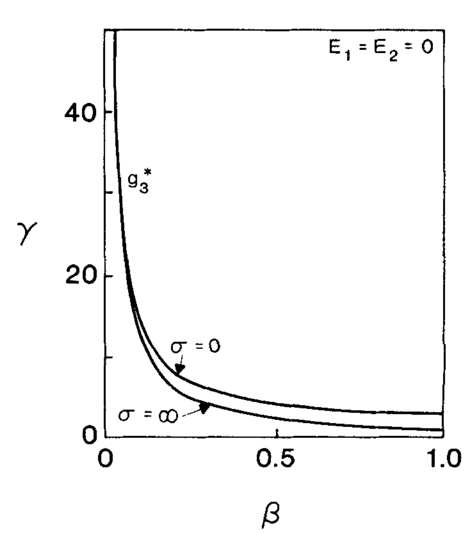

Figure 5. Dependence of uniqueness region on volume expansion parameter σ.

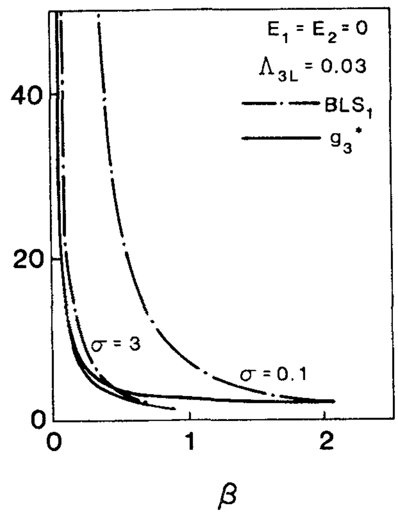

Figure 6. Dependence of multiplicity region in (γ, β) plane on σ.

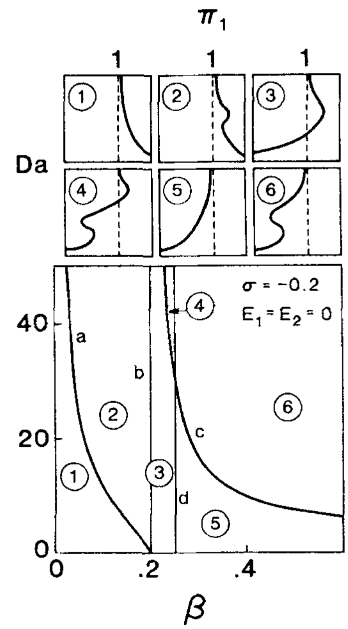

Figure 7. Division of (γ, β) plane into six regions.
Above, qualitatively different bifurcation diagrams of Da vs. Π_1

rather surprising feature, namely a pressure increase in the flow direction. An analysis of the momentum balance, Eq. 22, indicates that in this case the pressure decreases at any point in the reactor if

$$\beta > -\sigma/(1 + 2\sigma) \tag{45}$$

This condition is more likely to be satisfied for highly exothermic reactions, as the temperature increase tends to compensate for the reduced volume. However, if

$$\beta < -\sigma \tag{46}$$

then the pressure increases in the flow direction at any point in the reactor. In these cases the volume decrease by the reaction is larger than the volume increase due to the temperature rise. When neither of these two conditions is satisfied, that is,

$$-\sigma < \beta < -\sigma/(1 + 2\sigma) \tag{47}$$

then it can be shown that the pressure will still decrease in the flow direction for all

$$Da < Da_c = \frac{1}{\beta} J(y_c, 0) \tag{48}$$

where

$$y_c = 0.5(1 - \beta/\sigma) \tag{49}$$

When $Da > Da_c$, the pressure decreases in the upstream section of the reactor ($s < Da_c/Da$) and increases in the downstream section until the conversion is complete. The possible increase in the pressure due to the reaction increases the number of qualitatively different types of bifurcation diagrams over that when $\sigma > 0$. For all $\beta < -\sigma$, the outlet pressure exceeds the inlet pressure and a g_3^* curve, shown as curve a in Figure 7, separates between cases in which a unique flow rate, or equivalently Da, exists for any outlet pressure—shown as bifurcation diagram 1 in Figure 7—and those for which three flow rates exist for some outlet pressures—diagram 2 in Figure 7. The g_3^* curve (set of parameters satisfying Eq. 32) approaches $\gamma\beta = 1.256$ at $\gamma \rightarrow \infty$ and intersects the β axis at $\beta = -\sigma$. The value of Λ_3 is negative along this curve as $\Pi_1 > 1$. It increases with increasing γ, reaching the value of $0.162/\sigma$ for very large γ values.

Four basic types of Da vs. Π_1 diagrams, bifurcation diagrams 3–6 in Figure 7, exist for $\beta > -\sigma$. The (γ, β) regions corresponding to the different diagrams are separated by two curves. One is the vertical line

$$\beta = -\sigma/(1 + \sigma) \tag{50}$$

at which a limit point exists for $\Pi_1 = 1$. The second curve, c in Figure 7, is an H_3^* curve (a regular hysteresis variety) for all $\sigma < -0.178$. For all σ in (-0.178, 0) curve c consists of two separated segments of the H_3^* curve connected by a g_3^* curve at some β values greater than $-\sigma/(1 + \sigma)$.

A unique flow rate exists for any Π_1, for all (γ, β) values in regions 5 and 1. On the other hand, for all (γ, β) in regions 2, 3, and 4 thermoflow multiplicity exists for some $\Pi_1 > 1$. Up to three flow rates exist for some $\Pi_1 < 1$ for (γ, β) values in regions 4 and 6 bounded between the c curve and the BLS_1 (the set of parameters for which ignition occurs for $\Pi_1 = \Pi_L$).

The c curve approaches asymptotically $\gamma = 2.6$ for very large β and $\beta = -\sigma$ for $\gamma \rightarrow \infty$. The value of Λ_3 decreases monotonically with increasing β along curve c from $0.0374/\sigma^2$ at $\beta = -\sigma$ to zero at $\beta \rightarrow \infty$ and $\gamma = 2.6$. We conclude that if

$$\Lambda_{3L} > \frac{0.0374}{\sigma^2} \tag{51}$$

a unique dependence exists between the flow rate and Π_1 for all $\Pi_L < \Pi_1 < 1$.

The model predicts that for certain sets of parameters a solution exists for which the pressure within some points in the reactor is negative, even though the outlet pressure is positive.

Obviously, such a solution should be discarded, as the model is not valid for very low pressures and is invalid for negative pressures. The need to eliminate these solutions increases significantly the number of possible bifurcation diagrams. This feature is mainly of academic interest and is not likely to be encountered in practice. Thus, we refer the interested reader to Lee (1987).

Case d, an isothermal reaction involving volume decrease

We consider here an isothermal reaction accompanied by a volume change occurring in a packed-bed reactor. The corresponding steady state equations are

$$\frac{dx}{ds} = DaH(1 - x) \tag{52}$$

$$0.5\frac{d\Pi^2}{ds} = -\left(\frac{E_1}{Da} + \frac{E_2}{Da^2}\right)(1 + \sigma x) - \frac{E_3\sigma}{Da^2}\frac{dx}{dz} \tag{53}$$

Integration of Eqs. 52 and 53 gives the steady state relations

$$F_1 = 0.5(1 - \Pi_1^2) - \left(\frac{E_1}{Da} + \frac{E_2}{Da^2}\right) \cdot (1 + 0.5\sigma Da) - \frac{E_3\sigma}{Da} \quad Da \leq 1 \tag{54a}$$

$$F_2 = 0.5(1 - \Pi_1^2) - \left(\frac{E_1}{Da} + \frac{E_2}{Da^2}\right) \cdot \left(1 + \sigma - \frac{\sigma}{2Da}\right) - \frac{E_3\sigma}{Da^2} \quad Da > 1 \tag{54b}$$

Equation 54 indicates that a unique flow rate Da exists for any Π_1 when only one pressure drop mechanism is considered. Moreover, if the reaction does not involve a volume decrease ($\sigma \geq 0$), Π_1 always decreases as the inlet velocity increases and thermoflow multiplicity does not occur. When $\sigma < 0$, the frictional losses (E_1 and E_2 terms) reduce the pressure while the reduced linear velocity, caused by the volume decrease (E_3 term) increases it. The coupling between these two conflicting effects may lead to thermoflow multiplicity even in an isothermal reactor. A rather surprising finding.

Figure 8 shows all the possible bifurcation diagrams of Eq. 54 and the corresponding parameter regions for $\sigma = -0.5$. Multiplicity does not occur for any parameters in region 1, but it exists for some Π_1 for parameters in regions 2 and 3. Clearly, when the exit pressure is bounded ($\Pi_1 > \Pi_L$) only a part of the diagram is feasible.

The boundary between regions 1 and 2 is a hysteresis variety of F_2 for all E_2/E_1 larger than

$$\frac{E_2}{E_1} = \frac{2}{3}\frac{1 + \sigma}{(-\sigma)} \tag{55}$$

shown as solid point in Figure 8. It satisfies the expression

$$\frac{E_3}{E_1} = 0.5 + \frac{1 + \sigma}{(-\sigma)}\left(\frac{E_2}{E_1} + \sqrt{\frac{1.5E_2(-\sigma)}{E_1(1 + \sigma)}}\right) \tag{56}$$

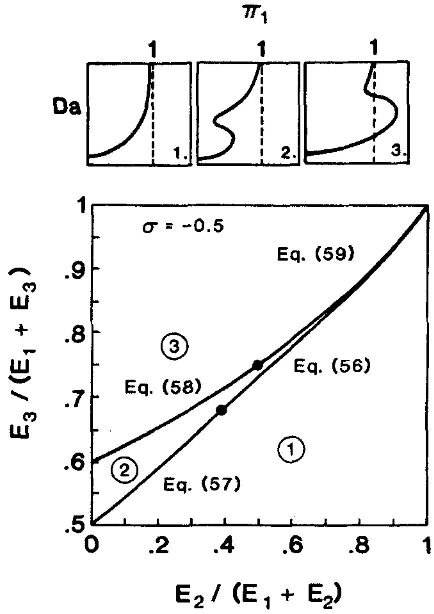

Figure 8. Division of E_i plane into regions with three different Da vs. Π_1 bifurcation diagrams (above).

For E_2/E_1 smaller than this value the boundary is a generalized hysteresis variety, given by the relation

$$\frac{E_3}{E_2} = \left(\frac{0.5}{-\sigma}\right)\left(1 + (2 + 0.5\sigma)\frac{E_2}{E_1}\right) \tag{57}$$

The boundary between regions 2 and 3 is the set of parameters at which an ignition point exists with equal inlet and exit pressures, that is, $\Pi_1 = 1$. This curve satisfies the relation

$$\frac{E_3}{E_1} = \left(1 + \frac{E_2}{E_1}\right)\frac{1 + \sigma}{-\sigma} \tag{58a}$$

for all

$$0 < \frac{E_2}{E_1} < \frac{2(1 + \sigma)}{-\sigma} \tag{58b}$$

and

$$\frac{E_3}{E_1} = 0.5 + \frac{1 + \sigma}{-\sigma}\frac{E_2}{E_1} + \sqrt{\frac{2E_2}{E_1}\frac{(1 + \sigma)}{(-\sigma)}} \tag{59a}$$

for

$$\frac{2(1 + \sigma)}{-\sigma} < \frac{E_2}{E_1} < \infty \tag{59b}$$

In practice E_2 is at least 50 times larger than E_3, and hence only bifurcation diagrams of type 1 can be obtained. We conclude that under practical conditions thermoflow multiplicity is not expected to exist in an isothermal packed-bed reactor in which a zero-order reaction is carried out. The multiplicity predicted in this section is mainly of academic interest.

Concluding Remarks

We have analyzed in this work several limiting models describing thermoflow multiplicity in an adiabatic packed-bed reactor for a reaction involving a change in volume. An analysis of more general cases was carried out by Lee (1987), but did not reveal any new surprising features due to the interaction among several pressure drop mechanisms.

The analysis indicates that for an exothermic reaction a volume increase enables the thermoflow multiplicity to occur at lower β values, that is, increases the probability of finding it for realistic parameter values. This finding is especially important in the analysis of the realistic second limiting model, which accounts only for the turbulent pressure drop. This model predicts that thermoflow multiplicity in an adiabatic reactor occurs only for unrealistically high heats of reactions if $\sigma = 0$. However, the multiplicity may be found for realistic heats of reaction when the reaction involves a volume increase.

Most previous studies of multitube and monolith reactors ignored the possibility that different flow rates may exist in parallel channels. This is a highly undesired behavior that may lead to nonuniform radial temperature profiles and to mechanical stresses, which may damage the reactor. This work indicates that this type of multiplicity may occur under practical operating conditions, and should be taken into consideration.

The possible existence of thermoflow multiplicity in an isothermal reactor for a reaction involving a decrease in volume is a very surprising finding. While this behavior occurs only for an unrealistic set of parameters, its existence is a vivid illustration of the difference between the feedback mechanism leading to thermoflow multiplicity and that leading to the common thermokinetic multiplicity.

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Notation

A = coefficient in Ergun equation
B = coefficient in Ergun equation
C = concentration
c = value of $\gamma\beta$ at $\gamma \rightarrow \infty$
c_p = heat capacity
Da^* = Damköhler number, Eq. 20
Da = smallest Da at which conversion is complete
E = activation energy
E_1, E_2, E_3 = dimensionless parameters, Eq. 20
F = function defining steady state
F_1 = function defining steady state for $Da \leq Da^*$
F_2 = function defining steady state for $Da \leq Da^*$
f_p = frictional pressure drop, Eq. 7
g^* = parameter set satisfying Eq. 32
g_i^* = g^* set for limiting cases *a, b, c,* and *d* for $i = 1, 2, 3$
H = Heaviside function
ΔH = heat of reaction
J = function, Eq. 25
$k(T)$ = reaction rate constant
L = length of reactor
P = pressure
p = parameter vector, Eq. 26
R = universal gas constant
r = reaction rate
s = dimensionless distance in reactor
T = temperature
u = velocity
X = temperature dependence of rate constant, Eq. 18
x = conversion
y = dimensionless temperature, Eq. 11
z = length coordinate

Greek letters

β = adiabatic temperature rise, Eq. 11
γ = dimensionless activation energy, Eq. 20
δ = parameter, Eq. 19
ϵ = an arbitrarily small positive number
Λ_j = parameter, Eq. 28
μ = viscosity
ν = stoichiometric coefficient
Π = dimensionless pressure, Eq. 15
ρ = density
σ = volume expansion parameter, Eq. 15

Subscripts

i = inert
L = limiting
T = total
o = inlet to reactor
1 = exit of reactor

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