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A HETEROGENEOUS CHEMICAL REACTOR WITH AN
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CATALYST PELLET: SECOND-ORDER CATALYTIC REACTIONS

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KYUNG JIN BAE

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A HETEROGENEOUS CHEMICAL REACTOR WITH AN INTERNALLY ISOTHERMAL BUT EXTERNALLY NON-ISOTHERMAL CATALYST PELLET: SECOND-ORDER CATALYTIC REACTIONS

By

Kyung Jin Bae

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ABSTRACT

A HETEROGENEOUS CHEMICAL REACTOR WITH AN INTERNALLY ISOTHERMAL BUT EXTERNALLY NON-ISOTHERMAL CATALYST PELLET: SECOND-ORDER CATALYTIC REACTIONS

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A 1-3-1 multiplicity pattern was found for the internally isothermal but externally non-isothermal catalyst semi-infinite slab with second-order catalytic reactions. The ranges of multiple steady states are generally rather narrow but expands slightly for certain physico-chemical parameters. For an isotropic and axisymmetric packed bed reactor with plug flow in the bulk fluid phase, axial convective heat transport and adiabatic conditions, a 3-1 multiple steady state pattern along the tube reactor was obtained.

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NOTATIONS

A, B, C	Chemical Species
a	Ratio of external surface to volume of catalyst particle
a_i	Defined by Equation (10.6a)
$\tilde{a}$	Shape factor (1 for semi-infininte slab, 2 for cylinder 3 for sphere)
$\tilde{B}$	Defined by Equation (8.25a)
Bi_h	Biot heat number $h\delta/\lambda_e$
Bi_m	Biot mass number $kg_j\delta/De_j$
b_1	The upper bound of Equation (8.31)
b_2	The lower bound of Equation (8.31)
c_i	A normalization constant
c_j	Concentration of component j
c^o_{jf}	Feed concentration of component j
C_{P_j}	Heat capacity of component j
Da	Damköhler number $(1-\tilde{\varepsilon}/\tilde{\varepsilon})\,a V_p\, \epsilon \rho S (N_T/L^2) k_f \tau$
De_j	Effective diffusivity of component j
Dr_j	Diffusion coefficient of component j in radial direction
Dz_j	Diffusion coefficient of component j in axial direction
d_i	Constant in the Fourier-type expansion
F(y)	Defined by Equation (8.18)
$F(\psi,k)$	Elliptic integral of the first kind

$\tilde{F}$	Defined by Equation (10.4)
$\mathfrak{F}[u(0)]$	Defined by Equation (8.53)
f_k	Defined by Equation (8.6a)
$G_k(\beta^L)$	Defined by Equations (8.35), (8.36), (8.40), and (8.41)
$g[u(0)]$	Defined by Equation (8.53b)
$H(u_j^o)$	Defined by Equation (10.12)
$(-\Delta H)$	Heat of reaction
h	Heat transfer coefficient
$h[u(o)]$	Defined by Equation (8.53a)
$\underline{\underline{J}}(\underline{d}^k)$	Jacobian matrix, defined by Equation (10.10)
K_j	Equilibrium constant $\bar{k}_j/k_j$
Ke	Reaction constant for the surface reaction, $k_3/\bar{k}_3$
$k(T)$	Arrhenius reaction rate constant
kg_j	Mass transfer coefficient for component j
k_j	Rate constant for forward reaction
$\bar{k}_j$	Rate constant for backward reaction
L^2	External surface area of catalyst particle
N	Total number of interior collocation points
Ne_j	Total effective flux of component j entering the solid phase
N_T	Total number of catalyst pellet inside the reactor
P	Pressure
$P_k(\xi)$	kth degree Jacobi polynomial
Q	Rate of heat transfer to the surroundings/reactor volume
q_e	Effective heat flux leaving (or entering) the catalyst pellet
R	Rate of reaction

Rg	Gas constant
R_j^o	Observable rate of reaction
$\hat{R}_j$	Turnover frequency, number of moles or molecules/cm^2 active surfact area/time (or intrisic rate)
r	Radial distance of the tubular reactor
S	Total active area/gm catalyst
$\tilde{S}$	Fraction of unoccupied catalyst surface
T	Temperature
T^o	Bulk phase temperature
T_f^o	Feed temperature
t	Time
u_j	Dimensionless concentration c_j/c_j^o
u_j^o	Dimensionless concentration defined relative to feed conditions c_j^o/c_{jf}^o
u_j^*	Defined by Equation (8.47a)
$\hat{V}$	Specific molar volume of the fluid
Vp	Catalyst pellet volume
<v>	Fluid mean velocity
$W(\xi^2)$	Arbitrary weighting function
x	Distance from the center of catalyst pellet
y	Dimensionless temperature T/T^o
y^o	Dimensionless temperature defined relative to feed conditions T^o/T_f^o
Z	Total length of the reactor
z	Distance along the reactor length

Superscripts

o	Bulk conditions

Subscripts

f	Feed conditions

Greek Symbols

β	Praeter temperature $De_j(-\Delta H)c_j^o/\lambda e T^o$
β^L	Defined by Equation (8.14a) $\beta Bi_m/Bi_h$
β^o	Dimensionless adiabatic temperature rise $(-\Delta H)C_{jf}^o/\rho^o \hat{C}_p^o T_f^o$
γ	Dimensionless activation energy E/RgT^o
γ^o	Dimensionless activation energy defined relative to feed conditions E/RgT_f^o
δ	Half-thickness of the catalyst particle
δ_{ik}	Kröonecker delta
ϵ	cm^3 solid/(cm^3 solid + cm^3 void)
$\tilde{\epsilon}$	cm^3 catalyst/(catalyst + fluid)
ζ	Dimensionless distance along the reactor length z/Z
η	Effectiveness factor
λe	Effective thermal conductivity
λ_r^o	Thermal conductivity in radial direction
λ_z^o	Thermal conductivity in axial direction
ξ	Dimensionless distance from center of pellet
ρ	Catalyst bulk density
$\rho(u)$	Defined by Equation (8.55d)
$\rho(y)$	Exp $[\gamma(1 - 1/y)]$
τ	Residence time $Z/\langle v\rangle$
ϕ^2	Thiele modulus $\rho\epsilon k(T^o)\delta^2 C_j^o/De$
Φ^2	Defined by Equation (8.25b)
$\psi_1(\beta^L)$	Defined by Equation (8.34)
$\psi_4(\beta^L)$	Defined by Equation (8.39)

INTRODUCTION

The strategy of operating heterogeneous chemical reactors depends largely on the nature of the steady states and on the stability of these steady states. The understanding of the reactor dynamics is essential for determining chemical reactor control policies. Normally, the analysis of chemical reactor dynamics is preceded by the analysis of these steady states.

For a heterogeneous chemical reactor, typified by a packed bed reactor, the model that is usually employed consists of material and energy balances, of the fluid phase and the solid phase. Not unless the fluid velocity changes drastically within the reactor, then the momentum conservation equation can be discounted. Hence, for a truly turbulent fluid having the mean velocity <v>, the fluid phase material balance for component j is

$$\frac{\partial c_j^\circ}{\partial t} = \frac{\partial}{\partial z}\left(D_{zj}\frac{\partial c_j^\circ}{\partial z}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(D_{rj}\frac{\partial c_j^\circ}{\partial r}\right) - \langle v\rangle\frac{\partial c_j^\circ}{\partial z} + \frac{1-\tilde{\epsilon}}{\tilde{\epsilon}}\, a N e_j \qquad (1)$$

subject to $c_j^\circ(0, r, z) = c_{j0}^\circ$ (1.1)

$$-D_{\ell j}\frac{\partial c_j^\circ}{\partial \ell} = \langle v\rangle\left[c_{jf}^\circ - c_j^\circ(t, \ell=0)\right], \ell = r, z \qquad (1.2)$$

$$\frac{\partial c_j^\circ}{\partial \ell} = 0 \quad , \quad \ell = R, Z \qquad (1.3)$$

Where $Ne_j \equiv$ Total effective flux of component j entering the solid phase.

Other symbols are defined in the notation section. Notably, this model presupposes axisymmetric concentration profile, i.e., no θ-dependency. The solid catalyst material balance for component j is

$$\frac{\partial c_j}{\partial t} + \underline{\nabla} \cdot \underline{Ne}_j = \epsilon \rho S \hat{R}_j \tag{2}$$

where $\hat{R}_j \equiv$ turnover frequency, no. of molecules or moles/cm^2 active surface area/time (or intrinsic rate)

$S \equiv$ total active area/gm catalyst

$\rho \equiv$ catalyst bulk density, (gm/cm^3)

$\epsilon \equiv$ cm^3 solid/(cm^3 solid + cm^3 void)

$\underline{Ne}_j \equiv - De_j \cdot \underline{\nabla} c_j$

$De_j \equiv$ effective diffusivity of component j

Assuming symmetric conditions,

$$\frac{\partial}{\partial \underline{n}} c_j = 0 \qquad \text{at} \quad \underline{x} = 0 \tag{2.1}$$

where $\frac{\partial}{\partial \underline{n}} \equiv$ derivative with respect to a normal

$\underline{x} = 0$, represents the center of symmetry.

If there is an external mass transfer resistance,

$$\underline{Ne}_j(\partial\Omega) \equiv - De_j \frac{\partial}{\partial \underline{n}} c_j = kg_j \, [c_j^\circ - c_j] \quad \text{at} \quad \underline{x} = \partial\Omega \tag{2.2}$$

where $\partial\Omega$ represents the external surface of the catalyst pellet.

The fluid phase energy balance is

$$\sum_{j=1}^{N} \rho_j^\circ \hat{C}_{p_j}^\circ \left(\frac{\partial T}{\partial t} + \langle v \rangle \frac{\partial T^\circ}{\partial z}\right) = \frac{\partial}{\partial z}\left(\lambda_z^\circ \frac{\partial T^\circ}{\partial z}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(\lambda_r^\circ \frac{\partial T^\circ}{\partial r}\right)$$
$$+\left(\frac{\partial \ln \hat{V}}{\partial \ln T}\right)_{P,c_j}\left[\frac{\partial P}{\partial t} + \langle v \rangle \frac{\partial P}{\partial z}\right] + \frac{1-\tilde{\epsilon}}{\tilde{\epsilon}} a q_e + Q \qquad (3)$$

where $Q \equiv$ rate of heat transfer to the surroundings/reactor volume.

$q_e \equiv$ effective heat flux leaving (or entering) the catalyst pellet

$\hat{V} \equiv$ specific molar volume of the fluid

Other symbols are defined in the notation section.

The heat balance for the catalyst pellet is

$$\sum_{j=1}^{N} \rho_j \hat{C}_{p_j} \frac{\partial T}{\partial t} + \underline{\nabla} \cdot q_e = \epsilon \rho S (-\Delta H) \hat{R}_j \qquad (4)$$

where $q_e \equiv -\lambda_e \underline{\nabla} T \equiv$ effective heat flux

$\lambda_e \equiv$ effective thermal conductivity

Assuming symmetric conditions,

$$\frac{\partial}{\partial \underline{n}} T = 0 \qquad \text{at} \quad \underline{x} = 0 \qquad (4.1)$$

and for an external heat transfer resistance,

$$q_e(\partial \Omega) = -\lambda_e \frac{\partial T}{\partial \underline{n}} = h\left[T^\circ - T\right] \quad \text{at} \quad \underline{x} = \partial \Omega \qquad (4.2)$$

Now, the link between the fluid phase and the solid phase is afforded by the concept of an effectiveness factor of species j, η_j. Thus

$$\eta_j = \frac{\int_{V_p} \hat{R}_j \, d^3\underline{r}}{V_p \hat{R}_j(C_j^\circ, T^\circ)} \qquad (5)$$

where $V_p \equiv$ catalyst pellet volume

$d^3\underline{r} \equiv$ differential catalyst pellet volume

Applying Gauss-Ostrograllskii's theorem,

$$\eta_j = \frac{\int_{\partial\Omega} \underline{n} \cdot \underline{N}e_j \, d^2\underline{r}}{V_p \, \epsilon \rho \, S \, \hat{R}_j(c_j^\circ, T^\circ)} \tag{5.1}$$

Clearly, the numerator in equation (5.1) is interpreted as the total moles of material j entering (or leaving) the external surface of the catalyst pellet. Hence, the fluid phase steady state balance can be rewritten as

$$0 = \frac{\partial}{\partial z}\left(D_{zj}\frac{\partial c_j^\circ}{\partial z}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(D_{rj}\frac{\partial c_j^\circ}{\partial r}\right) - \langle v \rangle \frac{\partial c_j^\circ}{\partial z}$$

$$- \frac{1-\tilde{\epsilon}}{\tilde{\epsilon}} \, a \, \eta_j \, \epsilon \rho \, S \, \hat{R}_j(c_j^\circ, T^\circ) \, V_p \frac{N_T}{\int_{\partial\Omega} d^2\underline{r}} \tag{5.2}$$

where $N_T \equiv$ total number of catalyst pellet inside the reactor. In the words of Carberry, the last term in equation (5.2) is referred to as the observable rate. Therefore, the solution to equation (5.2) requires the calculation of the effectiveness factor.

In this work, a method based on the theory of elliptic integrals and elliptic (Jacobian) functions is applied for calculating the effectiveness factor of a second order kinetics. The details of the diffusion-reaction model assumptions is postponed to another section. A simulation of the heterogeneous reactor model is also presented. Much of the works involving diffusion-reaction systems have been on first order kinetics and lately the focus of interest in

the literature have been on Langmurian form of the kinetic rate expression. A comprehensive review of research pertaining to diffusion-reaction systems up to 1975 is provided by Aris [7]. Upon examining this reference [7] and the recent literature, it is clear that studies on the second order kinetics is not fully explored.

When chemical reactions take place within a porous catalyst pellet, the system may have multiple steady state solutions for certain combinations of physico-chemical parameters. Many studies have treated internal and external transport resistances separately or together. In cases of gas-solid catalytic reactions, the external mass transfer resistance (Bi_m) is relatively much greater than the external heat transfer resistance (Bi_h), so that the major temperature gradient exists in the external film and the catalyst pellet may be considered to be isothermal. This internal pellet isothermality has been carefully examined for the first order reactions analytically [6,8] and experimentally [4,5]. Pereira et. al. analyzed the full non-isothermal diffusion-reaction equation by regular perturbation method for small Praeter temperature (β) and finite Bi_h/ ratios. The zeroth order solution of the full problem justifies the internal isothermality [6]. Also Cresswell studied the combined effects of internal and external resistances on the uniqueness of the steady states with internal isothermal model [8], while Hatfield and Aris [9] studied the combined effects of the full non-isothermal model with both linear and nonlinear kinetics.

A number of studies have been devoted to develop *a priori* bounds on physico-chemical parameter values for multiplicity of solutions [10-17]. But, because of the difficulty of handling coupled nonlinear differential equations, necessary and sufficient conditions could be obtained only for lumped parameter system while only sufficient conditions found for distributed system. Luss [16] developed *a priori* prediction of the unique steady state conditions with nonlinear heat generation term for arbitrary kinetics. Later, Van den Bosch and Luss [12] developed uniqueness and multiplicity criteria for lumped parameter model and for the intraparticle concentration gradient model. They found that for lumped model the higher the order of the reaction, the smaller was the parameter region where multiplicity could occur, and for the model with intraparticle concentration gradients, the multiplicity parameter region is smaller than that for a corresponding lumped model.

For first order reaction model, Pereira et. al. found analytically a 1-3-1 multiplicity pattern for relatively small β and relatively large Bi_m/Bi_h model and their analytic criteria were compared with exact numerical integration of the heat and mass balance equations [10]. Lately, Morbidelli and Varma [14] obtained explicit approximate bounds for the multiple region.

For langmuir-Hinshelwood type of kinetic model, the multiple steady state phenomenon depends on the adsorption

rate constant values. The assumption of fixed adsorption rate constants with temperature was a good approximation for the relatively small β cases. This assumption did not change the multiplicity pattern for larger β cases but changed the numerical range [11].

Studies on multiplicity of the steady state solutions is usually expressed in terms of the catalyst effectiveness factor [13, 14, 18-21]. Hlaváček and Kubíček [20] developed a simple approximation for evaluating the dependence of the effectiveness factor on the Thiele modulus. And Copelowitz and Aris [18] calculated the effectiveness factor for small and large Thiele modulus values asymptotically and applied the reasonable approximation to the rising part of the effectiveness factor versus Thiele modulus plot.

For bimolecular Langmuir-Hinshelwood Kinetics, Morbidelli and Varma [14] developed analytic solutions for effectiveness factor for the full range of Thiele modulus, in the limit of large adsorption inhibition constant, and Wong and Szépe [21] found that for this kinetics, multiple steady states might arise even when effectiveness factor is less than 1, and that with higher reaction temperatures and stronger surface chemisorption characteristics, multiplicities in endothermic reactions are likely to occur.

THE KINETIC MODEL

The kinetics of interest here is typical of a hydrogenation reaction involving an olefin, e.g., ethylene on a transition metal supported on γ-alumina.

Chemisorption

$$A + * \underset{\bar{k}_1}{\overset{k_1}{\rightleftarrows}} A\cdot * \qquad (6.1)$$

$$B + * \underset{\bar{k}_2}{\overset{k_2}{\rightleftarrows}} B\cdot * \qquad (6.2)$$

Surface reaction

$$A\cdot * + B\cdot * \underset{\bar{k}_3}{\overset{k_3}{\rightleftarrows}} \begin{matrix} & C & \\ / & & \backslash \\ * & & * \end{matrix} \qquad (6.3)$$

Product desorption

$$\begin{matrix} & C & \\ / & & \backslash \\ * & & * \end{matrix} \underset{\bar{k}_4}{\overset{k_4}{\rightleftarrows}} C + 2* \qquad (6.4)$$

Here, we suppose the surface-reaction is rate controlling. Thus, invoking the pseudo-steady state assumption.

$$\hat{R}_j = k_3 K_1 K_2 \left(C_A C_B - \frac{K_4}{K_e K_1 K_2} C_c \right) \tilde{S}^2 \qquad (6.5)$$

where $\tilde{S}^2 \equiv$ fraction of the surface that is unoccupied

$K_e \equiv \dfrac{k_3}{\bar{k}_3} \equiv$ reaction constant for the surface reaction

$K_j \equiv \dfrac{\bar{k}_j}{k_j} \equiv$ equilibrium constant

Assuming the forward reaction proceeds at a much faster rate than the backward reaction, and the surface does not exhibit poisoning (or $\tilde{S}^2$ is constant for all purposes), hence equation (6.5) is transformed into

$$\hat{R}_j = k_3 K_1 K_2 \tilde{S}^2 C_A C_B \qquad (6.6)$$

for an equimolar concentration of components A and B within the catalyst pellet void,

$$\tilde{R}_j = k(T)\, c_j^2 \tag{6.7}$$

We will assume the Arrhenius dependency for k.

THE INTERNALLY ISOTHERMAL, EXTERNALLY NON-ISOTHERMAL MODEL OF THE CATALYST PELLET

Hutchings and Carberry [1,2] have shown that the major seat of temperature difference will most likely be in the external fluid film, while the concentration gradient can be expected to prevail primarily within the porous catalyst. Lee and Luss have later refined this analysis [3]. Kehoe and Butt's data [4] and Butt et. al. [5] presented some results of an internally isothermal pellet but with a limiting external heat transfer rate. Their experiments yield various inter-intraphase temperature distribution data for a single pellet in the Ni/Kieselguhr catalyzed hydrogenation of benzyne. Hence with this consideration, the steady state material balance is

$$\underline{\nabla} \cdot De_j \cdot \underline{\nabla}\, c_j = \epsilon \rho S\, k(T)\, c_j^2 \tag{7.1}$$

where k(T) is the Arrhenius reaction rate constant. Upon assuming that the effective diffusivity is independent of pore geometry and the other diffusion effects, e.g. Knudsen and surface diffusion, thus for a semi-infinite catalyst slab,

$$De_j \frac{d^2 c_j}{dx^2} = \epsilon \rho S\, k(T)\, c_j^2 \tag{7.2}$$

For the symmetric pellet with a surrounding mass transfer film,

$$\left.\frac{dc_j}{dx}\right|_{x=0} = 0 \tag{7.3a}$$

$$-De_j \left.\frac{dc_j}{dx}\right|_{x=\delta} = kg_j \left[c_j^o - c_j|_{x=\delta} \right] \tag{7.3b}$$

where $\delta \equiv$ half the particle's thickness.

The energy balance is

$$\underline{\nabla} \cdot \lambda e \, \underline{\nabla} T = -\epsilon \rho S \, k(T) c_j^2 (-\Delta H) \tag{7.4}$$

Assuming an isotropic effective thermal conductivity, λe ,thus for the semi-infinite catalyst slab,

$$\lambda e \frac{d^2T}{dx^2} = -\epsilon \rho S \, k(T) c_j^2 (-\Delta H) \tag{7.5}$$

Again, with the symmetric pellet and a heat transfer film surrounding the pellet

$$\left.\frac{dT}{dx}\right|_{x=0} = 0 \tag{7.6a}$$

$$\lambda e \left.\frac{dT}{dx}\right|_{x=\delta} = h \left[T^o - T|_{x=\delta} \right] \tag{7.6b}$$

Integrating equations (7.5) and (7.6) yields

$$h\left[T|_{x=\delta} - T^o \right] = \epsilon \rho S \int_0^\delta (-\Delta H) \, k(T) c_j^2 \, dx \tag{7.7}$$

So, if the internal temperature gradient is zero, and the heat of reaction is temperature independent, equation (7.7) reduces to

$$h\left[T|_{x=\delta} - T^o \right] = \epsilon \rho S \, (-\Delta H) \, k(T|_{x=\delta}) \int_0^\delta c_j^2 \, dx \tag{7.8}$$

The material and energy balance equations can be casted into the following dimensionless form

$$u_j'' = \phi^2 e^{\gamma(1-\frac{1}{y})} u_j^2 \tag{7.9}$$

$$u_j'\Big|_{\xi=0} = 0 \tag{7.9a}$$

$$u_j'\Big|_{\xi=1} = Bi_m \left[1 - u_j\Big|_{\xi=1}\right] \tag{7.9b}$$

$$\frac{Bi_h}{\beta}(y-1) = \phi^2 \int_0 u_j^2 \, d\xi \cdot e^{\gamma(1-\frac{1}{y})} \tag{7.10}$$

where $\phi^2 \equiv \rho \epsilon k(T^\circ)\delta^2 C_j^\circ / De_j$ ≡ Thiele modulus

$u_j \equiv$ dimensionless concentration $\equiv C_j/C_j^o$

$y \equiv$ dimensionless temperature $\equiv T/T^o$

$\gamma \equiv$ dimensionless activation energy $\equiv E/(R_g T^o)$

$\xi \equiv x/\delta$

$\beta \equiv$ Praeter temperature $\equiv De_j(-\Delta H)C_j^\circ / \lambda_e T^\circ$

$Bi_m \equiv$ Biot mass number $\equiv kg_j\,\delta / De_j$

$Bi_h \equiv$ Biot heat number $\equiv h\delta / \lambda e$

In the perturbation framework of Varma et. al. [6], the full non-isothermal diffusion-reaction equations,

$$u'' = \phi^2 e^{\gamma(1-\frac{1}{y})} u^2 \quad , \quad \xi \in (0,1) \tag{7.11}$$

$$y'' = -\beta\phi^2 e^{\gamma(1-\frac{1}{y})} u^2 \quad , \quad \xi \in (0,1) \tag{7.12}$$

$$\xi = 1 \; : \; u' = Bi_m(1-u) \; ; \; y' = Bi_h(y-1) \qquad (7.13a,\ b)$$

$$\xi = 0 \; : \; u' = 0 \quad ; \quad y' = 0 \qquad (7.14a,\ b)$$

has the zero order term in the regular perturbation expansion yielding equations (7.9) and (7.10).

Let $R(u, y; \beta) \equiv u^2 \exp[\gamma(1 - \frac{1}{y})]$ (7.15)

$\beta \equiv$ perturbation parameter

thus assuming the following asymptotic sequences,

$$u \sim \sum_{j=0}^{\infty} \beta^j u_j \tag{7.16}$$

$$y \sim \sum_{j=0}^{\infty} \beta^j y_j \tag{7.17}$$

$$\begin{aligned} u'' &= \phi^2 R(u, y; \beta) \\ &\sim \phi^2 \{ R(u_0, y_0) + \beta [R_u(u_0, y_0) u_1 + R_y(u_0, y_0) y_1] \\ &\qquad + \beta^2 [2 R_u(u_0, y_0) u_2 + 2 R_y(u_0, y_0) y_2 \\ &\qquad\qquad + 2 u_1 y_1 R_{uy}(u_0, y_0) + u_1^2 R_{uu}(u_0, y_0) \\ &\qquad\qquad + y_1^2 R_{yy}(u_0, y_0)] + \cdots \} \\ &\sim u_0'' + \beta u_1'' + \beta^2 u_2'' + \cdots\cdots \end{aligned} \tag{7.18}$$

Hence, the zero order terms consist of the solution to the following equations:

$$y_0'' = 0 \tag{7.19}$$

$$\xi = 0 \quad : \quad y_0' = 0 \tag{7.19a}$$

$$\xi = 1 \quad : \quad y_0' = 0 \tag{7.19b}$$

thus y_0 = constant (7.20)

$$u_0'' = \phi^2 e^{\gamma(1 - \frac{1}{y_0})} u_0^2 \tag{7.21}$$

$$\xi = 0 \quad : \quad u_0' = 0$$

$$\xi = 1 \quad : \quad u_0' = Bi_m [1 - u_0] \tag{7.22}$$

y_0 is obtained from the first order term, thus

$$y'' = \phi^2 R(u_0, y_0) \tag{7.23}$$

$$\xi = 0 \quad : \quad y_1' = 0 \tag{7.23a}$$

$$\xi = 1 \quad : \quad y_1' = \frac{Bi_h}{\beta}(y_0 - 1) \tag{7.23b}$$

Upon integrating equation (7.23),

$$y_0 - 1 = \frac{\beta\phi^2}{Bi_h}\int_0^1 R(u_0, y_0)\, d\xi \tag{7.24}$$

The perturbation solution is not described here, but will be done in the future. The perturbation solution will provide stronger criteria (for small β) for the full non-isothermal problem.

NECESSARY AND SUFFICIENT CONDITIONS FOR UNIQUENESS OF SOLUTION

a. Dependency of Concentration on Temperature

Consider again the catalyst pellet model equations where both intraparticle diffusion and thermal conduction occur,

$$u_j'' = \phi^2 e^{\gamma(1-\frac{1}{y})} u_j^n \tag{8.1}$$

$$\equiv \phi^2 f(u_j ; y)$$

$$y'' = -\beta\,\phi^2\, e^{\gamma(1-\frac{1}{y})}\, u_j^n \tag{8.2}$$

with $$u_j'(0) = 0 \quad ; \quad y'(0) = 0 \tag{8.3}$$

$$u_j'(1) = Bi_m[1-u_j(1)] \quad ; \quad y'(1) = Bi_h[1-y(1)] \tag{8.4}$$

a-1. Variation of Concentration Profile with Temperature

Assume there exists a maximal solution u_{j2} and a minimal solution u_{j1} such that

$$u_{j2} \equiv u_j(y = y_2) \tag{8.5a}$$

$$u_{j1} \equiv u_j(y = y_1) \tag{8.5b}$$

and $$y_2 > y_1 \tag{8.5c}$$

If the differential equations satisfying these solutions are subtracted from each other, thus

$$u_{j2}'' - u_{j1}'' = \phi^2\{f_2 - f_1\} \tag{8.6}$$

where $$f_k \equiv e^{\gamma(1-\frac{1}{y_k})}\, u_{jk}^n \quad , \; k=1,2 \tag{8.6a}$$

Integrating from $\xi=0$ to $\xi=1$,

$$Bi_m\{u_{j1}(1) - u_{j2}(1)\} = \phi^2\int_0^1 \left(\frac{f_2-f_1}{y_2-y_1}\right)(y_2-y_1)\,d\xi \tag{8.7}$$

using the derivative definition

$$Bi_m\{u_{j1}(1) - u_{j2}(1)\} = \phi^2\int_0^1 \left.\frac{\partial f}{\partial y}\right|_{y*}(y_2-y_1)\,d\xi \tag{8.8}$$

where $y^* \in (y_1, y_2)$. With the n^{th} order kinetics ($n>0$), equation (8.8) is written as

$$\frac{\bar{Bi}_m}{\phi^2}\left\{u_{j_1}(1) - u_{j_2}(1)\right\} = \int_0^1 f(u_j^*, y^*)\left\{\frac{\gamma}{y^{*2}} + \frac{n}{u_j^*}\frac{\partial u_j}{\partial y}\bigg|_{y^*}\right\}(y_2 - y_1)\,d\xi \quad (8.9)$$

Since it was already assumed earlier that u_{j2} (a maximal solution) > u_{j1} (a minimal solution), therefore the left-hand side is negative. This indicates that,

$$\frac{\partial u_j}{\partial y}\bigg|_{y^*} < -\frac{u_j^*}{n}\frac{y^{*2}}{\gamma} < 0 \quad (8.10)$$

or, $$\frac{\partial u_j}{\partial y} < 0 \quad (8.11)$$

Another contradictory proof is to assume that if $\partial u_j / \partial y > 0$, the integral is positive. Thus, $u_{j2}(1) > u_{j1}(1)$ will make the left-hand side negative. This is a contradiction.

b. Bounds for y

By adding equations (8.1) and (8.2) the heat balance and the mass balance are uncoupled to yield

$$u_j(\xi) = \frac{y(1) + \beta u_j(1) - y(\xi)}{\beta} \quad (8.12)$$

For the internal isothermal-external non-isothermal model,

$$\frac{\bar{Bi}_h}{\beta}(y - 1) = u_j'(1) = \bar{Bi}_m\left[1 - u_j(1)\right] \quad (8.13)$$

and recognizing $y(1) \equiv y(\xi)$,thus,

$$u_j = \frac{1}{\beta^L}\left[1 + \beta^L - y\right] \quad (8.14)$$

where $$\beta^L \equiv \beta\,\bar{Bi}_m / \bar{Bi}_h \quad (8.14a)$$

Now, since $\frac{\partial y}{\partial u_j} < 0$ and $u_j \in (0,1)$, therefore

$$y \in [1, 1+\beta^L] \tag{8.15}$$

c. Necessary and Sufficient Conditions for Uniqueness of the Steady State: A Conservative Criteria

From the heat balance equation,

$$\begin{aligned} \frac{\bar{Bi}_h}{\beta}(y-1) &= u_j'(1) \\ &= \int_0^1 d(u_j') = \phi^2 \int_0^1 e^{\gamma(1-\frac{1}{y})} u_j^2 \, d\xi \end{aligned} \tag{8.16}$$

the effectiveness factor defined relative to the bulk conditions is

$$\eta = e^{\gamma(1-\frac{1}{y})} \int_0^1 u_j^2 \, d\xi \tag{8.17}$$

Hence,

$$\frac{\bar{Bi}_h}{\beta\phi^2} = \frac{\eta}{y-1} \equiv F(y) \tag{8.18}$$

$$\frac{dF}{dy} = \frac{(y-1)\frac{d\eta}{dy} - \eta}{(y-1)^2} \tag{8.19}$$

Furthermore,

$$F(y=1) = +\infty \tag{8.20a}$$

$$F(y=1+\beta^L) \overset{\rightarrow}{\cong} 0 \tag{8.20b}$$

Now, with equation (8.17),

$$\frac{dF}{dy} = \frac{\eta\left\{\frac{\gamma}{y^2}(y-1)-1\right\} + 2(y-1)e^{\gamma(1-\frac{1}{y})}\int_0^1 u_j(\xi;y)\frac{\partial u_j}{\partial y}\,d\xi}{(y-1)^2} \tag{8.21}$$

but, $\frac{\partial u_j}{\partial y} < 0$, hence

$$\frac{dF}{dy} = \frac{\eta\left\{\frac{\gamma}{y^2}(y-1)-1\right\} - 2(y-1)e^{\gamma(1-\frac{1}{y})}\mathrm{Abs}\left(\int_0^1 u_j \frac{\partial u_j}{\partial y} d\xi\right)}{(y-1)^2} \tag{8.21a}$$

It is clear from equation (8.21) that the necessary and sufficient condition for uniqueness of solution is

$$\frac{\gamma}{y^2}(y-1) - 1 \leq 0$$

or,
$$y^2 - \gamma y + \gamma \geq 0 \tag{8.22}$$

Inequality (8.22) is satisfied iff

$$\gamma \leq 4$$

which is also the necessary and sufficient condition for uniqueness of the steady state.

d. Van den Bosch and Luss Method for Uniqueness and Multiplicity of Steady States

If we define the effectiveness factor relative to the surface conditions,

$$\eta = u_j(1)^{-2} \int_0^1 u_j^2 \, d\xi \tag{8.23}$$

then the energy balance for the internal isothermal - external non-isothermal model results into

$$\begin{aligned}\frac{\bar{Bi}_h}{\beta}(y-1) &= \phi^2 \int_0^1 e^{\gamma(1-\frac{1}{y})} u_j^2 \, d\xi \\ &= \phi^2 e^{\gamma(1-\frac{1}{y})} u_j^2(1) \\ &= \frac{\eta\phi^2}{(\beta^L)^2} e^{\gamma(1-\frac{1}{y})} (1+\beta^L-y)^2 \end{aligned} \tag{8.24}$$

Let
$$\tilde{B} \equiv \frac{(\beta^L)^2 \bar{Bi}_h}{\beta\,\phi^2} \tag{8.25a}$$

$$\phi^2 \equiv e^{\gamma(1-\frac{1}{y})}(1+\beta^L-y) \tag{8.25b}$$

hence, $$\tilde{B} = F(y) \equiv \frac{(1+\beta^L-y)\eta\tilde{\Phi}^2}{(y-1)} \tag{8.26}$$

$$\ln F(y) = \ln\{\tilde{\Phi}^2(1+\beta^L-y)\} + \ln\eta - \ln(y-1) \tag{8.26a}$$

thus,

$$\frac{1}{F(y)}\frac{dF}{dy} = \frac{d}{dy}\ln[\tilde{\Phi}^2(1+\beta^L-y)] + \frac{d}{dy}\ln\eta - \frac{1}{y-1} \tag{8.27}$$

Since $F(y = 1) = +\infty$, $F(y = 1 + \beta^L) = 0$ and $F(y) \geq 0$, the necessary and sufficient condition for uniqueness of solution is

$$\frac{d}{dy}[\ln\tilde{\Phi}^2(1+\beta^L-y)] + \frac{d}{dy}\ln\eta - \frac{1}{y-1} \leq 0$$

or,

$$(y-1)\left[\frac{d}{dy}\{\ln\tilde{\Phi}^2(1+\beta^L-y)\} + \frac{d}{dy}\ln\eta\right] \leq 1 \quad \text{in } y\in(1, 1+\beta^L) \tag{8.28}$$

Using the identity

$$\begin{aligned}\frac{d\ln\eta}{dy} &= \frac{1}{2}\frac{d\ln\eta}{d\ln\phi}\cdot\frac{d\ln\tilde{\Phi}^2}{dy}\\ &= \frac{1}{2}\frac{d\ln\eta}{d\tilde{\Phi}}\left\{\frac{d\ln[\tilde{\Phi}^2(1+\beta^L-y)]}{dy} + \frac{1}{1+\beta^L-y}\right\}\end{aligned} \tag{8.29}$$

substituting equation (8.29) to the inequality (8.28)

$$(y-1)\left\{\frac{d\ln[\tilde{\Phi}^2(1+\beta^L-y)]}{dy}\left(1+\frac{1}{2}\frac{d\ln\eta}{d\ln\tilde{\Phi}}\right) + \frac{\frac{d\eta}{d\ln\tilde{\Phi}}}{2(1+\beta^L-y)}\right\} \leq 1 \tag{8.30}$$

$$\text{in} \quad y\in(1, 1+\beta^L)$$

Suppose we can bound *a priori*

$$b_2 \leq \frac{d \ln \eta}{d \ln \tilde{\Phi}} \leq b_1 \tag{8.31}$$

because $\frac{\partial u_j}{\partial y} < 0$ for an nth ($n > 0$) order kinetics, it follows $\frac{d \ln \eta}{d \ln \Phi} < 0$ and $b_1 \leq 0$. Van den Bosch and Luss [12] proved that for the slab, cylinder and sphere geometrics,

$$b_2 \geq -1 \tag{8.32}$$

It follows from the inequality (8.30) that a sufficient uniqueness criterion can be obtained by substituting $d \ln \eta / d \ln \Phi$ by its upper bound b_1. Hence, for the second order kinetics,

$$\begin{aligned} &(1 + \tfrac{b_1}{2})\, y^3 + [\beta^L + \gamma(1 + \tfrac{b_1}{2}) - (1 + \tfrac{b_1}{2})]\, y^2 \\ &\qquad - \gamma(1 + \tfrac{b_1}{2})(\beta^L + 2)\, y + \gamma(1 + \tfrac{b_1}{2})(1 + \beta^L) \geq 0 \\ &\qquad\qquad \text{for} \quad 1 \leq y \leq 1 + \beta^L \end{aligned} \tag{8.33}$$

For a conservative criteria, b_1 is set to zero, resulting into a model where intraparticle diffusion is neglected. This is tantamount to a lumped parameter model. Hence for $b_1 = 0$,

$$\frac{\beta^L \gamma}{1+\beta^L} \leq \Psi_1(\beta^L) \equiv \begin{cases} G_1(\beta^L) & \text{for } \beta^L \leq 1 \\ G_2(\beta^L) & \text{for } \beta^L \geq 1 \end{cases} \tag{8.34}$$

where

$$G_1(\beta^L) \equiv 2 + 2\sqrt{2}\left(1 - \frac{2\beta^{L2}}{[1+2(1+\beta^L)]^2}\right)^{1/2} + 3\,\frac{1-\beta^L + 2(1+\beta^L)}{[1+2(1+\beta^L)]^2} \tag{8.35}$$

$$G_2(\beta^L) \equiv 2+2\left[1+\frac{4(\beta^L+2)(\beta^{L2}+4\beta^L+2)}{(\beta^L+1)^2\,(\beta^L+4)^2}\right]^{\frac{1}{2}}+\frac{8(2+\beta^L)}{(1+\beta^L)(4+\beta^L)^2} \qquad (8.36)$$

For the case where $Bi_m \to \infty$,

$$\gamma \leq G_2(\beta^L \to \infty) = 4 \qquad (8.37)$$

It is clear that for $\beta^L \in (0, \infty)$, inequality (8.34) is satisfied for $\gamma \leq 4$. Hence, $\gamma \leq 4$ is the most conservative uniqueness criterion.

Multiple steady states exist for some $\tilde{B}$ values whenever inequality (8.30) is violated. Inspection of inequality (8.30) indicates that a sufficient condition for its violation for some y $\in$ (1, 1 + β^L) is to assume equal to b_2. Hence, multiplicity occurs for some $\tilde{B}$ values if

$$\left(1+\frac{b_2}{2}\right)y^3+\left[\beta^L+(\gamma-1)\left(1+\frac{b_2}{2}\right)\right]y-\gamma\left(1+\frac{b_2}{2}\right)(2+\beta)\,y$$
$$+\ \gamma\left(1+\frac{b_2}{2}\right)(1+\beta) \leq 0 \qquad (8.38)$$

for some y_s in (1, 1 + β^L).

A more conservative bound is obtained when $b_2 = -1$ (see Van den Bosch and Luss [12]). Hence,

$$\frac{\beta^L\gamma}{1+\beta^L} > \psi_4(\beta^L) \equiv \begin{cases} G_5(\beta^L) & \text{for } \beta^L \leq 1 \\ G_6(\beta^L) & \text{for } \beta^L \geq 1 \end{cases} \qquad (8.39)$$

where

$$G_5(\beta^L) \equiv 6+2\sqrt{6}\left(1+\frac{2\beta^{L^2}}{[2+3(1+\beta^L)]^2}\right)^{\frac{1}{2}} \qquad (8.40)$$
$$+\ \frac{5(1+\beta^L)\,[1-6(1+\beta^L)]}{[2+3(1+\beta^L)]^2}$$

$$G_6(\beta^L) \equiv 6+6\left\{1-\frac{2\beta^L+3}{(\beta^L+1)^2}\right\}^{\frac{1}{2}}-\frac{(2\beta^L+3)(2\beta^{L^2}+2\beta^L+3+4\beta^{L^2})}{(\beta^L+3)^2(\beta^L+1)} \quad (8.41)$$

In the case of $B_{im} \rightarrow \infty$ or $\beta^L \rightarrow \infty$, a condition for multiplicity of steady states for some values of $\tilde{B}$ is given by $\gamma \gtrsim 8$.

e. Exact Uniqueness and Multiplicity of Steady State Criteria

Before proceeding to derive the exact criteria, a proof of the uniqueness of the concentration distribution for a fixed temperature is set forth at the outset.

e-1. Bounds for u

Upon integration of equation (8.1)

$$u_j' = \phi^2 \int_0^{\xi} e^{\gamma(1-\frac{1}{y})} u_j^n \, d\xi \quad (8.42)$$

Since the integrand is positive,

$$u_j' \geq 0 \qquad \text{for} \quad \xi \in (0,1) \quad (8.43)$$

but, $u_j(1) = 1 - \frac{1}{Bi_m} u_j'(1)$

Hence, $0 \leq u_j(1) \leq 1$ (8.44)

as a corollary,

$$0 \leq u_j(0) \leq u_j(1) \leq 1 \quad (8.45)$$

e-2. Uniqueness of Internal Concentration Profile

Here again, the maximum principle is applied. Consider the maximal solution $\tilde{u}_2(\xi)$ and the minimal solution $\tilde{u}_1(\xi)$. Furthermore, let $\tilde{u}_2 > \tilde{u}_1$. Hence, given a y, and using a comparison theorem approach,

$$\tilde{u}_1(1) - \tilde{u}_2(1) = \phi^2 \int_0^1 \frac{R(\tilde{u}_2;y) - R(\tilde{u}_1;y)}{u_2 - u_1} (u_2 - u_1)\, d\xi \tag{8.46}$$

upon using the limit theorem,

$$\tilde{u}_1(1) - \tilde{u}_2(1) = \phi^2 \int_0^1 \left.\frac{\partial R}{\partial u}\right|_{u^*} (u_2 - u_1)\, d\xi \tag{8.47}$$

where $u^* \in (u_1, u_2)$

It is necessary and sufficient that if

$$\frac{\partial R}{\partial u} > 0 \tag{8.48}$$

then equation (8.47) is readily violated. For $R = e^{\gamma(1-\frac{1}{y})} u^2$, the uniqueness of u is quickly established.

e-3. The Solution

The elliptic integral was used by DeVera and Varma [22] to solve for the optimum bulk phase composition in an isothermal catalyst slab with a second order kinetics. This approach is extended here. Applying the Clairut's transformation to the material balance equation,

$$\frac{d}{d\xi}(u_j')^2 = 2\phi^2 \rho(y)\, u_j^2\, u_j' \tag{8.49}$$

where $$\rho(y) \equiv \exp\left[\gamma\left(1 - \frac{1}{y}\right)\right] \tag{8.49a}$$

and integrating from $\xi = 0$ to ξ

$$u_j' = \sqrt{\frac{2}{3}}\, \phi\, \rho^{\frac{1}{2}}(y) \sqrt{u^3 - u(0)^3} \tag{8.50}$$

Equation (8.50) is an elliptic integral form [23], whose solution is given by

$$F(\psi(u;u(0)),k) = \sqrt{\frac{2u(0)}{\sqrt{3}}}\,\phi\,\rho^{\frac{1}{2}}(y)\,\xi \tag{8.51}$$

where $F(\psi,k)$ $\equiv$ elliptic integral of the first kind

k $\equiv$ some modulus $\equiv (\sqrt{3}-3/2)/2\sqrt{3}$

$\cos\psi$ $\equiv [(\sqrt{3}+1)\,u(0)-u]\,/\,[(\sqrt{3}-1)\,u(0)+u]$

For $Bi_m \to \infty$, the centerline concentration is evaluated by using the boundary condition at $\xi = 1$, thus the transcendental form for u(0) is

$$F(\psi(1;u(0)),k) = \sqrt{\frac{2u(0)}{\sqrt{3}}}\,\phi\,\rho^{\frac{1}{2}}(y) \tag{8.52}$$

Now, y is eliminated from equation (8.52) by using the heat balance, and the result is casted into the form

$$\frac{\gamma}{2} = [g^{-1}(u(0))+1]\ln\left[\frac{1}{\phi}\sqrt{\frac{3}{2}}\,h(u(0))\right] \equiv \mathcal{F}(u(0)) \tag{8.53}$$

where

$$h(u(0)) \equiv 3^{-0.25}\,F(\psi(1;u(0)),k)\,/\sqrt{u(0)} \tag{8.53a}$$

$$g(u(0)) \equiv (\beta/Bi_h)\sqrt{1-u(0)^3}\;h(u(0)) \tag{8.53b}$$

Furthermore, since $0 \le u(0) \le 1$, therefore for

u(0) = 1,

$$\psi(1;u(0)=1) = \operatorname{Arcos}\frac{(\sqrt{3}+1)-1}{(\sqrt{3}-1)+1} = 0$$

$$F(0,k) = 0$$

$$h(u(0)=1) = 0$$

and, $\mathcal{F}(u(0)=1) = -\infty$

For $u(0) = 0$,

$$\varphi(1, u(0)=0) = \operatorname{Arcos}(-1) = \pi$$

$$F(\pi, k) = 2K$$

$$h(u(0)=0) = \frac{2K}{0} = +\infty$$

and $\mathcal{F}(u(0)=0) \cong \ln\sqrt{\frac{3}{2}}\,\frac{1}{\phi}\,h(u(0)) = +\infty$

It is clear that the necessary and sufficient condition for uniqueness of the steady state for all physico-chemical parameters is

$$\left\{ g_1 \ln\left[\frac{1}{\phi}\sqrt{\frac{3}{2}}\,h(u(0))\right] + g_2 \frac{d\ln h}{d\,u(0)} \frac{\beta}{Bi_h} \sqrt{1-u(0)^3}\, h(u(0)) \right.$$
$$\leq g_1 g_2 \ln\left[\frac{1}{\phi}\sqrt{\frac{3}{2}}\,h\right]$$
$$\text{for} \quad u(0) \in (0,1) \tag{8.54}$$

where

$$g_1(u(0)) \equiv \frac{\beta}{Bi_h}\left[\sqrt{1-u(0)^3}\,\frac{dh}{d\,u(0)} - \frac{3u(0)^2\,h(u(0))}{2\sqrt{1-u(0)^3}}\right] \tag{8.54a}$$

$$g_2(u(0)) \equiv 1 + \frac{\beta}{Bi_h}\sqrt{1-u(0)^3}\;h(u(0)) > 0 \tag{8.54b}$$

and

$$3^{0.25}\frac{dh}{d\,u(0)} \equiv \frac{-2\sqrt{3}\left\{(\sqrt{3}-1)u(0)+1\right\}^{-2}\left\{1-k^2\sin^2\varphi(1;u(0))\right\}^{-\frac{1}{2}}}{\sqrt{u(0)}\;\sin\varphi(1;u(0))}$$

$$- \frac{F(\psi(1; u(0)), k)}{2\, u(0) \sqrt{u(0)}} \tag{8.54c}$$

Exactly the same approach is applied for finite Bi_m. Here, the criteria for uniqueness is expressed in terms of the external concentration, i.e., u(1), instead of u(0). Thus, equation (8.53) assumes the form,

$$\mathcal{F}(u(1)) \equiv \left[g^{-1}(u(1))+1\right] \ln\left[\frac{1}{\phi}\sqrt{\frac{3}{2}}\, h(u(1))\right] = \frac{\gamma}{2} \tag{8.55}$$

where $h(u(1)) \equiv 3^{-0.25} F(\psi(u(1), u_0), k) / \sqrt{u_0}$ (8.55a)

$$u_0 = \left\{ u(1)^3 - \frac{3}{2\phi^2 \rho(u(1))} Bi_m^2 [1-u(1)]^2 \right\}^{1/3} \tag{8.55b}$$

$$g(u(1)) \equiv \frac{\beta}{Bi_h} \sqrt{u(1)^3 - u_0^3}\; h(u(1)) \geq 0 \tag{8.55c}$$

$$\rho(u(1)) \equiv \exp\left[\gamma\left(1 - \left\{1 + \frac{\beta Bi_m}{Bi_h}(1-u(1))\right\}^{-1}\right)\right] \tag{8.55d}$$

The bounds for u(1) are established by recognizing that since $0 \leq u_0 \leq 1$ and for the monotonic increasing kinetic rate function, $u' > 0$, thus $0 \leq u_0 < u \leq 1$. The lowest bound for u(1) is therefore the lowest root of

$$u_*(1)^3 - \frac{3\, Bi_m^2}{2\phi^2 \rho(u_*(1))} [1 - u_*(1)]^2 = 0 \tag{8.56}$$

Moreover, $\mathcal{F}(u_*(1)) = +\infty$ and $\mathcal{F}(u(1)=1) = -\infty$, hence the necessary and sufficient condition for uniqueness is

$$[1+g(u(1))]\frac{d\ln h(u(1))}{du(1)} \le \frac{1}{\phi}\sqrt{\frac{2}{3}}\,\frac{d\ln g(u(1))}{du(1)}\ln\left[\frac{1}{\phi}\sqrt{\frac{3}{2}}\,h(u(1))\right]$$

for $u_*(1) \le u(1) \le 1$ (8.57)

where

$$g'(u(1)) \equiv \frac{1}{\phi}\sqrt{\frac{3}{2}}\,\frac{\beta B\bar{i}_m}{B\bar{i}_h}\,\frac{h}{\rho}\left\{[1-u(1)]\frac{d\ln h}{du(1)} + \frac{[1-u(1)]\beta\gamma B\bar{i}_m}{2B\bar{i}_h\{1+\frac{\beta}{B\bar{i}_h}[1-u(1)]^2} - 1\right\} \quad (8.57a)$$

$$3^{0.25}\frac{dh}{du(1)} \equiv \frac{[d\varphi/du(1)]}{\sqrt{u_o}\sqrt{1-k^2\sin^2\varphi}} - \frac{F(\varphi(u(1),u_o),k)}{2u_o\sqrt{u_o}}\,\frac{du_o}{du_1} \quad (8.57b)$$

$$\frac{d\varphi}{du(1)} \equiv \frac{-2\left[u(1)\frac{du_o}{du(1)} - u_o\right]}{[(\sqrt{3}-1)u_o - u(1)]^2\sin\varphi(u(1))} \quad (8.57c)$$

$$\frac{du_o}{du(1)} \equiv u_o^{-2/3}\left\{u(1)^2 + \frac{B\bar{i}_m^{-2}}{2\phi^2}\,\frac{[1-u(1)]}{\rho(u(1))}\left[2 - \frac{(1-u(1))\gamma}{\left(1+\frac{\beta B\bar{i}_m}{B\bar{i}_h}[1-u(1)]^2\right)}\,\frac{\beta B\bar{i}_m}{B\bar{i}_h}\right]\right\} \quad (8.57d)$$

THE HETEROGENEOUS CHEMICAL REACTOR MODEL

Here, an adiabatic tubular type reactor with a plug flow velocity of the fluid phase model is employed. This assumption is generally valid for a high aspect ratio (i.e., reactor length/tube diameter). Hence, for the isotropic bed, with negligible pressure drop and axisymmetric flow, the steady state equation (5.2) reduces to

$$-\langle v\rangle\frac{dc_j^\circ}{dz} - \frac{1-\tilde{\epsilon}}{\tilde{\epsilon}}\,a\eta_j V_p\,\epsilon\rho S\,\frac{N_T}{L^2}\,\hat{R}_j(C_j^q, T^\circ) = 0 \quad (9.1)$$

The energy balance assumes that since the reactor is adiabatic and for a large aspect ratio, the radial transport of energy has a smaller contribution than the axial transport of energy. In this work, it is further assumed that the reactor bed is relatively dilute or low solids

density. This enables the model to neglect the axial thermal conduction contribution and thus, the energy transport is solely by a convective transport. For higher solids density, the axial thermal conduction contribution along the reactor length can no longer be neglected. This effect would definitely create more exotic behavior of the steady state multiplicity pattern; perhaps, more complex than the number of steady states in a single catalyst particle. Furthermore, the question of the steady state stability would be difficult to address. These studies will be later investigated in another research. With this model, the energy balance collapses into

$$-\rho^\circ \hat{C}_p^\circ \langle v \rangle \frac{dT^\circ}{dz} + \frac{1-\tilde{\epsilon}}{\tilde{\epsilon}}\, a\, \tilde{q}_e = 0 \tag{9.2}$$

where $\tilde{q}_e$ is the effective thermal conductivity flux entering or leaving the catalyst pellet.

Now, the heat balance in the solid phase, assuming an effective thermal conduction flux, is expressed as

$$\underline{\nabla} \cdot \tilde{\underline{q}}_e = \epsilon \rho S (-\Delta H) \hat{R}_j \tag{9.3}$$

and for a temperature independent heat of reaction,

$$\int_V \underline{\nabla} \cdot \underline{q}_e \, d^3\underline{r} = \int_{\partial\Omega} \underline{n} \cdot \underline{q}_e \, d^2\underline{r} = \epsilon \rho S (-\Delta H) \int_V \hat{R}_j \, d^3\underline{r} \tag{9.4}$$

but,

$$\frac{\tilde{q}_e}{N_T} \int_{\partial\Omega} d^2\underline{r} = \int_{\partial\Omega} \underline{n} \cdot \underline{q}_e \, d^2\underline{r} \tag{9.5}$$

and using the effectiveness factor definition and equations

(9.3) to (9.5), the energy balance in the fluid phase is transformed into

$$-\rho^{\circ}\hat{C}_p^{\circ}\langle v\rangle \frac{dT^{\circ}}{dz} + \frac{1-\tilde{\epsilon}}{\tilde{\epsilon}}\, a\, \frac{N_T}{L^2}(-\Delta H)\,\epsilon\rho S V_p \eta_j \hat{R}_j(C_j^{\circ}, T^{\circ}) = 0 \tag{9.6}$$

the initial boundary point conditions for equations (9.1) and (9.6) are provided by the feed conditions.

If the following dimensionless variables are defined

$Da \equiv$ Damköhler number $\equiv \frac{1-\tilde{\epsilon}}{\tilde{\epsilon}}\, a V_p\, \epsilon\rho S \frac{N_T}{L^2} k_f \tau$

$\tau \equiv$ residence time $\equiv Z/\langle v\rangle$

where $Z \equiv$ total length of the reactor

$C_{jf}^{\circ} \equiv$ feed concentration

$\gamma^{\circ} \equiv E/R_g T_f^{\circ} \equiv$ dimensionless activation energy defined relative to feed conditions

$T_f^{\circ} \equiv$ feed temperature,

hence, the dimensionless material and energy balances are expressed as

$$\frac{du_j^{\circ}}{d\zeta} + Da\,\eta_j(u_j^{\circ}, y^{\circ})\, e^{\gamma^{\circ}(1-\frac{1}{y^{\circ}})}\,[u_j^{\circ}]^2 = 0 \tag{9.7}$$

$$\frac{dy^{\circ}}{d\zeta} - \beta^{\circ} Da\,\eta_j(u_j^{\circ}, y^{\circ})\, e^{\gamma^{\circ}(1-\frac{1}{y^{\circ}})}\,[u_j^{\circ}]^2 = 0 \tag{9.8}$$

with initial conditions of $u_j^{o}(0) = 1$ and $y^{o}(0) = 1$. $\beta^{\circ} \equiv (-\Delta H)\, C_{jf}^{\circ} / [\rho^{\circ}\hat{C}_p^{\circ}\, T_f^{\circ}]$ is the dimensionless adiabatic temperature rise. Equations (9.7) and (9.8) are uncoupled to yield

$$y^{\circ} = 1 + \beta^{\circ}(1 - u_j^{\circ}) \tag{9.9}$$

Qualitatively, $u_j^{o} \leq 1$ for $0 \leq \zeta \leq 1$ and although the solution to equations (9.7) and (9.9) is unique at glance, the multiplicity of solutions to equation (9.7) depends on the continuity properties of the field, i.e., the second term in equation (9.7). From theory of first order ordinary differential equation, a unique solution is guaranteed if and only if the field is Lifschitz continuous. This requirement is satisfied sufficiently if the field is piecewise continuous in the interval and domain of interest. Since the field in equation (9.1) is not necessarily continuous because of the possibility of multiple solutions for the effectiveness factor, therefore the concentration profile of the fluid phase could likewise be multiple. Their number is equal to the number of steady states provided by the number of steady state effectiveness factor.

The steady state multiplicity pattern could change along the reactor length and it is largely governed by how the bulk fluid phase concentration change. It is possible to have a 3 to 1 pattern, a 1 to 3 to 1, etc.

NUMERICAL IMPLEMENTATION AND DISCUSSION OF RESULTS

a. Effectiveness Factor

The complexity of the transcendental functions for $Bi_m \to \infty$ in inequality (8.54) prevented the development of an *a priori* criteria for uniqueness. However since u(0) is bounded, the numerical implementation of equation (8.54) is not difficult but not practical if a quick estimate of the uniqueness criteria is derived, and the stronger criteria by Van den Bosch and Luss [12] would suffice. On the positive aspect, the violation of equation (8.54) can provide not an *a priori* criteria but provides for the calculation of the multiple steady states, their number, multiplicity patterns and the bifurcation points. The bifurcation points are obtained from the solution of

$$\frac{d\mathcal{F}}{du(0)} = \frac{d^2\mathcal{F}}{du(0)^2} = 0 \quad , \qquad 0 \leq u(0) \leq 1 \tag{10.1}$$

All the calculations involve a straight forward root searching, e.g., the half-interval method, and they are rather fast converging and not cumbersome. An example of these calculations are found in Appendix A.

As in the case of $Bi_m \rightarrow \infty$, no *a priori* criteria can be derived, however, the numerical calculation of the criteria given by equation (8.57) is easily implemented by a simple two-stage root searching technique. The first involves the calculation of $u_*(1)$ and the second involves the testing of the criteria for uniqueness, i.e., equation (8.57).

Figures 1 to 4 exhibit a plot of effectiveness factor versus Thiele modulus. The effectiveness factor is written as

$$\eta_j \equiv \frac{\text{Rate of reaction in the presence of diffusion}}{\text{Rate of reaction evaluated at bulk fluid phase conditions}}$$

$$= \begin{cases} \frac{1}{\phi}\sqrt{\frac{3}{2}}\sqrt{1-u(0)^3}\,\exp\left[\frac{\gamma}{2}\left(1-\frac{1}{y}\right)\right] & \text{for } Bi_m \rightarrow \infty \quad (10.2a) \\[2ex] \frac{Bi_m}{\phi^2}\left[1-u(1)\right] & \text{for finite } Bi_m \quad (10.2b) \end{cases}$$

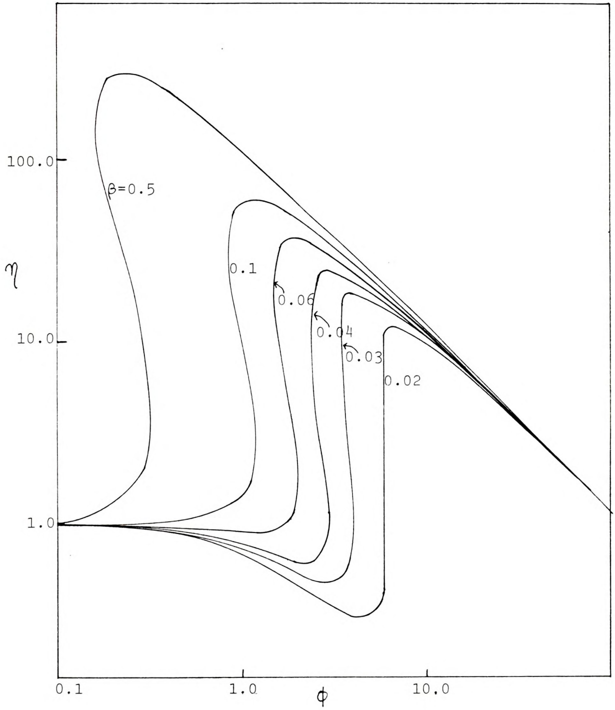

Figure 1 Effectiveness factor versus Thiele modules for various β.

$\gamma = 10.0$, $Bi_m = \infty$, $Bi_h = 1.0$

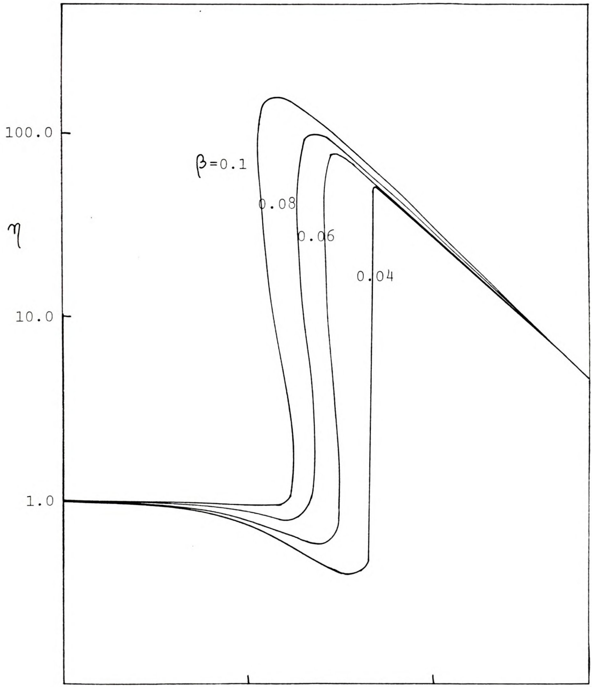

Figure 2 Effectiveness factor versus Thiele modules for various β.
$\gamma = 12.0$, $Bi_m = \infty$, $Bi_h = 2.0$

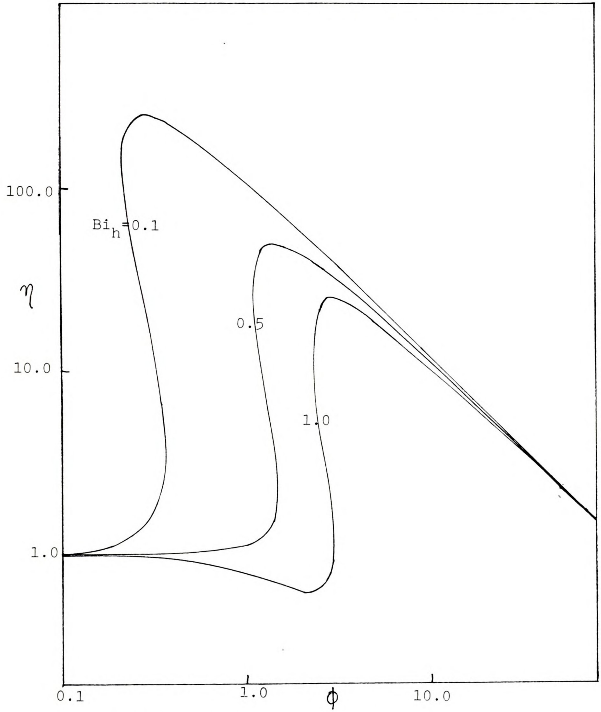

Figure 3 Effectiveness factor versus Thiele modules for various Bi_h.

$\gamma = 10.0$, $\beta = 0.04$, $Bi_m = \infty$

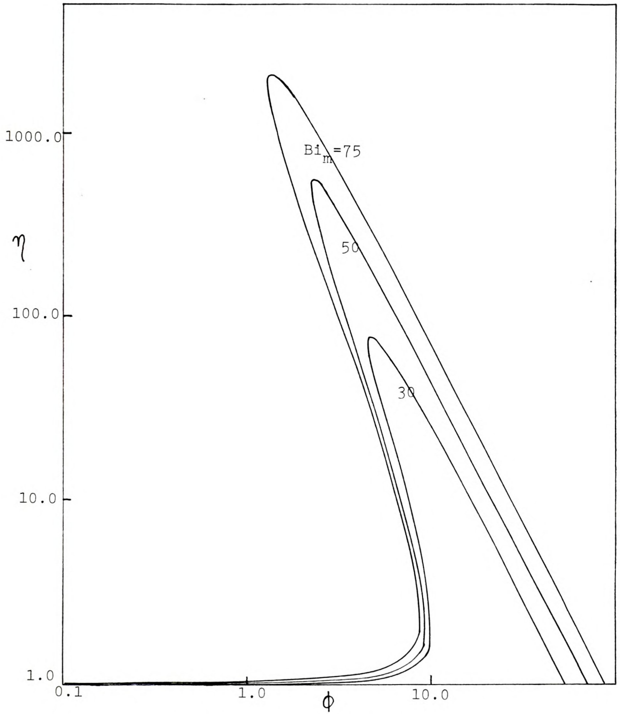

Figure 4 Effectiveness factor versus Thiele modules for various Bi_m.
γ = 20.0, β = 0.03, Bi_h = 0.5

For all the physico-chemical parameters reported here, the range of multiple steady states is relatively narrow. However, for a given value of Bi_h, γ and Bi_m, the range of multiple solutions expands as the Praeter temperature, β, increases (Figures 1 to 3). A similar situation exists for increasing Bi_m at a given value of β, γ and Bi_h (Figure 4). The range of multiple solutions also expands as the resistance to external heat transfer increases (compare Figures 1 and 2). There was no multiplicity pattern other than the 1-3-1 type that was found using the physico-chemical parameters reported here and those which are not reported here. Table 1 illustrates the uniqueness and multiplicity criteria comparison between the Van den Bosch and Luss analysis [12] and the elliptic integral approach. Except for very small values of the Praeter temperature, the Van den Bosch and Luss [12] analysis indeed present a workable criteria.

b. Concentration Profile Inside the Catalyst Pellet

Figures 5 to 8 show the concentration profiles using various physico-chemical parameters for the catalyst pellet. Figure 5 in particular compares a Fourier-type of orthogonal collocation solution (represented by Δ's) with the closed form solution. The trial solution for the orthogonal collocation is

$$u_j \sim \sum_{i=1}^{N+1} d_i \xi^{2i} \tag{10.3}$$

TABLE 1

Uniqueness and Multiplicity Criteria Comparison between Van den Bosch and Luss Analysis and the Elliptic Integral Solution

γ	Bim	Bin	β	Van den Bosch and Luss	Elliptic
10	∞	1.0	0.02	yes	no
			0.03	yes	yes
			0.04	yes	yes
			0.06	yes	yes
			0.1	yes	yes
			0.5	yes	yes
12	∞	2.0	0.04	yes	no
			0.06	yes	yes
			0.08	yes	yes
			0.1	yes	yes
10	∞	0.1	0.04	yes	yes
		0.5		yes	yes
		1.0		yes	yes
20	30	0.5	0.03	yes	yes
	50			yes	yes
	75			yes	yes

where $d_i \equiv$ a constant in the Fourier-type expansion

$N \equiv$ total number of interior collocation points

For the $Bi_m \rightarrow \infty$ case, the collocated differential equations (8.1) and (7.10) or the weighted residuals are

$$2\sum_{k=1}^{N+1}(k-1)(2k-3)\,d_k\,\xi_i^{2(k-2)} - \phi^2\rho(y)\left[\sum_{k=1}^{N+1}d_k\,\xi_i^{2(k-1)}\right]^2 = 0 \equiv \tilde{F}_i$$

for i = 1 → N (10.4)

$$\sum_{k=1}^{N+1} d_k - 1 = 0 \equiv \tilde{F}_{N+1} \qquad (10.5)$$

where $\rho(y) = \exp\left[\gamma\left(1-\frac{1}{y}\right)\right]$

$$y = 1 + \frac{\beta}{Bi_h}\phi^2\eta_j$$

and $\eta_j = \int_0^1 u_j^2(\xi\,;\,\phi, y)\,d\xi$

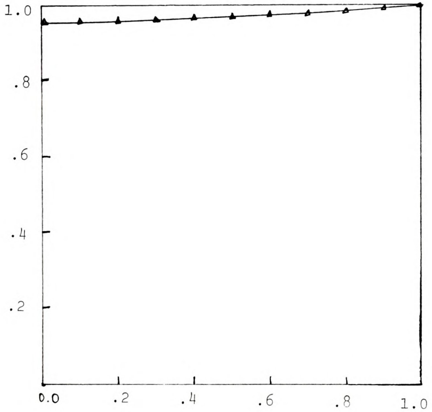

Figure 5 Concentration profile for a low ϕ.
$\gamma = 10.0$, $\beta = 0.03$, $\phi = 0.3$,
$Bi_m = \infty$, $Bi_h = 1.0$
(—— : analytic calculation,
Δ : collocation calculation)

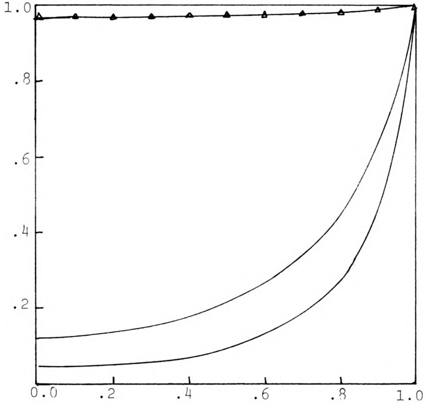

Figure 6 Concentration profile for a case of multiple solutions.
$\gamma = 10.0$, $\beta = 0.04$, $\phi = 0.22$,
$Bi_m = \infty$, $Bi_h = 0.1$
(—— : analytic calculation,
△ : collocation calculation)

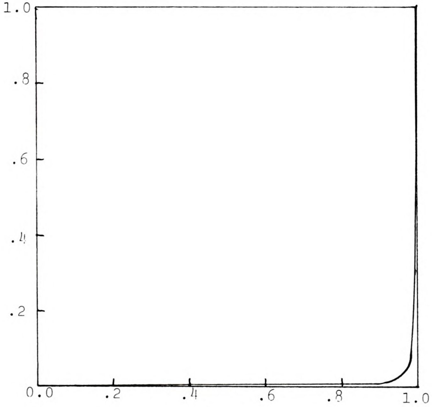

Figure 7 Concentration profile for a high ϕ.
$\gamma = 10.0$, $\beta = 0.03$, $\phi = 4.0$,
$Bi_m = \infty$, $Bi_h = 1.0$

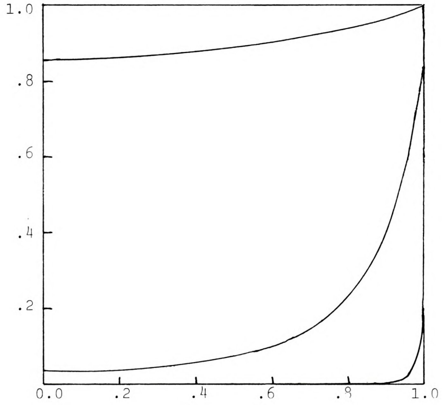

Figure 8 Concentration profile for a finite Biot mass number case. $\gamma = 20.0$, $\beta = 0.03$, $\phi = 0.5$, $Bi_m = 50.0$, $Bi_h = 0.5$

for the Fourier-type trial function

$$u_j^2 = \sum_{i=1}^{N+1} a_i^2 + \sum_{i=1}^{N+1} \sum_{\substack{k=1 \\ k \neq i}}^{N+1} a_i a_k \qquad (10.6)$$

where $$a_i \equiv d_i \xi^{2(i-1)} \qquad (10.6a)$$

Hence,

$$\eta_j = \sum_{i=1}^{N+1} d_i^2 \int_0^1 \xi^{4(i-1)} d\xi + \sum_{i=1}^{N+1} \sum_{\substack{k=1 \\ k \neq i}}^{N+1} d_i d_j \int_0^1 \xi^{2[i+k-2]}$$

or,

$$\eta_j = \sum_{i=1}^{N+1} \frac{d_i^2}{4(i-1)+1} + \sum_{i=1}^{N+1} \sum_{\substack{k=1 \\ k \neq j}}^{N+1} \frac{d_i d_k}{2(i+k-2)+1} \qquad (10.7)$$

The exterior boundary was collocated because the trial solution did not satisfy the exterior boundary condition. The collocation points ξ_i are obtained from the orthogonal property of the following Jacobi polynomial

$$\int_0^1 W(\xi^2) P_k(\xi^2) P_i(\xi^2) \xi^{\tilde{a}-1} d\xi = C_i \delta_{ik} \, , k = 1, 2, \cdots, i-1 \qquad (10.8)$$

and ξ_i satisfies $$P_k(\xi_i) = 0$$

where $P_k(\xi)$ is a kth degree Jacobi polynomial

δ_{ik} ≡ Krönecker delta

C_i ≡ a normalization constant

$\tilde{\alpha}$ ≡ shape factor (= 1 for semi-infinite slab, =2 for cylinder, = 3 for the sphere).

$W(\xi^2)$≡arbitrary weighting function (usually $1-\xi^2$ or simply 1).

These orthogonal points are calculated efficiently from the computer program developed by Michelsen and Villadsen

[24].

The solution for $\underline{d}$ are secured by a Newton-Raphson iteration, or

$$\underline{d}^{k+1} = \underline{d}^{k} - \underline{\underline{J}}^{-1}(\underline{d}^{k})\,\underline{\tilde{F}}(\underline{d}^{k}) \tag{10.9}$$

The Jacobian matrix is

$$\underline{\underline{J}}^{-1}(\underline{d}^{k}) \equiv \left[\frac{\partial \tilde{F}_i}{\partial d_\ell}\right]_{\underline{d}^{k}} \tag{10.10}$$

thus,

$$\begin{aligned}\frac{\partial \tilde{F}_i}{\partial d_k} &= 2(k-1)(2k-3)\,\xi_i^{(2k-4)} \\ &\quad - 2\phi^2\left[\sum_{k=1}^{N+1} d_k\,\xi_i^{2(k-1)}\right]\rho(y)\left\{\frac{\frac{\gamma\beta}{\overline{Bi}_h}(k-1)\left[\sum_{k=1}^{N+1} d_k\,\xi_i^{2(k-1)}\right]}{y^2}\right. \\ &\quad \left. + \,\xi_i^{2(i-1)}\right\} \qquad \text{for } i = 1 \rightarrow N\end{aligned} \tag{10.11}$$

$$\frac{\partial \tilde{F}_{N+1}}{\partial d_i} = 1 \tag{10.12}$$

Essentially, the calculation proceeds in the following fashion:

i) assume $\underline{d}$

ii) calculate y

iii) calculate the next guess via the Newton-Raphson iteration

iv) calculate the convergence tolerance

A specimen of the computer program using this technique is found in Appendix A.

The concentration profiles reveal that for a very diffusion-limited reaction, the profile becomes rather steep (Figure 7). An interesting case is when multiple steady states do arise, the upper branch steady state (in the context of the effectiveness factor plot) shows a steep profile. This must be safeguarded whenever instability indeed occur. The control policy should always be to keep the lower branch steady state.

c. The Tubular Reactor

The numerical implementation employs a discretization of the inverted fluid phase balance, i.e.,

$$\frac{d\zeta}{du_j^\circ} = -e^{-\gamma^\circ(1-\frac{1}{y^\circ})}\left\{Da\,\eta_j(u_j^\circ, y^\circ)[u_j^\circ]^2\right\}^{-1} \equiv H(u_j^\circ) \qquad (10.13)$$

It is assumed here that for an infinitesimal change in u_j^o, the effectiveness factor is approximately constant. Hence, by an IMSL DGEAR subroutine, the value of ζ at $u_j^o + \Delta u_j^o$ is obtained from

$$\int_{\zeta_k}^{\zeta_{k+1}} d\zeta = \int_{(u_j^\circ)_k}^{(u_j^\circ)_{k+1}} H(u_j^\circ)\, du_j^\circ \qquad (10.14)$$

and $\eta_j(u_j^\circ, y^\circ)$ at some $u_j^\circ \in (u_j^\circ, u_j^\circ + \Delta u_j^\circ)$ is evaluated from the previous discussions. In terms of the bulk phase conditions the physico-chemical parameters are redefined as

$$\phi^2 \equiv \phi_f^2\, e^{\gamma_f(1-\frac{1}{y^\circ})}\, u_j^\circ$$

$$\gamma \equiv \gamma_f / y^\circ$$

$$\beta \equiv \beta_f\, u_j^\circ / y^\circ$$

where ϕ_f^2 ≡ Thiele modulus evaluated at feed conditions

γ_f ≡ dimensionless activation energy evaluated at feed conditions

β_f ≡ adiabatic temperature rise evaluated at feed conditions

Figures 9 and 10 show the concentration profile of the bulk fluid phase reactant. The bulk phase temperature profile is not shown, but qualitatively, it increases along the reactor length. Clearly, the effectiveness factor decays along the reactor length, and therefore the conversion is decreasing, especially towards the reactor exit. Since the $du_j^o/d\zeta$ is steep at the vicinity of the reactor entrance, the majority of the catalytic activity is situated near the reactor entrance. Furthermore, a 3-1 multiplicity pattern for the reactor tube was found and noticeably, the lower steady state profile has the highest catalytic activity. Hence, for controllability and optimality, the choice should be the lower steady state but with the reactor size reduce to a sizeable fraction equivalent to some tolerable outlet conversion.

Finally, the case of high solids density should be interesting, because the inclusion of the axial thermal conductive heat transport can induce multiplicity patterns other than those obtained from a single particle. Furthermore, it should be realized that an internally isothermal, but externally non-isothermal

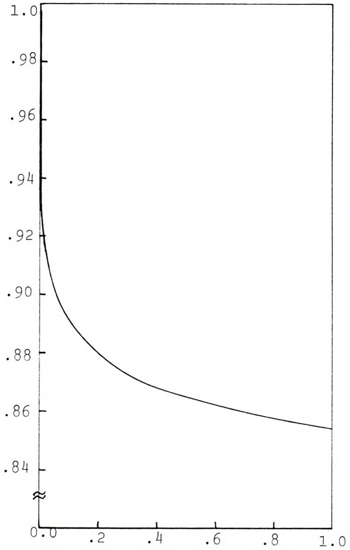

Figure 9 Concentration profile along the reactor length for unique solution case. $\gamma_f = 10.0$, $\beta_f = 0.04$, $\phi_f = 2.0$, $Bi_m = \infty$, $Bi_h = 0.1$, $\beta^{\circ} = 3.0$, $Da = 2.0$

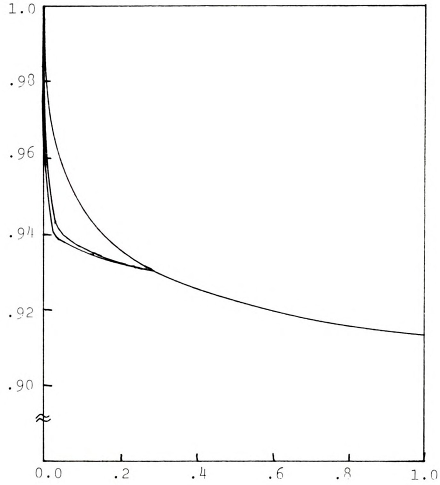

Figure 10 Concentration profile along the reactor length for the multiple solution case. $\gamma_f = 10.0$, $\beta_f = 0.04$, $\phi_f = 1.4$, $Bi_m = \infty$, $Bi_h = 0.5$, $\beta^{\circ} = 3.0$, $Da = 2.0$

catalyst pellet was used as a model here such that the consequences of these, as compared to the full non-isothermal case, is only but the later's shadow. However limited, it yet provides some insights into heterogeneous chemical reactor design.

APPENDICES

Appendix A. Computer Program and Sample Calculations

```
      PROGRAM FINITE(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C    THIS PROGRAM DETERMINES SURFACE AND CENTER
C    CONCENTRATION OF THE CATALYST PELLET, LOCATING
C    THEIR VALUES BY HALF-INTERVAL METHOD, FOR FINITE
C    BIOT MASS NUMBER CASE.
C
      DIMENSION DIFFER(2)
      PI=3.141592654
      TOL=1.0E-10
      TOLH=1.0E-12
      DN=1.0
      XK2=((SQRT(3.0)-(3.0/2.0))/2.0)/SQRT(3.0)
      COMK=1.598142025722
C
999   READ(5,*)GAM,BETA,PHI,BIM,BIH
      READ(5,*) SY1,DELY1,UPY1
      WRITE(6,30) GAM,BETA,PHI,BIM,BIH
30    FORMAT(/////,13X,"GAMMA=",F12.6,/,13X,"BETA=",F12.6,
     ./,13X,"PHI=",F12.6,/,13X,"BIOT MASS=",F12.6,/,13X,
     ."BIOT HEAT=",F12.6,/////)
      Y1=SY1
      READ(5,*) SY0,DELY0
C
C
1     V1=1.0+((BETA/BIH)*BIM*(1.0-Y1))
      T2=EXP((GAM/2.0)*(1.0-(1.0/V1)))
C
      ICOUNT=1
      Y0=SY0
21    T1=(SQRT(3.0)+1.0)*Y0-Y1
      T1=T1/((SQRT(3.0)-1.0)*Y0+Y1)
      PSI1=ACOS(T1)
      RT2=F(PSI1,XK2,COMK)*SQRT(1.5)/PHI
      RT21=SQRT(3.0)
      RT2=RT2/SQRT(RT21*Y0)
C
      DIFF=T2-RT2
      IF(ICOUNT.EQ.1) GOTO 101
      DIFFER(2)=DIFFER(1)
      DIFFER(1)=DIFF
      IF((DIFFER(1)*DIFFER(2)).LT.0.0) GOTO 103
      GOTO 102
C
101   DIFFER(1)=DIFF
      ICOUNT=2
      GOTO 102
103   Y0L=Y0
      Y0R=Y0-DELY0
      ITER=(ALOG(DN/TOLH)/ALOG(2.0))+1.0
      DO 50 I=1,ITER
      Y0=(Y0L+Y0R)/2.0
      T1=(SQRT(3.0)+1.0)*Y0-Y1
      T1=T1/((SQRT(3.0)-1.0)*Y0+Y1)
      PSI1=ACOS(T1)
      RT2=F(PSI1,XK2,COMK)*SQRT(1.5)/PHI
      RT21=SQRT(3.0)
      RT2=RT2/SQRT(RT21*Y0)
      DIF=T2-RT2
      IF(DIF.LE.0.0) GOTO 45
      Y0L=Y0
      GOTO 50
45    Y0R=Y0
50    CONTINUE
      IF(PSI1.GE.(PI/2.0)) GOTO 211
      PSI=PSI1
      GOTO 201
211   PSI=PI-PSI1
201   C1=SIN(PSI)**2.0
      C1=SQRT(1.0-(XK2*C1))
      C2=C1*SIN(PSI)
      C3=C2*(((SQRT(3.0)-1.0)*Y0)+Y1)**2.
```

```
      C4=C3*PHI*T2
      C5=3.0**0.75
      C6=C4/(C5*SQRT(3.0*Y0))
      CHECK1=C6-(RIM*(1.0-Y1))
      WRITE(6,65) Y1,Y0,V1,DIF,CHECK1
65    FORMAT(/,13X,"Y1=",F12.1 ,/,13X,"Y0=",F12.1 ,/,13X,
     *"TEMPERATURE=",E22.7,/,13X,"DIF=",F12.6,/,13X,"CHECK=",
     *E22.7)
102   Y0=Y0+DELY0
      IF(Y0.GE.Y1) GOTO 11
      GOTO 21
C
11    Y1=Y1-DELY1
      IF(Y1.LT.UPY1) GOTO 99
      GOTO 1
99    STOP
      END
C
C
C
      FUNCTION F(PSI1,XK2,COMK)
      PI=3.14159264
      IF(PSI1.GE.(PI/2.0)) GOTO 11
      GOTO 12
11    IF(PSI1.EQ.(PI/2.0)) GOTO 18
      PSI=PI-PSI1
      GOTO 13
12    PSI=PSI1
C
13    BIDEN=1.0
      FSUM=PSI
      T2M=PSI
      BINUM=1.0
      DO 10 M=1,100
      XM=FLOAT(M)
      BINUM=BINUM*(-0.5-XM+1.0)
      BIDEN=BIDEN*XM
      IF(BIDEN.LE.1.0E100) GOTO 31
      BINUM=BINUM/1.0E100
      BIDEN=BIDEN/1.0E100
31    BICOE=BINUM/BIDEN
      IF(ABS(BICOE).LE.1.0E-100) GOTO 20
      SINP=SIN(PSI)
      SINPSI=SINP**(2.0*XM-1.0)
      SK2=XK2**XM
      IF(ABS(SK2).LE.1.0E-80) GOTO 20
      T2M=(((2.0*XM-1.0)/(2.0*XM))*T2M)-(SINPSI*COS(PSI)/(
     +2.0*XM))
      IF(ABS(T2M).LE.1.0E-60) GOTO 20
      N=XM/2.0
      IF((2*N-M).EQ.0) GOTO 16
      FSUB=BICOE*(-SK2)*T2M
      GOTO 17
16    FSUB=BICOE*SK2*T2M
17    FSUM=FSUM+FSUB
      IF(ABS(FSUB).LE.1.0E-50) GOTO 20
10    CONTINUE
20    CONTINUE
      IF(PSI1.LT.(PI/2.0)) GOTO 15
      IF(PSI1.EQ.(PI/2.0)) GOTO 18
      FSUM=2.0*COMK-FSUM
      GOTO 15
18    FSUM=COMK
15    F=FSUM
      RETURN
      END
```

```
GAMMA=     20.000000
BETA=       .030000
PHI=       .700000
BIOT MASS=    75.000000
BIOT HEAT=      .500000



Y1= .9500000000
Y0= .1869741501
TEMPERATURE=            .1225000E+04
DIF=    .0000000
CHECK=          -.4412822E+00

Y1= .9400000000
Y0= .1268824328
TEMPERATURE=            .1270000E+04
DIF=    .0000000
CHECK=          -.1396961E+00

Y1= .9300000000
Y0= .0952849350
TEMPERATURE=            .1315000E+04
DIF=    .0000000
CHECK=           .3725551E+00

Y1= .9200000000
Y0= .0575555743
TEMPERATURE=            .1360000E+04
DIF=   -.0000000
CHECK=           .1116796E+01

Y1= .9100000000
Y0= .0391652021
TEMPERATURE=            .1405000E+04
DIF=   -.0000000
CHECK=           .2110975E+01
```

```
      PROGRAM COLLO(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C    THIS PROGRAM DETERMINES THE CENTER CONCENTRATION OF THE
C    CATALYST PELLET AND CONCENTRATION PROFILES WITHIN THE
C    PELLET, USING ORTHOGONAL POLYNOMIAL COLLOCATION METHOD.
C
      DIMENSION A(8,8),B(8,8),X(6),WKAREA(64),D(7)
      DIMENSION DIFFV(2),VROOT(5)
      X(1)=0.1163318689
      X(2)=0.3427240133
      X(3)=0.5506394029
      X(4)=0.7286685991
      X(5)=0.8678010538
      X(6)=0.9599350453
       READ(5,*) GAM,P2,BETA,BIH
      READ(5,*)D(1),D(2),D(3),D(4),D(5),D(6),D(7)
       B2=BETA*P2*P2/BIH
      TOL=0.000001
      N=6
      NP1=N+1
C
C    CALCULATE THE ROOT OF V FOR A GIVEN SET OF D VECTOR
C
      READ(5,*) DVV,CONV
       READ(5,*) NTEST
C
C    CALCULATE MULTIPLICITY FOR V(BOUND)
C
      DISCV=(GAM-4.0)*GAM
      DISCV=SQRT(DISCV)
      VOP=(GAM+DISCV)/2.0
      VOM=(GAM-DISCV)/2.0
      FVOP=GAM*(1.0-(1.0/VOP))
      FVOP=EXP(FVOP)/(VOP-1.0)
      FVOM=GAM*(1.0-(1.0/VOM))
      FVOM=EXP(FVOM)/(VOM-1.0)
    1  V=1.0
       T1I=0.0
      T1IJ=0.0
      DO 2 I=1,NP1
2     T1I=((D(I)*D(I))/((4.0*FLOAT(I-1))+1.0))+T1I
      DO 4 I=1,NP1
      DO 4 J=1,NP1
      IF(J.EQ.I) GOTO 4
      T1IJ=((D(I)*D(J))/((2.0*FLOAT(I+J-2))+1.0))+T1IJ
4     CONTINUE
      SM=T1I+T1IJ
      B2M=B2*SM
      B2M=1.0/B2M
      IF(B2M.LE.FVOM) V=VOP
C
C  ESTIMATE THE ROOT OF V(ROOT SEARCH)
C
      II=1
      J=0
5     H=GAM*(1.0-(1.0/V))
      H=EXP(H)
       XLHSV=(V-1.0)/H
       DIFFV(II)=XLHSV-(B2*SM)
      IF(II.EQ.1) GOTO 6
      IF((DIFFV(1)*DIFFV(2)).GT.0.0) GOTO 8
      J=J+1
      VROOT(J)=V-DVV
       IF(NTEST.NE.0) GOTO 555
       GOTO 15
C
C   CONDITIONS OF UNIQUE V
C
 555   IF(GAM.LE.4.0) GOTO 15
      IF(B2M.GT.FVOP) GOTO 15
      IF(B2M.LT.FVOM) GOTO 15
```

```
C    WHEN J=3 ROOT SEARCH STOPS BECAUSE THERE ARE ONLY 3
C    POSSIBLE ROOTS FOR V
C
      IF(J.EQ.3) GOTO 15
      GOTO 8
6     II=2
      V=V+DVV
      GOTO 5
8     DIFFV(1)=DIFFV(2)
      V=V+DVV
      GOTO 5
C
C    HALF-INTERVAL METHOD
C
  15   JIN=J
       DO 900 JJ=1,JIN
      VL=VROOT(JJ)
      VR=VL+DVV
      HL=GAM*(1.0-(1.0/VL))
      HL=EXP(HL)
       FL=((VL-1.0)/HL)-(B2*SM)
      IF(FL.LT.0.0) GOTO 110
C
C
C
103   V=(VL+VR)/2.0
      H=GAM*(1.0-(1.0/V))
      H=EXP(H)
       F=((V-1.0)/H)-(B2*SM)
      IF(ABS(F).LT.CONV) GOTO 18
      IF(F.GT.0.0) GOTO 104
      VR=V
      GOTO 103
104   VL=V
      GOTO 103
C
C   FL IS NEGATIVE
C
110   V=(VL+VR)/2.0
      H=GAM*(1.0-(1.0/V))
      H=EXP(H)
       F=((V-1.0)/H)-(B2*SM)
      IF(ABS(F).LT.CONV) GOTO 18
      IF(F.LT.0.0) GOTO 107
      VR=V
      GOTO 110
107   VL=V
      GOTO 110
C
C
  18   DHDV=(H*GAM)/(V*V)
       DO 30 J=1,N
      DO 30 I=1,NP1
      T2=0.0
      DO 20 K=1,NP1
20    T2=D(K)*(X(J)**FLOAT(2*(K-1)))+T2
      T3=(FLOAT((I-1)*((2*I)-3))*2.)*X(J)**FLOAT((2*I)-4)
       T7=0.0
       DO 220 K=1,NP1
       IF(K.EQ.I) GOTO 220
       T7=D(K)/((2.0*FLOAT(I+K-2))+1.0)
 220   CONTINUE
       DMDDI=D(I)/((2.0*FLOAT(I-1))-1.0)-T7
       DVDDI=B2*H*DMDDI
       DVDDI=DVDDI/(1.0-(B2*SM*DHDV))
  30   A(J,I)=T3-(P2*P2)*H*T2*(2.0*X(J)**FLOAT((2*I)-1) +
     .  ((GAM*DVDDI*T2)/(V*V)))
C
C
      DO 40 I=1,NP1
40    A(N+1,I)=1.0
```

```
      NP2=N+2
      DO 50 I=1,NP2
      A(N+2,I)=0.0
50    A(I,N+2)=0.0
C
      DO 60 J=1,N
      T4=0.0
      T5=0.0
      DO 55 K=1,NP1
      T4=((FLOAT((K-1)*((2*K)-3))*D(K))*(X(J)**FLOAT((2*K)
     .-4)))+T4
55    T5=(D(K)*(X(J)**FLOAT((2*K)-2)))+T5
60    B(J,N+2)=(2.*T4)-(((P2*P2)*H)*(T5*T5))
C
      B(N+1,N+2)=0.0
      DO 65 K=1,NP1
65    B(N+1,N+2)=D(K)+B(N+1,N+2)
      B(N+1,N+2)=B(N+1,N+2)-1.0
C
      DO 70 I=1,NP2
70    B(N+2,I)=0.0
C
      DO 80 J=1,NP1
      DO 80 I=1,NP1
      IF(I.NE.J) GOTO 75
      B(J,I)=1.0
      GOTO 80
75    B(J,I)=0.0
80    CONTINUE
C
      N2S=NP2*NP2
      DO 90 I=1,N2S
90    WKAREA(I)=0.0
C
      NN=NP1
       MM=NP2
      IA=MM
      IDGT=6
      CALL LEQT1F(A,MM,NN,IA,B,IDGT,WKAREA,IER)
C
      DO 100 K=1,NP1
100   D(K)=D(K)-B(K,NP2)
C
      ICOUNT=0
      DO 250 K=1,NP1
      IF(ABS(B(K,NP2)).LE.TOL) ICOUNT=ICOUNT+1
250   CONTINUE
      IF(ICOUNT.NE.NP1) GOTO 1
C
C   CONCENTRATION PROFILE
C
      WRITE(6,290)
 290  FORMAT(///,20X,"X",10X,"CONCENTRATION",//)
      THI=0.0
 261  Y=D(1)
      DO 260 I=2,NP1
      POWER=2.0*FLOAT(I)-2.0
260   Y=D(I)*(THI**POWER)+Y
      WRITE(6,300) THI,Y
 300  FORMAT(13X,F10.4,5X,F12.6)
      THI=THI+0.05
      IF(THI.GT.1.0) GOTO 800
      GOTO 261
C
C   NEW GUESS FOR D(I) WHEN V IS MULTIPLE
C
 800   IF(JIN.EQ.1) GOTO 999
C
       READ(5,*) (D(K),K=1,NP1)
C
900   CONTINUE
999   STOP
      END
```

```
             X          CONCENTRATION


          0.0000           .957059
           .0500           .957165
           .1000           .957482
           .1500           .958011
           .2000           .958752
           .2500           .959706
           .3000           .960872
           .3500           .962251
           .4000           .963844
           .4500           .965652
           .5000           .967675
           .5500           .969914
           .6000           .972371
           .6500           .975046
           .7000           .977941
           .7500           .981056
           .8000           .984394
           .8500           .987956
           .9000           .991743
           .9500           .995757
          1.0000          1.000000


:03 05/19/83   IB62628     357 Lines print.
ages print.  Cost at RG2 is   $   0.36
```

```
      PROGRAM PFR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C   CONCENTRATION PROFILE ALONG THE PLUG FLOW TUBULAR
C   REACTOR PACKED WITH CATALYSTS IS CALCULATED IN THIS
C   PROGRAM.
C
      REAL DIFF(2),UO(3),AIDA(3),THI(3)
      INTEGER N,METH,MITER,INDEX,IWK(2),IER,K
      REAL Y,WK(35),X,TOL,XEND,H
      COMMON GAM1,YZERO,DA,AIDAJ,UZE
      EXTERNAL FCN,FCNJ
C
C
C
      ITER=60
      DYO= 0.01
      SYO=0.00000001
      UPYO= 1.0
      COMK=1.598142025722
      XK2=((SQRT(3.0)-(3.0/2.0))/2.0)/SQRT(3.0)
      DELU=0.01
      READ(5,*) BETAB,DA
      READ(5,*) GAM1,BETA1,PHI1,BIOTH
      READ(5,*) UZERO,THI(1),THI(2),THI(3)
C
C    CALCULATION FOR EACH UZERO
C
      UZE=1.0-UZERO
80    YZERO=1.0+(BETAB*(1.0-UZERO))
      GAM=GAM1/YZERO
      BETA= BETA1*UZERO/YZERO
      PHI=(PHI1*EXP(GAM*(1.0-(1.0/YZERO)))*UZERO)**0.5
C
      J=0
      ICOUNT=1
      YO=SYO
C
C   FIND YOE AND V FOR EFFECTIVENESS FACTOR CALCULATION
C
1     T1=((SQRT(3.0)+1.0)*YO)-1.0
      T1=T1/(((SQRT(3.0)-1.0)*YO)+1.0)
      PSI1=ACOS(T1)
      T3=F(PSI1,XK2,COMK)
      T4=YO*SQRT(3.0)
      T21=T3/SQRT(T4)
      T2=(T21/PHI)*SQRT(1.5)
      T5=1.0-((YO*YO)*YO)
      V=1.0+(BETA/BIOTH)*SQRT(T5)*T21
      T6=(GAM/2.0)*(1.0-(1.0/V))
      RT2=EXP(T6)
      DIF=RT2-T2
      IF(ICOUNT.EQ.1) GOTO 11
      DIFF(2)=DIF
      GOTO 21
11    DIFF(1)=DIF
      ICOUNT=2
      GOTO 111
21    IF((DIFF(1)*DIFF(2)).LE.0.0) GOTO 31
      DIFF(1)=DIFF(2)
      GOTO 111
31    J=J+1
      UO(J) = YO
      YOL=UO(J)-DYO
      YOR=UO(J)
33    DO 50 I=1,ITER
      YOE=(YOL+YOR)/2.0
      T1=((SQRT(3.0)+1.0)*YOE)-1.0
      T1=T1/(((SQRT(3.0)-1.0)*YOE)+1.0)
      PSI1=ACOS(T1)
      T3=F(PSI1,XK2,COMK)
      T4=YOE*SQRT(3.0)
      T2=((T3/SQRT(T4))/PHI)*SQRT(1.5)
```

```
      T5=1.0-(YOE*YOE*YOE)
      V=1.0+(BETA/BIOTH)*SQRT(T5)*(T3/SQRT(T4))
      T6=(GAM/2.0)*(1.0-(1.0/V))
      RT2=EXP(T6)
      DIF=RT2-T2
      IF(DIFF(2).LE.0.0) GOTO 32
      IF(DIF.LE.0.0) GOTO 46
      YOR=YOE
      GOTO 50
46    YOL=YOE
      GOTO 50
32    IF(DIF.LE.0.0) GOTO 45
      YOL=YOE
      GOTO 50
45    YOR=YOE
50    CONTINUE
      WRITE(6,65) YOE,V,DIF
 65   FORMAT(/,13X,"YOE=",F12.10,/,13X,"TEMPERATURE=",
     .F14.8,/,13X,"DIF=",F16.6)
C
C
C    EFFECTIVENESS FACTOR
C
      TERM1=1.0/PHI
      TERM2=EXP((GAM/2.0)*(1.0-(1.0/V)))
      TERM3= SQRT(2.0/3.0)
      TERM41=(1.0-(YOE*YOE*YOE))
      TERM4= SQRT(TERM41)
      AIDA(J)=TERM1*TERM2*TERM3*TERM4
      WRITE(6,55) AIDA(J)
55    FORMAT(/,13X,"EFFECTIVENESS=",F12.8)
      DIFF(1)=DIFF(2)
111   YO=YO+DYO
      IF(YO.GT.UPYO) GOTO 99
      GOTO 1
C
C    CONCENTRATIONS AT EACH REACTOR LENGTH
C
99    DO 200 I=1,3
      IF(J.EQ.1.AND.I.NE.3) GOTO 200
      N=1
      X=UZE
      Y=THI(I)
      TOL=0.000001
      H=0.001
      METH=1
      MITER=0
      INDEX=1
      DO 10 K=1,10
      XEND=FLOAT(K)*DELU/10+UZE
      IF(J.EQ.1.AND.I.EQ.3) GOTO 190
      AIDAJ=AIDA(I)
      GOTO 180
190   AIDAJ=AIDA(J)
180   CALL DGEAR(N,FCN,FCNJ,X,H,Y,XEND,TOL,METH,MITER,INDEX,
     .IWK,WK,IER)
      IF(IER.GT.128) GOTO 20
10    CONTINUE
20    CONTINUE
      UZERO=1.0-UZE
      THI(I)=THI(I)+Y
      UZ=1.0-XEND
      WRITE(6,75) UZ,THI(I),AIDAJ
 75   FORMAT(///,13X,"UZERO=",F12.6,/,13X,"THI=",F12.6,/,13X,
     +"EFFECTIVENESS FACTOR=",F12.6)
200   CONTINUE
C
C
C
      IF(UZE.GT.1.0) GOTO 999
      IF(THI(1).GT.1.0.OR.THI(2).GT.1.0.OR.THI(3).GT.1.0)
     +GOTO 999
      UZERO=UZERO-DELU
```

```
      UZE=1.0-UZERO
      GOTO 80
C
C
999   STOP
      END
C
C
C
      FUNCTION F(PSI1,XK2,COMK)
      PI=3.141592654
      IF(PSI1.GE.(PI/2.0)) GOTO 11
      GOTO 12
11    IF(PSI1.EQ.(PI/2.0)) GOTO 18
      PSI=PI-PSI1
      GOTO 13
12    PSI=PSI1
C
13    BIDEN=1.0
      FSUM=PSI
      T2M=PSI
      BINUM=1.0
      DO 10 M=1,100
      XM=FLOAT(M)
      BINUM=BINUM*(-0.5-XM+1.0)
      BIDEN=BIDEN*XM
      IF(BIDEN.LE.1.0E100) GOTO 31
      BINUM=BINUM/1.0E100
      BIDEN=BIDEN/1.0E100
31    BICOE=BINUM/BIDEN
      IF(ABS(BICOE).LE.1.0E-100) GOTO 20
      SINP=SIN(PSI)
      SINPSI=SINP**(2.0*XM-1.0)
      SK2=XK2**XM
      IF(ABS(SK2).LE.1.0E-80) GOTO 20
      T2M=(((2.0*XM-1.0)/(2.0*XM))*T2M)-(SINPSI*COS(PSI)/(
     +2.0*XM))
      IF(ABS(T2M).LE.1.0E-80) GOTO 20
      N=XM/2.0
      IF((2*N-M).EQ.0) GOTO 16
      FSUB=BICOE*(-SK2)*T2M
      GOTO 17
16    FSUB=BICOE*SK2*T2M
17.   FSUM=FSUM+FSUB
      IF(ABS(FSUB).LE.1.0E-50) GOTO 20
10    CONTINUE
20    CONTINUE
      IF(PSI1.LT.(PI/2.0)) GOTO 15
      IF(PSI1.EQ.(PI/2.0)) GOTO 18
      FSUM=2.0*COMK-FSUM
      GOTO 15
18    FSUM=COMK
15    F=FSUM
      RETURN
      END
```

```
C
C
C
      SUBROUTINE FCN(N,X,Y,YPRIME)
      INTEGER N
      REAL Y,YPRIME,X
      COMMON GAM1,YZERO,DA,AIDAJ,UZE
      YPRIME=EXP(-GAM1*(1.0-(1.0/YZERO)))/(DA*AIDAJ*
     +(1.0-UZE)*(1.0-UZE))
      RETURN
      END
C
C
C
      SUBROUTINE FCNJ(N,X,Y,PD)
      INTEGER N
      REAL Y(N),PD(N,N),X
      RETURN
      END
```

```
YOE= .0014451905
TEMPERATURE=    5.95084237
DIF=        0.000000

EFFECTIVENESS= 44.20394969

YOE= .0181947796
TEMPERATURE=    2.28039119
DIF=         .000000

EFFECTIVENESS= 11.43206424

YOE= .4171244597
TEMPERATURE=    1.13480076
DIF=        0.000000

EFFECTIVENESS=  1.20357822



UZERO=     .990000
THI=     .000075
EFFECTIVENESS FACTOR=   44.203950



UZERO=     .990000
THI=     .000292
EFFECTIVENESS FACTOR=   11.432064



UZERO=     .990000
THI=     .002770
EFFECTIVENESS FACTOR=    1.203578

YOE= .0015558120
TEMPERATURE=    5.62562623
DIF=        0.000000

EFFECTIVENESS= 35.46469569

YOE= .0181870902
TEMPERATURE=    2.24302814
DIF=         .000000

EFFECTIVENESS=  9.53030197

YOE= .3599677158
TEMPERATURE=    1.15474818
DIF=        -.000000

EFFECTIVENESS=  1.18645495
```

```
UZERO=      .980000
THI=     .000230
EFFECTIVENESS FACTOR=   35.464696


UZERO=      .980000
THI=     .000875
EFFECTIVENESS FACTOR=    9.530302


UZERO=      .980000
THI=     .007895
EFFECTIVENESS FACTOR=    1.186455

YOE= .0017283939
TEMPERATURE=    5.25301887
DIF=          -.000000

EFFECTIVENESS= 28.40852006

YOE= .0175682262
TEMPERATURE=    2.23051404
DIF=           .000000

EFFECTIVENESS=  8.21935759

YOE= .3110138554
TEMPERATURE=    1.17450726
DIF=          -.000000

EFFECTIVENESS=  1.16564096


UZERO=      .970000
THI=     .000542
EFFECTIVENESS FACTOR=   28.408520


UZERO=      .970000
THI=     .002040
EFFECTIVENESS FACTOR=    8.219358


UZERO=      .970000
THI=     .017817
EFFECTIVENESS FACTOR=    1.165641
```

```
YOE= .0019935616
TEMPERATURE=    4.83562908
DIF=        -.000000

EFFECTIVENESS= 22.61875262

YOE= .0162490481
TEMPERATURE=    2.24836615
DIF=         .000000

EFFECTIVENESS=  7.36163081

YOE= .2700877915
TEMPERATURE=    1.19355393
DIF=        0.000000

EFFECTIVENESS=  1.14138995



UZERO=     .960000
THI=     .001174
EFFECTIVENESS FACTOR=   22.618753



UZERO=     .960000
THI=     .004354
EFFECTIVENESS FACTOR=    7.361631



UZERO=     .960000
THI=     .037397
EFFECTIVENESS FACTOR=    1.141390

YOE= .0024224507
TEMPERATURE=    4.36671049
DIF=        0.000000

EFFECTIVENESS= 17.74185493

YOE= .0141333163
TEMPERATURE=    2.31049110
DIF=         .000000

EFFECTIVENESS=  6.90601196

YOE= .2366469109
TEMPERATURE=    1.21124797
DIF=        0.000000

EFFECTIVENESS=  1.11323228
```

```
UZERO=      .950000
THI=      .002445
EFFECTIVENESS FACTOR=   17.741855



UZERO=      .950000
THI=      .008958
EFFECTIVENESS FACTOR=    6.906012



UZERO=      .950000
THI=      .076342
EFFECTIVENESS FACTOR=    1.113232

YOE= .0032401474
TEMPERATURE=    3.80965589
DIF=          0.000000

EFFECTIVENESS= 13.38010514

YOE= .0110275784
TEMPERATURE=    2.45970353
DIF=           .000000

EFFECTIVENESS=  6.95138032

YOE= .2099483041
TEMPERATURE=    1.22687901
DIF=          0.000000

EFFECTIVENESS=  1.08044015



UZERO=      .940000
THI=      .005001
EFFECTIVENESS FACTOR=   13.380105



UZERO=      .940000
THI=      .018130
EFFECTIVENESS FACTOR=    6.951380



UZERO=      .940000
THI=      .154062
EFFECTIVENESS FACTOR=    1.080440
```

```
YOE= .1891399813
TEMPERATURE=     1.23978371
DIF=           0.000000

EFFECTIVENESS=  1.04256630



UZERO=      .930000
THI=     .309364
EFFECTIVENESS FACTOR=     1.042566

YOE= .1733213659
TEMPERATURE=     1.24949420
DIF=           0.000000

EFFECTIVENESS=   .99985193



UZERO=      .920000
THI=     .619855
EFFECTIVENESS FACTOR=      .999852

YOE= .1616009484
TEMPERATURE=     1.25584484
DIF=           0.000000

EFFECTIVENESS=   .95331954



UZERO=      .910000
THI=    1.240753
EFFECTIVENESS FACTOR=      .953320
```

LIST OF REFERENCES

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