A STUDY OF MATHEMATICAL MODELS

FOR PSEUDO-HOMOGENEOUS CHEMICAL REACTORS

deur

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A STUDY OF MATHEMATICAL MODELS FOR PSEUDO-HOMOGENEOUS CHEMICAL REACTORS

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SYNOPSIS

In the pseudo-homogeneous models of chemical reactors, one assumes that the content of the reactor is homogeneous. These models are categorized as two-dimensional (axial and radial changes occur) and one-dimensional models (only axial changes occur).

In Chapter 1 we give a short survey of the existing literature. We also propose a modification of the one-dimensional model to reconcile the boundary conditions of the problem with the practical situation. Various numerical methods to solve the problems are also discussed.

In Chapter 2 a sufficient condition is derived which guarantees uniqueness for the one-dimensional problem. This result holds for general kinetics. An improved a-priori upper bound for the temperature solution is derived and this result is used to find an upper bound on the Damköhler-number

which gives an improvement of 10-30 times on existing results. Upper and lower function bounds on conversion are constructed and it is used to find a lower bound on the Damköhler-number. This result is new.

In Chapter 3 the bifurcation behaviour of the one-dimensional, two-dimensional and the modified one-dimensional model is examined numerically. A new method is introduced for the construction of an arc of limit points. This method enables one to examine the multiplicity behaviour of the problem as a function of the parameters.

The last chapter deals with the sensitivity of the solutions. Existing criteria are evaluated and we point out their shortcomings. We propose new criteria to evaluate sensitivity a-priori and numerically.

'n STUDIE VAN WISKUNDIGE MODELLE VIR PSEUDO-HOMOGENE CHEMIESE REAKTORE

deur

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SAMEVATTING

In die pseudo-homogene modelle van chemiese reaktore word aanvaar dat die reaktorinhoud 'n homogene kontinuum is. Hierdie modelle word onderverdeel in twee-dimensionele (aksiale en radiale veranderings in reaktor) en een-dimensionele modelle (slegs aksiale veranderings).

In Hoofstuk 1 word die literatuur kortliks bespreek. Ons stel ook 'n wysiging van die een-dimensionele model voor om die probleem se randvoorwaardes meer versoenbaar met die praktyk te maak. Verskillende numeriese tegnieke om die modelvergelykings op te los, word ook bespreek.

In Hoofstuk 2 word 'n voldoende voorwaarde afgelei om eenduidigheid van die een-dimensionele probleem te verseker. Hierdie resultaat is geldig vir algemene kinetika. 'n A-priori bo-grens vir die temperatuuroplossing word afgelei en hierdie resultaat word gebruik om 'n bogrens vir die Damköhler-

getal te vind wat 10-30 keer beter is as die bestaande resultate. Bo- en ondergrense van die omsetting word gekonstrueer en gebruik om 'n ondergrens vir die Damköhler-getal te vind. Hierdie resultaat is nog nie voorheen afgelei nie.

In Hoofstuk 3 word die bifurkasiegedrag van die een-dimensionele, twee-dimensionele en die gewysigde een-dimensionele model numeries bestudeer. 'n Nuwe numeriese metode word voorgestel om 'n baan van limietpunte te konstrueer. Hierdie metode stel mens in staat om die veelvuldigheid van die oplossings as 'n funksie van die probleem se parameters te ondersoek.

Die laaste hoofstuk handel oor die sensitiwiteit van die oplossings. Bestaande kriteria word evalueer en die tekortkominge word uitgewys. Ons stel nuwe kriteria voor om die sensitiwiteit a-priori en numeries te bepaal.

ACKNOWLEDGEMENT

I want to thank Nic van Rensburg for useful discussions.

LIST OF SYMBOLS

A - Cross-section area of reactor

A_{ij} - First derivative approximate in orthogonal collocation

B - $d_p L/r_o^2$

Bi - Biot number $h_w\ r_o/k_r$

B_{ij} - Second derivative approximate in orthogonal collocation

C - Concentration

C_0 - Inlet concentration

C_A - C/C_0

Cp - Specific heat

$\mathcal{D}_{as}$ - Axial dispersion coefficient

$\mathcal{D}_{ar}$ - Radial dispersion coefficient

$\mathcal{D}_m$ - Diffusion coefficient

d_p - Particle diameter of catalyst

E - Activation energy

$f(w,v)$ - Dimensionless rate of reaction $R(C,T)/R(C_0,T_0)$

$-\Delta H$ - Heat of reaction

h_w - Wall heat transfer coefficient

k_s - Axial thermal conductivity

k_r - Radial thermal conductivity

L - Length of reactor, m

Le - Lewis number Pe_{hs}/Pe_{ms}

NE - Number of elements in orthogonal collocation

$NCOL$ - Number of points in orthogonal collocation

n - Order of reaction

Pe_{ms} - $uL/\mathcal{D}_{as}$

Pe_{mr} - $d_p u/\mathcal{D}_{ar}$

Pe_{hs} - $Cp(\rho uL)/k_s$

Pe_{hr} - $Cp(\rho ud_p)/k_r$

R_g - Gas constant

R - Intrinsic rate of reaction

r_o - Radius of reactor, m

r' - Radial position, m

r - Radial position r'/r_o

s - Axial position z/L

T - Temperature in kelvin

T_0 - Inlet temperature in kelvin

t - Time

U - Global heat transfer coefficient

u - Mean linear velocity

v - Dimensionless temperature $(T-T_0)/T_0$

w - Conversion $(C_0-C)/C_0$

z - Axial position, m

Z - $\delta\beta'\alpha$

α - $LR(C_0,T_0)/(uC_0)$

β - $(-\Delta H)\ C_0\mathcal{D}_{as}/k_sT_0$

β' - $(-\Delta H)C_0/(\rho CpT_0)$ or $\beta Pe_{ms}/Pe_{hs}$

δ - E/R_gT_0

ϕ - $L^2R(C_0,T_0)/\mathcal{D}_{as}C_0$ or αPe_{ms}

γ - $2UL^2/(k_sr_o)$

γ' - $2UL/(uCp\rho r_o)$ or γ/Pe_{hs}

θ - Parameter in Keller's method

ρ - Density

χ - Labyrinth factor

Subscripts

a - Ambient value

h - Heat transfer

m - Mass transfer

0 - Initial value

r - Radial direction

s - Axial direction

CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 THE CHEMICAL REACTOR

In the chemical industry, most processes are concerned with the conversion of raw materials or reactants into products. These processes take place in a vessel, the chemical reactor. Most materials are in a gaseous or liquid form and the reactor is designed to convert these feeds into either gaseous or liquid products.

There is a wide variety of reactor types [107,110]. In this study we shall concentrate on the fixed bed reactor. This reactor consists of an array of tubes in a shell (See Figure 1.1). The tubes are packed with small particles, the catalyst. The catalyst particles are pretreated to get the required porosity and shape. In most cases the particles shapes are approximated as either cylindrical or spherical. In a large number of cases heat is generated when the chemical reaction takes place in the reactor. The facility exists to remove excess heat by pumping a cooling liquid through the shell side of the reactor.

Before we discuss the mathematical models of the fixed bed reactor, it is important to get a rough idea of the flow mechanisms inside the reactor.

The reactants are fed into the tubes and follow a complex flow pattern around the packed catalyst particles. Reactants go from the bulk or fluid phase to the catalyst phase where they are adsorped on the catalyst surface. The chemical reaction occurs mostly in the catalyst phase and products diffuse back into the bulk phase. Heat transfer occurs by means of

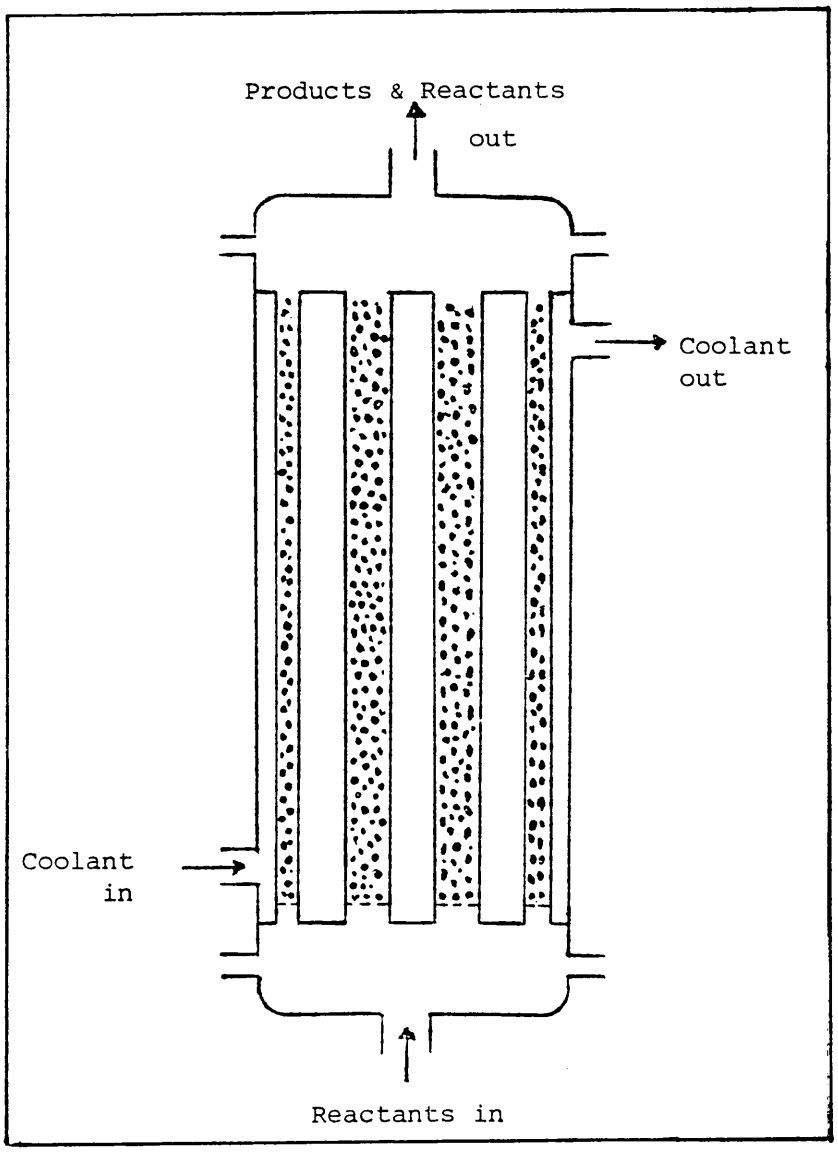

FIG. 1.1: Fixed Bed Reactor.

convection in the bulk phase in the axial direction, diffusion and conduction between adjacent particles in both the axial and radial directions. The conduction distinguishes heat transfer from mass transfer.

There exists a difference between the concentration of species in the catalyst phase and the adjacent bulk phase. Models which recognise these differences are heterogeneous models. In cases of effective heat and mass interchange between the phases, the catalyst and bulk phase do not denote markedly different heat and concentration levels and the whole continuum is assumed homogeneous. Models which describe this situation are of the pseudo-homogeneous type.

If radial gradients are significant, models which take both axial and radial effects in consideration, will prove better than one dimensional models which ignore radial effects. In [21,24,44] norms are suggested to facilitate the choice between one- or two-dimensional models.

1.2 PSEUDO-HOMOGENEOUS MODELS

The spectacular rise in fixed bed reactor capacity stresses the need for well designed units. As Froment [110] pointed out, the ammonia production increased more than tenfold from 1950 until 1970. This fact indicates the importance of appropriate models and the necessity to analyze these models to the fullest.

In [19,68] the pseudo-homogeneous models are suggested for the design of fixed bed reactors.

1.2.1 The Two-Dimensional Model

The steady state form of the two-dimensional model for the packed bed reactor is a boundary value problem.

PROBLEM A

$$\frac{1}{Pe_{ms}}\partial_{ss}w-\partial_s w+\frac{B}{Pe_{mr}}(\partial_{rr}w+\frac{1}{r}\partial_r w)+\alpha g(w)e^{\delta v/(1+v)}=0 \qquad (1)$$

$$\frac{1}{Pe_{hs}}\partial_{ss}v-\partial_s v+\frac{B}{Pe_{hr}}(\partial_{rr}v+\frac{1}{r}\partial_r v)+\beta'\alpha g(w)e^{\delta v/(1+v)}=0 \qquad (2)$$

with boundary conditions:

$$\left.\begin{aligned}\partial_s w &= Pe_{ms}w \quad ; \quad s = 0\\ \partial_s v &= Pe_{hs}v \quad ; \quad s = 0\end{aligned}\right] \qquad (3)$$

$$\partial_s w = \partial_s v = 0 \quad ; \quad s = 1 \qquad (4)$$

$$\partial_r w = \partial_r v = 0 \quad ; \quad r = 0 \qquad (5)$$

$$\left.\begin{aligned}\partial_r w &= 0 \quad ; \quad r = 1\\ \partial_r v &= Bi(v_a-v) \quad ; \quad r = 1\end{aligned}\right] \qquad (6)$$

For n-th order irreversible reactions $g(w) = (1-w)^n$.

w denotes conversion, that is the fraction of a reactant which has reacted. If C_0 denotes the inlet concentration, $w(s,r) = 1-C(s,r)/C_0$. $v(s,r) = T(s,r)/T_0-1$, where T_0 denotes the feed temperature. All the other parameters are constants. The subscripts s and r denote axial and radial directions, h and m heat and mass transfer respectively and v_a denotes a dimensionless ambient temperature. In general $Pe_{ms} = uL/\mathcal{D}_{as}$, $Pe_{hs} = Cp(\rho uL)/k_s$, $Pe_{mr} = d_p u/\mathcal{D}_{ar}$, $Pe_{hr} = Cp(\rho u d_p)/k_r$ where u is the axial velocity (mean), L is the length of the reactor, d_p is the catalyst diameter and $\mathcal{D}_{ar}$ and $\mathcal{D}_{as}$ are the dispersion coefficients (radial and axial). Cp is the heat capacity, k_r and k_s the conductivity (radial and axial) and ρ the density of the continuum. The boundary condition (3) ignores radial effects and is only an approximation [83].

For the derivation of this model, see Hill [107].

In the case of more than one reacting species, (but the feed is stoichiometric) (1)-(6) will be sufficient to describe the process, since the species differ from each other with a constant. If the feed is not stoichiometric additional mass-balances are required. The last term in (2) must also be updated if additional reactions occur.

1.2.2 The One-Dimensional Model

The following two-point boundary value problem describes the steady state one-dimensional case. It is derived under different assumptions than Problem A. See Hill [107].

PROBLEM B

$$w'' - Pe_{ms}w' + \phi g(w)e^{\delta v/(1+v)} = 0 \qquad (7)$$

$$v'' - Pe_{hs}w' + \beta\phi g(w)e^{\delta v/(1+v)} - \gamma v = 0 \qquad (8)$$

$$\left.\begin{aligned} w' &= Pe_{ms}w \ ; \quad s=0 \\ v' &= Pe_{hs}v \ ; \quad s=0 \end{aligned}\right] \qquad (9)$$

$$w' = v' = 0 \ ; \quad s=1 \qquad (10)$$

β denotes the heat which is involved in the chemical reaction. If the reaction is exothermic $\beta > 0$, if the reaction is endothermic, $\beta < 0$.
γ denotes an overall heat transfer coefficient between the shell- and tube-side fluids. When $\gamma>0$, the reactor is operated non-adiabatically. When no heat transfer takes place with the surrounding, the reactor is adiabatically operated ($\gamma=0$). This parameter can be regarded as a design variable. The Peclet numbers (Pe_{ms}, Pe_{mr}, Pe_{hs}, Pe_{hr}), as defined in this study, depend on the length of the reactor and the catalyst diameter. Since mean velocity and dispersion, as well as the physical properties of the fluid, will remain unchanged, Peclet numbers can also be categorized as design variables. The only operating variable is the Damköhler-number α (or ϕ). This parameter involves inlet temperature and concentration, the two variables most likely to fluctuate or change under operation.

This model plays a very important role in design [110]. Jensen [45] reported a list of comparison studies between experimental results and this model. In the bifurcation studies of Chapter 3 and the parameter sensitivity study of Chapter 4 we shall concentrate on the effect of changes in the Damköhler number.

1.3 ANALYSIS OF THE ONE-DIMENSIONAL MODEL

In this section we shall review known results on the existence, uniqueness, multiplicity, a-priori estimates and stability of solutions of the one-dimensional model. All these factors play an important role in the design of a chemical reactor.

1.3.1 Existence

The dynamic problem was studied by Pao [90] and Kuiper [46]. They proved the existence of solutions for the dynamic one-dimensional model. The existence of a solution of the steady state problem was studied by Gavalas [34,104] and Varma [61].

1.3.1.1 A-priori bounds

Varma [61,69] proved the following a-priori bounds:

$$0 \leq w(s) \leq 1 \qquad \text{I}$$

$$0 \leq v(s) \leq \beta \qquad \text{II}$$

If the reactions are of even order, it can be proved that Varma's results do not hold (Appendix C) unless the terms

$$g(w)e^{\delta v/(1+v)}$$

in (7) and (8) are replaced by

$$f(w,v) = \begin{cases} g(w)e^{\delta v/(1+v)}, & 0 \leq w \leq 1 \\ 0, & w \geq 1. \end{cases}$$

One can write (7)-(10) in integral form:

$$w(s) = \int_0^1 G_{ms}(s,t)\phi g(w(t))e^{\delta v(t)/(1+v(t))})dt \qquad (11)$$

$$v(s) = \int_0^1 G_{hs}(s,t)[\beta\phi g(w(t))e^{\delta v(t)/(1+v(t))} - \gamma v(t))dt \qquad (12)$$

where $G_i(s,t) = \begin{cases} 1/Pe_i \ , & 0 \leq t \leq s \\ (1/Pe_i)e^{Pe_i(s-t)} \ , & s < t \leq 1 \end{cases}$ $\quad i = ms, hs$

denotes the Green's function.

It is easy to prove that the integral operator T, defined by the right hand side of (11) and (12) has a fixed point, using Schauder's theorem and a-priori bounds I and II. See Hartman [105, p.424].

Gavalas [34,104] used the homotopy of T-I and I, the identity operator, to prove the existence of a fixed point. This approach stems from the work of M.A. Krasnoselskii.

1.3.2 Uniqueness

Most chemical reactors are operated in regions of uniqueness. This means that the design and operating variables are chosen to ensure the existence of only one solution. The Damköhler numbers α_* and α^* (or ϕ_* and ϕ^*) are sought such that uniqueness is guaranteed for $\alpha \leq \alpha_*$ and $\alpha \geq \alpha^*$. We shall refer to α_* and α^* as upper and lower bounds for uniqueness respectively. Several authors studied the uniqueness of Problem B.

In the following section we shall look briefly at the various approximations and assumptions and the resulting criteria for uniqueness.
In most cases assumptions and approximations were made to utilize standard analytical techniques.

1.3.2.1 Simplifications

Various simplifications to the differential equation of Problem B have been proposed in the literature. They are discussed briefly for the sake of completeness but no further attention will be given to these issues. A popular assumption is to choose $Pe=Pe_{ms}=Pe_{hs}$ ($Le=Pe_{hs}/Pe_{ms}=1$).
If one further assumes the reactor is adiabatic ($\gamma=0$), one can prove a linear relation between w(s) and v(s):

$$w(s) = \frac{v(s)}{\beta}$$

Under these simplifications, Problem B reduces to:

$$v'' - Pev' + \beta\phi(1-v/\beta)e^{\delta v/(1+v)} = 0 \quad ; \ 0<s<1 \tag{13}$$

$$v' = Pev \quad ; \ s=0 \tag{14}$$

$$v' = 0 \quad ; \ s=1 \tag{15}$$

Cohen [39] proved uniqueness of the solution of (13)-(15) if

$$\frac{d}{dv}\left(\frac{\beta\phi(1-v/\beta)}{v}e^{\delta v/(1+v)}\right) < 0 \tag{16}$$

He used the maximum-minimum principles of elliptic operators to prove the convergence of an upper and lower solution to a fixed point. Subsequently he used a perturbation analysis of the solution v in the region of the boundary layer at s=0 to arrive at (16).

Fleishman [22] studied the catalyst particle problem. He approximated the reaction term by a step function and matched the solutions in each domain continuously in a point. This step function approach did not compare very well with the numerical results of Parter et al. [53,54].

All in all, one can regard these assumptions as artificial and the analytical results are of limited value.

Another popular approach is to approximate Problem B as a sequence of continuously stirred tank reactors (CSTR). In each CSTR, conditions are identical (i.e. not a function of space variables) and mass and heat flows between adjacent cells make provision for both diffusion and convection. The multiplicity behaviour of a single cell was studied in 1956 [84]. The sequence-of-reactors-model uses the same approach and was studied by Varma [64] and Calo [10].

No literature on the validity of the above approach, either the convergence to the infinite dimensional case or the error of approximation, could be found. These issues need further examination by mathematicians.

1.3.2.2 Analytical Result of Varma and Amundson

We want to give a brief description of a result of Varma and Amundson [93] on an upper bound for the Damköhler number to guarantee uniqueness, since it is the only rigorous result. In Chapter 2 we prove a better result.

With the change of variables

$$w(s) = y(s)e^{Pe_{ms}s/2} \quad ; \quad v(s) = u(s)e^{Pe_{hs}s/2}$$

Problem B assumes a form which does not have any first derivatives. Let $y(s) = y_1(s)-y_2(s)$ and $u(s) = u_1(s)-u_2(s)$ be the difference between two solutions. Using the variational principle of the least eigenvalue of

the operator $L \equiv \frac{d^2}{ds^2}$ with the boundary operator

$$B_i = \begin{cases} (\frac{-d}{ds} + \frac{Pe_i}{2}) = 0 \quad ; \quad s = 0 \\ \\ (\frac{+d}{ds} + \frac{Pe_i}{2}) = 0 \quad ; \quad s = 1 \end{cases} \quad ,i = ms,hs$$

$\int_0^1 (yLy + p^2 uLu)ds < 0$, for p an arbitrary, real number, will not hold for y and u nontrivial if:

$$\alpha < \frac{[-\beta\mu_m a_3 + (\mu_h+\gamma)a_2] + \sqrt{[\beta\mu_m a_3 + (\mu_h+\gamma)a_2]^2 + 2\beta\mu_m(\mu_m+\gamma)a_1 a_3 e^{(Pe_{hs}-Pe_{ms})}}}{a_3[\ \beta\ a_1 e^{(Pe_{hs}-Pe_{ms})} + 2\beta a_2]}$$

where $\mu_{m,h}$ denotes the least eigenvalue for L and B_{ms} and L and B_{hs} respectively.

$$a_1 = \inf \frac{\partial f}{\partial w} < 0, \qquad a_2 = \sup \frac{\partial f}{\partial w} \leq 0$$

$$a_3 = \sup \frac{\partial f}{\partial v}$$

They also stated that no rigorous lower bounds on α could be obtained which would guarantee uniqueness [93]. Varma [93] derived this result for the special case Le=1 and he stated that the proof of the general case (Le≠1) is analogous. In Section 2.5 we shall compare our results with these bounds.

In Chapter 2 we shall derive an upper bound ϕ_* which is much sharper than the existing one. We shall also derive a lower bound on Damköhler numbers to guarantee uniqueness and we claim this to be the first result of its kind.

1.3.3 Multiplicity and Bifurcation

The analytical results for Problem B are limited to the very special cases of Le = 1 and γ = 0. Keller and Antman [101], Keller [40,78], Amann [3,4,5,6] and Laetsch [35,37,38] developed theories which give indications of the number of fixed points.

Most approaches rest on the work of Amann. To apply his methods, one must find maximum and minimum solutions of Problem B. Wildenauer [66] gave results for the existence of maximum and minimum solutions, but requires that f(w(s),v(s)) be concave on $s \in [0,1]$. Numerical results suggest the contrary.

We cannot find appropriate maximum and minimum solutions of Problem B. If there exist multiple solutions, they intersect and subsequent ordering is not possible.

We did not find any general results which were directly applicable to Problem B in the literature and we had to resort to numerical procedures. See Section 1.5.3.

1.3.4 Stability

Although we did not do any work on this aspect, we shall give a short survey of the literature for the sake of completeness. It must also be noted that our numerical bifurcation studies (Chapter 3) touched upon this matter, since a bifurcation point usually marks a change of stability. Different approaches to study the stability of the steady state solutions will be discussed. Endo [18], Gilles [31] and Eigenberger [14,15,17] gave a good review of the stability of different reactor types as well as the mechanisms which cause unstable behaviour.

In [9,28,33,99] the transient equations were numerically integrated for different initial values. The phase plane $w(s_1,t)$ - $v(s_1,t)$ for s_1 fixed, gives useful information on regions of stability. Although this approach is cumbersome it gives reliable information on the stability of the nonlinear equations.

In [2,9,17,56,67] the method of Lyapunov was used. Amundson [8] used perturbation analysis and Kastenberg [47] used the difference function $u(s,t)$ between the dynamic and steady state to construct eigenfunctions $\psi_1(s,t)$ and $\psi_2(s,t)$ on a slightly larger domain. Using the maximum principle of parabolic equations, he showed that $\psi_1(s,t)<u(s,t)<\psi_2(s,t)$.

The two comparison eigenfunctions are shown to converge to zero:

$$\lim_{t\to\infty} \psi_i(s,t)=0 \quad , \quad i=1,2.$$

Varma [63] used this approach to derive stability criteria. Luss [49,50] used the maximum principle of parabolic equations to derive criteria.

1.3.5 Parameter Sensitivity

Parameter sensitivity is an aspect which is of particular interest to the engineer. It describes the sensitivity of the steady state solutions to small perturbations in operating variables. If a system is in the sensitive region, a small perturbation in operating variables will give rise to a sharp increase in the temperature which can lead to burnout or deactivation of the catalyst.

Endo [18] suggested the use of the plug-flow model to study parameter sensitivity. This model results when $\mathcal{D}_{as} \to 0$, $k_s \to 0$ and one can write Problem B as:

$$-w' + \alpha f(w(s),v(s)) = 0 \tag{17}$$

$$-v' + \beta'\alpha f(w(s),v(s)) - \gamma' v(s) = 0 \tag{18}$$

$$\left.\begin{aligned} w(0) &= 0 \\ v(0) &= 0 \end{aligned}\right] \tag{19}$$

According to Endo, the motivation to use the plug-flow model is that most reactors are operated in regions of an unique solution where the plug-flow model (PFM) gives a reasonable description of reactor behaviour.

This is not generally true, since reactors can be operated in regions of multiple solutions. The second objection to Endo's suggestion is that more descriptive models than the PFM may give different criteria for parameter sensitivity.

In 1959 Barkelew [36] gave the first systematic description of parameter sensitivity. He used the PFM for his studies. Defining the dimensionless temperature as: $y = (T-T_0)\delta/T_0$ and assuming that $\delta >> y$, he approximated (17)-(19) as:

$$\frac{dy}{ds} = Zg(w)e^{y} - \gamma' y \tag{20}$$

$$\frac{dw}{ds} = \alpha g(w)e^{y} \tag{21}$$

$$\left.\begin{aligned} y(0) &= 0 \\ w(0) &= 0 \end{aligned}\right] \tag{22}$$

where $Z = \delta\beta'\alpha$

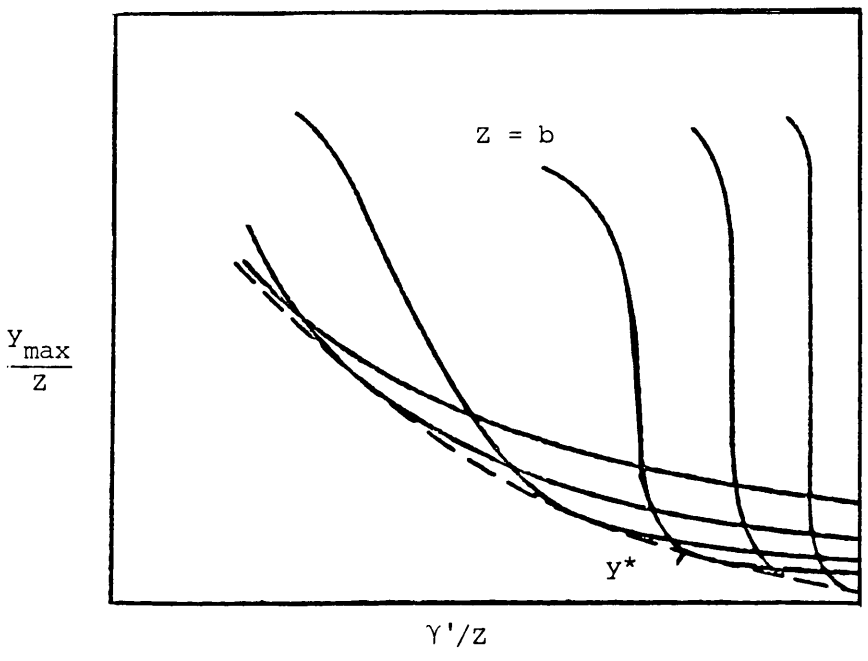

FIG. 1.2: Sensitivity Diagram

For over 700 choices of γ' and Z, (20)-(22) were integrated and diagrams, as shown in Figure 1.2, were constructed.

Consider Z = b. For $y_{max} < y^*$, the deviation in y_{max} for a change in γ'/Z is small, but for $y_{max} > y^*$, the change is more drastic. He proposed the following:

A reactor is stable with respect to small operating fluctuations if $y_{max} < y^*$, where y^* denotes the value which is tangential to the envelope.

Using Barkelew's diagram and assuming the PFM is adequate, one can compute the maximum radius of the tube which will still be parameter-insensitive.

Agnew and Potter [1] extended Barkelew's approach to the two-dimensional PFM. This model has more parameters and parameters were lumped as dimensionless groups to avoid complexity. The results were analogous to Barkelew's diagrams.

In 1970 Froment [23] studied the first order PFM for various parameter values. (18) is now divided by (17) to give:

$$\frac{dv}{dw} = \beta' - \frac{\gamma'(v)e^{-\delta v/(1+v)}}{\alpha(1-w)} \qquad (23)$$

The maximum temperature v_{max} for a first order reaction satisfies:

$$w_m = 1 - \frac{\gamma'}{\beta'\alpha}(v_{max})e^{-\delta v_{max}/(1+v_{max})} \qquad (24)$$

Using (24) $(1-w_m;\ v_{max})$-parameter-planes can be constructed for different choices of the parameters. In Figure 1.3 such a plane is shown.

Froment gave the following criterion for parametric sensitivity. The trajectory passing through the maxima of the $(1-w_m;v_{max})$ curves is critical. Inlet conditions which lead to v_{max} values to the right of this trajectory is sensitive.

In Figure 1.3 his proposition is illustrated.

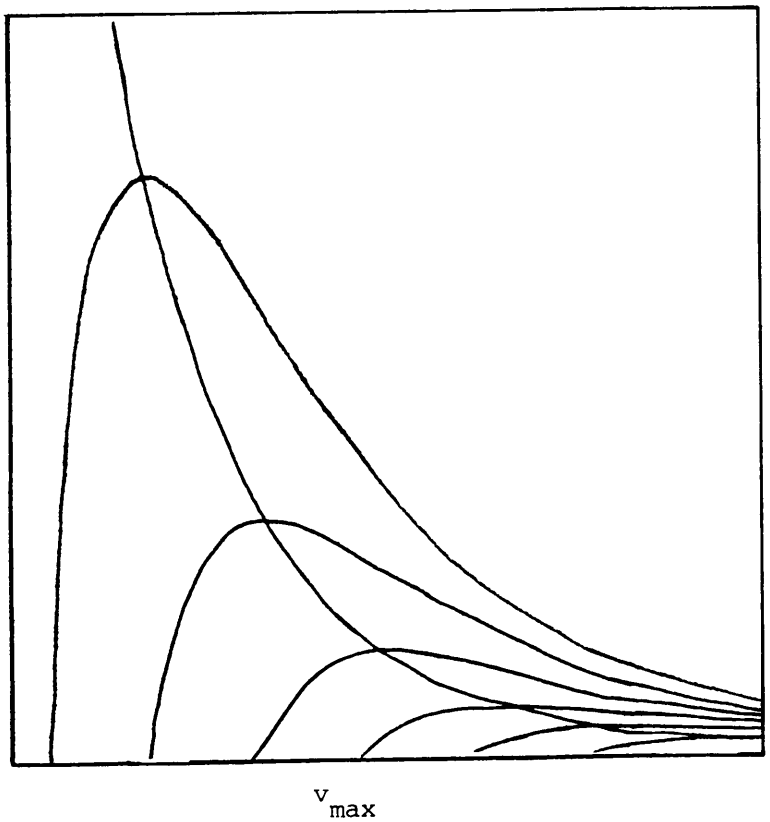

FIG. 1.3: Sensitivity Diagram

Varma and Morbidelli [89] gave the following criterion for sensitivity:
If $\frac{d^2v(s_1)}{dw(s)^2} > 0$ and $\frac{dv(s_2)}{ds} = 0$ where $s_1 < s_2$, run-away occurs.

Run-away is the term used to describe the sharp rise in temperature when a system is sensitive. Dente and Collina [102] defined their criterion only slightly different: If $\frac{d^2v(s_1)}{ds^2} > 0$ and $\frac{dv(s_2)}{ds} = 0$ where $s_1<s_2$, run-away occurs.

In 1978 El-Sawi et al [16] examined parameter sensitivity in an experimental fixed bed reactor for the production of vinylacetate from acetylene and acetic acid. They found that Barkelew's criterion is conservative and explained the phenomenon in terms of the poor correlation between the model and experiment.

In 1980 Emig et al [91] examined the same reaction and found that Barkelew's diagrams give realistic criteria. Agnew's diagrams were not conservative at large Z-values and these diagrams must be used with care. They suggest that one must first choose the best model and then analyze it for parameter sensitivity.

In Chapter 4 we derive conditions for parameter sensitivity for the one-dimensional model using the criterion of Dente and Collina. We also give a new criterion for parameter sensitivity which is applicable to any model.

1.4 MODIFICATION OF THE ONE-DIMENSIONAL MODEL

Before we introduce our modified one-dimensional model, we must first consider the aspect of dispersion. Secondly the status of the boundary conditions will be discussed since we propose a modification of the boundary conditions as well.

1.4.1 Dispersion

In the discussion which follows, we shall analyze the modelling of dispersion in more detail.

Wicke [72] gives a good description of dispersion. We concentrate on mass-dispersion, since heat transfer mechanisms are very complex and we will not suggest any changes to the energy balance.

Mass transfer comprises of convection and diffusion. The latter term contributes a small part to the total mass transfer and is of the form:

$$-\mathcal{D}_m A \frac{dC}{ds}$$

where $\mathcal{D}_m$ is the diffusion coefficient in the bulk medium. (A denotes the cross-flow area of the reactor tube). Dispersion consists of both diffusion and a hold-up term.

The latter term will be explained briefly. If mass-transfer consisted only of convection, a tracer-pulse, (an injection of a substance which must be tractable) as an approximation to the Dirac-delta function, will appear at

the outlet of the reactor unchanged (concentration as a function of time). No change should occur in the second moment of the distribution and every molecule of the tracer should have the same residence time. But in experiments a real tracer output showed a considerable increase in the second moment of its distribution. This fact suggests a hold-up in the reactor, due to the complex flow round the catalyst particles. It is exactly this time delay which forms the second term of dispersion. In more quantitative form, the dispersion $\mathcal{D}_{as}$ is:

$$\mathcal{D}_{as} = \chi\mathcal{D}_m + 0{,}5u\ d_p/(1+10\chi\mathcal{D}_m/(ud_p)) \qquad (25)$$

where χ is a "labyrinth factor" to correct for the diffusion along a curved path around the catalyst particles.

In Figure 1.4 we illustrate the mechanism of hold-up.

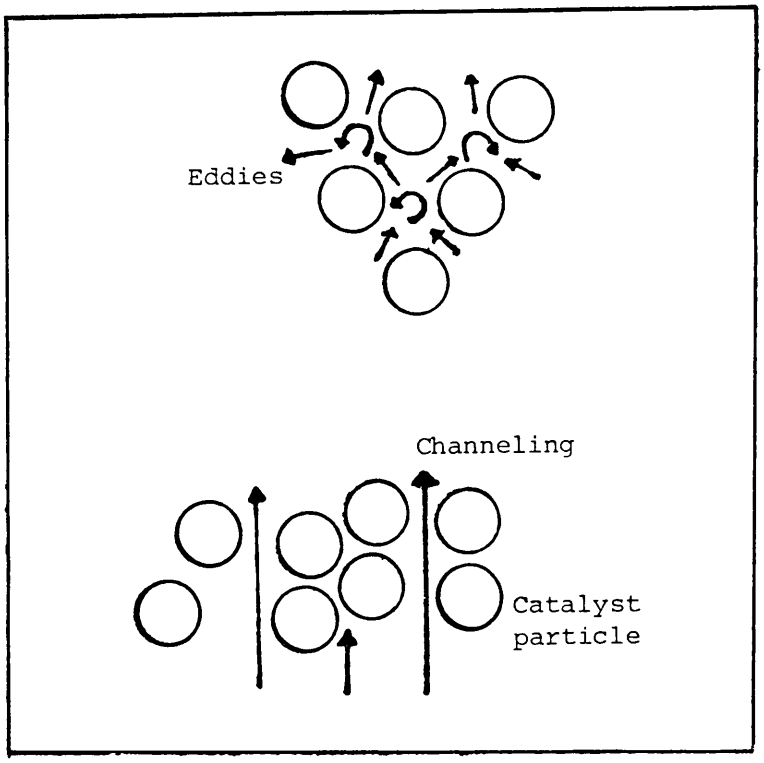

FIG. 1.4: Mechanism for Different Residence Times

Diffusion is the only process which will cause mass-flow upstream.

Remark: $\chi = 0,7$ for uniform packing [72].

1.4.2 Inlet Conditions

1.4.2.1 Reactor Inlet

Two types of reactor inlets are used in industry.

(a) Packed inlet

The inlet tube is packed with an inert material of the same physical dimensions as the catalyst. The flow pattern is established when it reaches the active part and the dispersion coefficient would have reached a constant value. Small variations in $\mathcal{D}_{as}$ due to the temperature effect on $\mathcal{D}_m$ may occur, but in most cases this effect is negligible.

(b) Unpacked inlet

The flow of reactants changes drastically when the active stage is entered and one will surmise a change in dispersion over a certain bed length until the flow is established for the packed tube.

1.4.2.2 Discussion of Boundary Conditions

The boundary conditions (9)-(10) were derived by Danckwerts [75] for a first order reaction. These conditions are still controversial and we shall give a short survey. Let C_0 denote the inlet concentration and u the mean velocity. A mass balance over the inlet gives:

$$uC_0 = uC(0^+) - \frac{\mathcal{D}}{L}\frac{dC(0^+)}{ds}, \tag{26}$$

where $\mathcal{D}$ is the "apparent" diffusion coefficient. He arrived intuitively at the outlet boundary condition.

Wehner and Wilhelm [73] considered the reactor system in three parts; the inlet stage (a), the reactor (b), and the outlet (c). The equations were set up for a first order isothermic reaction. We use Pe for the mass Peclet number (Pe_{ms}) where the subscripts a, b, c denote the fore, reactor and after sections respectively. The dimensionless concentration $C_A = C/C_0$ is used.

$$\frac{1}{Pe_a}\frac{d^2C_A}{ds^2} - \frac{dC_A}{ds} = 0 \qquad ; s < 0 \tag{27}$$

$$\frac{1}{Pe_b}\frac{d^2C_A}{ds^2} - \frac{dC_A}{ds} - \alpha C_A = 0 \quad ; 0 < s < 1 \tag{28}$$

$$\frac{1}{Pe_c}\frac{d^2C_A}{ds^2} - \frac{dC_A}{ds} = 0 \qquad ; s > 1 \tag{29}$$

$$C_A(-\infty) = 1 \tag{30}$$

$$C_A(0^-) - \frac{1}{Pe_a}\frac{dC_A(0^-)}{ds} = C_A(0^+) - \frac{1}{Pe_b}\frac{dC_A(0+)}{ds} \tag{31}$$

$$C_A(0^-) = C_A(0^+) \tag{32}$$

$$C_A(1^-) - \frac{1}{Pe_b}\frac{dC_A(1^-)}{ds} = C_A(1^+) - \frac{1}{Pe_c}\frac{dC_A(1^+)}{ds} \tag{33}$$

$$C_A(1^-) = C_A(1^+) \tag{34}$$

$C_A(\infty)$ is finite.

The boundary conditions provide for continuity and the conservation of mass. Solving (27)-(34) give:

$$\frac{1-C_A(s)}{(1-C_A(0))} = e^{Pe_a s} \quad ; \quad s \leq 0 \tag{35}$$

$$C_A(s) = Ae^{Pe_b s/2}\left((1+B)e^{BPe_b(1-s)/2} - (1-B)e^{BPe_b(s-1)/2}\right) ; \ 0 \leq s \leq 1 \tag{36}$$

where A and B are constants. Using the fact that $C_A(\infty)$ is finite,

$$C_A(s) = 2A \cdot B \cdot e^{Pe_b/2} = \text{constant}; \quad s \geq 1 \tag{37}$$

Since the solution for the after section is a constant, $\frac{dC_A(1^+)}{ds} = 0$ and it follows from (33)-(34) that:

$$\frac{dC_A(1^-)}{ds} = 0$$

Substituting for $C_A(s)$ from (35) into the total flux anywhere in the fore section gives:

$$C_A(s) - \frac{1}{Pe_a}\frac{dC_A}{ds} = 1. \tag{38}$$

Substituting this result in (31) gives the Danckwert's boundary condition at the inlet.

In 1959 Pearson [76] used a dispersion-coefficient in the reactor as shown in Figure 1.5.

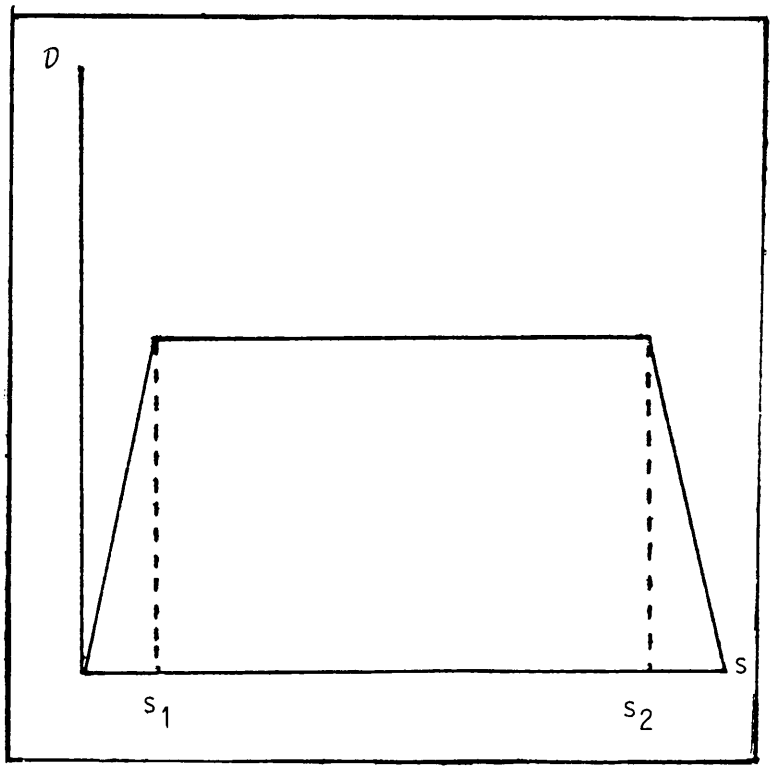

FIG. 1.5: Pearson's Variable Dispersion-Coefficient

Pearson showed that if $s_1 \to 0$ and $s_2 \to 0$, the Danckwert's boundary conditions result.

Bisschoff [103] generalized Wehner and Wilhelm's results for a reaction of general order. Van Cauwenberghe [74] considered the unsteady state and showed that the Danckwert's boundary conditions for the steady state are only valid if no diffusion occurs in the fore- and after sections.

Wissler [77] compared the one-dimensional axial dispersion model with the plug flow model under laminar flow conditions. If Pe_{ms} becomes large, the problem is transformed into an initial value problem (PFM). The solution is truncated at s=1.

In 1983 Nauman [52] suggested a modification of the Danckwert's boundary conditions. He used two tuning parameters κ and λ.

$$\frac{1-\kappa}{Pe_{ms}}\frac{dw}{ds} = w \; ; \qquad s=1 \qquad (39)$$

and

$$\frac{dw}{ds} = 0 \; ; \qquad s=1+\lambda \qquad (40)$$

The gradient at the outlet can be adjusted until it corresponds with the experimental results. The inlet parameter is changed until the model and experimental results are best correlated.

We consider Nauman's approach of an ad hoc nature and it lacks careful analysis of the model.

The objections to the Danckwert's boundary conditions are best summarized by Wicke [72].

(a) Which dispersion coefficient must be used at the inlet?

(b) No distinction is made between packed- and unpacked inlets.

1.4.3 Modification of Axial Dispersion Model

In the light of the objections rose by Wicke and the controversy around the Danckwert's boundary conditions in general, we propose modifications of the axial dispersion model in this section.

(a) Packed Inlet

The flow is fully established when it reaches the active zone. We assume no change occurs in the dispersion when the active zone is entered. A mass balance over the inlet gives

$$-\mathcal{D}_m\chi \frac{dC(0^-)}{dz} + uC(0^-) = uC(0^+) - \mathcal{D}_m\chi \frac{dC(0^+)}{dz} \qquad (41)$$

where $z = Ls$, $L \equiv$ length of reactor

It follows from the results of Wehner and Wilhelm that the flux is C_0u and

$$C_0 = C(0^+) - \frac{\mathcal{D}_m\chi}{uL} \frac{dC(0^+)}{ds} \qquad (42)$$

$$w(0^+) = \frac{\chi\mathcal{D}_m}{uL} \frac{dw(0^+)}{ds} \qquad (43)$$

Thus $Pe_{ms}(\text{inlet}) = uL/\chi\mathcal{D}_m$ and this Pe_{ms} differs from the Pe_{ms} defined for the rest of the active zone, i.e. $Pe_{ms} = uL/\mathcal{D}_{as}$. This result is also in accordance with Wicke's suggestion that the "dispersion" coefficient at the inlet is not the same as the dispersion in the reactor itself.

(b) Unpacked Inlet

The flow is not established and the dispersion coefficient becomes constant after bedlength ΔL, as shown in Figure 1.6.

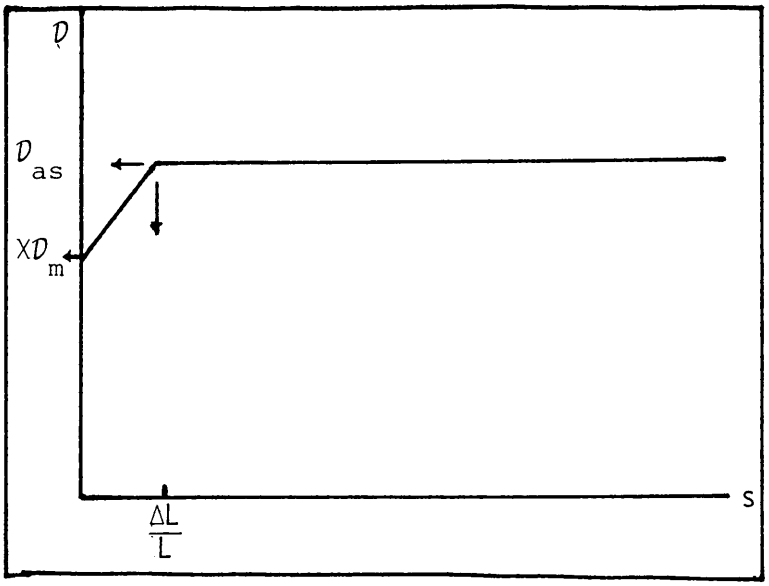

FIG. 1.6: Variation in Dispersion

A mass balance over the inlet gives the identical result as (43). The mass balance in the reactor changes:

$$\frac{\mathcal{D}(s)}{uL} w'' - w' + \alpha(1-w)e^{\delta v/(1+v)} = 0 ; \qquad 0 < s < 1 \qquad (44)$$

where
$$\mathcal{D}(s) = \begin{cases} \chi\mathcal{D}_m + sL\,\dfrac{(\mathcal{D}_{as}-\chi\mathcal{D}_m)}{\Delta L}, & \text{if} \quad s < \dfrac{\Delta L}{L} \\ \mathcal{D}_{as}, & \text{if} \quad 1 \geq s \geq \dfrac{\Delta L}{L} \end{cases}$$

To summarize: if the inlet is packed Problem B is used but (9) is substituted by (43). If the inlet is unpacked both (7) and (9) are substituted by (44) and (43) respectively.

The outlet conditions are correct if no diffusion occurs in the after section.

We constructed bifurcation diagrams for this modified model in Chapter 3, Section 3.7, but in the rest of this work we used the unmodified model.

1.5 NUMERICAL METHODS

In this section we shall discuss various numerical methods for the solution of the boundary value problems A and B as well as the construction of bifurcation diagrams. Sections 1.5.1 and 1.5.2 give a survey of known methods to solve boundary value problems.

1.5.1 One-Dimensional Model.

(a) Finite Difference Methods

(i) Implicit and explicit schemes

Due to the high nonlinearity extremely fine meshes are required to obtain good accuracy. In the literature very few authors used these methods to solve the boundary value problem.

(ii) Green's Function and Numerical Approximation of the Integral

Convergence is guaranteed if:

$$Pe_{ms}\left[\max_{\substack{0\le w(s)\le 1\\ 0\le v(s)\le \beta}}(f(w(s),v(s)))\right] < 1$$

$$Pe_{hs}\left[\max_{\substack{0\le w(s)\le 1\\ 0\le v(s)\le \beta}}(\beta f(w(s),v(s)-\gamma v(s))\right] < 1 \qquad \text{[see 95]}$$

When conversion is low and the temperature is close to ambient, this method gives reasonable results, but no convergence occurred in the case of high conversions.

(iii) Shooting Methods

Shooting methods [106,98] were used to solve the boundary value problem [60]. Outlet conditions (w(1),v(1)) are varied until the inlet boundary conditions are satisfied. If forward integration is used, the procedure becomes unstable [106]. The outlet values are corrected after every integration cycle (from s=1 to s=0) using a first order Taylor expansion. For a non-stoichiometrical system, the procedure is cumbersome, since N^2 equations must be integrated for every N-unknowns.

(iv) General Parameter Mapping Method

This method [86,95] is a variation of the shooting method. It is often used to construct bifurcation diagrams [42,45].

(v) Method of False Transient

The model equations are written in the unsteady state form and integrated until steady state is approached. Solving a parabolic partial differential equation, the methods of Saul'yev [51] or orthogonal collocation of the space variable with integration in time, can be used [12,62].

(b) Finite Elements

(i) Galerkin

The coefficients of the polynomial which approximates the solution over an element are obtained by either minimizing the residual over the whole element, or forcing it pointwise orthogonal. In the Galerkin method, the residual is weighted by the approximate over the whole interval. The integration of the nonlinear terms can be handled either by quadrature or finite difference approximations. It is specifically this limitation which makes other finite element methods more attractive.

(ii) Orthogonal Collocation (OC)

This method is by far the most popular [24,97,98] since it is

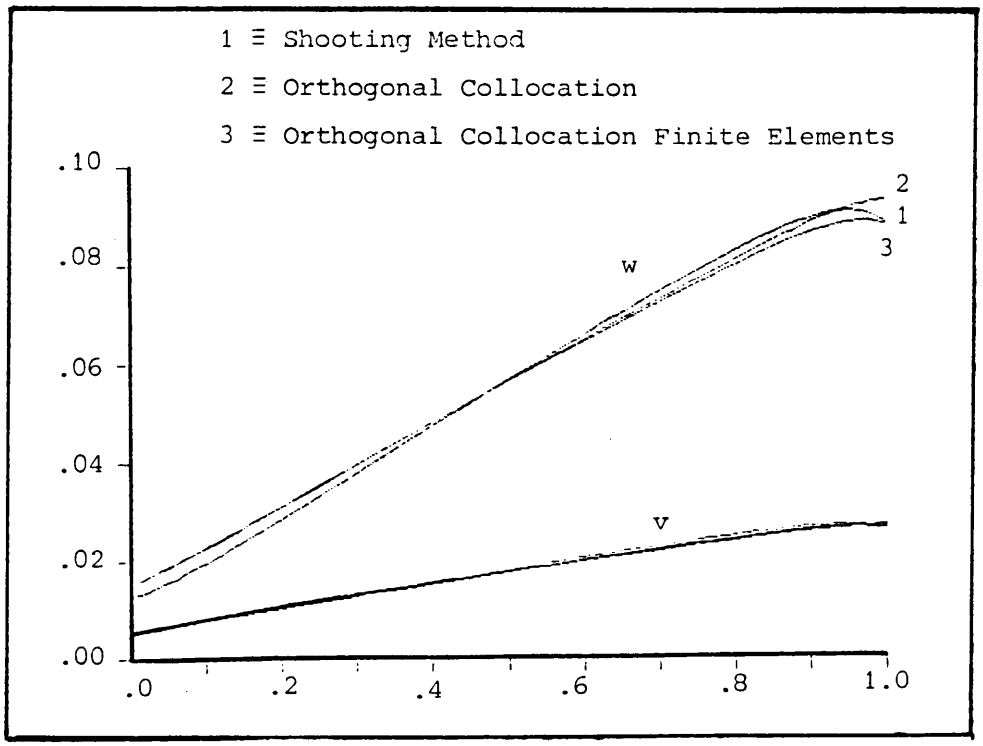

FIG. 1.7: Comparison Between Different Numerical Methods

suitable for highly nonlinear equations and was used extensively to solve the model equations [24,26,27,55,62,65]. For higher accuracy, the interval [0,1] can be divided into elements and at the nodes, the approximated function is smoothed (OCFE). If Hermitian polynomials are used, these continuity conditions at the nodes are satisfied automatically. Problem B was solved for $Pe_m = Pe_h = 5$, $\delta = 25$, $\beta = 0{,}5$, $\gamma = 5$ and $\phi = 0.25$, using: 1) a shooting method; 2) OC 3) OC on splines. The results are shown in Figure 1.7.

We did not do a detail study to compare the three methods, but we decided to use the OC and OCFE methods, due to their popularity.

1.5.2 Elliptic Partial Differential Equations (Two-dimensional model)

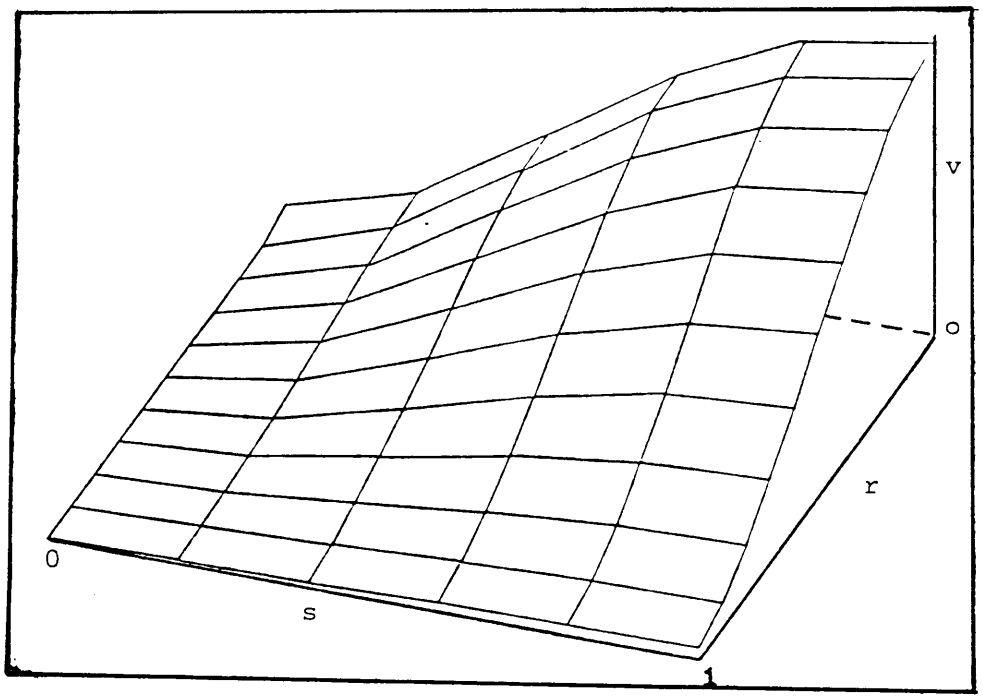

FIG. 1.8: Three-Dimensional Temperature Solution

Finlayson [98] gives a thorough discussion of OC and OCFE to solve this problem. In [83] they used the OC method to study the differences between one and two-dimensional models. Feick and Quon [21] used the Crank-Nicholson method to compare the one-dimensional, two-dimensional and heterogeneous models. Froment [20] also used an implicit finite difference method to compare theoretical and industrial values of radial effects. In Figure 1.8 a temperature solution in two dimensions, using OC, is shown.

1.5.3 Construction of Bifurcation Diagrams

One way of looking at the problem of the number of solutions of either Problems A or B, is to construct an arc of solutions. More precisely, both problems can be written in the following form:

$$F(u,\phi)=0$$

where $F:B\times R\rightarrow B$, for some Banach space B. By a smooth arc of solutions we mean the range in B of the function : $\phi\rightarrow u(\phi)$. If one can construct arcs for all possible values of the parameter ϕ, one will get a complete picture of the number of solutions. However, we shall not attempt to give a formal introduction to bifurcation theory and rather introduce the concept informally. In fact, we shall consider only the discretized versions of Problems A and B and we assume, as most authors do, that the results are valid for the original problem. (In general the validity of the approach has not yet been proved. See Section 3.9 for references.)

Let $G(u,\phi) = 0$

be the discretized version of Problems A and B, where $G:R^n\times R^n\times R\rightarrow R^n\times R^n$. As long as $G_u(u,\phi)$ is non-zero, the arc through (u,ϕ) is uniquely defined. If $G_u(u^0,\phi^0)$ becomes zero, we have a bifurcation point. In some cases (u^0,ϕ^0) marks the junction of two or more arcs and we refer to such a situation as simple and multiple bifurcation respec-

tively. (u^0,ϕ^0) can also be the point where two arcs merge smoothly, referred to as a limit point. In the latter case $G_\phi \in R(G_u)$ at (u^0,ϕ^0). To construct a bifurcation diagram numerically, the discretized problem (a set of algebraic equations) is solved at every value of a parameter. The Newton-type continuation procedure utilizes the Jacobi matrix in every step. This method fails when a non-isolated solution is approached. One can use any standard solution method to solve the discretized problem and keep track of the Jacobi matrix, switching to a method which is specifically designed for bifurcation points when necessary.

The bifurcation behaviour of the discretized version of Problem B was studied by several authors. Varma [60], used a shooting method. This method fails at bifurcation points and it is not clear how he computed these points. Hlavacek [42] used the general parameter mapping technique to construct the bifurcation diagrams. Jensen [45] mentions an approach whereby the determinant of the Jacobi matrix is extrapolated to zero.

Other authors studied integral equations in stead of the differential equations. Reddien [58] proposed a projection method to construct the bifurcation diagrams. Atkinson [88] used collectively compact operator approximations to the integral operator. Simpson [59] computed the least eigenvalues of the Jacobi matrix and obtained an estimate of the bifurcation point by extrapolation.

1.5.4 Our Results

In Chapter 3 we used the continuation method of Keller [96] to construct bifurcation diagrams for Problem A, Problem B and for the modified one-dimensional problem. We also describe the application of this method.

We used the principle of Keller's method to develop a new method to construct an arc of limit points for Problem B. No published results for the non-adiabatic case could be found, to compare our results with. The method in literature, which was used to construct the arcs, differs totally from our method.

1.6 SUMMARY OF NEW RESULTS

In Section 1.4.3 we propose a modification of the one-dimensional model. This model recognises the different elements of dispersion and will help to clear the controversy around the Danckwert's boundary conditions.

In Chapter 2 we derive a sufficient condition for uniqueness, for the one-dimensional model. Exploiting the characteristics of the reaction term, we derive sharper upper bounds on ϕ, to guarantee uniqueness. We also construct upper and lower function bounds on w solutions and using this result in conjunction with the uniqueness result, we construct a lower bound on ϕ. These results compare poorly with numerical values, but are the first of their kind.

In Chapter 3 we used Keller's arclength method to construct bifurcation diagrams for the one-dimensional, modified one-dimensional and two-dimensional models. A new method to construct an arc of limit points is introduced and results are reported.

In Chapter 4 we give an exact definition to parameter sensitivity. We use the criterion of Dente and Collina [102] to construct parameter-sensitivity diagrams and show that existing approaches in literature are inadequate to detect all parameter sensitive regions.

CHAPTER TWO

RIGOROUS BOUNDS FOR UNIQUENESS

2.1 INTRODUCTION

As Emig [91] pointed out, most industrial reactors are operated under conditions where the model has a unique solution. In the literature, numerically determined bifurcation diagrams are mostly used to determine sharp bounds for uniqueness. Apart from the shortcomings of numerical methods like inherent errors and the validity of dicretization, bifurcation points (or limit points) are only sufficient conditions for multiple solutions. Since bifurcation is local, no knowledge of independent solution branches will be gained from a bifurcation diagram. Hence the importance of analytical bounds is obvious. The effect of the Damköhler number on the uniqueness of the one-dimensional model attracted much attention in the past. This is expected since ϕ is an operating variable (see Section 1.2.2). In this chapter we shall also concentrate on this parameter.

For the non-adiabatic reactor model ($\gamma>0$), analytical results are limited (see Section 1.3.2). We shall derive a much improved upper bound $\phi_\star$ and, for the first time, a lower bound ϕ^*, using new methods.

In Section 2.2 we derive a sufficient condition for uniqueness. In Section 2.3 we show that for any given parameters β, δ and γ, there exists a $\phi_\star$. In Section 2.4 we improve the upper bound on $v(s)$ for the first order reaction. In Section 2.5 we compare our results with Varma's and for this example, our bounds are ten to thirty times better. This is a significant improvement.

In Section 2.6 we derive upper and lower function bounds for w. At high values of ϕ these solutions converge at s=1 and can prove valuable in error analysis and convergence of numerical approximations. In the last section we use this result to prove the existence of a ϕ^*. These bounds do not compare well with numerical results, but we claim it is the first result of it's kind.

An interesting fact which emerges from our approach is that if the specific properties of the functions in the differential equations are exploited, better results are achieved than using general or standard approaches.

2.2 GENERAL UNIQUENESS RESULT

2.2.1 Preliminaries

Let $(w_1(s),v_1(s))$ and $(w_2(s),v_2(s))$ denote two solutions of Problem B.
Define $\omega(s) = w_2(s) - w_1(s)$ and

$$\nu(s) = v_2(s) - v_1(s).$$

From the differential form of the model equations and the mean-value theorem, see Apostol [111, p. 254]:

$$\omega''(s)-Pe_{ms}\omega'(s)+\phi[\partial_v f(\bar{w}(s),\bar{v}(s))\nu(s)+\partial_w f(\bar{w}(s),\bar{v}(s))\omega(s)] = 0 \quad (1)$$

$$\nu''(s)-Pe_{hs}\nu'(s)+\beta\phi[\partial_v f(\bar{w}(s),\bar{v}(s))\nu(s)+\partial_w f(\bar{w}(s),\bar{v}(s))\omega(s)]-\gamma\nu(s) = 0 \quad (2)$$

$$\omega'(0) = Pe_{ms}\omega(0) \quad (3)$$

$$\omega'(1) = 0 \quad (4)$$

$$\nu'(0) = Pe_{hs}\nu(0) \quad (5)$$

$$\nu'(1) = 0 \quad (6)$$

where $\bar{w}(s)$ and $\bar{v}(s)$ in (1)-(2) result from the mean-value theorem. For these functions the only information we have are the facts that: $\bar{w}(s)\epsilon[w_1(s),w_2(s)]$ and $\bar{v}(s)\epsilon[v_1(s),v_2(s)]$. It is convenient to introduce the following notation:

$$\alpha(s) = \phi\partial_v f(\bar{w}(s),\bar{v}(s))$$

$$\rho(s) = -\phi\partial_w f(\bar{w}(s),\bar{v}(s))$$

$$L(s) = \alpha(s)v(s)-\rho(s)\omega(s)$$

$$Z(s) = \beta L(s)-\gamma v(s)$$

Note that α and ρ are strictly positive functions for any n-th order reaction.

2.2.2 Behaviour of the Difference Functions

In this section we shall prove that the following condition is sufficient for uniqueness. Throughout this section, it will be assumed that ω and v satisfy the boundary conditions (4) and (6).

Condition C: For any $s\epsilon[0,1]$, $Z(s)<0$ whenever $\omega(s)\geq 0$ and $v(s)>0$ and $Z(s)>0$ whenever $\omega(s)\leq 0$ and $v(s)<0$.

Proposition 1:

Suppose Condition C holds for the differential operator and at an $s_0\epsilon[0,1]$ the following hold:

i) $\omega(s_0) \geq 0$

ii) $\omega'(s_0) = 0$

iii) $\omega''(s_0) < 0$

iv) $\nu(s_0) > 0$

v) $\nu'(s_0) > 0$,

then there is $s_1 \in (s_0,1)$ such that:

i*) $\omega(s_1) < 0$

ii*) $\omega'(s_1) = 0$

iii*) $\omega''(s_1) \geq 0$

iv*) $\nu(s_1) < 0$

v*) $\nu'(s_1) < 0$

Proof

We shall make use of a sketch to elucidate the arguments.

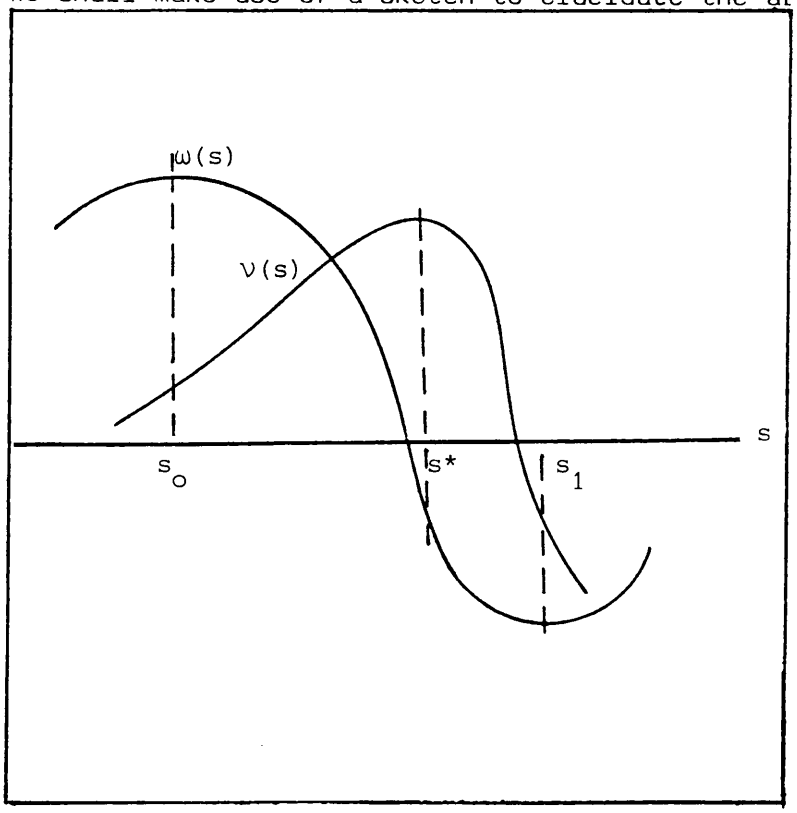

FIG. 2.1

Let s^* be the first point where $\nu'(s) = 0$, $s^* > s_0$.

Then $\nu''(s^*) \leq 0$, since $\nu'(s) > 0$ for $s \in (s_0, s^*)$.

This implies that $\omega(s^*) < 0$, because $\omega(s^*) \geq 0$ implies $Z(s^*) < 0$ and $\nu''(s^*)+Z(s^*) = 0$ is impossible.

We prove next that $\omega'(s^*)<0$.

Suppose $\omega'(s^*) \geq 0$. Since $\omega(s_0) \geq 0$ and $\omega(s^*) < 0$, there exists an $s_2 \in (s_0, s^*]$, such that:

$$\omega'(s_2) = 0 \text{ and } \omega(s_2) \leq 0 \text{ and } \omega''(s_2) \geq 0.$$

Since $\omega''(s_2) + L(s_2) = 0$, it follows that $\alpha(s_2)\nu(s_2)-\rho(s_2)\omega(s_2) \leq 0$. Hence $\nu(s_2) < 0$ which is impossible on the interval $(s_0, s^*]$. This contradicts the assumption, hence $\omega'(s^*) < 0$.

Let s_3 be the first zero of $\omega'(s)$, $s_3 > s^*$. Since $\omega(s^*)<0$ and $\omega'(s^*)<0$, $\omega(s_3)<0$ and $\omega''(s_3)\geq 0$. This proves i*-iii*.

It also follows that $\alpha(s_3)\nu(s_3)-\rho(s_3)\omega(s_3)\leq 0$, which implies $\nu(s_3)<0$. This proves iv*.

We next prove that $\nu'(s_3)<0$.

Suppose $\nu'(s_3) \geq 0$. Since $\nu(s^*) > 0$ and $\nu(s_3) < 0$, there exists an $s^{**} \in (s^*, s_3]$ such that $\nu'(s^{**}) = 0$, $\nu(s^{**}) < 0$ and $\nu''(s^{**}) \geq 0$. Therefore $\nu''(s^{**}) + Z(s^{**}) = 0$. This implies $Z(s^{**}) \leq 0$ which is impossible. Hence $\nu'(s_3) < 0$.

Q.e.d.

In future we shall refer to s_0 as a P-point and s_1 as an N-point.

Proposition 2

Suppose Condition C holds and s_0 denotes an N-point, then there exists a P-point $s_1 \in (s_0,1)$.

Proof

Let $\tau(s) = -\omega(s)$ and $\eta(s) = -\nu(s)$, then the proof is identical to the proof of Proposition 1.

2.2.3 Sufficient Condition for Uniqueness

Lemma 1

If Condition C holds for the differential operator, then Problem B has a unique solution.

Proof

Our approach will be to consider a number of possibilities and in each case show that the boundary value problem reduces to an initial value problem for the system of ordinary differential equations. (If for soms s, $w_1(s) = w_2(s)$, $v_1(s) = v_2(s)$, $w_1'(s) = w_2'(s)$ and $v_1'(s) = v_2'(s)$, it is well-known that $w_1 = w_2$ and $v_1 = v_2$).

The first possibility is $\omega(0) = \nu(0) = 0$. Then it follows from the boundary conditions that $\omega'(0) = \nu'(0) = 0$. Therefore we only have to consider the case either $\omega(0) \neq 0$ or $\nu(0) \neq 0$.

We can assume without loss of generality that $\omega(0)>0$ if $w_1(0) \neq w_2(0)$ and $w''(0)>0$ if $w_1(0) = w_2(0)$.

Note that if $\omega''(0) = 0$ and $\omega(0) = 0$, it follows from the differential equations that $\nu(0) = 0$. This case was already considered in the first part of the proof.

We shall prove that their exists a $s_1 \in (0,1)$ such that s_1 is a P-point. First, let $\omega(0)>0$. From the boundary condition, $\omega'(0)>0$. Let s_1 denote the first point where $\omega'(s_1) = 0$. At s_1, $\omega''(s_1)\leq 0$, therefore $L(s_1)\geq 0$, which implies $\nu(s_1)>0$. We shall now prove that $\nu'(s_1)>0$. Suppose $\nu'(s_1)\leq 0$, then $\nu(s)$ must have reached a maximum at $s^*\leq s_1$. At s^*, $Z(s^*)>0$ implies $\omega(s^*)<0$, which is a contradiction. Hence s_1 is a P-point.

Secondly, $\nu(0) \neq 0$ if $\omega(0) = 0$. From (3), $\omega'(0) = 0$. Let s_1 denote the first point where $\omega'(s_1) = 0$, $\omega(s_1)>0$. Using exactly the same arguments as in the first part, one can prove that s_1 is a P-point.

Consider the set of P-points on the interval $[0,1]$. Let p denote the sup of this set. ω' is a continuous function and since a P-point can be found arbitrarily close to p, it follows that $\omega'(p) = 0$. It is obvious from Propositions 1 and 2 that no N-point exists at $s_0>p$. It also follows from these propositions that an N-point exists arbitrarily close to p. Between every P-point and N-point $\nu'(s) = 0$, thus $\nu' = 0$ can be chosen arbitrarily close to p. Thus $\nu'(p) = 0$ since ν' is a continuous function.

We shall next prove that $\omega(p) = \nu(p) = 0$. Suppose $\omega(p) = k>0$. Then there is a neighbourhood of p where $\omega(s)> k$. But in this neighbourhood there must be an N-point where $\omega(s)<0$. By the same argument $\omega(p)<0$ is not possible. Hence $\omega(p) = 0$.

From Propositions 1 and 2 it follows that ν has positive and negative values arbitrarily close to p. As for ω it follows that $\nu(p) = 0$.

Since $\omega(p) = v(p) = \omega'(p) = v'(p) = 0$, the uniqueness theorem for the initial value problem implies uniqueness. Q.e.d.

2.3 UPPER BOUNDS FOR UNIQUENESS

In this section we shall prove the existence of an upper bound ϕ_* (See Section 1.3.2) and derive an estimate for it. It is important to note that $g(w) = (1-w)^n$ as used in Problem B is a decreasing function.

Lemma 2

If there exists a ϕ_1 such that v_{max} is an upper bound of v for all $\phi \leq \phi_1$, then there exists a ϕ_* such that Condition C holds for all $\phi \leq \phi_*$.

Proof

Let s denote a point where $w_2(s) \geq w_1(s)$ and $v_2(s) > v_1(s)$.

Then

$$Z(s) \leq \beta\phi g(w_2(s)) \frac{\delta e^{\delta v(s)/(1+v(s))}}{(1+v(s))^2} \cdot v(s) - \gamma v(s)$$

$$\leq v(s) \left(\frac{\beta\phi\delta e^{\delta v(s)/(1+v(s))}}{(1+v(s))^2} - \gamma\right)$$

Consider the function B defined by

$$B(v) = \frac{e^{\delta v/(1+v)}}{(1+v)^2}, \quad \text{then} \quad \frac{dB(v)}{dv} = \frac{e^{\delta v/(1+v)}}{(1+v)^4}[\delta - 2 - 2v]$$

If $\delta > 2(1+v)$, the function is increasing. Choose ϕ_* such that:

$$\phi_* = \min[\phi_1, \frac{\gamma(1+v_{max})^2 e^{-\delta v_{max}/(1+v_{max})}}{\beta\delta}] \tag{7}$$

Suppose $\delta \leq 2$, then max $B(v) = B(0)$ and one chooses ϕ_* such that:

$$\phi_* = \gamma/\beta\delta. \tag{8}$$

If $2<\delta<2(1+v)$, a maximum exists at $v = \delta/2-1$ and one can choose

$$\phi_* = \frac{\gamma\delta}{4\beta} e^{-(\delta-2)} \tag{9}$$

If s denotes a point where $w_2(s) \leq w_1(s)$ and $v_2(s)<v_1(s)$, the proof is identical.

Hence, for any set of parameters β, δ and γ, an upper bound ϕ_* exists.

Q.e.d.

Remark

For large δ, no accurate estimate can be made for $\phi*$

2.4 A NEW UPPER BOUND ON v(s)

It is obvious from the results in the last section that sharper "global" upper bounds on v will considerably improve the upper bound for uniqueness. In this section we shall derive a new upper bound on v for a first order reaction without solving the differential equation.

2.4.1 Preliminaries

In integral form, the model equations can be written as:

$$w(s) = \int_0^1 G_{ms}(s,t)\phi(1-w(t))e^{\delta v(t)/(1+v(t))}dt \tag{10}$$

$$v(s) = \int_0^1 G_{hs}(s,t)[\beta\phi(1-w(t))e^{\delta v(t)/(1+v(t))} - \gamma v(t)]dt \qquad (11)$$

where $G_i(s,t)$ denotes the Green's function as defined in Section 1.3.

The Pe_{ms} and Pe_{hs} numbers usually differ and we shall first consider the case $Pe_{ms} \leqslant Pe_{hs}$

$$v(s) < \int_0^1 G_{hs}(s,t)(\beta\phi(1-w(t))e^{\delta v(t)/(1+v(t))})dt$$

$$\leqslant \int_0^1 G_{ms}(s,t)(\beta\phi(1-w(t))e^{\delta v(t)/(1+v(t))})dt$$

$$= \beta w(s). \qquad (12)$$

If $Pe_{ms} > Pe_{hs}$, one can find a $P > 0$, such that

$$G_{ms}(s,t)P \geqslant G_{hs}(s,t) \quad (\text{e.g. } P = (1/Le)e^{Pe_{ms}})$$

and $v(s) < \beta P w(s)$ (13)

An upper bound on $v(s)$ in terms of $w(s)$ can be found such that $\psi v(s) < w(s)$, where

$$\psi = \begin{cases} 1/\beta & , \quad Le \geqslant 1 \\ 1/(P\beta) & , \quad Le < 1 \end{cases}$$

Definition: $H_\phi : H_\phi(v) = \phi(1-\psi v)e^{\delta v/(1+v)}$

It follows that $H_\phi v(s) > \phi(1-w(s))e^{\delta v(s)/(1+v(s))}$ for all solutions of (10)-(11).

We shall show that the function

$$J_\phi(v) = \beta H_\phi(v) - \gamma v$$

can be used to compute upper bounds for v without solving the boundary value problem.

2.4.2 Upper Bound

Lemma 3

If v_R has the property that $J_\phi(u)\leq 0$ for all $u\geq v_R$ then v_R is an upper bound for the temperature solution of Problem B.

Proof

We shall consider two possibilities: Either v is an increasing function or v has at least one local maximum in (0,1). Note that $v'(0)>0$.

In the first case $v''(1)\leq 0$. Since $v'(1) = 0$, it follows that

$$\beta\phi f(w(1),v(1)) - \gamma v(1)\geq 0.$$

Since

$$\beta\phi f(w(1),v(1)) - \gamma v(1)<J_\phi(v(1)),$$

it follows from the properties of J_ϕ that $v(1)<v_R$.

In the second case, we can use the same argument at every local maximum of v. Consequently $\max(v)<v_R$.

Q.e.d.

In Figure 2.2 three possible graphs for J_ϕ are shown for various ϕ. Note that $\phi_1 > \phi_2$ implies $J_{\phi_1} > J_{\phi_2}$.

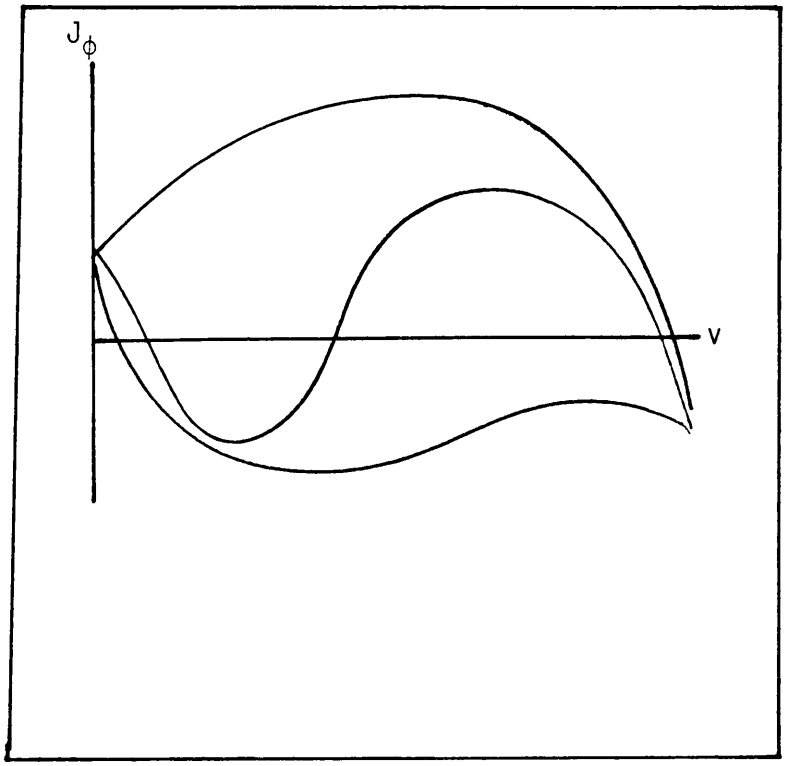

FIG. 2.2: $J_\phi(v)$

Proposition 3

If $\delta > 4\psi + 4$ then there exists an unique $\phi = \phi_R$ such that the local maximum of $J_{\phi_R} = 0$.

Proof

$$\frac{dJ_\phi(v)}{dv} = \frac{\beta\phi\delta(1-\psi v)e^{\delta v/(1+v)}}{(1+v)^2} - \gamma - \psi\beta\phi e^{\delta v/(1+v)}$$

$$\frac{d^2J_\phi(v)}{dv^2} = \frac{\phi\delta e^{\delta v/(1+v)}}{(1+v)^4}\left[\beta\delta-2\beta-2\psi\beta+v(-\beta\psi\delta-2\beta-2\beta\psi)\right]$$

The only point where the second derivative can change sign is at

$$v_0 = \frac{\delta-2-2\psi}{\psi\delta+2+2\psi} > 0,$$

since $\delta>2+2\psi$.

For $v<v_0$, the second derivative is strictly positive and for $v>v_0$ the second derivative is strictly negative. Note that $v_0<1/\psi$. It follows that J_ϕ can have at most one maximum for some $v>v_0$. Our aim is now to find a v^* and ϕ_R such that $J_{\phi_R}(v^*) = 0$ and $J'_{\phi_R}(v^*) = 0$.

Let $\beta\phi_R(1-\psi v^*)e^{\delta v^*/1+v^*}-\gamma v^* = 0$ (14)

$$\frac{\beta\phi_R\delta}{(1+v^*)^2}(1-\psi v^*)e^{\delta v^*/(1+v^*)}-\beta\psi\phi_R e^{\delta v^*/(1+v^*)}-\gamma = 0 \quad (15)$$

Substituting (14) in (15) and rearranging,

$$v^{*2}(-1-\psi\delta) + v^*(\delta-2)-1 = 0 \quad (16)$$

This equation can be solved for $\delta>4\psi+4$ and the roots are

$$v^*_{1,2} = \frac{(\delta-2)\pm\sqrt{\delta^2-4\delta(1+\psi)}}{2(1+\psi\delta)}.$$

From previous arguments it follows that the larger root v_2^* corresponds to a local maximum. Substituting this root into (14) we find that

$$\phi_R = \frac{\gamma v_2^* e^{-\delta v_2^*/(1+v_2^*)}}{\beta(1-\psi v_2^*)} \tag{17}$$

Q.e.d.

Define v_R as the smallest zero of $J_{\phi_R}(v)$ (see Figure 2.3). It follows from Lemma 3 and the properties of J_ϕ that v_R is an upper bound for the temperature solution v for all $\phi\leq\phi_R$.

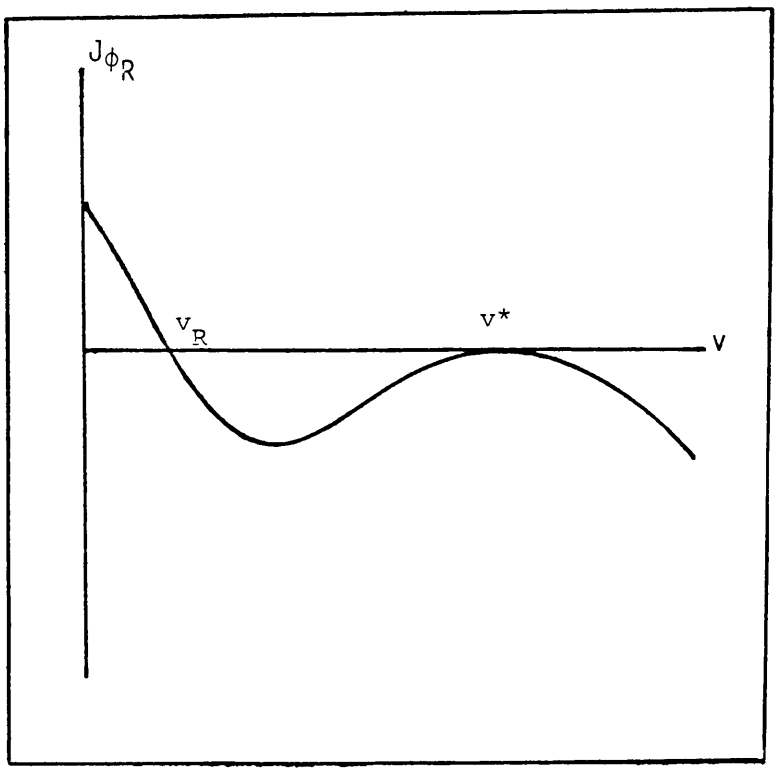

FIG. 2.3: $J_{\phi_R}(v)$

2.5 COMPARISON OF UPPER BOUNDS ON ϕ

Varma [60] derived analytical estimates for ϕ_* (See Section 1.3.2.2) and compared them with values obtained from bifurcation diagrams. In this section we shall compare our analytical results with those of Varma for the following set of parameters:

$$Pe_{ms} = Pe_{hs} = 5$$

$$\beta = 0,5$$

$$\delta = 25$$

We computed ϕ_R for different γ-values using (16) and (17). Then v_R, the smallest positive root of J_{ϕ_R} is determined numerically. This upper bound for v is now used in (7) to determine ϕ_*.

Table 2.1: Comparison of Upper Bounds

γ	Estimates for ϕ_*		
	Varma's Results		Our Results
	Numerical	Analytical	
5	0,05388	0,00109	0,0156
10	0,1244	0,001109	0,0312
12,5	0,17582	0,001198	0,039
15	0,2233	0,001282	0,0468

2.6 FUNCTION UPPER AND LOWER BOUNDS

In this section we shall construct functions which are upper and lower

bounds for the conversion solution of Problem B for the case of a first order reaction. We require these bounds to find a lower bound ϕ^*, such that Condition C holds for all $\phi \geq \phi^*$.

Notation

We shall use g for the solution of

$$g'' - Pe_{ms} g' + \phi(1-g) = 0$$

$$g' = Pe_{ms} g \quad ; s=0$$

$$g' = 0 \quad ; s=1$$

and h for the solution of

$$h'' - Pe_{ms} h' + \phi(1-h) e^{\delta\beta/(1+\beta)} = 0$$

$$h' = Pe_{ms} h \quad ; s=0$$

$$h' = 0 \quad ; s=1$$

We shall prove that $g \leq w \leq h$.

Proposition 4

If (w,v) is a solution of Problem B, $g \leq w$.

Proof

Let $g(s) > w(s)$, then it follows from the integral representations that

$$\int_0^1 G_{ms}(s,t)\phi(1-g(t))dt = g(s) > w(s) = \int_0^1 G_{ms}(s,t)\phi(1-w(t))e^{\delta v(t)/(1+v(t))}dt$$

Hence $\int_0^1 G_{ms}(s,t)\phi(w(t)-g(t))dt > 0$, which implies $g(t) < w(t)$ for some t.

Next we shall prove that $g(1)\leq w(1)$. Suppose $g(1)>w(1)$, then the solutions must intersect at $s_1<1$ and $g'(s_1)>w'(s_1)$

For $1>s>s_1$,

$g(s) > w(s)$,

$1-g(s) < 1-w(s)$ and thus

$1-g(s) < (1-w(s))e^{\delta v(s)/(1+v(s))}$.

Therefore

$$\int_{s_1}^{1} (1-g(s))ds < \int_{s_1}^{1} (1-w(s))e^{\delta v(s)/(1+v(s))}ds.$$

Hence

$$\int_{s_1}^{1} e^{Pe_{ms}(s_1-t)}\phi(1-g(t))dt <$$

$$\int_{s_1}^{1} e^{Pe_{ms}(s_1-t)}\phi(1-w(t))e^{\delta v(t)/(1+v(t))}dt \text{ and } g'(s_1) < w'(s_1).$$

This is a contradiction, hence $g(1)\leq w(1)$.

If $g(1)=w(1)$, then $g''(1)>w''(1)$. Thus $g(s)<w(s)$ in $(\delta,1)$ for some δ. Obviously this is also the case when $g(1)<w(1)$.

We shall now prove that it is impossible for g and w to intersect in (0,1). Suppose s_2 is a point of intersection. Either s_2 is a unique intersection point on (0,1) or is preceded by $s_1 \in (0,s_2)$ where $g(s_1)=w(s_1)$ and $g'(s_1)>w'(s_1)$.

Suppose there exists a unique $s_2 \in (0,1)$ such that $g(s_2)=w(s_2)$, $g'(s_2)<w'(s_2)$. For $0\leq s\leq s_2$

$g(s)\geq w(s)$

$(1-g(s))<(1-w(s))e^{\delta v(s)/(1+v(s))}$.

Hence

$$\int_0^{s_2} \phi(1-g(t))dt < \int_0^{s_2} \phi(1-w(t))e^{\delta v(t)/(1+v(t))}dt$$

At s_2, $g'(s_2)<w'(s_2)$, therefore $g(s_2)<w(s_2)$. But this is a contradiction.

The remaining possibility is that there exist an $s_2 \in (0,1)$ where $g(s_2)=w(s_2)$, $g'(s_2)<w'(s_2)$ and $s_1 \in (0,s_2)$ where $g(s_1)=w(s_1)$, $g'(s_1)>w'(s_1)$ and $s_2>s_1$.

At s_1, $g'(s_1)>w'(s_1)$, and $1-g(s)<(1-w(s))e^{\delta v(s)/(1+v(s))}$ for $s_1<s<s_2$.

Hence

$$g'(s_1)=\int_{s_2}^{1} e^{Pe_{ms}(s_1-t)}\,\phi(1-g(t))dt+\int_{s_1}^{s_2} e^{Pe_{ms}(s_1-t)}\,\phi(1-g(t))dt$$

$$< \int_{s_2}^{1} e^{Pe_{ms}(s_1-t)}\,\phi(1-w(t))e^{\delta v(t)/(1+v(t))}dt$$

$$+ \int_{s_1}^{s_2} e^{Pe_{ms}(s_1-t)}\,\phi(1-w(t)e^{\delta v(t)/(1+v(t))}dt$$

Thus $g'(s_1) < w'(s_1)$, which is a contradiction.

Q.e.d.

Proposition 5

If (w,v) is a solution of Problem B then $h>w$.

Proof

The arguments are exactly the same as in the proof of Proposition 4.

Q.e.d.

It is well-known that the functions g and h are given by:

$$h(s),g(s) = 1+M_2 \frac{Pe_{ms} e^{M_2-M_1+M_1 s}}{M_1 H} - \frac{Pe_{ms} e^{M_2 s}}{H} \qquad (18)$$

where $M_1 = \frac{Pe_{ms} + \sqrt{Pe_{ms}^2+4\phi'}}{2}$, $M_2 = \frac{Pe_{ms} - \sqrt{Pe_{ms}^2+4\phi'}}{2}$

$$H = M_2 e^{(M_2-M_1)} - M_2 - Pe_{ms} \frac{M_2}{M_1} e^{(M_2-M_1)} + Pe_{ms}.$$

$$\phi' = \begin{cases} \phi \text{ for } g \\ \phi e^{\delta\beta/(1+\beta)} \text{ for } h \end{cases}$$

2.7 A NEW LOWER BOUND ϕ^*

In this section we shall derive a new lower bound on ϕ for the case of a first order reaction.

In Lemma 4 we assume that $\nu(s) \leq \beta\omega(s)$. This assumption is strongly supported by numerical results, but we failed to prove it yet.

Lemma 4

Assume that $\nu(s) \leq \beta\omega(s)$. Then there exists a ϕ^* such that Condition C holds for all $\phi \geq \phi^*$.

Proof

$$Z(s) \leq \beta\phi(1-w(s))\left[\frac{\delta e^{\delta v(s)/(1+v(s))}}{(1+v(s))^2}\, v(s)\right] - \gamma v(s) - \beta\phi e^{\delta v(s)/(1+v(s))}\, \omega(s)$$

But from Proposition 4, it follows that $g(s) \leq w(s)$, for $s \in [0,1]$. Hence

$$Z(s) < v(s)\left[\beta\phi\delta(1-g(s))e^{\delta v(s)/(1+v(s))} - \gamma - \phi e^{\delta v(s)/(1+v(s))}\right]$$

$$< v(s)\left[\beta\phi\delta(1-g(0))e^{\delta v(s)/(1+v(s))} - \gamma - \phi e^{\delta v(s)/(1+v(s))}\right]$$

Using (18) one can choose ϕ^* such that

$(\beta\phi\delta(1-g(0))-\phi)e^{\delta v(s)/(1+v(s))} - \gamma \leq 0$

for all $\phi \geq \phi^*$ and $v(s) \in [0,\beta]$.

Q.e.d.

In Table 2.2 we compare our analytical bound with the numerical results of Varma [60] for an identical set of parameters as was used in Table 2.1.

Table 2.2: Comparison of Lower Bounds

γ	Numerical	Our Result
5	0,0919	3583,5
10	0,138	3573,0
12,5	0,18138	3567,7
15	0,2258	3563,0

Although these results compare poorly, they are the first of their kind.

CHAPTER THREE

BIFURCATION

3.1 INTRODUCTION

Numerical procedures are used to study the bifurcation behaviour of the reactor models. (See Section 1.5.3). The existence of multiple solutions of boundary value problems is well-known. In Section 3.2 some numerical methods to determine bifurcation points and bifurcation in finite dimensional space are discussed. In Section 3.3 our numerical approach is outlined. In Section 3.4 we discuss the results for the one-dimensional model (Problem B) and present the results. In Section 3.5 a new approach for the construction of arcs of bifurcation points (parameter-plane diagrams) is discussed and in the following section some results are shown. This method is new since it uses a totally different approach.

In Section 3.7 the bifurcation behaviour of the variable dispersion model is studied. The formulation of this model is also new, although a change in the boundary conditions along these lines were formerly suggested. In Section 3.8 we look at the two-dimensional model. No literature on the bifurcation behaviour of this model could be found. Regions of one, two and three solutions were found but no higher multiplicity than three. For certain choices of the parameters no solution was found. Due to the complexity of the problem we could link this problem to neither the numerical procedure nor the non-existence of a solution.

3.2 BIFURCATION IN FINITE DIMENSIONAL SPACE

We shall now discuss methods to construct arcs of solutions (as a function of a parameter) for the discretized problem. Consider the discretized version of a boundary value problem, parametrized by ϕ.

$$G(u(\phi),\phi) = 0, \tag{1}$$

where $u = (w,v)$ is the solution of (1).

Then (u,ϕ) is called a regular solution if $G_u(u,\phi)$ is nonsingular, otherwise (u,ϕ) is a bifurcation point. (u,ϕ) is a normal limit point if $G_u(u,\phi)$ is singular and

(a) $\dim N(G_u) = \operatorname{codim} R(G_u) = 1$. (b) $G_\phi \notin R(G_u)$

At a limit point two solution branches "meet smoothly". Jensen [45] stated without proof that Problem B only portrays limit point bifurcation and in the rest of this chapter we assume $G_\phi \notin R(G_u)$ at every bifurcation point.

We shall now explain Keller's method. It is a method used to trace out solution arcs, by varying a parameter of the problem. This method does not encounter any difficulties at limit points and bifurcation points, although this is often the case for other methods. (See Section 1.5.3). A new independent parameter s is introduced.

$$G(u(s),\phi(s)) = 0. \tag{2}$$

An additional equation is now required. Let

$$N_\theta(s) = \theta\|\dot{u}(s)\|^2 + (1-\theta)|\dot{\phi}(s)|^2 - 1 = 0 \tag{3}$$

where θ is an arbitrary constant $0<\theta<1$. The initial value for s is also arbitrary. (s is a form of arclength). Rewriting (2) and (3) we get

$$P(u(s),\phi(s),s) = \begin{bmatrix} G(u(s),\phi(s)) \\ N_\theta(u(s),s) \end{bmatrix} = 0 \tag{4}$$

If the derivative $u(s)$ is not known at s, an approximation of (3) is:

$$N3(s) = \theta\|u(s)-u(s_0)\|(\dot{u}(s_0)) + (1-\theta)|\phi(s)-\phi(s_0)|(\dot{\phi}(s_0)) - ds = 0. \tag{5}$$

If $x = (u,\phi)$, the Frechét derivative of P as a function of x only is represented by the Jacobi matrix.

$$P_x = \begin{bmatrix} G_u & G_\phi \\ N3_u & N3_\phi \end{bmatrix} \tag{6}$$

We shall need the following result.

LEMMA (Keller)

Let A be a linear operator $A: R^n \times R^n \to R^n \times R^\nu$.

$$A \equiv \begin{bmatrix} G_u & G_\lambda \\ C^* & D \end{bmatrix}$$

(a) If G_u is nonsingular then A is nonsingular iff:

1. $D - C^* G_u^{-1} G_\lambda$ is nonsingular.

(b) If G_u is singular and dim $N(G_u)$ = codim $R(G_u)$ = ν then A is nonsingular iff:

1. dim $R(G_\lambda) = \nu$
2. $R(G_\lambda) \cap R(G_u) = 0$
3. dim $R(C^*) = 0$
4. $N(G_u) \cap N(C^*) = 0$

(c) If G_u is singular and dim $N(G_u) > \nu$ then A is singular.

See Keller [96, p. 363].

Note: In the case of simple bifurcation the conditions in (b) can be stated as: $G_\lambda \notin R(G_u)$ and $C^* \notin R(G_u^*)$, where G_u^* is the dual element of G_u.

Assuming

$$G_u\dot{u}+G_\phi\dot{\phi} = 0$$

and $G_\phi \notin R(G_u)$, one concludes that $\dot{\phi} = 0$ and hence $u \in N(G_u)$.

Since

$$\|\dot{u}\|^2 + |\dot{\phi}|^2 > 0$$

it follows that $\dot{u}^T\dot{u} \neq 0$ and hence $\dot{u}^T \notin R(G_u{}^T)$.

It follows from the Lemma that P_x is nonsingular. Therefore a continuation procedure, using P_x will exhibit no problems at the limit points.

3.3 NUMERICAL PROCEDURES

We shall give a brief explanation of the method of orthogonal collocation, since it forms the basis for most of the numerical work in the following sections. (See Section 1.5.1 for references). Orthogonal collocation is a finite element used for the numerical solution of differential equations. The solution is approximated by a polynomial. In certain points on the interval $[0,1]$, called the collocation points, the polynomial is forced to satisfy the differential equation exactly. These conditions supply the necessary equations to solve for the coefficients of the polynomial.

Let the function $y(x)$ be approximated in NCOL points:

$$y(x_i)\ y_N(x_i) = \sum_{j=0}^{NCOL} C_j x_i{}^j, \qquad i = 1,2, \ldots NCOL.$$

Differentiating with respect to x gives:

$$y_N'(x) = \sum_{j=0}^{NCOL} C_j j x^{j-1}$$

Or in matrix form,

$$Y = XC$$

and

$$Y' = X'C$$

But

$$C = X^{-1}Y,$$

thus

$$Y' = X'X^{-1}Y.$$

Let $A = X'X^{-1}$,

then one can approximate the first derivative with a linear combination of the function values at NCOL-points

$$Y' = AY.$$

Following the same approach, one can derive an approximation of the second derivative in the form

$$Y'' = BY$$

where B is also a square matrix.

Let A_{ij} and B_{ij} denote the elements of A and B respectively. Using Villadsen's notation [94] for orthogonal collocation, the discretized version of Problem B for a first order reaction (and Le=1) can be written as:

$$\sum_{j=1}^{NCOL} A_{1j}u_j - Peu_1 = 0 \tag{7}$$

$$\sum_{j=1}^{NCOL} B_{ij}w_j - Pe \sum_{j=1}^{NCOL} A_{ij}w_j + \phi(1-w_i)\exp(\delta v_i/(1+v_i)) = 0 \tag{8}$$

$$\sum_{j=1}^{NCOL} B_{ij}v_j - Pe \sum_{j=1}^{NCOL} A_{ij}v_j + \beta\phi(1-w_i)\exp(\delta v_i/(1+v_i)) - \gamma v_i = 0 \tag{9}$$

$$\sum_{j=1}^{NCOL} A_{NCOL\,j}u_j = 0 \tag{10}$$

$$\sum_{j=1}^{NCOL} A_{NCOL-1,j}u_j = \Sigma A_{NCOL}u_j \tag{11}$$

$$\theta\left|u(s)-u(s_0)\right|us(s_0)+(1-\theta)\left|\phi(s)-\phi(s_0)\right|\phi s(s_0)-ds=0 \tag{12}$$

The method of Powell [92] was used to solve the resulting system of nonlinear algebraic equations. To compute us the system of equations (8)-(12) was differentiated with respect to s and an additional system was solved at each step of s.

$$\sum_{j=1}^{NCOL} A_{ij}(us_j) - Pe(us_1) = 0 \quad \left(us = \frac{du}{ds}\right) \tag{13}$$

$$\sum_{j=1}^{NCOL} B_{ij}ws_j - Pe \sum_{j=1}^{NCOL} A_{ij}ws_j + \frac{\phi\delta(1-w_i)}{(1+v_i)^2} e^{\delta v_i/(1+v_i)} vs_i - \phi e^{\delta v_i/(1+v_i)} ws_i + (1-w_i)e^{\delta v_i/(1+v_i)}\phi s = 0 \tag{14}$$

$$\sum_{j=1}^{NCOL} B_{ij}vs_j - Pe \sum_{j=1}^{NCOL} A_{ij}vs_j + \frac{(\beta\phi\delta(1-w_j)}{(1+vi)^2} \quad e^{\delta v_i/1+v_i} \tag{15}$$

$$-\gamma vs_i - \beta\phi e^{\delta v_i/1+v} ws_i + \beta(1-w_i)e^{\delta v_i/1+v_i}\phi s = 0$$

$$\sum_{j=1}^{NCOL} A_{NCOL,j}us_j = 0 \tag{16}$$

$$\sum_{j=1}^{NCOL} A_{NCOL-i,j}us_j = \sum_{j=1}^{NCOL} A_{NCOL,j}us_j \tag{17}$$

$$\theta(us(s)us(s)^T)+(1-\theta)\phi s(s)^2-1 = 0, \tag{18}$$

where $us = (\frac{dw}{ds}, \frac{dv}{ds})$

$$\phi s = \frac{d\phi}{ds}$$

We can summarize the procedure in the form of an algorithm.

1. Solve (2) for a known value of ϕ, using any standard procedure like a shooting method, imbedding techniques etc. [95].
2. Solve (13)-(18) to obtain $us(s_0)$ and $\phi s(s_0)$.
3. Increment s.
4. Solve (7)-(12) to obtain u(s) and $\phi(s)$.
5. Termination? If not return to step 2.

3.4 BIFURCATION DIAGRAMS OF PROBLEM B

Varma [60] constructed bifurcation diagrams using a shooting method, the way he computed the limit points is not clear from his article. His results appear to be identical to those of Figure 3.1 and Figure 3.2. For the adiabatic reactor (γ=0), a maximum of three solutions exist for $\phi \in (\phi_*, \phi^*)$ and only two limit points, at ϕ_* and ϕ^* respectively.

Luss [7] proved that multiple solution profiles do not intersect when $\gamma = 0$ and Le = 1. This simplifies the representation of a bifurcation diagram since an one-to-one relation exists between the function u and it's function values. Figure 3.1 is a true bifurcation diagram. In the non-adiabatic case numerical examples exist where the temperature and conversion profiles intersect [60]. A function value can no longer be uniquely assigned to a value of the function and the representation of the bifurcation behaviour is no longer an obvious matter. A possible way to overcome this problem is to construct diagrams for both temperature and conversion. If both profiles have intersections, it cannot be at s = 1 or s = 0. This is obvious from the uniqueness theorem for the initial value problem of ordinary differential equations.

We constructed the bifurcation diagrams for Problem B using the same set of parameters as in [60] and [93]. Our results (see Figure 3.1 and Figure 3.2) compare favourably. An orthogonal collocation method on splines was used with sixteen collocation points in total. The formulation differs slightly from (7)-(12), see [98]. A set of 33 equations was solved simultaneously at each step to give x(s) and the same number for xs(s). When fewer points were used an additional wiggle occurred in the bifurcation diagram, see Figure 3.3

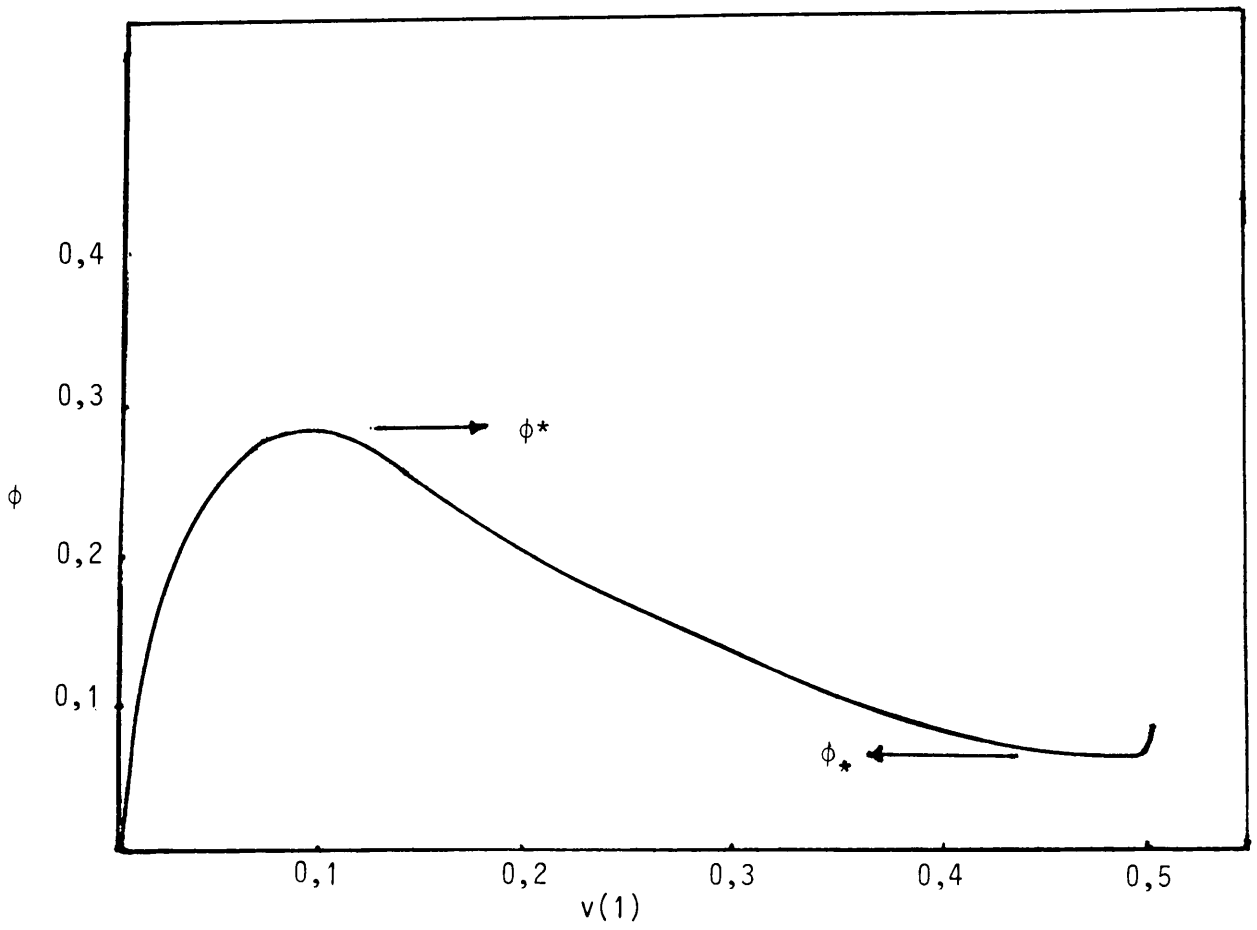

FIG. 3.1: Bifurcation Diagram of the Adiabatic Reactor

The program for the construction of these bifurcation diagrams is listed in Appendix A. This program is very versatile and the aspects of parametric sensitivity (see Chapter 4), stability and multiplicity can be examined at the same time. It can be very useful to engineers in the design stage of a reactor.

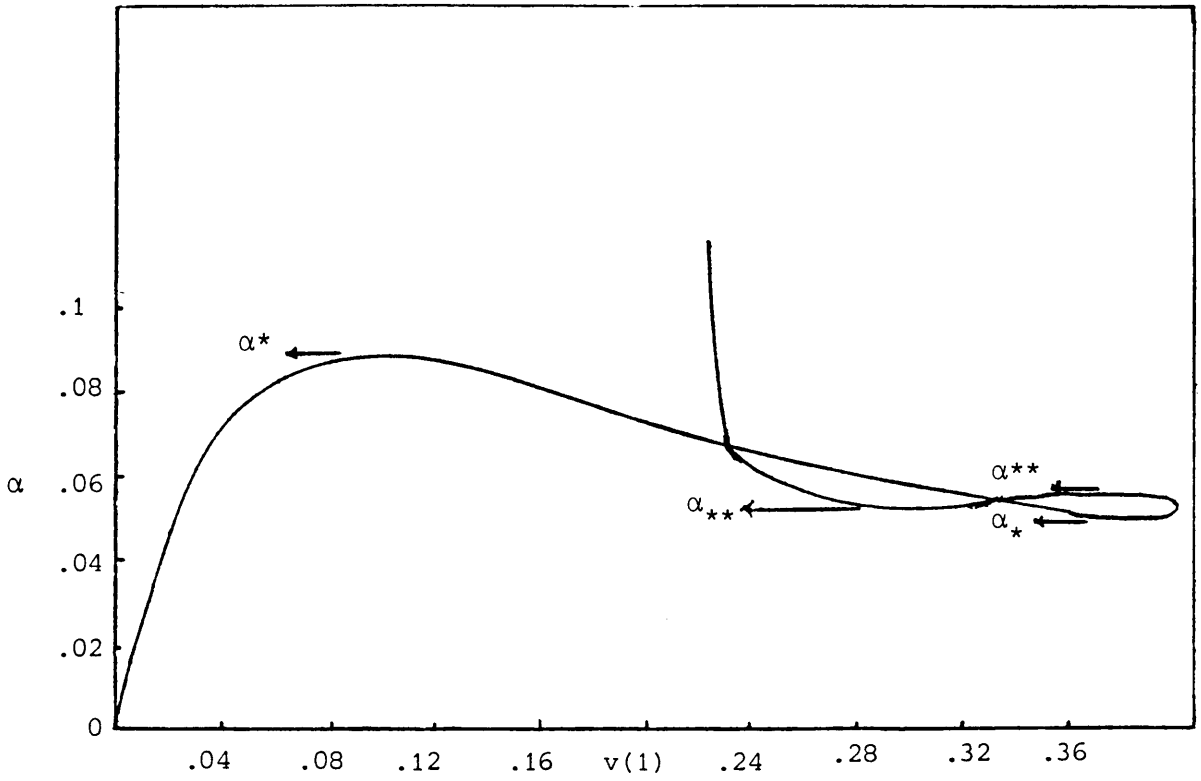

FIG. 3.2: Bifurcation Diagram of the Nonadiabatic Reactor Using 16 Collocation Points

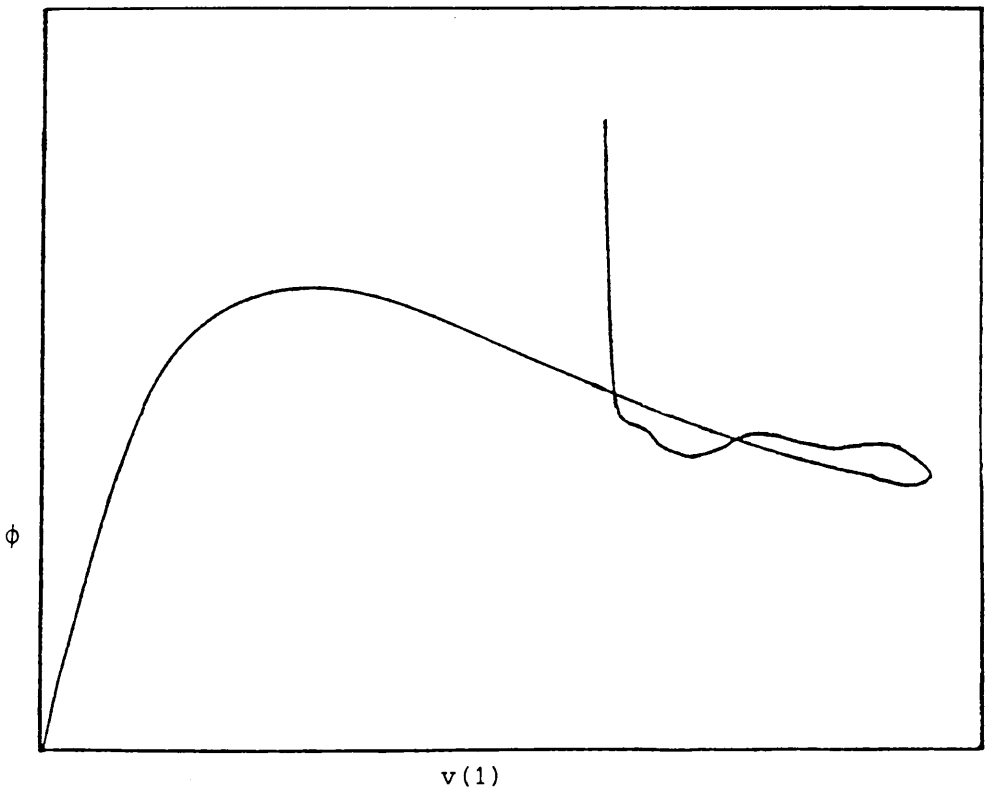

FIG. 3.3: Bifurcation Diagram of the Nonadiabatic Reactor Using 13 Collocation Points

3.5 CONSTRUCTION OF AN ARC OF LIMIT POINTS

Jensen [45] solved the adiabatic one-dimensional problem, constructing a bifurcation diagram at every Pe-value. Values of ϕ^* (or ϕ_*) and Pe for every diagram can be used to construct a diagram of ϕ versus Pe which marks the transition from one to three solutions. These arcs meet in a point called the trifurcation point [42].

This process can be repeated for the non-adiabatic reactor but it becomes very cumbersome to construct the parameter planes. The only attempt to do it for this reactor, was found in [42], but it was for the Frank-Kamenetskii type of temperature dependence [48]. It is also not permissible to construct the parameter planes solely from the temperature bifurcation diagrams for reasons already mentioned.

Using the same arguments as Keller [96], one can use Pe as a stepping parameter to trace an arc of limit points. In fact, any parameter can be used as independent variable, with any other as the dependent one to construct such a parameter plane. The procedure is as follows:

Instead of an arc-length, we set the determinant of the Jacobi matrix equal to zero. Let $M(u(Pe),\phi(Pe),Pe) \equiv \det G_u(u(Pe),\phi(Pe),Pe)$

$$P(u(Pe),\phi(Pe),Pe) = \begin{bmatrix} G(u(Pe),\phi(Pe),Pe) \\ \\ M(u(Pe),\phi(Pe),Pe) \end{bmatrix} = 0 \qquad (19)$$

Since u is a polynomial approximation over splines it is not easy to get an explicit expression for the determinant of the non-symmetric Jacobi matrix. Since we assume that $N(G_u) = 1$ there exists a $Z \in R^n x R^n$ such that $G_u(u,\phi) \cdot Z = 0$. Furthermore, Z can be normalized: $\|Z\| = 1$ or $Z_k = 1$. Since Z is non-zero, $G_u(u,\phi)$ is singular. (See [85] for more details.) We thus solve the following.

$$P(u(Pe),\phi(Pe),Pe) = \begin{bmatrix} G(u(Pe),\phi(Pe),Pe) \\ G_u(u(Pe),\phi(Pe),Pe) \cdot Z \\ Z_k - 1 \end{bmatrix} = 0 \qquad (20)$$

Using Pe as stepping parameter we initiate the procedure at a known limit point (using results from the bifurcation diagram). Since there exist more than one limit point at each Pe-number, the arc of lower or upper limit points in the case of the adiabatic reactor can be computed by either starting of with ϕ_* or ϕ^* respectively.

The procedure can be summarized in the form of an algorithm.

1. Compute the bifurcation diagram for the initial value of the independent parameter.
2. Supply an initial guess for u at a limit point.
3. Solve (20).
4. Increase Pe.
5. Termination of the arc? If not go to step 3.
6. Have all the limit point arcs been considered? If not, go to step 2.

3.6 RESULTS

To check the accuracy of this approach, a parameter plane was constructed for the same choice of parameters as Jensen [45], and Hlavacek [42]. The parameter plane in Figure 3.4 compares very well with their results.

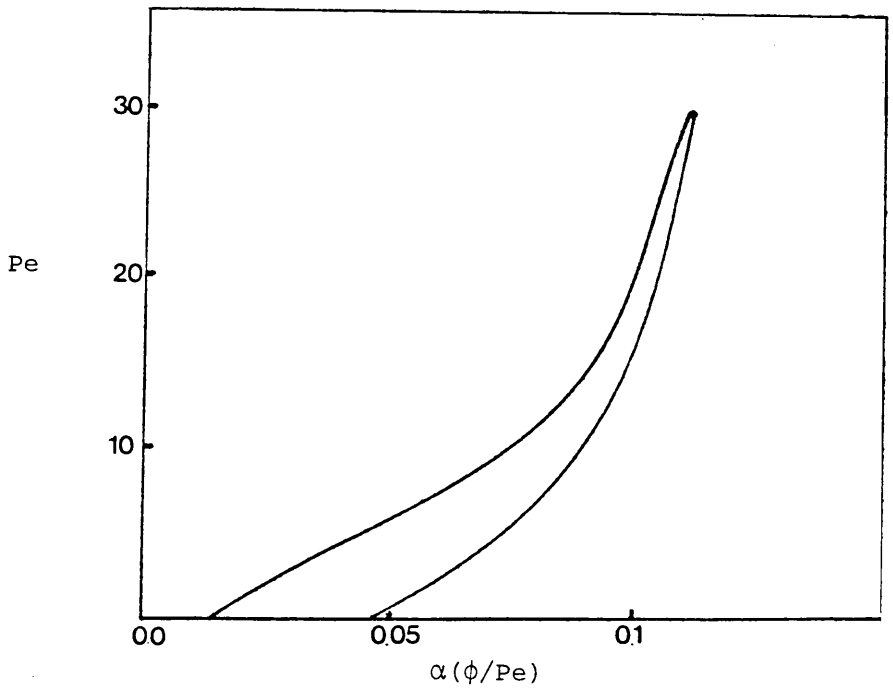

FIG. 3.4: Parameter Plane of an Adiabatic Reactor

No published results for the non-adiabatic reactor could be found. In Figure 3.5 a Pe versus ϕ diagram is shown.

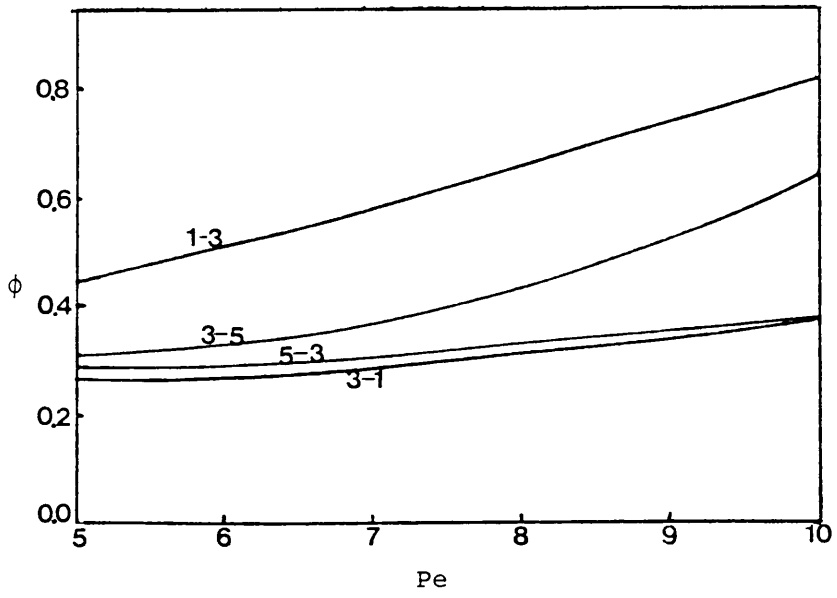

FIG. 3.5: Parameter Plane of a Non-Adiabatic Reactor

The numerical procedure broke down for Pe > 12 and for Pe < 3. The reason for the latter is probably the approach of a singularly perturbed problem. In the former case it is surmised that a true bifurcation point is approached. Possibly one can overcome by defining an arc-length for this problem and use the Newton chord method to jump over the singular points.

In Figure 3.6 the dimensionless heat transfer to the surroundings (γ) was varied independently, and ϕ was the dependent parameter.

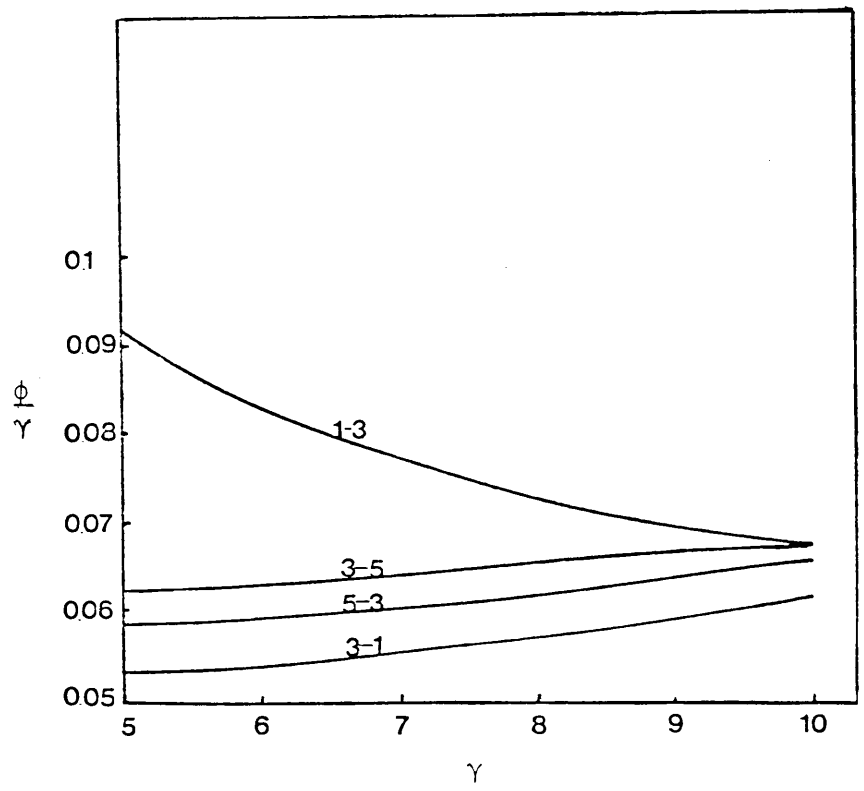

FIG. 3.6: Parameter Plane of γ vs. ϕ

For certain values of γ we compared our results with those of Varma [60]. Note that ϕ^{**} and ϕ_{**} denote the transition from five to three and three to five solutions respectively (See Figure 3.2).

Appendix B is a listing of a program to compute an arc of limit points.

Table 3.1

	$\gamma=0$	$\gamma=5$	$\gamma=10$
ϕ_*(Varma)	0,0708	0,2694	0,62218
ϕ_*(Our Result)	0,0700	0,2702	0,62207
ϕ^*(Varma)	0,280536	0,45969	0,693
ϕ^*(Our Result)	0,2800	0,46065	0,683

Table 3.2

	$\gamma=5$	$\gamma=10$
ϕ_{**}(Varma)	0,301368	0,659677
ϕ_{**}(Our Result)	0,295312	0,65728
ϕ^{**}(Varma)	0,322784	0,681204
ϕ^{**}(Our Result)	0,31556	0,681

3.7 ONE-DIMENSIONAL MODEL WITH VARIABLE DISPERSION

In Section 1.4 the issue of boundary conditions was discussed. Dispersion is an input variable, since the depth of catalyst bed over which the dispersion still increases and the initial diffusion of the feedstream will differ for different systems. For numerical purposes we defined a dispersion function with a radical change from inlet to final steady-state dispersion and another one with a slight change. In both cases the bed-length of unsteady state dispersion was 20%. This will be unrealistic in a large number of cases, but the choice is only illustrative.

The dispersion term was defined as: (u = linear velocity)

$$\mathcal{D}(s) = \begin{cases} \chi\mathcal{D}_m + s(\mathcal{D}_{as} - \chi\mathcal{D}_m)/0.2 & 0 \leq s \leq 0.2 \\ \mathcal{D}_{as} & 0.2 \leq s \leq 1 \end{cases}$$

The orthogonal collocation method was suitable to solve this system of equations with the additional complication of a nonlinear Laplacian. In Figure 3.7 we used $\chi\mathcal{D}_m = 0{,}5$ and $\mathcal{D}_{as} = 0{,}6$ with $uL = 3$. (Appropriate units for uL and $\mathcal{D}_m$, $\mathcal{D}_{as}$ must be used to render Pe_{ms} dimensionless).

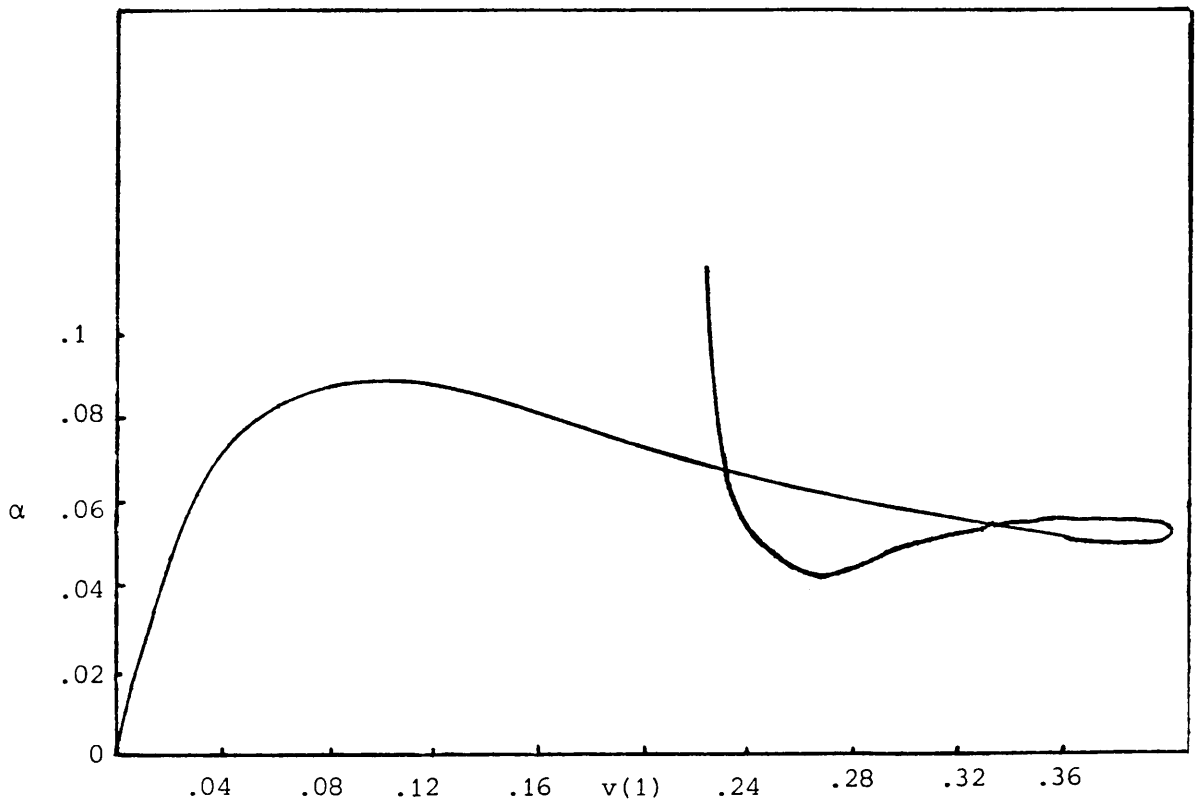

FIG. 3.7: Bifurcation Diagram for Slight Dispersion Variation

The diagram is similar to Figure 3.2 and for slight variations of the dispersion the behaviour is similar to the one-dimensional model. If $\chi\mathcal{D}_m$ = 0,1 and $\mathcal{D}_{as}$ = 0,6 (uL=3) we find totally different bifurcation behaviour. See Figure 3.8. The procedure broke down for (v(1),α) = (0.36297;0.00615). The multiplicity changes from one to two at α = 0,00615 and at α = 0.047934 four solutions exist until α = 0.0496717. For α > 0.088 no solutions could be found.

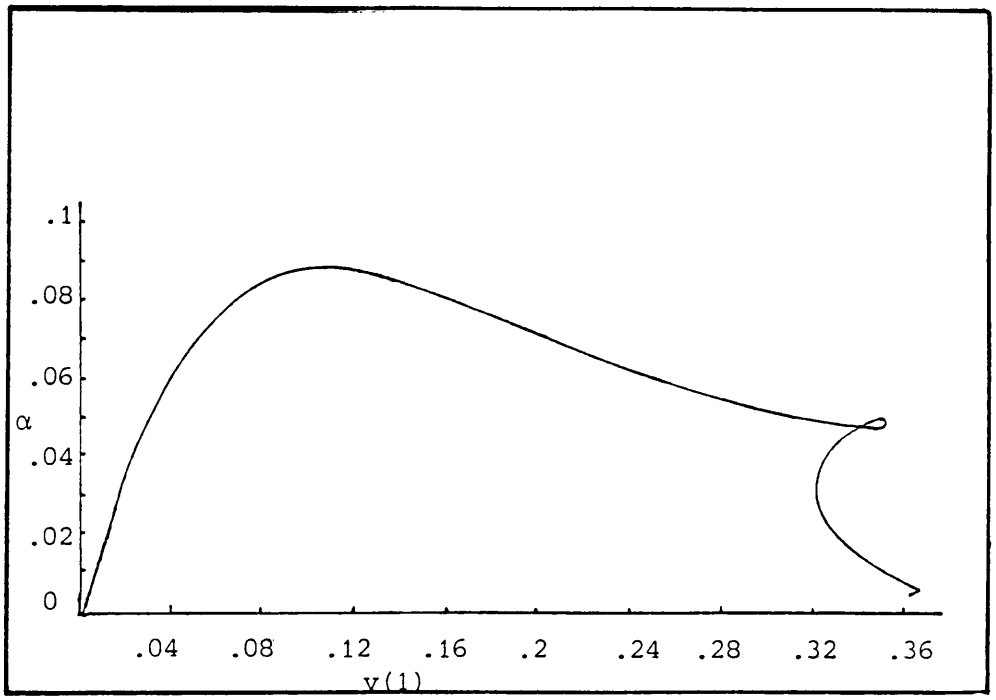

FIG. 3.8: Bifurcation Diagram for Drastic Dispersion Variation

The diagram is similar to the slight and non-variable dispersion case over the first part, i.e. $(v(1);\alpha) = (0;0) - (0{,}3388;0{,}048)$. The one-dimensional and the variable dispersion model will both correspond well with experimental results over this first part if the experiment approximates one-dimensional behaviour. For higher conversions in the experimental results, slight variations of the dispersion will also give good correspondence between the one-dimensional, the variational model and the experimental results. Deviations between the models and the experimental

results will occur for drastic dispersion variations. Unfortunately experimental results are limited and the true dispersion variation will not be known.

3.8 BIFURCATION-BEHAVIOUR OF THE TWO-DIMENSIONAL MODEL

The model equations were approximated in a way analogous to the one-dimensional equations. A double collocation procedure was used. The inlet conditions were assumed to be of the Danckwert-type. Actually a Bessel function describes the inlet axial condition correctly [83], but the approximate:

$$du/ds = Pe\ u$$

was used ($u = (w,v)$). The analysis of this problem will be very difficult and proofs of existence were not found in the literature. No published results on the numerical study of bifurcation were found either.

The orthogonal collocation method, was used. (See Appendix D). At higher values of Damköhler (Damköhler can be seen as an attenuation factor of the nonlinear term), the procedure fails to compute the steep conversion profiles accurately. We used symmetric polynomials in the radial direction which satisfied the boundary condition at $r = 0$ automatically. Three points in the radial and five points in the axial direction were used.

In Figure 3.9 only one solution was found over the range of Damköhler numbers. In Figure 3.10 the multiplicity changes from one to two but no higher multiplicity was found. In Figure 3.11 a maximum of three solutions was found.

This is in contrast with the one-dimensional model which has more complex bifurcation behaviour. At this stage we cannot attribute the simple bifurcation behaviour of the two-dimensional model to either the numerical procedure or an inherent property of the model itself. In all the cases only limit points were found. In the continuation process the solution arcs turned around when a point of no solution was reached and retraced the arc, although the arc-length parameter s was increased all the time.

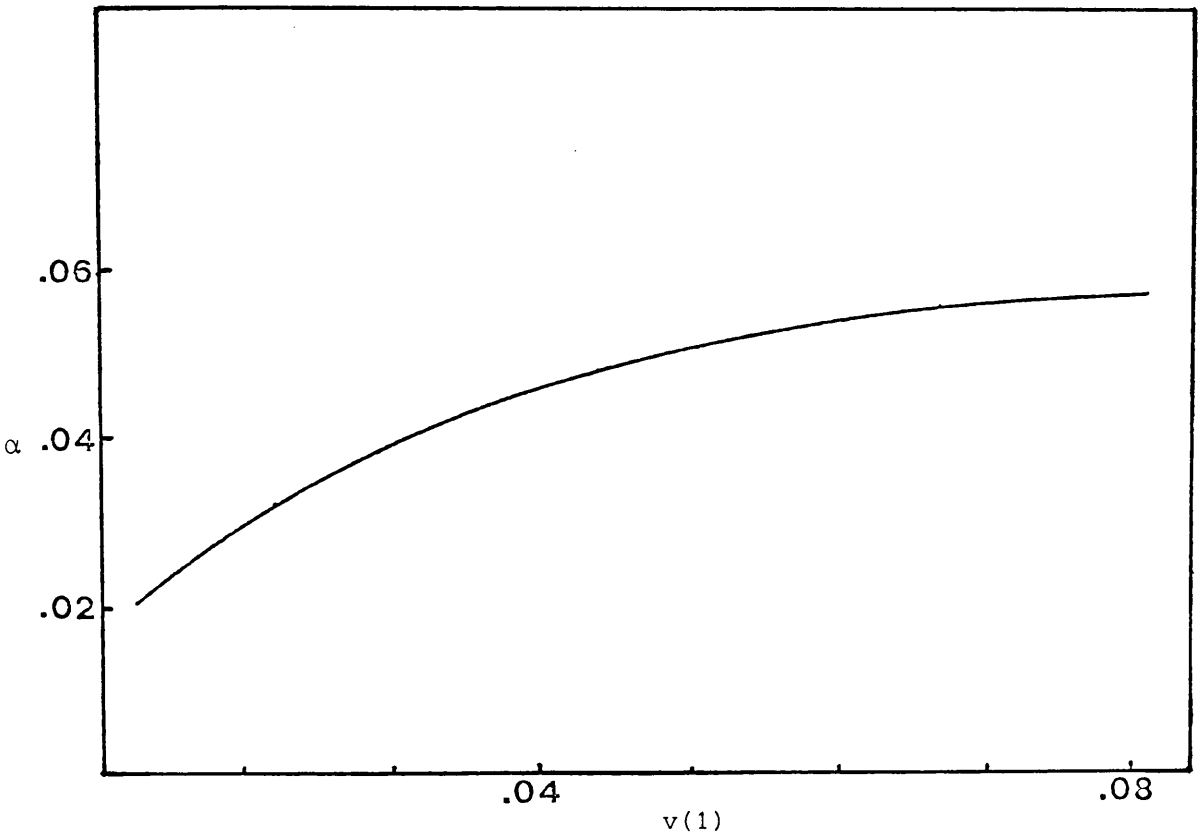

FIG. 3.9: Two-Dimensional Model- One Solution

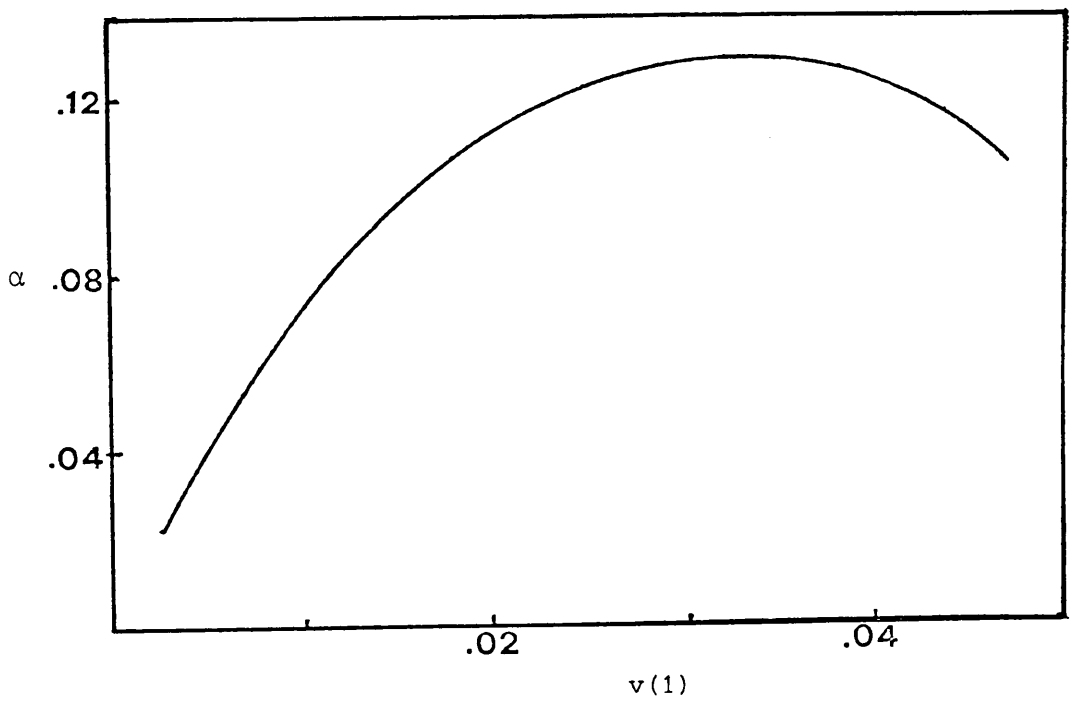

FIG. 3.10: Two-Dimensional Model-: One-Two Solutions

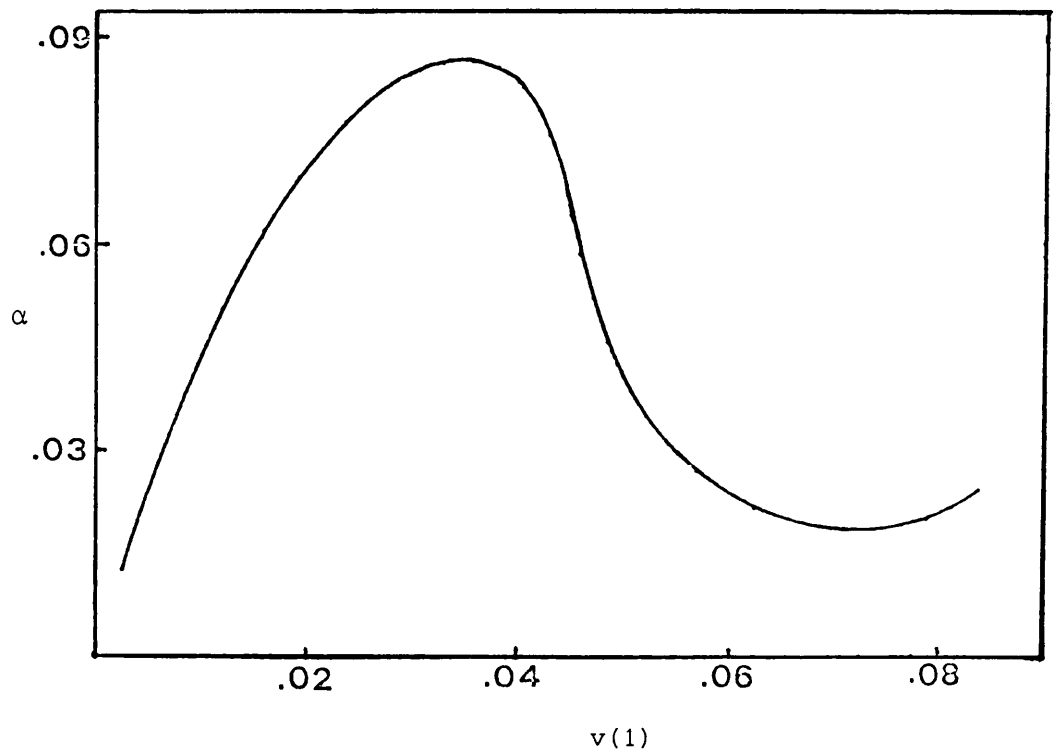

FIG. 3.11: Two-Dimensional Model-: One-Two-Three Solutions

3.9 REMARKS

The numerical procedures discussed in the previous sections are useful in the study of bifurcation behaviour. The validity of the results lies in a thorough study of the convergence properties of Powell's method using polynomial approximations. Weiss [79] studied the validity of a numerical approximation of the true bifurcation problem, Brezzi [108] studied the convergence properties of numerical methods for the computation of limit points and reported errors. To apply these results is not a simple task, and it is suggested that a more detailed study of the limit point approximations should be done.

A last aspect is the difference between a model's multiplicity and it's bifurcation behaviour. The existence of limit points are only sufficient conditions for multiplicity. Solution arcs which lie "independently" of the computed bifurcation curves, will not be discovered with the standard numerical procedure.

CHAPTER FOUR

PARAMETER SENSITIVITY

4.1 INTRODUCTION

Most reactors in practice are operated under steady state conditions. The whole process is controlled in such a way as to ensure either maximum yield [11,29,30] or profit. The effectiveness of the process will decrease if fluctuations occur in the product stream. Although minor fluctuations in the products will have less effect than large deviations, it is important to identify the origin of the fluctuations/variations and determine to what extent they will influence the product.

Parameter sensitivity describes the influence which operating variables have on the temperature and conversion profiles in the reactor. Operating variables are mostly the inlet concentration, inlet temperature and average velocity (flow speed). Inlet concentration is not always a control variable and it is important to know to what extent it will influence reactor performance.

If a reactor system is sensitive towards minor changes in the operating variables, it can be regarded as parameter sensitive. In [109] several criteria for parameter sensitivity are proposed.

Bilous and Amundson [see 89] have shown that the maximum temperature of a reactor may be very sensitive towards changes in the operating variables.

If the maximum temperature occurs within the reactor, (an internal maximum),this temperature is referred to as the "hot spot". Morbidelli and Varma [89] defined "run-away" as the occurrence of an inflexion point in the temperature versus conversion profile before the hot-spot.

The type of model plays an important role when parameter sensitivity is studied. Most authors [23,36,70,87,89,109] have concentrated on the one-dimensional plug-flow model and has linked parameter sensitivity to the existence of a positive second derivative prior to a local maximum in the temperature profile. In this chapter we shall give examples to point out the limitations of their conditions for sensitivity. The plug-flow model does not have multiple solutions since it is an initial value problem. Most authors base their choice of the plug-flow model on the fact that axial dispersion is negligible. Although Pe may be very large, the whole nature of the model changes when axial dispersion is considered since the boundary value problem can have multiple solutions. In Chapter 3 it was mentioned that the one-dimensional axial dispersion model has only limit point bifurcation. At the "first" limit point, (referring to the lower solution branch; see figure 4.3, ϕ^*) the temperature profile does not have a local maximum nor a positive second derivative for typical parameter values. But still, as $\phi \to \phi^*$ (ϕ^* the limit point value of ϕ), both

$$\sup \left|\frac{dw}{d\phi}\right| \quad \text{and} \quad \sup \left|\frac{dv}{d\phi}\right|$$

become large and are undefined at ϕ^*. If one keeps track of the smallest real part of the eigenvalues of the Jacobi matrix, a change from stable to unstable conditions occur as $\phi \to \phi^*$. The plug-flow model does not sense these parameter values as sensitive and is one of the main reasons why the axial dispersion model is used in this study of parameter sensitivity.

4.2 NECESSARY AND SUFFICIENT CONDITIONS FOR "RUN-AWAY"

It is convenient to check for run-away conditions without solving Problem B. In the derivation of these conditions for the one-dimensional axial dispersion model, the same criteria for "run-away" will be used as Dente & Collina. (see Section 1.3.5) In our analysis we shall need the following assumption, which is supported by numerical results:

v does not have a local minimum.

The first derivative of v(s) can be written as:

$$v'(s) = \int_s^1 e^{Pe_{hs}(s-t)}(\beta\phi g(w(t))e^{\delta v(t)/(1+v(t))}-\gamma v(t))dt.$$

If the right-hand-side is non-negative, (eg. $\gamma=0$), $v'(s)\geq 0$ for $s\ [0,1]$, hence $\gamma>0$ is a necessary condition for an internal maximum. If $v'(s_m)=0$, then $v'(s)\leq 0$ for $s_m\leq s\leq 1$ and $\beta\phi(g(w(s))e^{\delta v(s)/(1+v(s))}-\gamma v(s)$ will become negative at s_n, $s_m<s_n<1$.

The sufficient condition for an internal maximum is

C1: $\beta\phi g(w(1))e^{\delta v(1)/(1+v(1))}-\gamma v(1)<0$

Final conversion and outlet temperature can be measured and the existence of a local maximum temperature can be determined. If Condition C1 does not hold for $\gamma>0$, pseudo-adiabatic behaviour occurs and the maximum temperature is at the outlet. The evaluation of C1 plays an important role in the monitoring of the maximum reactor temperature.

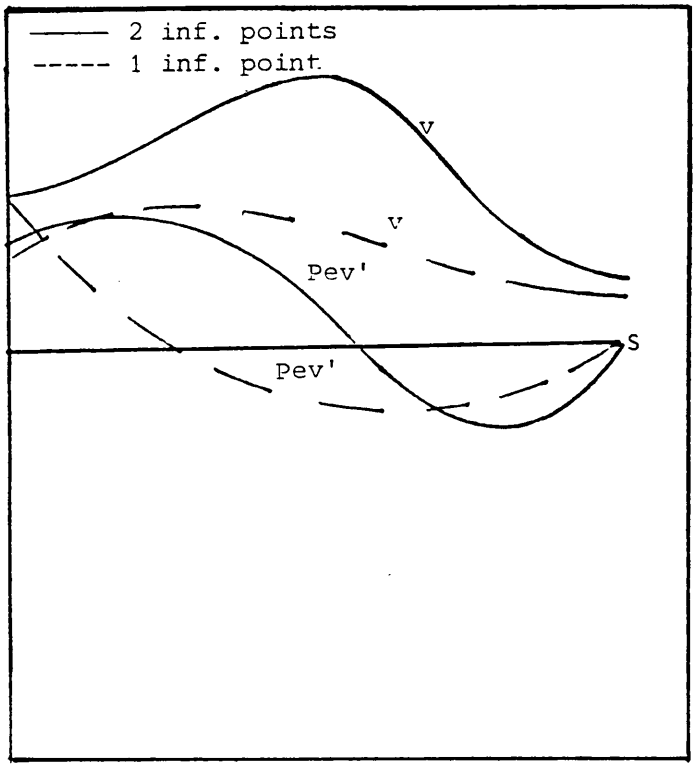

FIG. 4.1: Pe v'(s) and v(s)

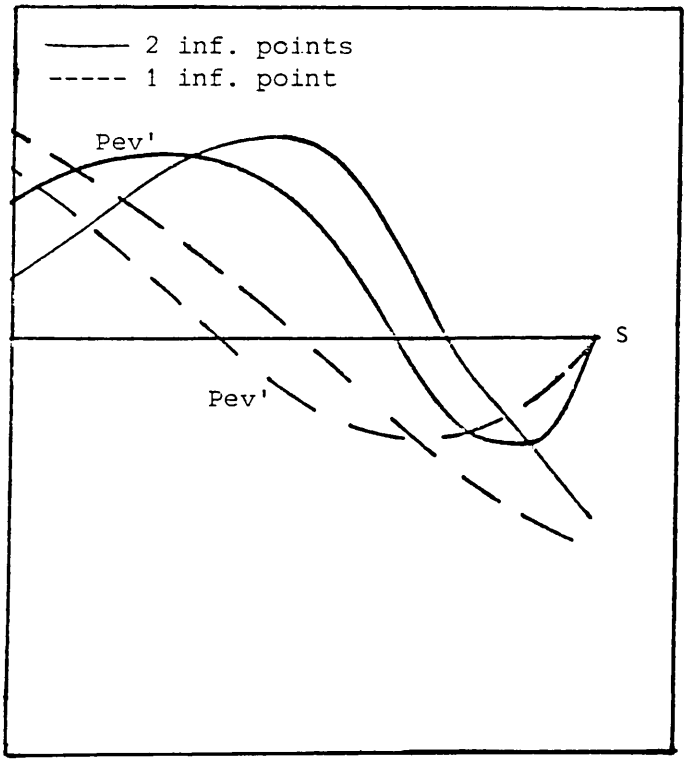

FIG. 4.2: $\beta\phi f(w(s),v(s))-\gamma v(s)$ and Pe v'(s)

A qualitative picture of v(s) and Pev'(s) is shown in Figure 4.1 for the case of a local maximum. Either one or two inflexion points exist. Note that we use Pe for Peclet number.

When $Pe_{hs}v'(s)$ reaches either a maximum or a minimum, v"(s)=0 and a qualitative picture of $Pe_{hs}v'(s)$ and $\beta\phi g(w(s))e^{\delta v(s)/(1+v(s))}-\gamma v(s)$ is shown in Figure 4.2. The full lines depict a typical parameter sensitive system, as defined by Dente & Collina. A sufficient condition for parameter sensitivity is v"(0)>0 and the existence of a local maximum in the temperature profile ("hot-spot").

C2: If C1 holds and $\beta\phi g(w(0))e^{\delta v(0)/(1+v(0))}-\gamma v(0)) < Pe_{hs}{}^2 v(0)$,

the system is parameter sensitive.

Therefore the measuring of inlet and outlet temperatures and concentrations is sufficient to detect parameter sensitivity conditions.

4.3 A NEW NORM OF PARAMETER SENSITIVITY

We shall propose a new norm of parameter sensitivity in this section.

As in Section 3.2 one can write Problem B in the form:

$$G(w(s),v(s),\phi(s)) = 0$$

Let $h(\phi) = \sup \left| \frac{dv}{d\phi} \right|$

As long as G_u is non-singular, $h(\phi)$ is uniquely defined and gives a clear picture of the influence of a parameter (or operating variable) on the solution. In the rest of this chapter we shall use this norm of parameter sensitivity, since most authors concentrate on the sensitivity of the temperature profile.

This norm is the first which relates sensitivity to the limit points. In the construction of the bifurcation diagram, $h(\phi)$ is calculated and will indicate sensitive regions easily. For ϕ close to the limit point values, the numerical calculation of $h(\phi)$ is omitted.

The discretized version of the two-dimensional model and the variable dispersion model can be easily analyzed by this method, while analytical conditions will be difficult to derive for them and usually give conservative operating limits.

4.4 RESULTS

In this section we shall compare different criteria as a function of ϕ. The approach of Adler & Emig [109] was omitted since the numerical calculation of v" was too inaccurate for the one-dimensional dispersion model.

We also calculated $h(\phi)$ for the two-dimensional model and the results can be regarded as the first attempt to quantify parametric sensitivity for the two-dimensional axial dispersion model.

We give the bifurcation diagram with the parametric sensitivity results to show the relation between sensitive regions and regions of multiple solutions.

4.4.1 One-Dimensional Model

In Figure 4.3 the bifurcation diagram for $Pe=Pe_{ms}=Pe_{hs}=5$, $\gamma=5$, $\delta=25$, $\beta=0,5$ as a function of ϕ, is shown for a first order reaction. $h(\phi)$ is shown in Figure 4.4 in conjunction with the analytical result (Condition C2). The values of v(s) and w(s) were used to test for Condition C2 and the value of

$$B(\phi)=Pe^2v(0)-\beta\phi(1-w(0))e^{\delta v(0)/(1+v(0))}+\gamma v(0)$$

was registered.

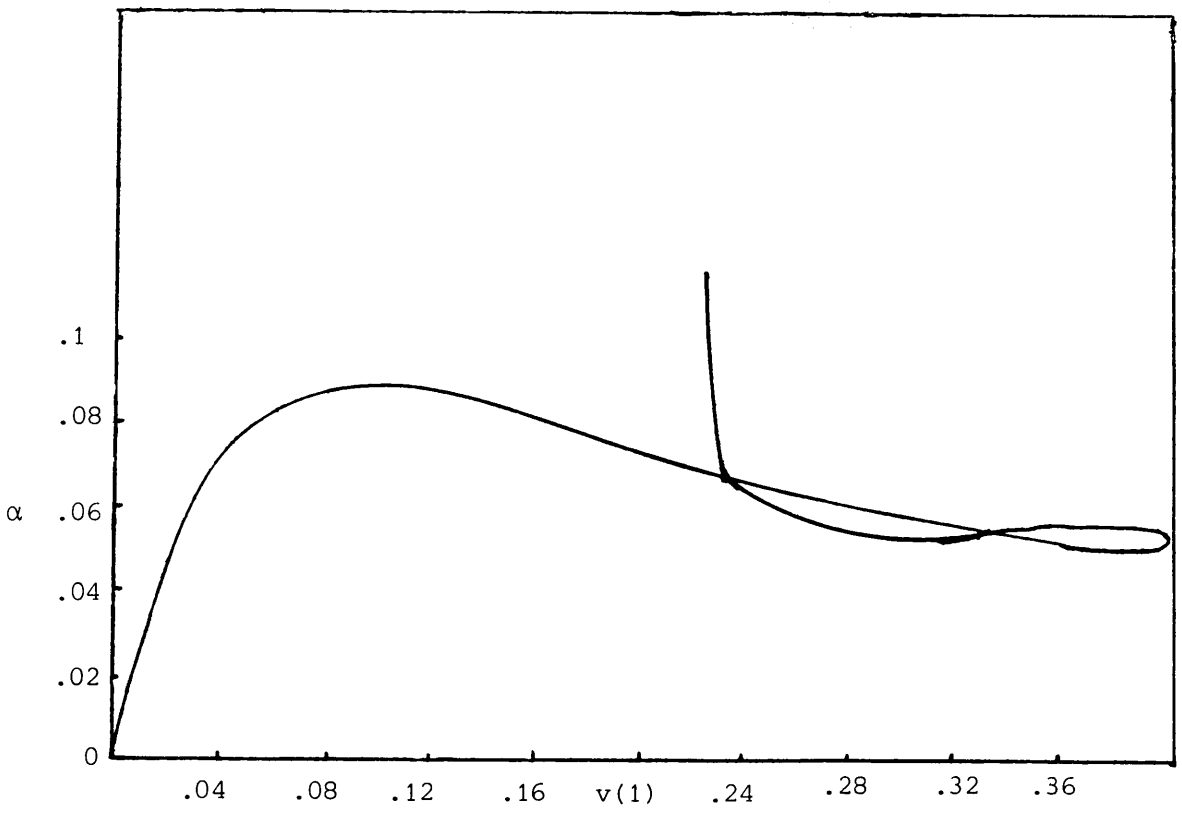

FIG. 4.3: Bifurcation Diagram

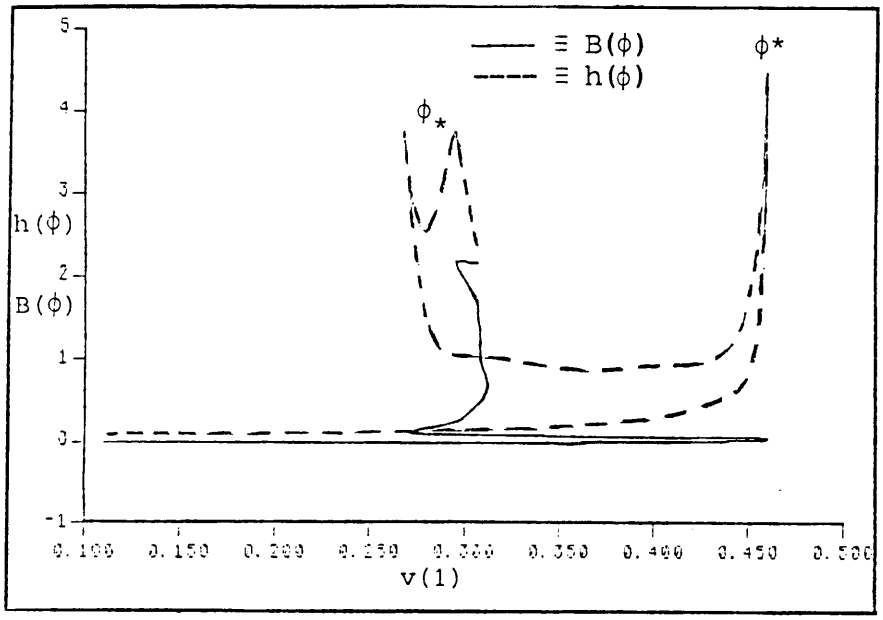

FIG. 4.4: h(ϕ) and the Analytical Result B(ϕ)

At $\phi=\phi^*$ (ϕ=0.459) h(ϕ) becomes infinite which indicates a very sensitive situation but the analytical criterium (B(ϕ)) does not sense it, since $v''(s)<0$ for all $s\in[0,1]$. At all the other limit points both h(ϕ) and B(ϕ) indicate parameter sensitivity.

4.4.2 Two-Dimensional Model

The sensitivity diagram of Figure 4.5 was constructed for the same set of parameters as the bifurcation diagram of Figure 3.9. In Figure 3.9 a limit point is approached as ϕ increases and the increase in h(ϕ) reflects of this behaviour.

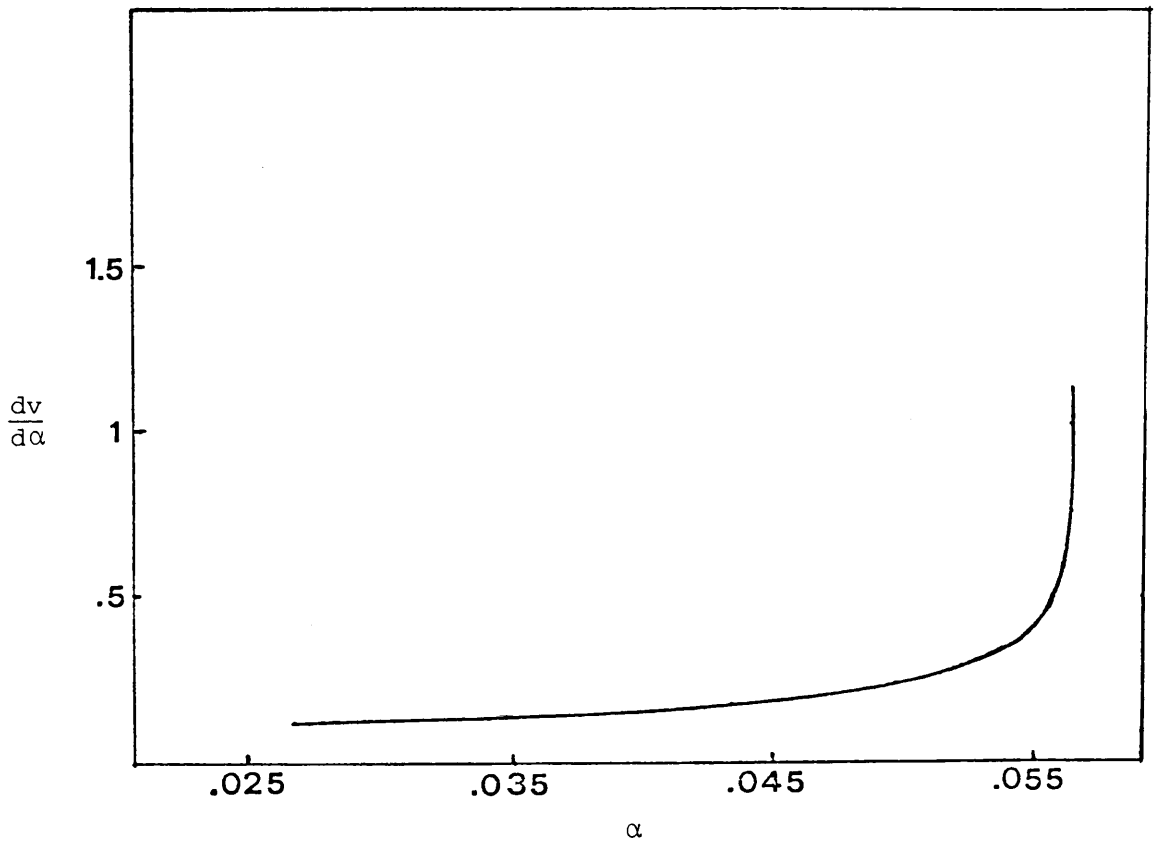

FIG. 4.5: Sensitivity Diagram For One Solution

The sensitivity diagrams in Figure 4.6 and Figure 4.7 correspond with the bifurcation diagrams of Figure 3.10 and Figure 3.11 respectively. Note that we plotted $\frac{dv}{d\alpha}$ and not $h(\phi)$ to point out the change in sign of $\frac{dv}{d\alpha}$ once $\phi > \phi^*$.

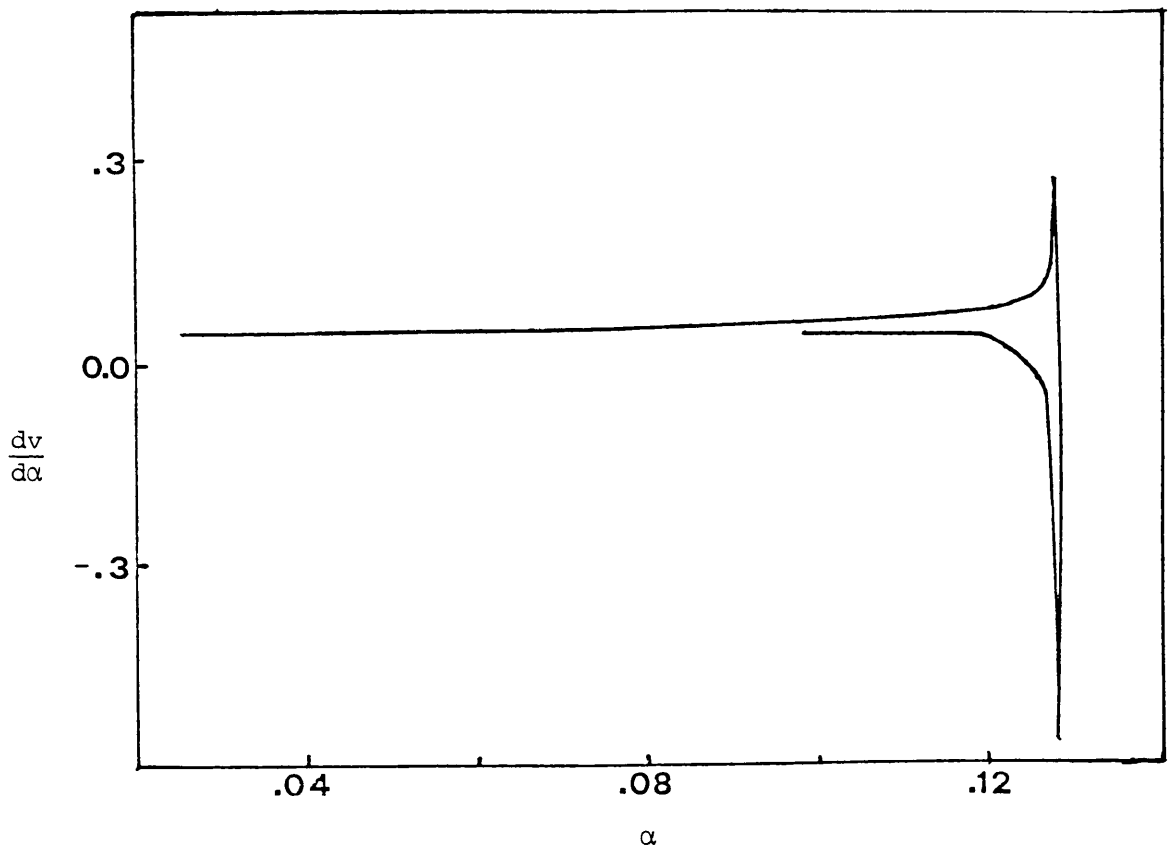

FIG. 4.6: Sensitivity Diagram For Two Solutions

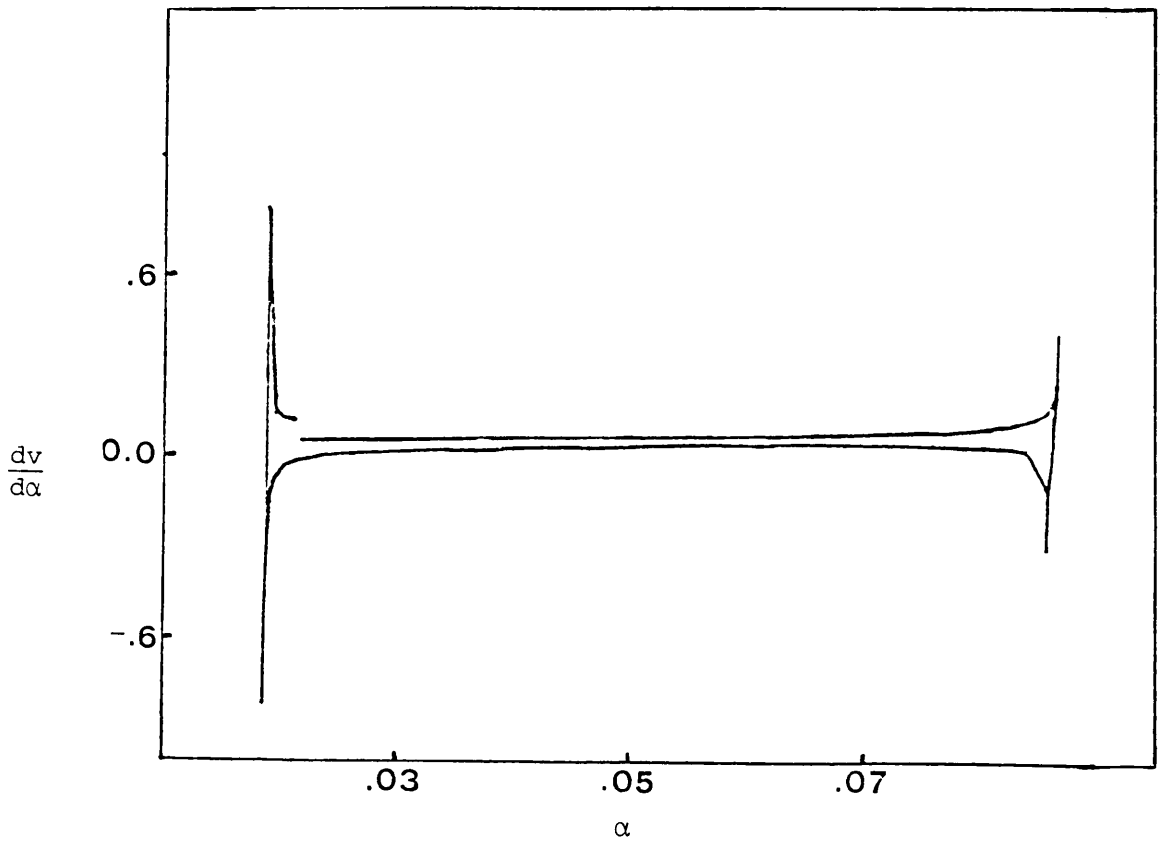

FIG. 4.7: Sensitivity Diagram For Three Solutions

4.5 DISCUSSION

At this stage no absolute definition for parameter sensitivity has been formulated. A-priori criteria are limited by the complexity of the model and the conservative limits it prescribes on operating variables. In the light of these facts, as well as the availability of high-speed computers, we strongly recommend a numerical approach towards parameter sensitivity. The results of Figure 4.4 - Figure 4.7 illustrate this approach. Neatly defined regions seperate the areas of sensitivity and non-sensitivity. These diagrams represent the effect of one variable on another and do not confuse one with the maze of other definitions and approaches.

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APPENDIX A

A listing of a Fortran program to compute bifurcation diagrams and do sensitivity checks.

FILE: KELS FORTRAN A1 UNIVERSITEIT VAN PRETORIA

```
C       THE CONSTRUCTION OF BIFURCATION CURVES FOR BOUNDARY VALUE PROB.
C       USING KELLER'S S-METHOD WITH SPLINES AND ORTHOGONAL COLLOCATIO
C       THE ALGEBRAIC EQUATIONS ARE SOLVED BY POWELLS METHOD
        INTEGER NSIG,NCOL,NE,N,ITMAX,IER,K,C,L,M,KC,ID,EL,IP,DJ,DI
C       NE = NUMBER OF ELEMENTS;NCOL=NUMBER OF COL.POINTS IN AN ELEMEN
C       N = SUM(NCOL-(NE-1))
C       M = N*(3*N+15)/2 ;WK(M):C = N-1;L = C/2 ; K = L/2.
        REAL X(33),WK(1881),PAR(105),FNORM,FFIN,DS
        REAL DC,AE,WV,CH,CH3,VE1,VE2,VE3,CH2,CH1
        DIMENSION DV(16),WV1(16)
        DIMENSION DIF1(20),DIF2(20),DIF3(20),VECT(20),DV2(16)
        DIMENSION ROOT(20),Y(300),Z(300),B(4,4),A(4,4)
        EXTERNAL FCN,POLI,DFOPR
        NSIG = 4
        NE = 5
        N = 33
        ITMAX = 100
        VE1 = C.
C       PAR(35) = BETA -DIMENSIONLESS ADIABATIC TEMPERATURE RISE
C       PAR(36) = DELTA-DIMENSIONLESS ACTIVATION ENERGY
C       PAR(37) = GAMMA-DIMENSIONLESS HEAT TRANSFER
C       PAR(38) = PECLET NUMBER : ONLY LE = 1 IS CONSIDERED.
C       X(1)-X(K) IS CONVERSION ;X(K+1)-X(L) IS TEMPERATURE.
C       PAR(34) = FUNCTIONAL; TO CALCULATE A(I,J) AND(B(I,J) ONLY ONCE.
C       PAR(39) = FUNCTIONAL TO DISTINGUISH BETWEEN CONVERSION AND TEM
C       ERATURE CALCULATIONS AND THEIR DERIVATIVES W.R.T. S.
        IEL  = C
        PAR(35)=0.5
        PAR(37) = 0.00
        PAR(34) = 1
        PAR(38) = 5.0
        PAR(36) = 25
C       SO = INITIAL VALUE OF STEPPING PARAMETER AND FFIN THE TERMINAL
C       VALUE. PAR(73) = INCREMENT IN STEPPING PARAMETER.
        FFIN = 0.4
        SO = 0.00
        PAR(73) = 0.015
        DS = PAR(73)
C       PAR(1) - PAR(16) IS CONVERSION; PAR(17) - PAR(32) IS TEMPERATU
C       PAR(34)-PAR(39) ARE OPERATING VARIABLES . PAR(33) = PI.
        PAR(33) = 0.2807e005
C       ************************************************************
C       READ INITIAL X(I)
C       ************************************************************
        PAR(39) = 1.
        S = SO
        CALL ZSPOW (FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
C       X(1)-X(16) = DX/DS; X(17)-X(32) IS DT/DS; X(33) IS D(FI)/DS.
   50   S = S+PAR(73)
        DO 20 I = 1,N
        PAR(I+39) = X(I)
        X(I) = PAR(I)
   20   CONTINUE
        PAR(39) = 2
        CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
```

```
C       ************************************************************
C       NEXT IS SEVERAL PAR. SENSITIVITY TESTS
C       ************************************************************
        NCOL = 4
        KO = NCOL-2
        CALL POLI (NCOL,KO,DIF1,DIF2,DIF3,ROOT,PAR)
        DO 949 EL = 1,KO
        DO 949 I = 1,NCOL
        CALL DFOPR (NCOL,I,EL,DIF1,DIF2,DIF3,ROOT,VECT)
        DO 949 J = 1,NCOL
        IF (EL.EQ.1) GO TO 958
        IF (EL.EQ.2) GO TO 959
  958   A(I,J) = VECT(J)
        GO TO 949
  959   B(I,J) = VECT(J)
  949   CONTINUE
        DO 951 EL = 1,NE
        DO 951 I = 1,NCOL
        DI = (EL-1)*3 + I
        DO 951 J = 1,4
        DJ = (EL-1)*3+J
        DV(DI) = A(I,J)*X(DJ)
        DV2(DI) = B(I,J)*X(DJ)
  951   CONTINUE
C       ************************************************************
C       DC = DENTE & COLLINA'S APPROACH
C       ************************************************************
        DC = 0.
        HV = 0.
C       DO 903 I = 1,15
C 903   DC1(I) = X(I+17)-X(I+16)
        DO 21 I = 1,16
        IF (DV2(I).GE.DC.AND.DV(I).GT.0.) DC = DV2(I)
   21   CONTINUE
        CH=ABS(X(33)-PAR(33))
        CH2 = (X(33)-PAR(33))
        IF (CH.LE.0.001.AND.X(33).GE.PAR(33)) CH2= 0.001
        IF (CH.LE.0.001.AND.X(33).LT.PAR(33)) CH2= -0.001
C       ************************************************************
C       HV = MAX((TEMP(S+DS)-TEMP(S))/((FI(S+DS)-FI(S))
C       ************************************************************
        DO 889 I = 1,16
        HV1(I)=ABS((X(I+16)-PAR(I+16))/CH2)
        IF (HV1(I).GE.HV) HV = HV1(I)
  889   CONTINUE
        CH3 = ABS(PAR(72))
        IF (CH3.LE.0.0001) CH3 = 0.0001
        VE2=ABS(PAR(71)/CH3)
C       ************************************************************
C       VE3 = ANALYTICAL RESULT; SEE CHAPTER 4
C       ************************************************************
        VE3=PAR(38)*PAR(38)*X(17)-PAR(35)*X(33)*(1.-X(1))*
     &  EXP(PAR(36)*X(17)/(1.+X(17)))+PAR(37)*X(17)
C       CH3 =(X(33)+PAR(33))/2.
C       CH4 = (X(32)+PAR(32))/2.
```

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```
      PAR(81)=PAR(81)*5.-X(33)*0.5*(1.-X(1))*EXP(25.*X(17)/(1.+X(17
     &+5.*X(17)
C     DO 782 I = 1,10
C     IT = 80 +I
      WRITE (1,22) X(33),VE3,HV,DC,VE2
   22 FORMAT (5F12.6,2X)
C 782 CONTINUE
      IF (S.GE.FFIN) GOTO 9000
      IF (IER.EQ.131) PAR(73) = PAR(73)-0.001
   40 DO 28 I = 1,N
      PAR(I) = X(I)
   28 X(I) = PAR(I+39)
      PAR (39) = 1
      CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,X,FNORM,AK,IER)
      GOTO 50
 9000 DO 26 I = 1,N
      WRITE (1,873) X(I)
  873 FORMAT (F12.8)
   26 CONTINUE
      STOP
      END
C     ************************************************************
C     IN THIS ROUTINE ARE THE NONLINEAR  EQUATIONS .
C     ************************************************************
      SUBROUTINE FCN (X,F,N,PAR)
      INTEGER L,K,M,N,KO,NE,O,OJ,DI,DJ,EL,EM,NCOL,KF,IT
      REAL X(N),F(N),PAR(105),THETA,DA
      DIMENSION DIF1(20),DIF2(20),VECT(20),DIF3(20),ROOT(20)
      DIMENSION A(10,10) ,B(10,10),HK(5)
      KF = (N-1)/2
      NE = 5
      OJ = NE-1
      K = (N-1)/2
      O = N-1
      KO = K-2
      HK(1)=1./0.2
      HK(2)=1./0.2
      HK(3)=1./0.2
      HK(4)=1./0.2
      HK(5)=1./0.2
      NCOL= 4
      M = NCOL-2
      EM = NCOL-1
      PAR(36) = 25.
      PAR(37) = 0.0
      PAR(38) =  5.00
      PAR(35) = 0.5
      PAR(101)=0.0
      PAR(102)=0.00
      PAR(103)=3.
      PAR(105)= PAR(103)/PAR(101)
      THETA = 0.7
      DO 15 I = 1,KF
      IT = 60+I
   15 PAR(IT) = 0.
```

```
      IF (PAR(34).GE.2.) GO TO 99
      GO TO 498
   99 DO 1 I = 1,N
    1 F(I) = 0.
      IF (PAR(39).GE.2.) GO TO 17
      GO TO 222
   17 DO 2 J = 1,NCOL
      PAR(81) = PAR(81)+HK(1)*HK(1)*B(1,J)*X(J+KF)
      F(1) = F(1)+HK(1)*A(1,J)*X(J)
      PAR(81)=F(1)
    2 F(1+KF)=F(1+KF)+HK(1)*A(1,J)*X(J+KF)
      F(1) =F(1)-PAR(105)*X(1)
      F(1+KF) = F(1+KF)-PAR(38)*X(1+KF)
      DO 3 EL = 1,NE
      DO 3 DI = 2,EM
      DO 4 DJ= 1,NCOL
      I = (EL-1)*(M+1)+DI
      IF (EL.EQ.1) DA = PAR(101) + ROOT(I)*PAR(102)
      IF (EL.GT.1) DA = PAR(101) + PAR(102)
      PAR(104) = DA/PAR(103)
      PAR(104) = 5.
      J = (EL-1)*(M+1)+DJ
      IT = 80+I
      PAR(IT)=PAR(IT)+HK(EL)*HK(EL)*B(DI,DJ)*X(J+KF)
      F(I)=F(I)+(HK(EL)*HK(EL)*B(DI,DJ)-HK(EL)*A(DI,DJ)*PAR(104))*X(J
    4 F(I+KF)=F(I+KF)+(HK(EL)*HK(EL)*B(DI,DJ)-HK(EL)*A(DI,DJ)*PAR(104
     & *X(J+KF)
      F(1) = F(I)+X(N)*(1.-X(I))*EXP(PAR(36)*X(I+KF)/(1.+X(I+KF)))
    3 F(I+KF)=PAR(35)*X(N)*(1.-X(I))*EXP(PAR(36)*X(I+KF)/(1.+X(I+KF))
     & -PAR(37)*X(I+KF)*F(I+KF)
C     ************************************************************
C     CONTINUITY AT NODES FOLLOWS NOW.
C     ************************************************************
      DO 5 EL = 1,OJ
      DO 5 DJ = 1,NCOL
      I = (EL-1)*(M+1)+NCOL
      J =(EL-1)*(M+1)+DJ
      L =EL*(M+1)+DJ
      IT = 80+I
      PAR(IT)=PAR(IT)+(HK(EL)*HK(EL)*B(4,DJ)*X(J+KF)+HK(EL+1)*HK(EL+1
     & *B(1,DJ)*X(L+KF))/2.
      F(I)= F(I)+HK(EL)*A(NCOL,DJ)*X(J)-HK(EL+1)*A(1,DJ)*X(L)
    5 F(I+KF)=F(I+KF)+HK(EL)*A(NCOL,DJ)*X(J+KF)-HK(EL+1)*A(1,DJ)*
     & X(L+KF)
C     ************************************************************
C     NOW FOLLOWS THE BOUNDARY CONDITION AT S = 1.
C     ************************************************************
      DO 6 DJ = 1,NCOL
      I = (NE-1)*(M+1)+NCOL
      J = (NE-1)*(M+1)+DJ
      IT = 1+80
      PAR(IT)=PAR(IT)+HK(NE)*HK(NE)*B(4,DJ)*X(J+KF)
      F(I) = F(I)+HK(NE)*A(NCOL,DJ)*X(J)
    6 F(I+KF)=F(I+KF)+HK(NE)*A(NCOL,DJ)*X(J+KF)
      DO 9 I = 1,3
```

```
    9   F(N) = F(N) + THETA*PAR(I+39)*(X(I)-PAR(I))
        F(N) = F(N)+(1.-THETA)*(X(N)-PAR(35))*PAR(M+39)-PAR(75)
        GO TO 500
C       ***********************************************************
C       NOW FOLLOWS THE  DERIVATIVES W.R.T. S
C       ***********************************************************
  222   DO 223 EL = 1,NE
        DO 223 DI = 2,EM
        DO 224 DJ = 1,NCOL
        I = (EL-1)*(M+1)+DI
        IF (EL.EQ.1)  DA = PAR(101)+ROOT(I)*PAR(102)
        IF (EL.GT.1)  DA = PAR(101)+PAR(102)
        PAR(104) = DA/PAR(103)
        PAR(104) = 0.
        J = (EL-1)*(M+1)+DJ
        F(I) = (HK(EL)*HK(EL)*B(DI,DJ)-HK(EL)*A(DI,DJ)*PAR(104))*X(J)+F(
  224   F(I+KF) = (HK(EL)*HK(EL)*B(DI,DJ)-HK(EL)*A(DI,DJ)*PAR(104))
     &  *X(J+KF)  +F(I+K)
        F(I) = F(I)+PAR(35)*PAR(36)*(1.-PAR(I))*EXP(PAR(36)*PAR(I+KF)/(
     &  1.+PAR(I+KF)))/((1.+PAR(I+KF))*(1.+PAR(I+KF)))*X(I+KF)-X(35)*
     &  EXP(PAR(36)*PAR(I+KF)/(1.+PAR(I+KF)))*X(I)+(1.-PAR(I))*
     &  EXP(PAR(36)*PAR(I+KF)/(1.+PAR(I+KF)))*X(N)
  223 F(I+KF) = F(I+KF)+(PAR(33)*PAR(35)*(1.-PAR(I))*EXP(PAR(36)*PAR(I+
     &  /(1.+PAR(I+KF)))/((1.+PAR(I+KF))*(1.+PAR(I+KF)))*PAR(36)-PAR(3
     &  *X(I+KF)-PAR(35)*PAR(35)*EXP(PAR(36)*PAR(I+KF)/(1.+PAR(I+KF)))
     &  *X(I)+(1.-PAR(I))*EXP(PAR(36)*PAR(I+KF)/(1.+PAR(I+KF)))
     &  *PAR(35)*X(N)
C       ***********************************************************
C       NOW FOLLOWS THE CONTINUOUS CONDITIONS.
C       ***********************************************************
        DO 225 EL = 1,OJ
        DO 225 DJ = 1,NCOL
        I = (EL-1)*(M+1)+NCOL
        J = (EL-1)*(M+1)+DJ
        L = EL*(M+1)+DJ
        F(I) = F(I)+HK(EL)*A(NCOL,DJ)*X(J)-HK(EL+1)*A(1,DJ)*X(L)
  225   F(I+KF) = F(I+KF)+HK(EL)*A(NCOL,DJ)*X(J+KF)-HK(EL+1)*A(1,DJ)*X(L+
C       ***********************************************************
C       NOW FOLLOWS THE BOUNDARY CONDITION AT S = 0.
C       ***********************************************************
        DO 226 J = 1,NCOL
        F(1) = F(1)+HK(1)*A(1,J)*X(J)
  226   F(1+KF) = F(1+KF)+HK(1)*A(1,J)*X(J+KF)
        F(1) = F(1)-PAR(105)*X(1)
        F(1+KF) = F(1+KF)-PAR(38)*X(1+KF)
C       ***********************************************************
C       NOW FOLLOWS THE BOUNDARY CONDITIONS AT S = 1
C       ***********************************************************
        I = (NE-1)*(M+1)+NCOL
        DO 227 DJ = 1,NCOL
        J = (NE-1)*(M+1)+DJ
        F(I) = F(I)+HK(NE)*A(NCOL,DJ)*X(J)
  227   F(I+KF) = F(I+KF)+HK(NE)*A(NCOL,DJ)*X(J)
        DO 228 I = 1,O
  228   F(N) = F(N)+THETA*X(I)*X(I)
```

```
      F(N) = F(N) + (1.-TJETA)*X(N)*X(N)-1.
      GO TO 500
  498 K = NCOL
      CALL POLI (K,KO,DIF1,DIF2,DIF3,ROOT,PAR)
      DO 130 ID= 1,2
      DO 130 I = 1,K
      CALL DFOPR (K,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
      DO 130 J = 1,K
      IF (ID.EQ.1) GO TO 198
      IF (ID.EQ.2) GO TO 199
  198 A(I,J) = VECT(J)
      GO TO 130
  199 B(I,J) = VECT(J)
  130 CONTINUE
      PAR(34)= 2.
      GO TO 99
  500 RETURN
      END
C
C     SUBROUTINE POLI : CALCULATES THE COLLOCATION POINTS .
C
      SUBROUTINE POLI(K,KO,DIF1,DIF2,DIF3,ROOT,PAR)
      DIMENSION DIF1(9),DIF2(9),DIF3(9),ROOT(9),PAR(100)
      INTEGER KO
      REAL AB,AD,AP,AL,BE,P,PN,PN1,PD,PD1,PP,PP1,Z1,Z0,Z
      KO = K-2
      AL = 0.
      BE = 0.
      AB = AL+BE
      AD =BE-AL
      AP = BE*AL
      DIF1(1) = (AD/(AB+2.)+1.)/2.
      DIF2(1) = 0.
      IF (KO.LT.2 ) GO TO 215
      DO 210 I = 2,KO
      Z1=I-1
      Z = AB+2*Z1
      DIF1(I) = (AB*AD/Z/(Z+2.)+1.)/2.
      IF (I.NE.2 ) GO TO 211
      DIF2(1) = (AB+AP+Z1)/Z/Z/(Z+1.)
      GO TO 210
  211 Z = Z*Z
      Y =Z1*(AB+Z1)
      Y = Y*(AP+Y)
      DIF2(I)=Y/Z/(Z-1.)
  210 CONTINUE
  215 P = 0.
      DO  220 I = 1,KO
  225 PD = 0.
      PN = 1.
      PD1 = 0.
      PN1 = 0.
      DO 230 J = 1,KO
      PP = (DIF1(J)-P)*PN-DIF2(J)*PD
      PP1 = (DIF1(J)-P)*PN1-DIF2(J)*PD1-PN
```

```
      PD = PN
      PD1 = PN1
      PN = PP
  230 PN1 = PP1
      ZO = 1.
      Z = PN/PN1
      IF (I.EQ.1 ) GO TO 221
      DO 222 J = 2,I
  222 ZO = ZO-Z/(P-ROOT(J-1))
  221 Z = Z/ZO
      P = P-Z
      IF (ABS(Z).GT.0.0000001) GO TO 220
      ROOT(I)= P
      P = P+ 0.0001
  220 CONTINUE
      DO 231 I = 1,KO
      J = KO+1-I
  231 ROOT(J+1) = ROOT(J)
      ROOT(1) = 0.
  235 ROOT (K) = 1.
  333 DO 240 I = 1,K
      P = ROOT(I)
      DIF1(I) = 1.
      DIF2(I) = 0.
      DIF3(I) = 0.
      DO 240 J = 1,K
      IF (J.EQ.I) GO TO 240
      Y = P-ROOT(J)
      DIF3(I)=Y*DIF3(I)+3.*DIF2(I)
      DIF2(I) =Y*DIF2(I) + 2.*DIF1(I)
      DIF1(I) = Y*DIF1(I)
  240 CONTINUE
  241 RETURN
      END
C
C     SUBROUTINE DFOPR . CALCULATES THE FIRST AND SECOND DERIVATIVES
C     APPROXIMATES .
      SUBROUTINE DFOPR (K,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
      DIMENSION VECT(9),ROOT(9),DIF1(9),DIF2(9),DIF3(9)
      REAL AX
      DO 320 J = 1,K
      IF (J.NE.I) GO TO 321
      IF (ID.NE.1) GO TO 305
      VECT(I) = DIF2(I)/DIF1(I)/2.
      GO TO 320
  305 VECT(I) = DIF3(I)/DIF1(I)/3.
      GO TO 320
  321 Y = ROOT(I)-ROOT(J)
      VECT(J) = DIF1(I)/DIF1(J)/Y
      IF (ID.EQ.2 ) VECT(J) = VECT(J)*(DIF2(I)/DIF1(I)-2./Y)
  320 CONTINUE
      GO TO 350
  310 Y = 0.
      DO 325 J = 1,K
      P = ROOT(J)
```

```
      AX = P*(1.-P)
      VECT(J) = AX/DIF1(J)**2
  325 Y = Y + VECT(J)
      DO 350 J = 1,K
  360 VECT(J) = VECT(J)/Y
  350 RETURN
      END
```

APPENDIX B

A listing of a FORTRAN program to compute an arc of limit points.

FILE: EXA FORTRAN A1 UNIVERSITEIT VAN PRETORIA

```
C       THE SOLUTION OF NONLINEAR ALGEBRAIC EQUATIONS
C       STEPPING ALONG A BIFURCATION CURVE USING COLLOCATION ON SPLINE
        INTEGER NSIG,N,EL,ITMAX,IER,K,O,L,M,KO,ID,INDIK
        INTEGER NCOL,MCOL,OR,EL,DI,DJ,NE
C       NSIG,ITMAX ARE INPUT FOR IMSL SUBROUTINE ZSPOW (SEE IMSL
C       MANUAL)
C       N = 13 POINTS FOR CONVERSION,13 FOR TEMPERATURE,1 FOR DAMKOHLER
C       PLUS 26 FOR THE JACOBIAN
C       NE = NUMBER OF ELEMENTS
C       NCOL = 2+ NUMBER OF INTERNAL COLLOCATION POINTS PER ELEMENT
C       INDIK : THE INDIK'TH X-VALUE IS SET TO 1. ( SEE SEIDEL IN REFE
C       RENCE )
        NSIG = 4
        ITMAX = 100
        N = 53
        REAL DEL,X(53),*K(4611),PAR(53),FNORM
        DIMENSION A(9,9),B(9,9),VECT(9),DIF1(9),DIF2(9),DIF3(9),ROOT(9,
        DIMENSION W(26),*KAREA(26)
        EXTERNAL FCN,POLI,DFOPR
C       PAR(4) = BETA-DIMENSIONLESS HEAT OF REACTION
C       PAR(5) = DELTA-DIMENSIONLESS ACTIVATION ENERGY
C       PAR(6) = GAMMA- HEAT TRANSFER COEFFICIENT
C       PAR(7) = PECLET NUMBER: ONLY LE = 1 IS CONSIDERED
C       X(N)   = FI:-DAMKOHLER*PECLET
C       X(1)-X(K) IS CONVERSION ;X(K+1)-X(L) IS TEMPERATURE.
C       ANY ONE OF THESE PAR(I) CAN BE USED AS INDEPENDENT VARIABLE.
        PAR(4) = 0.3
        PAR(5) =25.0
        PAR(6) = 5.0
        PAR(7) =  5.00
        PAR(8) = 1.0
C       ***************************************************************
C       READ INITIAL VALUES FOR X(I)
C       ***************************************************************
   66   CALL ZSPOW (FCN,NSIG,N,ITMAX,PAR,X,FNORM,*K,IER)
C       ***************************************************************
C       IN THIS EXAMPLE THE PROGRAM WAS TERMINATED WHEN GAMMA EXCEEDED
C       ***************************************************************
        IF (PAR(6).GT.15.0) GO TO 97
   77   PAR(2) = PAR(6)
        IF (PAR(6).EQ.5.) DEL = 1.0
        IF(PAR(6).GT.5.) DEL = 1.0
        PAR(6) = PAR(6) +DEL
        PAR(20) = X(N)/PAR(2)
C       ***************************************************************
C       WRITE RESULTS
C       ***************************************************************
        GO TO 66
   97   STOP
        END
C       ***************************************************************
C        IN THIS ROUTINE IS THE NONLINEAR EQUATIONS.
C       ***************************************************************
        SUBROUTINE FCN (X,F,N,PAR)
        INTEGER P,DI,DJ,OR,EL,NE,NCOL,MCOL,I,J,K,M,L,INDIK,O,ID,KO
```

```
      REAL X(N),F(N),PAR(21)
      DIMENSION DIF1(9),DIF2(9),DIF3(9),VECT(3),ROOT(9),A(9,9),B(9,9
      DIMENSION HK(4)
      INDIK =  26
      NE = 4
      NCOL = 4
      MCOL = NCOL - 1
      OR = NE-1
      M = NCOL-2
  110 O = N-1
  111 K = O/4
  112 L = O/2
      HK(1)=1./0.275
      HK(2)=1./0.275
      HK(3)=1./0.225
      HK(4)=1./0.225
      IF (PAR(8).GE.2.) GO TO 99
      GO TO 498
   99 DO 1 I = 1,N
    1 F(I) = 0.
C     ***************************************************************
C     BOUNDARY CONDITION AT S = 0
C     ***************************************************************
      DO 2 J = 1,NCOL
      F(1) = F(1) + HK(1)*A(1,J)*X(J)
      F(1+K) = F(1+K)+HK(1)*A(1,J)*X(J+K)
      F(1+L) = F(1+L)+HK(1)*A(1,J)*X(J+L)
    2 F(1+L+K) = F(1+L+K)+HK(1)*A(1,J)*X(J+L+K)
      F(1) = F(1)-PAR(7)*X(1)
      F(1+K)=F(1+K)-PAR(7)*X(1+K)
      F(1+L)=F(1+L)-PAR(7)*X(1+L)
      F(1+L+K) = F(1+L+K)-PAR(7)*X(1+L+K)
C     ***************************************************************
C     FUNCTIONS AT INTERNAL POINTS
C     ***************************************************************
      DO 3 EL = 1,NE
      DO 3 DI = 2,MCOL
      I =(EL-1)*(M+1) + DI
      DO 4 DJ = 1,NCOL
      J = (EL-1)*(M+1) + DJ
      F(I)=(-PAR(7)*HK(EL)*A(DI,DJ)+HK(EL)*HK(EL)*B(DI,DJ))*X(J)+F(I
      F(I+K)=(-PAR(7)*HK(EL)*A(DI,DJ)+HK(EL)*HK(EL)*B(DI,DJ))*X(J+K)
     & +F(I+K)
  101 F(I+L)=(-PAR(7)*HK(EL)*A(DI,DJ)+HK(EL)*HK(EL)*B(DI,DJ))*X(J+L)
     & +F(I+L)
    4 F(I+L+K)=(-PAR(7)*HK(EL)*A(DI,DJ)+HK(EL)*HK(EL)*B(DI,DJ))
     & *X(J+L+K)+F(I+L+K)
      F(I) = F(I)+X(N)*(1.-X(I))*EXP(PAR(5)*X(I+K)/(1.
     & +X(I+K)))
      F(I+K)=F(I+K)+X(N)*PAR(4)*(1.-X(I))*EXP(PAR(5)*
     & X(I+K)/(1.+X(I+K)))-PAR(6)*X(I+K)
  102 F(I+L)=F(I+L)+(PAR(5)*X(N)*(1.-X(I))*EXP(PAR(5)*
     & X(I+K)/(1.+X(I+K)))/((1.+X(I+K))*(1.+X(I+K))))*X(I+L+K)
     & -X(N)*EXP(PAR(5)*X(I+K)/(1.+X(I+K)))*X(I+L)
    3 F(I+L+K)=F(I+L+K)+(X(N)*PAR(4)*PAR(5)*(1.-X(I))*
```

```
     & EXP(PAR(5)*X(I+K)/(1.+X(I+K)))/((1.+X(I+K))*(1.+X(I+K)))-PAR(6
     & *X(I+L+K)-X(N)*PAR(4)*EXP(PAR(5)*X(I+K)/(1.+X(I+K)))*X(I+L)
C      ************************************************************
C      CONTINUITY EQUATIONS AT NODES
C      ************************************************************
       DO 5 EL = 1,OR
       I = (EL-1)*(M+1) + NCOL
       DO 5 DJ = 1,NCOL
       J = (EL-1)*(M+1) + DJ
       P = EL*(M+1) + DJ
       F(I) = F(I)+HK(EL)*A(NCOL,DJ)*X(J)-HK(EL+1)*A(1,DJ)*X(P)
       F(I+K)=F(I+K)+HK(EL)*A(NCOL,DJ)*X(J+K)-HK(EL+1)*A(1,DJ)*
     & X(P+K)
       F(I+L)=F(I+L)+HK(EL)*A(NCOL,DJ)*X(J+L)-HK(EL+1)*A(1,DJ)*X(P+L)
     5 F(I+L+K)=F(I+L+K)+HK(EL)*A(NCOL,DJ)*X(J+L+K)-HK(EL+1)*A(1,DJ)*
     & X(P+L+K)
C      ************************************************************
C      BOUNDARY CONDITION AT S = 1
C      ************************************************************
       DO 6 DJ = 1,NCOL
       J = (NE-1)*(M+1) + DJ
       F(K) = HK(NE)* A(NCOL,DJ)*X(J) + F(K)
   103 F(L)=HK(NE)*A(NCOL,DJ)*X(J+K)+F(L)
   105 F(L+K)=HK(NE)*A(NCOL,DJ)*X(J+L) + F(L+K)
     6 F(L+L)=HK(NE)*A(NCOL,DJ)*X(J+K+L)+F(L+L)
C      ************************************************************
C      SET V(K) =1. (TO FORCE JACOBIAN ZERO)
C      ************************************************************
   109 F(N) =X(L+INDIK)-1.
       GO TO 500
   498 CALL POLI (NCOL,KO,DIF1,DIF2,DIF3,ROOT,PAR)
       DO 130 ID= 1,2
       DO 130 I = 1,NCOL
       CALL DFOPR (NCOL,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
       DO 130 J = 1,NCOL
       IF (ID.EQ.1) GO TO 198
       IF (ID.EQ.2) GO TO 199
   198 A(I,J) = VECT(J)
       GO TO 130
   199 B(I,J) = VECT(J)
   130 CONTINUE
       PAR(8) = 2.
       GO TO 99
   500 RETURN
       END
```

APPENDIX C

THE EXISTENCE OF UNREALISTIC SOLUTIONS

All proofs to guarantee only realistic solutions, are only valid for odd order kinetics. In the case of zero and even order kinetics, unrealistic solutions exist.

A second order isothermic reaction was chosen. For a Pe=3 and ϕ=4 and unrealistic solutions were numerically determined.

$$w'' - 3w' + 4(w-1)^2 = 0$$
$$w' = 3w \quad ; s=0 \qquad (1)$$
$$w' = 0 \quad ; s=1$$

In the following section we will show that (1) has at least one unrealistic solution, i.e. w(s)>1.

Existence

One can rewrite (1) as

$$y(t) = -Z'(t)$$
$$y'(t) = -3y(t) + 4(Z(t)-1)^2$$
$$y(0) = 0 \qquad (2)$$
$$y(1) = 3Z(1)$$

where $t = 1-s$, $Z(t) = w(s)$.

If one considers (2) as an initial value problem, ignoring the boundary condition at t=1, it follows from previous results that for different choices of Z(0) different $y(1)$ and Z(1) will result. Suppose there exist Z_{01} and Z_{02} such that $y_1(1)<3Z_1(1)$ and $y_2(1)>3Z_2(1)$, then there exist a $Z_{01}<Z_0<Z_{02}$, such that (2) holds. Furthermore, if $Z_{01}>1$, then the solution is unrealistic.

Lemma 1

$$\max_{0\leq t\leq 1} Z(t) = Z(0)$$

Proof

At Z(0), $y(0) = 0$ and $y'(0) = 4(Z(0)-1)^2 > 0$.

Thus Z(0) is a local maximum. If there exist a Z(t), $t\in(0,1]$ where $Z(t)>Z(0)$, then there must also exist a $t^*\in(0,t)$ where $Z(t^*)$ is a local minimum. At t^*, $y(t^*) = 0$ and $y'(t^*)\leq 0$, but y' is non-negative for all Z(t). Since Z(t) never attains a local minimum, Z is a decreasing function of t and $\max_{0\leq t\leq 1} Z(t) = Z(0)$.

Lemma 2

There exist an unrealistic solution of (2) and $2<Z(0)<10$.

Proof

Let $Z_0 = 2$, $y_0 = 0$. Suppose there is a $t^* \in [0,1)$ where $y(t^*) = Z(t^*)$, then $Z(t)>y(t)$, for all $t<t^*$.

Thus $Z(t) > \frac{dZ(t)}{dt}$, $t<t^*$

$Z(t) > 2e^{-t}$, $t<t^*$

At $t = t^*$, $y'(t)>Z'(t)$

$-3y(t)+4(Z(t)-1)^2>Z'(t)$

$-3Z(t)+4Z^2(t)-8Z(t)+4>-Z(t)$

Thus $Z(t^*)<0,5$. It follows from Lemma 1 that the other root is not possible.

When $2e^{-t'} = 0,5$ then $Z(t')>0,5$ and thus $t'<t^*$.

Thus $-t' = -\ell n4<-\ell ne$

<-1

$t'>1$ and there does not exist a $t^* \in [0,1]$ such that $y(t^*) = Z(t^*)$.

Since $y(t)<Z(t)$ for $t \in [0,1]$ it follows that $y(1)<3Z(1)$.

This completes the first part of the proof.

Let $Z_0 = 10$, $y_0 = 0$. Suppose $y(t)<3Z(t)$, $t \in [0,1]$

Then $Z(t)>10e^{-3t}$.

And $4\int_0^1 (Z(t)-1)^2dt>4\int_0^{t'}(10e^{-3t}-1)^2dt$, where $10e^{-3t'} = 1$.

The integrand value of the r.h.s. > 30 = Pe Z(0).

Integration of y' gives: $y(1)-y(0) = 3Z(1)-3Z(0)+4\int_0^1 (Z-1)^2 dt$

If $3Z(0) < 4\int_0^1 (Z-1)^2 dt$, then

$y(1) > 3Z(1)$, which is a contradiction.

Thus, there exists a $t^* \epsilon (0,1]$ where

$y(t^*) = 3Z(t^*)$.

The possibility may exist that y and 3Z can intersect again at $t'' \epsilon (t^*,1)$.

This is only possible if $y'(t'') < 3Z'(t'')$.

$-3(3Z(t'')) + 4(Z(t'')-1)^2 < 3(-3Z(t''))$, which is impossible.

Thus $y(1) > 3Z(1)$

APPENDIX D

A listing of a Fortran program to compute bifurcation diagrams and do sensitivity checks for the two-dimensional model.

FILE: TWOD FORTRAN A1 UNIVERSITEIT VAN PRETORIA

```
C       ************************************************************
C       IN THIS PROGRAM BIFURCATION CURVES ARE CONSTRUCTED FOR THE
C       TWO-DIMENSIONAL PSEUDO-HOMOGENEOUS REACTOR MODEL. KELLER'S S-
C       METHOD IS USED WITH SHIFTED LEGENDRE POLYNOMIALS AXIALLY AND
C       SYMMETRICAL POLYNOMIALS RADIALLY. A PARAMETRIC SENSITIVITY TE
C       IS ALSO AVAILABLE.
C       ************************************************************
        INTEGER NSIG,NI,NJ,ITMAX,IER,K,O,L,M,KO,ID,INDIK,INDIL,N,TEL
        DIMENSION AR(10,10),BR(10,10),AZ(10,10),BZ(10,10)
        REAL KS,KSF,KSO,X(33),WK(1881),F(33),FNORM,PAR(105),PRMSP1,PRM
        REAL EUK
        EXTERNAL FCN,POLI,DFOPR
        NSIG = 4
        ITMAX = 100
        NI= 5
        NJ = 3
        N =2*(NI*NJ-2)+1
C       ************************************************************
C       H = N*(3*N+15)/2 ;WK(H):O = N-1;L = O/2 ; K = L/2.
C       ************************************************************
C       PAR(34)= FUNCTIONAL
C       PAR(35)= FUNCTIONAL
C       PAR(36)= PECLET Z-MASS
C       PAR(37)= PECLET R-MASS
C       PAR(38)= PECLET R-HEAT
C       PAR(39)= DELTA - DIMENSIONLESS ACTIVATION ENERGY.
C       PAR(40)= BETA - DIMENSIONLESS ADIABATIC TEMPERATURE RISE.
C       PAR(41)= GAMMA - DIMENSIONLESS HEAT TRANSFER.
C       PAR(42)= B - ASPECT RATIO .
C       PAR(43)= PECLET Z-HEAT.
C       PAR(44) = DKS ; INCREMENT IN KS, WHERE KS IS THE S-PARAMETER O
C       KELLER'S METHOD.
C       PAR(1)-PAR(16) = W(1)-W(16)
C       PAR(17)-PAR(32)= V(1)-V(16)
C       PAR(33) = FI
C       PAR(45)-PAR(60) = WS(1)-WS(16)
C       PAR(61)-PAR(76) = VS(1)-VS(16)
C       PAR(77) = DFI/DS
C       ************************************************************
        PAR(35) = 1
        PAR(36) = 5.00
        PAR(37) =30.00
        PAR(38) =30.00
        PAR(39) = 25.0
        PAR(40) = 0.5
        PAR(41) = 125.0
        PAR(42) = 10.0
        PAR(43) = 5.00
        PAR(44) =  0.04
        KSO = 0.0
        KSF =  0.2
C       ************************************************************
C       READ INITIAL PAR(I) USING ANY 2-D SOLVER AND GIVEN FI-VALUE
C       READ INITIAL X(I) ; GUESS FOR DW/DS , DV/DS AND DFI/DS.
C       ************************************************************
```

```
      PAR(80)=10
      PAR(34) = 1
      KS = KSO
   66 CALL ZSPOW (FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
   28 KS = KS + PAR(44)
      DO 23 I = 1,27
      PAR(I+44) = X(I)
      X(I) = PAR(I)
   23 CONTINUE
      PAR(34) = 2
      CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
      IF (ABS(X(27)-PAR(27)).LT.0.0001) GOTO 711
      PRMSP1= (X(15)-PAR(15))/(X(27)-PAR(27))
      EUK = 0.0
      DO 26 I =13,26
   26 EUK = EUK + X(I)**2
      EUK = EUK**0.5
      IF(ABS(X(27)-PAR(27)).LT.0.0001) GOTO 711
      PRMSP2 = (EUK-PAR(80))/(X(27)-PAR(27))
  711 WRITE (1,87) X(26),X(27)
   87 FORMAT(' ',2F12.5)
      IF (KS.GT.KSF) GOTO 97
      IF (X(12).GT.1.) GOTO 97
      IF (X(12).LT.0.) GOTO 97
      IF (IER.EQ.131) PAR(44) = PAR(44)-0.002
      DO 27 I = 1,27
      PAR(I) = X(I)
   27 X(I) = PAR(I+44)
      PAR(34) = 1
      CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
      PAR(80) = EUK
      GOTO 28
   97 STOP
      END
C     ***************************************************************
C     IN THIS ROUTINE ARE THE NONLINEAR EQUATIONS.
C     ***************************************************************
      SUBROUTINE FCN (X,F,N,PAR)
      DIMENSION T(32,32)
      INTEGER K,M,L,INDIK,ID,KO,NI,NJ,OI,OJ,IJ,KA,N,O,S,SO,KB,P,SA,
      INTEGER ADD,KP,Q
      REAL X(N),F(N),PAR(105),THETA
      DIMENSION AR(10,10),BR(10,10),AZ(10,10),BZ(10,10),DIF1(10)
      DIMENSION DIF2(10),DIF3(10),VECT(10),WORK(10),ROOT(10),ALFA(2
C     ***************************************************************
C     NI = OK AXIALLY ; NJ = OK RADIALLY.
C     OK = TOTAL NUMBER OF COLLOCATION POINTS
C     ***************************************************************
      DO 391 I=1,26
      DO 392 J=1,26
  392 T(I,J)=0
  391 CONTINUE
      NI = 5
      OI = NI-1
      NJ = 3
```

```
      OJ = NJ-1
      O = (NI*NJ-2)
      N = O*2+1
C     **********************************************************
C     THETA IS PARAMETER IN KELLER'S METHOD .
C     **********************************************************
      THETA = 0.55
      IF (PAR(35).GE.2.) GO TO 99
      GO TO 498
   99 DO 15 I = 1,N
   15 F(I)= 0.
C     **********************************************************
C     MAKE PROVISION HERE FOR THE SYMMETRICAL POLYNOMIALS FIRST AN
C     SECOND DERIVATIVES (AR, BR ) AS WELL AS THE ROOTS (WORT).
C     **********************************************************
      IF(PAR(34).GE.2) GOTO 252
      GOTO 253
  252 DO 1 I = 2,OI
      DO 2 J = 1,OJ
      KA=(I-1)*NJ+J-1
      KB = KA+O
      DO 3 P = 1,NJ
      S = (I-1)*NJ+P-1
      SO = S+O
      F(KA)=F(KA)+PAR(42)/2/PAR(37)*(AR(J,P)/WORT(J)+BR(J,P))*X(S)
    3 F(KB)=F(KB)+PAR(42)/2/PAR(38)*(AR(J,P)/WORT(J)+BR(J,P))*X(SO
      DO 4 L = 1,NI
      IF (L.EQ.1) ADD = 0
      IF (L.GT.1.AND.L.LT.NI) ADD = 1
      IF (L.GE.NI) ADD = 1
      S = (L-1)*NJ+J-ADD
      SO= S+ O
      F(KA) =F(KA)+(1/PAR(36)*BZ(I,L)-AZ(I,L))*X(S)
    4 F(KB) =F(KB)+(1/PAR(43)*BZ(I,L)-AZ(I,L))*X(SO)
      F(KA) = F(KA)+X(N)*(1.-X(KA))*EXP(PAR(39)*X(KB)/(1.+X(KB)))
      F(KB) = F(KB) +X(N)*PAR(40)*(1.-X(KA))*EXP(PAR(39)*X(KB)/(1.
     & +X(KB)))
    2 CONTINUE
    1 CONTINUE
C     **********************************************************
C     KELLER'S  N3-FUNCTION.  (SEE CHAPTER 3)
C     **********************************************************
      DO 220 I = 1,2O
  220 F(N)=F(N)+THETA*PAR(I+44)*(X(I)-PAR(I))
      F(N) = F(N) + (1.0-THETA)*PAR(N+44)*(X(N)-PAR(N))-PAR(44)
C     **********************************************************
C     NEXT FOLLOW THE BOUNDARY CONDITIONS.
C     **********************************************************
C     THE B.C. AT R = 0 IS AUTOMATICALLY SATISFIED.
C     **********************************************************
C     R = 1.
C     **********************************************************
      DO 7 I = 2,OI
      KA = (I-1)*NJ+NJ-1
      KB = KA+O
```

```
      DO 8 J = 1,NJ
      S= (I-1)*NJ+J-1
      SO = S+O
      T(KA,S)=T(KA,S)+AR(NJ,J)
      F(KA)=F(KA)+AR(NJ,J)*X(S)
      T(KB,SO)=T(KB,SO)+AR(NJ,J)
    8 F(KB)=F(KB)+AR(NJ,J)*X(SO)
      T(KB,KB)=T(KB,KB)+PAR(41)
      F(KB) = F(KB)+PAR(41)*X(KB)
    7 CONTINUE
C     ***************************************************************
C     BOUNDARY CONDITION AT Z = 0.
C     ***************************************************************
      DO 9 J = 1,OJ
      KA=J
      KB=KA+O
      DO 10 P =2,OI
      S = (P-1)*NJ+J-1
      SO = S+O
      T(KA,S)=T(KA,S)+AZ(1,P)
      F(KA)=F(KA)+AZ(1,P)*X(S)
      T(KB,SO)=T(KB,SO)+AZ(1,P)
   10 F(KB)= F(KB)+AZ(1,P)*X(SO)
      SA = (NI-1)*NJ+J-1
      SAO = SA+O
      T(KA,KA)=T(KA,KA)+AZ(1,1)-PAR(36)
      F(KA)=F(KA)+AZ(1,1)*X(KA)+AZ(1,NI)*X(SA)-PAR(36)*X(KA)
      T(KB,KB)=T(KB,KB)+AZ(1,1)-PAR(43)
    9 F(KB)=F(KB)+AZ(1,1)*X(KB)+AZ(1,NI)*X(SAO)-PAR(43)*X(KB)
C     ***************************************************************
C     BOUNDARY CONDITION AT Z = 1.
C     ***************************************************************
      DO 11 J = 1,OJ
      KA=(NI-1)*NJ+J-1
      KB = KA+O
      DO 12 P = 2,OI
      S = (P-1)*NJ+J-1
      SO =S+O
      T(KA,S)=T(KA,S)+AZ(NI,P)
      F(KA)= F(KA)+AZ(NI,P)*X(S)
      T(KB,SO)=T(KB,SO)+AZ(NI,P)
   12 F(KB)= F(KB)+AZ(NI,P)*X(SO)
      T(KA,KA)=T(KA,KA)+AZ(NI,NI)
      F(KA)=F(KA)+AZ(NI,1)*X(J)+AZ(NI,NI)*X(KA)
      T(KB,KB)=T(KB,KB)+AZ(NI,NI)
   11 F(KB) = F(KB)+AZ(NI,1)*X(J+O)+AZ(NI,NI)*X(KB)
      GO TO 500
  498 DO 503 IJ = 1,2
      IF (IJ.EQ.1 ) K = NI
      IF (IJ.EQ.2) K = NJ
      CALL POLI (K,KO,DIF1,DIF2,DIF3,ROOT,PAR)
      IF (IJ.EQ.2) GO TO 135
      GO TO 139
  135 DO 137 KP= 1,NJ
  137 WORT(KP) = ROOT(KP)
```

```
  139  DO 130 ID= 1,2
       DO 130 I = 1,K
       CALL DFOPR (K,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
       DO 130 J = 1,K
       IF (ID.EQ.1) GO TO 198
       IF (ID.EQ.2) GO TO 199
  198  IF (IJ.EQ.1) GO TO 201
       IF (IJ.EQ.2) GO TO 202
  201  AZ(I,J) = VECT(J)
       GO TO 130
  202  AR(I,J) = VECT(J)
       GO TO 130
  199  IF (IJ.EQ.1) GO TO 203
       IF (IJ.EQ.2) GO TO 204
  203  BZ(I,J) = VECT(J)
       GO TO 130
  204  BR(I,J) = VECT(J)
       GO TO 130
  130  CONTINUE
  503  CONTINUE
       PAR(35) = 2.
       GO TO 99
C      ************************************************************
C      IN THIS SECTION IS THE Dw/DS ,DT/DS AND DF1/DS FUNCTIONS.
C      ************************************************************
  253  DO 261 I = 2,GI
       DO 262 J = 1,GJ
       KA = (I-1)*NJ+J-1
       KB=KA+G
       DO 263 P = 1,NJ
       S = (I-1)*NJ+P-1
       SO = S + G
       F(KA) = F(KA)+PAR(42)/2/PAR(37)*(AR(J,P)/WORT(J)+BR(J,P))*X(S
  263  F(KB) = F(KB)+PAR(42)/2/PAR(38)*(AR(J,P)/WORT(J)+BR(J,P))*X(S
       DO 264 L = 1,NI
       IF(L.EQ.1) ADD = 0
       IF(L.GT.1.AND.L.LT.NI) ADD = 1
       IF(L.GE.NI) ADD = 1
       S = (L-1)*NJ+J-ADD
       SO = S + G
       F(KA) = F(KA)+(1/PAR(36)*BZ(I,L)-AZ(I,L))*X(S)
  264  F(KB) = F(KB)+(1/PAR(43)*BZ(I,L)-AZ(I,L))*X(SO)
       F(KA)=F(KA)-PAR(N)*EXP(PAR(39)*PAR(KB)/(1+PAR(KB)))*X(KA)
       F(KA)=F(KA)+PAR(39)*PAR(N)*(1-PAR(KA))*EXP(PAR(39)*PAR(KB)/(
     1 R(KB)))/(1+PAR(KB))**2*X(KB)
       F(KA)=F(KA)+(1-X(KA))*EXP(PAR(39)*PAR(KB)/(1+PAR(KB)))*X(N)
       F(KB)=((1-PAR(KA))*PAR(N)*PAR(39)*EXP(PAR(39)*PAR(KB)/(1+PAR
     1 )))/(1+PAR(KB))**2*X(KB)-PAR(N)*EXP(PAR(39)*PAR(KB)/(1+P
     1 AR(KB)))*X(KA)+(1-PAR(KA))*EXP(PAR(39)*PAR(KB)/(1+PAR(KB)
     1 ))*X(N))*PAR(40)+F(KB)
  262  CONTINUE
  261  CONTINUE
C      ************************************************************
C      THE BOUNDARY CONDITIONS
C      ************************************************************
```

```
C       R = 1
C       ***************************************************************
        DO 267 I = 2,OI
        KA = (I-1)*NJ+NJ-1
        KB = KA + O
        DO 268 J = 1,NJ
        S = (I-1)*NJ+J-1
        SO = S + O
        F(KA)=F(KA)+AR(NJ,J)*X(S)
  268   F(KB)=F(KB)+AR(NJ,J)*X(SO)
        F(KB)=F(KB)+PAR(41)*X(KB)
  267   CONTINUE
C       ***************************************************************
C       Z = O
C       ***************************************************************
        DO 269 J = 1,OJ
        KA = J
        KB = KA + O
        DO 270 P = 2,OI
        S = (P-1)*NJ+J-1
        SO = S+O
        F(KA)=F(KA)+AZ(1,P)*X(S)
  270   F(KB)=F(KB)+AZ(1,P)*X(SO)
        SA = (NI-1)*NJ+J-1
        SAO = SA + O
        F(KA)=F(KA)+AZ(1,1)*X(KA)+AZ(1,NI)*X(SA)-PAR(36)*X(KA)
  269   F(KB)=F(KB)+AZ(1,1)*X(KB)+AZ(1,NI)*X(SAO)-PAR(43)*X(KB)
C       ***************************************************************
C       Z = 1
C       ***************************************************************
        DO 271 J = 1,OJ
        KA=(NI-1)*NJ+J-1
        KB = KA + O
        DO 272 P = 2,OI
        S = (P-1)*NJ+J-1
        SO = S + O
        F(KA)=F(KA)+AZ(NI,P)*X(S)
  272   F(KB)=F(KB)+AZ(NI,P)*X(SO)
        F(KA)=F(KA)+AZ(NI,1)*X(J)+AZ(NI,NI)*X(KA)
  271   F(KB)=F(KB)+AZ(NI,1)*X(J+O)+AZ(NI,NI)*X(KB)
C       ***************************************************************
C       IN THE NEXT SECTION KELLER'S THETA FUNCTION IS COMPUTED
C       ***************************************************************
        DO 274 I = 1,26
  274   F(N) = F(N)+THETA*X(I)**2
        F(N)=F(N)+(1-THETA)*X(N)**2-1.0
  500   RETURN
        END
```