Modeling of a Non-Isothermal Tubular Reactor Packed with Immobilized Enzyme Systems

by

Mohammad Hassan Murad Chowdhury

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

January, 1995
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
MODELING OF A NONISOTHERMAL TUBULAR REACTOR
PACKED WITH IMMOBILIZED ENZYME SYSTEMS

BY

Mohammad Hassan Murad Chowdhury

A Thesis Presented to the
FACULTY OF THE COLLEGE OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE
In
CHEMICAL ENGINEERING

January, 1995
بِسْمِ اللَّهِ رَحِمَةَ الْبِلَادِ
This thesis, written by

MOHAMMAD HASSAN MURAD CHOWDHURY

under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING.

Thesis Committee

Mirza M. Hassan
Chairman (Dr. Mirza M. Hassan)

M. Atiqullah
Co-Chairman (Dr. M. Atiqullah)

Shafkat A. Beg
Member (Dr. Shafkat A. Beg)

Dr. Dulaihan K. Al-Harbi
Chairman, Chemical Engineering Department

Dr. Ala Al-Rabeh
Dean, College of Graduate Studies

Date: 8/1/1995
Dedicated to my Mother & late Father
ACKNOWLEDGEMENTS

The author expresses his extremely profound thanks and praise to ALLAH, the Almighty, the most Gracious, the most Merciful and peace be upon His Prophet (Sallahu alihi wa sallam).

The author highly appreciates Dr. Mirza M. Hassan, and Dr. M. Atiquullah from the Research Institute for their guidance, encouragement and help during the course of this work. Appreciation is also extended to Dr. Shafkat A. Beg for his help, encouragements and significant contributions.

The author acknowledges the Chemical Engineering Department of King Fahd University of Petroleum & Minerals (KFUPM) for providing him financial support and a congenial research environment. Acknowledgement is also due to the Data Processing Centre (DPC) at KFUPM for offering the computational facilities.

The author is deeply grateful to all his friends for their encouragement and moral support during his distant stay from home.
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xvi</td>
</tr>
<tr>
<td>ARABIC ABSTRACT</td>
<td>xviii</td>
</tr>
<tr>
<td>1 INTRODUCTION AND OBJECTIVES</td>
<td></td>
</tr>
<tr>
<td>1.1 Introduction and Objectives</td>
<td>1</td>
</tr>
<tr>
<td>1.2 References</td>
<td>4</td>
</tr>
<tr>
<td>2 LITERATURE REVIEW</td>
<td></td>
</tr>
<tr>
<td>2.1 Advantages and Application of Immobilized Biocatalyst</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Importance and Significance of Reactor Modeling</td>
<td>6</td>
</tr>
<tr>
<td>2.3 Selected Reactor Modeling Studies</td>
<td>7</td>
</tr>
<tr>
<td>on Immobilized Biocatalytic Systems</td>
<td></td>
</tr>
<tr>
<td>2.4 Analysis of Published Work</td>
<td>16</td>
</tr>
<tr>
<td>2.5 Description of the Problem</td>
<td>16</td>
</tr>
<tr>
<td>2.6 References</td>
<td>17</td>
</tr>
<tr>
<td>3 MATHEMATICAL MODEL FORMULATION</td>
<td></td>
</tr>
<tr>
<td>3.1 Problem Formulation</td>
<td>20</td>
</tr>
<tr>
<td>3.2 Solution of Model Equations</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>A GENERAL PARAMETRIC ANALYSIS</td>
</tr>
<tr>
<td>---</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>4.2</td>
<td>Approach to the Problem</td>
</tr>
<tr>
<td>4.3</td>
<td>Results and Discussion</td>
</tr>
<tr>
<td>4.4</td>
<td>References</td>
</tr>
<tr>
<td>5</td>
<td>DYNAMIC BEHAVIOR AND OPTIMAL FEED TEMPERATURE</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>5.2</td>
<td>Approach to the Problem</td>
</tr>
<tr>
<td>5.3</td>
<td>Results and Discussion</td>
</tr>
<tr>
<td>5.4</td>
<td>References</td>
</tr>
<tr>
<td>6</td>
<td>EFFECT OF IMMOBILIZED ENZYMES PARTICLES SHAPES ON REACTOR PERFORMANCE</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>6.2</td>
<td>Approach to the Problem</td>
</tr>
<tr>
<td>6.3</td>
<td>Results and Discussion</td>
</tr>
<tr>
<td>6.4</td>
<td>References</td>
</tr>
<tr>
<td>7</td>
<td>LOCAL WRONG - WAY BEHAVIOR</td>
</tr>
<tr>
<td>7.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>7.2</td>
<td>Approach to the Problem</td>
</tr>
<tr>
<td>7.3</td>
<td>Results and Discussion</td>
</tr>
</tbody>
</table>
8 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

8.1 Conclusions

8.2 Recommendations for Further Study

NOMENCLATURE

APPENDICES

A Derivation of the Collocation Equations

B Computer Programs

VITA
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Schematic diagram of an encapsulated enzyme Particle.</td>
<td>20</td>
</tr>
<tr>
<td>3.2</td>
<td>Tubular reactor packed with encapsulated enzyme particle.</td>
<td>21</td>
</tr>
<tr>
<td>4.1</td>
<td>Variation of dimensionless exit bulk substrate concentration, $C_b$ and dimensionless exit bulk temperature, $T_b$ (at $Z = 1.0$) as a function of dimensionless time, $(\tau)$ [Parameter values are given in Table 4.1].</td>
<td>37</td>
</tr>
<tr>
<td>4.2</td>
<td>Variation of dimensionless bulk substrate concentration, $C_b$ as a function of dimensionless reactor length, $Z$ [Parameter values are given in Table 4.1].</td>
<td>38</td>
</tr>
<tr>
<td>4.3</td>
<td>Variation of dimensionless bulk temperature $T_b$ as a function of dimensionless reactor length, $Z$ [Parameter values are given in Table 4.1].</td>
<td>39</td>
</tr>
<tr>
<td>4.4</td>
<td>Effect of dimensionless turn over number $K$ on variation of dimensionless bulk substrate concentration, $C_b$ as a function of dimensionless reactor length, $Z$ [Values of all parameters except $K$ are given in Table 4.1].</td>
<td>40</td>
</tr>
<tr>
<td>4.5</td>
<td>Effect of dimensionless turn over number $K$ on variation of dimensionless bulk temperature $T_b$ as a function of dimensionless reactor length, $Z$ [Values of all parameters except $K$ are given in Table 4.1].</td>
<td>41</td>
</tr>
<tr>
<td>4.6a</td>
<td>Variation of dimensionless substrate concentration inside particle, $C_P$ as a function of distance from the centerline of the particle, $r$ near the inlet of the reactor at $Z = 0.019$ [Parameter values are given in Table 4.1].</td>
<td>42</td>
</tr>
<tr>
<td>4.6b</td>
<td>Variation of dimensionless substrate concentration inside particle, $C_P$ as a function of distance from the centerline of the particle, $r$ at the middle of the reactor at $Z = 0.5$ [Parameter values are given in Table 4.1].</td>
<td>43</td>
</tr>
</tbody>
</table>
4.6c Variation of dimensionless substrate concentration inside particle, $C_p$ as a function of distance from the centerline of the particle, $r$ near the outlet of the reactor at $Z = 0.98$ [Parameter values are given in Table 4.1].

4.7a Variation of dimensionless temperature inside particle, $T_p$ as a function of distance from the centerline of the particle, $r$ near the inlet of the reactor at $Z = 0.019$ [Parameter values are given in Table 4.1].

4.7b Variation of dimensionless temperature inside particle, $T_p$ as a function of distance from the centerline of the particle, $r$ at the middle of the reactor at $Z = 0.5$ [Parameter values are given in Table 4.1].

4.7c Variation of dimensionless temperature inside particle, $T_p$ as a function of distance from the centerline of the particle, $r$ near the outlet of the reactor at $Z = 0.98$ [Parameter values are given in Table 4.1].

4.8 Effect of Peclet number for mass transfer, $Pe_m$ on dimensionless bulk substrate concentration, $C_b$ as a function of reactor length, $Z$ [Values of all parameters except $Pe_m$ and $Pe_h$ are given in Table 4.1].

4.9 Effect of Peclet number for heat transfer, $Pe_h$ on dimensionless bulk temperature, $T_b$ as a function of reactor length, $Z$ [Values of all parameters except $Pe_m$ and $Pe_h$ are given in Table 4.1].

4.10 Effect of mass transfer coefficient, $K_L$ (m/sec) on dimensionless bulk substrate concentration, $C_b$ as a function of reactor length, $Z$ [Values of all parameters except $K_L$ are given in Table 4.1].

4.11 Effect of heat transfer coefficient, $h$ (w/m² k) on dimensionless bulk temperature, $T_b$ as a function of reactor length, $Z$ [Values of all parameters except $h$ are given in Table 4.1].

4.12a Effect of $\alpha$ on dimensionless bulk substrate concentration, $C_b$ as a function of reactor length, $Z$ [Values of all parameters except $\alpha$ are given in Table 4.1].
Figure

4.12b Effect of $\alpha$ on dimensionless bulk temperature, $T_b$ as a function of reactor length, $Z$ [Values of all parameters except $\alpha$ are given in Table 4.1].

5.1 Effect of dimensionless Heat of Reaction, $\alpha$ on dimensionless Exit Conversion, $(1-C_b|_{Z=1})$ as a function of dimensionless Time, $\tau$.

5.2 Effect of dimensionless Heat of Reaction, $\alpha$ on Exit Bulk Temperature, $T_b|_{Z=1}$ (°C) as a function of dimensionless Time, $\tau$.

5.3 Effect of Biot number for mass, $Bi_m$ on Average Conversion, as a function of Feed Temperature, °C.

5.4 Variation of Optimum Feed Temperature, °C as a function of Biot number for mass, $Bi_m$ at $Pe_m = 5.0$.

5.5 Effect of Biot number for mass, $Bi_m$ on Average Conversion as a function of Peclet number for mass transfer, $Pe_m$.

5.6 Effect of Biot number for mass, $Bi_m$ on Optimum Feed Temperature, °C as a function of Peclet number for mass transfer, $Pe_m$.

5.7 Effect of dimensionless number $\alpha_1$ on Average Conversion as a function of Peclet number for mass transfer, $Pe_m$.

5.8 Effect of Stanton number, $St$ on Average Conversion as a function of Peclet number for mass transfer, $Pe_m$.

5.9 Variation of Temperature inside Immobilized Enzyme particle, °C as a function of Distance from the centerline of the particle, $r$ at $Z = 0.0199$.

5.10 Variation of Temperature inside Immobilized Enzyme particle, °C as a function of Distance from the centerline of the particle, $r$ at $Z = 0.5$. 
5.11 Variation of Temperature inside Immobilized Enzyme particle, 0°C as a function of Distance from the centerline of the particle, \( r \) at \( Z = 0.9801 \).

5.12 Variation of dimensionless Immobilized Enzyme Concentration, \( C_E \), as a function of dimensionless Time, \( \tau \) at \( r = 0.565 \) for different position of Bed.

5.13 Variation of Temperature inside Immobilized Enzyme Particle, 0°C as a function of dimensionless Time, \( \tau \) at \( r = 0.565 \) for different position of Bed.

6.1a Variation of dimensionless Exit Bulk Concentration, \( C_b \mid Z = 1 \) as a function of dimensionless Time, \( \tau \) for different geometries [Parameter values are given in Table 6.1].

6.1b Variation of dimensionless Exit Bulk Concentration, \( C_b \mid Z = 1 \) as a function of dimensionless Time, \( \tau \) for different geometries [\( Bi_{in} = Bi_h = 0.54 \) (Sphere), 0.36 (Cylindrical), 0.18 (Planar)]. Values of the other parameters are given in Table 6.1.

6.2a Variation of Exit Bulk Temperature, \( T_b \mid Z = 1 \) as a function of dimensionless Time, \( \tau \) for different geometries [Parameter values are given in Table 6.1].

6.2b Variation of Exit Bulk Temperature, \( T_b \mid Z = 1 \) as a function of dimensionless Time, \( \tau \) for different geometries [\( Bi_{in} = Bi_h = 0.54 \) (Sphere), 0.36 (Cylindrical), 0.18 (Planar)]. Values of the other parameters are given in Table 6.1.

6.3 Variation of Bulk Temperature \( T_b \), as a function of dimensionless Length along Bed (Reactor), \( Z \) [Parameter values are given in Table 6.1].

6.4 Variation of dimensionless Bulk Concentration, \( C_b \) as a function of dimensionless Length along Bed (Reactor), \( Z \) [Parameter values are given in Table 6.1].
Figure

6.5 Variation of dimensionless Exit Bulk Concentration, $C_b|z=1$ as a function of modified Biot number for mass transfer, $B_i^m*(n+1/3)$ [Values of all parameters except $B_i^m$ and $B_i^h$ are given in Table 6.1].

6.6 Variation of Exit Bulk Temperature, $T_b|z=1$ as a function of modified Biot number for heat transfer, $B_i^h*(n+1/3)$ [Values of all parameters except $B_i^h$ and $B_i^m$ are given in Table 6.1].

6.7 Variation of dimensionless Exit Bulk Concentration, $C_b|z=1$ as a function of Peclet number for mass transfer, $Pe_m$ [Values of all parameters except $Pe_m$ and $Pe_h$ are given in Table 6.1].

6.8 Variation of Exit Bulk Temperature, $T_b|z=1$ as a function of Peclet number for heat transfer, $Pe_h$ [Values of all parameters except $Pe_m$ and $Pe_h$ are given in Table 6.1].

6.9 Variation of dimensionless Exit Bulk Concentration, $C_b|z=1$ as a function of dimensionless Heat of Reaction, $\alpha$ [Values of all parameters except $\alpha$ are given in Table 6.1].

6.10 Variation of Exit Bulk Temperature, $T_b|z=1$ as a function of dimensionless Heat of Reaction, $\alpha$ [Values of all parameters except $\alpha$ are given in Table 6.1].

6.11a Variation of dimensionless Substrate Concentration inside particle, $C_p$ as a function of Distance from the centerline of the particle, $r$ at $Z = 0.0479$ [Parameter values are given in Table 6.1].

6.11b Variation of dimensionless Substrate Concentration inside particle, $C_p$ as a function of Distance from the centerline of the particle, $r$ at $Z = 0.5$ [Parameter values are given in Table 6.1].

6.11c Variation of dimensionless Substrate Concentration inside particle, $C_p$ as a function of Distance from the centerline of the particle, $r$ at $Z = 0.9908$ [Parameter values are given in Table 6.1].
Figure 6.12a Variation of Temperature inside particle, \( T_p \) as a function of Distance from the centerline of the particle, \( r \) at \( Z = 0.0479 \) [Parameter values are given in Table 6.1].

Figure 6.12b Variation of Temperature inside particle, \( T_p \) as a function of Distance from the centerline of the particle, \( r \) at \( Z = 0.5 \) [Parameter values are given in Table 6.1].

Figure 6.12c Variation of Temperature inside particle, \( T_p \) as a function of Distance from the centerline of the particle, \( r \) at \( Z = 0.9908 \) [Parameter values are given in Table 6.1].

7.1 Variation of bulk temperature as a function of dimensionless axial reactor length, \( Z \).

7.2 Variation of dimensionless bulk substrate concentration as a function of dimensionless axial reactor length, \( Z \).

7.3 Variation of bulk temperature as a function of dimensionless axial reactor length, \( Z \) for step decrease of the feed temperature from 50 °C to 15 °C.

7.4 Variation of bulk temperature as a function of dimensionless axial reactor length, \( Z \) for step decrease of the feed temperature from 90 °C to 15 °C.

7.5 Variation of maximum temperature rise as a function of Peclet number for mass and heat transfer, \( Pe_m, Pe_h \).

7.6 Variation of maximum temperature rise as a function of dimensionless heat of reaction, \( \alpha \).

7.7 Variation of maximum temperature rise as a function of Biot number for mass and heat transfer, \( Bi_m, Bi_h \).

7.8 Variation of maximum temperature rise as a function of dimensionless interfacial heat transfer coefficient, \( H \).

7.9 Variation of maximum temperature rise as a function of Stanton number, \( St \).
7.10 Variation of bulk temperature as a function of dimensionless axial reactor length, $Z$ for adiabatic condition.

7.11 Variation of dimensionless bulk substrate concentration as a function of dimensionless axial reactor length, $Z$ for adiabatic condition.
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Summary of the published works.</td>
<td>14</td>
</tr>
<tr>
<td>4.1</td>
<td>Base values of the parameters used in computation.</td>
<td>36</td>
</tr>
<tr>
<td>5.1</td>
<td>Base values of parameters used in the present modeling study.</td>
<td>63</td>
</tr>
<tr>
<td>6.1</td>
<td>Values of the parameters used in the present study.</td>
<td>88</td>
</tr>
<tr>
<td>7.1</td>
<td>Base values of the parameters used in computation.</td>
<td>115</td>
</tr>
</tbody>
</table>
THESIS ABSTRACT

FULL NAME OF STUDENT: MOHAMMAD HASSAN MURAD CHOWDHURY
TITLE OF STUDY: MODELING OF A NONISOTHERMAL TUBULAR REACTOR PACKED WITH IMMOBILIZED ENZYME SYSTEMS
MAJOR FIELD: CHEMICAL ENGINEERING DEPARTMENT

A generalized model, that includes the influence of overall transport and kinetic parameters, has been developed for a nonisothermal tubular reactor packed with immobilized enzyme. The substrate has been assumed to react with the enzyme following the Michaelis-Menten kinetics. Constant enzyme concentration as well as a first order enzyme deactivation rate has been considered. The resulting model equations have been solved using orthogonal collocation method.

The model has been used to simulate the influence of overall transport and kinetic parameters on (a) dynamic behavior of the reactor, (b) optimal feed temperature, (c) feed temperature perturbation in terms of wrong-way behavior, and (d) the shape of the biocatalyst particles.

The optimal feed temperature has been calculated by maximizing the average substrate conversion over a given operation period. For evaluating the wrong-way behavior, the feed temperature has been step decreased. For predicting the influence of variation in the shape of the biocatalyst particles, same surface area per unit volume has been chosen to be the basic criterion.

The present study shows that the transport and kinetic parameters appreciably affect the above categorized performance of the reactor depending on parametric values.
King Fahd University of Petroleum and Minerals
Department of Chemical Engineering

MASTER OF SCIENCE
ملخص الرسالة

اسم الطالب: محمد حسن مراد شوادي
عنوان الرسالة: تأثير كلي لمادة المتفاعلة مع صباغ انتزاعي ساكن
الخصوص الرئيسي: هندسة كيميائية
تاريخ الرسالة: ديسمبر 1994

تم تطوير نموذج عام لمادة المتفاعلات متغير الحرارة معًا بنظام انتزاعي ساكن. يأخذ هذا النموذج بعين
الأعراض التأثير الكلي لمادة النيكل (بارامترات) الناقل والحركة، وقد أظهرت أن حركة ميكونس-منشية تحقق حينما
تفاعل المادة المتفاعلة مع الأنتزاعي، كما أظهر أن تركيز الأنتزاع ثابت ومعدل التبنيت له من الدرجة الأولى، ثم حلت
المعادلات الناتجة بطريقة الارتداد المعتمد.

استخدام النموذج لمحاكاة التأثير الكلي لمادة النيكل والحركة على كل من الأنتزاع:
أ) السلوك الديناميكي لمادة التأثير النيكل للمفاعل.
ب) درجة حرارة التغذية الفضي.
ت) التقلانتة في درجة حرارة التغذية ممثلة بسلوك الطريق الحال.
ج) شكل حبيبات المتحجرات الجبيرة.

حسبت درجة الحرارة الفضي برفع معدل التحوليني للمادة المتفاعلة لأقصى قيمة له في فترة تشغيل معينة،
كما تم تقسيم سلوك الطريق الحالاً بالتفجيح التدريجي للدرجة حرارة التغذية، ولوقوع تأثير التغيير في شكل حبيبات
المحمور الجبيرة فقد أخذت نفس المساحة السطحية لوحدة الحجم معبرًا أساساً.
بينت الدراسة الجارية أن وسط المفاعل(symbol) المتفاعلة لها تأثير معتبر على أصناف الأداء السابق ذكره للمفاعل،
وأن ذلك يعتمد على قيم هذه الوسائط.

جامعة الملك فهد للبترول والمعادن
كلية الهندسة الكيميائية
ماجستير في العلوم
CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 Introduction and Objectives

Immobilized enzymes form an industrially important biocatalytic system because of several advantages (Cheetham, 1985; Gusek et al., 1990; Santoyo et al., 1993). They can be reused which leads to continuous operation and a uniform reaction environment. Large fluctuations in liquid loading does not appreciably change the cell concentration. This, in turn, offers improved process control, and enhanced reactor stability. Apart from these, with immobilized enzymes, very high cell concentrations can be achieved. The product and/or waste stream can be prevented from contamination. Also, unlike normal free cell culture, it is possible to maintain lower viscosity.

The above characteristics can be exploited, in principle, for process development using various types of reactors. However, using a tubular reactor offers several merits; such as higher average reaction rate than that would be in a continuous stirred tank reactor. The potential of enzyme loss is almost meagre because of absence of collisions between the biocatalyst particles and the impeller and liquid shearing (Santoyo et al., 1993). Moreover, a packed bed reactor has a high efficiency and conversion; as well as is easy to operate (Kiesser et al., 1990; Lin, 1991).

The mode of operating the reactor, that is isothermal versus nonisothermal holds practical importance. Changing the temperature of the reactor can compensate for the decreasing enzyme activity. Majority of enzymatic reactions are exothermic, and temperature is a convenient manipulating factor to control enzyme deactivation and
maximize substrate conversion. Therefore, nonisothermal operation has recently started to receive attention (Park et al., 1981; Lin, 1991).

Based on the above potentials, nonisothermal tubular reactor operating with immobilized enzymes appears to be a promising candidate for process development. However, for understanding the quantitative behavior of such a system, mathematical analyses and model simulation are important (Krishna and Ramachandran, 1975). For instance, the transient behavior of the reactor system can provide useful information to (Vieth and Davidson, 1976; Santoyo et al., 1993):

i. Understand the startup and shut down performance of a reactor;

ii. Describe reactor dynamics and control characteristic;

iii. Estimate the time required to reach a new steady state when a disturbance is introduced in a reactor system already in the steady state;

iv. Explore the possibility of multiple steady states of a given reaction system;

v. Analyze the regulation and control of the reactors by injected activators, inhibitors, or co-substrates; and

vi. Examine the loss of reactor potency.

In a nonisothermal reactor, the following transport processes will occur:

i. Transfer of the substrate and heat from the liquid bulk phase to the surface of the immobilized biocatalyst;

ii. Heat transfer from the source to the reactor wall; and

iii. Simultaneous diffusion and reaction of the substrate within the catalyst.

In the literature, studies dealing with the isothermal case are available (Marrazo et al., 1975; Santoyo et al., 1993). However, nonisothermal simulation results are limited. Lin (1991) modeled optimal feed temperature for a nonisothermal immobilized enzyme tubular reactor without properly incorporating the above transport processes. A general model capable of predicting the influence of varying operating conditions, transport and
kinetic parameters, and biocatalyst geometry will be formulated for a monosubstrate enzymatic process. Therefore, the objective of the present study is to analyze and simulate the behavior of a nonisothermal tubular reactor catalyzed by immobilized enzyme particle by including the relevant transport processes.

The overall objective of the present study is to analyze and simulate the behavior of a nonisothermal tubular reactor packed with immobilized monosubstrate enzyme deactivating following a first order rate expression. However, the specific objectives are to evaluate:

i. The influence of varying shapes of the immobilized enzyme particle (spherical, flat and cylindrical);

ii. Kinetic and mass transfer parametric effect;

iii. Optimum feed temperature based on a given reactor run time;

iv. Wrong-way behavior; and

v. Effect of catalyst deactivation.
1.2 References


CHAPTER 2

LITERATURE REVIEW

2.1 Advantages and Application of Immobilized Biocatalyst

The success of various chemical processes depends critically on catalysts including the enzymatic systems. Enzymes are structurally complex protein molecules. They are the biochemical equivalent of conventional catalysts. They have several advantages over their inorganic counter parts such as high activity, usually a high degree of specificity, and the ability to operate near ambient conditions. The immobilization of enzymes on supports provides the advantages of continuous operation, improved process control, and reduced costs resulting from enhanced stability and reuse of enzymes. Especially, the use of immobilized enzymes eliminates the costly enzyme recovery process and offers new opportunities for design and optimization of industrial enzyme reactor systems. Consequently, enzyme immobilization technology has rapidly advanced in recent years.

Application of immobilized enzymes range from the production of syrups from corn starch to artificial kidney devices, affinity chromatography on analytical biochemistry. Immobilized biocatalysts are used in chemical engineering processes, particularly in the fields of food and pharmaceutical production. The breakthrough in the application of immobilized microorganisms in waste water purification seems to be on its way. The two most important processes, as far as turn over is concerned, are the isomerization of glucose to fructose, using the glucose isomerize and the cleavage of pencilin using pencilin acylase. The growing patent literature shows that more processes can be expected in the near future.
2.2 Importance and Significance of Reactor Modeling

Knowledge of changes that occur in enzymatic kinetic parameters due to immobilization of the enzyme is essential in the design of immobilized enzyme reactors. Due to the presence of external and internal mass transfer effects, the intrinsic reaction kinetics of immobilized enzymes must be studied using a mathematical model which simultaneously consider the mass and heat transfer phenomena and reaction kinetics. A mathematical model is applicable to the analysis, design and simulation of heterogeneous enzymatic processes. The model develops the dynamic and steady state design equations for a reactor. It also requires various processes occurring in the reactor system.

The mode of operating the reactor, that is isothermal versus nonisothermal holds practical importance. Changing the temperature of the reactor can compensate for the decreasing enzyme activity. For understanding the quantitative behavior of such a system, mathematical analysis and model simulation are important. For instance, the transient behavior of the reactor system can generally provide useful information to:

i. Understand the startup and shut down performance of a reactor;

ii. Describe reactor dynamics and control characteristic;

iii. Estimate the time required to reach a new steady state when a disturbance is introduced in a reactor system already in the steady state;

iv. Explore the possibility of multiple steady states of a given reaction system;

v. Analyze the regulation and control of the reactors by injected activators, inhibitors, or cosubstrates; and

vi. Examine the loss of reactor potency.
2.3 Selected Reactor Modeling Studies on Immobilized Biocatalytic Systems

Engasser and Horvath (1973) investigated theoretically the effect of internal diffusion on the overall reaction rate in spherical particles and membranes containing immobilized enzymes for isothermal condition. First, a kinetic expression was derived in the absence of diffusion limitations, for reactions which take place in open system at high enzyme concentrations. This expression was used to compute the overall rate of diffusion limited reaction rate in spherical particles.

Marrazo et al. (1975) developed a mathematical model to describe the influence of axial dispersion, particle film mass transfer, intraparticle diffusion, and the chemical reaction of the substrate for enzymes immobilized in porous particles in packed columns, for first and zero order limits of Michaelis-Menten kinetics and isothermal condition. Steady state solutions were derived for both long and short column boundary conditions and plug flow. Theoretical predictions were compared with experimental results pertaining to hydrolysis of sucrose catalyzed by invertase bound to porous glass particles.

Davidson and Vieth (1975) studied in details the dynamics of a packed-bed reactor containing immobilized enzyme particles. The analysis consisted of:

i. Transient state behavior;

ii. Models for interphase and interfacial mass transfer between fluid and solid phases and interphase mass transfer for the solid phase;

iii. Detailed reaction rate model for the Bodenstein intermediates;

iv. Mass balances for substrates, Bodenstein intermediates, unoccupied enzyme active sites, and products; and

v. Models for enzyme denaturation and elution.

A generalized map of the range of validity of the steady-state hypothesis was established under conditions where multiple mass transfer gradients were present within
the reactor. The level of error involved in assuming the steady-state hypothesis was shown to depend on the relative magnitude of the kinetic parameters and the level of disturbance at the reactor inlet in terms of percent change in substrate inlet concentration. The error, however, appeared to be insensitive to the magnitude of the resistance to mass transfer as characterized by the modified Sherwood number. It was concluded that given any complete set of kinetic parameters, a transient, heterogeneous isothermal reactor model based on the steady state hypothesis may be used for predicting time varying concentration profiles for minor disturbances at the reactor inlet. Krishna and Ramachandran (1975) studied the effect of diffusional resistances (both inter and intramembrane) on the kinetic behavior of an immobilized two-enzyme system carrying out a consecutive sequence of reactions for the first order intrinsic kinetics.

Sadana (1979) reported an optimum temperature operation criterion for deactivating immobilized enzyme catalyzed reactions in an isothermal, and diffusion-free batch reactor. He found that his development applies to different types of enzymatic reactions which may or may not be reducible to the Michaelis-Menten type. Park et al. (1981) studied the optimal temperature control policy for an immobilized glucose isomerase packed-bed reactor. They considered the enzyme deactivation during the continuous reactor operation. They assumed steady state condition and plug-flow behavior of the reactor. The temperature of the reactor was varied externally from run to run. The kinetic parameters include reduced Michaelis-Menten constant, reduced maximum reaction rate, equilibrium constant and enzyme deactivation constant. Their functional relationships to temperature were determined experimentally. The optimization problem was formulated in terms of maximization of fructose productivity as the objective function. Approximately 8% improvement in terms of fructose productivity was achieved when the preprogrammed optimal temperature control policy was employed as compared to the reactor operation at an optimum constant temperature.
Manzon et al. (1987) formulated a design equation for packed-bed reactors operating under steady-state and plug flow condition, containing enzymes immobilized in spherical porous particles. They considered Michaelis-Menten kinetics and both the axial substrate profiles and effectiveness factor along the reactor length. The predicted behavior was compared to that shown by packed-bed reactors containing naringinase immobilized in Glycophase-coated controlled pore glass. The theoretically predicted results were found to fit well with experimentally measured values.

Experimental data for a fixed-bed reactor was obtained for the conversion of sucrose to glucose plus fructose using the enzyme invertase. The enzyme was immobilized by covalently binding it to a polymer matrix adsorbed in the pores of alumina (Geankoplis et al., 1987). A mathematical model, which included external film mass transfer, internal pore diffusion, axial dispersion, and enzymatic reaction with both substrate and product inhibition, was used to predict the performance of the fixed-bed reactor over a wide range of operating variables at isothermal condition. The tortuosity factor in the pores of the particle was experimentally determined, and the external mass transfer and axial dispersion coefficients were estimated from existing correlations. Comparison of the experimental data with the theoretical predictions from the model indicated a 70% loss of native invertase activity constant resulting from the immobilization and a 32% decrease for the Michaelis constant and the product and substrate inhibition constants.

Papathanasiou et al. (1988) presented a model for an isothermal fixed and fluidized bed immobilized enzyme bioreactor which included axial dispersion, mass-transfer effects, and a first order intraparticle chemical reaction. A complete parametric analysis was performed. The analysis revealed the importance of intraparticle and external mass transfer resistances, intraparticle chemical reaction and axial dispersion on the transient behavior of the reactor. Most importantly, the analysis revealed ways for parameter estimation and system identification via simple dynamic experiments. The
design and optimization implications were demonstrated using the derived solution to simulate the performance of an immobilized urease fluidized-bed bioreactor with a recycle loop.

Wrong-way behavior is one of the most surprising dynamic features of a packed-bed reactor. It refers to a transient temperature increase caused by a rapid reduction in the feed temperature or an increase in the feed rate. This temperature perturbation may shift the reactor to an undesired state or lead to a runaway. The wrong-way behavior is caused by the difference in the propagation speed of the concentration and temperature disturbances in the reactor. It occurs because a sudden change in the feed temperature decreases the conversion in the upstream section of the reactor. Consequently, the still-hot catalyst in the down-stream section is exposed to a higher reactant concentration than under the original steady-state operation, leading to an increase in the rate of heat generation by the reaction.

Pinjala et al. (1988) studied the conditions, under which the wrong way behavior occurs and its impact by using a pseudo homogeneous model that accounts for the axial dispersion in the packed bed reactor for a single first order irreversible reaction in a gas-solid nonenzymetic system. Chen and Luss (1989) studied the impact of the interfacial and intraparticle heat and mass transfer resistances on the wrong-way behavior. They started by comparing the predictions of a two phase model, which accounts only for the interfacial transport resistances but ignores the axial dispersion of heat and mass, with those of a pseudo homogeneous model, which accounts for the axial dispersion of heat and mass. After determining the conditions under which both models predict a similar dispersion of heat, they compared their predictions of the wrong-way behavior. They also examined a general model which accounts for both the interfacial transport resistances and axial dispersion.

Continuous synthesis of dipeptide Z-Tyr-Arg-NH₂ (Z-kyotorphin amide) was carried out using immobilized α-Chymotrypsin in a continuous fixed-bed reactor system
(Pere Clapes et al., 1989). As a prerequisite for designing a continuous reactor to perform such reactions, factors (cosolvent concentration and temperature) influencing reaction yields were optimized. Also, a kinetic study was carried out to obtain a reaction model and to estimate kinetic parameters.

Guzy et al. (1989) developed a mathematical model for describing the performance of a steady-state, packed-bed reactor, where an enzyme-catalyzed reaction occurred between two substrates. The reaction mechanism was assumed to be of the ping-pong or substituted-enzyme type. The model accounted for both axial backmixing in the bulk phase of the reactor and for internal diffusion in the pore phase of the catalyst. Using this model, performance was simulated for various configurations of the reactor, that is, from a continuous stirred tank reactor (CSTR) to an essentially plug flow type.

A study was made of phenol degradation by bacteria immobilized on particles of calcined diatomaceous earth in a draft tube, three-phase fluidized bed reactor (Andrew and Chase, 1989). A mathematical model was used to describe simultaneous diffusion and reaction of oxygen and phenol in the reactor. Liquid-solid mass transfer coefficients were determined experimentally. Experimental steady-state degradation data were used to calculate biofilm substrate diffusivities.

Guzy and Lotan (1990) analyzed in details the performance of a packed-bed immobilized enzyme reactor for multimolecular process. With numerical simulations, the effects of internal diffusion limitations, the depth of the pores, the substrates concentration in the feed, and kinetic parameters were evaluated. An experimental procedure for assessing their influence was described. Guzy and Lotan (1990) also developed an analytical model for describing the performance of packed bed enzymatic reactors operating with two cosubstrates and when one of the reaction products is inhibitory to the enzyme. The theoretical predictions were compared with those measured experimentally. They found some discrepancies when the inhibitory effect of the product was not included.
Kiesser et al. (1990) presented a model for a liquid fluidized bed reactor using immobilized enzymes with reversible Michaelis-Menten kinetics. The model was based on the axial dispersion model for bulk liquid phase. Inter- and intraparticle mass transfer as well as enzyme-catalyzed reaction inside the porous beads were considered.

Vasudevan and Weiland (1990) reported the experimental results in a fixed-bed reactor and a CSTR containing urease immobilized on a nonporous support and conducted in absence of diffusional limitations. Kinetic parameters were determined by separate batch experiments. The key observation was that the product ammonia attacked the free form of the enzyme, thereby illustrating the importance of mechanism in determining deactivation kinetics.

A counter-current bioreactor for splitting fats was studied using immobilized lipase (Kasugi et al., 1990). They reported the mass transfer effects of the two phase substrates and products in counter current reactors (fixed and fluidized bed reactors) using the immobilized lipase.

Lin (1991) modeled a packed-bed reactor to determine the optimal feed temperature of a nonisothermal immobilized enzymatic reaction with enzyme deactivation. The optimal feed temperature was obtained by maximizing the average substrate conversion over a given reaction period. Simulation showed that the optimal feed temperature strongly depended on the flow dispersion, the reaction activation energy, the corresponding enzyme inactivation energy and the heat of reaction. It was also observed that in a plug flow reactor the enzyme reaction generally exhibited a lower optimal feed temperature and higher substrate conversion than in a continuously stirred tank reactor. He considered unsteady state mass and heat balance only for bulk phase but not in the immobilized enzyme particle. According to his model equation, the reactor is not packed bed because catalyst particles are not stationary, they are flowing with the fluid. But he considered it as packed bed reactor.
Tsezos and Deutschmann (1992) developed a kinetic mass transfer model to describe the biosorption of metal ions by immobilized biomass from aqueous solution in a batch reactor. They showed that the developed kinetic mass transfer model could predict reasonably well batch kinetic experimental results under various experimental conditions and properties of the immobilized biomass.

Jung and Bauer (1992) modeled a solvent-free continuous transesterification in a fixed bed reactor with immobilized lipase, with special emphasis on the formulation of a kinetic equation based on heterogeneous catalysis. Hydrodynamic and mass transfer parameters, together with the reaction equation formed the basis of the reactor model. Residence time distribution and parameters of inter- and intraparticle mass transfer were determined by modeling of experiments performed in a fixed bed reactor under transient conditions.

Lortie and Pelletier (1992) compared between dispersion and plug-flow models for fixed-bed enzyme reactors. They used a plug-flow model to represent and analyze experimental data obtained with a fixed bed reactor in which axial dispersion was present. Data were generated for the dispersion model considering the external mass transfer and reaction rate. These data were then used to identify the parameters of the plug flow model with external mass-transfer resistance. The results obtained in this study showed that it was not necessary to consider the axial dispersion to describe an immobilized enzyme fixed-bed reactor at steady state.

Santoyo et al. (1993) formulated a mathematical model to analyze, design and simulate heterogeneous enzymatic processes occurring in a stirred tank reactor. The model formulated the unsteady-state design equations considering, for the substrate, diffusion in the spherical catalyst particles and reversible Michaelis-Menten kinetics. Although, the analysis was limited to selected cases, it could be extended to other support geometries, enzyme kinetics, and reactor configurations. To check the model, the
experimental data obtained with immobilized β-galactosidase were compared to those theoretically predicted.

Lortie (1994) reported the performance of CSTR and Fixed-bed reactors, containing immobilized enzyme obeying Michaelis-Menten kinetics using two dimensionless models at isothermal condition. He considered plug-flow model for Fixed-bed reactor and steady-state condition for CSTR. He concluded that a high conversion of the substrate was not compatible with an efficient use of the enzyme present in the reactor.

The results of the above mentioned published works are summerized in the following Table.

**Table 2.1: Summary of the published works.**

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Kinetic expression</th>
<th>Mass transfer parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Michaelis-Menten type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packed-bed (isothermal)</td>
<td>First- and zero-order Michaelis-Menten kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packed-bed (isothermal)</td>
<td>Generalized Michaelis-Menten; Briggs-Haldane kinetics</td>
<td>1 to 10</td>
<td></td>
</tr>
<tr>
<td>Packed-bed (isothermal)</td>
<td>First order limit of Michaelis-Menten kinetics</td>
<td>5 to 500</td>
<td></td>
</tr>
<tr>
<td>Batch (isothermal)</td>
<td>Simple Michaelis-Menten kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packed-bed (nonisothermal)</td>
<td>Reversible Michaelis-Menten</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed-bed (isothermal)</td>
<td>Reversible one-intermediate Michaelis-Menten kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed-bed (isothermal)</td>
<td>Michaelis-Menten; substrate inhibition; and substrate and product inhibition kinetics</td>
<td>0.2039 to 0.209</td>
<td></td>
</tr>
<tr>
<td>Packed-bed (nonisothermal), gas-solid reaction, non enzymatic system</td>
<td></td>
<td>160 to 2000</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.1: Summary of the published works. (Continued)

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Kinetic expression</th>
<th>Mass transfer parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed and fluidized-bed (isothermal)</td>
<td>First order reaction</td>
<td>0.01 to 20</td>
<td>0.01 to 100</td>
</tr>
<tr>
<td>Packed-bed (nonisothermal)</td>
<td>First order irreversible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed-bed (nonisothermal)</td>
<td>Michaelis-Menten kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packed-bed (isothermal)</td>
<td>Ping-pong type reaction mechanism</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluidized-bed (isothermal)</td>
<td>Monod kinetics with respect to oxygen and substrate inhibited kinetics w. r. t. phenol</td>
<td>2 to 35</td>
<td></td>
</tr>
<tr>
<td>Packed-bed (isothermal)</td>
<td>Ping-pong type mechanism, product inhibited</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluidized-bed (isothermal)</td>
<td>Reversible Michaelis-Menten kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packed bed and CSTR (isothermal)</td>
<td>Substrate inhibition and noncompetitive product inhibition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed- and fluidized-bed (isothermal)</td>
<td>Michaelis-Menten</td>
<td>0.01 to 1000</td>
<td></td>
</tr>
<tr>
<td>Packed-bed (nonisothermal)</td>
<td>Michaelis-Menten</td>
<td>0.01 to 1000</td>
<td></td>
</tr>
<tr>
<td>Batch reactor (isothermal)</td>
<td>Pseudo-first order</td>
<td>50 to 70</td>
<td>1.2 to 12</td>
</tr>
<tr>
<td>Fixed-bed (isothermal)</td>
<td>Michaelis-Menten kinetics</td>
<td>5 to 100</td>
<td></td>
</tr>
<tr>
<td>CSTR</td>
<td>Reversible Michaelis-Menten kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed bed and CSTR (isothermal)</td>
<td>Michaelis Menten Kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.4 Analysis of Published Work

Section 2.3 shows that most of the studies dealing with a biocatalytic packed-bed reactor have considered the isothermal. For the nonisothermal case, limited modeling work has been done. Specifically, no modeling study has been yet reported that has considered:

i. Transfer of the substrate and heat from the liquid bulk phase to the surface of the immobilized enzyme particles.

ii. Heat transfer from the source to the reactor wall;

iii. Simultaneous diffusion and reaction of the substrate within the catalyst; and

iv. Wrong way behavior.

2.5 Description of the Problem

Despite having the potential to control enzyme deactivation and maximize substrate conversion, an immobilized packed bed reactor has not been adequately modeled for nonisothermal condition. Therefore, a general model capable of predicting the influence of varying operating conditions, transport and kinetic parameters, and biocatalyst geometry should be developed for a nonisothermal immobilized enzyme tubular reactor, considering a monosubstrate enzymatic process and first order rate expression for enzyme deactivation. The model should also consider parametric effect, wrong-way behavior and optimization of feed temperature with respect to substrate conversion.
2.6 References


CHAPTER 3

MATHEMATICAL MODEL FORMULATION

3.1 Problem Formulation

The mathematical formulation of a given system requires basic understanding and identification of the various phenomena to deduce the model equations and reasonable assumptions to solve the resulting model equations.

Figures 3.1 and 3.2 show the schematic diagram of a spherical immobilized enzyme particle and the packed bed tubular reactor containing the immobilized enzyme particles, respectively. The semi-permeable membrane allows the substrate and the product to diffuse in and out, but retains the enzyme macromolecules.

![Diagram of semi-permeable membrane and enzyme solution]

Figure 3.1: Schematic diagram of an immobilized enzyme particle.
The various phenomena that are associated with the present unsteady state problem are:

i. Accumulation of substrate and heat in the bulk liquid;

ii. Transport of substrate and heat across the stagnant film which surrounds the immobilized enzyme particle (external mass and heat transfer);

iii. Diffusion of substrate, accumulation and reaction of the same in the immobilized enzyme particles;

iv. Diffusion, accumulation and generation of heat in the immobilized enzyme particles;

v. Axial dispersion of the substrate in the bulk liquid;

vi. Deactivation of immobilized enzyme; and

vii. Heat transfer between bulk fluid and the reactor wall.
To solve the model equations, the following assumptions have been made:

i. Wall temperature of the reactor is constant;

ii. Resistance of the membrane to any transport process is negligible;

iii. The reaction between the substrate and the enzyme follows Michaelis-Menten kinetics without product or substrate inhibition;

iv. All transport and physical properties are constant except the kinetic rate constants;

v. Enzyme activity is uniform throughout the particle having a first-order deactivation rate;

vi. Uniform distribution of the biocatalyst particles along the reactor bed; and

vii. Pressure drop across the reactor, radial concentration gradient in the bulk, and other mechanical effects are negligible.

With reference to Figures 3.1 and 3.2, a differential unsteady state mass balance, based on the above assumptions, in the immobilized enzyme particle gives:

\[
\frac{\partial c_p}{\partial t} = D_p \left( \frac{\partial^2 c_p}{\partial \vec{r}^2} + \frac{n \partial c_p}{\partial \vec{r}} \right) - \frac{k_p c_e c_p c_p}{c_p + k_m}
\]

(1)

where \( n = 0, 1, 2 \) for flat plate, cylinder and sphere, respectively.

The boundary conditions at the surface and center of the particle are as follows:

at \( \vec{r} = 0, \quad \frac{\partial c_p}{\partial \vec{r}} \bigg|_{r=0} = 0 \) \hspace{1cm} (2)

\[
\vec{r} = R, \quad D_p \frac{\partial c_p}{\partial \vec{r}} \bigg|_{r=R} = K_L \left( c_b - c_p \bigg|_{r=R} \right)
\]

(3)

Similarly, an unsteady state mass balance of the substrate in the bulk fluid phase gives:
\[
\varepsilon \frac{\partial c_b}{\partial t} = D_{ax} \varepsilon \frac{\partial^2 c_b}{\partial z^2} - u \frac{\partial c_b}{\partial z} - \left(1 - \varepsilon\right) \left(\frac{n+1}{R}\right) K_L \left(c_b - c_p|_{\gamma=R}\right) \tag{4}
\]

The boundary conditions at the entry and exit of the reactor are as follows:

at \( z = 0^+ \), \( \left. D_{ax} \varepsilon \frac{\partial c_b}{\partial z} \right|_{z=0^+} = -u \left( \left. c_b \right|_{z=0^+} - \left. c_b \right|_{z=0^-} \right) \) \tag{5}

\( z = L \), \( \frac{\partial c_b}{\partial z} \bigg|_{z=L} = 0 \) \tag{6}

An unsteady state energy balance in the immobilized enzyme particle gives:

\[
\rho_p \ c_{pp} \frac{\partial \bar{T}_p}{\partial t} = K_p \left( \frac{\partial^2 \bar{T}_p}{\partial \bar{r}^2} + \frac{n}{\bar{r}} \frac{\partial \bar{T}_p}{\partial \bar{r}} \right) + \frac{k_p \ c_p \ c_p}{c_p + k_m} \left( -\Delta H \right) \tag{7}
\]

The boundary conditions pertaining to Equation (7) at the surface and center of the particle are as follows:

at \( \bar{r} = 0 \), \( \left. \frac{\partial \bar{T}_p}{\partial \bar{r}} \right|_{\gamma=0} = 0 \) \tag{8}

\( \bar{r} = R \), \( K_p \left. \frac{\partial \bar{T}_p}{\partial \bar{r}} \right|_{\gamma=R} = h \left( \bar{T}_b - \left. \bar{T}_p \right|_{\gamma=R} \right) \) \tag{9}

An unsteady state energy balance in the bulk fluid phase gives the following:

\[
\varepsilon \rho_b \ c_{pb} \frac{\partial \bar{T}_b}{\partial t} = K_{ax} \varepsilon \frac{\partial^2 \bar{T}_b}{\partial z^2} - u \rho_b \ c_{pb} \frac{\partial \bar{T}_b}{\partial z} - h (1 - \varepsilon) \left(\frac{n+1}{R}\right) \left(\bar{T}_b - \left. \bar{T}_p \right|_{\gamma=R}\right) - \frac{2}{R_R} h_w \left( \bar{T}_b - \bar{T}_w \right) \tag{10}
\]

The appropriate boundary conditions for Equation (10) are:
\[
\text{at } z = 0^*, \quad K_{ax} \varepsilon \frac{\partial \tilde{T}_b}{\partial z} \bigg|_{z=0^*} = -u \rho_b c_{pb} \left( \tilde{T}_b \bigg|_{z=0} - \tilde{T}_b \bigg|_{z=0^*} \right)
\] (11)

\[
\text{at } z = L, \quad \frac{\partial \tilde{T}_b}{\partial z} \bigg|_{z=L} = 0 \quad (12)
\]

Deactivation of immobilized enzymes can be represented by a first order rate expression of the following form:

\[
\frac{d}{dt} \frac{d}{dt} c_E = -k_d c_E
\] (13)

The following initial conditions will be used in the present study:

\[
c_p(0, \tilde{r}) = c_{po}; \quad c_E(0) = c_{Eo}; \quad c_b(0, z) = c_{bo}
\]

\[
\tilde{T}_p(0, \tilde{r}) = \tilde{T}_{po}; \quad \tilde{T}_b(0, z) = \tilde{T}_{bo}
\] (14)

Equations (1) to (14) can be reduced to the corresponding dimensionless forms by introducing the following dimensionless parameters:

\[
C_p = \frac{c_p}{c_f}, \quad C_b = \frac{c_b}{c_f}, \quad C_E = \frac{c_E}{c_{Eo}}
\]

\[
Z = \frac{z}{L}; \quad r = \frac{\tilde{r}}{R}; \quad \tau = \frac{ut}{Le}; \quad k_p = k_{po} \exp \left( -\Delta E_i / R \tilde{T}_p \right)
\]

\[
T_p = \frac{\tilde{T}_p}{\tilde{T}_{po}}; \quad T_b = \frac{\tilde{T}_b}{\tilde{T}_{bo}}; \quad Pe_m = \frac{uL}{D_{ax} \varepsilon}; \quad Pe_h = \frac{uL\rho_b c_{pb}}{K_{ax} \varepsilon}
\]

Then Equations (1) to (14) can be written in the following dimensionless forms:

For the mass balance in the immobilized enzyme particle:
\[
\frac{\partial C_p}{\partial \tau} = \beta \left( \frac{\partial^2 C_p}{\partial r^2} + n \frac{\partial C_p}{\partial r} \right) - \frac{D_{a1} E C_p}{C_p + K} \exp \left( -\frac{1}{T_p} \right)
\]  

Equations (15) has the following boundary conditions:

at \( r = 0 \), \( \frac{\partial C_p}{\partial r} \bigg|_{r=0} = 0 \)  

(16)

\[ r = 1, \quad \frac{\partial C_p}{\partial r} \bigg|_{r=1} = Bi_m (C_b - C_p \bigg|_{r=1}) \]  

(17)

For the bulk fluid phase, the nondimensionalized mass balance equation becomes:

\[
\frac{\partial C_b}{\partial \tau} = \frac{1}{Pe_m} \frac{\partial^2 C_b}{\partial Z^2} - \frac{\partial C_b}{\partial Z} - \alpha_b (C_b - C_p \bigg|_{r=1})
\]  

(18)

The nondimensionalized boundary conditions for Equation (18) are:

at \( Z = 0^+ \), \( \frac{\partial C_b}{\partial Z} \bigg|_{Z=0^+} = -Pe_m (C_b \bigg|_{Z=0^+} - C_b \bigg|_{Z=0^+}) \)  

(19)

at \( Z = 1 \), \( \frac{\partial C_b}{\partial Z} \bigg|_{Z=1} = 0 \)  

(20)

For the immobilized enzyme particles, the dimensionless energy balance equation is:

\[
\frac{\partial T_p}{\partial \tau} = \beta_1 \left( \frac{\partial^2 T_p}{\partial r^2} + \frac{n}{r} \frac{\partial T_p}{\partial r} \right) + \frac{D_{a1} E C_p}{C_p + K} \exp \left( -\frac{1}{T_p} \right)
\]  

(21)

For Equation (21), the dimensionless boundary conditions are:

at \( r = 0 \), \( \frac{\partial T_p}{\partial r} \bigg|_{r=0} = 0 \)  

(22)
\[ r = 1, \quad \left. \frac{\partial T_p}{\partial r} \right|_{r=1} = Bi_h \left( T_b \mid_{r=1} - T_p \mid_{r=1} \right) \]  \hspace{1cm} (23)

For the bulk fluid phase, the dimensionless energy balance equation is:

\[ \frac{\partial T_b}{\partial \tau} = \frac{1}{Pe_h} \frac{\partial^2 T_b}{\partial Z^2} - \frac{\partial T_b}{\partial Z} - \left( T_b \mid_{Z\to 0} - T_p \mid_{Z=1} \right) - St \left( T_b - T_w \right) \] \hspace{1cm} (24)

The dimensionless boundary conditions for Equation (24) are:

at \( Z = 0^+ \), \quad \left. \frac{\partial T_b}{\partial Z} \right|_{Z=0} = -Pe_h \left( T_b \mid_{Z=0} - T_p \mid_{Z=0} \right) \hspace{1cm} (25)

\[ Z=1 \quad \left. \frac{\partial T_b}{\partial Z} \right|_{Z=1} = 0 \hspace{1cm} (26) \]

For the first-order rate of deactivation of the enzyme, Equation (13) reduces to the following dimensionless form:

\[ \frac{d C_E}{d \tau} = -D_{a2} C_E \exp \left( -\frac{\gamma}{T_p} \right) \] \hspace{1cm} (27)

The initial conditions in the dimensionless form may be written as follows:

\[ C_p (0,r) = C_{p0}, \quad C_E (0) = C_{E0}, \quad C_b (0,Z) = C_{b0}, \]
\[ T_p (0,r) = T_{p0}, \quad T_b (0,Z) = T_{b0} \]  \hspace{1cm} (28)
3.2 Solution of Model Equations

The resulting model equations are parabolic partial differential equations. The associated boundary conditions are of Neumen type, which for this particular case, are represented by Dankwerts boundary conditions.

In simulation problems related to a tubular reactor, orthogonal collocation has been found effective to solve numerically the partial differential model equations of the above type. Therefore, the above model equations have been solved using this numerical technique. The details of the model equations in collocation form has been given in the Appendix A.
CHAPTER 4

A GENERAL PARAMETRIC ANALYSIS

4.1 Introduction

Immobilized enzymes have several advantages and form an industrially important biocatalytic system (Cheetam, 1985; Gusek et al., 1990; Santoyo et al., 1993). They can be reused which lead to continuous operation with a uniform reaction environment. Large fluctuations in liquid loading do not appreciably change the cell concentration, which in turn, improve process control and reactor sensitivity. A high cell concentration can be achieved, and the product and or waste stream can be prevented from contamination. Further, in the free cell culture, it is possible to maintain lower viscosity. The above characteristics can be exploited, in principle, for process development using various types of reactors. The tubular reactor in particular, has the advantage of higher average reaction rate, compared to that in a continuous stirred tank reactor. Here, the potential of enzyme loss is almost meager because of absence of collisions between biocatalyst particles and impeller and liquid shearing (Santoyo et al., 1993). Moreover, a packed bed reactor offers high efficiency and conversions, and also easier to operate (Krishna and Ramachandran, 1975; Vieth and Davidson, 1976; Park et al., 1981; Kiesser et al., 1990; Lin, 1991).

Majority of enzymatic reactions are exothermic and temperature turns out to be a convenient manipulating factor to control enzyme deactivation and maximize substrate conversion. This can, in turn, significantly affect the overall performance of biological reactor. Therefore, nonisothermal operation has recently started to receive much attention
(Krishna and Ramachandran, 1975; Vieth and Davidson, 1976; Park et al., 1981; Kiessler et al., 1990; Lin, 1991; Santoyo et al., 1993).

Mathematical analyses and model simulations help understand the quantitative behaviour of biological systems and predict the overall performance. The solution of the unsteady state model equations, describing the nonisothermal behavior of the bulk fluid and the enzyme solution in the encapsulated enzyme particle, can provide the following (Krishna and Ramachandran, 1975; Vieth and Davidson, 1976; Santoyo et al., 1993):

i. Help understand the start-up and shut down performances of a reactor;

ii. Describe reactor dynamics and control characteristics;

iii. Estimate the time required to reach a new steady state when a disturbance is introduced into a reactor system already in the steady state;

iv. Explore the possibility of multiple steady states of a given system;

v. Analyze the regulation and control of reactors by injected activators, inhibitors, or cosubstrates; and

vi. Examine the loss of reactor potency.

In a nonisothermal reactor, the following transport processes will occur:

a. Transfer of the substrate and heat from the bulk liquid phase to the surface of the immobilized biocatalyst;

b. Heat transfer from the source to the reactor wall; and

c. Simultaneous diffusion and reaction of the substrate within the biocatalyst.

In the literature, studies dealing with the isothermal cases are available (Marrazo et al., 1975; Ilias et al., 1981; 1983; Santoyo et al., 1993). However, nonisothermal simulations results are limited. Lin (1991) predicted the optimal feed temperature for a nonisothermal immobilized enzyme tubular reactor by considering an axial dispersion model for the bulk liquid and temperature. His model provides useful informations, however, the internal diffusional resistance to mass and heat transfer inside the biocatalyst particle was ignored in the analysis. These resistances could be very
significant in many circumstances and change the overall performance of the system. Therefore, the objective of the present study is to analyze and simulate the behavior of a nonisothermal immobilized enzyme tubular reactor by including the appropriate and relevant transport processes.

In the present study, a general model capable of predicting the influence of varying operating conditions, transport and kinetic parameters will be formulated for a monosubstrate enzymatic process.

4.2 Approach to the Problem

The mathematical model as described in chapter 3 has been used with the exception that there is no deactivation of the enzyme solution. This would mean that \( k_d = 0 \), in equation (13) of chapter 3 and \( C_E = 1 \) for all values of time. Further, \( n = 2 \), since we are considering spherical particle only.
4.3 Results and Discussion

The performance of a nonisothermal tubular reactor packed with spherical encapsulated enzyme particles has been modeled in terms of different dimensionless kinetic and transport parameters. Table 4.1 lists the base values of the parameters considered for the present study. The above set of equations (15-27) has been solved by the method of orthogonal collocation. The solution procedure, described by Finlayson (1972) and Hassan and Beg (1987), has been used to solve the above equations.

At the start-up (\( \tau = 0 \)), we have considered the following:

i. The reactor bed temperature equals the feed temperature, that is, \( T_{b0} = T_{p0} = T_0 \) (0.06);

ii. No substrate feeds the reactor, that is, \( C_{p0} = C_{b0} = 0 \); and

iii. The reactor is subject to a step increase in the substrate feed concentration, that is, \( C_{b_f} = C_b \bigg|_{Z=0^-} = 1 \).

Figure 4.1 shows the dynamic behavior of the reactor in terms of two dimensionless output variables, the exit concentration and temperature. The dimensionless exit concentration initially increases to a maximum, then decreases till it reaches the steady state value. On the other hand, the dimensionless exit temperature, unlike the concentration, changes little with time. The difference in response between concentration and temperature may be explained as follows.

The feed experiences two different transport processes as soon as it enters the reactor. One is the convective bulk and axial transport, the other is the combined diffusional and hydrodynamic boundary layer mass transport from the bulk to the center of the spherical enzyme particles. The convective transport occurs because of the overall fluid motion whereas the latter happens due to the existing concentration gradient of the
substrate between the bulk fluid and the catalyst particle. The substrate concentration at
the exit of the reactor increases as long as the combined convective and bulk transport
predominates over the other. But the situation starts to revert when the substrate, carried
by the combined diffusional and hydrodynamic boundary layers mass transport process,
begins to participate in the enzyme-catalyzed reaction.

At the start-up, the reactor temperature equals the feed temperature. Consequently,
the temperature gradient between the bulk fluid and the catalyst is insignificant. However,
the gradients begin to develop when the exothermic catalytic reaction starts occurring in
the enzyme capsule. The convective and axial heat transport process conveys the heat of
reaction to the exit of the reactor. Under the given simulation conditions, the
dimensionless exit temperature appears to be little affected by the transported heat of
reaction.

Figure 4.1 also shows that the reactor reaches steady state at a dimensionless time
of about 17.5 under the given values of the kinetic and transport parameters.

Figures 4.2 and 4.3 illustrate the development of concentration and temperature
profiles, respectively, along the length of the reactor as a function of dimensionless time,
τ. The axial substrate concentration decreases while the axial temperature increases. This
happens because the enzyme-catalyzed reaction generates heat while the substrate is
consumed. The decrease in axial substrate concentration is almost continuous along the
bed of the reactor. However, the temperature profiles start flattening particularly beyond
the middle of the reactor. This predicts that heat of reaction is generated more at the first
half of the reactor than at the next half.

Figures 4.4 and 4.5 demonstrate the specific effects of introducing the Michaelis-
Menten kinetic term. In this regard, the kinetic term has been converted to zero and first
order expressions by considering \( K << C_p \) and \( K >> C_p \), respectively. A zero-order
system shows more overall conversion than a first-order one (Figure 4.4). Consequently,
the exit temperature for a zero-order system will be higher than that of a first-order
system (Figure 4.5). For all intermediate values of K, the exit conversion and temperature will be bounded between these two limits. The value of the exit conversion is particularly important from the application viewpoint. The higher the conversion, the easier and cheaper will be the unit operation involved in separating the spent biocatalysts from the exit stream.

Figure 4.6 plots the dimensionless concentration profile inside the encapsulated catalyst particle as a function of dimensionless time in the following locations:

i. Near the inlet (Figure 4.6a);

ii. At the middle (Figure 4.6b); and

iii. Near the exit of the reactor (Figure 4.6c).

Figure 4.6a shows that the dimensionless substrate concentration inside enzyme capsule decreases toward the centre of the catalyst particle, irrespective of the time scale. But for a given position in the particle, the concentration initially increases, then decreases till reaching the steady state value. Figures 4.6b and 4.6c predict the same overall phenomena as Figure 4.6a. However, the difference is that the time, during which the particle substrate concentration increases, lengthens, and ultimately assumes a limiting value as the axial reactor position deviates from the inlet. This dimensionless limiting value is found to be about 4 corresponding to the current simulation conditions.

Figures 4.7a, 4.7b and 4.7c demonstrate the dimensionless catalyst particle temperature profiles near the inlet, at the middle and approaching the exit of the reactor, respectively. These figures confirm that at any axial position along the reactor length, the time-dependent temperature profiles, unlike the corresponding concentration profiles, are nearly flat. Therefore, isothermal condition can be considered to exist in the catalyst particles throughout the reactor till achieving the steady state. At any position inside the particles, the temperature increases up to the steady state value. This behavior differs from that of the particle concentration.
Figure 4.8 shows the effect of axial mass dispersion, in terms of Peclet number for mass $\text{Pe}_m$, on the dimensionless bulk substrate concentration. Based on the overall effects, the reactor can be divided into these distinct regions which are:

i. Region I, $0.0 \leq Z \leq 0.42$;  
ii. Region II, $0.42 \leq Z \leq 0.56$; and  
iii. Region III, $0.56 \leq Z \leq 1.0$;

In Region I, at a given position in the reactor, the concentration increases with the increase in $\text{Pe}_m$. This means that the more the backmixing effect, the more is the concentration. This behavior is more pronounced toward the inlet of the reactor.

In Region II, the concentration profiles almost overlap on one another, irrespective of the widely varying values of the Peclet numbers. This physically signifies that in this region, the concentration profiles do not depend on the state of the backmixing.

In the Region III, the influence of axial mass dispersion is opposite to that in Region I. The exit substrate concentration decreases with the increase in Peclet number, that is, backmixing effects. In the limiting case, a plug flow reactor ($\text{Pe}_m \rightarrow \infty$) shows lower exit concentration than a continuous stirred tank reactor ($\text{Pe}_m \rightarrow 0$). Therefore, conversion will be more in a plug flow tubular reactor than in a stirred tank reactor.

Figure 4.9 predicts the influence of axial thermal dispersion, in terms of Peclet number for heat $\text{Pe}_h$, on the dimensionless bulk reactor temperature. On the basis of the overall thermal effects, the reactor can be axially divided into two major regions:

i. Region I, $0.0 \leq Z \leq 0.62$; and  
ii. Region II, $0.62 \leq Z \leq 1.0$

In Region I, corresponding to a given axial position, the bulk temperature, unlike the bulk concentration, increases with the decrease in $\text{Pe}_h$, which is more conspicuous toward the inlet of the reactor. This physically signifies that the elevation in local axial temperature is inversely related to thermal backmixing effects.
In Region II, the thermal backmixing effect do not appreciably influence the local axial temperature profile corresponding to the given simulation conditions. However, globally speaking, a lower $Pe_h$ shows a flatter temperature profile than a higher $Pe_h$.

Figure 4.10 illustrates how the external mass transfer coefficient $K_L$ affects the steady state dimensionless concentration profile. With the increase of $K_L$, Biot number for mass $Bi_m$ and dimensionless parameter $\alpha_1$, the concentration profile steepens. This, in turn, increases the overall conversion. Under the given simulation conditions, the resistance to mass transfer becomes negligible for $K_L > 1.6 \times 10^{-3}$ m/s.

Figure 4.11 predicts the influence of external heat transfer coefficient $h$ on steady state dimensionless temperature profiles. For the present simulation study, the effect of external heat transfer coefficient becomes negligible for $h > 2.16 \times 10^4$ w/m$^2$ k. On the whole, as the external heat transfer coefficient increases, the bulk temperature tends to be uniform throughout the reactor, indicating that isothermal condition is going to prevail.

Figures 4.12a and 4.12b show the effect of dimensionless heat of reaction $\alpha$ on dimensionless concentration and temperature profiles, respectively. For a given axial position, the concentration, unlike the temperature, decreases with the increase in $\alpha$. For a given $\alpha$, the concentration profile is concave upward whereas the temperature profile is linear or nearly convex upward. In other words, the dimensionless bulk concentration decreases along the reactor length, but the temperature increases.
Table 4.1: Base values of the parameters used in computation.

<table>
<thead>
<tr>
<th>Mass transfer parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_i_m$</td>
<td>0.54</td>
</tr>
<tr>
<td>$P_e_m$</td>
<td>$1.0*10^4$</td>
</tr>
<tr>
<td>$\alpha_1$ ($K_L = 1.6*10^{-4}$ m/s)</td>
<td>2.88</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.296</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heat transfer parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_i_h = B_i_m$</td>
<td>0.54</td>
</tr>
<tr>
<td>$P_e_h = 0.25 P_e_m$</td>
<td>2500</td>
</tr>
<tr>
<td>$H$ ($h = 2.16*10^2$ w/m$^2$ k)</td>
<td>2.88</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>0.296</td>
</tr>
<tr>
<td>$St$</td>
<td>0.1</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$Da_1$</td>
<td>$5.0*10^6$</td>
</tr>
<tr>
<td>$K$</td>
<td>0.5</td>
</tr>
<tr>
<td>$C_E$</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 4.1  Variation of dimensionless exit bulk substrate concentration, $C_b$ and dimensionless exit bulk temperature, $T_b$ (at $Z = 1.0$) as a function of dimensionless time, ($\tau$) [Parameter values are given in Table 4.1].
Figure 4.2 Variation of dimensionless bulk substrate concentration, $C_b$ as a function of dimensionless reactor length, $Z$ [Parameter values are given in Table 4.1].
Figure 4.3 Variation of dimensionless bulk temperature $T_b$ as a function of dimensionless reactor length, $Z$ [Parameter values are given in Table 4.1].
Figure 4.4 Effect of dimensionless turn over number K on variation of dimensionless bulk substrate concentration, $C_b$, as a function of dimensionless reactor length, Z [Values of all parameters except K are given in Table 4.1].
Figure 4.5 Effect of dimensionless turn over number $K$ on variation of dimensionless bulk temperature $T_b$ as a function of dimensionless reactor length, $Z$ [Values of all parameters except $K$ are given in Table 4.1].
Figure 4.6a  Variation of dimensionless substrate concentration inside particle, $C_p$, as a function of distance from the centerline of the particle, $r$ near the inlet of the reactor at $Z = 0.019$ [Parameter values are given in Table 4.1].
Figure 4.6b  Variation of dimensionless substrate concentration inside particle, $C_p$, as a function of distance from the centerline of the particle, $r$ at the middle of the reactor at $Z = 0.5$ [Parameter values are given in Table 4.1].
Figure 4.6c  Variation of dimensionless substance concentration inside particle, $C_p$, as a function of distance from the centerline of the particle, $r$ near the outlet of the reactor at $Z = 0.98$ [Parameter values are given in Table 4.1].
Figure 4.7a Variation of dimensionless temperature inside particle, $T_p$ as a function of distance from the centerline of the particle, $r$ near the inlet of the reactor at $Z = 0.019$ [Parameter values are given in Table 4.1].
Figure 4.7b Variation of dimensionless temperature inside particle, $T_p$ as a function of distance from the centerline of the particle, $r$ at the middle of the reactor at $Z = 0.5$ [Parameter values are given in Table 4.1].
Figure 4.7c Variation of dimensionless temperature inside particle, $T_p$ as a function of distance from the centerline of the particle, $r$ near the outlet of the reactor at $Z = 0.98$ [Parameter values are given in Table 4.1].
Figure 4.8  Effect of Peclet number for mass transfer, $P_e_m$ on dimensionless bulk substrate concentration, $C_b$ as a function of reactor length, $Z$ [Values of all parameters except $P_e_m$ and $P_e_h$ are given in Table 4.1].
Figure 4.9 Effect of Peclet number for heat transfer, $P_e_h$ on dimensionless bulk temperature, $T_b$ as a function of reactor length, $Z$ [Values of all parameters except $P_e_m$ and $P_e_h$ are given in Table 4.1].
Figure 4.10 Effect of mass transfer coefficient, $K_L$ (m/sec) on dimensionless bulk substrate concentration, $C_b$ as a function of reactor length, $Z$ [Values of all parameters except $K_L$ are given in Table 4.1].
Figure 4.11 Effect of heat transfer coefficient, $h$ (w/m$^2$ k) on dimensionless bulk temperature, $T_b$ as a function of reactor length, $Z$ [Values of all parameters except $h$ are given in Table 4.1].
Figure 4.12a Effect of $\alpha$ on dimensionless bulk substrate concentration, $C_b$ as a function of reactor length, $Z$ [Values of all parameters except $\alpha$ are given in Table 4.1].
Figure 4.12b Effect of $\alpha$ on dimensionless bulk temperature, $T_b$, as a function of reactor length, $Z$ [Values of all parameters except $\alpha$ are given in Table 4.1].
4.4 References


CHAPTER 5

DYNAMIC BEHAVIOR AND OPTIMAL FEED TEMPERATURE

5.1 Introduction

Immobilized biocatalyst technology has been steadily advancing because of its several advantages over the free-cell process (Cheetham, 1985; Gusek et al., 1990; Webb and Atkinson, 1992; Santoyo et al., 1993). For example, immobilized enzymes can be reusable and they ensure continuous operation and uniform reaction environment. Further, the large fluctuations in the feed does not substantially change the cell concentration. This, in turn, offers improved process control and better reactor stability. The products can be prevented from contamination and easily separated from the used catalysts. Additionally, with immobilized enzymes, higher cell concentration and lower solution viscosity can be maintained.

To harness the above advantages into beneficial industrial applications, the reactor-type is to be judiciously selected. From the perspective of process development, a tubular reactor offers several merits over a continuous stirred tank reactor. These include:

i. Higher average reaction rate;

ii. Less enzyme loss due to absence of collisions between the biocatalyst particles, the impeller and liquid shearing (Santoyo et al., 1993); and

iii. Higher efficiency, conversion, and easier process operation (Kiesser et al., 1990; Lin, 1991).

Therefore, the application of a tubular reactor packed with immobilized enzymes has constituted an important and active research area (Marrazo et al., 1975; Devera and
Varma, 1979; Atiqullah et al., 1990; Lin, 1991; Jung and Bauer, 1992; Lortie and Pelletier, 1992; Lortie, 1994; Backer and Baron, 1994).

Most of the enzymatic reactions are exothermic. Also, the enzymes deactivate with the rise of temperature causing the activity to decrease. These characteristics have prompted optimization studies in immobilized enzymatic reactions which are selectively reviewed for a packed-bed tubular reactor as follows.

Park et al. (1981) reported a linearly rising temperature control policy for maximizing the productivity of fructose for a relatively short operation period. They assumed that the packed bed reactor behaved as a plug-flow reactor. Therefore, they neglected the effects of axial dispersion or backmixing. They considered the reversible enzymatic isomerization of glucose to fructose with a first order deactivation rate of the enzymes. Kim et al. (1982) treated the optimization problem of Park et al. (1981) considering the effect of enzyme loading on the overall conversion. The same assumption of plug-flow behavior was retained. This assumption significantly simplifies the mathematical formulation of the optimal temperature control policy. But it does not necessarily hold for a real packed bed reactor (Levenspiel, 1980; Smith, 1981). Moreover, none of the above studies simulated the dynamic behavior of the reactor. They directly assumed steady state without confirming if a tubular reactor packed with immobilized enzymes would really reach the steady state provided the enzymes deactivate.

The optimal temperature control policy is difficult to implement in an industrial packed-bed reactor, primarily because of controlling the substrate temperature which varies along the reactor bed. Therefore, Lin (1991) investigated numerically the possibility of finding an optimal feed temperature for such a system. For this purpose, he maximized the substrate conversion averaged over a given operation period.

All the above authors related the findings of their simulation studies to an immobilized, packed-bed tubular reactor without considering the mass and heat transport resistances internal and external to the immobilized biocatalyst particles. The importance
of these aspects are well documented in the available literature (Marrazo et al., 1975; Lee et al., 1979; Krishna and Ramachandran, 1975; Devera and Varma, 1979; Bodalo et al., 1986, Atiquallah et al., 1990; Lortie and Andre', 1990; Tsezos and Deutschmann, 1992; Lortie and Pelletier, 1992; Jung and Bauer, 1992; Lortie, 1994; Backer and Baron, 1994).

Unlike the optimal temperature control policy, an optimal feed temperature is easier to implement in an industrial enzymatic packed-bed reactor. This underscores that the optimal feed temperature problem should be formulated considering the effects of overall transport resistances as well as the heat transfer occurring across the reactor tube. Therefore, the objective of the present study is to simulate the optimal feed temperature for an immobilized packed-bed, tubular reactor based on a generalized model which overcomes the limitations of the previous studies. The simulation results will also be explained in terms of overall mass transfer, heat transfer and kinetic parameters.

5.2 Approach to the Problem

The mathematical model as described in Chapter 3 by Equations (1) to (28) has been used. Here n = 2, because spherical particle has been considered for packing the reactor.
5.3 Results and Discussion

A generalized model has been formulated to predict the dynamic behavior and to find the optimal feed temperature for an immobilized, packed-bed tubular reactor under varying mass transfer, heat transfer and kinetic parametric values. Table 5.1 lists the values of the model parameters for which the model equations have been solved using orthogonal collocation. The details of this numerical technique (orthogonal collocation) are available elsewhere (Finlayson, 1972; Hassan and Beg, 1987; Atiquallah et al., 1990; 1992).

At the start-up ($\tau = 0$), we have considered the following:

i. The reactor bed temperature equals the feed temperature, that is, $T_{bo} = T_{po} = T_0 (0.0596)$;

ii. The enzyme solution and the bulk fluid are free of substrate, that is, $C_{po} = C_{bo} = 0$; and

iii. The reactor is subjected to a step increase in the substrate feed concentration, that is, $C_{b_{inf}} = C_{b}|_{Z=0^-} = 1$.

Figure 5.1 shows the influence of dimensionless heat of reaction $\alpha$ on the dynamic behavior of the reactor. This has been expressed in terms of variation of the exit conversion as a function of dimensionless time. Corresponding to the given parameter values (Table 5.1), the conversion momentarily hikes up at $\tau \approx 0.2$, irrespective of $\alpha$. Upto $\tau \approx 0.2$, the reactor retains the initial condition set at the start of the reactor. This situation can be compared with that of the induction period of a typical complex reaction. After this critical dimensionless time, the conversion decreases with the progress of time. However, the dimensionless heat of reaction affects this decreasing behavior. The larger value of $\alpha$ implies a larger increase in temperature of enzyme solution which would tend to deactivate the enzyme much earlier and thereby reducing the conversion.
Figure 5.2 illustrates the effect of increasing dimensionless heat of reaction $\alpha$ on the reactor exit temperature. Under the given simulation conditions (Table 5.1), the exit bulk temperature rises because of increase in adiabatic temperature rise. For $\alpha = 0.04$, the exit bulk temperature does not continuously rise as it does for $\alpha = 0.01$ and 0.02. After substantial increment, the temperature tends to fall which may be attributed to the occurrence of the enzyme deactivation process.

Figure 5.3 demonstrates the variational influence of the feed temperature on the average conversion. In this context, the average conversion has been calculated using the following Equation:

$$\text{Average Conversion} = \frac{1}{\tau_f} \int_0^{\tau_f} (1 - C_b|_{Z=1}) \, d\tau$$

(29)

Corresponding to each mass transfer Biot number $Bim$, an optimal feed temperature occurs which maximizes the average conversion. The optimal feed temperature strongly depends on Biot number. Figure 5.4 shows the effect of Biot number on optimum feed temperature. The results show that two modes of transport mechanism (external or internal) mass/heat transport resistances control the optimum feed temperature. Variations with Biot number below $Bim=7$, the external mass/heat transport resistance controls the overall process, while the internal diffusional resistance controls the overall process for $Bim > 7$. In the internal diffusion control regime ($Bim > 7$) the increase in Biot number would decrease the conversion and temperature which would reduce the effect of deactivation thus allowing the system to operate with relatively higher feed temperature as shown in Figure 5.4. On the other hand in the external mass/heat transport control regime an increase in the Biot number would imply lowering of the transport resistance thereby increasing conversion and temperature which would progressively reduce the optimum feed temperature.
Figure 5.5 illustrates the influence of $P_{em}$ on average conversion for various $B_{im}$. Corresponding to the given parametric values (Table 5.1), the average conversion initially increases up to $P_{em} \approx 50$. This critical value of $P_{em}$ does not strongly depend on $B_{im}$. For $P_{em} > 50$, all the curves become fairly asymptotic, indicating minor influence of backmixing on average conversion. However, for $P_{em} < 50$ increasing backmixing decreases the average conversion. On the other hand, the average conversion decreases with the increase in $B_{im}$, irrespective of the state of backmixing in the reactor. This means that decrease in intraparticle mass transfer resistance or increase in external mass transfer resistance will favor the average conversion.

Figure 5.6 predicts the variation of the optimal feed temperature as a function of the for mass transfer Peclet number $P_{em}$ for various $B_{im}$. The qualitative nature of Figure 5.6 fairly remains the same, irrespective of variations in $B_{im}$. However, as the extent of backmixing decreases with the increase in $P_{em}$, the optimal feed temperature drops abruptly till it becomes asymptotic at $P_{em} \approx 100$ for the given simulation conditions (Table 5.1).

Figure 5.7 shows the effect of axial dispersion ($P_{em}$) on average substrate conversion for various values of external mass transport resistance parameter ($\alpha_1$). The effect of axial dispersion is negligible beyond a value of $P_{em} > 50$ which was also shown in Figure 5.5. The average conversion, however, increases with decrease in external mass transport resistance (Higher values of $\alpha_1$) for all values of $P_{em}$.

Figure 5.8 demonstrates the effect of Peclet number on the average substrate conversion for various Stanton numbers. The effect of $P_{em}$ is similar to the one described for Figures 5.5 and 5.7. However, for a given $P_{em}$ the decrease in Stanton
number increases the average substrate conversion because the adiabatic reactor (St = 0) would offer larger temperature rise and therefore, a higher conversion.

Figures 5.9 to 5.11 predict the dynamic temperature profile of a biocatalyst particle at three locations of the reactor: near the inlet, at the middle and close to the exit, respectively. It is found that irrespective of the location of the reactor bed, the catalyst particle approximately remains isothermal. However, with the increase in time, the particle inside temperature near the entry initially increases up to a particular value beyond which it starts to decrease. On the otherhand, near the middle and exit, the particle inside temperature keeps on rising monotonically.

Figure 5.12 shows the dynamic behavior of the dimensionless enzyme concentration at a location $\tau = 0.565$ of the biocatalyst pellet, near the inlet, at the middle and close to the exit of the reactor. For the first two locations, the enzyme concentration dramatically falls, but near the exit, the enzyme concentration virtually remains unaffected up to the operational time considered ($\tau = 2$). This indicates that the enzyme deactivation front is moving gradually towards the exit of the reactor.

Figure 5.13 predicts the dynamic behavior of temperature at a location of $\tau = 0.565$ of the biocatalyst pellet at various positions along the length of the reactor. Near the entry of the reactor, the temperature, unlike the enzyme concentration, initially increases, then decreases with the progress of time. However, close to the middle and exit positions, the temperature continuously increases. For the temperature profile near the inlet of the reactor, the temperature starts to drop after $\tau = 1.4$. This may be attributed to the complete deactivation of enzyme at this location as shown in Figure 5.12. However, for other locations, the temperature continues to rise due to the fact that the enzyme has not yet been fully deactivated (Refer to Figure 5.12).
Table 5.1: Base values of parameters used in the present modeling study.

<table>
<thead>
<tr>
<th>Mass transfer parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$Bi_m$</td>
<td>10.0</td>
</tr>
<tr>
<td>$Pe_m$</td>
<td>5.0</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>2.88</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.760</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heat transfer parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$Bi_h$ = $Bi_m$</td>
<td>10.0</td>
</tr>
<tr>
<td>$Pe_h$ (= 0.25 $Pe_m$)</td>
<td>1.25</td>
</tr>
<tr>
<td>$H$ = $\alpha_1$</td>
<td>2.88</td>
</tr>
<tr>
<td>$St$</td>
<td>0.1</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.02</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>0.760</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$Da_1$</td>
<td>$9.5 \times 10^7$</td>
</tr>
<tr>
<td>$Da_2$</td>
<td>$1.1 \times 10^{43}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>7.6</td>
</tr>
<tr>
<td>$K$</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figure 5.1 Effect of dimensionless Heat of Reaction, $\alpha$ on dimensionless Exit Conversion, $(1-C_b|_{z=1})$ as a function of dimensionless Time, $\tau$. 
Figure 5.2  Effect of dimensionless Heat of Reaction, $\alpha$ on Exit Bulk Temperature, $T_b|_{Z=1}$ (°C) as a function of dimensionless Time, $\tau$. 
Figure 5.3 Effect of Biot number for mass, $B_i_m$ on Average Conversion, as a function of Feed Temperature, $^\circ$C.
Figure 5.4 Variation of Optimum Feed Temperature, °C as a function of Biot number for mass, $\text{Bi}_m$ at $\text{Pe}_m = 5.0$. 
Figure 5.5 Effect of Biot number for mass, $B_i m$, on Average Conversion as a function of Peclet number for mass transfer, $P_e m$. 

\[
\left(\frac{L}{r_f}\int_0^1 (1 - C_b) \, dr\right) 
\]
Figure 5.6  Effect of Biot number for mass, Bi_m on Optimum Feed Temperature, °C as a function of Peclet number for mass transfer, Pe_m.
Figure 5.7 Effect of dimensionless number $\alpha_1$ on Average Conversion as a function of Peclet number for mass transfer, $Pe_m$. 
Figure 5.8  Effect of Stanton number, St on Average Conversion as a function of Peclet number for mass transfer, Pe_m.
Figure 5.9 Variation of Temperature inside Immobilized Enzyme particle, °C as a function of Distance from the centerline of the particle, $r$ at $Z = 0.0199$. 
Figure 5.10 Variation of Temperature inside Immobilized Enzyme particle, °C as a function of Distance from the centerline of the particle, r at Z = 0.5.
Figure 5.11 Variation of Temperature inside Immobilized Enzyme particle, °C as a function of Distance from the centerline of the particle, r at Z = 0.9801.
Figure 5.12 Variation of dimensionless Immobilized Enzyme Concentration, $C_E$, as a function of dimensionless Time, $\tau$ at $r = 0.565$ for different position of Bed.
Figure 5.13 Variation of Temperature inside Immobilized Enzyme Particle, °C as a function of dimensionless Time, \( \tau \) at \( r = 0.565 \) for different position of Bed.
5.4 References


CHAPTER 6

EFFECT OF IMMOBILIZED ENZYMES PARTICLES SHAPES ON REACTOR PERFORMANCE

6.1 Introduction

In recent years there has been an increased interest for developing various techniques for immobilizing enzymes. Utilization of immobilized enzymes, which are encapsulated by semi-permeable membrane, is a problem of immense industrial and technological importance. One way of immobilizing the enzyme in the aqueous phase is by encapsulating it inside a semi-permeable membrane of a suitable material like nylon or cellulose nitrate. Each microcapsule can then be considered as a catalyst particle to be used in a packed bed reactor (Ramachandran, 1974).

Immobilized enzymatic reaction in a packed bed reactor is of particular interest to biochemical industries because of its ease of operation and relatively high conversion. Inspite of the fact that the industrial application of packed bed encapsulated enzyme reactors has been well established, very little effort has been directed toward the mathematical modeling of such systems (Cheetam, 1985; Gusek et al., 1990; Kiesser et al., 1990; Webb and Atkinson, 1992; Santoyo et al., 1993). Mathematical modeling and simulation of the transient and steady state cases for such systems would involve various rate controlling steps which include axial dispersion of mass and heat, internal and external mass and heat transport and the associated biochemical reaction. Various investigators have presented mathematical models which considered one or more of these mechanisms in various combinations (Ramachandran, 1974; Krishna and Ramachandran,
1975, Marrazo et al., 1975, Park et al., 1981, Lin, 1991, Jung and Bauer, 1992, Santoyo et al., 1993). Recently, Hassan et al. (1995) presented a comprehensive model which considered axial dispersion of heat and mass, internal and external heat and mass transport and Michaelis-Menten kinetics for a bioreactor packed with spherical shaped encapsulated enzyme. However, the shape of the particles which is a very important parameter to define the performance of such systems has received very little consideration.

This communication analyses the influence of geometry of encapsulated enzyme particles on the performance of the tubular reactor packed with immobilized enzyme systems. The selection of the size and shape of the encapsulated particles are very important in defining the performance characteristic of packed bed reactors. Not only that the shape and size of the particles will define the pressure drop, but also the mechanism of mass and heat transport. The effect of particle shape on local and overall mass transfer rates from individual particles was extensively studied by various investigators (Pasternak and Gauvin, 1960; Skelland and Cornish, 1963; Beg, 1973; 1975; 1976; Copper et al., 1986). Similarly studies have also been covered for heat transfer performance (Wasch and Forment, 1972; Melanson and Dixon, 1985; Dixon, 1988; Renken and Poulidakos, 1988; Borkink and Westerterp, 1992). As the effect of shape on heat and mass transfer from individual geometry has been well established, one would expect the geometry and size of the packing will have a significant effect in a reactor packed with immobilized enzymes. For such systems therefore, the effect of various mechanism like axial dispersion, internal and external mass and heat transfer, reaction kinetics will be strongly coupled thereby, making it difficult to obtain necessary predictions. The inclusion of the effect of the geometry of immobilized enzyme particles will further complicated the analysis.

The objective of the present study is to analyse and simulate the behavior of a nonisothermal tubular reactor packed with immobilized enzyme particles by including the
appropriate and relevant transport processes to determine the effect of shape of the individual particle. A general model capable of predicting the influence of varying operating conditions, transport and kinetic parameters has been formulated for a monosubstrate enzymatic process to illustrate the effect of geometry of individual particle.

6.2 Approach to the Problem

The mathematical model as described in Chapter 3 has been used with the exception that there is no deactivation of the enzyme solution. This would mean that \( k_d = 0 \), in Equation (13) of Chapter 3 and \( C_E = 1 \) for all values of time. Here, \( n = 0, 1 \) and 2 for planar, cylindrical and spherical geometry respectively.
6.3 Results and Discussion

Numerical simulation was performed to analyze the effect of encapsulated enzyme particle shape on the reactor performance for various parameters of practical significance. Same surface area per unit volume was chosen as the basis to compare the reactor performance packed with particles of spherical, cylindrical and planar (flat plate) geometries. Table 6.1 lists the base values of the parameters considered for the present study. The model equations have been solved using orthogonal collocation method, the details of which are available elsewhere (Hassan and Beg, 1987).

At the start-up (τ = 0), we have considered the following:

i. The reactor bed temperature equals the feed temperature, that is,
   \[ T_{po} = T_{bo} = T_0 \] (0.0596);

ii. The bulk fluid and the enzyme solution are free of substrate, that is, \( C_{po} = C_{bo} = 0 \); and

iii. The reactor is subject to a step increase in the substrate feed concentration, that is, \( C_{bf} = C_b \bigg|_{z=0^-} = 1 \).

Figures 6.1a and 6.1b show the approach to steady state of the exit bulk substrate concentration for different Biot numbers for planar, cylindrical and spherical particles. It may be observed from Figure 6.1a that for the case of higher Biot number (when the intraparticle mass transfer resistance is high), the effect of the shape of the encapsulated enzyme particle is very significant. However, for the case when the intraparticle resistance is small (low Biot number) the shape of the particle has virtually no effect. The steady state conversion, which is reached after about \( \tau \approx 15 \), is highest for spherical particle and lowest for the flat plate. Note that although the surface area per unit volume is considered same for all geometries, the particle size, Biot number and parameter \( \beta \) would be different for different geometries, thereby, contributing to varying performances for various geometric shapes.
The approach of the exit bulk temperature to steady state for the three geometries are shown in Figure 6.2a and 6.2b at different Biot numbers of heat transfer. In the present simulation, Biot number for heat and mass has been considered equal from analogy. These figures indicate again that the effect of particle geometry will be pronounced only at large Biot numbers when the intraparticle heat transfer resistance is significant. The temperature rise is found to be maximum for the spherical shape due to higher conversion.

The steady state bulk temperature profile along the length of the reactor is shown in Figure 6.3 for spherical, cylindrical and planar geometry. This figure predicts that the temperature rise is higher although the bed for the spherical geometry. On the other hand, the temperature profiles are very similar for the cylindrical and planar geometry near the inlet of the bed up to \( Z < 0.25 \), after which the temperature becomes higher for the cylindrical particles. Such behavior can be explained from the steady state bulk concentration profiles shown in Figure 6.4. The conversion is higher although the reactor for spherical shaped encapsulated enzyme particles, which contributes to higher temperatures in the reactor. The conversion for the cylindrical and planar particles are nearly same at \( Z < 0.25 \) after which the cylindrical particles offer larger conversion. This, in other words, correspond to the temperature profiles of Figure 6.3.

Figure 6.5 shows the effect of Biot number on the reactor performance for various particle shapes. The steady state exit bulk concentrations has been plotted against a modified Biot number for mass transport, \( \text{Bi}_{m}^{*} = \text{Bi}_{m}(n+1/3) \), where \( n = 0, 1 \) and 2 for flat plate, cylindrical and spherical geometry, respectively. It may be mentioned here that for the same surface area per unit volume, which has been taken as the common basis, the effective particle size will become different which will yield different Biot numbers. However, the modified Biot numbers, \( \text{Bi}_{m}^{*} \) remain same for all shapes. In the low Biot number regime where \( \text{Bi}_{m}^{*} < 5 \), external mass transfer resistance is significant and, therefore, the effect of geometry is minimal. On the other hand, at intermediate numbers
the intraparticle diffusion resistance also becomes important and the effect of geometry becomes significant. It is observed that spherical particles always yield higher conversion and the flat plate geometry gives the lowest conversion. The effect of Biot number for a particular geometry can also be observed in this figure. In case of flat plate for example, there is a slow rise in the exit bulk substrate concentration up to dimensionless Biot number of 5, which is followed by a sharper increase up to $B_i m^*$ of 10. There is little effect of Biot number beyond this value on the steady state conversion in the reactor. In this region, $B_i m^* > 10$, the intraparticle diffusional resistance is very high, substrate cannot reach the enzyme solution easily to react and the exit concentration approaches the feed concentration. It is, therefore, realised that for flat plate $B_i m^* < 5$ is external mass transfer control regime while $B_i m^* > 10$ is intraparticle diffusion control regime. Biot numbers between 5 to 10 indicate a dual resistance regime. The qualitative nature for the spherical and cylindrical geometries is similar, however, numerical computations have been performed for a maximum value of $B_i m^* = 15$ which appears to be below the upper limit of the intraparticle diffusion resistance regime for these geometries. The solution becomes very oscillatory beyond this value with the present numerical scheme.

Figure 6.6 shows the effect of modified Biot number for heat transfer $B_i h^* = B_i h^{(n+1)/3}$ on the steady state exit bulk temperature for flat plate, cylindrical and spherical geometries. The temperature difference is negligible for different geometries in the range of $B_i h^* < 5$ which is external heat transfer control regime. Between $B_i h^*$ of 5 and 10 there is significant effect of the particle geometry, the spherical shape showing the maximum temperature while the flat plate shows the minimum temperature. This would be expected since the conversion is maximum in the case of spherical geometry as shown in Figure 6.5. For Biot number greater than 10 for a flat plate, the system becomes totally intraparticle heat transfer controlled and the temperature approaches the feed temperature.

The effect of axial dispersion in terms of Peclet number for mass transfer on the steady state exit bulk substrate concentration is shown in Figure 6.7 for the three
geometries. At low Peclet number implying more mixing, the differences in the exit concentrations for different particle shape would be minimum, because the system is approaching a continuous stirred tank reactor and the effect of geometric shape would become negligible. At large Peclet number, the system approaches plug flow, the effect of axial dispersion disappear for any specific geometry. However, as can be seen from this figure spherical and flat plate geometry always offer the highest and lowest conversion respectively at $Pe_m > 10^2$. In the intermediate range of Peclet numbers, the cylindrical and flat plate geometries show the highest and lowest conversion, respectively.

Figure 6.8 shows the effect of axial dispersion of heat on the steady state exit bulk temperature for the three geometries. The effect of Peclet number for heat transfer is, in other words, follows the concentration plot shown in Figure 6.7. Whenever the conversion is higher, the temperature is higher and vice versa.

The effect of dimensionless heat of reaction, ($\alpha$) on the exit bulk concentration and temperature is shown in Figures 6.9 and 6.10, respectively. With the increase in $\alpha$, both the conversion and the temperature increase. When $\alpha$ is very low or very high the effect of geometry is insignificant. In the moderate range of $\alpha$, the spherical particle shows highest conversion and temperature while the flat plate shows the lowest conversion and temperature.

The steady state concentration profile within the encapsulated enzyme particles are shown at three locations, that is, near the inlet ($Z = 0.0479$), at the center ($Z = 0.5$) and near the exit ($Z = 0.9908$) of the reactor in Figures 6.11a, 6.11b and 6.11c, respectively for all three geometries. Near the inlet of the reactor, the concentration profile for the flat plate and cylinder are similar, displaying high substrate concentrations and negligible variation within the enzyme solution. On the other hand, for spherical shape encapsulation there is a sharp rise in the substrate concentration from the centre to the surface. Near the center of the reactor ($Z = 0.5$), the concentration profile for the cylinder and spherical particles is close with a moderate rise in concentration from the center to
the surface. For the flat plate, the concentration is quite high and does not change appreciably along the length of the particle from center to surface. Near the exit of the bed (Figure 6.11c) all three geometries show significant change in the concentration within the encapsulated enzyme solution. The concentration is largest for the flat plate and smallest for the spherical geometry.

The corresponding steady state temperature profiles within the encapsulated enzyme particles are shown at three locations, near the inlet, at the center and near the exit of the reactor in Figures 6.12a, 6.12b and 6.12c, respectively for all geometries. These figures show that the temperature changes are synchronized with the concentration changes which means that higher conversion would give rise to higher temperature and vice versa.
Table 6.1: Values of the parameters used in the present study.

<table>
<thead>
<tr>
<th>Mass transfer parameters</th>
<th>Spherical particle</th>
<th>Cylindrical particle</th>
<th>Planar particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_i_m$</td>
<td>8.0</td>
<td>5.333</td>
<td>2.6666</td>
</tr>
<tr>
<td>$P_e_m$</td>
<td>$1.0 \times 10^4$</td>
<td>$1.0 \times 10^4$</td>
<td>$1.0 \times 10^4$</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>2.88</td>
<td>2.88</td>
<td>2.88</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.296</td>
<td>0.666</td>
<td>2.664</td>
</tr>
</tbody>
</table>

Heat transfer parameters

| $B_{ih} = B_i_m$         | 8.0                | 5.333                | 2.6666         |
| $P_{eh}$ ($= 0.25 P_e_m$) | 2500.0             | 2500.0               | 2500.0         |
| $H$                      | 2.88               | 2.88                 | 2.88           |
| $St$                     | 0.1                | 0.1                  | 0.1            |
| $\alpha$                 | 0.02               | 0.02                 | 0.02           |
| $\beta_1$                | 0.296              | 0.666                | 2.664          |

Kinetic parameters

| $D_{a1}$                 | $5.0 \times 10^6$ | $5.0 \times 10^6$ | $5.0 \times 10^6$ |
| $K$                      | 0.5                | 0.5                 | 0.5             |
Figure 6.1a Variation of dimensionless Exit Bulk Concentration, $C_b|_{Z=1}$ as a function of dimensionless Time, $\tau$ for different geometries [Parameter values are given in Table 6.1].
Figure 6.1b  Variation of dimensionless Exit Bulk Concentration, $C_b|_{z=1}$ as a function of dimensionless Time, $\tau$ for different geometries [$\text{Bi}_m = \text{Bi}_h = 0.54$ (Sphere), 0.36 (Cylindrical), 0.18 (Planar). Values of the other parameters are given in Table 6.1].
Figure 6.2a Variation of Exit Bulk Temperature, $T_{b|z=1}$ as a function of dimensionless Time, $\tau$ for different geometries [Parameter values are given in Table 6.1].
Figure 6.2b Variation of Exit Bulk Temperature, $T_b|_{Z=1}$ as a function of dimensionless Time, $\tau$ for different geometries [$B_{in} = B_{in} = 0.54$ (Sphere), 0.36 (Cylindrical), 0.18 (Planar). Values of the other parameters are given in Table 6.1].
Figure 6.3 Variation of Bulk Temperature $T_B$, as a function of dimensionless Length along Bed (Reactor), Z [Parameter values are given in Table 6.1].
Figure 6.4 Variation of dimensionless Bulk Concentration, $C_b$ as a function of dimensionless Length along Bed (Reactor), $Z$ [Parameter values are given in Table 6.1].
Figure 6.5 Variation of dimensionless Exit Bulk Concentration, $C_b|_{z=1}$ as a function of modified Biot number for mass transfer, $Bi_m^*(n+1/3)$ [Values of all parameters except $Bi_m$ and $Bi_h$ are given in Table 6.1].
Figure 6.6 Variation of Exit Bulk Temperature, $T_b|_{Z=1}$ as a function of modified Biot number for heat transfer, $Bi_h^*(n+1/3)$ [Values of all parameters except $Bi_h$ and $Bi_m$ are given in Table 6.1].
Figure 6.7 Variation of dimensionless Exit Bulk Concentration, $C_b|_{Z=1}$ as a function of Peclet number for mass transfer, $P_e_m$ [Values of all parameters except $P_e_m$ and $P_e_H$ are given in Table 6.1].
Figure 6.8 Variation of Exit Bulk Temperature, $T_b|_{Z=1}$ as a function of Peclet number for heat transfer, $Pe_h$ [Values of all parameters except $Pe_m$ and $Pe_h$ are given in Table 6.1].
Figure 6.9 Variation of dimensionless Exit Bulk Concentration, $C_b|_{Z=1}$ as a function of dimensionless Heat of Reaction, $\alpha$ [Values of all parameters except $\alpha$ are given in Table 6.1].
Figure 6.10 Variation of Exit Bulk Temperature, $T_b|_{Z=1}$ as a function of dimensionless Heat of Reaction, $\alpha$ [Values of all parameters except $\alpha$ are given in Table 6.1].
Figure 6.11a Variation of dimensionless Substrate Concentration inside particle, $C_p$ as a function of Distance from the centerline of the particle, $r$, at $Z = 0.0479$ [Parameter values are given in Table 6.1].
Figure 6.11b Variation of dimensionless Substrate Concentration inside particle, \( C_p \) as a function of Distance from the centerline of the particle, \( r \) at \( Z = 0.5 \). Parameter values are given in Table 6.1.
Figure 6.11c  Variation of dimensionless Substrate Concentration inside particle, $C_p$ as a function of Distance from the centerline of the particle, $r$ at $Z = 0.9908$ [Parameter values are given in Table 6.1].
Figure 6.12a  Variation of Temperature inside particle, $T_p$ as a function of Distance from the centerline of the particle, $r$ at $Z = 0.0479$ [Parameter values are given in Table 6.1].
Figure 6.12b Variation of Temperature inside particle, $T_p$ as a function of Distance from the centerline of the particle, $r$ at $Z = 0.5$ [Parameter values are given in Table 6.1].
Figure 6.12c  Variation of Temperature inside particle, $T_p$, as a function of Distance from the centerline of the particle, $r$ at $Z = 0.9908$ [Parameter values are given in Table 6.1].
6.4 References


CHAPTER 7

LOCAL WRONG-WAY BEHAVIOR

7.1 Introduction

The overall performance of an immobilized, packed-bed reactor concerns the mode of its operation. The literature reports operating such a reactor either following an optimum temperature control policy (Park et al., 1981; Kim et al., 1982) or using an optimal feed temperature (Lin, 1991; Atiqullah et al., 1994). Between these two options, the latter is easier to apply to an industrial packed-bed reactor. Atiqullah et al. (1994), unlike Lin (1991), have shown that the overall mass transfer, heat transfer and kinetic parameters significantly influence the optimal feed temperature. From the above study, the parametric range related to the optimal feed temperature can be determined. But to evaluate the robustness of this study, the effects of thermal perturbation must be determined.

In what follows, we selectively review the findings of the studies dealing with the sudden temperature perturbation for gaseous feed(s) reacting with a solid catalyst in a packed-bed reactor.

A sudden decrease in feed temperature or increase in feed velocity leads to wrong-way behavior. Wrong-way behavior is a unique dynamic feature that originates from the difference in the propagation speed of concentration and temperature disturbances. Under this situation, the sudden decrease in the feed temperature lowers the conversion in the upstream section of the reactor. Consequently, the still-hot catalyst in the down-stream section possesses a higher reactant concentration than under the original steady-state
operation. This increases the reaction exotherm. Simulation studies have predicted the following:

i. The key parameters which influence the wrong-way behavior are the dimensionless adiabatic temperature rise, activation energy, heat transfer capacity, coolant temperature, magnitude of temperature drop and length of the reactor (Mehta et al., 1981).

ii. The interphase heat and mass transfer resistances may lead to steady-state multiplicity, depending on the parametric values, as well as ignite a low-temperature steady-state or create a transient high-temperature wave, initially moving upstream (Pinjala et al., 1988; Chen and Luss, 1989).

iii. For gaseous reactants adsorbing on the catalyst surface, the wrong-way behavior generates an upstream-moving temperature front. Resultantly, the reaction adsorption may appreciably increase the temperature above that attained in its absence, and ignite the reactor (Il'in and Luss, 1992).

iv. For a multi-reaction system having multiple steady states, the temperature waves, slowly moving upstream, may decrease the yield of the desired product, and cause reactor shutdown. Also, the overall adverse effects are more pronounced than those for the single reactant (Il'in and Luss, 1993).

Like the gas-solid reactive system, the immobilized enzyme-substrate is also a two-phase system. The catalyst is the common solid phase whereas the substrate, unlike a gas, is a liquid reactant. Therefore, a sudden decrease in feed temperature may introduce wrong-way behavior in an immobilized, packed-bed reactor as well. However, the review of the literature does not show any work in this area, unlike the gas-solid system.

The advantages of immobilized biocatalyst (Cheetam, 1985; Gusek et al., 1990; Webb and Atkinson, 1992; Santoyo et al., 1993; Hassan et al., 1995), using a tubular reactor, and operating at an optimal feed temperature (Lin, 1991; Atiqullah et al., 1994) cannot be adequately exploited unless we have studied the overall thermal perturbation
and wrong-way behavior for this kind of system. This prompts us to undertake the present study in which we would like to evaluate the influence of selected transport and kinetic parameters on this surprising dynamic feature for a tubular reactor packed with immobilized enzyme.

This present study is likely to help formulate desirable control policies, and start-up and shut-down procedures for an immobilized packed-bed reactor to minimize the adverse impact of the thermal perturbation.

7.2 Approach to the Problem

The mathematical model as described in Chapter 3 has been used with the exception that there is no deactivation of the enzyme solution. This would mean that $k_d = 0$, in Equation (13) of Chapter 3 and $C_E = 1$ for all values of time. Further, $n = 2$, since we are considering spherical particle only.
7.3 Results and Discussion

The influence of thermal perturbation in the form of a sudden decrease of the feed temperature has been simulated for an immobilized, packed-bed tubular reactor under various heat transfer, mass transfer and kinetic parametric values. Table 7.1 lists the base values of the parameters which did not change during simulation. However, when the effect of a particular parameter was investigated, only its values were changed, keeping other parameters constant. Orthogonal collocation, the details of which are available elsewhere (Finlayson 1972; Hassan and Beg 1987; Atiqullah et al., 1990; 1992; 1994), has been used for solving the model equations.

Initially ($\tau = 0$) the reactor is operating at steady state condition corresponding to a step change in feed concentration, that is,

$$C_{bf} = C_b \bigg|_{z=0^-} = 1.$$  

with a temperature of 70 °C. The reactor is then subjected to step decrease in feed temperature from 70 °C to 15 °C.

Figure 7.1 shows the influence of step decreasing the feed temperature from 70 °C to 15 °C on the dynamic thermal behavior of the reactor. At selected points along the reactor bed, the temperature initially exceeds that shown by the original steady state corresponding to 70 °C. Then with the progress of time, the axial temperature profile keeps on falling below the original steady-state temperature profile till reaching the new steady-state. Unlike a typical gas-solid system, the transient temperature rise does not appear in the form of sharp spikes (Mehta et al., 1981; Pinjala et al., 1988; Chen and Luss, 1989; Il'in and Luss, 1992; 1993). Rather, it fluctuates around the original steady-state temperature profile. Also, the fluctuating behavior decays with time. Based on the results of multi-reaction gas-solid system (Il'in and Luss, 1993), it can be stated that the
crests of this fluctuation, which represents the wrong-way, will amplify for a multi-substrate, multi-enzymatic system.

Figure 7.2 illustrates the impact of the above dynamic temperature fluctuations on the dimensionless bulk substrate concentration. The concentration declines, unlike the temperature, without any fluctuation. The step decrease in the feed temperature lowers the overall post-perturbation final conversion and the axial temperature. Note that the variation of the temperature and concentration profile is opposite to each other, the former increases while the latter decreases.

Figures 7.3 and 7.4 demonstrate the influence of step decrease of the feed temperature to 15 °C from initial values of 50 and 90 °C, respectively. Corresponding to each of the above feed temperature, that is, 50, 70, and 90 °C, the reactor shows similar dynamic thermal behavior.

Figure 7.5 shows how the variation in axial mass and heat dispersion vary the maximum temperature rise resulting from the step decrease of the feed temperature from 70 °C to 15 °C. The qualitative behavior of the plot of maximum temperature rise as a function of the Peclet numbers for heat and mass remains similar. This means that as the overall axial dispersion of mass and heat increases with the increase in \( P_e_m \) and \( P_e_h \), the maximum temperature rise also increases. However, the temperature rise is found to sharply occur corresponding to a critical value of the Peclet numbers for mass and heat transfer. Under the given simulation condition (Table 7.1), these are predicted to be \( P_e_m \sim 100 \) and \( P_e_h \sim 500 \), respectively.

Figure 7.6 predicts that the dimensionless heat of reaction \( \alpha \) does not initially affect the maximum temperature rise up to \( \alpha \approx 0.015 \) for the given simulation conditions. However, for \( \alpha > 0.015 \), the maximum temperature starts to decline.

Figure 7.7 illustrates the effect of Biot numbers for heat and mass transfer \( \text{Bi}_h \) and \( \text{Bi}_m \), respectively on the maximum axial temperature rise. Under the given simulation conditions, the maximum temperature rise increases up to \( \text{Bi}_m, \text{Bi}_h \approx 8 \), then decreases
up to $\text{Bi}_\text{m}$, $\text{Bi}_h \approx 15$, it again increases till $\text{Bi}_\text{m}$, $\text{Bi}_h \approx 55$. Exceeding this value, it gradually decreases.

Figures 7.8 and 7.9 predict the influence of dimensionless heat transfer coefficient $H$ and Stanton number $St$ on the maximum axial temperature rise. With the increase of $H$ and $St$, the temperature rise decreases somewhat linearly. Figure 7.9 particularly shows the temperature rise, that is, the local wrong-way behavior will be more critical for an adiabatic reactor ($St = 0$), the effects of which are detailed in Figures 7.10 and 7.11. Note the significance of this finding while it has been reported that adiabatic operation favors the time-averaged, overall exit conversion of the reactor (Atiquullah et al., 1994).

Figure 7.10 shows relatively pronounced wrong-way behavior compared to that shown by Figure 7.1. The new steady-state temperature profile, like the previous case (Figure 7.1), replicates the original temperature profile but stabilizes at a much lower value.

Figure 7.11 illustrates the accompanied effect on the dimensionless bulk concentration. The feed temperature perturbation does not virtually change the concentration profile. This indicates that the substrate has stopped reacting. Therefore, the reactor is to be shutdown.
Table 7.1: Base values of parameters used in computation.

<table>
<thead>
<tr>
<th>Mass transfer parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_i_m$</td>
<td>0.54</td>
</tr>
<tr>
<td>$P_e_m$</td>
<td>$1.0 \times 10^4$</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>2.88</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.296</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heat transfer parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_i_h$ = $B_i_m$</td>
<td>0.54</td>
</tr>
<tr>
<td>$P_e_h$ = $0.25P_e_m$,</td>
<td>2500</td>
</tr>
<tr>
<td>$H$</td>
<td>2.88</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>0.296</td>
</tr>
<tr>
<td>$St$</td>
<td>0.1</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$Da_1$</td>
<td>$5 \times 10^6$</td>
</tr>
<tr>
<td>$K$</td>
<td>0.5</td>
</tr>
<tr>
<td>$C_E$</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 7.1 Variation of bulk temperature as a function of dimensionless axial reactor length, $Z$. 
Figure 7.2 Variation of dimensionless bulk substrate concentration as a function of dimensionless axial reactor length, $Z$. 

\[ \tau = 0.0, 0.1, 0.25 \]
Figure 7.3 Variation of bulk temperature as a function of dimensionless axial reactor length, Z for step decrease of the feed temperature from 50 °C to 15 °C.
Figure 7.4 Variation of bulk temperature as a function of dimensionless axial reactor length, $Z$ for step decrease of the feed temperature from 90 °C to 15 °C.
Figure 7.5 Variation of maximum temperature rise as a function of Peclet number for mass and heat transfer, $P_{em}$, $P_{eh}$.
Figure 7.6 Variation of maximum temperature rise as a function of dimensionless heat of reaction, $\alpha$. 
Figure 7.7 Variation of maximum temperature rise as a function of Biot number for mass and heat transfer, $B_{im}$, $B_{ih}$. 
Figure 7.8 Variation of maximum temperature rise as a function of dimensionless interfacial heat transfer coefficient, $H$. 
Figure 7.9 Variation of maximum temperature rise as a function of Stanton number, St.
Figure 7.10 Variation of bulk temperature as a function of dimensionless axial reactor length, $Z$ for adiabatic condition.
Figure 7.11  Variation of dimensionless bulk substrate concentration as a function of dimensionless axial reactor length, Z for adiabatic condition.
7.4 References


CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

8.1 Conclusions

From the present study of the "Modeling of a Nonisothermal Tubular Reactor Packed with Immobilized Enzyme Systems", the following conclusions can be made.

8.1.1 A General Parametric Analysis

Based on the used parametric values, the present simulation study concludes the following concerning a nonisothermal, enzyme-catalyzed, packed-bed reactor:

i. If the reactor is initially substrate-free and has the same temperature as the feed, the dimensionless exit concentration, unlike the corresponding bulk temperature, will first reach a maximum, then will decrease till reaching the steady state.

ii. The steady state bulk substrate concentration progressively decreases along the reactor bed. On the other hand, the temperature increases, but only up to a critical bed length beyond which the effect of reaction exotherm decreases.

iii. A zero order system will show more overall conversion and exit temperature than a first order one. For a typical Michaelis-Menten kinetics, the conversion and temperature will be bounded between these two limits.
iv. At any axial position along the reactor bed, the dynamic biocatalyst temperature profiles, unlike the concentration profiles, are nearly flat. This shows that the encapsulated enzyme particles, at any time, can be considered isothermal.

v. The influence of mass transfer backmixing effects on concentration profile is more pronounced toward the entry of the reactor than approaching the exit. The exit substrate concentration decreases with the increase in Pe_m, that is, backmixing effects. Therefore, in the limiting case, a plug flow reactor will show more conversion than a perfect mixer.

vi. The rise in axial bulk temperature is inversely proportional to the thermal backmixing effects around the reactor inlet. Toward the reactor exit, the thermal backmixing effects do not influence the axial temperature.

vii. With the increase of the external mass transfer coefficient K_L and the Biot number for mass transfer Bi_m, the axial concentration profile steeply decreases. Under the given simulation condition, the external resistance to mass transfer and heat transfer was found to be negligible beyond a critical value of K_L and external heat transfer coefficient h, respectively.

viii. At any given axial position, the concentration, unlike the temperature, decreases with the increase in dimensionless heat of reaction α.

8.1.2 Dynamic Behavior and Optimal Feed Temperature

The overall performance of a nonisothermal tubular reactor packed with immobilized enzymes has been modeled in terms of pertinent transport and kinetic parameters. The biocatalytic reaction has been assumed to follow the irreversible Michaelis-Menten kinetics having a first order deactivation rate. Based on the considered parametric values (Table 5.1), the model predicts the following:
i. The feed temperature influences the conversion averaged over a given operation period such that an optimal temperature exists. This optimal temperature strongly depends on the mass transfer and heat transfer Biot numbers.

ii. For a given value of $B_{im}$ or $B_{ih}$, the optimal feed temperature sharply drops with the increase in $Pe_m$, up to a value of $Pe_m \approx 50$ beyond which the backmixing does not influence the optimal feed temperature.

iii. The average conversion increases with decrease in Biot number and Stanton number and with increase of external mass transfer resistance parameter $\alpha_1$.

iv. From the analysis of the effect of dimensionless heat of reaction $\alpha$ on the temperature and conversion it was concluded that higher values of $\alpha$ will accelerate the deactivation process thereby reducing the conversion and temperature at a much earlier stage.

v. The biocatalyst particles fairly remain isothermal, independent of the location of the reactor bed.

8.1.3 Effect of Immobilized Enzymes particles Shapes on Reactor Performance

The following conclusions may be drawn from the theoretical analysis to define the performance of tubular reactor packed with immobilized enzyme particles:

i. A generalized mathematical model has been developed for a tubular reactor packed with immobilized enzyme particles of various shapes taking into consideration axial dispersion in the bulk fluid, external and internal mass and heat transfer resistances and Michaelis-Menten kinetics for reaction in the enzyme solution.

ii. The effect of particle geometry is only significant at modified Biot number ($B_{im}^*, B_{ih}^*$) larger than five.

iii. The temperature and conversion decreases with increase of Biot number.
iv. For a specific modified Biot number spherical particle offers maximum conversion and temperature while particle with planar geometry gives minimum conversion and temperature.

8.1.4 Local Wrong-Way Behavior

The present study simulating the influence of a step decrease of the feed temperature of a nonisothermal, immobilized packed-bed reactor concludes the following:

i. Subject to the above feed temperature perturbation, the axial temperature profile inside the reactor fluctuates around the original steady-state temperature profile. This fluctuation decays with time such that the new steady-state temperature profile stabilizes at a much lower value, replicating the original temperature profile. The crests of the fluctuating temperature profile lying above the original temperature profile represent the local wrong-way behavior.

ii. The wrong-way behavior is much critical for an adiabatic reactor, and less pronounced than that of a typical gas-solid system.

iii. The maximum temperature rise, representing the local wrong-way behavior, increases in a similar manner with the increase in axial dispersion for heat and mass, that is, $Pe_h$ and $Pe_m$, respectively. In each case, a critical value exists at which the temperature rise fairly accelerates.

iv. The dimensionless heat of reaction decreases the temperature rise only beyond a critical value. On the other hand, increasing the dimensionless heat transfer coefficient $H$ and Stanton number $St$ reduces it fairly linearly.

v. The axial temperature rise varies as a function of Biot numbers of heat and mass, that is $Bi_h$ and $Bi_m$, respectively, in a manner that differs from that of $Pe_m$, $Pe_h$, $H$ and $St$. In this case, the temperature rise initially increases sharply with the increase in $Bi_h$ and $Bi_m$; then decreases till $Bi_h$ and $Bi_m$ reach a critical value. Beyond this value,
the temperature rises gradually goes up till $\text{Bi}_h$, $\text{Bi}_m \approx 55$. For $\text{Bi}_h$, $\text{Bi}_m > 55$, it again starts to decrease.

8.2 Recommendations for Further Study

Based on the results of the present study, the following future work is recommended:

i. In the present study, the wall temperature of the reactor has been considered constant. But for practical consideration, it is rather difficult to maintain constant temperature along the reactor wall for an exothermic enzymatic reaction. Therefore, the model should be extended for varying temperature along the reactor wall.

ii. In the model formulation, the resistance of the membrane to any transport process has been assumed to be negligible. This resistance should be included in the model equation to make the predictions more realistic.

iii. Another assumption in our model is all transport and physical properties are constant. Heat capacity of the substrate and enzyme solution and intra-particle thermal conductivity depend on temperature. For the exothermic enzymatic reactions, this assumption should be eliminated by considering temperature dependent heat capacity and intra-particle thermal conductivity.

iv. The overall problem, especially the wrong-way behavior, should be extended to multi-substrate, multi-enzyme biochemical reaction.

v. The influence of reactor residence time (length/velocity) on wrong-way behavior should be studied.

vi. The performance of the reactor should be identified based on mass transfer, heat transfer kinetic controlled regions. A more systematic approach should be followed in this matter.
NOMENCLATURE

\( Bi_m \)  \quad \text{Biot number for mass transfer} \quad \frac{K_i R}{D_p}

\( Bi_h \)  \quad \text{Biot number for heat transfer} \quad \frac{h R}{K_p}

\( c_b \)  \quad \text{Substrate concentration in the bulk fluid}

\( C_b \)  \quad \text{Dimensionless substrate concentration in the bulk fluid} \quad \frac{c_b}{c_{bf}}

\( c_{bo} \)  \quad \text{Initial substrate concentration}

\( c_{b} |_{z=0} \)  \quad \text{Substrate concentration at the reactor inlet} = c_{bf}

\( c_{b} |_{z=L} \)  \quad \text{Substrate concentration at the reactor outlet}

\( c_p \)  \quad \text{Substrate concentration inside the particle}

\( C_p \)  \quad \text{Dimensionless substrate concentration inside the particle} \quad \frac{c_p}{c_{bf}}

\( c_E \)  \quad \text{Enzyme concentration}

\( c_{Eo} \)  \quad \text{Initial enzyme concentration}

\( C_E \)  \quad \text{Dimensionless enzyme concentration} \quad \frac{c_E}{c_{Eo}}

\( c_{pb} \)  \quad \text{Heat capacity of the bulk fluid}

\( c_{pp} \)  \quad \text{Heat capacity of the biocatalyst particle}

\( D_{e1} \)  \quad \text{Damkohler number for enzyme reaction} \quad \frac{L_E k_{vo} c_{Eo}}{u c_{bf}}

\( D_{e2} \)  \quad \text{Damkohler number for enzyme deactivation} \quad \frac{L_E k_{do}}{u}

\( D_{ax} \)  \quad \text{Axial mass transfer dispersion coefficient}
\( D_p \) \quad \text{Intra-particle diffusion coefficient}

\( \Delta E_1 \) \quad \text{Activation energy}

\( \Delta E_2 \) \quad \text{Deactivation energy}

\( h \) \quad \text{Heat transfer coefficient for bulk fluid}

\( h_w \) \quad \text{Heat transfer coefficient for reactor wall}

\( (-\Delta H) \) \quad \text{Heat of reaction}

\( H \) \quad \text{Dimensionless number defined as}\( \left( \frac{n+1}{R} \right) h(1-\varepsilon) \frac{L}{u\rho_v c_{pb}} \)

\( K_{ax} \) \quad \text{Axial heat transfer dispersion coefficient}

\( k_{do} \) \quad \text{Initial deactivation rate constant}

\( k_d \) \quad \text{Temperature-dependent deactivation rate constant}

\( k_d = k_{do} \exp\left(-\frac{\Delta E_2}{R_s T_p}\right) \)

\( k_{po} \) \quad \text{Pre exponential factor for enzyme reaction rate constant}

\( k_p \) \quad \text{Temperature-dependent enzyme reaction rate constant}

\( k_p = k_{po} \exp\left(-\frac{\Delta E_1}{R_s T_p}\right) \)

\( K_p \) \quad \text{Intra-particle thermal conductivity}

\( k_m \) \quad \text{Michaelis-Menten constant}

\( K \) \quad \text{Dimensionless turnover number}\( \frac{k_m}{c_{po}} \)

\( K_L \) \quad \text{External mass transfer coefficient}

\( L \) \quad \text{Length of the reactor, 120 cm}

\( Pe_m \) \quad \text{Peclet number for mass}\( \frac{uL}{D_{ax}\varepsilon} \)

\( Pe_h \) \quad \text{Peclet number for heat}\( \frac{uL\rho_v c_{pb}}{K_{ax}\varepsilon} \)

\( R \) \quad \text{Radius of spherical biocatalyst particle}
\[ R_R \] Radius of the reactor of tube

\[ \bar{r} \] Radial coordinate of the spherical geometry

\[ r \] Dimensionless radial coordinate of the spherical geometry \( \frac{\bar{r}}{R} \)

\[ R_g \] Universal gas constant

\[ St \] Stanton number \( \frac{2h_w}{R_R} \frac{L}{u \rho_b c_{pb}} \)

\[ T_o \] Dimensionless feed substrate temperature

\[ \bar{T}_o \] Reference temperature \( \frac{\Delta E_i}{R_p} \)

\[ \bar{T}_w \] Reactor wall temperature

\[ \bar{T}_p \] Substrate temperature inside particle

\[ \bar{T}_{po} \] Initial temperature of the enzyme solution inside the biocatalyst particle

\[ \bar{T}_b \] Substrate temperature in the bulk

\[ T_W \] Dimensionless reactor wall temperature \( \frac{\bar{T}_w}{\Delta E_i} \)

\[ T_b \] Dimensionless substrate temperature in the bulk \( \frac{\bar{T}_b}{\Delta E_i} \)

\[ \bar{T}_{bo} \] Initial substrate temperature in the bulk liquid

\[ T_p \] Dimensionless substrate temperature in the bulk \( \frac{\bar{T}_p}{\Delta E_i} \)
\( t \) Time

\( u \) Superficial velocity, 0.8 cm/sec

\( z \) Axial distance along the reactor

\( Z \) Dimensionless axial distance along reactor \( \frac{z}{L} \)

Greek symbols

\( \varepsilon \) Bed voidage

\( \alpha \) Dimensionless heat of reaction (adiabatic temperature rise)

\[
\frac{c_{bf} (-\Delta H) R_g}{\rho_p c_{pp} \Delta E_1}
\]

\( \alpha_i \) Dimensionless number defined as

\[
\frac{n + 1}{R} \frac{K_L L (1 - \varepsilon)}{u}
\]

\( \beta \) Dimensionless number defined as

\[
\frac{L \varepsilon D_p}{u R^2}
\]

\( \beta_i \) Dimensionless number defined as

\[
\frac{L \varepsilon}{u R^2} \frac{K_p}{\rho_p c_{pp}}
\]

\( \gamma \) Ratio of deactivation energy to activation energy \( \frac{\Delta E_2}{\Delta E_1} \)

\( \tau \) Dimensionless time \( \frac{uL}{L \varepsilon} \)

\( \rho_p \) Density of the biocatalyst particle

\( \rho_b \) Substrate density in the bulk fluid phase
APPENDIX A

Derivation of the collocation equations

The dimensionless partial differential equations (15) to (27) can be reduced to ordinary differential equations by the method of Orthogonal Collocation.

In the present collocation method, the concentration profile in the spherical particle is approximated by the symmetric trial function:

\[ C_p(\tau, \tau) = C_p(0, \tau) + (1 - r^2) \sum_{i=1}^{N} a_i(\tau) P_{i-1}(r^2) \]  

(28)

where \( a_i(\tau) \) are functions of time (or constants) and \( P_j \) are the orthogonal polynomials defined by:

\[ \int_0^1 w(r^2) P_j(r^2) P_i(r^2) r^{i-1} \, dr = C_i \delta_{ij} \]  

(29)

where \( w(r^2) = 1 - r^2 \)

\[ j = 1, 2 \ldots \quad i - 1 \]

The constant \( C_i \) in Eqn. (29) is as defined by Villadsen and Steward (1967) and \( \delta_{ij} \) is unity if \( i = j \) and zero otherwise.

The concentration profiles in the bulk fluid phase has been approximated by non-symmetric polynomials of the type

\[ C_b(Z, \tau) = (1 - Z)C_b(0, \tau) + ZC_b(1, \tau) + Z(1 - Z) \sum_{i=1}^{N} a_i(\tau) P_{i-1}(Z) \]  

(30)

where \( a_i \) are arbitrary co-efficients and \( P_j \) are the non-symmetric polynomials defined by the condition
\[
\int_0^w(Z)P_n(Z)P_m(Z)\,dZ = 0
\]

\(n = 0, 1, \ldots, m-1\)

\(w(Z) = 1\) in the present study.

Equations (15)-(27) can be expressed in the collocation form as follows:

For the mass balance in the immobilized enzyme particle

\[
\frac{dC_{pk}}{d\tau} = \beta \sum_{i=1}^{N+1} B_{k,i} C_{pi} - \frac{D_{al} C_{Ek} C_{pk}}{C_{pk} + K} \exp\left(-\frac{1}{T_{pk}}\right)
\]

\(k = 1, 2, 3, \ldots, N\)

\[
\sum_{i=1}^{N+1} A_{1,i} C_{pi} = 0
\]

\[
\sum_{i=1}^{N+1} A_{N+1,i} C_{pi} = Sh\left(C_{ij}\left(\tau\right) - C_{p,N+1}\right)
\]

For the mass balance of bulk fluid phase

\[
\frac{dC_{bj}}{d\tau} = \frac{1}{P_{em}} \sum_{i=1}^{M} BX_{j,i} C_{bi} + \sum_{i=1}^{M} AX_{j,i} C_{bi} - \alpha_{i}\left(C_{ij} - C_{p,N+1}\right)
\]

\[
\sum_{i=1}^{M} AX_{1,i} C_{bi} = -P_{em}\left(C_{b_{i+1}} - C_{bi}\right)
\]
\[ \sum_{i=1}^{M+2} A X_{f_{i+2}, i} C_{b_i} = 0 \]  
(36)

For the energy balance in the immobilized enzyme particle

\[ \frac{d T_{pk}}{d \tau} = \beta_i \sum_{i=1}^{N+1} B_{k,i} T_{p_i} + \frac{D_{a,i} C_{Ek} C_{pk}}{C_{pk} + K} \exp \left( -\frac{1}{T_{pk}} \right) \]  
(37)

\[ k = 1, 2, 3 \ldots \ldots, N \]

\[ \sum_{i=1}^{N+1} A_{1,i} T_{p_i} = 0 \]  
(38)

\[ \sum_{i=1}^{N+1} A_{N+1,i} T_{p_i} = Nu \left( T_{b_j} (\tau) - T_{p,N+1} \right) \]  
(39)

For the energy balance of bulk fluid phase

\[ \frac{d T_{bj}}{d \tau} = \frac{1}{P_{eh}} \sum_{i=1}^{M+2} B X_{j,i} T_{bi} - \sum_{i=1}^{M+2} A X_{j,i} T_{bi} - H \left( T_{bj} - T_{p,N+1} \right) - St \left( T_{bj} - T_w \right) \]  
(40)

where \( j = 2, 3, \ldots, M+1 \)

\[ \sum_{i=1}^{M+2} A X_{1,i} T_{bi} = -P_{eh} \left( T_{bi}^{t_{2+}^+} - T_{bl} \right) \]  
(41)
\[
\sum_{i=1}^{M+1} \alpha X_{i,z,j} T_{bi} = 0
\]

(42)

For the deactivation rate of enzyme

\[
\frac{d C_{Ek}}{d \tau} = -D_{a2} C_{Ek} \exp\left(-\frac{\gamma}{T_{pk}}\right)
\]

(43)

where \( k = 1, 2, \ldots, N \)

where \( M \) and \( N \) are the number of internal collocation points for the bulk fluid phase and for the immobilized enzyme particle respectively.

Equations (30)-(43) can be rearranged to give the following expressions in terms of internal collocation points:

For the mass balance in the immobilized enzyme particle

\[
\frac{d C_{pk}}{d \tau} = \beta \left[ \sum_{i=1}^{N} B_{k,i} - \frac{B_{k,N+1} A_{N+1,i}}{R_p} \right] C_{pi} + \frac{\beta Sh B_{k,N-1}}{R_p} C_{bj} - \frac{D_{a2} C_{Ek} C_{pk}}{C_{pk} + K} \exp\left(-\frac{1}{T_{pk}}\right)
\]

(44)

where \( R_p = A_{N+1,N+1} + Sh \)

The substrate concentration at the surface of the particle is,

\[
C_{p,N+1} = \frac{Sh C_{bj}(\tau) - \sum_{i=1}^{N} A_{N+1,i} C_{pi}}{R_p}
\]

(45)
\[
\frac{dC_{b,i}}{d\tau} = \sum_{i=2}^{M+1} \left[ \left( \frac{1}{P_{em}} BX_{j,i} - AX_{j,i} \right) + \left( \frac{1}{P_{em}} BX_{j,i} - AX_{j,i} \right) \right] R_3 AX_{M+2,i} - R_4 AX_{i,i} \] + \\
\left[ \left( \frac{1}{P_{em}} BX_{j,M+2} - AX_{j,M+2} \right) \right] C_{b,i} \\
-P_{em} C_{b,i} \left[ R_2 \left( \frac{1}{P_{em}} BX_{j,i} - AX_{j,i} \right) - R_1 \left( \frac{1}{P_{em}} BX_{j,M+2} - AX_{j,M+2} \right) \right] \\
-\alpha_i \left[ 1 - \frac{Sh}{R_{p}} \right] C_{b,i} \\
-\sum_{i=1}^{N} \left( \frac{\alpha_i}{R_{p}} \right) A_{N+1,i} C_{P,i}
\] (46)

where 
\[
R = AX_{M+2,M+2} \left( AX_{1,1} - P_{em} \right) - AX_{M-2,1} AX_{1,M+2} \\
R_1 = AX_{M-2,1} / R \\
R_2 = \left( AX_{1,1} - P_{em} \right) / R \\
R_3 = AX_{1,M+2} / R \\
R_4 = AX_{M-2,M+2} / R
\]

The inlet concentration (at \(Z=0^+\)) in the external bulk fluid phase, \(C_{b,1}\) and exit concentration, \(C_{b,M+2}\) may be written respectively as

\[
C_{b,1} = R_3 \sum_{i=2}^{M+1} AX_{M-2,i} C_{b,i} - R_4 \sum_{i=2}^{M+1} AX_{1,i} C_{b,i} - R_1 P_{em} C_{b,1} \bigg|_{Z=0^+}. \quad (47)
\]

\[
C_{b,M+2} = R_1 \sum_{i=2}^{M+1} AX_{1,i} C_{b,i} - R_2 \sum_{i=2}^{M+1} AX_{M-2,i} C_{b,i} + R_1 P_{em} C_{b,1} \bigg|_{Z=0^+}. \quad (48)
\]
For the energy balance in the catalyst particle

\[
\frac{d T_{pk}}{d \tau} = \beta_l \left( \sum_{i=1}^{N} B_{k,i} - \sum_{i=1}^{N} \frac{A_{N+1,i}}{R_p} \right) T_{pi} \\
+ \frac{\beta_l B_{k,N+1} T_{pk}}{R'_p} \\
+ \frac{D_{21} C_{Ek} \alpha C_{pk}}{C_{pk}} \exp \left( -\frac{1}{T_{pk}} \right)
\]

(49)

where \( R'_p = A_{N+1,N+1} + Nu \).

The temperature at the surface of the particle is

\[
T_{p,N+1} = \frac{Nu T_{bj} - \sum_{i=1}^{N} A_{N+1,i} T_{pi}}{R'_p}
\]

(50)

For the energy balance of bulk fluid phase

\[
\frac{d T_{bj}}{d \tau} = \sum_{i=2}^{M+1} \left( \frac{1}{P_{eb}} BX_{j,i} - AX_{j,i} \right) + \left( \frac{1}{P_{eb}} BX_{j,1} - AX_{j,1} \right) \left( R'_{j} AX_{N+2,i} - R'_{j} AX_{j,i} \right)
\]
\[
\left(\frac{1}{Pe_h} BX_{j,M+2} - AX_{j,M+2}\right) \left(R'_1 AX_{i,j} - R'_2 AX_{M+2,i}\right)\right]\] 
\[
-P_{eh} T_{b,i} \left[ R'_2 \left(\frac{1}{Pe_h} BX_{j,1} - AX_{j,1}\right) - R'_1 \left(\frac{1}{Pe_h} BX_{j,M+2} - AX_{j,M+2}\right)\right] 
- H \left[ 1 - \frac{Nu}{R'_p} \right] T_{b,j} 
- \sum_{i=1}^{N} \left[ H \left(\frac{R'_i}{R'_p}\right) A_{N+1,i} T_{P,i}\right] 
- \text{St} \left( T_{b_j} - T_w \right)
\]

(51)

where \( R' = AX_{M+2,M+2} \left(AX_{1,1} - P_{eh}\right) - AX_{M+2,1} AX_{1,M+2} \)
\( R'_1 = AX_{M+2,i} / R' \)
\( R'_2 = \left(AX_{1,1} - P_{eh}\right) / R' \)
\( R'_3 = AX_{1,M+2} / R' \)
\( R'_4 = AX_{M+2,M+2} / R' \)

The inlet concentration (at \( Z=0^+ \)) in the external bulk fluid phase, \( T_{b,i} \) and exit concentration, \( T_{b,M+2} \) may be written respectively as

\[
T_{b,i} = R'_3 \sum_{i=2}^{M+1} AX_{M+2,i} T_{bi} - R'_1 \sum_{i=2}^{M+1} AX_{1,i} T_{bi} - R'_4 P_{eh} T_{b} \bigg|_{Z=0^+}
\]

(52)

\[
T_{b,M+2} = R'_4 \sum_{i=2}^{M+1} AX_{1,i} T_{bi} - R'_2 \sum_{i=2}^{M+1} AX_{M+2,i} T_{bi} + R'_1 P_{ew} T_{b} \bigg|_{Z=0^+}
\]

(53)

The collocation matrices A, B, AX and BX have been generated by procedures described by Finlayson (1972).
References


APPENDIX B

Computer Programs
**FOR SPHERICAL PARTICLE WITHOUT DEACTIVATION (DA2=0.0)

**BASE CASE

**ANALYSIS OF A NONISOTHERMAL TUBULAR REACTOR

---------------------------------------------------------------

C: THE METHOD OF ORTHOGONAL COLLOCATION HAS BEEN EMPLOYED HERE.
C: TO REDUCE THE DEFINING PARTIAL DIFFERENTIAL EQUATIONS TO
C: NON-LINEAR O.D.E.S. THE SET OF N.L.O.D.E IS THEN SOLVED.
C: N HAS BEEN USED AS A PARAMETER

C: N=(MM+2)*(NI+1)  *****REDEFINE FOR NONISOTHERMAL CASE*****
C: WHERE MM IS THE NUMBER OF INTERNAL COLL. POINTS FOR EXTERNAL
C: PHASE AND NI IS THE NUMBER OF INTERNAL COLL. POINTS FOR PARTICLE.

---------------------------------------------------------------

C: PARAMETER(N=140)
IMPLICIT REAL*8(A-H,O-Z)
INTEGER METH,MITER,IKW(N),IER,K
REAL*8 Y(N),WK(N+1),T,TOL,TEND,
REAL*8 PARAM(50),DUMMY(1,1)
COMMON/DATA/CLT,AMPL,CHZ,PEM,ALFA,SH,TBAR,S1,CK,SK,P,CON1,NI,
COMMON/DATA/THZ,PEH,ALFAI,CNH,T1,PH,CON1T,S1,TW,BETA,DA1,DA2,
,GAMMA
COMMON AX(30,30),BX(30,30),X(50),VMAX
COMMON CH(50,50),F(30),A(50,50),B(50,50),PG(50,50)
COMMON TH(50,50),TFC(50,50),TACT(60)
DIMENSION CONV(50)
EXTERNAL FCN,FCN1

C: *****************COLLOCATION PARAMETERS***********************
C: MM IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR BED
C: NI IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR PARTICLE

C: MM=8
M1=MM+1
M2=MM+2
M20=M2*2.0
M30=M2*3.0
M40=M2*4.0
M50=M2*5.0
M60=M2*6.0
M70=M2*7.0
M80=M2*8.0
M90=M2*9.0
M100=M2*10.0


```fortran
N110=M2*11.0
N120=M2*12.0
N130=M2*13.0
N140=M2*14.0

C
N1=N1+1
C
DO 9 I=1,M2
   DO 9 J=1,M2
  9 READ(5,*)AX(I,J)
C
DO 5 I=1,M2
   DO 5 J=1,M2
  5 READ(5,*)BX(I,J)
C
C X( 1)=  0.2957581E+00
C X( 2)=  0.5652353E+00
C X( 3)=  0.7844035E+00
C X( 4)=  0.9300014E+00
C X( 5)=  1.0000000E+01
A( 1, 1)=-0.5071712E+01
A( 1, 2)=  0.8658617E+01
A( 1, 3)=-0.6367129E+01
A( 1, 4)=  0.4695816E+01
A( 1, 5)=-0.1865592E+01
A( 2, 1)=-0.1034610E+01
A( 2, 2)=-0.2653762E+01
A( 2, 3)=  0.6392034E+01
A( 2, 4)=-0.3711387E+01
A( 2, 5)=  0.1407729E+01
A( 3, 1)=  0.5229562E+00
A( 3, 2)=  0.3168659E+01
A( 3, 3)=  0.1912086E+01
A( 3, 4)=  0.6623901E+01
A( 3, 5)=-0.2066112E+01
A( 4, 1)=-0.3860729E+00
A( 4, 2)=  0.1861797E+01
A( 4, 3)=-0.6701922E+01
A( 4, 4)=-0.1605993E+01
A( 4, 5)=  0.6832509E+01
A( 5, 1)=  0.7615325E+00
A( 5, 2)=-0.3486199E+01
A( 5, 3)=-0.1026042E+02
A( 5, 4)=-0.3356176E+02
A( 5, 5)=  0.2600000E+02
B( 1, 1)=  0.3446540E+02
B( 1, 2)=  0.4414925E+02
B( 1, 3)=-0.1426772E+02
B( 1, 4)=  0.7002486E+01
B( 1, 5)=-0.2418620E+01
B( 2, 1)=  0.1397961E+02
B( 2, 2)=-0.5231625E+02
```
B( 2, 1)= 0.4803702E+02
B( 2, 4)= -0.1517764E+02
B( 2, 5)= 0.4677069E+01
B( 3, 1)= -0.3108303E+01
B( 3, 2)= 0.3360006E+02
B( 3, 3)= -0.9452824E+02
B( 3, 4)= 0.8089441E+02
B( 3, 5)= -0.1685794E+02
B( 4, 1)= 0.1837682E+01
B( 4, 2)= -0.1257995E+02
B( 4, 3)= 0.9744605E+02
B( 4, 4)= -0.2666901E+03
B( 4, 5)= 0.1999845E+03
B( 5, 1)= 0.3854616E+02
B( 5, 2)= -0.1703650E+03
B( 5, 3)= 0.4579635E+03
B( 5, 4)= -0.7941446E+03
B( 5, 5)= 0.4680000E+03

C
T=0.0

C: *************** INITIAL CONDITION **************

C
DO 4 I=1,M50
4 CONTINUE
Y(1)=1.0
Y(1)=0.0

4 CONTINUE
DO 43 I=1,M2
CONV(1)=0.0
43 CONTINUE
M51=M50 +1
DO 415 I=M51,M100
Y(I)=0.0600
415 CONTINUE
M101=M100 +1
DO 416 I=M101,N
Y(I)=1.0
416 CONTINUE

C

C: ********** IMSL VARIABLES **********************
C: -------- TFIN = FINAL TIME  ---------------
C: -------- DTPRNT = PRINT INTERVAL ------------
C:
TFIN = 40.0
DTPRNT =2.00
NPRINT = INT(TFIN/DTPRNT)

C

C:
TOL =0.00001
H=0.000001
METH=2
MITER=0
INDEX=1

C:*********************** FOR DIVPAG **********************
IER=0
NPARAM=50
CALL SSET(NPARAM,0.0,PARAM,1)
PARAM(1)=11
PARAM(4)=10000
PARAM(12)=METH
PARAM(13)=HITER
PARAM(19)=0

C: ****** PARAMETERS FOR THE PROBLEM **********
C
C    CHZ=1.00
THZ=0.0600
PEM=1.0E+04
PEH=PEM*0.25
ALFA=2.880
C    ALFA=8.0
ALFAH=ALFA
C    ALFAH=2.880E+00
SII=0.54
C    SIH=5.0
C    CNH=0.025
CNH=SII
ST=0.1
C    ST=0.1
Tw=0.0600
C    SL=10.
C    BETA=0.04
BETA=1.0E-02
C    BETA=1.0E-02*SL/4.0
TBAR=60.0
C    VMAX=0.02
DA1=5.0E+06
C    DA1=5.0E+06*4.0/SL
DA2=0.0
C    GAMMA=76000.0/10000.0
FACT=10000.0/2.0
C
C    NOTE: SI= 25.0 FOR ZERO ORDER AND SI=4.0 FOR OTHER KINETICS
C
C    SI=4.0
C    SI=45.0
CK=2.0
C    CK=CK/SL
SK=2.0
M=1.0/PEM
MI=1.0/PEH
C    CON1=0.760
CON1=0.296
CON11=CON1
C    CON11=25.
C
C  ****** END OF PARAMETERS ****************************
c

****** INPUT FOR X VALUE AND AX & BX MATRIX ******

X(1)=0.0
X(2)=0.0199
X(3)=0.1017
X(4)=0.2372
X(5)=0.4083
X(6)=0.5917
X(7)=0.7628
X(8)=0.8983
X(9)=0.9801
X(10)=1.0

WRITE(7,2001)
WRITE(7,2002) PEM
WRITE(7,2003) ALFA
WRITE(7,2004) TBAK
WRITE(7,2005) SI
WRITE(7,2006) CK
WRITE(7,2007) SK
WRITE(7,2008) CON1
WRITE(7,2018) CON1
WRITE(7,2009) PEM
WRITE(7,2010) ALFA
WRITE(7,2011) TBAK
WRITE(7,2012) VMAX
WRITE(7,2013) VMAX
WRITE(7,2014) SI
WRITE(7,2015) CK
WRITE(7,2016) SK
WRITE(7,2017) CON1
WRITE(7,2018) CON1
WRITE(7,2019) CNH
WRITE(7,2020) CHZ

WRITE(7,2001)
WRITE(7,2002) PEM
WRITE(7,2003) ALFA
WRITE(7,2004) TBAK
WRITE(7,2005) SI
WRITE(7,2006) CK
WRITE(7,2007) SK
WRITE(7,2008) CON1
WRITE(7,2018) CON1
WRITE(7,2009) PEM
WRITE(7,2010) ALFA
WRITE(7,2011) TBAK
WRITE(7,2012) VMAX
WRITE(7,2013) VMAX
WRITE(7,2014) SI
WRITE(7,2015) CK
WRITE(7,2016) SK
WRITE(7,2017) CON1
WRITE(7,2018) CON1
WRITE(7,2019) CNH
WRITE(7,2020) CHZ
**FUNCTION TEFILMS FORTRAN A**

**KING ABDUL UNIVERSITY OF ELBOUL AND MINERALS, DUNHAN**

```fortran
7810 FORMAT(5X, 'DIMLESS FEED CONC., CI2 = ', E14.7)
WRITE(7, 7011) TII2
7811 FORMAT(5X, 'DIMLESS FEED TEMP., TII2 = ', E14.7)
WRITE(7, 7010)
7810 FORMAT(5X, '********END OF THE PARAMETERS FOR THIS RUN**********')
WRITE(6, 3001)
3001 FORMAT(1X, 'TIME CONC. TEMP CONV')
TACT(M2) = Y(I*6*M2)*TACT-273.0
WRITE(6, 3002) T, Y(M2), TACT(M2), CONV(M2)
WRITE(7, 1003) T
WRITE(7, 1004)
WRITE(7, 1071)
TACT(M2) = Y(I*6*M2)*TACT-273.0
DO 1112 I = 1, M2
1112 TACT(I) = Y(I+5*M2)*TACT-273.0
DO 1113 I = 1, M2
1113 TACT(I*M2) = Y(I+6*M2)*TACT-273.0
DO 1114 I = 1, M2
1114 TACT(I+2*M2) = Y(I+7*M2)*TACT-273.0
DO 1115 I = 1, M2
1115 TACT(I+3*M2) = Y(I+8*M2)*TACT-273.0
DO 1116 I = 1, M2
1116 TACT(I+4*M2) = Y(I+9*M2)*TACT-273.0
DO 1115 I = 1, M2
WRITE(7, 1016) X(I), Y(I), Y(I+M2), Y(I+2*M2), Y(I+3*M2), Y(I+4*M2),
, CONV(I)
WRITE(9, 1006) X(I), Y(I+5*M2), Y(I+6*M2), Y(I+7*M2),
, Y(I+8*M2), Y(I+9*M2)
WRITE(9, 1006) X(I), TACT(I), TACT(I*M2), TACT(I+2*M2), TACT(I+3*M2),
, TACT(I+4*M2)
1115 CONTINUE
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
C
K1=K+1

CH(K,J)=P’BX(J,K1)+AX(J,K1)+((P’BX(J,1)-AX(J,1))*(R1*AX(NP,K1)-
&RH*AX(1,K1))+((P’BX(J,M2)-AX(J,M2))*(R1*AX(1,K1)-R2*AX(NP,K1)))

22 CONTINUE

CH(M1,J)=PEH*CHZ*RH*(P’BX(J,1)-AX(J,1))
CH(M2,J)=PEH*CHZ*R1*(P’BX(J,M2)-AX(J,M2))

23 CONTINUE

DO 203 J=2,NI
DO 202 K=1,MM
K1=K+1

TH(K,J)=PH’*BX(J,K1)-AX(J,K1)+((PH’*BX(J,1)-AX(J,1))*(RT3*AX(MP,K1)-
&RT4*AX(1,K1))+((PH’*BX(J,M2)-AX(J,M2))*(RT5*AX(1,K1)
&-RT2*AX(M2,K1)))

202 CONTINUE

TH(M1,J)=PEH*THZ*RT3*(PH’*AX(J,1)-AX(J,1))
TH(M2,J)=PEH*THZ*R1*(PH’*AX(J,M2)-AX(J,M2))

203 CONTINUE

RP=A(N1,N1)+SH
RPT=A(N1,N1)+CNH

C11=ALFA*(1.0-(SH/RP))
T11=ALFAH*(1.0-(CNH/RPT))
C12=-(ALFA/RP)*A(N1,1)
C13=-(ALFA/RP)*A(N1,2)
C14=-(ALFA/RP)*A(N1,3)
C15=-(ALFA/RP)*A(N1,4)
T12=-(ALFAH/RPT)*A(N1,1)
T13=-(ALFAH/RPT)*A(N1,2)
T14=-(ALFAH/RPT)*A(N1,3)
T15=-(ALFAH/RPT)*A(N1,4)

DO 12 J=1,NI
 DO 13 I=1,NI
 PC(I,J)=CON1*(B(J,1)-(R(J,N1)*A(N1,1)/RP))
 TPC(I,J)=CON1*(B(J,1)-(R(J,N1)*A(N1,1)/RPT))

13 CONTINUE

PC(N1,J)=CON1*SH*B(J,N1)/RP
 TPC(N1,J)=CON1*CNH*B(J,N1)/RPT

12 CONTINUE

DO 10 K=1,NPRINT
 TEND=DPRINT*FLOAT(K)

CALL DIVPAG(INDEX,N,FCN,FCNJ,DUMMY,T,TEND,TOL,FARAM,Y)

DO 123 I=1,M2
 CONV(I)=1.0-Y(I)

123 CONTINUE
TACT(M2)=Y(6*2)*FACT-273.0
WRITE(6,3002) T,Y(M2),TACT(M2),CONV(M2)
WRITE(6,3002) T,Y(M2),Y(6*2),CONV(M2)
1002 FORMAT(1X,F10.4,2X,F6.4,2X,F6.4,2X,F10.4)
WRITE(7,1003) T
1003 FORMAT(10X,'TIME = ',F10.4,/,)
WRITE(7,1004)
WRITE(9,3004)
1004 FORMAT(3X,'XVALUE',5X,'BULK',5X,'PARTL1',
   ,5X,'PARTL2',5X,'PARTL3',5X,'PARTL4',5X,'CONV',/,)
WRITE(9,2071)
WRITE(9,2071)
2071 FORMAT(2X,'Y=0.296',
   ,5X,'Y=0.565',5X,'Y=0.784',5X,'Y=0.934',/,)
WRITE(7,1071)
1071 FORMAT(2X,'Y=0.296',
   ,5X,'Y=0.565',5X,'Y=0.784',5X,'Y=0.934',/,)
DO 1005 I=1,M2
WRITE(7,1016)X(I),Y(I),Y(I+1),Y(I+2),Y(I+3),Y(I+4),CONV(I)
1005 CONTINUE
DO 2222 M2=1,M2
2222 TACT(I)=Y(1+5*M2)*FACT-273.0
DO 2223 I=1,M2
2223 TACT(1+M2)=Y(1+6*M2)*FACT-273.0
DO 2224 I=1,M2
2224 TACT(1+2*M2)=Y(1+7*M2)*FACT-273.0
DO 2225 I=1,M2
2225 TACT(1+3*M2)=Y(1+8*M2)*FACT-273.0
DO 2226 I=1,M2
2226 TACT(1+4*M2)=Y(1+9*M2)*FACT-273.0
DO 3005 I=1,M2
WRITE(9,1006)X(I),TACT(I),TACT(I+M2),TACT(I+2*M2),TACT(I+3*M2),TACT(I+4*M2)
3005 CONTINUE
WRITE(10,1003) T
WRITE(10,9004)
9004 FORMAT(3X,'XVALUE',5X,'CPR',
   ,5X,'CPR2',5X,'CPR3',5X,'CPR4',/,)
WRITE(9,9071)
9071 FORMAT(1X,'Y=0.296',
   ,5X,'Y=0.565',5X,'Y=0.784',5X,'Y=0.934',/,)
DO 9005 I=1,M2
WRITE(10,1006)X(I),Y(I+10*M2),Y(I+11*M2),Y(I+12*M2),Y(I+13*M2)
9005 CONTINUE
1006 FORMAT(4X,F6.4,5(1X,F10.6))
1016 FORMAT(4X,F6.4,6(1X,F10.6))
IF (IER.GT.128) GO TO 20
10 CONTINUE
GO TO 30
20 CONTINUE
C
WRITE(6,1002)N,IER
C
1001 FORMAT(1X,F8.3,10F7.3/, (9X,10F7.3))
1002 FORMAT(1X,'NO. OF CELLS = ',I5,' IER VALUE = ',1.5)
C
30 CONTINUE
131 CONTINUE
STOP
END
C
C
SUBROUTINE FCN(N,T,Y,YPRIME)
IMPLICIT REAL*(A-H,O-Z)
REAL*8 TERN,
REAL*8 SUMA1(30),YPRIME(N),Y(N),T
REAL*8 SUMT(30)
COMMON/DATA/CLT,AMPL,CHZ,PEN,ALFA,SH,TBAR,SI,CK,SH,F,CONH,MM,N1
COMMON/DATA/TIHZ,PEH,ALTAH,CHN,T1,PH,CONIT,ST,IV,RTFA,DA1,DA2
,GAMMA
COMMON AX(30,30),BX(30,30),X(50),VMAX
COMMON CH(50,50),F(30),A(50,50),B(50,50),FC(50,50)
COMMON TIH(50,50),TFC(50,50)
DIMENSION CONV(50)
INTEGER N
C
CHZ= 1.0
M1=MM+1
M2=MM+2
M20=M2*2.0
M30=M2*3.0
M40=M2*4.0
M50=M2*5.0
M60=M2*6.0
M70=M2*7.0
M80=M2*8.0
M90=M2*9.0
M100=M2*10.0

************************************************************************
M110=M2*11.0
M120=M2*12.0
M130=M2*13.0
M140=M2*14.0

************************************************************************
C
N1=N1+1
C
R=(AX(M2,M2)/AX(M2,11)-(AX(1,M2)/AX(1,1)-PEM))
R1=1.0/(R*(AX(1,1)-PEM))
R2=1.0/(R*(AX(M2,11)))
R3=((R2*AX(M2,M2))-1.0)/AX(M2,1)
R4=(R1*AX(M2,M2))/AX(M2,1)
C
C
************************************************************************
C: **************************************************
C
RT=(AX(M2,M2)/AX(M2,1))-(AX(1,M2)/(AX(1,1)-PEH))
RT1=1.0/(RT*(AX(1,1)-PEH))
RT2=1.0/(RT*(AX(M2,1)))
RT3=((RT2*AX(M2,M2))-1.0)/AX(M2,1)
RTH=(RT1*AX(M2,M2))/AX(M2,1)
C:
C: **************************************************
C
DO 23 J=2,M1
DO 22 K=1,MM
K1=K+1
CH(K,J)=P*BX(J,K1)-AX(J,K1)+((P*BX(J,1)-AX(J,1))*(R1*AX(M2,K1)-
&RT4*AX(1,K1)))+((P*BX(J,M2)-AX(J,M2))*(R1*AX(1,K1)-R2*AX(M2,K1))}
22 CONTINUE
CH(M1,J)=PEH*CHZ*RT4*(P*BX(J,1)-AX(J,1))
CH(M2,J)=PEH*CHZ*R1*(P*BX(J,M2)-AX(J,M2))
23 CONTINUE
C:
C
DO 203 J=2,M1
DO 202 K=1,MM
K1=K+1
TH(K,J)=PH*BX(J,K1)-AX(J,K1)+((PH*BX(J,1)-AX(J,1))*(RT3*AX(M2,K1)-
&RT4*AX(1,K1)))+((PH*BX(J,M2)-AX(J,M2))*(RT1*AX(1,K1)
&RT2*AX(M2,K1))}
202 CONTINUE
TH(M1,J)=PEH*THZ*RTH*(PH*BX(J,1)-AX(J,1))
TH(M2,J)=PEH*THZ*RTH*(PH*BX(J,M2)-AX(J,M2))
203 CONTINUE
RP=A(N1,N1)+SH
RPT=A(N1,N1)+CNH
C
C11=ALFA*(1.0-(SH/RP))
T11=ALFAH*(1.0-(CNH/RPT))
C12=(-ALFA/RP)*A(N1,1)
C13=(-ALFA/RP)*A(N1,2)
C14=(-ALFA/RP)*A(N1,3)
C15=(-ALFA/RP)*A(N1,4)
T12=(-ALFAH/RPT)*A(N1,1)
T13=(-ALFAH/RPT)*A(N1,2)
T14=(-ALFAH/RPT)*A(N1,3)
T15=(-ALFAH/RPT)*A(N1,4)
C
DO 12 J=1,N1
DO 13 I=1,N1
PC(I,J)=CON1*(B(J,1)-B(J,N1)*A(N1,1)/RP)
TPC(I,J)=CON1*(B(J,1)-B(J,N1)*A(N1,1)/RPT)
13 CONTINUE
PC(N1,J)=-CON1*SH*B(J,N1)/RP
TPC(N1,J)=-CON1*CNH*B(J,N1)/RPT
12 CONTINUE
10 DO 21 J=2,M1
    SUMA1(J)=0.0
    SUMT1(J)=0.0
21 CONTINUE
DO 25 J=2,M1
DO 25 I=1,M4
   II=I+1
   SUMA1(J)=SUMA1(J)+CH(1,I)*Y(I)
   SUMT1(J)=SUMT1(J)+TII(1,I)*Y(5*M2+II)
25 CONTINUE
DO 700 I=1,M4
   II=I+M2*(I-1)
   12=M2*I
   YPRIME(II)=0.0
   YPRIME(12)=0.0
700 CONTINUE
DO 800 I=2,M1
   YPRIME(I)=0.0
   YPRIME(I+5*M2)=0.0
   YPRIME(I)=SUMA1(I)-CH(M1,I)*CH(M2,I)-&C11*Y(I)+C12*Y(I+M2)+C13*Y(I+2*M2)+C14*Y(I+3*M2)+C15*Y(I+4*M2)
   &+PC(1,1)*Y(I+6*M2)-PC(5,1)*Y(I)-
   &+PC(4,1)*Y(I+4*M2)-PC(5,1)*Y(I)-
   &Mitchel Menken
   &{(DAI*Y(I+10*M2))}*EXP(-1.0/Y(I+6*M2))*Y(I+M2)/&Y(I+M2)+SK
   &yprime(I+2*M2)=PC(1,2)*Y(I+2*M2)+PC(2,2)*Y(I+2*M2)+ PC(3,2)*Y(I+3*M2)+&Y(I+4*M2)*Y(I+5*M2)+&+PC(4,2)*Y(I+4*M2)-PC(5,2)*Y(I)-
   &{(DA1*Y(I+11*M2))}*EXP(-1.0/Y(I+7*M2))*Y(I+2*M2)/&Y(I+2*M2)+SK
   &YPRIME(I+3*M2)=PC(1,3)*Y(I+3*M2)+PC(2,3)*Y(I+2*M2)+ PC(3,3)*Y(I+3*M2)+&Y(I+4*M2)*Y(I+5*M2)+&+PC(4,3)*Y(I+4*M2)-PC(5,3)*Y(I)-
   &{(DA1*Y(I+12*M2))}*EXP(-1.0/Y(I+8*M2))*Y(I+3*M2)/&Y(I+3*M2)+SK
   &YPRIME(I+4*M2)=PC(1,4)*Y(I+4*M2)+PC(2,4)*Y(I+2*M2)+ PC(3,4)*Y(I+4*M2)+&Y(I+4*M2)*Y(I+5*M2)+&+PC(4,4)*Y(I+4*M2)-PC(5,4)*Y(I)-
   &{(DA1*Y(I+13*M2))}*EXP(-1.0/Y(I+9*M2))*Y(I+4*M2)/&Y(I+4*M2)+SK
   &YPRIME(1+5*M2)=0.0
   &YPRIME(1+6*M2)=0.0
   &YPRIME(1+7*M2)=0.0
   &YPRIME(1+8*M2)=0.0
   &YPRIME(1+9*M2)=0.0
c
VPRIIME(1+5*M2)=SUM11(1)-TH(M1,1)+TH(M2,1)-
& TH1*(Y(1+5*M2)+T12*(Y(1+6*M2)+T13*(Y(1+7*M2)
&+T14*(Y(1+8*M2)+T15*(Y(1+9*M2)=ST*Y(1+5*M2) - T1)

c
VPRIIME(1+6*M2)=TPC(1,1)*Y(1+6*M2)+TPC(2,1)*Y(1+7*M2)
&+ TPC(3,1)*Y(1+8*M2)
&+ TPC(4,1)*Y(1+9*M2)-TPC(5,1)*Y(1+5*M2)+

c
MITCHEL MENTEN
&ABETA*(DA1*Y((1+10*M2))*EXP(-1.0/Y((1+6*M2)))*Y((1+7*M2))/
&(Y(1+2*M2)*SK)
VPRIIME(1+7*M2)=TPC(1,2)*Y(1+6*M2)+TPC(2,2)*Y(1+7*M2)
&+ TPC(3,2)*Y(1+8*M2)
&+ TPC(4,2)*Y(1+9*M2)-TPC(5,2)*Y(1+5*M2)+

c
MITCHEL MENTEN
&ABETA*(DA1*Y((1+11*M2))*EXP(-1.0/Y((1+7*M2)))*Y((1+2*M2))/
&(Y(1+2*M2)*SK)
VPRIIME(1+8*M2)=TPC(1,3)*Y(1+6*M2)+TPC(2,3)*Y(1+7*M2)
&+ TPC(3,3)*Y(1+8*M2)
&+ TPC(4,3)*Y(1+9*M2)-TPC(5,3)*Y(1+5*M2)+

c
MITCHEL MENTEN
&ABETA*(DA1*Y((1+12*M2))*EXP(-1.0/Y((1+8*M2)))*Y((1+3*M2))/
&(Y(1+3*M2)*SK)
VPRIIME(1+9*M2)=TPC(1,4)*Y(1+6*M2)+TPC(2,4)*Y(1+7*M2)
&+ TPC(3,4)*Y(1+8*M2)
&+ TPC(4,4)*Y(1+9*M2)-TPC(5,4)*Y(1+5*M2)+

c
MITCHEL MENTEN
&ABETA*(DA1*Y((1+13*M2))*EXP(-1.0/Y((1+9*M2)))*Y((1+4*M2))/
&(Y(1+4*M2)*SK)
VPRIIME(1+10*M2)=-DA2*Y(1+10*M2)*EXP(-GAMMA/Y(1+6*M2))
VPRIIME(1+11*M2)=-DA2*Y(1+11*M2)*EXP(-GAMMA/Y(1+7*M2))
VPRIIME(1+12*M2)=-DA2*Y(1+12*M2)*EXP(-GAMMA/Y(1+8*M2))
VPRIIME(1+13*M2)=-DA2*Y(1+13*M2)*EXP(-GAMMA/Y(1+9*M2))

Y(1)= SUM2 - R*PEH*G12
Y(M2)= SUM3 + R*PEM*CHZ
SUM4=0.0
SUM5=0.0
DO 551 I=2,M1
SUM2=SUM2 + (R3*AX(M2,1) - RH*AX(1,1))*Y(I)
551 SUM3=SUM3 + (R1*AX(1,1) - R2*AX(M2,1))*Y(I)
Y(1)= SUM2 - R*PEH*G12
Y(M2)= SUM3 + R*PEM*CHZ
SUM4=0.0
SUM5=0.0
DO 556 I=2,M1
SUM4=SUM4 + (RT3*AX(M2,1) - RT4*AX(1,1))*Y(I+5*M2)
556 SUM5=SUM5 + (RT1*AX(1,1) - RT2*AX(M2,1))*Y(I+5*M2)

CONTINUE
Y(M2*5+1) = SUM4 - RT1*PM1*THZ
Y(M2*5+M2) = SUM5 + RT1*PM1*THZ

C
RETURN
END

C
C

SUBROUTINE FCNJ(N,T,Y,PD)
IMPLICIT REAL*8(A-H,O-Z)
INTEGER N
REAL*8 Y(N),PD(N,N),T
RETURN
END
**FOR OPTIMIZATION**
**SPHERE WITH DEACTIVATION**
**BASE CASE**

THE METHOD OF ORTHOGONAL COLLOCATION HAS BEEN EMPLOYED HERE TO REDUCE THE DEFINING PARTIAL DIFFERENTIAL EQUATIONS TO NON-LINEAR O.D.E.S. THE SET OF N.L.O.D.E.'S IS THEN SOLVED.

N HAS BEEN USED AS A PARAMETER

\[ N = (M+2)(N+1) \] ******REDIFINE FOR NONISOHERMAL CASE******

WHERE MM IS THE NUMBER OF INTERNAL COLL. POINTS FOR EXTERNAL PHASE AND NI IS THE NUMBER OF INTERNAL COLL. POINTS FOR PARTICLE.

PARAMETER(N=140)
IMPLICIT REAL*8(A-H,O-Z)
INTEGER METH,MITER,1W(N),IER,K
REAL*8 Y(N),WK(N*N+13*N+1),T,TOL,TEND,H
REAL*8 PARAM(50),DUMMY(1,1)
COMMON/DATA/CLT,AML,CHZ,PEM,ALFA,S1,TBAR,S1,CH,SK,T,CON1,MM,NI
COMMON/DATA/THZ,PEH,ALFAH,CLNH,TI,PH,CON1,T,ST,TW,RIIA,DAI,DAP,
,CAMMA
COMMON AX(30,30),BK(30,30),X(50),VMAX
COMMON CH(50,50),G(30),A(50,50),R(50,50),FA(50,50)
COMMON TH(50,50),TFG(50,50),TACT(50)
DIMENSION CONV(50)
EXTERNAL FCN,FCNJ

******COLLOCATION PARAMETERS***********

MM IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR BED
NI IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR PARTICLE

MM=8
M1=MM+1
M2=MM+2
M20=M2*2.0
M30=M2*3.0
M40=M2*4.0
M50=M2*5.0
M60=M2*6.0
M70=M2*7.0
M80=M2*8.0
M90=M2*9.0
M100=M2*10.0

************************************************
M110=M2*11.0
M120=M2*12.0
M130=M2*13.0
M140=M2*14.0

************************************************
C
N1=4
N1=N1+1
C
DO 9 I=1,M2
DO 9 J=1,M2
9 READ(5,*)AX(I,J)
C
DO 5 I=1,M2
DO 5 J=1,M2
5 READ(5,*)BX(I,J)
C
X( 1)= 0.2957581F+00
X( 2)= 0.5652353E+00
X( 3)= 0.7844835E+00
X( 4)= 0.9340014E+00
X( 5)= 1.0000000E+01
A( 1, 1)= -0.5071712E+01
A( 1, 2)= 0.8658617E+01
A( 1, 3)= -0.6367129E+01
A( 1, 4)= 0.4645816E+01
A( 1, 5)= -0.1865592E+01
A( 2, 1)= 0.1434610E+01
A( 2, 2)= -0.2653762E+01
A( 2, 3)= 0.6392033E+01
A( 2, 4)= -0.3711387E+01
A( 2, 5)= 0.1407724E+01
A( 3, 1)= 0.5229562E+00
A( 3, 2)= -0.3168659E+01
A( 3, 3)= -0.1912086E+01
A( 3, 4)= 0.6623901E+01
A( 3, 5)= -0.2066112E+01
A( 4, 1)= 0.3860729E+00
A( 4, 2)= 0.1861479E+01
A( 4, 3)= -0.6701922E+01
A( 4, 4)= -0.1605993E+01
A( 4, 5)= 0.6812509E+01
A( 5, 1)= 0.7615325E+00
A( 5, 2)= -0.3668199E+01
A( 5, 3)= 0.1026842E+02
A( 5, 4)= -0.3356176E+02
A( 5, 5)= 0.2600000E+02
B( 1, 1)= -0.3484510E+02
B( 1, 2)= 0.4414925E+02
B( 1, 3)= -0.1426772E+02
B( 1, 4)= 0.7002886E+01
B( 1, 5)= -0.2418620E+01
B( 2, 1)= 0.1397981E+02
R( 2, 2)=0.5231625E+02
R( 2, 3)= 0.4831762E+02
R( 2, 4)=0.1517764E+02
R( 2, 5)= 0.4677060E+01
R( 3, 1)=0.3108303E+01
R( 3, 2)=0.3360006E+02
R( 3, 3)=0.9528201E+02
R( 3, 4)= 0.8089141E+02
R( 3, 5)=0.1605794E+02
R( 4, 1)=0.1837682E+01
R( 4, 2)=0.1257895E+02
R( 4, 3)=0.9746056E+02
R( 4, 4)=0.2866910E+03
R( 4, 5)=0.1999845E+03
R( 5, 1)= 0.3854616E+02
R( 5, 2)=0.1703650E+03
R( 5, 3)=0.4579635E+03
R( 5, 4)=0.7944466E+03
R( 5, 5)=0.4680001E+03

T=0.0

C: *****************************************************************
C: INITIAL CONDITION
C: *****************************************************************
C
DO 4 I=1,M50
C
Y(I)=1.0
Y(I)=0.0
4 CONTINUE

DO 43 I=1,M2
C CONV(I)=0.0
43 CONTINUE

M51=M50 +1
DO 115 I=M51,M100
Y(I)=0.0596
115 CONTINUE

M101=M100 +1
DO 116 I=M101,N
Y(I)=1.0
116 CONTINUE

C

C: **** IMLV VARIABLES
C: ------- TFIN = FINAL TIME -------
C: ------- DTPTNT = PRINT INTERVAL -------
C
TFIN = 2.0
DTPTNT =0.1
NPRINT = INT(TFIN/DTPTNT)

C
TOL =0.00001
H=0.000001
METH=2
MITER=0
INDEX=1

C: FOR DIVPAC
IER=0
NPARAM=50
CALL SSSET(NPARAM,0.0,PARAM,1)
PARAM(1)=H
PARAM(4)=10000
PARAM(12)=METII
PARAM(13)=MITER
PARAM(19)=0

C
C ******* PARAMETERS FOR THE PROBLEM *********
C
C
C HZ=1.00
HZ=0.0596
PEM=5.0E+00
PEH=PEM*0.25
ALFA=2.880
C
ALFA=8.0
ALFAI=ALFA
C
ALFAI=2.880E+00
SI=10.0
C
CNI=0.025
CNI=SI
ST=0.1
C
ST=0.1
TH=0.0596
C
BETA=0.04
BETA=0.02
TBAR=60.0
C
VMAX=0.02
DA1=9.5E+07
C
DA1=5.0E+06
DA2=1.1E+13
GAMMA=76000.0/10000.0
FACT=10000.0/2.0
C
GAMMA=76000.0/12017.0
C
FACT=12017.0/2.0
C
C
C NOTE : SI= 25.0 FOR ZERO ORDER AND SI=4.0 FOR OTHER KINETICS
C
C
C
SI=4.0
C
SI=5.0
CK=2.0
SK=CK/SI
P=1.0/PEM
PH=1.0/PEH
CON1=.760
C
CON1=.296
CON1T=CON1
C
CON1T=25.
C
C
C ******* END OF PARAMETERS ********************
C
C
C
C ******* INPUT FOR X VALUE AND AX & RX MATRIX *******
C
C
C
C
X(1)=0.0
X(2)=0.0199
X(3)=0.1017
X(4)=0.2372
X(5)=0.4083
X(6)=0.5917
X(7)=0.7628
X(8)=0.8983
X(9)=0.9801
X(10)=1.0

WRITE(7,2001)
2001 FORMAT(5X,'**********VALUES OF THE PARAMETERS FOR THIS RUN**********
...
WRITE(7,2009) PEH
7009 FORMAT(5X,'PECLET NO. FOR HEAT,PEH =',E14.7)
WRITE(7,2003) ALFA
7003 FORMAT(5X,'ALFA =',E14.7)
WRITE(7,7008) ALFAH
7008 FORMAT(5X,'ALFAH =',E14.7)
WRITE(7,2004) TRAR
7004 FORMAT(5X,'TRAR =',E14.7)
WRITE(7,2014) VMAX
7014 FORMAT(5X,'VMAX =',E14.7)
WRITE(7,2005) SI
7005 FORMAT(5X,'INLET CONC., SI =',E14.7)
WRITE(7,2006) CK
7006 FORMAT(5X,'CONSTANT K, CK =',E14.7)
WRITE(7,2007) SK
7007 FORMAT(5X,'CK/SI =',E14.7)
WRITE(7,2008) CON1
7008 FORMAT(5X,'CON1 =',E14.7)
WRITE(7,2018) CON11
7018 FORMAT(5X,'CON11 =',E14.7)
WRITE(7,7000) CNH
7000 FORMAT(5X,'NUSSELT NUMBER,CNH =',E14.7)
WRITE(7,7001) SH
7001 FORMAT(5X,'SHERWOOD NUMBER,SH =',E14.7)
WRITE(7,7002) ST
7002 FORMAT(5X,'STANTON NUMBER,ST =',E14.7)
WRITE(7,7003) TW
7003 FORMAT(5X,'DIMLESS WALL TEMP.,TW =',E14.7)
WRITE(7,7004) DA1
7004 FORMAT(5X,'DAMKHOLER NO. FOR ACT.,DA1 =',E14.7)
WRITE(7,7005) DA2
7005 FORMAT(5X,'DAMKHOLER NO. FOR DEA.,DA2 =',E14.7)
WRITE(7,7006) BETA
7006 FORMAT(5X,'BETA =',E14.7)
WRITE(7,7007) GAMMA
7007 FORMAT(5X,'GAMMA =',E14.7)
WRITE(7,7010) CHZ
7010 FORMAT(5X,'DIMLESS FEED CONC.,CHZ =',E14.7)
WRITE(7,7011) THZ
1011 FORMAT(5X,'DIMLESS FEED TEMP.,THZ =',I14.7)
WRITE(7,1010)
2010 FORMAT(5X,'*****END OF THE PARAMETERS FOR THIS RUN*****',/)
WRITE(6,3001)
3001 FORMAT(1X,' TIME CONC. TEMP CONV')
TACT=M2*Y(6*M2)*FACT-273.0
WRITE(6,3002) T,Y(M2),TACT(M2),CONV(M2)
WRITE(7,1003) T
WRITE(7,1004)
WRITE(7,1071)
TACT=M2*Y(6*M2)*FACT-273.0
DO 1112 I=1,M2
1112 TACT(I)=Y(1+5*M2)*FACT-273.0
DO 1113 I=1,M2
1113 TACT(I+1)=Y(1+6*M2)*FACT-273.0
DO 1114 I=1,M2
1114 TACT(I+2)=Y(1+7*M2)*FACT-273.0
DO 1115 I=1,M2
1115 TACT(I+3)=Y(1+8*M2)*FACT-273.0
DO 1116 I=1,M2
1116 TACT(I+4)=Y(1+9*M2)*FACT-273.0
DO 1015 I=1,M2
WRITE(7,1016)X(1),Y(1),Y(1+M2),Y(1+2*M2),Y(1+3*M2),Y(1+4*M2),
,CONV(I)
WRITE(9,1006)X(1),Y(1+5*M2),Y(1+6*M2),Y(1+7*M2),
,Y(1+8*M2),Y(1+9*M2)
WRITE(9,1006)X(1),TACT(1),TACT(1+M2),TACT(1+2*M2),TACT(1+3*M2),
,TACT(1+4*M2)
1015 CONTINUE
C
C
C ***************************************************************************
C
R=(AX(M2,M2)/(AX(M2,1))-(AX(1,M2)/(AX(1,1)-PEH))
R1=1.0/(R*(AX(1,1)-PEH))
R2=1.0/(R*(AX(M2,1)))
R3=((R2*AX(M2,M2))-1.0)/AX(M2,1)
R4=(R1*AX(M2,M2))/AX(M2,1)
C
C ***************************************************************************
C
RT=(AX(M2,M2)/(AX(M2,1))-(AX(1,M2)/(AX(1,1)-PEH))
RT1=1.0/(RT*(AX(1,1)-PEH))
RT2=1.0/(RT*(AX(M2,1)))
RT3=((RT2*AX(M2,M2))-1.0)/AX(M2,1)
RT4=(RT1*AX(M2,M2))/AX(M2,1)
C
C***************************************************************************
C
DO 23 J=2,M1
DO 22 K=1,MM
K1=K+1
C

CH(K,J)=PBX(J,K1)-AX(J,K1)+((PBX(J,1)-AX(J,1))*R3*AX(M2,K1)-
& RH*AX(1,K1))+((PBX(J,2)-AX(J,M2))*R1*AX(1,K1)-R2*AX(M2,K1))
22 CONTINUE
CH(M1,J)=PEH*CHZ*RH*(PBX(J,1)-AX(J,1))
CH(M2,J)=PEH*CHZ*R1*(PBX(J,M2)-AX(J,M2))
21 CONTINUE
DO 203 J=2,N1
DO 202 K=1,N1
K1=K+1
TH(K,J)=PH*PBX(J,K1)-AX(J,K1)+((PH*PBX(J,1)-AX(J,1))*R13*AX(M2,K1)-
& RTN*AX(1,K1))+((PH*PBX(J,M2)-AX(J,M2))*R11*AX(1,K1)
& R2*AX(M2,K1))
202 CONTINUE
TH(M1,J)=PEH*THZ*RTN*(PH*PBX(J,1)-AX(J,1))
TH(M2,J)=PEH*THZ*R1*(PH*PBX(J,M2)-AX(J,M2))
203 CONTINUE
RP=A(N1,N1)*SH
RPT=A(N1,N1)*CNH
C11=ALF*(1.0-SH/RP))
T11=ALFAH*(1.0-CNHI/RPT))
C12=-ALFA/RP)*A(N1,1)
C13=(ALFA/RP)*A(N1,2)
C14=-ALFA/RP)*A(N1,3)
C15=(ALFA/RP)*A(N1,4)
T12=-ALFAH/RPT)*A(N1,1)
T13=(ALFAH/RPT)*A(N1,2)
T14=-ALFAH/RPT)*A(N1,3)
T15=(ALFAH/RPT)*A(N1,4)
DO 12 J=1,N1
DO 13 I=1,N1
PC(I,J)=CON1*(B(J,1)-(B(J,N1)*A(N1,1)/RP))
TPC(I,J)=CON1*(B(J,1)-(B(J,N1)*A(N1,1)/RPT))
13 CONTINUE
PC(N1,J)=CON1*SH*B(J,N1)/RP
TPC(N1,J)=CON1*CNH*B(J,N1)/RPT
12 CONTINUE
G:**********
G:**********
DO 10 K=1,NPRINT
TEND=DI1PRINT*FLOAT(K)
CALL DVFAG(INDEX,N,FCN,FCNJ,DUMMY,T,TEND,TOL,PARAM,Y)
DO 123 I=1,M2
CONV(I)=1.0-Y(I)
123 CONTINUE
TACT=M2=Y(6*M2)*FACT-273.0
WRITE(6,3002) T,Y(M2),TACT(M2),CONV(M2)
c    WRITE(6,3002) T,Y(M2),Y(6*M2),CONV(M2)
1002 FORMAT(1X,F10.4,2X,F6.4,2X,F6.4,2X,F6.4)
      WRITE(7,1003) T
1003 FORMAT(10X,'TIME = ',F10.4,/) 
      WRITE(7,1004)
1004 FORMAT(3X,'XVALUE',5X,'BULK',5X,'PART1',
          ,5X,'PART2',5X,'PART3',5X,'PART4',5X,'CONV',/) 
      WRITE(9,1003) T
      WRITE(9,3004)
1004 FORMAT(3X,'XVALUE',5X,'TBULK',5X,'TPRTH',
          ,5X,'TPRTL2',5X,'TPRTL3',5X,'TPRTH',/) 
      WRITE(9,2071)
2071 FORMAT(2N3,'Y=0.296',
          ,5X,'Y=0.565',5X,'Y=0.784',5X,'Y=0.934',/) 
      WRITE(7,1071)
1071 FORMAT(2N3,'Y=0.296',
          ,5X,'Y=0.565',5X,'Y=0.784',5X,'Y=0.934',/) 
      DO 1005 I=1,M2
          WRITE(7,1016)X(I),Y(I),Y(1+M2),Y(1+2*M2),Y(1+3*M2),Y(1+4*M2).
          .CONV(I)
1005 CONTINUE
      DO 2222 M2 = 1,M2
          TACT(I)=Y(1+5*M2)*FACT-273.0
          2222 TACT(I+1*M2)=Y(1+6*M2)*FACT=273.0
          DO 2224 I=1,M2
              TACT(I+2*M2)=Y(1+7*M2)*FACT-273.0
              2224 TACT(I+3*M2)=Y(1+8*M2)*FACT-273.0
              DO 2226 I=1,M2
                  TACT(I+4*M2)=Y(1+9*M2)*FACT-273.0
                  2226 TACT(I+5*M2)=Y(1+10*M2)*FACT-273.0
                  DO 3005 M2 = 1,M2
                      WRITE(9,1006)X(I),TACT(I),TACT(I+M2),TACT(I+2*M2),TACT(I+3*M2),
                      .TACT(I+4*M2)
                      .TACT(I+5*M2)
                      WRITE(9,1006)X(I),Y(I+5*M2),Y(I+6*M2),Y(I+7*M2),Y(I+8*M2),
                      .Y(I+9*M2)
3005 CONTINUE
      WRITE(10,1003) T
      WRITE(10,9004)
9004 FORMAT(3X,'XVALUE',5X,'CEPR1',
          ,5X,'CEPR2',5X,'CEPR3',5X,'CEPR14',/) 
      WRITE(10,9071)
9071 FORMAT(14X,'Y=0.296',
          ,5X,'Y=0.565',5X,'Y=0.784',5X,'Y=0.934',/) 
      DO 9005 I=1,M2
          WRITE(10,1006)X(I),Y(I+10*M2),Y(I+11*M2),Y(I+12*M2),Y(I+13*M2)
9005 CONTINUE
1006 FORMAT(14X,F6.4,5(1X,F10.6))
1016 FORMAT(14X,F6.4,6(1X,F10.6))
     IF(IER.GT.128) GO TO 20
10 CONTINUE
     GO TO 30
30 CONTINUE
     WRITE(6,1002)N,IER
! ENZYMES FORTRAN A1 KLG FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHARAN

1001 FORMAT(1X,F8.3,10F7.3,/,9X,10F7.3))
1002 FORMAT(1X,'NO. OF CELLS = ',15,' IER VALUE = ',15)

C
C
30 CONTINUE
131 CONTINUE
STOP
END
C
C
SUBROUTINE FCN(N, T, Y, YP)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 TERMT
REAL*8 SUMA(N), YP(N), T
REAL*8 SUMT(N)
COMMON/CLT, ANPL, CHZ, PEM, ALFA, SII, TR, SI, CHE, SK, P, CONH, HM, NI
COMMON/THZ, PEM, ALFA, AHN, TH, INH, ST, IW, RM, DA, DA2,
,CMMA
COMMON AX(30,30), BX(30,30), X(50), VMAX
COMMON CH(50,50), F(30), A(50,50), R(50,50), TF(50,50)
COMMON TH(50,50), TPC(50,50)
DIMENSION CONV(50)
INTEGER N

C
CHZ= 1.0
M1=MM+1
M2=MM+2
M20=M2*2.0
M30=M2*3.0
M40=M2*4.0
M50=M2*5.0
M60=M2*6.0
M70=M2*7.0
M80=M2*8.0
M90=M2*9.0
M100=M2*10.0

**************************************************************************
M110=M2*11.0
M120=M2*12.0
M130=M2*13.0
M140=M2*14.0

**************************************************************************
C
N1=NI+1
C
R=(AX(M2,M2)/AX(M2,1))-(AX(1,M2)/(AX(1,1)-PEM))
R1=1.0/(R*(AX(1,1)-PEM))
R2=1.0/(R*(AX(M2,1)))
R3=((R2*AX(M2,M2))-1.0)/AX(M2,1)
Rn=(R1*AX(M2,M2))/AX(M2,1)
C
C **************************************************************************
C
C **************************************************************************
C
C
RT=(AX(M2,M2)/AX(M2,1))-(AX(1,M2)/(AX(1,1)-PFH))
RT1=1.0/(RT*(AX(1,1)-PEH))
RT2=1.0/(RT*(AX(M2,1)))
RT3=((RT2*AX(M2,M2))-1.0)/AX(M2,1)
RT4=(RT1*AX(M2,M2))/AX(M2,1)

******************************************************************************

DO 23 J=2,M1
DO 22 K=1,MM
K1=K+1

CH(K,J)=P*BX(J,K1)-(AX(J,K1)+{((P*BX(J,1)-AX(J,1))*(R3*AX(M2,K1)-
&RT4*AX(1,K1)))+{((P*BX(J,M2)-AX(J,M2))*(RT1*AX(1,K1)-R2*AX(M2,K1)))}}
22 CONTINUE
CH(M1,J)=PEM*CHZ*RT4*(P*BX(J,1)-AX(J,1))
CH(M2,J)=PEM*CHZ*RT1*(P*BX(J,M2)-AX(J,M2))
23 CONTINUE

DO 203 J=2,M1
DO 202 K=1,MM
K1=K+1

TH(K,J)=PH*BX(J,K1)-(AX(J,K1)+{(PH*BX(J,1)-AX(J,1))*(RT3*AX(M2,K1)-
&RT4*AX(1,K1)))+{(PH*BX(J,M2)-AX(J,M2))*(RT1*AX(1,K1))}
&-RT2*AX(M2,K1))
202 CONTINUE
TH(M1,J)=PEM*THZ*RT4*(PH*BX(J,1)-AX(J,1))
TH(M2,J)=PEM*THZ*RT1*(PH*BX(J,M2)-AX(J,M2))
203 CONTINUE
RP=A(N1,N1)+SH
RPT=A(N1,N1)*CNH

C11=ALFA*(1.0-(SH/RP))
T11=ALFAH*(1.0-(CNH/RPT))
C12=-(ALFA/RP)*A(N1,1)
C13=-(ALFA/RP)*A(N1,2)
C14=-(ALFA/RP)*A(N1,3)
C15=-(ALFA/RP)*A(N1,4)
T12=-(ALFAH/RPT)*A(N1,1)
T13=-(ALFAH/RPT)*A(N1,2)
T14=-(ALFAH/RPT)*A(N1,3)
T15=-(ALFAH/RPT)*A(N1,4)

DO 12 J=1,N1
DO 13 I=1,N1
PC(I,J)=CON1*(B(J,1)-B(J,N1)*A(N1,1)}/RP))
TPC(I,J)=CON1*T*(B(J,1)-B(J,N1)*A(N1,1)/RPT)
13 CONTINUE
PC(N1,J)=-CON1*SH*B(J,N1)/RP
TPC(N1,J)=-CON1*CNH*B(J,N1)/RPT
12 CONTINUE

******************************************************************************
DO 21 J=2,M1
   SUMA1(J)=0.0
   SUMT1(J)=0.0
21 CONTINUE
   DO 25 J=2,M1
      DO 25 I=1,NM
         11=I+1
         SUMA1(J)=SUMA1(J)+CH(I,J)*Y(I1)
         SUMT1(J)=SUMT1(J)+TH(I,J)*Y(5*M2+11)
25 CONTINUE
   DO 700 I=1,14
      11=1+M2*(I-1)
      12=M2*I
      YPRIME(11)=0.0
      YPRIME(12)=0.0
700 CONTINUE
   DO 800 I=2,M1
      YPRIME(I)=0.0
      YPRIME(I+5*M2)=0.0
      YPRIME(I)=SUMA1(I)-CH(M1,1)+CH(M2,1)-
      &C11*Y(1)*C12*Y(1+M2)+C13*Y(1+2*M2)+C14*Y(1+3*M2)+C15*Y(1+4*M2)
      &+PC(1,1)*Y(1+M2)+PC(2,1)*Y(1+2*M2)+PC(3,1)*Y(1+3*M2)
      &+PC(4,1)*Y(I+4*M2)-PC(5,1)*Y(I)-
      &MITCHEL MENTEN
      &D(1)*Y(I+10*M2)*EXP(-1.0/Y(1+6*M2))*Y(1+M2)
      &/(Y(I+M2)+SK)
      &D(1)*Y(I+11*M2)*EXP(-1.0/Y(1+7*M2))*Y(1+2*M2)
      &/(Y(I+2*M2)+SK)
      &D(1)*Y(I+12*M2)*EXP(-1.0/Y(1+8*M2))*Y(1+3*M2)
      &/(Y(I+3*M2)+SK)
      &D(1)*Y(I+13*M2)*EXP(-1.0/Y(1+9*M2))*Y(1+4*M2)
      &/(Y(I+4*M2)+SK)
      YPRIME(I)=0.0
      YPRIME(I+6*M2)=0.0
      YPRIME(I+7*M2)=0.0
      YPRIME(I+8*M2)=0.0
      YPRIME(I+9*M2)=0.0
      YPRIME(I+5*M2)=SUMT1(I)-TH(M1,1)+TH(M2,1)-
&T11*Y(1+5*M2)+T12*Y(1+6*M2)+T13*Y(1+7*M2)
&+T14*Y(1+8*M2)+T15*Y(1+9*M2)-ST*(Y(1+5*M2) - Y(1))

C:
YPRI/M/A*(1+6*M2)#=TPC(1,1)*Y(1+6*M2)+TPC(2,1)*Y(1+7*M2)
&+TPC(3,1)*Y(1+8*M2)
&+TPC(4,1)*Y(1+9*M2)-TPC(5,1)*Y(1+5*M2)+

C: MITCHEL MENTEN
@&BETA*(DA1*Y(1+10*M2))#*EXP(-1.0/Y(1+6*M2))*Y(1+7*M2)/
&*Y(1+5*M2)*SK
YPRI/M/A*(1+7*M2)=TPC(1,2)*Y(1+6*M2)+TPC(2,2)*Y(1+7*M2)
&+TPC(3,2)*Y(1+8*M2)
&+TPC(4,2)*Y(1+9*M2)-TPC(5,2)*Y(1+5*M2)+

C: MITCHEL MENTEN
@&BETA*(DA1*Y(1+11*M2))#*EXP(-1.0/Y(1+7*M2))*Y(1+2*M2)/
&*Y(1+5*M2)*SK
YPRI/M/A*(1+8*M2)=TPC(1,3)*Y(1+6*M2)+TPC(2,3)*Y(1+7*M2)
&+TPC(3,3)*Y(1+8*M2)
&+TPC(4,3)*Y(1+9*M2)-TPC(5,3)*Y(1+5*M2)+

C: MITCHEL MENTEN
@&BETA*(DA1*Y(1+12*M2))#*EXP(-1.0/Y(1+8*M2))*Y(1+3*M2)/
&*Y(1+5*M2)*SK
YPRI/M/A*(1+9*M2)=TPC(1,4)*Y(1+6*M2)+TPC(2,4)*Y(1+7*M2)
&+TPC(3,4)*Y(1+8*M2)
&+TPC(4,4)*Y(1+9*M2)-TPC(5,4)*Y(1+5*M2)+

C: MITCHEL MENTEN
@&BETA*(DA1*Y(1+13*M2))#*EXP(-1.0/Y(1+9*M2))*Y(1+4*M2)/
&*Y(1+5*M2)*SK
YPRI/M/A*(1+10*M2)=DA2*Y(1+10*M2)*EXP(-GAMMA/Y(1+6*M2))
YPRI/M/A*(1+11*M2)=DA2*Y(1+11*M2)*EXP(-GAMMA/Y(1+7*M2))
YPRI/M/A*(1+12*M2)=DA2*Y(1+12*M2)*EXP(-GAMMA/Y(1+8*M2))
YPRI/M/A*(1+13*M2)=DA2*Y(1+13*M2)*EXP(-GAMMA/Y(1+9*M2))

C: YPRIM/A*(1+10*M2)=DA2*Y(1+10*M2)*EXP(-GAMMA/0.06)
C: YPRIM/A*(1+11*M2)=DA2*Y(1+11*M2)*EXP(-GAMMA/0.06)
C: YPRIM/A*(1+12*M2)=DA2*Y(1+12*M2)*EXP(-GAMMA/0.06)
C: YPRIM/A*(1+13*M2)=DA2*Y(1+13*M2)*EXP(-GAMMA/0.06)
C: YPRIM/A*(1+10*M2)=-2.5E-07
C: YPRIM/A*(1+11*M2)=-2.5E-07
C: YPRIM/A*(1+12*M2)=-2.5E-07
C: YPRIM/A*(1+13*M2)=-2.5E-07

RRR: CONTINUE

C:
SUM2=0.0
SUM3=0.0
DO 555 1=2,M1
SUM2=SUM2+(R3*AX(M2,1)-R4*AX(1,1))*Y(1)
555 SUM3=SUM3+(R1*AX(1,1)-R2*AX(M2,1))*Y(1)
Y(1)=SUM2-RH*PEM*CHZ
Y(M2)=SUM3+R1*PEM*CHZ
SUM4=0.0
SUM5=0.0
DO 556 1=2,M1
SUM4=SUM4+(R3*AX(M2,1)-R4*AX(1,1))*Y(1+5*M2)
556 SUM5=SUM5+(R1*AX(1,1)-R2*AX(M2,1))*Y(1+5*M2)
Y(M2*5+1)=SUM4-RH*PEM*THIZ
Y(M2*5+M2)=SUM5+RT1*PEM*THIZ
SUBROUTINE FCNJ(N, T, Y, PD)
IMPLICIT REAL*8(A-H,O-Z)
INTEGER N
REAL*8 Y(N), PD(N,N), T
RETURN
END
* FOR FLAT PLATE WITHOUT DEACTIVATION
* BASE CASE
* EFFECT OF GEOMETRY

THE METHOD OF ORTHOGONAL COLLOCATION HAS BEEN EMPLOYED HERE TO REDUCE THE DEFINING PARTIAL DIFFERENTIAL EQUATIONS TO NON-LINEAR O.D.E.S. THE SET OF N.L.O.D.E IS THEN SLED.

N HAS BEEN USED AS A PARAMETER

N=(MM+2)*(N1+1) \textbf{**REDINE FOR NONISOThERMAL CASE****}

WHERE MM IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR EXTERNAL PHASE AND N1 IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR PARTICLE

PARAMETER(N=140)
IMPLICIT REAL*(A-H,O-Z)
INTEGER M,HH, MTER, IMPH, IMPH, ICT,N
REAL*8 Y(I),NK(N*N+13*N+1),T,TOL,TEND,N
REAL*8 PARAM(50),DUMMY(1,1)
COMMON/CLT,AMPL,CHZ,PEH,ALFA,SH,TBAR,ST1,ST1,SK,SK,F,CON1,MM,N1
COMMON/HTZ,PEH,ALFA,CNH,T1,PHI,CON1,SY,TW,BETA,DA1,DA2,
,GAMMA
COMMON AX(j30,30),EX(30,30),X(50),VMAX
COMMON CII(50,50),CII(30,30),A(50,50),B(50,50),CI50,50)
COMMON TH(50,50),THC(50,50),TACT(60)
DIMENSION CONV(50)
EXTERNAL FCN, FCNJ

**********COLLOCATION PARAMETERS**********

MM IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR BED
N1 IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR PARTICLE

MM=8
M1=MM+1
M2=MM+2
M20=M2*2.0
M30=M2*3.0
M40=M2*4.0
M50=M2*5.0
M60=M2*6.0
M70=M2*7.0
M80=M2*8.0
M90=M2*9.0
M100=M2*10.0
**`````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````````
B( 3, 3) = -0.6513217E+02
B( 3, 4) = 0.4656660E+02
B( 3, 5) = -0.9005158E+01
B( 4, 1) = 0.2846666E+01
B( 4, 2) = -0.1366350E+02
B( 4, 3) = 0.7858660E+02
B( 4, 4) = -0.1936370E+03
B( 4, 5) = 0.1258952E+03
B( 5, 1) = 0.5334667E+02
B( 5, 2) = -0.1788093E+03
B( 5, 3) = 0.3745448E+03
B( 5, 4) = -0.5570821E+03
B( 5, 5) = 0.3080000E+03

C
T=0.0

C **************** INITIAL CONDITION **************
C
DO 4 I=1,M50
C  Y(I)=1.0
  Y(I)=0.0
4 CONTINUE
C  INITIAL CONVERSION IS ZERO
C
DO 43 I=1,M2
C  CONV(I)=0.0
43 CONTINUE
C  CONV(1)=1.0-Y(1)
43 CONTINUE
M51=M50 +1
DO 415 I=M51,M100
Y(I)=0.0596
415 CONTINUE
M101=M100 +1
DO 416 I=M101,N
Y(I)=1.0
416 CONTINUE

C

C ******** IMSL VARIABLES **********************
C
C ------- TFIN = FINAL TIME  -----------------
C ------- DTPRNT = PRINT INTERVAL  ----------
C
TFIN = 30.0
DTPRNT =1.0
NPRINT = INT(TFIN/DTPRNT)
C
TOL =0.00001
H=0.000001
METH=2
MITER=0
INDEX=1
C
C*******************************************************************
C FOR DIVPAG *********************************************************
IER=0
NPARAM=50
CALL SSET(NPARAN,0.0,PARAM,1)
PARAM(1)=11
PARAM(4)=10000
PARAM(12)=METH
PARAM(13)=METER
PARAM(19)=0

C:

***** PARAMETERS FOR THE PROBLEM *******

C:

CHZ=1.0E-06
HIZ=0.0596
PHI=1.0E+04
PHI=PHI*0.25

C

ALFA=8.000
ALFA=2.880
ALFAR=ALFA
SH=8.0/3.0

C

SH=5.0/3.0

C

CNH=0.025
CNH=SH
ST=0.1
TW=0.0596
BETA=2.0E-02

C

BETA=1.0E-02
TBAR=60.0

C

VMAX=0.02
DA1=5.0E+06

C

DA1=5.0E+07
DA2=0.0
GAMMA=76000.0/10000.0
FACT=10000.0/2.0

C:

NOTE : S1= 25.0 FOR ZERO ORDER AND S1=4.0 FOR OTHER KINETICS

C

S1=4.0
S1=4.5.0
CK=2.0
SK=CK/S1
P=1.0/PEM
PH=1.0/PEH

C

CON1=1.800
CON1=2.664
CON11=CON1

C:

****** END OF PARAMETERS ****************************

C:

C:

****** INPUT FOR X VALUE AND AX & RX MATRIX *******

C

X(1)=0.0
X(2)=0.0199
X(3)=0.1017
X(4)=0.2372
X(5)=0.4083
X(6)=0.5917
X(7)=0.7628
X(8)=0.8983
X(9)=0.9801
X(10)=1.0

WRITE(7,2001)
2001 FORMAT(5X,'*****VALUES OF THE PARAMETERS FOR THIS RUN*****',//)
WRITE(7,2002) PFM
2002 FORMAT(5X,'PECLET NO. FOR MASS,PFM =',E14.7)
WRITE(7,7009) PEN
2009 FORMAT(5X,'PECLET NO. FOR HEAT,PEN =',E14.7)
WRITE(7,2003) ALFA
2003 FORMAT(5X,'ALFA =',E14.7)
WRITE(7,7008) ALFAH
2008 FORMAT(5X,'ALFAH =',E14.7)
WRITE(7,2004) TBAR
2004 FORMAT(5X,'TBAR =',E14.7)
WRITE(7,2014) VMAX
2014 FORMAT(5X,'VMAX =',E14.7)
WRITE(7,2005) S1
2005 FORMAT(5X,'INLET CONC., S1 =',E14.7)
WRITE(7,2006) CK
2006 FORMAT(5X,'CONSTANT K , CK =',E14.7)
WRITE(7,2007) SK
2007 FORMAT(5X,'CK/S1 =',E14.7)
WRITE(7,2008) CON1
2008 FORMAT(5X,'CON1 =',E14.7)
WRITE(7,2018) CON1T
2018 FORMAT(5X,'CON1T =',E14.7)
WRITE(7,7000) CNH
2000 FORMAT(5X,'NUSELT NUMBER,CNH =',E14.7)
WRITE(7,7001) SH
2001 FORMAT(5X,'SHERWOOD NUMBER,SH =',E14.7)
WRITE(7,7002) ST
2002 FORMAT(5X,'STANTON NUMBER,ST =',E14.7)
WRITE(7,7003) TW
2003 FORMAT(5X,'DIMLESS WALL TEMP.,TW =',E14.7)
WRITE(7,7004) DA1
2004 FORMAT(5X,'DIMKHOLER NO. FOR ACT.,DA1 =',E14.7)
WRITE(7,7005) DA2
2005 FORMAT(5X,'DIMKHOLER NO. FOR DFA.,DA2 =',E14.7)
WRITE(7,7006) BETA
2006 FORMAT(5X,'RETA =',E14.7)
WRITE(7,7007) GAMMA
2007 FORMAT(5X,'GAMMA =',E14.7)
WRITE(7,7010) CHZ
2010 FORMAT(5X,'DIMLESS FEED CONC.,CHZ =',E14.7)
WRITE(7,7011) THZ
2011 FORMAT(5X,'DIMLESS FEED TEMP.,THZ =',E14.7)
WRITE(7,2010)
2010 FORMAT(5X,'*****END OF THE PARAMETERS FOR THIS RUN*****',//)
WRITE(6,3001)
3001 FORMAT(1X,' TIME CONC. TEMP CONV')

CONV(M2)=1.0-Y(M2)
TAC(N2) = Y(6*N2)*FACT-273.0
WRITE(6,3002) 1,Y(N2),TAC(N2),CONV(N2)
WRITE(6,3002) T,Y(N2),Y(6*N2),CONV(N2)
WRITE(7,1003) 1
WRITE(7,1004)
WRITE(7,1071)
TAC(N2) = Y(6*N2)*FACT-273.0
DO 1112 I=1,N2
1112 TAC(I) = Y(I+5*N2)*FACT-273.0
DO 1113 I=1,N2
1113 TAC(I+1*N2) = Y(I+6*N2)*FACT-273.0
DO 1114 I=1,N2
1114 TAC(I+2*N2) = Y(I+7*N2)*FACT-273.0
DO 1115 I=1,N2
1115 TAC(I+3*N2) = Y(I+8*N2)*FACT-273.0
DO 1116 I=1,N2
1116 TAC(I+4*N2) = Y(I+9*N2)*FACT-273.0
DO 1015 I=1,N2
WRITE(7,1016) X(1),Y(1),Y(I+M2),Y(I+2*M2),Y(I+3*M2),Y(I+4*M2),
,CONV(1)
WRITE(9,1006) X(1),TAC(1),TAC(I+M2),TAC(I+2*M2),TAC(I+3*M2),
,TAC(I+4*M2)
1015 CONTINUE

R = (AX(N2,M2)/AX(M2,1)) - (AX(1,M2)/(AX(1,1) - PEM))
R1 = 1.0/(R*(AX(1,1) - PEM))
R2 = 1.0/(R*(AX(M2,1)))
R3 = ((R2*AX(M2,M2)) - 1.0)/AX(M2,1)
Rn = (R1*AX(M2,M2))/AX(M2,1)

RT = (AX(N2,M2)/AX(M2,1)) - (AX(1,M2)/(AX(1,1) - PEM))
RT1 = 1.0/(RT*(AX(1,1) - PEM))
RT2 = 1.0/(RT*(AX(M2,1)))
RT3 = ((RT2*AX(M2,M2)) - 1.0)/AX(M2,1)
RTn = (RT1*AX(M2,M2))/AX(M2,1)

DO 23 J=2,M1
DO 22 K=1,NN
K=K+1

CH(K,J) = P*BX(J,K) - AX(J,K) + ((P*BX(J,1) - AX(J,1)))*(R1*AX(M2,K) -
&RH*AX(1,K1)) + ((P*BX(J,M2) - AX(J,M2)))*(R1*AX(1,K1) - R2*AX(M2,K1))
22 CONTINUE

CH(M1,J) = PEM*CHZ*RH*(P*BX(J,1) - AX(J,1))
CH(M2,J) = PEM*CHZ*R1*(P*BX(J,M2) - AX(J,M2))
23 CONTINUE


DO 203 J=2,M1
DO 202 K=1,M1
K1=K+1
C
TH(K,1)=PHIRX(J,K1)-AX(J,K1)*(PHIRX(J,1)-AX(J,1))**RI3g*AX(M2,K1)-
&RTH(R1*AX(1,K1))+(PHIRX(J,M2)-AX(J,M2))**RI1g*AX(1,K1)
K=R2g*AX(M2,K1))
202 CONTINUE
TH(J1,J)=PEH*THZ*RIg*(PHIRX(J,1)-AX(J,1))
TH(M2,J)=PEH*THZ*RIg*(PHIRX(J,M2)-AX(J,M2))
203 CONTINUE
C
RP=A(N1,N1)+SH
RPT=A(N1,N1)+CNH
C
C11=ALFA*(1.0-(SH/RP))
T11=ALFA*(1.0-(CNH/RPT))
C12=-ALFA/RPT)*A(N1,1)
C13=-ALFA/RPT)*A(N1,2)
C14=-ALFA/RPT)*A(N1,3)
C15=-ALFA/RPT)*A(N1,4)
T12=-ALFA/RPT)*A(N1,1)
T13=-ALFA/RPT)*A(N1,2)
T14=-ALFA/RPT)*A(N1,3)
T15=-ALFA/RPT)*A(N1,4)
C
DO 12 J=1,N1
DO 13 I=1,N1
PC(1,J)=CONT*(B(J,1)-B(J,N1)*A(N1,1)/RP))
TPC(1,J)=CONT*(B(J,1)-B(J,N1)*A(N1,1)/RPT))
13 CONTINUE
PC(N1,J)=-CONT*SH*B(J,N1)/RP
TPC(N1,J)=-CONT*CNH*B(J,N1)/RPT
12 CONTINUE
C
******************************************************************************
C
DO 10 K=1,NPRINT
TEND=DI*PRINT*FLOAT(K)
C
CALL DIVPAK(INDEX,N,FCN,FCNJ,DUMMY,T,TEND,TOL,PARAM,Y)
C
DO 123 I=1,M2
CONV(1)=1.0-Y(1)
123 CONTINUE
TACT(M2)=Y(6*M2)*TACT=273.0
WRITE(6,3002)T,Y(M2),TACT(M2),CONV(M2)
C
WRITE(6,3002)T,Y(M2),Y(6*M2),CONV(M2)
1002 FORMAT(1X,F10.4,2X,RF.4,2X,RF.4,2X,RF.4)
C
1002 FORMAT(1X,F10.4,3(2X,RF.4))
WRITE(7,1003)T
1003 FORMAT(10X,'TIME=',F10.4,1,2X)
WRITE(7,1004)
1004 FORMAT(3X,'XVALUE',5X,'BULKA',5X,'PARTL1').
.5X,'PARTL2',5X,'PARTL3',5X,'PARTL4',5X,'CONV',./
WRITE(9,1003) T
WRITE(9,3004)
FORMAT(3X,'KVALUE',5X,'TRNLK',5X,'TRPL1',
      5X,'TRPL2',5X,'TRPL3',5X,'TRPL4',./)
WRITE(9,2071)
FORMAT(24X,'Y=0.165',
      5X,'Y=0.478',5X,'Y=0.739',5X,'Y=0.919',./)
WRITE(7,1071)
FORMAT(24X,'Y=0.165',
      5X,'Y=0.478',5X,'Y=0.739',5X,'Y=0.919',./)
NO 1005 I=1,M2
WRITE(7,1016)X(I),Y(I),Y(I+1*M2),Y(I+2*M2),Y(I+3*M2),Y(I+4*M2),Y(I+5*M2),
CONTINUE
CC Y(I+9*M2)
CONTINUE WRITE(10,1003) T
WRITE(10,9004)
FORMAT(3X,'KVALUE',5X,'CEPR1',
      5X,'CEPR2',5X,'CEPR3',5X,'CEPR4',./)
WRITE(10,9071)
FORMAT(14X,'Y=0.165',
      5X,'Y=0.478',5X,'Y=0.739',5X,'Y=0.919',./)
DO 9005 I=1,M2
WRITE(10,1006)X(I),Y(I+10*M2),Y(I+11*M2),Y(I+12*M2),Y(I+13*M2)
CONTINUE
FORMAT(/,4X,F6.4,5(1X,F10.6))
FORMAT(/,4X,F6.4,6(1X,F10.6))
IF(IER,GT,128) GO TO 20
CONTINUE
GO TO 30
CONTINUE
WRITE(6,1002)IER
CC
FORMAT(1X,F8.3,10F7.3,./(9X,10F7.3))
FORMAT(1X,'NO. OF CELLS =',15,' IER VALUE = ',15)
CC
30 CONTINUE
111 CONTINUE
STOP
END

SUBROUTINE FCN(N, T, Y, YPRIME)
  IMPLICIT REAL*8(A-H, O-Z)
  REAL*8 TEND
  REAL*8 SUMA1(30), YPRIME(N), Y(N, 1)
  REAL*8 SUMF1(30)
  COMMON/DATA/CLT, AMP, CLZ, PEM, ALFA, SH, EBAR, ST, CI, SI, P, CON1, M1, N1
  COMMON/DATA/THZ, PEH, ALFAN, GT, TI, RN, CON11, ST, TV, RETA, DAT, GAUS, GAMMA
  COMMON AX(30, 30), BX(30, 30), X(50), VMX
  COMMON CNH(50, 50), F(30), A(50, 50), B(50, 50), PC(50, 50)
  COMMON TH(50, 50), TPC(50, 50)
  DIMENSION Conv(50)
  INTEGER N

  CHZ = 1.0
  M1 = M1 + 1
  M2 = M2 + 2
  M3 = M3 + 2.0
  M4 = M4 + 3.0
  M5 = M5 + 4.0
  M6 = M6 + 5.0
  M7 = M7 + 6.0
  M8 = M8 + 7.0
  M9 = M9 + 8.0
  M10 = M10 + 9.0
  M11 = M11 + 10.0

  N1 = N1 + 1

  R1 = (AX(M2, M2)/AX(M2, 1)) - (AX(1, M2)/(AX(1, 1) - PHI))
  R1 = 1.0/(R1*(AX(1, 1) - PHI))
  R2 = 1.0/(R2*(AX(M2, 2)))
  R3 = (R2*AX(M2, M2) - 1.0)/AX(M2, 1)
  Rh1 = (R1*AX(M2, M2))/AX(M2, 1)

  RT1 = (AX(M2, M2)/AX(M2, 1)) - (AX(1, M2)/(AX(1, 1) - PHI))
  RT1 = 1.0/(RT1*(AX(1, 1) - PHI))
  RT2 = 1.0/(RT2*(AX(M2, 1)))
  RT3 = (RT2*AX(M2, M2) - 1.0)/AX(M2, 1)
  RT4 = (RT1*AX(M2, M2))/AX(M2, 1)
DO 23 J=2, M1
DO 22 K=1, MM
K1=K+1

CII(K,J)=P*BX(J,K1)-AX(J,K1)+((P*B*X(J,1)-AX(J,1))*R1*AX(K2,K1)-
R1*AX(K1,K1))+((P*B*X(J,1)-AX(J,1))*R1*AX(K1,K1)-
R1*AX(K2,K1))

22 CONTINUE

CII(K1,J)=PHI*CH*(R4*(P*B*X(J,1)-AX(J,1))
CII(K1,J)=PHI*CH*(R1*(P*B*X(J,1)-AX(J,1))

23 CONTINUE

DO 203 J=2, M1
DO 202 K=1, MM
K1=K+1

CII(K,J)=P*BX(J,K1)-AX(J,K1)+((P*B*X(J,1)-AX(J,1))*R13*AX(K2,K1)-
R13*AX(K1,K1))+((P*B*X(J,1)-AX(J,1))*R13*AX(K1,K1)-
R13*AX(K2,K1))

202 CONTINUE

CII(K1,J)=PHI*THI*PHI*(P*B*X(J,1)-AX(J,1))
CII(K1,J)=PHI*THI*PHI*(P*B*X(J,1)-AX(J,1))

203 CONTINUE

RP=A(N1,N1)+SH
RPT=A(N1,N1)+CMH

C11=ALFA*((1.0-(SH/RP))
111=ALFA*(1.0-(CMH/RPT))
C12=-(ALFA/RP)*A(N1,1)
C13=-(ALFA/RP)*A(N1,2)
C14=-(ALFA/RP)*A(N1,3)
C15=-(ALFA/RP)*A(N1,4)
T12=-(ALFA/RPT)*A(N1,1)
T13=-(ALFA/RPT)*A(N1,2)
T14=-(ALFA/RPT)*A(N1,3)
T15=-(ALFA/RPT)*A(N1,4)

DO 12 J=1, N1
DO 13 I=1, N1
PC(I,J)=CON1*(B(J,1)-(B(J,N1)*A(N1,1)/RPT))
TPC(I,J)=CON1*(B(J,1)-(B(J,N1)*A(N1,1)/RPT))

12 CONTINUE

PC(N1,J)=CON1*SH*B(J,N1)/RP
TPC(N1,J)=CON1*CMH*B(J,N1)/RPT

13 CONTINUE

DO 21 J=2, M1
SUMA1(J)=0.0
SUMT1(J)=0.0

21 CONTINUE

DO 25 J=2, M1
DO 25 I=1, MM
11=1+1
SUMA1(J)=SUMA1(J)+CH(I,J)*Y(11)
SUM1(J)=SUM1(J)+TH(I,J)*Y(5*M2+11)

25 CONTINUE

C
DO 100 I=1,14
11+M2*1
I2=M2*1
YPRIME(I1)=0.0
YPRIME(I2)=0.0
100 CONTINUE

C
DO 800 I=2,M1
C
YPRIME(I)=0.0
C
YPRIME(I+5*M2)=0.0
YPRIME(I)=SUMA1(I)+CH(N1,1)+CH(N2,1)-
&*C11*Y(1)+C12*Y(I+M2)+C13*Y(I+2*M2)+C14*Y(I+3*M2)+C15*Y(I+4*M2)
C
YPRIME(I+M2)=PC(1,1)*Y(I+M2)+PC(2,1)*Y(I+2*M2)+PC(3,1)*Y(I+3*M2)
&+PC(4,1)*Y(I+4*M2)-PC(5,1)*Y(I-)
C
MISTHEL MINTEN
&*(DA1*Y(I+10*M2)*EXP(-1.0/Y(1+6*M2))*Y(1+M2))/
&*(Y(I+M2)+SK)
C
YPRIME(I+2*M2)=PC(1,2)*Y(I+M2)+PC(2,2)*Y(I+2*M2)+PC(3,2)*Y(I+3*M2)
&+PC(4,2)*Y(I+4*M2)-PC(5,2)*Y(I-)
C
&*(DA1*Y(I+1*M2))*EXP(-1.0/Y(I+5*M2))*Y(I+2*M2))/
&*(Y(I+2*M2)+SK)
C
YPRIME(I+3*M2)=PC(1,3)*Y(I+M2)+PC(2,3)*Y(I+2*M2)+PC(3,3)*Y(I+3*M2)
&+PC(4,3)*Y(I+4*M2)-PC(5,3)*Y(I-)
C
&*(DA1*Y(I+12*M2))*EXP(-1.0/Y(I+7*M2))*Y(I+3*M2))/
&*(Y(I+3*M2)+SK)
C
YPRIME(I+4*M2)=PC(1,4)*Y(I+M2)+PC(2,4)*Y(I+2*M2)+PC(3,4)*Y(I+3*M2)
&+PC(4,4)*Y(I+4*M2)-PC(5,4)*Y(I-)
C
&*(DA1*Y(I+13*M2))*EXP(-1.0/Y(I+8*M2))*Y(I+4*M2))/
&*(Y(I+4*M2)+SK)
C
YPRIME(1+5*M2)=0.0
YPRIME(1+6*M2)=0.0
YPRIME(1+7*M2)=0.0
YPRIME(1+8*M2)=0.0
YPRIME(1+9*M2)=0.0
YPRIME(1+5*M2)=SUM1(I)-TH(M1,1)+TH(M2,1)-
&T11*Y(1+5*M2)+T12*Y(1+6*M2)+T13*Y(1+7*M2)
&+T14*Y(I+8*M2)+T15*Y(I+9*M2)-ST(Y(1+5*M2)-T2)
C
YPRIME(1+6*M2)=TPC(1,1)*Y(1+6*M2)+TPC(2,1)*Y(1+7*M2)
&+TPC(3,1)*Y(1+8*M2)
&+TPC(4,1)*Y(I+9*M2)-TPC(5,1)*Y(1+5*M2)+
C MITCHEL HENTEN

&beta*(DA1*Y(110*M2))**EXP(-1.0/(Y(146*M2)**Y(1+P2))
&X*(Y(1+M2)**SK)
YPRIM1(147*M2) = TPG(1,2)**Y(1+M2)**TPG(2,2)**Y(1+M2)
&X = TPG(1,1)**Y(1+M2)**TPG(2,2)**Y(1+M2)
C MITCHEL HENTEN

&beta*(DA1*Y(111*M2))**EXP(-1.0/(Y(147*M2)**Y(1+M2))
&X*(Y(1+M2)**SK)
YPRIM1(118*M2) = TPG(1,1)**Y(1+M2)**TPG(2,2)**Y(1+M2)
&X = TPG(1,1)**Y(1+M2)**TPG(2,2)**Y(1+M2)
C MITCHEL HENTEN

&beta*(DA1*Y(112*M2))**EXP(-1.0/(Y(148*M2)**Y(1+M2))
&X*(Y(1+M2)**SK)
YPRIM1(119*M2) = TPG(1,1)**Y(1+M2)**TPG(2,2)**Y(1+M2)
&X = TPG(1,1)**Y(1+M2)**TPG(2,2)**Y(1+M2)
C MITCHEL HENTEN

&beta*(DA1*Y(113*M2))**EXP(-1.0/(Y(149*M2)**Y(1+M2))
&X*(Y(1+M2)**SK)
YPRIM1(114*M2) = TPG(1,1)**Y(1+M2)**TPG(2,2)**Y(1+M2)
&X = TPG(1,1)**Y(1+M2)**TPG(2,2)**Y(1+M2)
C MITCHEL HENTEN

&beta*(DA1*Y(114*M2))**EXP(-1.0/(Y(150*M2)**Y(1+M2))
&X*(Y(1+M2)**SK)
YPRIM1(115*M2) = TPG(1,1)**Y(1+M2)**TPG(2,2)**Y(1+M2)
&X = TPG(1,1)**Y(1+M2)**TPG(2,2)**Y(1+M2)

END CONTINUE

SUM2 = 0.0
SUM3 = 0.0
DO 551 I = 2, N1
SUM2 = SUM2 + (R3*AX(N2,1) - RN*AX(1,1))**Y(1)
551 SUM2 = SUM2 + (R1*AX(1,1) - R2*AX(N2,1))**Y(1)
Y(1) = SUM2 - RN*PEH*CHZ
Y(M2) = SUM2 + RT1*PEH*CHZ
SUM4 = 0.0
SUM5 = 0.0
DO 556 I = 2, N1
SUM4 = SUM4 + (RT3*AX(N2,1) - RT4*AX(1,1))**Y(M2)
556 SUM5 = SUM5 + (RT1*AX(1,1) - RT2*AX(N2,1))**Y(M2)
Y(M2+5+1) = SUM4 - RT4*PEH*THZ
Y(M2+5+2) = SUM5 + RT1*PEH*THZ
C RETURN
C C SUBROUTINE FCNJ(N,T,Y,FD)
IMPLICIT REAL*(A-H,O-Z)
INTEGER N
REAL*8 Y(N),FD(N,N),T
RETURN
END
** FOR CYLINDRICAL PARTICLE WITHOUT DEACTIVATION **
** BASE CASE **
** EFFECT OF GEOMETRY **

THE METHOD OF ORTHOGONAL COLLOCATION HAS BEEN EMPLOYED HERE
TO REDUCE THE DEFINING PARTIAL DIFFERENTIAL EQUATIONS TO
NON-LINEAR O.D.E.S. THE SET OF N.I.O.D.E IS THEN SOLVED.

N HAS BEEN USED AS A PARAMETER

\( N = (M+2) \times (N+1) \) REDIFINING FOR NONISOThERMAL CASE**
WHERE \( M \) IS THE NUMBER OF INTERNAL COLL. POINTS FOR EXTERNAL
PHASE AND \( N \) IS THE NUMBER OF INTERNAL COLL. POINTS FOR PARTICLE.

** PARAMETER(N=140) **

PARAMETER(N=140)
INTEGER(METH,NMTER,WS(N),IERR)
REALS(Y(N),WK(N)+13*N+1),T,TOL,TEND,H
REALS(PARAM(50),DUMMY(1,1))
COMMON/DATA/CLT,AMPI,CHZ,PEH,ALFA,SH,TBAR,S,CV,K,P,CONJ,IA,B
COMMON/DATA/THZ,PEH,ALFAH,CHH,T1,PH,CONJ,IS,T,K,DATA,DA,DAP,
,GAMMA
COMMON AX(30,30),AX(30,30),X(50),VMAX
COMMON GH(50,50),F(30),A(30,30),B(30,50),E(30,50)
COMMON TH(50,50),TPC(30,50),TACT(60)
DIMENSION CONV(50)
EXTERNAL FCN,FCNJ

** COLLOCATION PARAMETERS **

** N\( M = 8 \)
** N = M + 1 \)
M2 = M + 2
M20 = M2 * 2.0
M30 = M2 * 3.0
M40 = M2 * 4.0
M50 = M2 * 5.0
M60 = M2 * 6.0
M70 = M2 * 7.0
M80 = M2 * 8.0
M90 = M2 * 9.0
M100=M2*10.0

********************************************************************
M110=M2*11.0
M120=M2*12.0
M130=M2*13.0
M140=M2*14.0

********************************************************************
C:
N1=4
N1=N1+1
C:
DO 9 I=1,M2
DO 9 J=1,M2
9 READ(5,*)AX(I,J)
C:
DO 5 I=1,M2
DO 5 J=1,M2
5 READ(5,*)BX(I,J)

********************************************************************
C:
X( 1)=0.2389648E+00
C:
X( 2)=0.5261587E+00
C:
X( 3)=0.7639309E+00
C:
X( 4)=0.9274913E+00
C:
X( 5)=0.1000000E+01
A( 1, 1)=-0.4184716E+01
A( 1, 2)=0.6700685E+01
A( 1, 3)=-0.4274691E+01
A( 1, 4)=0.2877766E+01
A( 1, 5)=-0.1190455E+01
A( 2, 1)=-0.1554554E+01
A( 2, 2)=-0.1900567E+01
A( 2, 3)=0.5283625E+01
A( 2, 4)=-0.2831399E+01
A( 2, 5)=0.1042796E+01
A( 3, 1)=0.6162676E+00
A( 3, 2)=0.3258648E+01
A( 3, 3)=-0.1309199E+01
A( 3, 4)=0.5671614E+01
A( 3, 5)=-0.1720215E+01
A( 4, 1)=-0.4776065E+00
A( 4, 2)=0.2025616E+01
A( 4, 3)=-0.6529153E+01
A( 4, 4)=-0.1078177E+01
A( 4, 5)=0.6059321E+01
A( 5, 1)=0.9607694E+00
A( 5, 2)=-0.3859333E+01
A( 5, 3)=0.1024480E+02
A( 5, 4)=0.3133592E+02
A( 5, 5)=0.2400000E+02
B( 1, 1)=-0.2367752E+02
B( 1, 2)=0.2914784E+02
B( 1, 3)=-0.7760893E+01
B( 1, 4)=0.3429999E+01
B( 1, 5)=-0.1134307E+01
B( 2, 1)=0.1488800E+02
R( 2, 2)=-0.4368600E+02
R( 2, 3)= 0.3597721E+02
R( 2, 4)=-0.1021462E+02
R( 2, 5)= 0.3034894E+01
R( 3, 1)=-0.3576610E+01
R( 3, 2)= 0.3286165E+02
R( 3, 3)=-0.7890704E+02
R( 3, 4)= 0.6264560E+02
R( 3, 5)=-0.1262339E+02
R( 4, 1)= 0.2206231E+01
R( 4, 2)=-0.1288139E+02
R( 4, 3)= 0.8755812E+02
R( 4, 4)=-0.2377294E+03
R( 4, 5)= 0.1603464E+03
R( 5, 1)= 0.4396265E+02
R( 5, 2)=-0.1716195E+03
R( 5, 3)= 0.4138163E+03
R( 5, 4)=-0.6701594E+03
R( 5, 5)= 0.3810000E+03

C

T=0.0

C: ********************************** INITIAL CONDITION ***************

C
DO 44 I=1,M50
C  Y(I)=1.0
Y(I)=0.0
44 CONTINUE
DO 45 I=1,M2
CONV(I)=0.0
45 CONTINUE
M51=M50 +1
DO 48 I=M51,M100
Y(I)=0.0596
48 CONTINUE
M101=M100 +1
DO 49 I=M101,N
Y(I)=1.0
49 CONTINUE

C

C: ******** IMSL VARIABLES ***************

C: -------- TFIN = FINAL TIME -----------
C: -------- DTPRNT = PRINT INTERVAL -------

C
TFIN = 30.0
DTPRNT =1.0
NPRINT = INT(TFIN/DTPRNT)

C
TOL =0.00001
H=0.000001
METH=2
MITER=0
INDEX=1
IER=0
NPARAM=50
CALL SSET(NPARAM,0.0,PARAM,1)
PARAM(1)=H
PARAM(4)=10000
PARAM(12)=HETH
PARAM(13)=NITR
PARAM(19)=0

*** PARAMETERS FOR THE PROBLEM **********

C
C    CIH=1.00
CNH=0.0596
C   PEM=1.0E+04
C   PEH=PEM*0.25
C
C   ALFA=8.000
ALFA=2.880
ALFAI=ALFA
C   ALFAI=2.880E+00
SIH=8.0*2.0/3.0
SIH=5.0*2.0/3.0
C   CNH=0.025
CNH=SIH
C   ST=10.0
ST=0.1
TW=0.0596
C   BETA=3.0E-02
BETA=2.0E-02
TBAR=60.0
C   VMAX=0.02
DA1=5.0E+06
DA1=5.0E+07
DA2=0.0
C   GAMMA=76000.0/10000.0
FACT=10000.0/2.0
C
C   NOTE : SI= 25.0 FOR ZERO ORDER AND SI=SI FOR OTHER KINETICS
C
C
C   SI=4.0
SI=45.0
C   CK=2.0
SK=CK/SI
C   P=1.0/PEM
P=1.0/PEH
C   CON1=0.550
CON1=0.666
CON1=CON1
C
C   END OF PARAMETERS ****************************
C
C
C   INPUT FOR X VALUE AND AX & BX MATRIX *********
C
C
X(1)=0.0
WRITE(7,2001)
2001 FORMAT(5X,'********VALUES OF THE PARAMETERS FOR THIS RUN********',/)
WRITE(7,2002) PFM
2002 FORMAT(5X,'PECLET NO. FOR MASS, PFM  =',E14.7)
WRITE(7,2009) PFM
2009 FORMAT(5X,'PECLET NO. FOR HEAT, PFM =',E14.7)
WRITE(7,2003) ALFA
2003 FORMAT(5X,'ALFA  =',E14.7)
WRITE(7,2008) ALFAH
2008 FORMAT(5X,'ALFAH =',E14.7)
WRITE(7,2004) TBAR
2004 FORMAT(5X,'TBAR  =',E14.7)
WRITE(7,2014) VMAX
2014 FORMAT(5X,'VMAX =',E14.7)
WRITE(7,2005) S1
2005 FORMAT(5X,'S1  =',E14.7)
WRITE(7,2006) CK
2006 FORMAT(5X,'CK  =',E14.7)
WRITE(7,2007) SK
2007 FORMAT(5X,'SK  =',E14.7)
WRITE(7,2008) CON1
2008 FORMAT(5X,'CON1 =',E14.7)
WRITE(7,2018) CON1T
2018 FORMAT(5X,'CON1T =',E14.7)
WRITE(7,2009) CNH
2009 FORMAT(5X,'CNH =',E14.7)
WRITE(7,2001) SH
2001 FORMAT(5X,'SH =',E14.7)
WRITE(7,2002) SII
2002 FORMAT(5X,'SII =',E14.7)
WRITE(7,2003) ST
2003 FORMAT(5X,'ST =',E14.7)
WRITE(7,2004) TW
2004 FORMAT(5X,'TW =',E14.7)
WRITE(7,2008) DA1
2008 FORMAT(5X,'DA1 =',E14.7)
WRITE(7,2005) DA2
2005 FORMAT(5X,'DA2 =',E14.7)
WRITE(7,2006) DETA
2006 FORMAT(5X,'DETA =',E14.7)
WRITE(7,2007) GAMMA
2007 FORMAT(5X,'GAMMA =',E14.7)
WRITE(7,2010) CHZ
2010 FORMAT(5X,'CHZ =',E14.7)
WRITE(7,2011) THZ
2011 FORMAT(5X,'THZ =',E14.7)
WRITE(7,2010)
1110 FORMAT(5X, '**********END OF THE PARAMETERS FOR THIS RUN********',./,./) 
1111 WRITE(6,3001) 
1111 FORMAT(1X, 'TIME CONC. TEMP COMP') 
  CONV(M2)=1.0-Y(M2) 
  TACT(M2)=Y(6*M2)*FACT-273.0 
  WRITE(6,3002) 1,Y(M2),TACT(M2),CONV(M2) 
  WRITE(7,1004) 1 
  WRITE(7,1071) TACT(M2)=Y(6*M2)*FACT-273.0 
  DO 1112 I=1,M2 
1112 TACT(I)=Y(I+5*M2)*FACT-273.0 
  DO 1113 I=1,M2 
1113 TACT(I+M2)=Y(I+6*M2)*FACT-273.0 
  DO 1114 I=1,M2 
1114 TACT(I+2*M2)=Y(I+7*M2)*FACT-273.0 
  DO 1115 I=1,M2 
1115 TACT(I+3*M2)=Y(I+8*M2)*FACT-273.0 
  DO 1116 I=1,M2 
1116 TACT(I+4*M2)=Y(I+9*M2)*FACT-273.0 
  DO 1015 I=1,M2 
1015 WRITE(7,1016)X(I),Y(I),Y(I+M2),Y(I+2*M2),Y(I+3*M2),Y(I+4*M2), 
  ,CONV(I) 
  WRITE(9,1005)X(I),Y(I+5*M2),Y(I+6*M2),Y(I+7*M2), 
  ,Y(I+8*M2),Y(I+9*M2) 
  WRITE(9,1006)X(I),TACT(I),TACT(I+M2),TACT(I+2*M2),TACT(I+3*M2), 
  ,TACT(I+4*M2) 
1015 CONTINUE 

*************************************************************************************** 

*************************************************************************************** 

R=(AX(M2,M2)/AX(M2,1))-(AX(1,M2)/(AX(1,1)-PEN)) 
R1=1.0/(R*(AX(1,1)-PEN)) 
R2=1.0/(R*(AX(M2,M2))) 
R3=((R2*AX(M2,M2))-1.0)/AX(M2,1) 
R4=(R1*AX(M2,M2))/AX(M2,1) 

*************************************************************************************** 

R=(AX(M2,M2)/AX(M2,1))-(AX(1,M2)/(AX(1,1)-PEN)) 
R1=1.0/(R*(AX(1,1)-PEN)) 
R2=1.0/(R*(AX(M2,M2))) 
R3=((R2*AX(M2,M2))-1.0)/AX(M2,1) 
R4=(R1*AX(M2,M2))/AX(M2,1) 

*************************************************************************************** 

DO 23 J=2,M1 
DO 22 K=1,MM 
K1=K+1 


CH(K,J)=P*RX(J,K1)-AX(J,K1)+((P*RX(J,1)-AX(J,1))*R1*AX(1,K1)-
&AX(J,1,K1)))*((P*RX(J,M2)-AX(J,M2))*R1*AX(1,K1)-R2*AX(M2,K1))
22 CONTINUE
CH(1,J1)=PHI*CHZ*RH*(P*RX(J,1)-AX(J,1))
CH(M2,J)=PHI*CHZ*R1*(P*RX(J,M2)-AX(J,M2))
23 CONTINUE

DO 203 J=2,M1
DO 202 K=1,N1
K4=K+1
TH(K,J)=PHI*RX(J,K1)-AX(J,K1)+((PHI*RX(J,1)-AX(J,1))*R1*AX(1,K1)-
&RT4*AX(1,K1))) + ((PHI*RX(J,M2)-AX(J,M2))*R1*AX(1,K1)
&-RT2*AX(M2,K1))
202 CONTINUE
TH(1,J1)=PHI*THZ*RT4*(PHI*RX(J,1)-AX(J,1))
TH(M2,J)=PHI*THZ*R1*(PHI*RX(J,M2)-AX(J,M2))
203 CONTINUE

RP=A(N1,N1)+SH
RP1=A(N1,N1)+CNH

C11=ALFA*(1.0-(SH/RP))
111=ALFAH*(1.0-(CNH/RP1))
C12=-((ALFA/RP)*A(N1,1))
C13=-((ALFA/RP)*A(N1,2))
C14=-((ALFA/RP)*A(N1,3))
C15=-((ALFA/RP)*A(N1,4))
T12=-((ALFAH/RP1)*A(N1,1))
T13=-((ALFAH/RP1)*A(N1,2))
T14=-((ALFAH/RP1)*A(N1,3))
T15=-((ALFAH/RP1)*A(N1,4))

DO 12 J=1,N1
DO 13 I=1,N1
PC(I,J)=CON1*(B(J,1)-(B(J,N1)*A(N1,1)/RP))
TCP(I,J)=CON11*(B(J,1)-(B(J,N1)*A(N1,1)/RP1))
13 CONTINUE
PC(N1,J)=-CON1*SH*B(J,N1)/RP
TCP(N1,J)=-CON11*CNH*B(J,N1)/RP1
12 CONTINUE

***********************************************************************

DO 10 K=1,NPRINT
10 ENDFPRINT*FLOAT(K)

CALL DIVPAC(INDEX,N,FON,FONJ,DUMMY,T,TEND,TOL,PAR2,PARAM)

DO 123 I=1,M2
CONV(I)=1.0-Y(I)
123 CONTINUE
TACT=M2=Y(6*M2)*TACT-273.0
WRITE(6,3002) T,Y(M2),TACT(M2),CONV(M2)
WRITE(6,3002) T,Y(N2),Y(6*M2),CONV(M2)

*****************************************************************************
WRITE(7,1003) T

 FORMAT(10X,'TIME=',F10.4,/,)
WRITE(7,1004)

 FORMAT(3X,'XVALUE',5X,'BULK',5X,'PART1',
       ,5X,'PART2',5X,'PART3',5X,'PART4',5X,'CONV',/,)
WRITE(9,1003) T
WRITE(9,3004)

 FORMAT(3X,'XVALUE',5X,'IBULK',5X,'TPR1',
       ,5X,'TPR2',5X,'TPR3',5X,'TPR4',/,)
WRITE(9,2071)

 FORMAT(2X,'Y=0.239',
       ,5X,'Y=0.526',5X,'Y=0.764',5X,'Y=0.921',/,)
WRITE(7,1071)

 FORMAT(2X,'Y=0.239',
       ,5X,'Y=0.526',5X,'Y=0.764',5X,'Y=0.921',/,)
DO 1005 I=1,M2
WRITE(7,1016)(X(I),Y(I),Y(1+M2),Y(1+2*M2),Y(1+3*M2),Y(1+4*M2),
       ,CONV(I))

 CONTINUE

 DO 2222 I=1,M2
   TACT(I)=Y(1+5*M2)*FACT-C273.0
   DO 2223 I=1,M2
     TACT(I+M2)=Y(1+6*M2)*FACT-C273.0
     DO 2224 I=1,M2
       TACT(I+2*M2)=Y(1+7*M2)*FACT-C273.0
       DO 2225 I=1,M2
         TACT(I+3*M2)=Y(1+8*M2)*FACT-C273.0
         DO 2226 I=1,M2
           TACT(I+4*M2)=Y(1+9*M2)*FACT-C273.0
           DO 3005 I=1,M2
             WRITE(9,1006)(X(I),Y(I+M2),Y(I+6*M2),Y(I+7*M2),Y(I+8*M2),
             ,Y(I+9*M2))
             WRITE(10,1003) T
       WRITE(10,9004)

 FORMAT(3X,'XVALUE',5X,'CEPRI1',
       ,5X,'CEPRI2',5X,'CEPRI3',5X,'CEPRI4',/,)
WRITE(10,9071)

 FORMAT(1X,'Y=0.239',
       ,5X,'Y=0.526',5X,'Y=0.764',5X,'Y=0.921',/,)
DO 9005 I=1,M2
WRITE(10,1006)(X(I),Y(I+10*M2),Y(I+11*M2),Y(I+12*M2),Y(I+13*M2))

 CONTINUE

 FORMAT(/,X,F6.4,5(1X,F10.6))

 CONTINUE

 IF(IER.GT.128) GO TO 20
 CONTINUE

 GO TO 30
 CONTINUE

 WRITE(6,1002) N,IER
SUBROUTINE FCN(N,T,Y,YPrime)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 TERM1
REAL*8 SUM1(30), YPrime(N), Y(N), T
REAL*8 SUMT1(30)
COMMON/DATA/Cl.T, AMPL, CHZ, PEN, ALFA, SIH, TBAR, S1, C, S, P, CONT1, M1, M11
COMMON/DATA/T1Z, PEN, ALFA, CNH, T1, PI, CONT1, S1, TW, R1A, HA1, DAP1
COMMON AX(30,30), BX(30,30), X(50), VMAX
COMMON CH(50,50), F(30), A(50,50), B(50,50), PC(50,50)
COMMON TH(50,50), PC(50,50)
DIMENSION CONV(50)
INTEGER N

CHZ = 1.0
M1 = M1*1
M2 = M2*2
M30 = M3*1.0
M40 = M4*0.0
M50 = M5*0.0
M60 = M6*1.0
M70 = M7*0.0
M80 = M8*0.0
M90 = M9*0.0
M100 = M1*10.0

**-----------------------------------**
M110 = M1*11.0
M120 = M1*12.0
M130 = M1*13.0
M140 = M1*14.0
**-----------------------------------**

N1 = N1 + 1

R = (AX(M2,M2)/AX(M2,1)) - (AX(1,M2)/(AX(1,1) - PEM))
R1 = 1.0 / (R*(AX(1,1) - PEM))
R2 = 1.0 / (R*(AX(M2,1)))
R3 = ((R2*AX(M2,M2)) - 1.0) / AX(M2,1)
R4 = (R1*AX(M2,M2)) / AX(M2,1)

**-----------------------------------**

**-----------------------------------**
```
RT=(AX(M2,M2)/AX(M2,1))-(AX(1,M2)/(AX(1,1)-PEH))
RT1=1.0/(RT*(AX(1,1)-PEH))
RT2=1.0/(RT*(AX(M2,1)))
RT3=((-RT2*AX(M2,M2))-1.0)/AX(M2,1)
RT4=(R11*AX(M2,M2))/AX(M2,1)

C
C******************************************************************************
C
DO 23 J=2,M1
DO 22 K=1,N1
K1=K+1

CH(K,J)=P*BX(J,K1)-AX(J,K1)*((P*BX(J,1)-AX(J,1))**(R1*AX(M2,K1)-
  &R1*AX(1,K1)))+((P*BX(J,M2)-AX(J,M2))**(R1*AX(1,K1)-R2*AX(M2,K1))
22 CONTINUE
CH(M1,J)=PEH*CHZ*RH*P*BX(J,1)-AX(J,1))
CH(M2,J)=PEH*CHZ*RH*P*BX(J,M2)-AX(J,M2))
23 CONTINUE
C
C
DO 203 J=2,M1
DO 202 K=1,N1
K1=K+1

TH(K,J)=PHI*BX(J,K1)-AX(J,K1)*((PHI*BX(J,1)-AX(J,1))**(R13*AX(M2,K1)-
  &RTH*AX(1,K1)))+((PHI*BX(J,M2)-AX(J,M2))**(R13*AX(1,K1)
  &-RT2*AX(M2,K1)))
202 CONTINUE
TH(M1,J)=PEH*THZ*RT1*(PHI*BX(J,1)-AX(J,1))
TH(M2,J)=PEH*THZ*RT1*(PHI*BX(J,M2)-AX(J,M2))
203 CONTINUE
RP=A(N1,N1)+SH
RPT=A(N1,N1)+CNH

C11=ALFA*(1.0-(SH/RP))
T11=ALFAH*(1.0-(CNH/RPT))
C12=-(ALFA/RP)*A(N1,1)
C13=-(ALFA/RP)*A(N1,2)
C14=-(ALFA/RP)*A(N1,3)
C15=-(ALFA/RP)*A(N1,4)
T12=-(ALFAH/RPT)*A(N1,1)
T13=-(ALFAH/RPT)*A(N1,2)
T14=-(ALFAH/RPT)*A(N1,3)
T15=-(ALFAH/RPT)*A(N1,4)

DO 12 J=1,N1
DO 13 I=1,N1
PC(I,J)=CON1*(B(J,1)-B(J,N1)*A(N1,1)/RP))
TCP(I,J)=CON1*(B(J,1)-B(J,N1)*A(N1,1)/RP)
13 CONTINUE
PC(N1,J)=CON1*SH*B(J,N1)/RP
TCP(N1,J)=CON1*CNH*B(J,N1)/RP
12 CONTINUE
C******************************************************************************
```
10 DO 21 J=2,M1
  SUMA1(J)=0.0
  SUMT(J)=0.0
21 CONTINUE
DO 25 J=2,M1
DO 25 I=1,M1
   I1=I+1
   SUMA(J)=SUMA(J)+CH(I,J)*Y(I)
   SUMT(J)=SUMT(J)+TH(I,J)*Y(5*M2+11)
25 CONTINUE

DO 700 I=1,N1
   M2=M2*(1-1)
   YPRIME(I)=0.0
   YPRIME(I)=0.0
700 CONTINUE

DO 800 I=2,M1
  YPRIME(I)=0.0
  YPRIME(I)*(M2)=0.0
  YPRIME(I)=SUMA(I-1)-CH(M1,I)+CH(M1,I-1)
  &C11*Y(I-1)*C12*Y(I)*M2+C13*Y(I+1)*M2+C14*Y(I+2)*M2+C15*Y(I+1)*M2

  YPRIME(I)=PC(I,1)*Y(I+M2)+PC(I,2)*Y(I+2*M2)+PC(I,3)*Y(I+3*M2)+PC(I,4)*Y(I+4*M2)
  &PC(I,5)*Y(I+5*M2)+PC(I,6)*Y(I+6*M2)+PC(I,7)*Y(I+7*M2)+PC(I,8)*Y(I+8*M2)+PC(I,9)*Y(I+9*M2)+PC(I,10)*Y(I+10*M2)

MICHIEL MENTEN
&{DA1*Y(I+10*M2)*EXP(-1.0/Y(I+10*M2))} Y(I+10*M2)
&{(Y(I+10*M2)+SK)

  YPRIME(I+2*M2)=PC(I,1)*Y(I+M2)+PC(I,2)*Y(I+2*M2)+PC(I,3)*Y(I+3*M2)+PC(I,4)*Y(I+4*M2)
  &PC(I,5)*Y(I+5*M2)+PC(I,6)*Y(I+6*M2)+PC(I,7)*Y(I+7*M2)+PC(I,8)*Y(I+8*M2)+PC(I,9)*Y(I+9*M2)+PC(I,10)*Y(I+10*M2)

&{DA1*Y(I+11*M2)*EXP(-1.0/Y(I+11*M2))} Y(I+11*M2)
&{(Y(I+11*M2)+SK)

  YPRIME(I+3*M2)=PC(I,1)*Y(I+M2)+PC(I,2)*Y(I+2*M2)+PC(I,3)*Y(I+3*M2)+PC(I,4)*Y(I+4*M2)
  &PC(I,5)*Y(I+5*M2)+PC(I,6)*Y(I+6*M2)+PC(I,7)*Y(I+7*M2)+PC(I,8)*Y(I+8*M2)+PC(I,9)*Y(I+9*M2)+PC(I,10)*Y(I+10*M2)

&{DA1*Y(I+12*M2)*EXP(-1.0/Y(I+12*M2))} Y(I+12*M2)
&{(Y(I+12*M2)+SK)

  YPRIME(I+4*M2)=PC(I,1)*Y(I+M2)+PC(I,2)*Y(I+2*M2)+PC(I,3)*Y(I+3*M2)+PC(I,4)*Y(I+4*M2)
  &PC(I,5)*Y(I+5*M2)+PC(I,6)*Y(I+6*M2)+PC(I,7)*Y(I+7*M2)+PC(I,8)*Y(I+8*M2)+PC(I,9)*Y(I+9*M2)+PC(I,10)*Y(I+10*M2)

&{DA1*Y(I+13*M2)*EXP(-1.0/Y(I+13*M2))} Y(I+13*M2)
&{(Y(I+13*M2)+SK)

  YPRIME(I+5*M2)=0.0
  YPRIME(I+6*M2)=0.0
  YPRIME(I+7*M2)=0.0
  YPRIME(I+8*M2)=0.0
  YPRIME(I+9*M2)=0.0
YPRIME(1+6*M2) = SUM1(1+11*(M1,1)+11*(M2,1)) -
 & T11*(Y(1+6*M2)+T12*Y(1+6*M2)+T13*Y(1+7*M2)
 &+ T14*Y(1+8*M2)+T15*Y(1+9*M2)-ST1*(Y(1+5*M2) - Y1)

YPRIME(1+6*M2) = TPC(1,1)*Y(1+6*M2)+TPC(2,1)*Y(1+7*M2)
 &+ TPC(3,1)*Y(1+8*M2)
 &+ TPC(4,1)*Y(1+9*M2)-TPC(5,1)*Y(1+5*M2)

MITCHEL MENTEN

&BEITA*(DA1*Y(1+10*M2))*EXP(-1.0/Y(1+6*M2))*Y1*Y2)
 &/(Y(1+2*M2))+SK
 YPRIME(1+7*M2) = TPC(1,2)*Y(1+6*M2)+TPC(2,2)*Y(1+7*M2)
 &+ TPC(3,2)*Y(1+8*M2)
 &+ TPC(4,2)*Y(1+9*M2)-TPC(5,2)*Y(1+5*M2)

MITCHEL MENTEN

&BEITA*(DA1*Y(1+11*M2))*EXP(-1.0/Y(1+7*M2))*Y(1+2*M2)
 &/(Y(1+2*M2))+SK
 YPRIME(1+8*M2) = TPC(1,3)*Y(1+6*M2)+TPC(2,3)*Y(1+7*M2)
 &+ TPC(3,3)*Y(1+8*M2)
 &+ TPC(4,3)*Y(1+9*M2)-TPC(5,3)*Y(1+5*M2)

MITCHEL MENTEN

&BEITA*(DA1*Y(1+12*M2))*EXP(-1.0/Y(1+8*M2))*Y(1+3*M2)
 &/(Y(1+3*M2))+SK
 YPRIME(1+9*M2) = TPC(1,4)*Y(1+6*M2)+TPC(2,4)*Y(1+7*M2)
 &+ TPC(3,4)*Y(1+8*M2)
 &+ TPC(4,4)*Y(1+9*M2)-TPC(5,4)*Y(1+5*M2)

MITCHEL MENTEN

&BEITA*(DA1*Y(1+13*M2))*EXP(-1.0/Y(1+9*M2))*Y(1+4*M2)
 &/(Y(1+4*M2))+SK
 YPRIME(1+10*M2) = PARAM2*Y(1+10*M2)*EXP(-GAMMA/Y(1+6*M2))

YPRIME(1+11*M2) = PARAM2*Y(1+11*M2)*EXP(-GAMMA/Y(1+7*M2))

YPRIME(1+12*M2) = PARAM2*Y(1+12*M2)*EXP(-GAMMA/Y(1+8*M2))

YPRIME(1+13*M2) = PARAM2*Y(1+13*M2)*EXP(-GAMMA/Y(1+9*M2))

YPRIME(1+10*M2) = 0.0
YPRIME(1+11*M2) = 0.0
YPRIME(1+12*M2) = 0.0
YPRIME(1+13*M2) = 0.0

CONTINUE

SUM2 = SUM2 + (R3*AX(M2,1) - R4*AX(1,1))*Y(1)

SUM3 = SUM3 + (R1*AX(1,1) - R2*AX(M2,1))*Y(1)

Y(1) = SUM2 - R4*PEH*CHIZ
Y(M2) = SUM3 + R1*PEH*CHIZ

SUMM = SUM2
SUMM = SUM3
SUMM = SUM2 + (R3*AX(M2,1) - R4*AX(1,1))*Y(1+5*M2)

SUM5 = SUM5 + (R1*AX(1,1) - R2*AX(M2,1))*Y(1+5*M2)

Y(M2+5+1) = SUM4 - R4*PEH*THIZ
Y(M2+5+2) = SUM5 + R1*PEH*THIZ

RETURN

END
SUBROUTINE FCNJ(N,T,Y,P0)
IMPLICIT REAL*(A-H,O-Z)
INTEGER N
REAL*8 Y(N),P0(N,N),T
RETURN
END
FOR SPHERICAL PARTICLE WITHOUT DEACTIVATION(DA=0.0)
FOR WRONG WAY BEHAVIOR
FIRST RUN THIS PROGRAM THEN RUN ENZYMESI FORTRAN PROGRAM
BASE CASE

THE METHOD OF ORTHOGONAL COLLOCATION HAS BEEN EMPLOYED HERE
TO REDUCE THE DEFINING PARTIAL DIFFERENTIAL EQUATIONS TO
NON-LINEAR O.D.E.S. THE SET OF N.I.O.D.E IS THEN SOLVED.

N HAS BEEN USED AS A PARAMETER

N=(MM+2)*(NI+1) *****REDEFINE FOR NONISOTHERMAL CASE*****

WHERE MM IS THE NUMBER OF INTERNAL COLL.POINTS FOR EXTERNAL
PHASE AND NI IS THE NUMBER OF INTERNAL COLL.POINTS FOR PARTICLE.

PARAMETER(N=140)
IMPLICIT REAL*8(A-H,O-Z)
INTEGER METH,MTER,INU(N),IER,K
REAL*8 Y(N),WK(4*N+13*N+1),I,TOL,TEND,II
REAL*8 PARAM(50),DUMMY(1,1)
COMMON/DATA/CLT,AMPL,CH1,P1,ALFA,SH,TBAR,S1,CK,SK,G,CON1,MM,NI
COMMON/DATA/T17,PEH,ALFAH,CH1H,TH1,PH,CON1T,ST1,TH1,MA,T,DA,DAP.
.GAMMA
COMMON AX(30,30),BX(30,30),MAX
COMMON CH(50,50),G(30),A(50,50),B(50,50),RC(50,50)
COMMON TH(50,50),TPC(50,50)
EXTERNAL FCN,FCNJ

**********COLLOCATION PARAMETERS**********

MM IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR RTD
NI IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR PARTICLE

MM=8
MM=MM+2
M2=MM+2
M2=M2*2.0
M3=M2*3.0
M4=M2*4.0
M5=M2*5.0
M6=M2*6.0
M7=M2*7.0
M8=M2*8.0
M9=M2*9.0
M100=M2*10.0

********
M110=M2*11.0
M120=M2*12.0
M130=M2*13.0
M140=M2*14.0

********
C:
Ni=4
Ni=Ni+1

DO 9 I=1,M2
DO 9 J=1,M2
9 READ(5,*)AX(I,J)

DO 5 I=1,M2
DO 5 J=1,M2
5 READ(5,*)BX(I,J)

C: **********
C: X( 1)= 0.2957581E+00
C: X( 2)= 0.4652353E+00
C: X( 3)= 0.8790000E+00
C: X( 4)= 0.9300000E+01
C: X( 5)= 0.1000000E+01
A( 1, 1)=-0.5071712E+01
A( 1, 2)= 0.0658617E+01
A( 1, 3)=-0.6367129E+01
A( 1, 4)= 0.4695816E+01
A( 1, 5)= 0.1865592E+01
A( 2, 1)=-0.1430602E+01
A( 2, 2)=-0.2653762E+01
A( 2, 3)= 0.4292020E+01
A( 2, 4)=-0.3712510E+01
A( 2, 5)=-0.1107724E+01
A( 3, 1)= 0.5229562E+00
A( 3, 2)=-0.3168659E+01
A( 3, 3)=-0.1912068E+01
A( 3, 4)= 0.6623901E+01
A( 3, 5)= 0.2066411E+01
A( 4, 1)=-0.3860729E+00
A( 4, 2)= 0.1861472E+01
A( 4, 3)=-0.7019224E+01
A( 4, 4)= 0.1690993E+01
A( 4, 5)= 0.6832500E+01
A( 5, 1)= 0.7614375E+00
A( 5, 2)=-0.3468199E+01
A( 5, 3)= 0.1026822E+02
A( 5, 4)=-0.3335176E+02
A( 5, 5)= 0.2600000E+02
B( 1, 1)= 0.3445690E+02
B( 1, 2)= 0.4414925E+02
B( 1, 3)= 0.1426772E+02
B( 1, 4)= 0.7002486E+01
B( 1, 5)= 0.2418620E+01
B( 2, 1)= 0.1397981E+02
R( 2, 2) = -0.5231625E+02
R( 2, 3) = -0.4883702E+02
R( 2, 4) = -0.1517760E+02
R( 2, 5) = 0.4677060E+01
R( 3, 1) = 0.3108303E+01
R( 3, 2) = 0.3360106E+02
R( 3, 3) = -0.9452824E+02
R( 3, 4) = 0.8089441E+02
R( 3, 5) = -0.1685794E+02
R( 4, 1) = 0.1837682E+01
R( 4, 2) = 0.1257895E+02
R( 4, 3) = 0.9744685E+02
R( 4, 4) = 0.2866901E+03
R( 4, 5) = 0.1999815E+03
R( 5, 1) = 0.3654661E+02
R( 5, 2) = -0.1703605E+03
R( 5, 3) = 0.4579635E+03
R( 5, 4) = 0.7941146E+03
R( 5, 5) = 0.4689000E+03

C
C F=0.0
C
C *************** INITIAL CONDITION ***************
C
DO 4 I=1,N50
C
Y(I)=1.0
Y(I)=0.0
4 CONTINUE
M51=M50+1
DO 115 I=M51,M100
Y(I)=0.0686
115 CONTINUE

M101=M100+1
DO 116 I=M101,N
Y(I)=1.0
116 CONTINUE
C
C *********** IMSL VARIABLES ***********************
C
-- --- TFIN = FINAL TIME --- --
C --- --- DPRINT = PRINT INTERVAL --- ---
C
TFIN = 40.0
DPRINT = 2.0
NPRINT = INT(TFIN/DPRINT)
C
TOL = 0.00001
H=0.00001
METII=2
MITER=0
INDEX=1
C*************** FOR DIVPAG **************
IER=0
NPARAM=50
CALL SSET(NPARAM,0.0,PARAM,1)
PARAM(1)=11
PARAM(10)=10000
PARAM(12)=NTERM
PARAM(13)=MTER
PARAM(19)=0

C: ****** PARAMETERS FOR THE PROBLEM ***********

C
CHZ=1.00
FHZ=0.0686
THZ=0.05383
THZ=0.057
PEM=1.0E+04
PEM=100.0
PEM*PEM*0.25
C
ALFA=8.0
ALFA=1.00
ALFA=2.880
ALFA=ALFA
ALFA=ALFA
C
ALFA=ALFA
ALFA=ALFA*1.00
ALFA=ALFA*1.00
SH=0.94
SH=5.4000E-01/1.0
CNH=0.025
CNH=SH*1.00
ST=0.0
ST=0.1
TW=0.0686
C
TW=0.05383
C
BETA=0.017
BETA=1.0E-02
TBAR=60.0
C
VMAX=0.02
DA1=5.0E+06
C
DA1=5.0E+07
C
DA1=9.5E+07
C
DA1=10.5E+07
C
DA2=1.0E+35
DA2=0.0
C
GAMMA=76900.0/12000.0
GAMMA=76000.0/10000.0
C
GAMMA=5.0
C
NOTE:  SI= 25.0 FOR ZERO ORDER AND SI=4.0 FOR OTHER KINETICS
C
C
SI=1.0
C
SI=1.0
CK=2.0
SK=CK/SI
P=1.0/PEM
PH=1.0/PEH
C
CON1=0.760
C
CON1=1.0
C
CON1=0.296*1.0
CON11=CON1*1.00

C

******** END OF PARAMETERS ************

C

******** INPUT FOR X VALUE AND AX & BX MATRIX ********

C

X(1)=0.0
X(2)=0.0199
X(3)=0.1017
X(4)=0.2372
X(5)=0.4083
X(6)=0.5917
X(7)=0.7628
X(8)=0.8983
X(9)=0.9801
X(10)=1.0

C

WRITE(7,2001)
2001 FORMAT(5X,'*********VALUES OF THE PARAMETERS FOR THIS RUN*********
WRITE(7,2002) PEM
2002 FORMAT(5X,'PECLET NO. FOR MASS, PEM =',E14.7)
WRITE(7,2003) PEH
2003 FORMAT(5X,'PECLET NO. FOR HEAT, PEH =',E14.7)
WRITE(7,2004) ALFA
2004 FORMAT(5X,'ALFA =',E14.7)
WRITE(7,2005) ALFAH
2005 FORMAT(5X,'ALFAH =',E14.7)
WRITE(7,2006) TBAR
2006 FORMAT(5X,'TBAR =',E14.7)
WRITE(7,2007) VMAX
2007 FORMAT(5X,'VMAX =',E14.7)
WRITE(7,2008) SI
2008 FORMAT(5X,'SI =',E14.7)
WRITE(7,2009) CK
2009 FORMAT(5X,'CK =',E14.7)
WRITE(7,2010) CONS
2010 FORMAT(5X,'CONS =',E14.7)
WRITE(7,2011) CI
2011 FORMAT(5X,'CI =',E14.7)
WRITE(7,2012) CNH
2012 FORMAT(5X,'CNH =',E14.7)
WRITE(7,2013) NUS
2013 FORMAT(5X,'NUS =',E14.7)
WRITE(7,2014) SHER
2014 FORMAT(5X,'SHER =',E14.7)
WRITE(7,2015) STANT
2015 FORMAT(5X,'STANT =',E14.7)
WRITE(7,2016) TW
2016 FORMAT(5X,'TW =',E14.7)
WRITE(7,2017) DA1
2017 FORMAT(5X,'DA1 =',E14.7)
WRITE(7,2018) DA2
2018 FORMAT(5X,'DA2 =',E14.7)
WRITE(7,2019) BETA
PROGRAM FORMAT(5X,'BETA',-1,E14.7)
WRITE(7,7007) GAMMA
FORMAT(5X,'GAMMA',-1,E14.7)
WRITE(7,7010) CHZ
FORMAT(5X,'DIMLESS FEED CONC.,CHZ',-1,E14.7)
WRITE(7,7011) THZ
FORMAT(5X,'DIMLESS FEED TEMP.,THZ',-1,E14.7)
WRITE(7,7010)
FORMAT(5X,'END OF THE PARAMETERS FOR THIS RUN',/)
WRITE(6,3001)
FORMAT(1X,'TIME CONC. TEMP')
WRITE(6,3002) T,Y(M2),Y(6*M2)

C WRITE(7,1003) T
C WRITE(7,1004)
C WRITE(7,1071)
C DO 1015 I=1,M2
C WRITE(7,1006)X(I),Y(I),Y(I+M2),Y(I+2*M2),Y(I+3*M2),Y(I+4*M2)
C WRITE(9,1006)X(I),Y(I+5*M2),Y(I+6*M2),Y(I+7*M2),
C Y(I+8*M2),Y(I+9*M2)
C 1015 CONTINUE
C
C R=(AX(M2,M2)/AX(M2,1))-(AX(1,M2)/(AX(1,1)-PEH))
R1=1.0/(R*(AX(1,1)-PEH))
R2=1.0/(R*(AX(M2,1)))
R3=((R2*AX(M2,M2))-1.0)/AX(M2,1)
Rh=(R1*AX(M2,M2))/AX(M2,1)
C
C RT=(AX(M2,M2)/AX(M2,1))-(AX(1,M2)/(AX(1,1)-PEH))
RT1=1.0/(RT*(AX(1,1)-PEH))
RT2=1.0/(RT*(AX(M2,1)))
RT3=((RT2*AX(M2,M2))-1.0)/AX(M2,1)
RT4=(RT1*AX(M2,M2))/AX(M2,1)
C
C DO 23 J=1,M1
C DO 22 K=1,MM
K1=K+1
C
CH(K,J)=P*BX(J,K1)-AX(J,K1)+((P*BX(J,1)-AX(J,1)))*(R1*AX(M2,K1)-
&Rh*AX(1,K1))+(P*BX(J,M2)-AX(J,M2))*(R1*AX(1,K1)-R2*AX(M2,K1))
22 CONTINUE
CH(M1,J)=PEH*CHZ*R4*(P*BX(J,1)-AX(J,1))
CH(M2,J)=PEH*CHZ*R1*(P*BX(J,M2)-AX(J,M2))
23 CONTINUE
C
DO 203 J=2,M1
DO 202 K=1, NM1
   K1=K+1
   C1: TH(K, J)=PHI*BX(J, K1)-AX(J, K1)*((PHI*BX(J, 1)-AX(J, 1))*R12*AX(1, K1)-
      &R13*AX(1, K1))+(PHI*BX(J, M2)-AX(J, M2))*R11*AX(1, K1)
      &-R22*AX(M2, K1))
202 CONTINUE
TH(N, J)=PHI*H*Z*RTH*(PHI*BX(J, 1)-AX(J, 1))
TH(M, J)=PHI*H*Z*RTH*(PHI*BX(J, M2)-AX(J, M2))
203 CONTINUE

C
RP=A(N1, N1)+SH
RPT=A(N1, N1)+CNHI
C11=ALFA*(1.0-(SH/RP))
T11=ALFA/(1.0-(CNHI/RPT))
C12=-(ALFA/RP)*A(N1, 1)
C13=-(ALFA/RP)*A(N1, 2)
C14=-(ALFA/RP)*A(N1, 3)
C15=-(ALFA/RP)*A(N1, 4)
T12=-(ALFA/RPT)*A(N1, 1)
T13=-(ALFA/RPT)*A(N1, 2)
T14=-(ALFA/RPT)*A(N1, 3)
T15=-(ALFA/RPT)*A(N1, 4)

DO 12 J=1, N1
   DO 13 I=1, N1
      PC(I, J)=CON1*B(I, J)-B(J, N1)*A(N1, I)/RP
      TPC(I, J)=CON1*B(I, J)-B(J, N1)*A(N1, I)/RPT
13 CONTINUE
PC(N1, J)=CON1*SH*B(J, N1)/RP
TPC(N1, J)=CON1*PHI*B(J, N1)/RPT
12 CONTINUE

******************************************************************************

DO 10 J=1, NPRINT
   TEND=DIPTEN*FLOAT(K)
   CALL DIVPAG( INDEX, N, FCN, FCNI, NUMAY, T, TEND, TOI, PARAH, Y)
   WRITE(6,3002) T, Y(M2), Y(M2)
   3002 FORMAT(1X,F10.4,2(2X,F6.4))
   3003 FORMAT(1X,'TIME = ',F10.4,1X)
   3004 FORMAT(2X,'XVALUE',5X,'BULK',5X,'PARTL1',
      5X,'PARTL2',5X,'PARTL3',5X,'PARTLH',7X)
   WRITE(9,1003) T
   WRITE(9,1004)
   WRITE(9,3004)
   WRITE(9,1004)
   WRITE(9,3004)
   WRITE(9,3004)
C FORMAT(24X,'Y=0.296').
C 5X, 'Y=0.565', 5X, 'Y=0.704', 5X, 'Y=0.934' /.
C WRITE(7,1071)
C FORMAT(24X,'Y=0.296').
C 5X, 'Y=0.565', 5X, 'Y=0.704', 5X, 'Y=0.934' /.
C DO 1005 I=1,N2
C WRITE(7,1006)X(I),Y(I),Y(I+M2),Y(I+2*M2),Y(I+3*M2),Y(I+4*M2)
C 1005 CONTINUE
C DO 3005 I=1,N2
C WRITE(9,1006)X(I),Y(I+5*M2),Y(I+6*M2),Y(I+7*M2),Y(I+8*M2),Y(I+9*M2)
C 3005 CONTINUE
C WRITE(10,1003) T
C WRITE(10,9003)
C FORMAT(3X,'XVALUE',5X,'CEPR11',
C 5X,'CEPR12',5X,'CEPR13',5X,'CEPR14',/)
C WRITE(10,9011)
C FORMAT(19X,'Y=0.296',
C 5X, 'Y=0.565', 5X, 'Y=0.704', 5X, 'Y=0.934' /)
C DO 9005 I=1,N2
C WRITE(10,1006)X(I),Y(I+10*M2),Y(I+11*M2),Y(I+12*M2),Y(I+13*M2)
C 9005 CONTINUE
C FORMAT(4X,F6.4,5(1X,F10.6))
C IF(IER.GT.128) GO TO 20
C CONTINUE
C GO TO 30
C CONTINUE
C WRITE(6,1002)N,IER
C C FORMAT(1X,F6.3,10F7.3),/(9X,10F7.3))
C FORMAT(1X,1F7.4)
C FORMAT(1X,'NO. OF CELLS = ',I5,' IER VALUE = ',I5)
C 30 CONTINUE
C CONTINUE
C WRITE(11,1003) T
C DO 456 I=1,100
C WRITE(11,3333) Y(I)
C 456 CONTINUE
C STOP
C END
C C SURROUNDS, FCN(N,I,Y,YPRIME)
C IMPLICIT REAL*8(A-H,O-Z)
C REAL*8 TERM
C REAL*8 SUMAT(30),YPRIME(N),Y(N),I
C REAL*8 SUMT(30)
C COMMON/DATA/CLT,AMPL,CIZ,PEH,ALFA,SH,FRAR,S,CK,SK,I,CONH,MM,NI
C COMMON/DATA/FH2,PEH,ALFAH,CNI,TH,PH,CONIT,S,T,RF1A,DA1,DA2,
C COMMON AX(30,30),BX(30,30),X(50),VMAX
C COMMON CH(50,50),F(30),A(50,50),B(50,50),PCI(50,50)
C COMMON TH(50,50),TPC(50,50)
INTEGER N

CHZ= 1.0
R1=M1+1
M2=M1+2
N20=M2*2.0
N30=M2*3.0
N40=M2*4.0
N50=M2*5.0
N60=M2*6.0
N70=M2*7.0
N80=M2*8.0
N90=M2*9.0
M100=M2*10.0

******************************************************************************
M110=M2*11.0
M120=M2*12.0
M130=M2*13.0
M140=M2*14.0

******************************************************************************

N1=N1+1

R=(AX(N2,M2)/AX(M2,1))-(AX(1,N2)/(AX(1,1)-R1*M1))
R1=1.0/(R*(AX(1,1)-R1))
R2=1.0/(R*(AX(N2,1)))
R3=((R2*AX(N2,M2))-1.0)/AX(M2,1)
R4=(R1*AX(N2,M2))/AX(M2,1)

******************************************************************************

RT=(AX(N2,M2)/AX(M2,1))-(AX(1,N2)/(AX(1,1)-R1*M1))
RT1=1.0/(R1*(AX(1,1)-R1))
RT2=1.0/(RT*(AX(M2,1)))
RT3=((RT2*AX(M2,M2))-1.0)/AX(M2,1)
RT4=(RT1*AX(M2,M2))/AX(M2,1)

******************************************************************************

DO 23 J=2,M1
DO 22 K=1,MM
K1=K+1

CH(K,J)=P*BX(J,K1)-AX(J,K1)*((P*BX(J,1)-AX(J,1))**(R1*AX(N2,K1)-
&RT*AX(1,K1)))+((P*BX(J,M2)-AX(J,M2))**(R1*AX(1,K1)-R2*AX(M2,K1))))
22 CONTINUE
CH(M1,J)=P*CHZ*RT4*(P*BX(J,1)-AX(J,1))
CH(M2,J)=P*CHZ*R1*(P*BX(J,M2)-AX(J,M2))
23 CONTINUE

******************************************************************************

DO 203 J=2,M1
DO 202 K=1,MM
K1=K1+1

TH(K,J)=PH*RX(J,K1)-AX(J,K1)+((PH*RX(J,1)-AX(J,1))*(R13*AY(1,M1)-
&RT*AX(1,K1))+((PH*RX(J,M2)-AX(J,M2))*(R13*AX(1,M1)
&-RT*AX(M2,K1)))

202 CONTINUE
TH(M1,J)=PEH*THZ*RTH*(PH*RX(J,1)-AX(J,1))
TH(M2,J)=PH*THZ*RTH*(PH*RX(J,M2)-AX(J,M2))

293 CONTINUE
RP=AN1,N1+SH
RP=AN1,N1+CNH

C11=ALFA*(1.0-(SH/RP))
T11=ALFA*F(1.0-(CNH/RP))
C12=-(ALFA/RP)*AN1,1
C13=-(ALFA/RP)*AN1,2
C14=-(ALFA/RP)*AN1,3
C15=-(ALFA/RP)*AN1,4
T12=-(ALFA/RP)*AN1,1
T13=-(ALFA/RP)*AN1,2
T14=-(ALFA/RP)*AN1,3
T15=-(ALFA/RP)*AN1,4

DO 12 J=2,M1
DO 13 I=1,N1
PC(I,J)=C01*(B(J,1)-(B(J,N1)*AN1,1)/RP))
TPC(I,J)=C01*(B(J,1)-(B(J,N1)*AN1,1)/RP)

13 CONTINUE
PC(N1,J)=C01*SH*B(J,N1)/RP
TPC(N1,J)=C01*CNH*B(J,N1)/RP

12 CONTINUE

******************************************************************************

10 DO 21 J=2,M1
SUMA1(J)=0.0
SUMT1(J)=0.0
21 CONTINUE
DO 25 J=2,M1
DO 25 I=1,MM
I=I+1
SUMA1(J)=SUMA1(J)+CH(I,J)*Y(I)
SUMT1(J)=SUMT1(J)+TH(I,J)*Y(5*M2+I)
25 CONTINUE

DO 700 I=1,14
I=I+M2*(I-1)
I2=M2*I
YPRIME(I1)=0.0
YPRIME(I2)=0.0
700 CONTINUE

DO 800 I=2,M1
YPRIME(I)=0.0
800 CONTINUE

YPRIME(I+5*M2)=0.0
YPRIME(I)=SUMA1(I)-CH(N1,1)+CH(M2,1)-
\[ A C_{11} Y(1) + C 1_{12} Y(1 + M2) + C 1_{13} Y(1 + 2M2) + C 1_{14} Y(1 + 3M2) + C 1_{15} Y(1 + 5M2) + C 1_{16} Y(1 + 7M2) \]

\[ \text{VPRIME}(1 + M2) = PC(1,1) Y(1 + M2) + PC(2,1) Y(1 + 2M2) + PC(3,1) Y(1 + 3M2) + PC(4,1) Y(1 + 4M2) + PC(5,1) Y(1 + 5M2) + PC(6,1) Y(1 + 6M2) + PC(7,1) Y(1 + 7M2) \]

\[ \text{YPRIME}(1 + 2M2) = PC(1,2) Y(1 + M2) + PC(2,2) Y(1 + 2M2) + PC(3,2) Y(1 + 3M2) + PC(4,2) Y(1 + 4M2) + PC(5,2) Y(1 + 5M2) + PC(6,2) Y(1 + 6M2) + PC(7,2) Y(1 + 7M2) \]

\[ \text{YPRIME}(1 + 3M2) = PC(1,3) Y(1 + M2) + PC(2,3) Y(1 + 2M2) + PC(3,3) Y(1 + 3M2) + PC(4,3) Y(1 + 4M2) + PC(5,3) Y(1 + 5M2) + PC(6,3) Y(1 + 6M2) + PC(7,3) Y(1 + 7M2) \]

\[ \text{YPRIME}(1 + 4M2) = PC(1,4) Y(1 + M2) + PC(2,4) Y(1 + 2M2) + PC(3,4) Y(1 + 3M2) + PC(4,4) Y(1 + 4M2) + PC(5,4) Y(1 + 5M2) + PC(6,4) Y(1 + 6M2) + PC(7,4) Y(1 + 7M2) \]

\[ \text{YPRIME}(1 + 5M2) = PC(1,5) Y(1 + M2) + PC(2,5) Y(1 + 2M2) + PC(3,5) Y(1 + 3M2) + PC(4,5) Y(1 + 4M2) + PC(5,5) Y(1 + 5M2) + PC(6,5) Y(1 + 6M2) + PC(7,5) Y(1 + 7M2) \]

\[ \text{YPRIME}(1 + 6M2) = PC(1,6) Y(1 + M2) + PC(2,6) Y(1 + 2M2) + PC(3,6) Y(1 + 3M2) + PC(4,6) Y(1 + 4M2) + PC(5,6) Y(1 + 5M2) + PC(6,6) Y(1 + 6M2) + PC(7,6) Y(1 + 7M2) \]

\[ \text{YPRIME}(1 + 7M2) = PC(1,7) Y(1 + M2) + PC(2,7) Y(1 + 2M2) + PC(3,7) Y(1 + 3M2) + PC(4,7) Y(1 + 4M2) + PC(5,7) Y(1 + 5M2) + PC(6,7) Y(1 + 6M2) + PC(7,7) Y(1 + 7M2) \]

\[ \text{YPRIME}(1 + 5M2) = \text{SUM}(1,1) - \text{TH}(M1,1) + \text{TH}(M2,1) \]

\[ \text{YPRIME}(1 + 4M2) = PC(1,4) + 1 + 2 + Y(1 + 6M2) + Y(1 + 3M2) + 1 + 7M2 \]

\[ \text{YPRIME}(1 + 3M2) = PC(1,3) + 1 + 2 + Y(1 + 6M2) + Y(1 + 3M2) + 1 + 7M2 \]

\[ \text{YPRIME}(1 + 2M2) = PC(1,2) + 1 + 2 + Y(1 + 6M2) + Y(1 + 3M2) + 1 + 7M2 \]

\[ \text{YPRIME}(1 + M2) = PC(1,1) + 1 + 2 + Y(1 + 6M2) + Y(1 + 3M2) + 1 + 7M2 \]

\[ \text{YPRIME}(1 + 7M2) = PC(1,1) \text{EXP}(-1,0,1 + 4M2) * Y(1 + 5M2) + 1 + 7M2 \]

\[ \text{YPRIME}(1 + 6M2) = PC(1,1) \text{EXP}(-1,0,1 + 4M2) * Y(1 + 5M2) + 1 + 7M2 \]

\[ \text{YPRIME}(1 + 5M2) = PC(1,1) \text{EXP}(-1,0,1 + 4M2) * Y(1 + 5M2) + 1 + 7M2 \]

\[ \text{YPRIME}(1 + 4M2) = PC(1,1) \text{EXP}(-1,0,1 + 4M2) * Y(1 + 5M2) + 1 + 7M2 \]

\[ \text{YPRIME}(1 + 3M2) = PC(1,1) \text{EXP}(-1,0,1 + 4M2) * Y(1 + 5M2) + 1 + 7M2 \]

\[ \text{YPRIME}(1 + 2M2) = PC(1,1) \text{EXP}(-1,0,1 + 4M2) * Y(1 + 5M2) + 1 + 7M2 \]

\[ \text{YPRIME}(1 + M2) = PC(1,1) \text{EXP}(-1,0,1 + 4M2) * Y(1 + 5M2) + 1 + 7M2 \]
&+ TFC(3,4)*Y(1+8*M2)
&+TFC(4,4)*Y(1+9*M2)+TFC(5,4)*Y(1+5*M2)+
C MITCHEL MENTEN
&RETA*(DA1*Y(1+3*M2))*EXP(-1.0/Y(1+9*M2))*Y(1+4*M2)/
&{Y(1+4*M2)+SK)
YPRIME(1+10*M2)=DA2*Y(1+10*M2)*EXP(-GAUSS/Y(1+6*M2))
YPRIME(1+11*M2)=DA2*Y(1+11*M2)*EXP(-GAUSS/Y(1+7*M2))
YPRIME(1+12*M2)=DA2*Y(1+12*M2)*EXP(-GAUSS/Y(1+8*M2))
YPRIME(1+13*M2)=DA2*Y(1+13*M2)*EXP(-GAUSS/Y(1+9*M2))
C YPRIME(1+10*M2)=0.0
C YPRIME(1+11*M2)=0.0
C YPRIME(1+12*M2)=0.0
C YPRIME(1+13*M2)=0.0
C CONTINUE
C
SUM2=0.0
SUM3=0.0
DO 555  I=2,M1
SUM2=SUM2 + (R3*AX(M2,1) - R4*AX(1,1))*Y(I)
555 SUM3=SUM3 + (R1*AX(1,1) - R2*AX(M2,1))*Y(I)
Y(I)= SUM2 - R4*PEH*CHZ
Y(M2)= SUM3 + R1*PEH*CIH
SUM4=0.0
SUM5=0.0
DO 556  I=2,M1
SUM4=SUM4 + (RT3*AX(M2,1) - RT4*AX(1,1))*Y(I+5*M2)
556 SUM5=SUM5 + (RT1*AX(1,1) - RT2*AX(M2,1))*Y(I+5*M2)
Y(M2+5+M2)= SUM4 - RT4*PEH*NIZ
Y(M2+5+M2)= SUM5 + RT1*PEH*THZ
C
RETURN
END
C
C
SUBROUTINE FCN(N,I,Y,PD)
IMPLICIT REAL*8(A-H,O-Z)
INTEGER N
REAL*8 Y(N),PD(N,N),T
RETURN
END
FOR WRONG WAY BEHAVIOR
FOR SPHERICAL PARTICLE WITHOUT DEACTIVATION
RAS CASE

THE METHOD OF ORTHOGONAL COLLOCATION HAS BEEN EMPLOYED HERE
TO REDUCE THE DEFINING PARTIAL DIFFERENTIAL EQUATIONS TO
NON-LINEAR O.D.E.S. THE SET OF N.I.O.D.E IS THEN SOLVED.

N HAS BEEN USED AS A PARAMETER

N=(M+2)*(Ni+1) REDFIND FOR NONISOETHERAL CASE

WHERE M IS THE NUMBER OF INTERNAL COLLOC. POINTS FOR EXTERNAL
PHASE AND Ni IS THE NUMBER OF INTERNAL COLLOC. POINTS FOR PARTICI

PARAMETER(N=140)
IMPLICIT REAL*8(A-H,O-Z)
INTEGER METH,MITER,IK(N),IER,K
REAL*8 Y(N),WK(N+13*N+1),T,TOL,TEND,H
REAL*8 PARAM(50),DUMMY(1,1)
COMMON/DATA/CLT,AMPL,CIZ,PEM,ALFA,SH,IBAR,SI,CI,SK,IP,CON1,MM,N
COMMON/DATA/THZ,PEH,ALFAH,CHH,TH,PH,CON11,S*,TW,DELA,DAL,DAP, 
,GAMMA
COMMON AX(30,30),BX(30,30),X(50),VMAX
COMMON CHI(50,50),F(30),A(50,50),B(50,50),PC(50,50)
COMMON TH(50,50),TPC(50,50),TACT(60)
DIMENSION CONV(50)
EXTERNAL FCN,FCNJ

**********COLLOCATION PARAMETERS**********

MM IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR RED
Ni IS THE NUMBER OF INTERNAL COLLOCATION POINTS FOR PARTICI

MM=R
M1=M+1
M2=M+2
M20=M2*2.0
M30=M2*3.0
M40=M2*4.0
M50=M2*5.0
M60=M2*6.0
M70=M2*7.0
M80=M2*8.0
M90=M2*9.0
M100 = M2*10.0

M110 = M2*11.0
M120 = M2*12.0
M130 = M2*13.0
M140 = M2*14.0

C
N1 = 4
N1 = N1 + 1
C
DO 9 I = 1, M2
   DO 9 J = 1, M2
   9 READ(5, *) AX(I, J)
C
DO 5 I = 1, M2
   DO 5 J = 1, M2
   5 READ(5, *) BX(I, J)
C
X(1) = 0.2957581E+00
X(2) = 0.5652353E+00
X(3) = 0.7844835E+00
X(4) = 0.9300014E+00
X(5) = 0.1000000E+01
A(1, 1) = -0.5071712E+01
A(1, 2) = 0.8658617E+01
A(1, 3) = -0.6367129E+01
A(1, 4) = 0.4615819E+01
A(1, 5) = -0.1865929E+01
A(2, 1) = -0.1434610E+01
A(2, 2) = 0.2653762E+01
A(2, 3) = 0.6392034E+01
A(2, 4) = -0.3713387E+01
A(2, 5) = 0.1407772E+01
A(3, 1) = 0.5229526E+00
A(3, 2) = -0.3186593E+01
A(3, 3) = -0.1912086E+01
A(3, 4) = 0.6623901E+01
A(3, 5) = -0.2066112E+01
A(4, 1) = -0.3860729E+00
A(4, 2) = 0.1861479E+01
A(4, 3) = -0.6701922E+01
A(4, 4) = -0.1605933E+01
A(4, 5) = 0.6832509E+01
A(5, 1) = 0.7615325E+00
A(5, 2) = -0.3468199E+01
A(5, 3) = 0.1026842E+02
A(5, 4) = -0.3356176E+02
A(5, 5) = 0.2600000E+02
B(1, 1) = -0.3446590E+02
B(1, 2) = 0.4414925E+02
B(1, 3) = -0.1426772E+02
B(1, 4) = 0.7002986E+01
B(1, 5) = -0.2418620E+01
B(2, 1) = 0.1397981E+02
B(2,2)=-0.5231625E+02  
B(2,3)=0.4883702E+02  
B(2,4)=-0.1517764E+02  
B(2,5)=0.4677060E+01  
B(3,1)=-0.3108303E+01  
B(3,2)=-0.3360006E+02  
B(3,3)=-0.9452824E+02  
B(3,4)=0.808941E+02  
B(3,5)=0.1685794E+02  
B(4,1)=0.1837682E+01  
B(4,2)=0.1257895E+02  
B(4,3)=0.9714605E+02  
B(4,4)=0.2866901E+03  
B(4,5)=0.199985E+03  
B(5,1)=0.3854616E+02  
B(5,2)=0.1703650E+03  
B(5,3)=0.457635E+03  
B(5,4)=0.7941456E+03  
B(5,5)=0.4680000E+03

c:
T=0.0

C: ********************************INITIAL CONDITION ***************
         DO 47 I=1,100
         READ(* Y(I)
 47 CONTINUE
               DO 43 I=1,M2
               CONV(I)=1.0-Y(I)
 43 CONTINUE

C:
DO 4 M=1,50
     Y(M)=1.0
    Y(I)=0.0
 4 CONTINUE

C: M51=M50+1
  NO 415 I=M51,M100
C:
Y(I)=0.06
 415 CONTINUE
      M101=M100+1
      DO 416 I=M101,N
      Y(I)=1.0
 416 CONTINUE

C:

C: **************************** IMSL VARIABLES ********************
C: ---------- TFIN = FINAL TIME ---------------
C: ---------- DT PRINT = PRINT INTERVAL ----------
C:
      TFIN = 30.0
      DT PRINT =2.00
      NPRINT = INT(TFIN/DT PRINT)
C:
      TOL =0.00001
      H=0.000001
      METH=2
MITER=0
INDEX=1

******************************************************************************
** FOR DIVPAC ******************************************************************************

IER=0
NPARAM=50
CALL SSE(NPARAM,0.0,PARAM,1)
PARAM(1)=H
PARAM(2)=10000
PARAM(12)=METH
PARAM(13)=MITER
PARAM(19)=0

C

C ***** PARAMETERS FOR THE PROBLEM *********

C

CHZ=1.00
THZ=0.059
THZ=0.0538
THZ=0.0686
PBM=1000.0
PBM=1.0E+02
PBM=1.0E+04
PBM=0.25*PBM

ALPHA=8.0
ALPHA=2.88
ALPHA=2.80E+00
ALPHA=ALPHA*ALPHA
SH=0.54
SH=0.0000E-01/1.0
C=0.025
C=SH*1.0
C
ST=0.0
ST=0.1
TW=0.0576
BETA=1.0E-02
BETA=0.017
TBAR=50.0
TBAR=60.0
VMAX=0.02
DA1=5.0E+07
DA1=9.5E+07
DA1=10.5E+07
DA1=5.0E+06
DA2=0.0
DA2=1.1E+03

GAMMA=5.0
GAMMA=76000.0/10000.0
GAMMA=76000.0/10000.0
GAMMA=76000.0/12017.0
C

C NOTE : SI = 25.0 FOR ZERO ORDER AND SI=4.0 FOR OTHER KINETICS

C

SI=4.0

SI=45.0
CK=2.0
SK=CK/SI
P=1.0/PEH
PH=1.0/PEH

C
CONI=1.0
CONI=0.296*1.0
C
CONI=0.760
CONI=CONI*1.0

C
******** END OF PARAMETERS **********************
C
C
C
******** INPUT FOR X VALUE AND AX & BX MATRIX ********
C
X(1)=0.0
X(2)=0.0199
X(3)=0.1017
X(4)=0.2372
X(5)=0.4083
X(6)=0.5917
X(7)=0.7628
X(8)=0.8983
X(9)=0.9801
X(10)=1.0

C
WRITE(7,2001)
2001 FORMAT(5X,'********VALUES OF THE PARAMETERS FOR THIS RUN********',/)
WRITE(7,2002) PEM
2002 FORMAT(5X,'PECLET NO. FOR MASS,PEM =',E14.7)
WRITE(7,2009) PEH
2009 FORMAT(5X,'PECLET NO. FOR HEAT,PEH =',E14.7)
WRITE(7,2003) ALFA
2003 FORMAT(5X,'ALFA =',E14.7)
WRITE(7,2008) ALFAH
2008 FORMAT(5X,'ALFAH =',E14.7)
WRITE(7,2004) TBAR
2004 FORMAT(5X,'TBAR =',E14.7)
WRITE(7,2005) SI
2005 FORMAT(5X,'INLET CONC., SI =',E14.7)
WRITE(7,2006) CK
2006 FORMAT(5X,'CONSTANT K , CK =',E14.7)
WRITE(7,2007) SK
2007 FORMAT(5X,'CK/SI =',E14.7)
WRITE(7,2008) CONI
2008 FORMAT(5X,'CONI =',E14.7)
WRITE(7,2018) CONIT
2018 FORMAT(5X,'CONIT =',E14.7)
WRITE(7,2000) CNH
2000 FORMAT(5X,'NUSSELT NUMBER,CNH =',E14.7)
WRITE(7,2001) SH
2001 FORMAT(5X,'SHERWOOD NUMBER,SH =',E14.7)
WRITE(7,2002) ST
2002 FORMAT(5X,'STANTON NUMBER,ST =',E14.7)
WRITE(7,2003) TW
2003 FORMAT(5X,'DIMLESS WALL TEMP.,TW =',E14.7)
WRITE(7,7004) DA1
/04 FORMAT(5X,'DANKIOILER NO.FOR ACT.,DA1 = ',E14.7)
WRITE(7,7005) DA2
/05 FORMAT(5X,'DANKIOILER NO.FOR DEA.,DA2 = ',E14.7)
WRITE(7,7006) BETA
/06 FORMAT(5X,'BETA = ',E14.7)
WRITE(7,7007) GAMMA
/07 FORMAT(5X,'GAMMA = ',E14.7)
WRITE(7,7010) CHZ
/10 FORMAT(5X,'DIMLESS FEED CONC.,CHZ = ',E14.7)
WRITE(7,7011) TIZ
/11 FORMAT(5X,'DIMLESS FEED TEMP.,TIZ = ',E14.7)
WRITE(7,7010)
/10 FORMAT(5X,'***END OF THE PARAMETERS FOR THIS RUN***',/)
WRITE(6,3001)
/01 FORMAT(1X,' TIME CONC. TEMP CONV')
CONV(M2)=1-Y(M2)
TACT(M2)=Y(6*M2)*FACT-273.0
WRITE(6,3002) T,Y(M2),TACT(M2),CONV(M2)
WRITE(6,3002) T,Y(M2),Y(6*M2),CONV(M2)
WRITE(7,1003) T
WRITE(7,1071) TACT(M2)=Y(6*M2)*FACT-273.0
DO 1112 I=1,M2
1112 TACT(I)=Y(I+5*M2)*FACT-273.0
DO 1113 I=1,M2
1113 TACT(I+M2)=Y(I+6*M2)*FACT-273.0
DO 1114 I=1,M2
1114 TACT(I+2*M2)=Y(I+7*M2)*FACT-273.0
DO 1115 I=1,M2
1115 TACT(I+3*M2)=Y(I+8*M2)*FACT-273.0
DO 1116 I=1,M2
1116 TACT(I+4*M2)=Y(I+9*M2)*FACT-273.0
DO 1015 I=1,M2
WRITE(7,1016)X(I),Y(I),Y(I+M2),Y(I+2*M2),Y(I+3*M2),Y(I+4*M2),
CONV(I)
WRITE(9,1006)X(I),Y(I+5*M2),Y(I+6*M2),Y(I+7*M2),
WRITE(9,1006)X(I),TACT(I),TACT(I+M2),TACT(I+2*M2),TACT(I+3*M2),
TACT(I+4*M2)
1015 CONTINUE
C
C
C

R=(AX(M2,M2)/AX(M2,1)-(AX(1,M2)/AX(1,1)-PEM))
R1=1.0/(R*(AX(1,1)-PEM))
R2=1.0/(R*(AX(M2,1)))
R3=((R2*AX(M2,M2))-1.0)/AX(M2,1)
Ru=(R1*AX(M2,M2))/AX(M2,1)
C
C
C
C
C
RT = (AX(M2, M2)/AX(M2, 1)) - (AX(1, M2)/(AX(1, 1) - PH1))
RT1 = 1.0/(RT*(AX(1, 1) - PH1))
RT2 = 1.0/(RT*(AX(M2, 1)))
RT3 = ((RT2*AX(M2, M2)) - 1.0)/AX(M2, 1)
RT4 = (RT1*AX(M2, M2))/AX(M2, 1)

C:

DO 23 J = 2, N1
DO 22 K = 1, MM
K1 = K + 1
C:

CH(K, J) = PH*BX(J, K1) - AX(J, K1) + (((PH*BX(J, 1) - AX(J, 1)) + (R3*AX(M2, K1) -
& PH*AX(1, K1))) + ((PH*BX(J, M2) - AX(J, M2))*(R1*AX(1, K1) - R3*AX(M2, K1))))

22 CONTINUE
CH(M1, J) = PH*CHZ*RH*(PH*BX(J, 1) - AX(J, 1))
CH(M2, J) = PH*CHZ*R1*(PH*BX(J, M2) - AX(J, M2))

23 CONTINUE
C:

DO 203 J = 2, N1
DO 202 K = 1, MM
K1 = K + 1
C:

TH(K, J) = PH*BX(J, K1) - AX(J, K1) + (((PH*BX(J, 1) - AX(J, 1)) + (R13*AX(M2, K1) -
& PH*AX(1, K1))) + ((PH*BX(J, M2) - AX(J, M2))*(R1*AX(1, K1) -
& R2*AX(M2, K1))))

202 CONTINUE
TH(M1, J) = PH*THZ*RH4*(PH*BX(J, 1) - AX(J, 1))
TH(M2, J) = PH*THZ*R11*(PH*BX(J, M2) - AX(J, M2))

203 CONTINUE
C:

RP = A(N1, N1)*SH
RPT = A(N1, N1)*CNH

C11 = ALFA*(1.0 - (SH/RP))
T11 = ALFAH*(1.0 - (CNH/RPT))
C12 = -(ALFA/RP)*A(N1, 1)
C13 = -(ALFA/RP)*A(N1, 2)
C14 = -(ALFA/RP)*A(N1, 3)
C15 = -(ALFA/RP)*A(N1, 4)
T12 = -(ALFAH/RPT)*A(N1, 1)
T13 = -(ALFAH/RPT)*A(N1, 2)
T14 = -(ALFAH/RPT)*A(N1, 3)
T15 = -(ALFAH/RPT)*A(N1, 4)
C:

DO 12 J = 1, N1
DO 13 I = 1, N1
PC(1, J) = CON1*(B(J, I) - (B(J, N1)*A(N1, I)/RP))
TPC(1, J) = CON1*(B(J, I) - (B(J, N1)*A(N1, I)/RPT))
13 CONTINUE
PC(N1, J) = -CON1*SH*B(J, N1)/RP
TPC(N1, J) = -CON1*CNH*B(J, N1)/RPT
12 CONTINUE
C:
C: elligence FORTRAN A1 KING FAD UNIVERSITY OF PERINEUM AND MINERALS, PAMIRAN

C: *******************************************************************************
C: DO 10 K=1,NPRINT
C: IEND=DFPRINT*FLOAT(K)
C: CALL DIVHAP(INDEX,N,FCH,FCHJ,DAHNNY,T,THH,TOI,TAN,V,Y)
C:
C: *******************************************************************************
C: DO 123 I=1,M2
C: CONV(I)=1.0-Y(I)
C: 123 CONTINUE
C: TACT(M2)=Y(6*M2)*FACT=273.0
C: WRITE(6,3002) Y(M2),TACT(M2),CONV(M2)
C: WRITE(6,3002) Y(M2),Y(6*M2),CONV(M2)
C: 3002 FORMAT(1X,F10.4,2X,F6.4,F6.4,F6.4)
C: WRITE(7,1003) T
C: 1003 FORMAT(10X,'TIME =',F10.4,10X)
C: WRITE(7,1004)
C: 1004 FORMAT(3X,'XVALUE',5X,'BULK',5X,'PART1'),
C: ,5X,'PART2',5X,'PART3',5X,'PART4',5X,'CONV',10X)
C: WRITE(9,1003) T
C: WRITE(9,3004)
C: 1004 FORMAT(3X,'XVALUE',5X,'TBULK',5X,'TPRTH'),
C: ,5X,'TPRTH1',5X,'TPRTH2',5X,'TPRTH3',5X,'TPRTH4',10X)
C: WRITE(9,2071)
C: 2071 FORMAT(24X,'Y=0.296',
C: ,5X,'Y=0.565',5X,'Y=0.784',5X,'Y=0.934',10X)
C: WRITE(7,1071)
C: 1071 FORMAT(24X,'Y=0.296',
C: ,5X,'Y=0.565',5X,'Y=0.784',5X,'Y=0.934',10X)
C: DO 1005 I=1,M2
C: WRITE(7,1016)X(I),Y(I),Y(I+M2),Y(I+2*M2),Y(I+3*M2),Y(I+4*M2),
C: ,CONV(I)
C: 1005 CONTINUE
C: DO 2222 I=1,M2
C: 2222 TACT(I)=Y(I+5*M2)*FACT=273.0
C: DO 2223 I=1,M2
C: 2223 TACT(I+1*M2)=Y(I+6*M2)*FACT=273.0
C: DO 2224 I=1,M2
C: 2224 TACT(I+2*M2)=Y(I+7*M2)*FACT=273.0
C: DO 2225 I=1,M2
C: 2225 TACT(I+3*M2)=Y(I+8*M2)*FACT=273.0
C: DO 2226 I=1,M2
C: 2226 TACT(I+4*M2)=Y(I+9*M2)*FACT=273.0
C: DO 3005 I=1,M2
C: 3005 WRITE(9,1006)X(I),TACT(I),TACT(I+1*M2),TACT(I+2*M2),TACT(I+3*M2),
C: ,TACT(I+4*M2)
C: WRITE(9,1006)X(I),Y(I+5*M2),Y(I+6*M2),Y(I+7*M2),Y(I+8*M2),Y(I+9*M2)
C: 1005 CONTINUE
C: WRITE(10,1003) T
C: WRITE(10,9004)
C: 9004 FORMAT(3X,'XVALUE',5X,'CEPRT1',
C: ,5X,'CEPRT2',5X,'CEPRT3',5X,'CEPRT4',10X)
C: WRITE(10,9071)
SUBROUTINE FCN(N,T,Y,YPRIME)
  IMPLICIT REAL*8(A-I,0-Z)
  REAL*8 TERN
  REAL*8 SUM1(30),YPRIME(N),Y(N),T
  REAL*8 SUMF(30)
  COMMON DATA/CLT,AMPL,CHZ,FEM,ALFA,SH,TBAR,S ,CK,SI,F,CON1,MN,N1
  COMMON DATA/THZ,PFH,ALTAR,CNH,TI,PH,CON11,S,TW,RF,TO,DA1,DA2.
  COMMON AK(30,30),RK(30,30),X(50),VMAX
  COMMON CH(50,50),F(30),A(50,50),R(50,50),FG(50,50)
  COMMON TH(50,50),TPC(50,50)
  INTEGER N

CHZ= 1.0
M1=M1+1
M2=M2+2
M20=M2*2.0
M30=M2*3.0
M40=M2*4.0
M50=M2*5.0
M60=M2*6.0
M70=M2*7.0
M80=M2*8.0
M90=M2*9.0
M100=M2*10.0

**************************************************************************
M110=M2*11.0
M120=M2*12.0
M130=M2*13.0
M140=M2*14.0
**************************************************************************

C
N1 = N1 + 1

R = (AX(M2, M2)/AX(M2, 1) - (AX(1, M2)/(AX(1, 1) - PEM))
R1 = 1.0/(R*(AX(1, 1) - PEM))
R2 = 1.0/(R*(AX(M2, 1)))
R3 = ((R2*AX(M2, M2)) - 1.0)/AX(M2, 1)
R4 = (R1*AX(M2, M2))/AX(M2, 1)

RT = (AX(M2, M2)/AX(M2, 1) - (AX(1, M2)/(AX(1, 1) - PEM)))
RT1 = 1.0/(RT*(AX(1, 1) - PEM))
RT2 = 1.0/(RT*(AX(M2, 1)))
RT3 = ((RT2*AX(M2, M2)) - 1.0)/AX(M2, 1)
RT4 = (RT1*AX(M2, M2))/AX(M2, 1)

DO 23 J = 2, M1
DO 22 K = 1, MM
K1 = K + 1

CH(K, J) = P*BX(J, K1) - AX(J, K1) + (P*BX(J, 1) - AX(J, 1))*R3*AX(M2, K1) - & R4*AX(1, K1) + (P*BX(J, M2) - AX(J, M2))*R1*AX(1, K1) - R2*AX(M2, K1))

22 CONTINUE
CH(M1, J) = PEM*CHZ*R4*(P*BX(J, 1) - AX(J, 1))
CH(M2, J) = PEM*CHZ*R1*(P*BX(J, M2) - AX(J, M2))

23 CONTINUE

DO 203 J = 2, M1
DO 202 K = 1, MM
K1 = K + 1

TH(K, J) = P*BX(J, K1) - AX(J, K1) + (P*BX(J, 1) - AX(J, 1))*R3*AX(M2, K1) - & R4*AX(1, K1) + (P*BX(J, M2) - AX(J, M2))*R1*AX(1, K1) & - R2*AX(M2, K1))

202 CONTINUE
TH(M1, J) = PEM*THZ*RT4*(P*BX(J, 1) - AX(J, 1))
TH(M2, J) = PEM*THZ*RT1*(P*BX(J, M2) - AX(J, M2))

203 CONTINUE
RF = A(N1, N1) + SH
RPT = A(N1, N1) + CNH

C11 = ALFA*(1.0 - (SH/RP))
T11 = ALFAH*(1.0 - (CNH/RPT))
C12 = -ALFAH/RF)*A(N1, 1)
C13 = -ALFAH/RF)*A(N1, 2)
C14 = -ALFAH/RF)*A(N1, 3)
C15 = -ALFAH/RF)*A(N1, 4)
T12 = -ALFAH/RPT)*A(N1, 1)
T13 = -ALFAH/RPT)*A(N1, 2)
T14 = -ALFAH/RPT)*A(N1, 3)
I15=-((ALFAH/RPT)*A(N1,H))

DO 12 J=1,N1
DO 13 I=1,N1
PC(I,J)=CON1*(B(I,J)-(B(J,N1)*A(N1,1)/RPT))
TPC(I,J)=CON11*(B(I,J)-(B(J,N1)*A(N1,1)/RPT))
13 CONTINUE
PC(N1,J)=-CON1*SH*B(J,N1)/RPT
TPC(N1,J)=-CON11*CNH*B(J,N1)/RPT
12 CONTINUE

* ******************************************

10 DO 21 J=2,M1
   SUMA1(J)=0.0
   SUNT1(J)=0.0
21 CONTINUE

DO 25 J=2,M1
   DO 25 I=1,M1,4
   11=I+1
   SUMA1(J)=SUMA1(J)+CH(I,J)*Y(11)
   SUNT1(J)=SUNT1(J)+TH(I,J)*Y(5*M2+11)
25 CONTINUE

DO 700 I=1,14
   I1=I+M2*(1-1)
   I2=M2*I
   YPRIME(I1)=0.0
   YPRIME(I2)=0.0
700 CONTINUE

DO 800 I=2,M1
   YPRIME(1)=0.0
   YPRIME(1+5*M2)=0.0
   YPRIME(I)=SUMA1(I)-CH(M1,1)+CH(M2,1)-
   &C11*Y(I)+C12*Y(1+M2)+C13*Y(1+2*M2)+C14*Y(1+3*M2)+C15*Y(1+4*M2)
   &C
   YPRIME(I+M2)=PC(1,1)*Y(I+M2)+PC(2,1)*Y(1+2*M2)+PC(3,1)*Y(1+3*M2)
   &PC(4,1)*Y(1+4*M2)+PC(5,1)*Y(I)
   &C
   MITCHEL MENTEN
   &(DA1*Y(I+10*M2))*EXP(-1.0/Y(1+6*M2))*Y(I+M2)/
   &(Y(I+M2)+SK)
   &C
   YPRIME(I+2*M2)=PC(1,2)*Y(I+M2)+PC(2,2)*Y(I+2*M2)+PC(3,2)*Y(I+3*M2)
   &PC(4,2)*Y(I+4*M2)-PC(5,2)*Y(I)
   &C
   &(DA1*Y(I+11*M2))*EXP(-1.0/Y(I+7*M2))*Y(I+2*M2)/
   &(Y(I+2*M2)+SK)
   &C
   YPRIME(I+3*M2)=PC(1,3)*Y(I+M2)+PC(2,3)*Y(I+2*M2)+PC(3,3)*Y(I+3*M2)
   &PC(4,3)*Y(I+4*M2)-PC(5,3)*Y(I)
   &C
   &(DA1*Y(I+12*M2))*EXP(-1.0/Y(I+8*M2))*Y(I+3*M2)/
   &(Y(I+3*M2)+SK)
   &C
   YPRIME(I+4*M2)=PC(1,4)*Y(I+M2)+PC(2,4)*Y(I+2*M2)+PC(3,4)*Y(I+3*M2)
   &PC(4,4)*Y(I+4*M2)-PC(5,4)*Y(I)
   &C
   &D
&+ PC(4,4)*Y(1+4*M2)-PC(5,4)*Y(1)-
&*(DA1*Y(1+13*M2))*EXP(-1.0/Y(1+9*M2))*Y(1+4*M2)/
&*(Y(1+4*M2)+SK)

c
YPRIME(1+5*M2)=0.0
YPRIME(1+6*M2)=0.0
YPRIME(1+7*M2)=0.0
YPRIME(1+8*M2)=0.0
YPRIME(1+9*M2)=0.0

YPRIME(1+5*M2)=SUM1(Y(1+1*M1)+SUM2(1)+SUM3(1)
&+T11*Y(1+5*M2)+T12*Y(1+6*M2)+T13*Y(1+7*M2)
&+T14*Y(1+8*M2)+T15*Y(1+9*M2)-ST*(Y(1+5*M2)-TW)

c
YPRIME(1+6*M2)=TPC(1,1)*Y(1+6*M2)+TPC(2,1)*Y(1+7*M2)
&+ TPC(3,1)*Y(1+8*M2)
&+TPC(h,1)*Y(1+9*M2)-TPC(5,1)*Y(1+5*M2)+

c MITCHEL MENTEN
&+T16*Y(1+10*M2)))*EXP(-1.0/Y(1+6*M2))*Y(1+6*M2)/
&*(Y(1+4*M2)+SK)
YPRIME(1+7*M2)=TPC(1,2)*Y(1+6*M2)+TPC(2,2)*Y(1+7*M2)
&+ TPC(3,2)*Y(1+8*M2)
&+TPC(h,2)*Y(1+9*M2)-TPC(5,2)*Y(1+5*M2)+

c MITCHEL MENTEN
&+T17*Y(1+11*M2)))*EXP(-1.0/Y(1+7*M2))*Y(1+7*M2)/
&*(Y(1+4*M2)+SK)
YPRIME(1+8*M2)=TPC(1,3)*Y(1+6*M2)+TPC(2,3)*Y(1+7*M2)
&+ TPC(3,3)*Y(1+8*M2)
&+TPC(h,3)*Y(1+9*M2)-TPC(5,3)*Y(1+5*M2)+

c MITCHEL MENTEN
&+T18*Y(1+12*M2)))*EXP(-1.0/Y(1+8*M2))*Y(1+8*M2)/
&*(Y(1+4*M2)+SK)
YPRIME(1+9*M2)=TPC(1,4)*Y(1+6*M2)+TPC(2,4)*Y(1+7*M2)
&+ TPC(3,4)*Y(1+8*M2)
&+TPC(h,4)*Y(1+9*M2)-TPC(5,4)*Y(1+5*M2)+

c MITCHEL MENTEN
&+T19*Y(1+13*M2)))*EXP(-1.0/Y(1+9*M2))*Y(1+9*M2)/
&*(Y(1+4*M2)+SK)
YPRIME(1+10*M2)=-DA2*Y(1+10*M2)*EXP(-GAMMA/Y(1+6*M2))
YPRIME(1+11*M2)=-DA2*Y(1+11*M2)*EXP(-GAMMA/Y(1+7*M2))
YPRIME(1+12*M2)=-DA2*Y(1+12*M2)*EXP(-GAMMA/Y(1+8*M2))
YPRIME(1+13*M2)=-DA2*Y(1+13*M2)*EXP(-GAMMA/Y(1+9*M2))

c
YPRIME(1+10*M2)=0.0
YPRIME(1+11*M2)=0.0
YPRIME(1+12*M2)=0.0
YPRIME(1+13*M2)=0.0

END

CONTINUE

SUM2=0.0
SUM3=0.0
DO 555 1=2,M1
SUM2=SUM2 + (R3*AX(M2,1) - RH*AX(1,1))*Y(1)
555 SUM3=SUM3 + (R1*AX(1,1) - R2*AX(M2,1))*Y(1)
Y(1)= SUM2 - RH*PEM*CIUZ
Y(M2) = SUM1 + RT1*PEH*CIIZ
SUM1 = 0.0
SUM5 = 0.0
DO 556 I = 2, M1
   SUM4 = SUM4 + (RT3*AX(M2,1) - RT4*AX(1,1))*Y(I+5*M2)
556 SUM5 = SUM5 + (RT1*AX(1,1) - RT2*AX(M2,1))*Y(I+5*M2)
Y(M2*5+1) = SUM4 - RT4*PEH*THZ
Y(M2*5+M2) = SUM5 + RT1*PEH*THZ
C
RETURN
END

SUBROUTINE FCNJ(N, T, Y, PD)
IMPLICIT REAL*8(A-H, O-Z)
INTEGER N
REAL*8 Y(N), PD(N, N), T
RETURN
END
C******************************************************************************
C PROGRAM TO GENERATE X, A AND B MATRICES FOR NONSYMMETRIC PLANE
C GEOMETRY
C DATA REQUIRED K=1,NMAX=20(MAXIMUM NUMBER OF POINTS),ALFA=ALPHA=0.0
C AND CGAM=0.1333333E+01
C******************************************************************************
C
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION X(25),RECA(25),RECB(25),A(25,25),B(25,25),WG(25),WR(25)
*,WL(25),C(25),Q(25)
DIMENSION XS(25),AS(25,25),RS(25,25),XX(25)
READ(5,*),K,NMAX,ALF,BET,CGAM

C100 FORMAT(2I3,3E14.7)
101 FORMAT(1X,E14.7)
DO 555 I=1,25
DO 555 J=1,25
R(I,J)=0.0
555 A(I,J)=0.0
DO 1 N=2,NMAX
WRITE(6,102)
102 FORMAT(1H0)
CALL ABSCI(N,ALF,BET,X,RECA,RECB)
CALL ABGH(K,N,ALF,BET,CGAM,X,A,B,WG,WR,WL,C)
P=1.0
DO 8 I=1,N
8 P=P*X(I)
Q(N)=P
C WRITE(6,101)(X(I),I=1,N)
DO 230 I=1,N
I1=I+1
XX(I1)=X(I)
230 CONTINUE
XX(1)=0.0
N2=N+2
XX(N2)=1.0
DO 231 I=1,N2
231 WRITE(6,191)I,XX(I)
191 FORMAT(10X,'X(',12,E15.7)
C WRITE(6,101)(WG(I),I=1,N)
IF (ALF=1.0E-06) 2,2,4
4 N1=N+1
WRITE(6,101)(WR(I),I=1,N1)
N2=N+2
IF (BET=1.0E-06) 2,2,6
6 IF (K=1) 2,7,2
7 WRITE(6,101)(WL(I),I=1,N2)
2 NK=N+3-K
DO 11 I=1,NK
1010 FORMAT(10X,'AX(',12,E15.7)
1111 FORMAT(10X,'BX(',12,E15.7)
11 WRITE(6,1010)(I,J,A(I,J),J=1,NK)
DO 611 I=1,NK
1011 FORMAT(10X,'BX(',12,E15.7)
611 WRITE(6,1111)(I,J,B(I,J),J=1,NK)
IF (N,N.E.7) GO TO 1
FILE: MATRIX A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHIRAN

DO 812 J1=1,NK
DO 811 J1=1,NK
AS(11,J1)=2.*DSORT(X(11))*A(11,J1)
811 BS(11,J1)=4.0*X(11)*B(11,J1)+2.0*3.0*A(11,J1)
812 WRITE(6,101)(AS(11,J1),J1=1,NK)
DO 813 J2=1,NK
813 WRITE(6,101)(BS(12,J2),J2=1,NK)
1 CONTINUE
Q(1)=(BET+1.)/(ALF+BET+2.)
DO 10 I=1,NMAX
10 C(I)=C(I)*Q(1)**2
NMAX=NMAX+1
DO 12 I=1,NMAX
2 IN=NMAX-I
12 C(IN+1)=C(IN)
C(1)=CGAM
WRITE(6,101)(RECA(I),I=1,NMAX)
WRITE(6,101)(RECB(I),I=1,NMAX)
WRITE(6,101)(C(I),I=1,NMAX)
STOP
END

C******************************************************************************
C
C SUBROUTINE ABCW(K,N,ALF,BET,CGAM,X,A,B,PI1,PI2,PI3,C)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION X(1),A(25,25),B(25,25),C(1),PI1(1),PI2(1),PI3(1),P1(25)
& P2(25),P3(25)
DIMENSION XS(25),AS(25,25),BS(25,25)
N1=N+1
N2=N+2
DO 50 I=1,N
L=N2-1
L1=N1-1
50 X(L)=X(L1)
X(1)=0.0
X(N2)=1.0
DO 1 I=K,N2
PI1(K)=1.
PI2(K)=0.
PI3(K)=0.
X1=X(I)
DO 2 J=K,N2
IF (J-I) 3,4,3
1 PI1(J+1)=PI1(J)
PI2(J+1)=PI2(J)
PI3(J+1)=PI3(J)
GO TO 2
2 CONTINUE
P1(1)=PI1(N2+1)
P2(1)=PI2(N2+1)
P3(1)=PI3(N2+1)

SUBROUTINE ARSC1(N, ALF, BET, ROOT, A, B)
IMPLICIT REAL*8 (A-H, O-Z)
DIMENSION ROOT(1), A(25), B(25)
C=ALF+BET
A(1)=(BET+1.)/(C+2.)
A(2)=1.-(ALF+BET)/(C+H.)/(C+2.)/2.
B(1)=0.
B(2)=(ALF+1.)*(BET+1.)/(C+3.)/(C+2.)*2
DO 1 I=3, N
   A1=I
   A2=2*I
   A(I)=(1.-C*(ALF+BET)/(C+A2)/(C+A2-2.))/2.
   B(I)=(A1-1.)*(A1+ALF-1.)*(A1+BET-1.)*(A1+C-1.)/(A2+C-1.)*2
&   (A2+C-2.)*2/(A2+C-3.)
1 XL=0.
NX=0
5 XR=XL+(1.-XC)/FLOAT(N-NX+1)
   CALL SSN(N, A, B, XL, NL, PNL, QNL)
6 CALL SSN(N, A, B, XR, NR, PNR, QNR)
   IF(NL-NR=1)10, 3, 4
10 XL=XR
   GO TO 5
4 XR=(XR+XL)/2.
   GO TO 6
3 X=XR-(XR-XL)/FLOAT(NX-PNL)*PNR
16 CALL SSN(N, A, B, X, NX, PNX, QNX)
   XN=X-PNX/QNX
   IF(DABS(.1.-X/XN)=1.8E-06)12, 12, 11
12 NX=N-NL+1
   ROOT(NX)=XN
   IF(NX-H)=10, 99, 99
11 IF(XN-XL=1)7, 7, 8
   IF(XN-XR=1)9, 7, 7
9 X=XR
   GO TO 16
7 IF(NL-NX=1)13, 11, 11
13 X=XR-(XR-X)/FLOAT(NR-PNL)*PNR
   GO TO 16
14 X=XL-(XL-X)/FLOAT(NL-PNL)*PNL
   GO TO 16
99 RETURN
END

SUBROUTINE SSN(N, A, B, X, NS, PN, QN)
IMPLICIT REAL*8 (A-H, O-Z)
DIMENSION A(25), B(25), P(50), Q(50)
NS=0
P(1)=A(1)-X
Q(1)=-1.
IF(P(1))3, 3, 2
2 NS=NS+1
3 P(2)=(A(2)-X)*P(1)-B(2)
   IF(P(2)*P(1))5, 5, 4
4 NS=NS+1
5 Q(2)=-(A(2)-X)-P(1)
   IF(N-2)7,7,8
8 DO 1 I=3,N
   P(I)=(A(I)-X)*P(I-1)-B(I)*Q(I-2)
   IF(P(I)*P(I-1))1,1,6
6 NS=NS+1
1 Q(I)=(A(I)-X)*Q(I-1)-P(I-1)-B(I)*Q(I-2)
7 PN=P(N)
   QN=Q(N)
RETURN
END
VITA

Name: Mohammad Hassan Murad Chowdhury

Family Name: Chowdhury

Religion: Islam

Nationality: Bangladeshi

Personal Data: Born in November 08, 1966.

Education: Obtained Bachelor of Science in Chemical Engineering from Bangladesh University of Engineering & Technology (BUET), Dhaka, Bangladesh in 1991.

Publications:


