DELBRIDGE, Henry Thomas, 1945-
OPTIMIZATION OF CHEMICAL REACTORS WITH
FEED DISTRIBUTION.

Rice University, Ph.D., 1970
Engineering, chemical

University Microfilms, A XEROX Company, Ann Arbor, Michigan
RICE UNIVERSITY

OPTIMIZATION OF CHEMICAL REACTORS
WITH FEED DISTRIBUTION

by

HENRY THOMAS DELBRIDGE

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING

Thesis Director's signature:

[Signature]

Houston, Texas

May, 1970
TO JAN
ACKNOWLEDGMENTS

I wish to express my sincere gratitude and appreciation to
the following people and organizations:

My wife, Jan, whose contributions were invaluable.

Professor D. C. Dyson, my thesis advisor, for his interest
and helpful suggestions.

Professor R. Jackson and Professor A. Miele for serving on
my thesis committee.

My colleagues, especially J. E. Bailey, for their advice
and friendship.

Scottie Taylor for typing this manuscript.

Robert Simon for drafting the figures.

The National Science Foundation, Systems Grant No. GU-1153
and Individual Grant No. GK-12522.

Rice University for a Graduate Fellowship.

The National Aeronautics and Space Administration for a NASA
Traineeship.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>1</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>NOMENCLATURE</td>
<td>v</td>
</tr>
<tr>
<td>CHAPTER 1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER 2. INFINITESIMAL FEED BYPASS IN AN ISOTHERMAL TUBULAR REACTOR</td>
<td>12</td>
</tr>
<tr>
<td>2.1. Reaction systems to be analyzed</td>
<td>12</td>
</tr>
<tr>
<td>2.2. The reactor model</td>
<td>13</td>
</tr>
<tr>
<td>2.3. Analysis for the Case A reaction system</td>
<td>16</td>
</tr>
<tr>
<td>2.4. Analysis for the Case B and Case C reaction systems</td>
<td>19</td>
</tr>
<tr>
<td>CHAPTER 3. FEED DISTRIBUTION FOR A REACTION SYSTEM WHICH INCLUDES A FIRST ORDER SIDE REACTION</td>
<td>24</td>
</tr>
<tr>
<td>3.1. Equations for the isothermal reactor</td>
<td>24</td>
</tr>
<tr>
<td>3.2. The optimal feed distribution problem</td>
<td>28</td>
</tr>
<tr>
<td>3.2.a. $m_f$ is a fixed parameter</td>
<td>28</td>
</tr>
<tr>
<td>3.2.b. $m_f$ is a free parameter</td>
<td>34</td>
</tr>
<tr>
<td>3.3. The free endpoint reactor with no feed distribution</td>
<td>35</td>
</tr>
<tr>
<td>3.4. Results and conclusions</td>
<td>36</td>
</tr>
<tr>
<td>CHAPTER 4. FEED DISTRIBUTION FOR A REACTION SYSTEM WHICH INCLUDES A SECOND ORDER SIDE REACTION - $q_{20}$ IS A FIXED PARAMETER</td>
<td>51</td>
</tr>
<tr>
<td>4.1. Formulation of the optimization problem</td>
<td>52</td>
</tr>
<tr>
<td>4.2. Discussion of results</td>
<td>57</td>
</tr>
<tr>
<td>4.3. Is the Hamiltonian maximized with respect to $x_3$</td>
<td>61</td>
</tr>
<tr>
<td>4.4. Consideration of $v = \dot{x}_3$ as the control</td>
<td>62</td>
</tr>
<tr>
<td>4.5. Attainable region study</td>
<td>66</td>
</tr>
</tbody>
</table>
CHAPTER 5. FEED DISTRIBUTION FOR A REACTION SYSTEM WHICH INCLUDES A SECOND ORDER SIDE REACTION - $\phi_{20}$ IS A FREE PARAMETER ........................................... 79

5.1. The objective function ........................................... 79

5.2. The optimal dump reactor ........................................... 79

5.2.a. Calculation of the derivatives of $x_{1f}$ and $x_{2f}$ with respect to $\Theta$ by a method of variational calculus ........................................... 80

5.2.b. Calculation of the derivatives of $x_{1f}$ and $x_{2f}$ with respect to $\Theta$ by a finite difference approximation ........................................... 82

5.2.c. Results ......................................................... 83

5.3. The optimal distributed reactor ................................... 84

5.3.a. Solution by means of a variational method ........ 84

5.3.b. Solution by means of a finite difference method 88

5.3.c. Results ......................................................... 91

5.4. Comparison of the optimal distributed reactor and the optimal dump reactor ........................................... 93

REFERENCES .......................................................... 111

APPENDIX I. DETERMINATION OF THE FIRST VARIATION IN THE OBJECTIVE FUNCTION INDUCED BY VARIATIONS IN THE CONTROL VARIABLE ........................................... 113

APPENDIX II. DETAILED INFORMATION CONCERNING OPTIMAL TRAJECTORIES FOR VARIOUS $m_f$ ........................................... 115

APPENDIX III. DETERMINATION OF $\phi_{0}$ FOR THE ISOTHERMAL REACTOR WITH NO FEED DISTRIBUTION ........................................... 118

APPENDIX IV. THE DEPENDENCE OF THE SOLUTION OF A SYSTEM OF ORDINARY DIFFERENTIAL EQUATIONS ON THE INITIAL CONDITIONS AND THE PARAMETER ........................................... 119

APPENDIX V. THE FIRST AND SECOND DERIVATIVES OF $f_1$ AND $f_2$ ........ 121

APPENDIX VI. PARTIAL DERIVATIVES OF $x_3 = u (x_1, x_2, \Lambda, \Theta)$ ... 124

APPENDIX VII. DERIVATIVES OF $\Lambda = f_3$ ........................................... 126
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.A</td>
<td>Parameter Values for the Different Reaction Systems</td>
<td>13</td>
</tr>
<tr>
<td>2.B</td>
<td>Effects of a Small Feed Bypass to m = m₁</td>
<td>19</td>
</tr>
<tr>
<td>3.A</td>
<td>Kinetic Data</td>
<td>26</td>
</tr>
<tr>
<td>3.B</td>
<td>Results for mᵢ = 4.0, g₁ = 12.0075, g₂ = 12.1469, g₃ = 1.7451</td>
<td>33</td>
</tr>
<tr>
<td>3.C</td>
<td>Properties of the Optimal Trajectory</td>
<td>35</td>
</tr>
<tr>
<td>3.D</td>
<td>Improvement of the Objective Function Realizable by Optimal Control</td>
<td>38</td>
</tr>
<tr>
<td>4.A</td>
<td>Properties of Optimal Trajectories for Various φ</td>
<td>59</td>
</tr>
<tr>
<td>4.B</td>
<td>Departures from the Singular Trajectory with ν = 0</td>
<td>65</td>
</tr>
<tr>
<td>5.A</td>
<td>Occurrence of the Double Root Phenomenon for Different Kinetic Parameters</td>
<td>92</td>
</tr>
<tr>
<td>5.B</td>
<td>Percentage Improvement in the Objective Function for Various Kinetics</td>
<td>95</td>
</tr>
<tr>
<td>5.C</td>
<td>Maximum Improvement for Various φ</td>
<td>97</td>
</tr>
<tr>
<td>5.D</td>
<td>Summary of φ = 0 Results</td>
<td>98</td>
</tr>
</tbody>
</table>
## NOMENCLATURE

### Roman Letters

- **A**: $2 \times 2$ matrix given by equation (5.8).
- **A<sub>i</sub>**: Chemical substance $i$.
- **a<sub>i</sub>**: Molar flowrate of substance $A_i$ at position $m$ for $i = 1, 3, 4, 5$ (Chapter 2).
- **b<sub>1</sub>**: $k_1/q_1$.
- **E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>**: Activation energies.
- **F**: Objective function in terms of dimensionless quantities; $x_1 (m_r) - \Phi x_2 (m_r)$.
- **F<sub>D</sub>**: $F$ for the dump policy (and the best choice of $\Theta$ if $\Theta$ is a free parameter).
- **F<sub>OPT</sub>**: $F$ for the optimal choice of $x_3$ (and the best choice of $\Theta$ if $\Theta$ is a free parameter).
- **F<sub>1</sub>**: Objective function for the optimal control policy (Chapter 3).
- **F<sub>2</sub>**: Objective function for the "time - optimal" dump policy (refer to Section 3.3).
- **F<sub>3</sub>**: Objective function for the dump policy (Chapter 3).
- **ΔF**: $F_{OPT} - F_D$.
- **\(\hat{F}\)**: Objective function in terms of the exit stream molar flowrates.
- **\(\delta \hat{F}\)**: First variation in $\hat{F}$ caused by a variation in $q$.
- **f<sub>1</sub>, f<sub>2</sub>**: Derivative of $x_1$ and $x_2$ with respect to the independent variable ($m$ or $t$), respectively, expressed in terms of $x_1$, $x_2$, $x_3$, $\Theta$.
- **f<sub>3</sub>**: Derivative of $\Lambda$ with respect to the independent variable ($m$ or $t$), expressed in terms of $x_1$, $x_2$, $x_3$, $\Lambda$, $\Theta$.
- **f<sub>1</sub>, f<sub>2</sub>, f<sub>3</sub>**: $f_1$, $f_2$, $f_3$ written in terms of $x_1$, $x_2$, $\Lambda$, $\Theta$; see equations (5.19) through (5.21).
- **G<sub>i</sub>**: $g_1 m_r = (K_i m_r)/q_{10}$ for $i = 1, 2, 3$.
- **g<sub>i</sub>**: $K_i/q_{10}$ for $i = 1, 2, 3$.
- **H**: Hamiltonian function when $x_3$ is regarded as the control variable.
- **\(\overline{H}\)**: Hamiltonian function when $\dot{x}_3$ is regarded as the control variable.
\( h_1, h_2, h_3 \) Derivative of \( f_1^*, f_2^*, f_3^* \) with respect to the parameter \( \Theta \); see equations (5.9) and (5.25).

\( I \) Percentage improvement in the objective function.

\( K_1, K_2, K_3 \) Kinetic parameters; see equations (3.1) and (4.1).

\( K_{10}, K_{20}, K_{30} \) Arrhenius frequency factors.

\( k_1, k_2 \) Kinetic constants; see equations (1.1), (1.5), (1.6), (2.1).

\( k_3 \) \( k_1 + n_1 k_2 \) (Chapter 2).

\( k_{10}, k_{20}, k_{30} \) Arrhenius frequency factors.

\( l_1, l_2, l_3 \) Derivative of \( x_1, x_2, \Lambda \) with respect to the parameter \( \Theta \); see equations (5.7) and (5.22).

\( m \) Mass of catalyst in the part of the reactor to the left of a cross-sectional plane; see Figs. 2.1 and 3.1.

\( m_f \) Total mass of catalyst in the reactor.

\( m_{fe} \) Optimal \( m_f \) for the dump reactor (Chapter 3).

\( m_1 \) Point of injection of the infinitesimal feed bypass (Chapter 2); position in the reactor where \( x_3 \) is exactly 1 and \( \gamma H/\lambda x_3 = 0 \) (Chapter 3, 4, 5).

\( \bar{m} \) See equation (2.46).

\( N \) Number of stages in an adiabatic cascade reactor.

\( n_1, n_2 \) Stoichiometric coefficients in reaction 2 of Chapter 2.

\( n_3 \) Order of reaction 2 in Chapter 2.

\( Q_1 \) Total flowrate of the reactant A_1 fed to the reactor (Chapter 2).

\( q \) Portion of \( Q_1 \) that enters the reactor in the section \( [0, m] \) (Chapter 2); total molar flowrate of the reaction mixture at position \( m \) (Chapter 3, 4, 5).

\( \delta q \) First variation in \( q \) (Chapter 2).

\( q_i \) Molar flowrate of substance A_i at position \( m \) for \( i = 1, 2, 3, 4, 5 \) (Chapter 3, 4, 5).

\( q_{10}, q_{20} \) Molar feed flowrates of A_1 and A_2, respectively.

\( R \) Universal Gas Constant, 1.987 calories per degree mole.
\( r_1 \) Rate of formation of A\textsubscript{3} per unit mass of catalyst.

\( r_2 \) Rate of formation of A\textsubscript{4} per unit mass of catalyst (Chapter 2); rate of formation of A\textsubscript{5} per unit mass of catalyst (Chapter 3, 4, 5).

\( T \) Temperature in degrees Kelvin.

\( t \) Dimensionless position, \( \frac{m}{m_f} \).

\( t_D \) Position at which the entire feed stream of A\textsubscript{1} is injected for the delayed dump policy; see equation (4.28).

\( t_1 \) \( \frac{m_1}{m_f} \) (Chapter 4, 5).

\( u \) Rate of addition of reactant A\textsubscript{1} at position \( m \) (Chapter 2); value of \( x_3 \) for which \( \lambda_H/\lambda x_3 = 0 \) (Chapter 4, 5).

\( V \) Maximum value of \( v \).

\( v \) \( x_3 \), a possible control variable.

\( W \) \( 3 \times 3 \) matrix given by equation (5.24).

\( w_1, w_2 \) See equation (2.43).

\( x \) Amount of Q\textsubscript{1} that has been converted in the section \( [0, m] \) (Chapter 2).

\( x_1, x_2 \) Fraction of q\textsubscript{10} that has been converted by reactions 1 and 2, respectively, in the section \( [0, m] \) (Chapter 1, 3, 4, 5).

\( x_3 \) Fraction of q\textsubscript{10} that has entered the reactor in the section \( [0, m] \).

\( x_{1f} \) \( x_i (m_f) \) for \( i = 1, 2, 3 \).

\( x_3^0 \) Reference control policy.

\( y_1, y_2, y_3 \) \( x_1, x_2, \Lambda \).

**Greek Letters**

\( \gamma \) Mole fraction of A\textsubscript{1} in the reaction mixture (Chapter 2).

\( \gamma_i \) Mole fraction of substance A\textsubscript{i} in the reaction mixture (Chapter 3, 4, 5).

\( \varepsilon \) Very small portion of Q\textsubscript{1} (Chapter 2).

\( \Theta \) Feed ratio, \( q_{20}/q_{10} \).
\( \Theta_D \) Optimal \( \Theta \) for the dump reactor (Chapter 5).

\( \Theta_{OPT} \) Optimal \( \Theta \) for the distributed reactor (Chapter 5).

\( \Theta_o \) Reference value of \( \Theta \).

\( \Delta \Theta \) \( \Theta \) increment used for finite difference expressions (Chapter 5).

\( \Lambda \) \( \frac{\lambda_2}{\lambda_1} \).

\( \lambda_1, \lambda_2, \lambda_3 \) Adjoint variables corresponding to the three state variables.

\( \xi_1, \xi_2, \xi_3 \) \( x_1, x_2, \Lambda; y_1, y_2, y_3 \).

\( \varphi_+ \) \( x_3 \).

\( \varphi \) Penalty for formation of the waste product relative to the profit realizable from production of the main product.

\( \varphi_D \) See equation (4.27).

\( \varphi_E \) See equation (4.30).

\( \varphi_2 \) See equation (5.2).

\( \varphi_o \) Value of \( \varphi \) corresponding to the "time - optimal" dump reactor for which \( m_f \rightarrow 0^+ \).

\( \varphi^{(1)} \) \( -\Lambda(m_f) \).

\( \varphi^{(2)} \) \( 1_1 (m_f)/l_2 (m_f) \).

\( \varphi^{(3)} \) See equation (5.33).
Chapter 1. INTRODUCTION

As early as 1939 Leitenberger [1] considered the problem of determining the optimum temperature profile in a plug-flow tubular reactor. Several investigators [2 - 5] have explored the case of a single reversible exothermic reaction in such a reactor and have found that the optimal control is a profile of decreasing temperature. Bilous and Amundson [6] studied a system of consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(1.1)

where B is the desired product and the kinetic constants $k_i$ are of the Arrhenius form

$$k_i = k_{10} \exp(-E_i/RT).$$

(1.2)

A declining temperature profile is required for cases in which $E_2 > E_1$ [7].

A declining temperature profile can be achieved by either direct or indirect temperature control. Indirect temperature control, e.g., the use of cooling coils, is conceptually sound, but indirectly cooled reactors are often costly to build and operate. A simple method of direct temperature control consists of the delayed addition of cold reactant feed at various points along the reactor length.

Dyson et al. [8] and Dyson and Horn [9] have considered this quenching or cold shot technique in the N-stage adiabatic cascade reactor shown in Figure 1.1. They have treated the problem of determining the minimum mass of catalyst required to achieve a specified degree of conversion for a single reversible exothermic reaction with
general kinetics; the controls are the inlet temperature, the catalyst distribution, and the cold shot distribution. Of course, the $N$-stage cascade reactor with main feed preheating and interstage cooling is equivalent to a single tubular reactor with cold feed injections at $N-1$ points along its length.

Dyson and Horn [10] also have treated a tubular reactor for a single reversible exothermic reaction where the controls are the continuous distribution of a subsidiary cold feed stream along the reactor (see Fig. 1.2) and the inlet temperature of the reactor. The reactor is equipped with a heat exchanger which preheats the portion of the main feed stream that is not distributed. Obviously this reactor and preheater assembly is equivalent to the $N$-stage adiabatic cascade reactor (Fig. 1.1) for the case where $N$ is infinite. In order to maximize the exit conversation for a distributed feed reactor of given reactor volume (or amount of catalyst) and given exit flowrate, in general, the cold feed must be distributed along the first portion of the reactor according to a singular control policy. In the second portion of the reactor, no more cold feed is available; thus, the rate of addition is zero.

The previous problem has been extended to the case where the temperature is constrained from above [11]. In general, the cold feed is added to the first part of the reactor such that the temperature is the maximum allowable temperature. In the second portion of the reactor, the cold feed is added in such a way that the reaction rate is maximized with respect to variations in the mass flowrate at each point. In the last section, no cold feed is added at all.

Graves [12] also has treated the optimum distributed feed
reactor for the reaction system

\[ A_1 + A_2 \leftrightarrow A_3 + A_4 \quad \text{Reaction 1} \]

\[ A_1 \rightarrow A_5 \quad \text{Reaction 2} \]

where \( A_1 \) is the distributed reactant, \( A_3 \) is the desired product, and \( A_5 \) is a waste product. All of the feed stream of reactant \( A_2 \) is preheated before entering the reactor, but none of the feed stream of reactant \( A_1 \) is. It is desired to maximize the objective function

\[ F = x_1 - \phi x_2 \quad (1.4) \]

at the outlet of the adiabatic reactor where \( x_1 \) is the fractional conversion of \( A_1 \) by means of reaction 1 and \( \phi \) is the cost of producing the waste product \( (A_5) \) relative to the profit realizable from producing \( A_3 \). The direct control variable is the rate of addition of cold \( A_1 \) and the indirect control variable is the preheater duty. The optimal trajectory consists of a singular trajectory followed by a non-singular trajectory for which the rate of addition is zero.

The injection of cold feed into a warmer reaction mixture produces two different effects. First, the temperature of the reaction mixture is lowered. Secondly, the composition of the reaction mixture is altered. The compositional effect of feed distribution can be studied by considering an isothermal reactor with feed distribution.

Several authors [13, 14] have investigated the performance of a plug-flow tubular reactor in which no axial dispersion occurs and the reactions taking place are

\[ A_1 + A_2 \xrightarrow{k_1} A_3 \]

\[ 2A_1 \xrightarrow{k_2} A_5 \quad (1.5) \]
where $A_3$ is the desired product and $A_5$ is the waste product. The feed stream of reactant $A_2$ enters the reactor in the normal manner, but the feed stream of $A_1$ can be distributed along the length of the reactor (see Fig. 1.3).

Messikomer [13] has treated the situation where the feed stream of $A_1$ is injected at five equally spaced points along the length of the reactor; the first injection point is the beginning of the reactor while the fifth injection point is 80% down the reactor length. He has found that in order to maximize the yield of $A_3$ for a given mass of catalyst it is necessary to distribute the reactant $A_1$ in unequal parts. The yield for the reactor with the optimum feed distribution is greater than the yield for the reactor with no feed distribution.

The idea of a continuous feed distribution policy has been examined by van de Vusse and Voetter [14] for the reaction system (1.5). For the maximum yield problem the optimum feed distribution function has been determined by the method of parametric expansion [15]. The optimum reactor has been compared with three other reactor arrangements: the traditional tube with no feed distribution, the distributed feed reactor in which the concentration of $A_1$ is constant for the entire reactor, and the distributed feed reactor in which the ratio of the concentration of $A_1$ to the concentration of $A_2$ is constant. The authors have concluded that the reactor which is optimal in the sense of maximum yield is not necessarily optimal in the sense of maximum product selectivity.

Especially for complex reaction systems, it would be desirable to have a test to determine if the conventional feed arrangement (i.e.,
no distribution of reactants) is non-optimal. Several authors \[16, 17\] have developed such a criterion, which involves the evaluation of the adjoint variables of optimization theory for the reactor without feed distribution.

Horn and Tsai \[16\] have developed a very general approach for determining the effects of mixing (bypass, recycle, general feed bypass, channeling, local mixing) on tubular reactor performance. Their approach can be used to see if, for a particular reaction system, it is profitable to distribute one or more reactants along the length of an isothermal reactor. The adjoint variables corresponding to reactant conversions in the isothermal reactor without feed distribution can be evaluated and then can be used to determine whether or not an infinitesimal feed bypass of a reactant causes an infinitesimal increase in the objective function. If the effect of a small feed bypass of any reactant is beneficial, then the reactor without feed distribution can be improved by distribution of at least one reactant.

A second criterion for distinguishing cases in which the delayed addition of reactants is advantageous has been derived by Jackson and Senior \[17\]. Adjoint variables corresponding to reactant concentrations, product concentrations, and reactant flowrates can be calculated for the isothermal tubular reactor with no feed distribution. In order for the conventional feed policy to be optimal it is necessary that each adjoint variable corresponding to a reactant concentration takes its largest value at the beginning of the reactor. If this necessary condition is not satisfied by one or more adjoints corresponding to a reactant concentration, then feed distribution is called for.
Jackson and Senior [17] have examined a conventional feed reactor in which reactions

\[
\begin{align*}
A_1 + A_2 & \xrightarrow{k_1} A_3 \\
2A_1 + A_2 & \xrightarrow{k_2} A_5
\end{align*}
\]  

(1.6)

are occurring. The objective is to maximize the exit concentration of product \( A_3 \). The adjoint corresponding to the concentration of reactant \( A_2 \) takes its maximum value at the beginning of the reactor, but the adjoint corresponding to the concentration of \( A_1 \) does not. Therefore, the necessary condition for optimality of the "dump" policy is not satisfied. Distribution of the feed stream of \( A_1 \) should improve the yield of \( A_3 \).

Senior [18] has studied the problem of determining the optimum distribution of \( A_1 \) for the reaction system (1.6). He has assumed the addition of reactant \( A_1 \) has no direct influence on the concentrations of the other substances in the reaction mixture. The absence of a dilution effect is a characteristic of reactions occurring in a dilute solution of an inert solvent. The rate of addition of \( A_1 \) is the control variable, and this rate can be constrained in two different ways. The first possible constraint is that the rate of addition is bounded from above. The second possible constraint is that the total amount of reactant \( A_1 \) to be added to the reactor is bounded. Senior has found that the optimum distribution policy subject to both constraints does not contain a section where the maximum rate of addition is required (if the upper bound on the rate is large); hence, the constraint on the rate of addition can be ignored. Also, every optimal trajectory includes a singular segment. For one particular set
of reasonable kinetic and physical parameters the optimal value of the objective function (the exit concentration of $A_3$) is 131% greater than the value for the policy of no feed distribution.

In all the previous work concerning continuous feed distribution the control variable has been the rate of addition of the distributed reactant. In this work a new control variable will be used. The new control variable is defined as the fraction of the feed flowrate of the distributed reactant entering the tubular reactor between the beginning and the current position down the reactor. Another feature of this work is consideration of the dilution effect that Jackson and Senior neglected. Also, an objective function that includes a penalty for waste product formation is used throughout this work.

Chapter 2 examines the effect of infinitesimal feed bypass on the performance of an isothermal tubular reactor for three different reaction systems. The method suggested by Horn and Tsai [16] is used in this analysis.

Chapter 3 consists of solving the optimum distribution (of $A_1$) problem for an isothermal tubular reactor in which reaction system (1.3) takes place. Both the free endpoint problem and the fixed endpoint problem are discussed.

In Chapter 4 the optimum distribution is determined for a reactor with a reaction system consisting of a reversible main reaction that is first order with respect to the distributed reactant and a irreversible waste reaction that is second order. The attainable region of end states is constructed from optimal end states corresponding to different magnitudes of the penalty cost for forming waste product.

Chapter 5 treats the optimum distribution problem of Chapter 4
with the feed flowrate of the undistributed reactant being considered as a free parameter. This problem is approached using a method of variational calculus and then an approximate method.
FIGURE 1.1  N-STAGE ADIABATIC CASCADE REACTOR WITH A MAIN FEED PREHEATER AND COLD FEED BYPASS FOR INTERSTAGE COOLING
FIGURE 1.2  TUBULAR REACTOR WITH MAIN FEED PREHEATER AND DISTRIBUTED SUBSIDIARY FEED
FIGURE 1.3 ISO THERMAL REACTOR WITH FEED DISTRIBUTION
Chapter 2. INFINITESIMAL FEED BYPASS IN AN
ISOTHERMAL TUBULAR REACTOR

In the operation of most tubular reactors the feed stream enters the reactor at its very beginning. If the reaction system involves a main reaction and a side reaction, it is quite common that product selectivity is poor for the normal feed arrangement. For these systems it seems possible that the reactor's performance may be improved by injecting some of the feed stream at various points along the length of the reactor.

2.1 Reaction systems to be analyzed

In this chapter three different reaction systems will be studied to determine whether or not the performance of an isothermal tubular reactor can be improved by the delayed injection of an infinitesimal portion of the feed stream of reactant $A_1$. Each reaction consists of two independent irreversible reactions

\[ \begin{align*}
A_1 & \xrightarrow{k_1} A_3 \quad \text{Reaction 1} \\
{n_1} A_1 & \xrightarrow{k_2} A_4 + n_2 A_5 \quad \text{Reaction 2}
\end{align*} \]

(2.1)

where $k_1$ and $k_2$ are kinetic constants. The kinetics of the reaction system are such that the rate of formation of $A_3$ per unit mass of catalyst is given by

\[ r_1 = k_1 \gamma \]

(2.2)

and the rate of formation of $A_5$ per unit mass of catalyst is

\[ r_2 = k_2 \gamma^{n_3} \]

(2.3)
where $\gamma$ is the mole fraction of substance $A_1$ in the reaction mixture. Three combinations of the $n_1$, $n_2$, and $n_3$ values will be investigated and they are listed in Table 2.A. Note that $n_1$ and $n_3$ are not equal for Case B.

### Table 2.A
Parameter Values for the Different Reaction Systems

<table>
<thead>
<tr>
<th>Case</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>$n_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

2.2 The reactor model

The reactor under consideration is an isothermal plug-flow reactor with no axial dispersion. Let $m$ represent the mass of catalyst in the part of the reactor to the left of the cross-sectional plane labelled $m$ in Figure 2.1. The total mass of catalyst in the reactor is $m_f$. Thus, $m$ is a measure of position along the length of the idealized tubular reactor. In the equivalent well-stirred batch reactor $m$ represents batch time.

$Q_1$ is the total flowrate of the reactant $A_1$ fed to the reactor. An infinitesimal flowrate of the reactant, defined as $\epsilon$, bypasses the beginning of the reactor and enters at $m = m_1$. The flowrate of the reactant entering at $m = 0$ is $Q_1 - \epsilon$.

The flowrate of substance $A_i$ at position $m$ is defined as $a_1(m)$ for $i = 1, 3, 4, \text{ and } 5$. Let $q(m)$ represent the portion of $Q_1$ that enters the reactor in the section $[0, m]$. The boundary conditions for these flowrates are
\[ a_1(o) = q(o) = q_1 - \varepsilon \]  \hspace{1cm} (2.4)

\[ a_i(o) = 0 \text{ for } i = 3, 4, 5. \]  \hspace{1cm} (2.5)

Knowledge of all these flowrates is sufficient to describe the state of the reactor.

The number of dependent variables in this formulation can be greatly reduced by use of a variable corresponding to the amount of \( q_1 \) that has been converted in the section \([0, m]\). This conversion variable is defined as

\[ x(m) = a_3(m) + n_1 a_4(m). \]  \hspace{1cm} (2.6)

The state of the reactor is determined by the three variables \( a_3, x, \) and \( q \). Therefore, the state equations and their boundary conditions are

\[ \dot{a}_3 = r_1 \hspace{1cm}; \hspace{1cm} a_3(o) = 0 \]  \hspace{1cm} (2.7 a, b)

\[ \dot{x} = r_1 + n_1 r_2 \hspace{1cm}; \hspace{1cm} x(o) = 0 \]  \hspace{1cm} (2.8 a, b)

\[ \dot{q} = u \hspace{1cm}; \hspace{1cm} q(o) = q_1 - \varepsilon \]  \hspace{1cm} (2.9 a, b)

where \( \cdot \) denotes the derivative with respect to \( m \).

The objective function to be maximized is

\[ \hat{F} = \hat{F}(m_r) = a_3(m_r) - \varphi a_4(m_r) \]  \hspace{1cm} (2.10)

where \( \varphi \) is the economic penalty for formation of the waste product, \( A_4 \). It is assumed that \( \varphi \geq 0 \). The objective function written in terms of \( a_3 \) and \( x \) is

\[ \hat{F} = \hat{F}(m_r) = \left[ \frac{n_1 + \varphi}{n_1} \right] a_3(m_r) - \frac{\varphi}{n_1} x(m_r). \]  \hspace{1cm} (2.11)
There are three adjoint variables (or Lagrangian multipliers), \( \lambda_1, \lambda_2, \) and \( \lambda_3 \), corresponding to the three state variables, \( a_3, x, \) and \( q \). The adjoint equations are

\[
\begin{align*}
\dot{\lambda}_1 &= -\lambda_1 \frac{\partial r_1}{\partial a_3} - \lambda_2 \left[ \frac{\partial r_1}{\partial a_3} + n_1 \frac{\partial r_2}{\partial a_3} \right] \\
\dot{\lambda}_2 &= -\lambda_1 \frac{\partial r_1}{\partial x} - \lambda_2 \left[ \frac{\partial r_1}{\partial x} + n_1 \frac{\partial r_2}{\partial x} \right] \\
\dot{\lambda}_3 &= -\lambda_1 \frac{\partial r_1}{\partial q} - \lambda_2 \left[ \frac{\partial r_1}{\partial q} + n_1 \frac{\partial r_2}{\partial q} \right]
\end{align*}
\]

(2.12)

(2.13)

(2.14)

and from the definition of the objective function their boundary conditions are

\[
\lambda_1(m_f) = \frac{n_2 + \varphi}{n_1}, \quad \lambda_2(m_f) = -\frac{\varphi}{n_1},
\]

\[
\lambda_3(m_f) = 0.
\]

(2.15 a, b, c)

Since there is no mole number change in reaction 2 (i.e., \( n_1 = 1 + n_2 \)), the mole fraction of \( A_1 \) can be expressed as

\[
\chi(m) = \frac{q(m) - x(m)}{q(m)}.
\]

(2.16)

Recall that \( r_1 \) and \( r_2 \) are functions of \( \chi \) only. Therefore, from (2.12), it follows that \( \dot{\lambda}_1 = 0 \). The value of \( \lambda_1 \) is known at \( m_f \); hence,

\[
\lambda_1(m) = \frac{n_1 + \varphi}{n_1} \quad \text{for all } m.
\]

(2.17)

The policy of no feed bypass \( (q(m) = Q_1 \text{ for all } m) \) yields a certain value of the objective function \( \dot{\hat{f}} \). Consider a perturbation of the no-bypass policy in the form of an infinitesimal feed bypass to
position \( m_1 > 0 \); i.e.,

\[
\delta q (m) = \begin{cases} 
- \varepsilon & \text{for } 0 \leq m < m_1 \\
0 & \text{for } m_1 \leq m \leq m_f 
\end{cases} \tag{2.18}
\]

where \( \varepsilon \) is arbitrarily small. In Appendix I it is shown that the first variation in \( \hat{r} \) for this type of perturbation is given by

\[
\delta \hat{r} = \int_0^{m_f} \left\{ \lambda_1 \frac{\partial r_1}{\partial q} + \lambda_2 \left[ \frac{\partial r_1}{\partial q} + n_1 \frac{\partial r_2}{\partial q} \right] \right\} \delta q \, dm.
\]

\[
\hat{r} = 0 \tag{2.19}
\]

Equation (2.19) can be rewritten using equations (2.14) and (2.18) to give

\[
\delta \hat{r} = + \varepsilon \left[ \lambda_3 (m_1) - \lambda_3 (0) \right] \delta q = 0 \tag{2.20}
\]

We see that improvement of the objective function by a small feed bypass to position \( m_1 \) is possible if and only if there exists a value of \( m_1 > 0 \) such that

\[
\left[ \lambda_3 (m_1) - \lambda_3 (0) \right] \delta q = 0 > 0 \tag{2.21}
\]

Now the three reaction systems (see equations (2.1) through (2.3) and Table 2.A) will be analyzed to see if inequality (2.21) can be satisfied.

2.3 Analysis for the Case A reaction system

For Case A \( (n_1 = n_3 = 1, n_2 = 0) \), the reaction system consists of the following reactions

\[
A_1 \xrightarrow{k_1} A_3 \quad \text{Reaction 1} \tag{2.22}
\]

\[
A_1 \xrightarrow{k_2} A_4 \quad \text{Reaction 2}
\]
for which
\[ r_i = k_i \gamma \quad \text{for } i = 1, 2 \quad . \quad (2.23) \]

In order to evaluate \( \lambda_3 (m) \) for the policy of no feed bypass (\( \epsilon = 0 \)) it is necessary to determine the variables \( x(m) \), \( \lambda_1 (m) \), and \( \lambda_2 (m) \) first. Equations (2.8 a), (2.23), and (2.16) are combined to give
\[ \dot{x} = \left[ k_1 + k_2 \right] \left[ \frac{Q_1 - x}{Q_1} \right] \quad (2.24) \]
which, together with boundary condition (2.8 b), can be integrated with the result that
\[ x(m) = Q_1 \left[ 1 - \exp \left( -\frac{k_3 m}{Q_1} \right) \right] \quad (2.25) \]
where \( k_3 \equiv k_1 + k_2 \).

From (2.23) and (2.16) we see that
\[ \frac{\partial r_i}{\partial x} \bigg|_{\epsilon = 0} = -\frac{k_1}{Q_1} \quad \text{for } i = 1, 2 \quad . \quad (2.27) \]
Equation (2.17) reduces to \( \lambda_1 = 1 + \varphi \) for this case \( (n_1 = 1) \).

Thus, equation (2.13) becomes
\[ \dot{\lambda}_2 = \frac{k_1}{Q_1} \left[ 1 + \varphi \right] + \frac{k_3}{Q_1} \lambda_2 \quad (2.28) \]
and this equation can be integrated using boundary condition (2.15 b) to give
\[ \lambda_2 (m) = \begin{cases} \frac{k_1 - k_2 \varphi}{k_3} \exp \left[ \frac{k_3}{Q_1} (m - m_f) \right] - \frac{k_1}{k_3} \left[ 1 + \varphi \right] \end{cases} \quad . \quad (2.29) \]
From (2.23) and (2.16) it follows that

$$\left. \frac{\partial r_i}{\partial q} \right|_{\epsilon = 0, \frac{q^2}{q^2_1}} = \frac{k_i x}{\epsilon = 0, \frac{q^2}{q^2_1}} = \frac{k_i x}{q^2} \quad \text{for } i = 1, 2. \quad (2.30)$$

This result is combined with equations (2.14), (2.17), and (2.29) to give

$$\dot{\lambda}_3 = -\frac{k_1 x}{q^2_1} \left[ 1 + \phi \right] - \frac{k_3 x}{q^2_1} \left\{ \left[ \frac{k_1 - k_2 \phi}{k_3} \right] \exp \left[ \frac{k_3}{q_1} (m - m_f) \right] - \frac{k_1}{k_3} \left[ 1 + \phi \right] \right\},$$

which simplifies to

$$\dot{\lambda}_3 = \frac{x}{q^2_1} \left[ \frac{k_2 \phi - k_1}{q^2} \right] \exp \left[ \frac{k_3}{q_1} (m - m_f) \right]. \quad (2.31)$$

Since the exponential term in equation (2.31) is positive for all values of $m$, the quantity $k_2 \phi - k_1$ determines the sign of $\dot{\lambda}_3$ for all $m$ and consequently the sign of $\delta \hat{F}$ (the improvement in the objective function for a small feed bypass to position $m_1$) for any $m_1 > 0$. The relationships among $\delta \hat{F}$, $\hat{F}$ for $\epsilon = 0$, and the quantity $k_2 \phi - k_1$ are summarized in Table 2.3.
Table 2.B

Effects of a Small Feed Bypass to $m = m_1$

<table>
<thead>
<tr>
<th>$k_2 \gamma - k_1$</th>
<th>$\delta \hat{F}$</th>
<th>$\hat{F}$ for $\epsilon = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive</td>
<td>Positive</td>
<td>Negative</td>
</tr>
<tr>
<td>Zero</td>
<td>Zero</td>
<td>Zero</td>
</tr>
<tr>
<td>Negative</td>
<td>Negative</td>
<td>Positive</td>
</tr>
</tbody>
</table>

We desire a situation where both $\delta \hat{F}$ and $\hat{F}$ for $\epsilon = 0$ are positive. This situation does not occur for this reaction system ($n_1 = n_3 = 1$, $n_2 = 0$); hence, a small feed bypass is not beneficial and we infer that any sort of bypass policy (e.g., continuous feed distribution) is not beneficial.

2.4 Analysis of the Case B and Case C reaction systems

The reaction systems to be studied are

$$A_1 \xrightarrow{k_1} A_3$$
$$n_1 A_1 \xrightarrow{k_1} A_4 + n_2 A_5$$

for which

$$r_1 = k_1 \gamma ; \quad r_2 = k_2 \gamma^2 . \quad \text{(2.32)}$$

For Case B, $n_1 = 1$ and $n_2 = 0$ while, for Case C, $n_1 = 2$ and $n_2 = 1$.

Equations (2.8 a) and (2.32) can be combined to yield

$$\dot{x} = k_1 \gamma + n_1 k_2 \gamma^2 .$$

Since $\gamma = \left[ Q_1 - x \right] / Q_1$ for $\epsilon = 0$,

$$\dot{\gamma} = - \frac{k_1}{Q_1} \gamma - \frac{n_1 k_2}{Q_1} \gamma^2 . \quad \text{(2.33)}$$
Using the boundary condition $\Upsilon(0) = 1$, we find that

$$\Upsilon(m) = \frac{k_1}{k_3 e^{+b_1 m} - n_1 k_2}$$

(2.34)

and

$$x(m) = \frac{k_3 q_1 \left[ e^{+b_1 m} - 1 \right]}{k_3 e^{+b_1 m} - n_1 k_2}$$

(2.35)

where $k_3 = k_1 + n_1 k_2$ and $b_1 = k_1 / q_1$

(2.36)

From (2.32) and (2.16), we see that

$$\left. \frac{\lambda r_1}{k_1} \right|_{\xi = 0} = -\frac{k_1}{q_1}; \quad \left. \frac{\beta r_2}{k_1} \right|_{\xi = 0} = -\frac{2k_2}{q_1} \Upsilon$$

(2.37)

Thus, equation (2.13) becomes

$$\dot{\lambda}_2 = \frac{k_1}{q_1} \left[ \frac{n_1 + \phi}{n_1} \right] + \left[ \frac{k_1 + 2n_1 k_2 \Upsilon}{q_1} \right] \lambda_2$$

(2.38)

Using the expression for $\Upsilon(m)$ given by equation (2.34), we find that

$$\frac{k_1 + 2n_1 k_2 \Upsilon}{q_1} = b_1 \left[ \frac{k_3 e^{+b_1 m} + n_1 k_2}{k_3 e^{+b_1 m} - n_1 k_2} \right]$$

(2.39)

Substitution of equation (2.39) into equation (2.38) yields a first order differential equation with a variable coefficient. The value of $\lambda_2(m_1)$ is given by equation (2.15b); hence, the differential equation can be integrated by means of the integrating factor method [19] to give
\[ \lambda_2 (m) = - \frac{\varphi}{n_1} \left[ \frac{e^{+b_1 m}}{e^{+b_1 m_l}} \right] \left[ \frac{k_3 e^{+b_1 m_l} - n_1 k_2}{k_3 e^{+b_1 m_l} - n_1 k_2} \right]^2 \]  
\[ - \left( \frac{n_1 + \varphi}{n_1} \right) \left[ \frac{e^{+b_1 m_l}}{e^{+b_1 m_l}} \right] \left[ \frac{k_3 e^{+b_1 m_l} - e^{+b_1 m}}{k_3 e^{+b_1 m_l} - e^{+b_1 m}} \right] \left[ \frac{k_3 e^{+b_1 m_l} - n_1 k_2}{k_3 e^{+b_1 m_l} - n_1 k_2} \right]. \]  

From (2.32) and (2.16), it follows that
\[ \frac{\delta r_1}{\delta q} \bigg|_{\xi = 0} = \frac{k_1 x}{q_1^2}; \quad \frac{\delta r_2}{\delta q} \bigg|_{\xi = 0} = \frac{2k_2 \gamma x}{q_1^2}. \]  

Combination of equations (2.14), (2.17), (2.40), and (2.41) lead to the following equation
\[ \dot{\lambda}_3 = \left[ \frac{n_1 + \varphi}{n_1} \right] \left[ \frac{k_1 x}{q_1^2} \right] \left\{ \left[ \frac{w_1 (m_r - m) - 1}{w_2 (m_r)} \right] \right\} \left[ \frac{w_1 (m_r - m) - 1}{w_2 (m_r)} \right]^2 \left[ k_1 + 2n_1 k_2 \gamma \right] \frac{x}{q_1^2}. \]  

where \( w_1 (m) \equiv e^{+b_1 m} \) and \( w_2 (m) \equiv \frac{1}{q_1} \left[ k_3 w_1 (m) - n_1 k_2 \right]. \)

Inspection of equation (2.42) reveals that \( \dot{\lambda}_3 (0) \equiv 0 \) since \( x (0) = 0 \). A sufficient condition for \( \lambda_3 (m \neq 0) > 0 \) is the inequality
\[ \left[ \frac{w_1 (m_r - m) - 1}{w_2 (m_r)} \right] \left[ \frac{w_2 (m_r)}{w_2 (m_r)} \right] \left[ 1 + 2n_1 \gamma \frac{k_2}{k_1} \right] \geq 1, \]
or, using equation (2.39),

$$\left[ w_1 (m_f - m) - 1 \right] \left[ \frac{k_3 w_1 (m) + n_1 k_2}{k_3 w_1 (m_f) - n_1 k_2} \right] \geq 1 . \quad (2.44)$$

The inequality expressed by (2.44) can be rewritten as

$$\frac{e^{b_1 m_f}}{e + 2b_1 m} \geq 1 + \frac{k_1}{n_1 k_2} \quad (m \neq 0) . \quad (2.45)$$

If there exists a positive value of $m$ (call it $\bar{m}$) for which the inequality (2.45) becomes an equality, then it is guaranteed that $\lambda_3 (m)$ is positive for $0 < m \leq \bar{m}$ and $\delta \varphi > 0$ for any $m_1 \leq \bar{m}$. This sufficiency condition is written in more concise mathematical notation below.

$$\bar{m} = \frac{1}{2b_1} \left\{ b_1 m_f - \ln \left[ 1 + \frac{k_1}{n_1 k_2} \right] \right\} \quad (2.46)$$

$$\bar{m} > 0 \Rightarrow \delta \varphi > 0 \text{ for } 0 < m_1 \leq \bar{m} \quad (2.47)$$

We see that $\bar{m}$ is positive whenever the dimensionless reactor length $\frac{k_1 m_f}{Q_1}$ is large or the dimensionless kinetic ratio $\frac{k_1}{n_1 k_2}$ is small.

If the sufficient condition is not satisfied (i.e., $\bar{m} \leq 0$), then $\lambda_3$ must be evaluated by integrating equation (2.42) to see if the inequality (2.21) is satisfied.

Therefore, it is quite possible that the performance of an isothermal tubular reactor in which a Case B or Case C reaction system occurs can be improved by an infinitesimal bypass of the feed stream of reactant $A_1$. If an infinitesimal feed bypass is profitable, it would be wise to explore the idea of continuous feed distribution.
FIGURE 2.1  INFINITESIMAL FEED BYPASS IN A ISOTHERMAL TUBULAR REACTOR
Chapter 3. FEED DISTRIBUTION FOR A REACTION SYSTEM WHICH INCLUDES A FIRST ORDER SIDE REACTION

Graves [12] has explored the optimal feed distribution problem for the exothermic reaction system

\[ \frac{K_1}{K_2} A_1 + A_2 \xrightleftharpoons{\text{Reaction 1}} A_3 + A_4 \]

\[ K_3 A_1 \rightarrow A_5 \quad \text{Reaction 2} \]

which is more complex than those discussed in Chapter 2 because the main reaction is reversible and more than one reactant is present in the reactor. These reactions take place in a tubular reactor equipped with a heat exchanger that preheats the feed stream of reactant \( A_2 \). The cold feed stream of \( A_1 \) is distributed along the length of the reactor.

Most of Graves' work is concerned with the optimal distribution of the \( A_1 \) feed stream in an adiabatic reactor where the preheater duty and the total mass of catalyst are free parameters and the flowrates and temperatures of the two feed streams are fixed quantities. Graves found that there was a significant improvement to be gained by distribution of the substance \( A_1 \) along the length of the adiabatic reactor but that an isothermal reactor without feed distribution is even better. For this reason we will investigate the optimal distribution of the reactant \( A_1 \) along an isothermal reactor for the reaction system (3.1). Both the fixed and the free endpoint reactors will be examined.

3.1 Equations for the isothermal reactor

As in Chapter 2 the reactor under consideration is an isothermal
plug-flow tubular reactor with no axial dispersion. The position in the reactor is represented by the variable $m$ and the length of the reactor by $m_f$ (see Fig. 3.1). The feed stream of reactant $A_1$ may be distributed along the length of the reactor, but the feed stream of $A_2$ may not. The variables $q_{10}$ and $q_{20}$ are defined as the molar feed flowrates of $A_1$ and $A_2$ respectively, and these feed parameters are fixed.

It is assumed that the kinetics of the reaction system are such that the rate of formation of $A_3$ per unit mass of catalyst can be written as

$$ r_1 = K_1(T) y_1 y_2 - K_2(T) y_3 y_4 $$

(3.2)

and the rate of formation of $A_5$ per unit mass of catalyst is given by

$$ r_2 = K_3(T) y_1 $$

(3.3)

where $y_1$ is the mole fraction of substance $A_1$ in the reaction mixture. $K_i$ is a temperature dependent kinetic parameter which is of the Arrhenius form

$$ K_i = K_{i0} \exp \left( -\frac{E_i}{RT} \right) \quad i = 1, 2, 3 $$

(3.4)

where $E_i$ is the activation energy and $T$ is the absolute temperature. The values of $K_{i0}$ and $E_i$ used for this study are listed in Table 3.A.
### Table 3.4

**Kinetic Data**

<table>
<thead>
<tr>
<th></th>
<th>$K_{910}$ in kg. mole per hr. - ton catalyst</th>
<th>$E$ in cal. per gm. mole - degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$3.452 \times 10^{14}$</td>
<td>25,470.</td>
</tr>
<tr>
<td>2</td>
<td>$2.042 \times 10^{25}$</td>
<td>45,870.</td>
</tr>
<tr>
<td>3</td>
<td>$4.33 \times 10^7$</td>
<td>13,930.</td>
</tr>
</tbody>
</table>

Let $x_1 (m)$ and $x_2 (m)$ be defined as the fraction of $q_{10}$ that has been converted in the section $[0, m]$ by reactions 1 and 2, respectively. Let $x_3 (m)$ represent the fraction of $q_{10}$ that has entered the reactor in the section $[0, m]$. The control variable $x_3 (m)$ is subject to the following constraints:

1. $x_3$ is a piecewise continuous function of $m$.
2. $x_3$ is a non-decreasing function of $m$; $x_3 \geq 0$.
3. $x_3 (m_f) \leq 1.0$. \hspace{1cm} (3.5)

In this formulation $x_3$ is the control variable, but in Graves' formulation $\frac{dx_3}{dm}$ is considered to be the control with $x_3$ being regarded as the third state variable. Using the derivative as the control leads to a problem of singular control. Some aspects of the singular control problem will be discussed in Chapter 4. At this point, it is asserted that the results of the two different formulations are identical and that singular control considerations can be avoided by using $x_3$ as the control variable.

If the molar flowrate of species $A_1$ in the reactor is represented by $q_1 (m)$, then we may write
\[ q_1 (m) = q_{10} \left[ x_3 (m) - x_1 (m) - x_2 (m) \right] \]  
(3.6)

\[ q_2 (m) = q_{10} \left[ \Theta - x_1 \right] \]  
(3.7)

\[ q_3 (m) = q_4 (m) = q_{10} x_1 (m) \]  
(3.8)

\[ q_5 (m) = q_{10} x_2 (m) \]  
(3.9)

\[ q (m) = \sum_{i=1}^{5} q_i (m) = q_{10} \left[ x_3 (m) + \Theta \right] \]  
(3.10)

where \( \Theta = q_{20}/q_{10} \) and \( q (m) \) is the total molar flowrate of the reaction mixture.

Component balances for \( A_3 \) and \( A_5 \) yield

\[ \frac{dq_3}{dm} = \dot{x}_3 = r_1 \quad ; \quad \frac{dq_5}{dm} = \dot{x}_5 = r_2 \]  
(3.11)

Combining equations (3.8), (3.9), and (3.11), we get the state equations

\[ \dot{x}_1 = f_1 (x_1, x_2, x_3) = g_1 \gamma_1 \gamma_2 - g_2 \gamma_3^2 \]  
(3.12)

\[ \dot{x}_2 = f_2 (x_1, x_2, x_3) = g_3 \gamma_1 \]  
(3.13)

where \( g_i = K_i/q_{10} \) for \( i = 1, 2, 3 \) and

\[ \gamma_i (m) = q_i (m)/q (m) \text{ for } i = 1, 2, 3, 4, 5. \]  
(3.14)

The state equations in explicit form are

\[ \dot{x}_1 = f_1 = \frac{g_1 \left[ x_3 - x_1 - x_2 \right] \left[ \Theta - x_1 \right] - g_2 x_1^2}{\left[ x_3 + \Theta \right]^2} \]  
(3.15)
\[ \dot{x}_2 = f_2 = \frac{g_3 \left[ x_3 - x_1 - x_2 \right]}{x_3 + \theta} \]  

(3.16)

The boundary conditions for the state variables are

\[ x_1(0) = x_2(0) = 0 \]  

(3.17)

The performance of the reactor is determined by evaluating the following objective function

\[ \hat{F} = \hat{F}(m_r) = q_3(m_r) - \varphi q_2(m_r) \]

or, equivalently,

\[ F = F(m_r) = x_1(m_r) - \varphi x_2(m_r) \]  

(3.18)

where \( \varphi \) is the economic penalty for formation of the waste product \( A_2 \) relative to the profit realizable from producing the desired product \( A_3 \). Negative values of \( \varphi \), corresponding to situations where both \( A_3 \) and \( A_2 \) are profitable products, are allowable.

3.2 The optimal feed distribution problem

We will examine the isothermal reactor for which the feed stream of \( A_1 \) is distributed along the length of the reactor. The objective function is to be maximized by the proper choice of \( x_3 \) at all points in the reactor. The parameter \( m_r \) is considered as a fixed quantity in Section 3.2.a and as a free quantity in Section 3.2.b.

3.2.a \( m_r \) is a fixed parameter

It is possible to construct two adjoint variables \( \lambda_1 \) and \( \lambda_2 \) corresponding to the state variables \( x_1 \) and \( x_2 \), respectively. The adjoints satisfy the equations listed below.

\[ \dot{\lambda}_1 = -\lambda_1 \frac{\delta f_1}{\delta x_1} - \lambda_2 \frac{\delta f_2}{\delta x_1} \]  

(3.19)
\[ \dot{\lambda}_2 = -\lambda_1 \frac{\lambda f_1}{\partial x_2} - \lambda_2 \frac{\lambda f_2}{\partial x_2} \]  \hspace{1cm} (3.20)

Since the initial state space is constrained according to equation (3.17) and the objective function is defined by equation (3.18), it is required that the adjoints have the boundary conditions

\[ \lambda_1 (m_r) = +1 \quad ; \quad \lambda_2 (m_r) = -\varphi \]  \hspace{1cm} (3.21)

As the problem stands now there are four equations and five variables \((x_1, x_2, x_3, \lambda_1, \text{ and } \lambda_2)\). The Pontryagin Maximum Principle \([20]\) or a method from the calculus of variations \([21]\) can be applied in order to obtain a relationship between \(x_3\) and the four other variables.

The Hamiltonian function for this problem is defined as

\[ H = H (m) = \lambda_1 f_1 + \lambda_2 f_2 \]  \hspace{1cm} (3.22)

The Maximum Principle states that the Hamiltonian must be maximized with respect to allowable variations in \(x_3\) for each value of \(m\); this is a necessary condition for optimality. A much weaker necessary condition for optimality is that \(H\) is constant for all \(m\).

Now suppose that \(0 < x_3 < 1\) for a point on the optimal trajectory. \(H\) is to be maximized with respect to variations in \(x_3\) at this point; therefore, it is true that

\[ \frac{\partial H}{\partial x_3} = \lambda_1 \frac{\lambda f_1}{\partial x_3} + \lambda_2 \frac{\lambda f_2}{\partial x_3} = 0 \]  \hspace{1cm} (3.23)

It can be shown easily that in our case there is only one value of \(x_3\) which satisfies equation (3.23) for fixed values of \(x_1, x_2, \lambda_1, \text{ and } \lambda_2\); and equation (3.23) can be rearranged to express \(x_3\) as an explicit
function of $x_1$, $x_2$, $\lambda_1$, and $\lambda_2$. To be certain that $H$ is maximized and not minimized we will always test to see that the inequality

$$\frac{\lambda^2 H}{\delta x_3^2} = \lambda_1 \frac{\delta^2 f_1}{\delta x_3^2} + \lambda_2 \frac{\delta^2 f_2}{\delta x_3^2} < 0 \quad (3.24)$$

is met.

Inspection of equation (3.23) reveals that only the ratio $\lambda_2 : \lambda_1$ is required in order to evaluate $x_3$ when $0 < x_3 < 1$. This fact suggests that the ratio of the adjoints instead of the two individual adjoints should be used in calculating the optimal trajectory. The new adjoint variable is defined as

$$\lambda = \lambda (m) = \frac{\lambda_2 (m)}{\lambda_1 (m)} \quad (3.25)$$

and it is assumed that $\lambda_1 (m) \neq 0$ for all $m$. Since $\lambda_1$ is a continuous function of $m$ and $\lambda_1 (m_0) = +1$, this assumption can be rewritten as $\lambda_1 (m) > 0$ for all $m$.

Some spot checks were made during the computation of the optimal trajectories, and condition (3.26) was always met. The adjoint equation, deduced from equations (3.19) and (3.20), and the adjoint boundary condition, deduced from equation (3.21), are written below.

$$\dot{\lambda} = \lambda \left[ \frac{\delta f_1}{\delta x_1} - \frac{\delta f_2}{\delta x_2} \right] + \lambda^2 \frac{\delta f_2}{\delta x_1} - \frac{\delta f_1}{\delta x_2} \quad (3.27)$$

$$\lambda (m_0) = - \varphi \quad (3.28)$$

The general form of the control $x_3 (m)$ is depicted in Figure 3.2. Graves found for the adiabatic problem that $x_3 (0) > 0$ for the fixed endpoint case $[12]$; this is also true for the isothermal
problem. For the first part \(0 \leq m < m_1\) the control \(x_3\) is determined by using equation (3.23). The value of \(x_3\) at \(m = m_1\) is exactly one.

Recall the constraints that \(x_3 \geq 0\) and \(x_3 \leq 1.0\); therefore, \(x_3(m) = 1.0\) for the final portion of the trajectory \((m \leq m_f)\). The condition \(x_3(m_f) \leq 1.0\) indicates that it is not necessary for the optimal trajectory to contain a segment on which \(x_3(m) = 1.0\).

A mixed boundary value problem has been constructed. The state variables are known at \(m = 0\) while the adjoint \(\Lambda\) is known at \(m = m_f\). The value of \(x_3(0)\) is unknown, but it is determined by the value of \(\Lambda(0)\) according to equation (3.23). The computational algorithm for solving this problem is as follows:

1.) Specify \(g_1, g_2, g_3, m_f, \Theta, \) and \(\varphi\).

2.) Guess \(x_3(0)\) or \(\Lambda(0)\).

3.) Calculate the trajectory using the Maximum Principle subject to the restrictions on \(x_3\).

4.) Is \(\Lambda(m_f) = -\varphi\)? If not, use the calculated value of \(\Lambda(m_f)\) to guess a new value of \(x_3(0)\) or \(\Lambda(0)\). If \(\Lambda(m_f) = -\varphi\), the optimal trajectory has been evaluated.

The state equations and the adjoint equations are solved numerically by using the modification by Hamming of Milne's classical modified predictor-corrector method \([22]\). It is a stable forth order integration procedure that requires only two derivative evaluations per step. The predictor-corrector method is not self-starting; therefore, a special fourth order Runge-Kutta procedure suggested byRalston \([23]\) is used to provide the starting values required by Hamming's method.

The optimal control policy and the conversion profiles for a
representative situation ( $\Theta = 5.0$, $\varphi = 2.0$, $m_r = 4.0$, $T = 812^\circ K$, $\theta_1 = 12.0075$, $\theta_2 = 12.1469$, $\theta_3 = 1.7151$ ) are shown in Figure 3.3. The values of $x_3 (0)$ and $m_1$ are 0.0005552 and 3.197, respectively. The values of $x_1 (m_r)$ and $x_2 (m_r)$ are 0.6799 and 0.1406, respectively; the objective function is 0.3988. If the feed stream of $A_1$ were not distributed (i.e., $x_3 (m) = 1.0$ for all $m$), the values of $x_1 (m_r)$ and $x_2 (m_r)$ would be 0.6728 and 0.2352 resulting in an objective function of 0.2024 (see Fig. 3.4). Therefore, the objective function corresponding to the "dump" policy has been increased 97% by the use of the optimal control policy.

The optimal trajectory for another situation ( $\Theta = 10.0$, $\varphi = 1.0$, $m_r = 4.0$, $\theta_1 = 12.0075$, $\theta_2 = 12.1469$, $\theta_3 = 1.7151$ ) is depicted in Figure 3.5. The values of $x_3 (0)$ and $m_1$ are 0.17833 and 1.4633, respectively. The values of $x_1 (m_r)$ and $x_2 (m_r)$ are 0.7742 and 0.1455; consequently, the objective function $F$ is 0.6286. The values of $x_1 (m_r)$ and $x_2 (m_r)$ for the dump trajectory ($x_3 = 1.0$) are 0.7771 and 0.1569 resulting in an objective function of 0.6202 (see Fig. 3.6). For this situation the improvement in the objective function is 1.4%.

Table 3.B is a summary of the results for the reactor where $m_r = 4.0$, $\theta_1 = 12.0075$, $\theta_2 = 12.1469$, and $\theta_3 = 1.7151$. An interesting phenomenon is observed for the case in which $\Theta = 5.0$ and $\varphi = 3.0$. The value of the objective function for the dump policy is -0.0328 while the value of $F$ for the optimal control policy is + 0.2656. Thus, an unprofitable reactor is transformed into a profitable one. We conclude that this phenomenon is even more pronounced as $\varphi$ is increased and $\Theta$ is decreased.
### Table 3.B

Results for \( m_r = 4.0, \theta_1 = 12.0075, \theta_2 = 12.1469, \theta_3 = 1.7151 \)

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>( \varphi )</th>
<th>( x_3 (0) )</th>
<th>( m_1 )</th>
<th>( x_1 (m_r) )</th>
<th>( x_2 (m_r) )</th>
<th>( F )</th>
<th>( x_1 (m_r) )</th>
<th>( x_2 (m_r) )</th>
<th>( F )</th>
<th>( % \text{ INCREASE IN } F )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.</td>
<td>0.</td>
<td>0.0036930</td>
<td>2.4125</td>
<td>0.7091</td>
<td>0.1723</td>
<td>0.7091</td>
<td>0.6728</td>
<td>0.2352</td>
<td>0.6728</td>
<td>5.40</td>
</tr>
<tr>
<td>5.</td>
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<tr>
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<td>0.0011657</td>
<td>2.8903</td>
<td>0.7010</td>
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<td>0.4376</td>
<td>24.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
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<td>0.0005552</td>
<td>3.197</td>
<td>0.6799</td>
<td>0.1406</td>
<td>0.3988</td>
<td>0.2024</td>
<td>97.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
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<td>0.0002951</td>
<td>3.459</td>
<td>0.6416</td>
<td>0.1253</td>
<td>0.2656</td>
<td>-0.0328</td>
<td>SEE TEXT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>0.</td>
<td>0.42963</td>
<td>0.7071</td>
<td>0.7779</td>
<td>0.1532</td>
<td>0.7779</td>
<td>0.7771</td>
<td>0.1569</td>
<td>0.7771</td>
<td>1.0</td>
</tr>
<tr>
<td>10.</td>
<td>0.5</td>
<td>0.26085</td>
<td>1.1373</td>
<td>0.7769</td>
<td>0.1491</td>
<td>0.7024</td>
<td>0.6986</td>
<td>0.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
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<td>0.17833</td>
<td>1.4633</td>
<td>0.7742</td>
<td>0.1455</td>
<td>0.6288</td>
<td>0.6202</td>
<td>1.4</td>
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<td>1.7359</td>
<td>0.7699</td>
<td>0.1420</td>
<td>0.5569</td>
<td>0.5417</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
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<td>0.09718</td>
<td>1.9788</td>
<td>0.7639</td>
<td>0.1386</td>
<td>0.4867</td>
<td>0.4632</td>
<td>5.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>3.0</td>
<td>0.05721</td>
<td>2.4246</td>
<td>0.7449</td>
<td>0.1310</td>
<td>0.3518</td>
<td>0.3063</td>
<td>14.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2. b. \( m_f \) is a free parameter

It is well known that the Hamiltonian \( H \) is constant for the optimal control policy and this constant is zero when \( m_f \) is a free parameter. Thus,

\[
H(m) = 0 \quad \forall \quad m \in [0, m_f]
\]

(3.29)

when the control policy and the length of the reactor are chosen properly.

Graves \([12]\) has shown for the adiabatic reactor that there exists no solution to the problem when \( m_f \) is free. The objective function increases monotonically with \( m_f \), and in the corresponding sequence of controls \( x_3(0) \rightarrow 0 \) as \( m_f \rightarrow \infty \), the limiting control being \( x_3 \equiv 0 \) (i.e., the addition of \( A_1 \) is delayed forever). Graves produced substantial numerical evidence as well as an analytical proof. A similar proof can be given for the isothermal reactor; knowing this in advance we did not investigate any reactors with very large values of \( m_f \). However, the trend \( (x_3(0) \rightarrow 0 \text{ as } m_f \rightarrow \infty) \) is clear from the numerical example discussed in the following paragraph.

Consider the isothermal reactor for which \( \Theta = 10.0, \phi = 3.0, \quad g_1 = 12.0075, \quad g_2 = 12.1469, \quad \text{and} \quad g_3 = 1.7151. \) The optimal trajectories for six different values of \( m_f \) have been calculated according to the procedure outlined in Section 3.2. a. The characteristic properties of these trajectories are summarized in Table 3. C (see Appendix II for detailed information). The Hamiltonian \( H \) is plotted versus \( x_3(0) \) in Figure 3.7. By extrapolation of the data we verify that \( H \) is zero.
Table 3.5
Properties of the optimal trajectory

<table>
<thead>
<tr>
<th>$m_r$</th>
<th>$x_3(0)$</th>
<th>$m_1$</th>
<th>$F$</th>
<th>$H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2580</td>
<td>0.42963</td>
<td>0.7071</td>
<td>0.34728</td>
<td>0.010422</td>
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<tr>
<td>2.7038</td>
<td>0.26085</td>
<td>1.1373</td>
<td>0.35023</td>
<td>0.003840</td>
</tr>
<tr>
<td>3.0348</td>
<td>0.17832</td>
<td>1.4633</td>
<td>0.35112</td>
<td>0.001794</td>
</tr>
<tr>
<td>3.3095</td>
<td>0.12947</td>
<td>1.7359</td>
<td>0.35149</td>
<td>0.000946</td>
</tr>
<tr>
<td>3.5534</td>
<td>0.09718</td>
<td>1.9788</td>
<td>0.35116</td>
<td>0.000531</td>
</tr>
<tr>
<td>4.0000</td>
<td>0.05721</td>
<td>2.4246</td>
<td>0.35181</td>
<td>0.000186</td>
</tr>
</tbody>
</table>

when $x_3(0)$ is zero and $m_r$ is infinite. The form of the optimal control for the free endpoint problem can be deduced from Figure 3.8, which depicts the optimal control policy for three different finite values of $m_r$. The optimal control policy for the free $m_r$ situation is such that $x_3(0) \rightarrow 0$, $x_3(0) \rightarrow 0$, $m_1 \rightarrow \infty$, and $m_r \rightarrow \infty$.

3.3 The free endpoint reactor with no feed distribution

It has been established that for the reactor with optimally distributed $A_1$ there exists no solution to the free endpoint problem (i.e., the "time-optimal" reactor), the objective function being monotonic increasing in $m_r$. We now consider for purposes of comparison the single input reactor (i.e., the case where all the feed enters at $m = 0$; $x_3 = 1$) for which it is well known that there exists an optimal $m_r$.

Recalling that

$$F = F(m_r) = x_1(m_r) - \phi x_2(m_r)$$  \hspace{1cm} (3.30)

the optimal value of $m_r$ is chosen in such a way that

$$\frac{dF}{dm_r} = f_1(m_r) - \phi f_2(m_r) = 0$$  \hspace{1cm} (3.31)

provided that $-1 < \phi < \phi_0$, where
\[ \phi_o \equiv \frac{g_1 \Theta}{g_3 \left[ 1 + \Theta \right]} \]  
(3.32)

(see Appendix III). When \( \Phi \geq \Phi_o \) (\( \Phi_o \) is positive), the value of \( F \) is negative for any \( m_r > 0 \); hence, the optimal value of \( m_r \) is zero, that is, it does not pay to react at all! Furthermore, if \( \Phi \leq -1 \), the optimal \( m_r \) is infinite because \( x_1 \to 0, x_2 \to 1 \), and \( F \to -\Phi \) as \( m_r \to \infty \).

In a situation where \( \Theta, g_1, g_2, \) and \( g_3 \) are fixed it is possible to discover the optimal \( m_r \) for any value of \( \Phi \) by calculating only one dump trajectory. The derivatives \( f_1 \) and \( f_2 \) for such a dump trajectory are depicted in Figure 3.9; both \( f_1 \) and \( f_2 \) approach zero (from negative and positive values, respectively) as \( m \) becomes infinite. The ratio \( f_1/f_2 \) for the same trajectory is plotted in Figure 3.10; the ratio approaches \(-1\) as \( m \) becomes infinite. Therefore, from equation (3.31) it follows that each point on the single dump trajectory is the optimal endpoint for the value of \( \Phi \) given by

\[ \Phi = \frac{f_1(m_r)}{f_2(m_r)} \]  
(3.33)

where \(-1 < \Phi \leq \Phi_o \). According to the reasoning above, Figure 3.10 is actually a plot of \( \Phi \) versus optimal \( m_r \).

In summary, the "time-optimal" reactor without feed distribution is of finite length unless \( \Phi \leq -1 \).

3.4 Results and conclusions

There are at least three ways of distributing the \( A_1 \) feed stream to an isothermal reactor of specified \( m_r \). The first method is to distribute the feed so that the Pontryagin Maximum Principle (or the Weierstrass necessary condition) is satisfied; the resulting control
policy is presumably the optimal policy. The second possibility is to inject all the feed at a point along the reactor such that the effective \( m_f \) \( (m_f' \) is the optimal \( m_f \) for the reactor without feed distribution. ¹

The third method consists of not distributing the feed at all; i.e., dumping it into the reactor at \( m = 0 \).

These three control policies have been examined for the case where \( m_f = 4.0 \), \( a_1 = 12.0075 \), \( a_2 = 12.1469 \), and \( a_3 = 1.7151 \). Two different values of \( \Theta \) and at least five different values of \( \Phi \) have been studied. The effectiveness of the different control strategies for the \( \Theta = 5.0 \) case is shown in Figure 3.11. The improvement of the objective functions corresponding to the two dump control schemes that can be realized by using the optimal control is summarized in Table 3.D.

Although only one set of kinetic parameters \( g_i \) have been examined, it is possible to make the several general conclusions concerning the effect of feed distribution in an isothermal reactor in which the reaction system (3.1) occurs. The following conclusions are made for the circumstance where \( m_f \) and the \( g_i \) values are specified constants:

¹This control policy is possible only if the value of the optimal endpoint for the "dump" reactor is less than the specified value of \( m_f \) under consideration.
<table>
<thead>
<tr>
<th>$\Theta$</th>
<th>$\Phi$</th>
<th>$F_1$</th>
<th>$m_f$</th>
<th>$F_2$</th>
<th>$F_3$</th>
<th>$\frac{F_1 - F_2}{F_2} \times 100$</th>
<th>$\frac{F_1 - F_3}{F_3} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.</td>
<td>0.</td>
<td>0.70913</td>
<td>1.9646</td>
<td>0.70613</td>
<td>0.67280</td>
<td>0.42 %</td>
<td>5.40 %</td>
</tr>
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<td>0.62558</td>
<td>1.6864</td>
<td>0.62051</td>
<td>0.55519</td>
<td>0.82</td>
<td>12.68</td>
</tr>
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<td>0.43758</td>
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</tr>
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<tr>
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<td>2.41</td>
<td>14.85</td>
</tr>
</tbody>
</table>
1.) A characteristic of the optimal control, $x_3(0)$, increases as $\Theta$ increases (constant $\Phi$) and decreases as $\Phi$ increases (constant $\Theta$).

2.) Another characteristic of the optimal control, $m_1$, decreases as $\Theta$ increases (constant $\Phi$) and increases as $\Phi$ increases (constant $\Theta$).

3.) The optimal value of $m_r$ for the dump reactor increases as $\Theta$ increases (constant $\Phi$) and decreases as $\Phi$ increases (constant $\Theta$).

4.) $F_1$, the objective function for the optimal control policy; $F_2$, the objective function corresponding to the "time-optimal" dump policy; and $F_3$, the objective function for the normal dump policy, increase as $\Theta$ increases (constant $\Phi$) and decrease as $\Phi$ increases (constant $\Theta$).

5.) $F_1 \to 0$ as $\Phi \to \infty$ (constant $\Theta$).

6.) $F_2 = 0$ for $\Phi \geq \Phi_0 > 0$ (constant $\Theta$).

7.) $F_1 > F_2$ at constant $\Phi$ and $\Theta$.

8.) $F_1 > F_3$ at constant $\Phi$ and $\Theta$ when the specified $m_r$ is greater than the dump "time-optimal" value of $m_r$.

9.) The quantities $F_1 - F_2$ and $F_1 - F_3$ ($m_r > m_{fe}$) decrease as $\Theta$ increases (constant $\Phi$) and increase as $\Phi$ increases (constant $\Theta$, $\Phi < \Phi_0$).
FIGURE 3.1 ISOTHERMAL TUBULAR REACTOR WITH FEED DISTRIBUTION
FIGURE 3.3: OPTIMAL CONTROL POLICY AND CORRESPONDING CONVERSION ( $\theta = 5.0$, $\phi = 2.0$, $g_1 = 12.0075$, $g_2 = 12.1469$, $g_3 = 1.7151$, $m_f = 4.0$ )
FIGURE 3.4  DUMP TRAJECTORY \((x_3 \equiv 1)\) FOR THE CASE WHERE
\[\theta = 5.0, \quad \phi = 2.0, \quad g_1 = 12.0075, \quad g_2 = 12.1469, \quad g_3 = 1.7151, \quad m_f = 4.0\]
FIGURE 3.5 OPTIMAL CONTROL POLICY AND CORRESPONDING CONVERSION PROFILES \((\theta = 10.0, \phi = 1.0, g_1 = 12.0075, g_2 = 12.1469, g_3 = 1.7151, m_f = 4.0)\)
FIGURE 3.6  DUMP TRAJECTORY (x₃=1) FOR THE CASE WHERE
θ = 10.0,  φ = 1.0,  g₁ = 12.0075,  g₂ = 12.1469, g₃ = 1.7151,
mₚ = 4.0
FIGURE 3.7  THE HAMILTONIAN AS A FUNCTION OF $X_3(0)$
($\theta = 10.0$, $\phi = 3.0$, $g_1 = 12.0075$, $g_2 = 12.1469$, $g_3 = 1.7151$)
FIGURE 3.8 OPTIMAL CONTROL POLICIES FOR THREE VALUES OF $m_f$ ($\theta = 10.0$, $\phi = 3.0$, $g_1 = 12.0075$, $g_2 = 12.1469$, $g_3 = 1.7151$)
FIGURE 3.9 THE DERIVATIVES $f_1$ AND $f_2$ FOR A TYPICAL DUMP TRAJECTORY ($\theta = 5.0$, $g_1 = 12.0075, g_2 = 12.1469, g_3 = 1.7151$)
FIGURE 3.10  THE RATIO $f_1/f_2$ FOR A TYPICAL DUMP TRAJECTORY
($\theta = 5.0, g_1 = 12.0075, g_2 = 12.1469, g_3 = 12.1469$)
FIGURE 3.11  OBJECTIVE FUNCTION FOR THREE POSSIBLE CONTROL POLICIES (θ = 5.0, g₁ = 12.0075, g₂ = 12.1469, g₃ = 1.715)
Chapter 4. FEED DISTRIBUTION FOR A REACTION SYSTEM WHICH INCLUDES A SECOND ORDER SIDE REACTION - $q_{20}$ IS A FIXED PARAMETER

In the previous chapter we studied a reaction system consisting of a reversible exothermic main reaction and an irreversible isomerization which is the costly side reaction. In this chapter we will investigate a similar reaction system

\[ A_1 + A_2 \xrightarrow{K_1} A_3 + A_4 \quad \text{Reaction 1} \]

\[ 2A_1 \xrightarrow{K_3} A_5 \quad \text{Reaction 2} \]

(4.1)

which includes a reversible main reaction and an irreversible dimerization that produces a waste product, $A_5$. The feed stream of the reactant $A_1$ is to be distributed so that the performance of the idealized isothermal reactor is maximized.

As the results of Chapter 3 indicate, the free endpoint ($m_r$) problem of determining the optimal policy for distributing the feed stream of $A_1$ is ill-posed for the reaction system (3.1); i.e., the reactor turns out to be infinitely long. To avoid this possibility, only the fixed endpoint problem will be considered for the reaction system (4.1).

The molar feed flowrates, $q_{10}$ and $q_{20}$, will be regarded as fixed parameters throughout this chapter. Various combinations of the kinetic parameters ($g_1, g_2, g_3$), the feed ratio ($\Theta$), the cost associated with formation of $A_5$ ($\Gamma$), and the reactor size ($m_r$) will be inspected in order to find the circumstances under which feed distribution is most beneficial.
In this chapter it will be shown that the end states associated with the optimal trajectories for different values of the waste penalty \( \Phi \) constitute the boundary of the attainable region in the end state space for an isothermal reactor in which the feed distribution policy is the only variable.

### 4.1 Formulation of the optimization problem

The reactor under consideration is an isothermal plug-flow tubular reactor with no axial dispersion. The variable \( m \) represents the mass of catalyst to the left of the cross-sectional plane labelled \( m \) in Figure 3.1; \( m_T \) is the total mass of catalyst contained in the reactor. The feed stream of \( A_1 \) may be distributed along the length of the reactor, but the feed stream of \( A_2 \) may not.

The kinetics of the reaction system are such that the rate of formation of \( A_3 \) per unit mass of catalyst is

\[
    r_1 \ (m) = K_1 \ \frac{\gamma_1 \ (m)}{\gamma_2 \ (m)} - K_2 \ \frac{\gamma_3 \ (m)}{\gamma_4 \ (m)} \quad (4.2)
\]

and the rate of formation of \( A_5 \) per unit mass of catalyst is given by

\[
    r_2 \ (m) = K_3 \left( \frac{\gamma_1 \ (m)}{\gamma_4 \ (m)} \right)^2 \quad (4.3)
\]

where \( \gamma_1 \) is the mole fraction of \( A_1 \) and \( K_1 \) is a kinetic constant.

The variables \( x_1 \ (m) \), \( x_2 \ (m) \), and \( x_3 \ (m) \) are dimensionless state variables and are given by

\[
    x_1 \ (m) = \frac{q_3 \ (m)}{q_1 \ (m)}; \quad x_2 \ (m) = \frac{2q_5 \ (m)}{q_1 \ (m)} \quad (4.4 \ a, \ b)
\]

\[
    x_3 \ (m) = \frac{q_1 \ (m) + q_3 \ (m) + 2q_5 \ (m)}{q_1 \ (m)} \quad (4.5)
\]

where \( q_1 \) is the molar flowrate of \( A_1 \). As in Chapter 3 we will take \( x_3 \) to be the control variable on the assumption that it will turn out to be
non-decreasing. Occasionally this assumption is found to be false; in these cases \( v = \dot{x}_3 \) is used as the control and \( x_3 \) becomes strictly a state variable. Decisions regarding departures from a singular control segment arise when we take \( v \) as the control.

Component balances for \( A_3 \) and \( A_5 \) lead to

\[
\frac{dq_3}{dm} = r_1(m) ; \quad \frac{dq_2}{dm} = r_2(m) \quad . \tag{4.6 a, b}
\]

Equations (4.6a) and (4.6b) are combined with equations (4.2) and (4.3) to give

\[
\frac{dx_1}{dm} = g_1 \gamma_1(m) \gamma_2(m) - g_2 \left[ \gamma_3(m) \right]^2 \tag{4.7}
\]

\[
\frac{dx_2}{dm} = 2g_3 \left[ \gamma_1(m) \right]^2 \tag{4.8}
\]

where \( g_i \equiv K_i/q_{i0} \). At this point of the development it is convenient to introduce the dimensionless position \( t \), which is the ratio \( m/m_f \).

Since \( \gamma_i = q_i / \sum_{i=1}^{5} q_i \) and the \( q_i \) variables can be expressed in terms of \( x_1 \), \( x_2 \), and \( x_3 \), equations (4.7) and (4.8) may be transformed into

\[
\dot{x}_1 = f_1(x_1, x_2, x_3) = \frac{G_1 \left[ x_3 - x_1 - x_2 \right] \left[ \Theta - x_1 \right] - \Theta x_2^2}{\left[ x_3 + \Theta - 0.5x_2 \right]^2} \tag{4.9}
\]

\[
\dot{x}_2 = f_2(x_1, x_2, x_3) = \frac{2\Theta \left[ x_3 - x_1 - x_2 \right]^2}{\left[ x_3 + \Theta - 0.5x_2 \right]^2} \tag{4.10}
\]

where \( \Theta = q_{20}/q_{10} \) and \( G_i \equiv g_i m_f \) for \( i = 1, 2, \) and \( 3 \). In this chapter and the next, the symbol \( \dot{} \) denotes the derivative with respect
to t, the dimensionless position. The boundary conditions on \( x_1 \) and \( x_2 \) are

\[
x_1 (0) = x_2 (0) = 0. \tag{4.11}
\]

The objective function

\[
F = F(t = 1) = x_1 (t = 1) - \varphi x_2 (t = 1) \tag{4.12}
\]

is to be maximized by the proper choice of \( x_3 \) at every position \( t \).

Since \( A_2 \) is a waste product which may be difficult to separate from the product stream, \( \varphi \) ordinarily will be greater than or equal to zero.

However, it is conceivable that \( A_2 \) might have some worth in which case \( \varphi \) would be negative.

The adjoint variables \( \lambda_1 \) and \( \lambda_2 \) (i.e., the Lagrangian multipliers) satisfy the equations

\[
\begin{align*}
\dot{\lambda}_1 &= -\lambda_1 \frac{\partial f_1}{\partial x_1} - \lambda_2 \frac{\partial f_2}{\partial x_1} \tag{4.13} \\
\dot{\lambda}_2 &= -\lambda_1 \frac{\partial f_1}{\partial x_2} - \lambda_2 \frac{\partial f_2}{\partial x_2} \tag{4.14}
\end{align*}
\]

From the definition of the objective function, it is required that the adjoint boundary conditions are

\[
\begin{align*}
\lambda_1 (t = 1) &= +1 \quad ; \quad \lambda_2 (t = 1) = -\varphi. \tag{4.15}
\end{align*}
\]

Only the ratio \( \lambda_2 : \lambda_1 \) is needed in the numerical procedure used to calculate the optimal trajectory; therefore, if \( \lambda_1 \) is non-zero, a new adjoint variable is constructed such that

\[
\lambda_\upph (t) \equiv \lambda_2 (t)/\lambda_1 (t) \tag{4.16}
\]

\[
\begin{align*}
\dot{\lambda}_\upph &= \lambda_\upph \left[ \frac{\partial f_1}{\partial x_1} - \frac{\partial f_2}{\partial x_2} \right] + \lambda_\upph^2 \frac{\partial f_2}{\partial x_1} - \frac{\partial f_1}{\partial x_2} \tag{4.17}
\end{align*}
\]
\[ (t = 1) = - \varphi \quad . \]  

(4.18)

The Hamiltonian function is given by

\[ H = H(t) = \lambda_1 f_1 + \lambda_2 f_2 \quad . \]  

(4.19)

The Weierstrass necessary condition or the Pontryagin Maximum Principle requires that \( H \) is maximized with respect to allowable variations in \( x_3 \) for each value of \( t \) on the optimal trajectory. Also, the Hamiltonian is constant along the optimal trajectory.

The general form of the control policy is the same as that of Figure 3.2. The first part of the policy, where \( 0 < x_3 < 1 \), is predicted by the Maximum Principle in a very straightforward manner. Since \( x_3 \) is in the interior of its range and \( H \) is to be maximized, it is necessary that

\[ \frac{\partial H}{\partial x_3} = \lambda_1 \frac{\partial f_1}{\partial x_3} + \lambda_2 \frac{\partial f_2}{\partial x_3} = 0 \]  

(4.20)

\[ \frac{\partial^2 H}{\partial x_3^2} = \lambda_1 \frac{\partial^2 f_1}{\partial x_3^2} + \lambda_2 \frac{\partial^2 f_2}{\partial x_3^2} < 0 \]  

(4.21)

for the optimal value of \( x_3 \). The state equations are constituted such that only one value of \( x_3 \) satisfies equation (4.20). Consequently, if the root of equation (4.20) satisfies condition (4.21), the root assuredly causes \( H \) to be maximized. The first part of the control policy ends as \( x_3 \) reaches one at \( t = t_1 \). For the remainder of the reactor \((t_1 < t \leq 1)\), \( x_3 \) remains at one since it is not allowed to decrease. Since the control is constant for this section, the Hamiltonian is constant (and equal to the constant associated with the first part of
the control policy). However, it is not certain that \( H \) is maximized with respect to \( x_3 \). If \( H \) is not maximized for all points on the second part of the trajectory we can say nothing a priori concerning whether or not the control is optimal (in the class of controls for which \( \dot{x}_3 \geq 0 \)); this question may be resolved by considering \( v = \dot{x}_3 \) to be the control and studying the singular segment. This procedure was followed in some cases and the optimality of the "coasting" segment (i.e., the final portion of the trajectory where \( x_3 = 1 \) and \( v = 0 \)) was confirmed. Details will be given later.

As was mentioned in Chapter 3, it is conceivable that \( x_3 \) could be less than 1 at \( t = 1 \). This is quite likely to occur for cases where \( G_3 \gg G_1 \) and \( \theta > 0 \). There should be no problem concerning whether or not \( H \) is maximized since the coasting segment is never reached.

The state variables \( x_1 \) and \( x_2 \) are known at \( t = 0 \). The values of \( x_3 (0) \) and \( \Lambda (0) \) are unknown, but they are related according to equation (4.20). Optimal trajectories have been computed using the following algorithm:

1.) Specify \( G_1, G_2, G_3, \Theta, \) and \( x_3 (0) \).

2.) Determine the value of \( \Lambda (0) \) using equation (4.20) and the specified value of \( x_3 (0) \).

3.) Calculate the optimal trajectory using equation (4.20) to evaluate \( x_3 \) for \( 0 < t < t_1 \) and using \( x_3 = 1 \) for \( t_1 \leq t \leq 1 \). The three differential equations are solving by using Hamming's predictor-corrector method.

4.) \( \Phi = -\Lambda (1) \).

If the optimal trajectory for a specific value of \( \Phi \) is sought, we can iterate on \( x_3 (0) \) until \( \Lambda (1) \) has the proper value or we can interpolate
the results of several optimal trajectories corresponding to values of 
\( \phi \) which are close to the desired value.

4.2 Discussion of results

The results of a representative situation are presented here. The kinetics and the reactor volume are such that \( G_1 = 10.0 \), \( G_2 = 1.0 \), and \( G_3 = 10.0 \); the first reaction displays a moderate degree of reversibility and the second reaction is competitive with the first. The feed flowrates \( q_{10} \) and \( q_{20} \) are equal; thus, \( \Theta = 1.0 \).

Consider the case where \( \phi \) is approximately zero (\( \phi = -0.0594 \)). If the feed stream of \( A_1 \) were not distributed (\( x_3 = 1.0 \) \( \forall t \)), then the exit values of \( x_1 \) and \( x_2 \) would be 0.4387 and 0.5060, respectively. Using this control policy (the "dump" policy), \( F \) would be 0.4688, and 94.47\% of the reactant \( A_1 \) would be converted to products. The optimal control policy is shown in Figure 4.1; it is characterized by \( x_3 (0) = 0.15 \) and \( t_1 = 0.6306 \). The values of \( x_1 (1) \) and \( x_2 (1) \) are 0.5190 and 0.3505, respectively, which result in an objective function of 0.5398. The conversion is 84.95\%. We see that optimal control brings about a positive change in \( F \) of 0.0710 or a 15.1\% improvement over the dump policy.

Suppose the value of \( \phi \) were larger, say \( \phi = +0.9225 \), a high penalty circumstance. Using the dump control policy, the value of \( F \) would be -0.0281; i.e., the reactor would be uneconomical to operate. The optimal control (see Fig. 4.2) for this value of \( \phi \) is such that \( x_3 (0) = 0.075 \) and \( x_3 (1) = 0.6849 \); 31.51\% of the feed stream bypasses the reactor completely. The values of \( x_1 (1) \) and \( x_2 (1) \) for the optimal control are 0.4108 and 0.1245, respectively; \( F \) is 0.2959. The optimal control results in a positive change in \( F \) of 0.3240 over the dump policy.
An uneconomical reactor has been converted into a moderately profitable one by means of feed distribution.

The properties of the optimal trajectories for various $\varphi$ are summarized in Table 4.A. As $\varphi$ increases, $x_3(0)$ decreases and $t_1$ increases ($t_1 = 1.0$ for $x_3(0) = 0.1078$). As $x_3(0) \rightarrow 1.0$, $x_1(1)$ and $x_2(1)$ approach their dump values and $\varphi \rightarrow -0.772$. The assumption that $\lambda_1 \neq 0$ was verified for all these trajectories.

In Figure 4.3 there is a comparison of $F_{OPT}$, the value of $F$ for the optimal control, and $F_D$, the value of $F$ for the dump policy, over a large range of $\varphi$. $F_{OPT}$ is positive for all finite $\varphi$. The quantity $F_{OPT} - F_D$ is zero for $\varphi \leq -0.772$, but it increases as $\varphi$ becomes larger.
Table 4.A

Properties of optimal trajectories for various $\varphi$

$G_1 = 10.0$, $G_2 = 1.0$, $G_3 = 10.0$; $\Theta = 1.0$

<table>
<thead>
<tr>
<th>$\varphi$</th>
<th>$x_3 (0)$</th>
<th>$t_1$</th>
<th>$x_3 (1)$</th>
<th>$x_1 (1)$</th>
<th>$x_2 (1)$</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-0.772)</td>
<td>1.000</td>
<td>0.</td>
<td>1.0</td>
<td>0.4387</td>
<td>0.5060</td>
<td>(0.829)</td>
</tr>
<tr>
<td>-0.7659</td>
<td>0.800</td>
<td>0.0153</td>
<td>1.0</td>
<td>0.4401</td>
<td>0.5041</td>
<td>0.8262</td>
</tr>
<tr>
<td>-0.7596</td>
<td>0.700</td>
<td>0.0273</td>
<td>1.0</td>
<td>0.4424</td>
<td>0.5011</td>
<td>0.8230</td>
</tr>
<tr>
<td>-0.7494</td>
<td>0.500</td>
<td>0.0448</td>
<td>1.0</td>
<td>0.4466</td>
<td>0.4955</td>
<td>0.8179</td>
</tr>
<tr>
<td>-0.7346</td>
<td>0.400</td>
<td>0.0717</td>
<td>1.0</td>
<td>0.4535</td>
<td>0.4862</td>
<td>0.8107</td>
</tr>
<tr>
<td>-0.7007</td>
<td>0.300</td>
<td>0.1169</td>
<td>1.0</td>
<td>0.4646</td>
<td>0.4707</td>
<td>0.7944</td>
</tr>
<tr>
<td>-0.6310</td>
<td>0.200</td>
<td>0.2031</td>
<td>1.0</td>
<td>0.4823</td>
<td>0.4443</td>
<td>0.7827</td>
</tr>
<tr>
<td>-0.4081</td>
<td>0.105</td>
<td>0.4051</td>
<td>1.0</td>
<td>0.5080</td>
<td>0.3959</td>
<td>0.6696</td>
</tr>
<tr>
<td>-0.0594</td>
<td>0.150</td>
<td>0.6306</td>
<td>1.0</td>
<td>0.5190</td>
<td>0.3505</td>
<td>0.5398</td>
</tr>
<tr>
<td>0.2488</td>
<td>0.125</td>
<td>0.8186</td>
<td>1.0</td>
<td>0.5151</td>
<td>0.3100</td>
<td>0.4380</td>
</tr>
<tr>
<td>0.4826</td>
<td>0.105</td>
<td>-</td>
<td>0.9715</td>
<td>0.4884</td>
<td>0.2423</td>
<td>0.3715</td>
</tr>
<tr>
<td>0.5322</td>
<td>0.100</td>
<td>-</td>
<td>0.9217</td>
<td>0.4771</td>
<td>0.2202</td>
<td>0.3599</td>
</tr>
<tr>
<td>0.9225</td>
<td>0.075</td>
<td>-</td>
<td>0.6849</td>
<td>0.4108</td>
<td>0.1245</td>
<td>0.2959</td>
</tr>
<tr>
<td>1.8817</td>
<td>0.050</td>
<td>-</td>
<td>0.4628</td>
<td>0.3212</td>
<td>0.0551</td>
<td>0.2175</td>
</tr>
<tr>
<td>3.3520</td>
<td>0.035</td>
<td>-</td>
<td>0.3319</td>
<td>0.2510</td>
<td>0.0267</td>
<td>0.1615</td>
</tr>
<tr>
<td>11.326</td>
<td>0.015</td>
<td>-</td>
<td>0.1516</td>
<td>0.1278</td>
<td>0.0047</td>
<td>0.0746</td>
</tr>
</tbody>
</table>
This set of kinetic parameters \((G_1 = G_3 = 10.0, G_2 = 1.0)\) has been investigated for two other values of the feed parameter \(\Theta, 3.9\) and \(10.0\). The effects of the parameter \(\Theta\) on the final state \((x_1(1)\) and \(x_2(1))\) attained by optimal control are displayed in Figure 4.4. Each of the three curves is associated with a different value of \(\Theta\), and each point of an individual curve represents the final state for the optimal control with a particular \(x_3(0)\). The value of \(\Phi\) for which a final state is optimal can be determined by the equation

\[
\Phi = \frac{dx_1(1)}{dx_2(1)} \quad .
\]

(4.22)

Inspection of Figure 4.4 reveals the following trends:

1.) As \(\Theta\) increases, the value of \(\Phi\) associated with the optimal control where \(x_3(0) \rightarrow 1.0\) increases.

2.) As \(\Theta\) increases (at constant \(\Phi\)), the quantity \(F_{OPT} - F_D\) decreases until it reaches zero.

Other sets of \(G_1, G_2, G_3\), and \(\Theta\) have been studied with the hope of eventually being able to formulate an expression for \(F_{OPT} - F_D\) as a function of \(g_1, g_2, g_3, m_f, \Phi, \) and \(\Theta\), which are the parameters of the problem. The following general conclusions can be made on the basis of numerous investigations:

1.) \(\frac{\partial}{\partial \Theta} \left[ F_{OPT} - F_D \right] \leq 0\) \(\text{Constant } G_1, \Phi\)

2.) \(\frac{\partial}{\partial \Phi} \left[ F_{OPT} - F_D \right] > 0\) \(\text{Constant } G_1, \Theta\)

3.) \(\frac{\partial}{\partial m_f} \left[ F_{OPT} - F_D \right] \geq 0\) \(\text{Constant } g_1, \Phi, \Theta\)
No general conclusions concerning the effects of the kinetic parameters $g_i$ (or $G_i$) on $F_{OPT} - F_D$ can be made. This should not be too surprising; the state equations (equations (4.9) and (4.10) are non-linear and strongly coupled. A very large number of $G_1$, $G_2$, $G_3$, and $\Theta$ combinations would have to be studied before any generalizations regarding the kinetic parameters could be made.

4.3 Is the Hamiltonian maximized with respect to $x_3$?

For the first part of an optimal trajectory ($0 \leq t < t_1$), the Hamiltonian is maximized with respect to variations in $x_3$ provided that the inequality (4.21) is fulfilled. The inequality was satisfied for every trajectory that was calculated. Instead of checking the inequality, we could have verified that $H$ is maximized when $x_3$ is chosen according to \( \frac{\partial H}{\partial x_3} = 0 \). A sample case ($G_1 = 2.0$, $G_2 = 0.0$, $G_3 = 900.0$, $\Theta = 5.49$, $\phi = -0.00379$, $x_3(0) = 0.125$, and $t_1 = 0.8535$) is illustrated in Figure 4.5. Indeed $H$ is maximized with respect to variations in $x_3$.

Along the second part of an optimal trajectory ($t_1 \leq t \leq 1$), $H$ is constant since $\dot{x}_3 = 0$, but $H$ may not be maximized with respect to $x_3$; that is, a lower value of $x_3$ may yield a greater value of $H$ than $x_3 = 1$ does. The sample case mentioned in the previous paragraph is examined in Figure 4.6. The Hamiltonian is maximized by $x_3 = 1$ for all points on the second part of the trajectory; therefore, the control is optimal in the class of control subject to the condition $0 \leq x_3 \leq 1$ only (no restraint on $\dot{x}_3$). A second sample case ($G_1 = 5.0$, $G_2 = 2.5$, $G_3 = 12.5$, $\Theta = 1.182$, $\phi = -0.6977$, $x_3(0) = 0.70$, and $t_1 = 0.03559$) is shown in Figure 4.7. In this case, $H$ is maximized by $x_3 = 1$ for $t_1 \leq t < 0.33$, but $H$ is maximized by $x_3 = 0$ for $0.33 < t \leq 1.00$. Thus, the control policy calculated for this case is not optimal in the class of controls.
which allow $\dot{x}_3 < 0$. However, if $v = \dot{x}_3$ were chosen as the control, the Maximum Principle would be satisfied on the "coasting" segment and the control indeed would be optimal in the class of non-decreasing controls.

This phenomenon of $U$ not being maximized with respect to $x_3$ for the coasting segment of an optimal trajectory is exceptional. The cases studied indicate that this condition occurs only when $x_3(0)$ is close to 1 and $t_1$ is close to 0.

4.4 Consideration of $v = \dot{x}_3$ as the control

Instead of using $x_3$ as the control variable we could have used $\dot{x}_3 (v = \dot{x}_3)$ as the control subject to the restriction $0 \leq v \leq V$. It is assumed that $V$ is very large. With $v$ as the control, $x_3$ is regarded as the third state variable which is restricted such that $0 \leq x_3 \leq 1$; $x_3(1) = 1$.

The adjoint variable corresponding to the state variable $x_3$ is $\lambda_3$, and it must satisfy the equation

$$\lambda_3 = -\lambda_1 \frac{\partial f_1}{\partial x_3} - \lambda_2 \frac{\partial f_2}{\partial x_3} \quad (4.23)$$

Since $x_1(0) = x_2(0) = 0$ and $x_3(0) = 0$, the transversality condition requires that $\lambda_3(0) = 0$.

According to this formulation, the Hamiltonian is

$$\bar{H} = \bar{H}(t) = \lambda_1 f_1 + \lambda_2 f_2 + \lambda_3 v \quad (4.24)$$

or

$$\bar{H} = H + \lambda_3 v$$

where $H$ is the Hamiltonian when $x_3$ is considered to be the control. Recall that $f_1$ and $f_2$ are functions of $x_1$, $x_2$, and $x_3$; consequently, $\bar{H}$ is linear.

\[\text{There is no fixed} \ m_f \text{ problem for which } x_3(0) = 0.\]
in the control $v$. If $\lambda_3 > 0$, $H$ will be maximized by $v = V$. If $\lambda_3 < 0$, the Hamiltonian will be maximized by $v = 0$. If $\lambda_3 = 0$, the proper value of $v$ cannot be determined directly from the Hamiltonian; this is a singular control situation.

There exists a singular trajectory for which

$$\lambda_3 = 0 ; \quad \dot{\lambda}_3 = 0.$$  \hfill (4.25 a, b)

Since $\lambda_3 (0) = 0$, we will start on the singular trajectory; however, the optimal point of departure from the singular trajectory is unknown. Comparison of equation (4.25b) and the equation $\frac{\lambda H}{\delta x_3} = 0$ reveals that they are identical. Thus, it is conjectured that we remain on the singular trajectory until $x_3$ reaches 1. When $x_3$ reaches 1, it must remain there; hence, the control $v$ is zero and $\lambda_3$ must be negative for the remainder of the trajectory in order for $H$ to be maximized with respect to $v$.

To test the conjecture concerning the point of departure from the singular trajectory we will examine a typical singular trajectory and the effect of leaving it at various points. The parameters for the case to be examined are $G_1 = G_3 = 10.0$, $G_2 = 1.0$, $\theta = 1.0$, and $\varphi = -0.05943$. The singular trajectory is initiated with $x_3 (0) = 0.15$, $v = 1.70$, and $\lambda (0) = -1.41667$. The singular trajectory can be followed up to $t = 0.63058$ ($v = 1.23$) at which point $x_3$ attains the value 1 and the singular trajectory must be left with $v = 0$ for the rest of the trajectory.

First we will consider departures from the singular trajectory with $v = 0$. Departures from the singular segment at $t = 0.16$, 0.32, 0.48, and 0.63058 are considered (see Table 4.8 for the results). In each case, $\lambda_3$ is negative for the entire $v = 0$ segment; hence, once we leave the singular trajectory with $v = 0$ we do not return (i.e., the singular
trajectory is unstable). The largest value of the objective function is obtained for the \( v = 0 \) departure at \( t = 0.63058 \); therefore, since \( F \) should be maximized, the best point for a \( v = 0 \) departure is \( t = t_1 \), the point on the singular trajectory for which \( x_3 = 1 \).
### Table 4.B

Departures from the singular trajectory with \( v = 0 \)

<table>
<thead>
<tr>
<th>DEPARTURE POINT</th>
<th>0.16</th>
<th>0.32</th>
<th>0.48</th>
<th>0.63058</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_3 ) AT THE DEPARTURE PT.</td>
<td>0.39693</td>
<td>0.61287</td>
<td>0.81461</td>
<td>1.00000</td>
</tr>
<tr>
<td>( x_1 ) (1)</td>
<td>0.29003</td>
<td>0.39811</td>
<td>0.47159</td>
<td>0.51904</td>
</tr>
<tr>
<td>( x_2 ) (1)</td>
<td>0.09259</td>
<td>0.17599</td>
<td>0.26584</td>
<td>0.35053</td>
</tr>
<tr>
<td>( \lambda_2 ) (1) = ( \Lambda ) (1)</td>
<td>0.85300</td>
<td>0.63586</td>
<td>0.33811</td>
<td>0.05943</td>
</tr>
<tr>
<td>( \lambda_3 ) (1)</td>
<td>-0.86940</td>
<td>-0.69618</td>
<td>-0.46030</td>
<td>-0.23584</td>
</tr>
<tr>
<td>( \bar{H} )</td>
<td>0.01151</td>
<td>0.04043</td>
<td>0.07982</td>
<td>0.11357</td>
</tr>
<tr>
<td>( \Phi ) FOR ( \Phi = -0.05943 )</td>
<td>0.29553</td>
<td>0.40857</td>
<td>0.48739</td>
<td>0.53987</td>
</tr>
</tbody>
</table>
Graves has shown that the singular trajectory for the adiabatic problem is unstable with respect to the $v = V$ departure. We expect the same to be true for this problem. Since we primarily are interested in the case of $V$ being infinite, this would mean that $x_3$ could jump to the value 1 at $t = 1$. The variables $x_1$ and $x_2$ however would be continuous across the jump so this type of termination would not affect the objective function.

One major difference between the two possible controls ($x_3$ and $\dot{x}_3$) involves the final $v = 0$ segment that is predicted by both approaches. You will recall that $H$ was not necessarily maximized with respect to variations in $x_3$ on the $v = 0$ segment (see Section 4.3 and, in particular, Fig. 4.7). With $\dot{x}_3$ as the control, if $\lambda_3 < 0$ on the $v = 0$ segment, then $\bar{H}$ is maximized with respect to variations in $v$. For the situation shown in Fig. 4.7, $\bar{H}$ is maximized with respect to $v$ ($\lambda_3 < 0$ for $t_1 \leq t \leq 1$ and $\lambda_3(t_1) = 0$) while $H$ is not maximized with respect to $x_3$.

4.5 Attainable region study

The final state of an isothermal reactor is described by the values of $x_{1f}$, $x_{2f}$, $x_{3f}$, $q_{10}$, and $q_{20}$. For a situation where the kinetic parameters $G_1$, $G_2$, and $G_3$ and the feed flowrate $q_{10}$ and $q_{20}$ are fixed quantities, we can represent the final state as a point in the $(x_{1f}, x_{2f}, x_{3f})$ space. If we are not concerned with the value of $x_{3f}$, that is, the objective function is dependent on $x_{1f}$ and $x_{2f}$ only, then the final state is described by a point in the $(x_{1f}, x_{2f})$ plane.

\[ x_{1f} = x_i(m_f) = x_i(t = 1) \text{ for } i = 1, 2, 3. \]
We want to determine what final states can be attained when the feed stream of $A_1$ can be distributed in any manner as long as $\dot{x}_3 \geq 0$ and $0 \leq x_3 \leq 1$ for all $t$. In other words, find the attainable region (of final states) for an isothermal reactor with feed distribution.

Two specific types of control policies are used to generate final states which form a closed curve in the final state space. It is conjectured that these states are on the boundary of the attainable region. The first sort of control policy is the control which is optimal in the sense that an objective function of the linear form

$$F = x_{1f} - \varphi x_{2f}$$

is maximized. Corresponding to each value of $\varphi$ (e.g., $\varphi > \varphi_D$) for which $F$ is maximized there is a unique value of $x_3(0)$ which describes the optimal control policy for that $\varphi$. The limiting quantity $\varphi_D$ is defined as

$$\varphi_D = \lim_{x_3(0) \to 1} \left[ \frac{dx_{1f}}{dx_{2f}} \right]$$

where the optimal final state $(x_{1f}, x_{2f})$ is regarded as a function of $x_3(0)$ only.

The second type of control policy used to generate a locus of points in the final state space is the delayed dump policy. For this policy $x_3$ is given by

$$x_3(t) = \begin{cases} 0 & \forall \ t \in \left[ 0, t_D \right) \\ 1 & \forall \ t \in \left[ t_D, 1 \right] \end{cases}$$

(4.28)
where $t_D$ is the point at which the entire feed stream of $A_1$ is injected. Upon closer inspection of this policy it appears that such a policy is the control which is optimal in the sense that a linear objective function is minimized. There is an unique value of $t_D$ corresponding to each value of $\varphi$ for which the linear objective function given by equation (4.26) is minimized, provided that $\varphi_0 < \varphi < \varphi_E$. The quantities $\varphi_0$ and $\varphi_E$ are given by

$$\varphi_0 = \lim_{t_D \to 1^-} \left[ \frac{dx_{1f}}{dx_{2f}} \right] = \frac{a_1 \theta}{2a_3}$$

$$\varphi_E = \lim_{t_D \to 0^+} \left[ \frac{dx_{1f}}{dx_{2f}} \right]$$

where $x_{1f}$ and $x_{2f}$ are considered as functions of $t_D$ only. $\varphi_0$ is the value of $\varphi$ corresponding to the "time-optimal" dump reactor for $m_f \to 0^+$ (see Section 3.3 and Appendix III).

The dump policy ($x_3 = 1 \ \forall \ t \in [0, 1]$) is the limiting delayed dump policy for $t_D \to 0^+$ and the optimal control for $F$ being maximized for $\varphi = \varphi_D$. The final state $(x_{1f}, x_{2f})$ produced by the dump policy has the following properties:

1.) For $\varphi \geq \varphi_D$, the linear objective function given by equation (4.26) is maximized.

2.) For $\varphi \geq \varphi_E$, the linear objective function is minimized.

The no reaction policy ($x_3 = 0 \ \forall \ t \in [0, 1]$) is the delayed dump policy for the limiting case of $t_D \to 1^-$; it also is the optimal control for $F$ be maximized for $\varphi \to \infty$, which requires that $x_3(0) \to 0$. The final state for this policy is $x_{1f} = x_{2f} = 0$. 
For \( \Phi \leq \Phi_0 \), the linear objective function is minimized by the no reaction policy; the value of \( F \) is zero.

Therefore, by both minimizing and maximizing the linear objective function for all values of \( \Phi (\Phi < +\infty \) ) it is possible to generate a closed curve in the \((x_{1f}, x_{2f})\) plane. We assert that the closed curve forms the boundary of the attainable region. The most reasonable method of testing this assertion is to generate the closed curve for a particular set of kinetic and feed parameters and then attempt to attain a final state outside the closed curve by perturbing a control policy which produces a point on the curve. Of course, only certain types of perturbations are permissible because of the restrictions \( x_3 \geq 0 \) and \( 0 \leq x_3 \leq 1 \).

This perturbation procedure has been carried out for the case where \( G_1 = G_3 = 10.0, G_2 = 1.0, \) and \( \Theta = 1.0 \). The final states which are produced by optimal control policies for all values of \( \Phi \) and \( F \) being both minimized and maximized certainly do form a closed curve (see Fig. 4.8). The values of \( \Phi_D \) and \( \Phi_E \) are \(-0.772\) and \(+1.9302\), respectively. Equation (4.29) predicts that \( \Phi_0 = 0.5 \) exactly, and that value is confirmed in Fig. 4.8. Perturbations of the control policies associated with points A through H in Fig. 4.8 produce final states that are inside the closed curve. Hence, for this test case the assertion that the closed curve is the boundary of the attainable region is valid, and there is good reason to believe that the phenomenon will occur for any set of kinetic and feed parameters.

The attainable region for \( G_1 = G_3 = 10.0, G_2 = 1.0, \) and \( \Theta = 10.0 \) (see Fig. 4.9) is markedly smaller than the attainable region for the \( \Theta = 1.0 \) case (refer to Fig. 4.8). The values of \( \Phi_D \) and \( \Phi_E \) for the \( \Theta = 10.0 \) case are \( 1.31 \) and \( 11.21 \), respectively.
FIGURE 4.1  OPTIMAL CONTROL POLICY
AND CORRESPONDING CONVERSION PROFILES ($\theta=1.0$, $\phi=-0.0594$, $G_1 = G_3 = 10.0$, $G_2 = 1.0$)
\[ X_3(0) = 0.0750 \quad X_1(1) = 0.4108 \]
\[ X_3(1) = 0.6849 \quad X_2(1) = 0.1245 \]
\[ F = 0.2959 \]

**FIGURE 4.2** OPTIMAL CONTROL POLICY AND CORRESPONDING CONVERSION PROFILES (\( \theta = 1.0 \), \( \phi = 0.9225 \), \( G_1 = G_3 = 10.0 \), \( G_2 = 1.0 \))
FIGURE 4.3  COMPARISON OF OPTIMAL CONTROL POLICY AND DUMP POLICY \( (\theta = 1.0, \ G_1 = G_3 = 10.0, \ G_2 = 1.0) \)
Figure 4.4: Final states corresponding to optimal control with various $x_3(o)$ and $\theta (G_1=0.5, G_2=1.0)$.
FIGURE 4.5  THE HAMILTONIAN AS A FUNCTION OF \( x_3 \) FOR THE FIRST PART OF THE OPTIMAL TRAJECTORY ( \( \theta = 5.49, \phi = -0.00379, G_1 = 2.0, G_2 = 0, G_3 = 900.0 \) )
Figure 4.6 $H$ as a function of $x_3$ for the second part of the optimal trajectory ($\theta = 5.49$, $\phi = 0.00379$, $G_1 = 2.0$, $G_2 = 0$, $G_3 = 900$, $t = 0.8535$)
FIGURE 4.7  \( H \) AS A FUNCTION OF \( x_3 \) FOR THE SECOND PART OF THE OPTIMAL TRAJECTORY (\( \theta = 1.182 \), 
\( \phi = -0.69774 \), \( G_1 = 5.0 \), \( G_2 = 2.5 \), \( G_3 = 12.5 \))
**Figure 4.8** Attainable Region for $\theta = 1.0$, $G_1 = G_3 = 10.0$, $G_2 = 1.0$
FIGURE 4.9  ATTAINABLE REGION FOR $\theta = 10.0$, \\
$G_1 = G_3 = 10.0$, $G_2 = 1.0$
Chapter 5. FEED DISTRIBUTION FOR A REACTION SYSTEM WHICH INCLUDES A SECOND ORDER SIDE REACTION - \(q_{20}\) IS A FREE PARAMETER

In Chapter 4 we determined the optimal feed distribution for an isothermal tubular reactor in which the reaction system (4.1) takes place. The feed flowrates \(q_{10}\) and \(q_{20}\) were regarded as fixed quantities. It is conceivable that either or both flowrates could be freely chosen. Hence, we will explore the case in which \(q_{20}\) is a free parameter and \(q_{10}\) is fixed. Equivalently, \(\theta\) is a free parameter while \(q_{10}\) is fixed.

5.1 The objective function

The objective function

\[
F = F(t = 1) = x_1(1) - \varphi x_2(1)
\]

is to be maximized by the proper choice of the control \(x_3(t)\) and the free parameter \(\theta (\theta \geq 0)\). As in Chapter 4, \(x_3\) is constrained such that \(0 \leq x_3 \leq 1\) and \(\frac{dx_3}{dt} \geq 0\).

5.2 The optimal dump reactor

Consider \(G_1', G_2', G_3',\) and \(q_{10}\) as fixed quantities. For a given value of \(\varphi\) we wish to find the value of \(\theta\) for which \(F\) is maximized. This value of \(\theta\) is unique and positive whenever \(\varphi > \varphi_z\). The limiting value \(\varphi_z\) is defined by

\[
\varphi_z = \lim_{\theta \to 0} \left[ \frac{dx_{1f}}{d\theta} \right] = \lim_{\theta \to 0} \left[ \frac{dx_{2f}}{d\theta} \right] x_3 \equiv 1
\]

where \(x_{1f}\) and \(x_{2f}\) denote \(x_1(1)\) and \(x_2(1)\), respectively. For all
\[ \varphi \leq \varphi, \text{ F is negative for all positive } \theta \text{ and } F \text{ reaches its largest value (zero) when } \theta = 0. \]

For each \( \theta > 0 \), it is possible to evaluate the derivatives of \( x_{1f} \) and \( x_{2f} \) with respect to \( \theta \) by means of either a method from the calculus of variations or a procedure involving a finite difference approximation. These methods will be discussed in a later part of this section. Upon the evaluation of the derivatives, the equation

\[
\frac{dF}{d\theta} = \frac{dx_{1f}}{d\theta} - \varphi \frac{dx_{2f}}{d\theta} = 0 \quad (5.3)
\]

yields the value of \( \varphi \) corresponding to the objective function that is maximized by the value of \( \theta \) under investigation. In order to be certain that \( F \) has been maximized and not minimized with respect to \( \theta \) the second derivative of \( F \) with respect to \( \theta \) should be calculated; it should be negative (and always was in the examples calculated).

Normally, the value of \( \varphi \) is specified and the best value of \( \theta \) is unknown. The optimal \( \theta \) can be found by searching the range of possible \( \theta \) values \( (\theta > 0) \) until we find a value for which equation (5.3) and the second derivative of \( F \) test are satisfied.

5.2 a. Calculation of the derivatives of \( x_{1f} \) and \( x_{2f} \) with respect to \( \theta \) by a method of variational calculus

For the dump reactor the state equations can be written as

\[
\frac{dx_1}{dt} = \dot{x}_1 = f_1(x_1, x_2, x_3, \theta) \quad x_3 \equiv 1 \quad (5.4)
\]

\[
\frac{dx_2}{dt} = \dot{x}_2 = f_2(x_1, x_2, x_3, \theta) \quad x_3 \equiv 1 \quad (5.5)
\]
where \( f_1 \) and \( f_2 \) are given explicitly by equations (4.9) and (4.10).

Recall that \( x_1(0) = x_2(0) = 0 \).

The variation in the state variables \( x_1 \) and \( x_2 \) caused by a variation in the parameter \( \Theta \) is described by

\[
\dot{\mathbf{l}}(t) = A(t) \mathbf{l}(t) + \mathbf{h}(t); \quad \mathbf{l}(0) = 0 \quad (5.6 \text{ a, b})
\]

where \( \mathbf{l}(t) = \begin{bmatrix} l_1(t), l_2(t) \end{bmatrix}^T = \begin{bmatrix} \frac{dx_1}{d\Theta}(t), \frac{dx_2}{d\Theta}(t) \end{bmatrix}^T \),

\[
A(t) = \begin{bmatrix}
\frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} \\
\frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2}
\end{bmatrix}
\]

\( x_3 \equiv 1 \quad (5.7) \)

and \( \mathbf{h}(t) = \begin{bmatrix} h_1(t), h_2(t) \end{bmatrix}^T = \begin{bmatrix} \frac{\partial f_1}{\partial \Theta}(t), \frac{\partial f_2}{\partial \Theta}(t) \end{bmatrix}^T \),

\( x_3 \equiv 1 \quad (5.8) \)

(see Appendix IV). The elements of the matrix \( A \) and the vector \( \mathbf{h} \) are written out in Appendix V.

We desire the values of \( l_1 \) and \( l_2 \) at \( t = 1 \) for a set value of \( \Theta \); hence, we simultaneously integrate the state equations (5.4) and (5.5) and the equations for \( l_1 \) and \( l_2 \) using the boundary condition \( x_1(0) = x_2(0) = l_1(0) = l_2(0) = 0 \). The integration of these four equations by means of the Hamming predictor-corrector method requires approximately 10 seconds on the Burroughs B-5500 for a typical calculation.
5.2 b. Calculation of the derivatives of $x_{1f}$ and $x_{2f}$ with respect to $\Theta$ by a finite difference approximation

The value of $\Theta$ for which the derivatives $\frac{dx_{1f}}{d\Theta}$ and $\frac{dx_{2f}}{d\Theta}$ are to be determined is designated as $\Theta_0$. The derivatives can be approximated by using one of two centered finite difference expressions [24] given below:

$$\left. \frac{dx_{1f}}{d\Theta} \right|_{\Theta = \Theta_0} = \frac{1}{2\Delta\Theta} \left[ x_{1f}(\Theta_0 + \Delta\Theta) - x_{1f}(\Theta_0 - \Delta\Theta) \right] + o(\Delta\Theta^2) \text{ for } k = 1, 2 \tag{5.10}$$

$$\left. \frac{dx_{2f}}{d\Theta} \right|_{\Theta = \Theta_0} = \frac{1}{12\Delta\Theta} \left[ x_{2f}(\Theta_0 - 2\Delta\Theta) - 8x_{2f}(\Theta_0 - \Delta\Theta) + 8x_{2f}(\Theta_0 + \Delta\Theta) - x_{2f}(\Theta_0 + 2\Delta\Theta) \right] + o(\Delta\Theta^4) \text{ for } k = 1, 2 \tag{5.11}$$

Also, the second derivative with respect to $\Theta$ can be approximated by the following finite-difference formula:

$$\left. \frac{dx_{kf}}{d\Theta^2} \right|_{\Theta = \Theta_0} = \frac{1}{\Delta\Theta^2} \left[ x_{kf}(\Theta_0 - \Delta\Theta) - 2x_{kf}(\Theta_0) + x_{kf}(\Theta_0 + \Delta\Theta) \right] + o(\Delta\Theta^2) \text{ for } k = 1, 2 \tag{5.12}$$

For practically all the calculations, the fourth order formula for the first derivative with respect to $\Theta$ has been used rather than the second order expression. The dump reactor state equations (5.4) and (5.5) are integrated for the $\Theta$ values of $\Theta_0 - 2\Delta\Theta$, $\Theta_0 - \Delta\Theta$, $\Theta_0$, $\Theta_0 + \Delta\Theta$, and $\Theta_0 + 2\Delta\Theta$. 

\[ \Theta_0, \ \Theta_0 + \Delta \Theta, \ \text{and} \ \Theta_0 + 2 \Delta \Theta; \] these ten differential equations can be solved simultaneously. The resulting \( x_{1f} \) and \( x_{2f} \) values are then inserted into equations (5.11) and (5.12) from which the first and second derivatives with respect to \( \Theta \) are obtained. This method requires about 5 seconds on the B-5500; therefore, it is roughly twice as fast as the variational calculus method of finding the desired derivatives. It should be remembered that the slower method is also an exact method.

5.2 c. Results

Most of the results for the optimal dump problem will be presented in Section 5.4, where the dump reactor for which \( \Theta \) is chosen optimally will be compared with the distributed reactor for which the control \( x_3 \) and the parameter \( \Theta \) are optimal selections. However, the results of one optimal dump study are presented in this section.

The dimensionless kinetic constants are \( G_1 = G_3 = 2.0 \) and \( G_2 = 1.0 \). The values of \( x_{1f} \) and \( x_{2f} \) for a large range of \( \Theta \) values are displayed in Figure 5.1. Using the finite difference method discussed in Section 5.2, b, the \((\Theta, \Phi)\) pairs for which \( F \) is maximized with respect to \( \Theta \) have been found (see Fig. 5.2). From Fig. 5.2, we see that the value of \( \Phi_2 \) is approximately \(-0.69\). Consequently, for \( \Phi \leq -0.69 \), \( F \) is maximized by \( \Theta = 0 \) (i.e., reactant \( A_2 \) should not be fed to the reactor at all).

Several general conclusions pertaining to the optimal dump reactor can be made on the basis of the representative case just described and numerous others. It has been concluded that:

1.) \( \Phi_2 \geq -1 \) for any combination of \( G_1, G_2, \) and \( G_3 \).
2.) For \( \varphi \leq \varphi_Z \), the optimal value of \( \Theta \) and the objective function are both zero. \( F \) would be negative for any positive value of \( \Theta \).

3.) The optimal value of \( F \) is positive, provided that

\[ \varphi > \varphi_Z . \]

4.) As \( \varphi \) increases ( \( \varphi > \varphi_Z \)), the optimal \( \Theta \) increases and the optimal \( F \) decreases.

5.3 The optimal distributed reactor

The quantities \( G_1, G_2, G_3, q_{10}, \) and \( \varphi \) are specified, and we wish to find the combination of the control \( x_3 \) and the free parameter \( \Theta \) which maximizes the objective function. As in the dump reactor problem of the previous section, there are two methods that may be applied to the distributed reactor problem; they are the method from the calculus of variations and the method involving finite difference approximations. The variational method is discussed first.

5.3. a. Solution by means of a variational method

In order to maximize \( F \) with respect to the control \( x_3 \), the Hamiltonian

\[ H = H(t) = \lambda_1 \varphi_1 (x_1, x_2, x_3, \Theta) + \lambda_2 \varphi_2 (x_1, x_2, x_3, \Theta) \]

(5.13)
must be maximized by the proper choice of \( x_3(t) \) at all positions \( t \).

The control is constrained such that \( 0 \leq x_3 \leq 1 \) and \( \dot{x}_3 \geq 0 \). According to the analysis of Section 4.1, the optimal control policy for a fixed value of \( \Theta \) can be represented as

\[ x_3(t) = \begin{cases} u(x_1, x_2, \mathcal{L}, \Theta) & \text{for } 0 \leq t \leq t_1 \\ 1 & \text{for } t_1 \leq t \leq 1 \end{cases} \]

(5.14)
where \( u \) is the value of \( x_3 \) for which \( \frac{\lambda H}{\lambda x_3} = 0 \), \( \Lambda \) is the quotient \( \lambda_2/\lambda_1 \), and \( t_1 \) is the position at which \( u = 1 \) exactly. \( u (x_1, x_2, \Lambda, \Theta) \) is written out in Appendix VI.

The differential equations for \( x_1, x_2, \) and \( \Lambda \) are written as

\[
\begin{align*}
\dot{x}_1 &= f_1 (x_1, x_2, x_3, \Theta) \\
\dot{x}_2 &= f_2 (x_1, x_2, x_3, \Theta) \\
\dot{\Lambda} &= f_3 (x_1, x_2, x_3, \Lambda, \Theta)
\end{align*}
\]  

(5.15)  
(5.16)  
(5.17)

where \( x_3 \) is given by equation (5.14) and

\[
f_3 = \Lambda \left[ \frac{\lambda f_1}{\lambda x_1} - \frac{\lambda f_2}{\lambda x_2} \right] + \Lambda^2 \frac{\partial f_2}{\partial x_1} - \frac{\partial f_1}{\partial x_2}
\]  

(5.18)

(see Appendix V for the explicit expressions of \( \frac{\lambda f_1}{\lambda x_1} \) and the rest as functions of \( x_1, x_2, x_3, \) and \( \Theta \)). It is possible to rewrite the differential equations in terms of \( x_1, x_2, \Lambda, \) and \( \Theta \) only by inserting equation (5.14) into equations (5.15) through (5.17). The resulting equations are of the form

\[
\begin{align*}
\dot{x}_1 &= f_1^* (x_1, x_2, \Lambda, \Theta) \\
\dot{x}_2 &= f_2^* (x_1, x_2, \Lambda, \Theta) \\
\dot{\Lambda} &= f_3^* (x_1, x_2, \Lambda, \Theta)
\end{align*}
\]  

(5.19)  
(5.20)  
(5.21)

The solution of these equations are dependent upon \( t, \) the initial conditions, and the parameter \( \Theta \). The variation of the solution caused by a variation of the parameter \( \Theta \) (no variation in the initial conditions) is represented by the column vector \( \text{J} \) whose components are
\[ l_1 (t) = \frac{\lambda x_1}{\lambda \theta} (t) \quad ; \quad l_2 (t) = \frac{\lambda x_2}{\lambda \theta} (t) \quad ; \quad l_3 (t) = \frac{\lambda \Lambda}{\lambda \theta} (t) \quad . \]

The differential vector equation and boundary condition for \( l \) are

\[ \dot{l} (t) = W (t) l (t) + h (t) \quad ; \quad l (0) = 0 \quad (5.23 \text{ a, b}) \]

for which the \( 3 \times 3 \) matrix \( W \) is given by

\[
W (t) = \begin{bmatrix}
\frac{\lambda f_{11}}{\delta x_1} & \frac{\lambda f_{12}}{\delta x_2} & \frac{\lambda f_{13}}{\delta \Lambda} \\
\frac{\lambda f_{21}}{\delta x_1} & \frac{\lambda f_{22}}{\delta x_2} & \frac{\lambda f_{23}}{\delta \Lambda} \\
\frac{\lambda f_{31}}{\delta x_1} & \frac{\lambda f_{32}}{\delta x_2} & \frac{\lambda f_{33}}{\delta \Lambda}
\end{bmatrix} \quad (5.24)
\]

and

\[ h_i (t) = \frac{\lambda f_{i3}}{\lambda \theta} \text{ for } i = 1, 2, 3. \quad (5.25) \]

The derivatives of the \( f_i^* (x_1, x_2, \Lambda, \theta) \) with respect to each argument can be written out explicitly as a function of the arguments; but the explicit expressions are quite complicated and must be derived for two situations, \( x_3 = u (x_1, x_2, \Lambda, \theta) \) and \( x_3 = 1 \). It is easier to evaluate the derivatives of \( f_i^* (x_1, x_2, \Lambda, \theta) \) by the chain rule differentiation of \( f_i (x_1, x_2, x_3, \theta) \), \( f_2 (x_1, x_2, x_3, \theta) \), and \( f_3 (x_1, x_2, x_3, \Lambda, \theta) \). Suppose a vector \( y \) is defined such that

\[ y_1 = x_1 \quad ; \quad y_2 = x_2 \quad ; \quad y_3 = \Lambda \quad (5.26) \]

and another vector \( \xi \) is defined such that
\[ p_1 = y_1 ; \quad p_2 = y_2 ; \quad p_3 = y_3 ; \quad p_4 = x_3. \]  \hspace{1cm} (5.27)

Therefore, using the chain rule for differentiation, we get
\[ \frac{\lambda f_i^*}{\delta y_k} = \frac{\lambda f_i}{\delta y_k} + \frac{\lambda f_4}{\delta x_3} \frac{\lambda p_4}{\delta y_k} \quad i, k = 1, 2, 3 \]  \hspace{1cm} (5.28)
\[ \frac{\lambda f_i^*}{\lambda \theta} = \frac{\lambda f_i}{\lambda \theta} + \frac{\lambda f_4}{\delta x_3} \frac{\lambda p_4}{\lambda \theta} \quad i = 1, 2, 3 \]  \hspace{1cm} (5.29)

From equation (5.14) we observe that
\[ \frac{\lambda p_4}{\delta y_k} = \frac{\lambda x_3}{\delta y_k} = \begin{cases} \frac{\lambda u (y, \theta)}{\delta y_k} & 0 \leq t < t_1 \\ 0 & t_1 \leq t \leq 1 \end{cases} \]  \hspace{1cm} (5.30)

and
\[ \frac{\lambda p_4}{\lambda \theta} = \frac{\lambda x_3}{\lambda \theta} = \begin{cases} \frac{\lambda u (y, \theta)}{\lambda \theta} & 0 \leq t < t_1 \\ 0 & t_1 \leq t \leq 1 \end{cases} \]  \hspace{1cm} (5.31)

Equations (5.15) and (5.16) reveal that
\[ \frac{\lambda f_i}{\delta y_3} = \frac{\lambda f_4}{\delta \lambda} = 0 \quad \text{for } i = 1, 2. \]  \hspace{1cm} (5.32)

The formulas for \( \frac{\lambda f_4}{\delta x_1}, \frac{\lambda f_4}{\delta x_2}, \frac{\lambda f_4}{\delta x_3}, \) and \( \frac{\lambda f_4}{\lambda \theta} \) with \( i = 1 \) or \( 2 \) are listed in Appendix V. The derivatives of \( u \) and \( f_3 \) are derived in Appendices VI and VII, respectively.

For a set value of \( \Theta \), equations (5.15) through (5.17) and equation (5.23a) with \( x_3 \) given by equation (5.14) can be integrated simultaneously using the fourth order Hamming predictor-corrector
procedure. The resulting trajectory is optimal with respect to \( x_3 \) for the value of \( \varphi \), call it \( \varphi^{(1)} \), that is equal to \( -\Lambda \) (1). Also, the trajectory yields the value of the quotient \( l_1 (1)/l_2 (1) \), which we define as \( \varphi^{(2)} \). If \( x_3 (0) \) and \( \Theta \) are chosen correctly, then \( \varphi^{(1)} = \varphi^{(2)} \) and the trajectory is optimal with respect to both \( x_3 \) and the free parameter \( \Theta \) for \( \varphi = \varphi^{(1)} = \varphi^{(2)} \).

In the normal situation, \( \varphi \) is specified; consequently, a two-dimensional search in the \((x_3 (0), \Theta)\) space must be conducted in order to find the trajectory for which \( \varphi^{(1)} = \varphi \) and \( \varphi^{(2)} = \varphi \). The values of \( x_3 (0) \) and \( \Theta \) used to initiate this search are crucial. If they are not reasonably close to the correct values, the search will either diverge or converge with agonizing slowness.

A second approach involves an one-dimensional search. A value of \( x_3 (0) \) is chosen and then a search is conducted for a value of \( \Theta \) which yields a \( \varphi^{(1)} = \varphi^{(2)} \) situation. This procedure is repeated for several values of \( x_3 (0) \) until several optimal \((x_3 (0), \Theta)\) pairs corresponding to different values of \( \varphi \) are known. Then the optimal values of \( x_3 (0) \) and \( \Theta \) for a specific value of \( \varphi \) can be obtained by means of interpolation (e.g., a 5-point Lagrangian interpolation). Normally, this approach is very effective; however, for some combinations of the kinetic parameters \((G_1, G_2, \text{ and } G_3)\), there is no \( \Theta \) such that \( \varphi^{(1)} = \varphi^{(2)} \) when low values of \( x_3 (0) \) are examined. Also, when larger values of \( x_3 (0) \) are considered for the same kinetics, two values of \( \Theta \) are optimal values (see Fig. 5.3).

5.3. b. Solution by means of a finite difference method

The reasoning involved in this method is best explained by examining the portion of the \((x_{1f}, x_{2f})\) plane which contains the final
state that is optimal with respect to both the control $x_3$ and the free parameter $\Theta$ for a specific value of $\varphi$. Suppose, for example, that $\varphi = 0$ and the optimal final state is point C in Figure 5.4; the optimal pair of $x_3(0)$ and $\Theta$ values is designated as $(x_3^0(0), \Theta_o)$. The points A through E are the final states which are optimal with respect to $x_3$ for $\Theta$ values of $\Theta_o - 2 \Delta \Theta$, $\Theta_o - \Delta \Theta$, $\Theta_o$, $\Theta_o + \Delta \Theta$, and $\Theta_o + 2 \Delta \Theta$, respectively. If the control function associated with point C is designated as $x_3^0$, then the points F, G, H, and I are the final states for which the control is $x_3^0$ and $\Theta$ is $\Theta_o - 2 \Delta \Theta$, $\Theta_o - \Delta \Theta$, $\Theta_o + \Delta \Theta$, and $\Theta_o + 2 \Delta \Theta$, respectively. Regardless of the exact form of the curve connecting points F, G, C, H, and I (the dashed curve in Fig. 5.4), the tangent to that curve at point C must coincide with the tangent to the curve connecting points A through E (the solid curve in Fig. 5.4). The slope of the dashed curve is given by

$$\varphi(3) \equiv \left[ \frac{dx_{1f}}{d \Theta} / \frac{dx_{2f}}{d \Theta} \right] \bigg|_{x_3 \equiv 0} \quad (5.33)$$

and the slope of the solid curve is $\varphi(2)$. We see that

$$\varphi(1) = \varphi(2) = \varphi(3) = \varphi = 0$$

at point C. Therefore, for any specified value of $\varphi$, there exists an optimal $(x_3(0), \Theta)$ pair for which $\varphi(1) = \varphi(3) = \varphi$.

The simplest way to evaluate $\varphi(3)$ for a particular $(x_3(0), \Theta)$ combination is to use the following finite difference formula:
\[
\varphi(3) \equiv \begin{bmatrix}
    x_{1f}(\theta - 2\Delta\theta) - 8x_{1f}(\theta - \Delta\theta) + 8x_{1f}(\theta + \Delta\theta) \\
    - x_{1f}(\theta + 2\Delta\theta) \\
    x_{2f}(\theta - 2\Delta\theta) - 8x_{2f}(\theta - \Delta\theta) + 8x_{2f}(\theta + \Delta\theta) \\
    - x_{2f}(\theta + 2\Delta\theta)
\end{bmatrix}
\delta x_3 \equiv 0
\]

(5.34)

In order to evaluate \( \varphi(1) \) and \( \varphi(3) \) for a particular combination of \( x_3(0) \) and \( \Theta (\Theta \equiv \Theta_o) \), it is necessary to simultaneously integrate the two state equations for \( \Theta = \Theta_o - 2\Delta\Theta \), \( \Theta_o - \Delta\Theta \), \( \Theta_o \), \( \Theta_o + \Delta\Theta \), and \( \Theta_o + 2\Delta\Theta \) and the adjoint equation for \( \Theta = \Theta_o \) with the control given by equation (5.14) and the \( x_1, x_2 \), and \( \Delta \) values for \( \Theta = \Theta_o \). The finite difference evaluation of \( \varphi(1) \) and \( \varphi(3) \) is approximately twice as fast as the variational determination of \( \varphi(1) \) and \( \varphi(2) \).

In the normal situation \( \varphi \) is specified and the \((x_3(0), \Theta)\) pair for which \( \varphi(1) = \varphi(3) = \varphi \) must be found. As indicated in Section 5.3.a, a 2-dimensional search in the \((x_3(0), \Theta)\) space is very difficult. A more workable scheme is the following:

1.) Choose a value of \( x_3(0) \) and then search for a value of \( \Theta \) for which \( \varphi(1) = \varphi(3) \).

2.) Repeat for several values of \( x_3(0) \).

3.) Interpolate these results to obtain the solution for the specified \( \varphi \).

This is the method used for virtually all of the calculations for the distributed reactor with \( \Theta \) being considered as a free parameter.
5.3. c. Results

In many kinetic situations (e.g., $g_1 = g_2 = 1.0$ and $g_3 = 25.0$) the quantity $\varphi(3) - \varphi(1)$, when evaluated for a specific value of $x_3(0)$, depends on $\Theta$ in the manner shown in Figure 5.5. There is only one value of $\Theta$ for which $\varphi(3) = \varphi(1)$ for a particular value of $x_3(0)$. Of course the combination of $x_3(0)$ and $\Theta$ which result in $\varphi(3) = \varphi(1)$ is the optimal $(x_3(0), \Theta)$ pair for $\varphi = \varphi(3) = \varphi(1)$.

There are other kinetic situations where $\varphi(3) - \varphi(1)$ does not have the form indicated in Figure 5.5. Depending upon the value of $x_3(0)$ being considered there are zero, one, or two $\Theta$ values for which $\varphi(3) = \varphi(1)$. Consider the case where $g_1 = g_3 = 2.0$ and $g_2 = 1.0$. When $x_3(0)$ is less than 0.799, it is not possible to find a finite $\Theta$ for which $\varphi(3) = \varphi(1)$ (see Fig. 5.6). For $x_3(0) = 0.799$ there is one value of $\Theta$, namely 2.4, which yields $\varphi(3) = \varphi(1)$ (see Fig. 5.7). If $x_3(0)$ is greater than 0.799, two separate values of $\Theta$ are optimal values corresponding to different values of $\varphi$. For example, in the case of $x_3(0) = 0.850$, there is a solution at $\Theta = 1.346$ ($\varphi = -0.1764$) and another solution at $\Theta = 6.102$ ($\varphi = 1.399$).

Whether or not this double root phenomenon occurs for any values of $x_3(0)$ is dependent on the values of $g_1$, $g_2$, and $g_3$. Table 5.A summarized the frequency of this phenomenon occurring in the kinetic situations that were studied.

Figure 5.3 is a plot of the optimal values of $x_3(0)$ and
Table 5.A Occurrence of the double root phenomenon
for different kinetic parameters

<table>
<thead>
<tr>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
<th>DOES THE DOUBLE ROOT SITUATION OCCUR?</th>
<th>VALUE OF $x_3(0)$ BELOW WHICH NO ROOTS EXIST</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>1.</td>
<td>5.</td>
<td>YES (?)</td>
<td>0.50</td>
</tr>
<tr>
<td>2.</td>
<td>1.</td>
<td>2.</td>
<td>YES</td>
<td>0.799</td>
</tr>
<tr>
<td>5.</td>
<td>2.5</td>
<td>12.5</td>
<td>YES</td>
<td>0.485</td>
</tr>
<tr>
<td>5.</td>
<td>12.5</td>
<td>12.5</td>
<td>YES</td>
<td>0.645</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>12.5</td>
<td>YES</td>
<td>0.29</td>
</tr>
<tr>
<td>1.</td>
<td>1.</td>
<td>25.</td>
<td>NO</td>
<td>-</td>
</tr>
<tr>
<td>1.</td>
<td>0.</td>
<td>100.</td>
<td>NO</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.</td>
<td>900.</td>
<td>NO</td>
<td>-</td>
</tr>
</tbody>
</table>
\( \Theta \) versus \( \Phi \) for the kinetics described by \( G_1 = G_3 = 2.0 \) and \( G_2 = 1.0 \).

A similar plot for the case where \( G_1 = G_2 = 1.0 \) and \( G_3 = 25.0 \) is shown in Figure 5.8. The values of \( t_1 \) and \( F \) for the optimal trajectories of the latter kinetics situation appear in Figure 5.9.

Eight different sets of kinetic parameters \((G_1, G_2, \text{ and } G_3)\) have been investigated thoroughly. On the basis of these studies, the following conclusions concerning the optimal distributed reactor are made:

1.) \( F > 0 \) although it may be very small when \( \Phi \) is large.
2.) \( t_1 < 1 \).
3.) \( x_3(1) = 1 \).
4.) As the optimal \( \Theta \) approaches 0, the optimal \( x_3(0) \) approaches zero for systems which do not display the double root phenomenon.
5.) For systems which exhibit the double root phenomenon, the optimal \( x_3(0) \) approaches one as the optimal \( \Theta \) approaches zero.
6.) \( x_3(0) \to 1 \) as the optimal \( \Theta \) approaches infinity.
7.) As \( \Phi \) increases, \( t_1 \) and \( \Theta \) increases and \( F \) decreases.

5.4 Comparison of the optimal distributed reactor and the optimal dump reactor

For all positive and most negative values of \( \Phi \) the performance of the optimal distributed reactor for the case that \( \Theta \) is a free parameter is better than that of the optimal dump reactor for the same \( \Phi \), \( G_1 \), \( G_2 \), and \( G_3 \). The most convenient measure of the improvement in the objective function that can be affected by the distribution of the feed stream of \( A_1 \) is the quantity \( I \) given by
\[ I = \frac{\Delta F}{F_D} \times 100\% \quad (5.35) \]

for which \( \Delta F \) is the difference between the objective function for the optimal distributed reactor and the objective function \( (F_D) \) for the optimal dump reactor. Both \( \Delta F \) and \( I \) for a large range of \( \varphi \) and a typical kinetic situation \( (G_1 = G_2 = 2.5 \text{ and } G_3 = 12.5) \) are shown in Figure 5.10. The largest percentage improvement is 1.9% which occurs for \( \varphi = + 0.02 \); the optimal \( \Theta \) and \( x_3(0) \) for the distributed reactor are 2.80 and 0.50, respectively. Figure 5.11 indicates that the optimal value of \( \Theta \) for the distributed reactor \( (\Theta_{\text{OPT}}) \) is less than or equal to the optimal \( \Theta \) for the dump reactor \( (\Theta_D) \) for all values of \( \varphi \). Also, the quotient \( \frac{\Theta_D - \Theta_{\text{OPT}}}{\Theta_D} \) reaches its largest value in the neighborhood of \( \varphi = 0 \); therefore, we infer that the quotient is maximized at the value of \( \varphi \) associated with maximum percentage improvement in the objective function. This inference has been verified for each of the eight sets of kinetic parameters that were studied.

The percentage improvement in the objective function depends on the values of \( \varphi, G_1, G_2, \text{ and } G_3 \). Referring to Table 5.B we see that the largest value of \( I \) for both \( \varphi = -0.25 \) and \( \varphi = 0 \) occurs for the case where \( G_1 = 2.0, G_2 = 0, \text{ and } G_3 = 900.0 \). For \( \varphi = +0.25 \) through \( \varphi = +1.50, I \) is largest when \( G_1 = 5.0, G_2 = 2.5, \) and \( G_3 = 12.5 \). Using the results indicated in the table to predict I for a set of kinetic parameters that has not been examined is
Table 5.B Percentage improvement in the objective function for various kinetics

<table>
<thead>
<tr>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
<th>-0.25</th>
<th>0</th>
<th>0.25</th>
<th>0.50</th>
<th>0.75</th>
<th>1.00</th>
<th>1.25</th>
<th>1.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>1.</td>
<td>2.</td>
<td>0.005</td>
<td>0.0625</td>
<td>0.15</td>
<td>0.18</td>
<td>0.21</td>
<td>0.215</td>
<td>0.20</td>
<td>0.19</td>
</tr>
<tr>
<td>5.</td>
<td>12.5</td>
<td>12.5</td>
<td>0.158</td>
<td>0.474</td>
<td>0.702</td>
<td>0.89</td>
<td>0.895</td>
<td>0.81</td>
<td>0.69</td>
<td>0.57</td>
</tr>
<tr>
<td>2.</td>
<td>1.</td>
<td>5.</td>
<td>0.39</td>
<td>0.693</td>
<td>0.66</td>
<td>0.87</td>
<td>0.31</td>
<td>0.215</td>
<td>0.15</td>
<td>0.115</td>
</tr>
<tr>
<td>5.</td>
<td>2.5</td>
<td>12.5</td>
<td>0.94</td>
<td>1.33</td>
<td>1.59</td>
<td>1.575</td>
<td>1.37</td>
<td>1.10</td>
<td>0.87</td>
<td>0.68</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>12.5</td>
<td>1.33</td>
<td>1.89</td>
<td>1.35</td>
<td>0.61</td>
<td>0.295</td>
<td>0.161</td>
<td>0.100</td>
<td>0.068</td>
</tr>
<tr>
<td>1.</td>
<td>1.</td>
<td>25.</td>
<td>3.00</td>
<td>5.07</td>
<td>0.072</td>
<td>0.009</td>
<td>0.003</td>
<td>0.0015</td>
<td>0.001</td>
<td>≤ 0.001</td>
</tr>
<tr>
<td>1.</td>
<td>0.</td>
<td>100.</td>
<td>3.9</td>
<td>9.42</td>
<td>0.007</td>
<td>0.001</td>
<td>≤ 0.001</td>
<td>≤ 0.001</td>
<td>≤ 0.001</td>
<td>≤ 0.001</td>
</tr>
<tr>
<td>2.</td>
<td>0.</td>
<td>900.</td>
<td>4.79</td>
<td>14.68</td>
<td>0.002</td>
<td>≤ 0.001</td>
<td>≤ 0.001</td>
<td>≤ 0.001</td>
<td>≤ 0.001</td>
<td>≤ 0.001</td>
</tr>
</tbody>
</table>
very risky since Table 5.3 itself provides at least one example of how unreliable predictions can be. For the case where \( \phi = +0.25 \), the first five sets of parameters suggest that \( \frac{\dot{I}}{I K_1} \) and \( \frac{\dot{I}}{I K_2} \) are negative and \( \frac{\dot{I}}{I K_3} \) is positive. Using these relationships and the fact that \( I = 0.08\% \) for \( \vec{G} = (1.0, 1.0, 25.0) \), it could be predicted that \( I > 0.08 \) for \( \vec{G} = (1.0, 0., 100.0) \). In fact, \( I \) is much less than 0.08 and the prediction fails. Therefore, such predictions should be made only if the untested \( \vec{G} \) is in the neighborhood of a \( \vec{G} \) vector which has been examined.

The study of the different combinations of \( G_1, G_2 \), and \( G_3 \) was carried out with the idea of finding a set of parameters for the maximum \( I \) is large. The largest improvement found was 14.9% when \( \phi = -0.01 \) and \( \vec{G} = (2., 0., 900.;) \). The maximum \( I \) for the different \( G \) vectors are shown in Table 5.3. These results suggest that \( I \) is large when \( \phi \) is zero and \( K_3 \) is much greater than \( K_1 \) and \( K_2 \) (the ratio \( K_1 : K_2 \) apparently is not very important). Accordingly, the \( \phi = 0 \) results were analyzed more thoroughly (refer to Table 5.4). We infer that \( I \) is large when \( K_3 \gg K_1, K_3 \gg K_2 \), and \( \phi \) is close to zero. In these situations \( x_3 \) (0) is nearly zero, \( \theta_d \gg \theta_{OPT} \), \( t_1 \) is close to one, \( x_1 \) (1) is very small, and \( x_2 \) (1) is almost one.

Thus, we conclude that the distribution of \( A_1 \) along the length of the isothermal reactor for which \( \theta \) is a free parameter leads to a significant improvement over the dump reactor only in extreme situations; i.e., when the waste
<table>
<thead>
<tr>
<th>$G_1$</th>
<th>$G_2$</th>
<th>$G_3$</th>
<th>MAX. VALUE OF I</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>1.</td>
<td>2.</td>
<td>0.213%</td>
<td>0.885</td>
</tr>
<tr>
<td>2.</td>
<td>1.</td>
<td>5.</td>
<td>0.72</td>
<td>0.107</td>
</tr>
<tr>
<td>5.</td>
<td>12.5</td>
<td>12.5</td>
<td>0.90</td>
<td>0.62</td>
</tr>
<tr>
<td>5.</td>
<td>2.5</td>
<td>12.5</td>
<td>1.61</td>
<td>0.348</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>12.5</td>
<td>1.89</td>
<td>0.02</td>
</tr>
<tr>
<td>1.</td>
<td>1.</td>
<td>25.</td>
<td>5.38</td>
<td>-0.03</td>
</tr>
<tr>
<td>1.</td>
<td>0.</td>
<td>100.</td>
<td>9.66</td>
<td>-0.01</td>
</tr>
<tr>
<td>2.</td>
<td>0.</td>
<td>900.</td>
<td>14.9</td>
<td>-0.01</td>
</tr>
</tbody>
</table>
Table 5.D Summary of \( \varphi = 0 \) results

<table>
<thead>
<tr>
<th>( G_1 )</th>
<th>( G_2 )</th>
<th>( G_3 )</th>
<th>( I ) (°)</th>
<th>( x_3(0) )</th>
<th>( \Theta )</th>
<th>( t_1 )</th>
<th>( x_1(1) )</th>
<th>( x_2(1) )</th>
<th>( x_1(1) )</th>
<th>( x_2(1) )</th>
<th>( F )</th>
<th>( \Theta_D )</th>
<th>( \Theta_D - \Theta_{opt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>1.</td>
<td>2.</td>
<td>0.0625</td>
<td>0.808</td>
<td>1.802</td>
<td>0.157</td>
<td>0.293</td>
<td>0.249</td>
<td>0.542</td>
<td>0.293</td>
<td>1.835</td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>12.5</td>
<td>12.5</td>
<td>0.474</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>1.</td>
<td>5.</td>
<td>0.693</td>
<td>0.610</td>
<td>2.075</td>
<td>0.332</td>
<td>0.2555</td>
<td>0.385</td>
<td>0.640</td>
<td>0.2555</td>
<td>2.292</td>
<td>0.218</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>2.5</td>
<td>12.5</td>
<td>1.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>12.5</td>
<td>1.89</td>
<td>0.491</td>
<td>2.696</td>
<td>0.445</td>
<td>0.247</td>
<td>0.471</td>
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reaction is strongly favored by the kinetics. In most situations the selection of the value of the free parameter \( \Theta \) is far more important in determining how to operate the isothermal reactor than is the distribution of the reactant \( A_1 \).
FIGURE 5.1  FINAL STATES FOR THE DUMP REACTOR ($G_1 = G_3 = 2.0$,
$G_2 = 1.0$)
FIGURE 5.2
PROPERTIES OF THE OPTIMAL DUMP REACTOR
($G_1 = G_3 = 2.0$, $G_2 = 1.0$)
FIGURE 5.3  OPTIMAL \((x_3(o), \theta)\) PAIRS FOR VARIOUS \(\phi\) \((G_1 = G_3 = 2.0, G_2 = 1.0)\)
FIGURE 5.4 \( \phi^{(1)} = \phi^{(2)} = \phi^{(3)} = 0 \) AT POINT C
FIGURE 5.5  TYPICAL PLOT OF $\phi^{(3)} - \phi^{(1)}$ FOR VARIOUS $\theta$ VALUES AT CONSTANT $x_3(0)$
FIGURE 5.6  PLOT OF $\phi^{(3)} - \phi^{(1)}$ VERSUS $\theta$ ( $x_3(o)=0.50$, $G_1=G_3=2.0$, $G_2=1.0$ )
FIGURE 5.7  PLOT OF $\phi^{(3)} - \phi^{(1)}$ VERSUS $\theta$  
( $x_3(0) = 0.799$, $G_1 = G_3 = 2.0$, $G_2 = 1.0$)
Figure 5.8 Optimal values of $x_3(0)$ and $\theta$ for various $\phi$

($G_1 = G_2 = 1.0$, $G_3 = 25.0$)
FIGURE 5.9 VALUES OF $t_1$ AND $F$ CORRESPONDING OPTIMAL TRAJECTORIES FOR VARIOUS $\phi$

($G_1 = G_2 = 1.0$, $G_3 = 25.0$)
FIGURE 5.10
IMPROVEMENT IN THE OBJECTIVE FUNCTION
($g_1 = g_2 = 2.5$, $g_3 = 12.5$)
FIGURE 5.11 COMPARISON OF $\phi_{OPT}$ AND $\phi_D$ ($G_1=G_2=2.5$, $G_3=12.5$)
REFERENCES


Appendix I. DETERMINATION OF THE FIRST VARIATION IN THE
OBJECTIVE FUNCTION INDUCED BY VARIATIONS IN
THE CONTROL VARIABLE

State equations (2):
\[ \dot{x} = f(x, u) \quad ; \quad x(0) = \xi \]  \hspace{1cm} (I.1 a, b)

Objective function:
\[ F = F(x(m_f)) \]  \hspace{1cm} (I.2)

Adjoint equations (2):
\[ \dot{\lambda} = -\lambda \frac{\delta f}{\delta x} \quad ; \quad \lambda (m_f) = \frac{\lambda F}{\delta x (m_f)} \]  \hspace{1cm} (I.3 a, b)

where \( x, \xi, \) and \( \xi \) are column vectors of dimension 2. \( \lambda \) and \( \delta \) are row vectors of dimension 2. \( \frac{\delta f}{\delta x} \) is a 2 x 2 matrix. The element in the \( i \)th row and the \( j \)th column is \( \frac{\delta f_i}{\delta x_j} \).

According to the Lagrange multiplier theorem, we may write
\[ F = F - \int_0^{m_f} \lambda (m) \left[ \dot{x} - f(x, u) \right] \, dm \]  \hspace{1cm} (I.4)

where \( \lambda \) is a column vector of Lagrange multipliers. For variations in \( x \) and \( u \),
\[ \delta F = \frac{\delta F}{\delta x (m_f)} \delta x (m_f) - \int_0^{m_f} \lambda \left[ \delta \dot{x} - \frac{\delta f}{\delta x} \delta x - \frac{\delta f}{\delta u} \delta u \right] \, dm. \]  \hspace{1cm} (I.5)

Integration by parts yields
\[ -\int_0^{m_f} \lambda \delta x \, dm = -\lambda (m_f) \delta x (m_f) + \lambda (0) \delta x (0) \]
\[ + \int_0^{m_f} \lambda \delta x \, dm \]  \hspace{1cm} (I.6)
Substitution of equation (I.6) into equation (I.5) gives

\[
\delta F = \left[ \frac{\partial F}{\partial x} (m_x) - \lambda (m_x) \right] \delta x (m_x) + \lambda (0) \delta x (0) \\
+ \int_{0}^{m_f} \left[ \lambda + \lambda \frac{f_x}{3x} \right] \delta x \, dm + \int_{0}^{m_f} \lambda \frac{f_x}{3u} \delta u \, dm .
\]  

(1.7)

If \( \lambda \) is chosen to be equal to \( \mu \) (the adjoint vector), then equation (I.7) becomes

\[
\delta F = \mu(0) \delta x (0) + \int_{0}^{m_f} \mu \frac{f_x}{3u} \delta u \, dm .
\]  

(1.8)

The choice of \( u \) has no effect on \( x (0) \); therefore,

\[
\delta F = \int_{0}^{m_f} \left[ \mu_1 \frac{f_{1x}}{3u} + \mu_2 \frac{f_{2x}}{3u} \right] \delta u \, dm .
\]  

(1.9)
Appendix II. DETAILED INFORMATION CONCERNING OPTIMAL TRAJECTORIES FOR VARIOUS $m_f$

Values of the fixed parameters:

$\Theta = 10.0$, $\Phi = 3.0$, $\epsilon_1 = 12.0075$, $\epsilon_2 = 12.1469$,

$\epsilon_3 = 1.7151$

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Appendix III. DETERMINATION OF $\varphi_o$ FOR THE ISOTHERMAL REACTOR WITH NO FEED DISTRIBUTION

From Chapter 3, it is known that

$$f_1 = \left( g_1 \left[ x_3 - x_1 - x_2 \right] \left[ \Theta - x_1 \right] - g_2 x_1^2 \right) \left[ x_3 + \Theta \right]^{-2}$$  \hspace{1cm} (III.1)

$$f_2 = g_2 \left[ x_3 - x_1 - x_2 \right] \left[ x_3 + \Theta \right]^{-1}$$  \hspace{1cm} (III.2)

By definition,

$$\varphi_o = \frac{f_1}{f_2} \bigg|_{m=0, x_3 = 1}$$  \hspace{1cm} (III.3)

Since $x_1 = x_2 = 0$ at $m = 0$, we can write

$$\varphi_o = \frac{g_1 \Theta \left[ 1 + \Theta \right]^{-2}}{g_3 \left[ 1 + \Theta \right]^{-1}}$$

or

$$\varphi_o = \frac{g_1 \Theta}{g_3 \left[ 1 + \Theta \right]}$$  \hspace{1cm} (III.4)
Appendix IV. THE DEPENDENCE OF THE SOLUTION OF A SYSTEM OF ORDINARY DIFFERENTIAL EQUATIONS ON THE INITIAL CONDITIONS AND THE PARAMETER

Consider the initial value problem

\[ \dot{\mathbf{y}} = \mathbf{f} (\mathbf{y}, P) ; \quad \mathbf{y} = \mathbf{a} \quad \text{at} \quad x = 0 \]

(IV.1 a, b)

where \( P \) is the parameter of the problem. If \( \mathbf{f} \) is continuously differentiable with respect to \( \mathbf{y} \) and \( P \), then there exists an unique solution \[ \mathbf{y} = \mathbf{y} (x, \mathbf{a}, P) \]. (IV.2)

The derivatives of the solution with respect to the initial values \( \mathbf{a} \) along a solution \( \mathbf{y} \) are given by

\[ \frac{\partial \mathbf{y}}{\partial \mathbf{a}} (x) = \frac{\partial \mathbf{y}}{\partial \mathbf{a}} \]

(IV.3)

For small changes in the initial conditions,

\[ \frac{\partial \mathbf{y}}{\partial \mathbf{a}} (x) = \mathbf{A} (x) \frac{\partial \mathbf{y}}{\partial \mathbf{a}} (x) \]

(IV.4)

\[ \frac{\partial \mathbf{y}}{\partial \mathbf{a}} (0) = \mathbf{I} \] (IV.5)

where the matrix \( \mathbf{A} (x) \equiv \frac{\partial \mathbf{f}}{\partial \mathbf{y}} \) is evaluated for \( \mathbf{y} = \mathbf{y} \);

\( \mathbf{I} \) is the identity or unit matrix.

\[ ^{1} \] All vectors are assumed to be column vectors. Matrices of the form

\[ \begin{bmatrix} \frac{P_1}{Q_1} & \cdots & \frac{P_1}{Q_1} \\ \vdots & \ddots & \vdots \\ \frac{P_n}{Q_n} & \cdots & \frac{P_n}{Q_n} \end{bmatrix} \]

\[ \frac{\partial P}{\partial Q} \] are understood to be
Similarly, it can be shown that if equation (IV.1) is linearized about a solution \( \overline{y} \) for small changes in the parameter \( P \) then

\[
\dot{\overline{l}}(x) = A(x) \overline{l} + h(x) ; \quad \overline{l}(0) = 0 \quad (IV.6 \ a, \ b)
\]

where \( \overline{l}(x) \equiv \frac{\overline{y}}{P} \) and \( h(x) \equiv \frac{\overline{f}}{P} \); the matrix \( A(x) \) and the vectors \( \overline{l}(x) \) and \( h(x) \) are evaluated along \( \overline{y} \).

Suppose \( \overline{l}(x) \) is of the form \( \overline{l}(x) \) \( q(x) \). In order for equations (IV.4), (IV.5), (IV.6 a), and (IV.6 b) to be satisfied, it is necessary that

\[
q(x) = \int_0^x \overline{l}^{-1}(\tau) h(\tau) \, d\tau . \quad (IV.7)
\]

Therefore, we can write

\[
\overline{l}(x) = \frac{\overline{y}}{P} = \overline{l}(x) \int_0^x \overline{l}^{-1}(\tau) h(\tau) \, d\tau . \quad (IV.8)
\]
Appendix V. THE FIRST AND SECOND DERIVATIVES OF $f_1$ AND $f_2$

For Chapters 4 and 5, $f_1$ and $f_2$ are

$$f_1(x_1, x_2, x_3, \Theta) = \frac{a_1 \left[ x_3 - x_1 - x_2 \right] \left[ \Theta - x_1 \right] - a_2 x^2}{x^2} \quad (V.1)$$

$$f_2(x_1, x_2, x_3, \Theta) = \frac{2a_3 \left[ x_3 - x_1 - x_2 \right]^2}{x^2} \quad (V.2)$$

where $X = x_3 + \Theta - 0.5x_2$ . \quad (V.3)

From equations (V.1) and (V.3),

$$\frac{\partial f_1}{\partial x_1} = \frac{a_1 \left[ 2x_1 + x_2 - x_3 - \Theta \right] - 2a_2}{x^2} \quad (V.4)$$

$$\frac{\partial f_1}{\partial x_2} = - \frac{a_1 \left[ \Theta - x_1 \right] \left[ x_1 + 0.5x_2 + \Theta \right] + a_2 x^2}{x^3} \quad (V.5)$$

$$\frac{\partial f_1}{\partial x_3} = \frac{a_1 \left[ \Theta - x_1 \right] \left[ 2x_1 + 1.5x_2 - x_3 + \Theta \right] + 2a_2 x^2}{x^3} \quad (V.6)$$

$$\frac{\partial f_1}{\partial \Theta} = \frac{a_1 \left[ x_3 - x_1 - x_2 \right] \left[ 2x_1 - 0.5x_2 + x_3 - \Theta \right] + 2a_2}{x^3} \quad (V.7)$$

Similarly, from equations (V.2) and (V.3) we get

$$\frac{\partial f_2}{\partial x_1} = - \frac{4a_3 \left[ x_3 - x_1 - x_2 \right]}{x^2} \quad (V.8)$$

$$\frac{\partial f_2}{\partial x_2} = - \frac{2a_3 \left[ x_3 - x_1 - x_2 \right] \left[ x_1 + x_3 + 2\Theta \right]}{x^3} \quad (V.9)$$
\[
\frac{\partial^2 r_2}{\partial x_1 \partial x_2} = \frac{2\bigg[a_1 \bigg(x_1 + 0.5x_2 + \Theta\bigg) - 2a_2x_1\bigg]}{x^3}
\]  

(v.13)

\[
\frac{\partial^2 r_2}{\partial x_1 \partial x_3} = \frac{\partial^2 r_1}{\partial x_1 \partial \Theta} = -\frac{a_1 \bigg[4x_1 + 1.5x_2 - x_3 - \Theta\bigg] - 4a_2x_1}{x^3}
\]  

(v.14)

From equation (v.5),

\[
\frac{\partial^2 r_1}{\partial x_2^2} = -\frac{a_1 \bigg[\Theta - x_1\bigg] \bigg[3x_1 + x_2 + x_3 + 4\Theta\bigg] - 3a_2x_1^2}{2x^4}
\]  

(v.15)

\[
\frac{\partial^2 r_1}{\partial x_2 \partial x_3} = \frac{3a_1 \bigg[\Theta - x_1\bigg] \bigg[x_1 + 0.5x_2 + \Theta\bigg] + 3a_2x_1^2}{x^4}
\]  

(v.16)

\[
\frac{\partial^2 r_1}{\partial x_2 \partial \Theta} = -\frac{3a_1 \bigg[\Theta - x_1\bigg] \bigg[x_1 + 0.5x_2 + \Theta\bigg] - a_1 x \bigg[0.5x_2 + 2\Theta\bigg]}{x^4} + \frac{3a_2x_1^2}{x^4}
\]  

(v.17)
From equation (V.8),

\[
\frac{\partial f}{\partial x_1} = \frac{4G_3}{x^2}
\]  

(V.18)

\[
\frac{\partial^2 f}{\partial x_1 \partial x_2} = \frac{4G_3}{x^3} \left[ x_1 + 0.5x_2 + \Theta \right]
\]  

(V.19)

\[
\frac{\partial^2 f}{\partial x_1 \partial x_3} = -\frac{4G_3}{x^3} \left[ 2x_1 + 1.5x_2 - x_3 + \Theta \right]
\]  

(V.20)

\[
\frac{\partial^2 f}{\partial x_1 \partial \Theta} = \frac{8G_3}{x^3} \left[ x_3 - x_1 - x_2 \right]
\]  

(V.21)

From equation (V.9),

\[
\frac{\partial^2 f}{\partial x_2^2} = G_3 \left[ \frac{x_1 + x_3 + 2 \Theta}{x^4} \right] \left[ \frac{3x_1 + 2x_2 - x_3 + 2 \Theta}{x^4} \right]
\]  

(V.22)

\[
\frac{\partial^2 f}{\partial x_2 \partial x_3} = \frac{2G_3}{x^4} \left\{ 3 \left[ x_3 - x_1 - x_2 \right] \left[ x_1 + x_3 + 2 \Theta \right] - 2x^2 \right\}
\]  

(V.23)

\[
\frac{\partial^2 f}{\partial x_2 \partial \Theta} = \frac{2G_3}{x^4} \left[ x_3 - x_1 - x_2 \right] \left[ 3x_1 + x_2 + x_3 + 4 \Theta \right]
\]  

(V.24)
Appendix VI. PARTIAL DERIVATIVES OF $x_3 = u(x_1, x_2, \Lambda, \Theta)$

For $0 \leq t \leq t_1$, $x_3 = u(x_1, x_2, \Lambda, \Theta)$. In explicit terms, $u$ is given by

$$u(x_1, x_2, \Lambda, \Theta) = \frac{1}{B} \left[ g_1 \left( \Theta - x_1 \right) \left[ 2x_1 + 1.5x_2 + \Theta + 2g_2 x_1^2 \right] - 4g_3 \Lambda \left[ x_1 + x_2 \right] \left[ x_1 + 0.5x_2 + \Theta \right] \right]$$

\[(VI.1)\]

where

$$B = B(x_1, x_2, \Lambda, \Theta) \equiv g_1 \left[ \Theta - x_1 \right] - 4g_3 \Lambda \left[ x_1 + 0.5x_2 + \Theta \right].$$

\[(VI.2)\]

Using equations (VI.1) and (VI.2), we obtain

$$\frac{\partial u}{\partial x_1} = \frac{1}{B^2} \left[ 2g_1^2 \left[ \Theta - x_1 \right] + 2g_2 g_1 x_1 \left[ 2 \Theta - x_1 \right] + 4g_1 g_3 \Lambda \left[ x_1 + 0.5x_2 + \Theta \right] \left[ 3x_1 + 0.5x_2 - \Theta \right] - 8g_2 g_3 x_1 \Lambda \left[ x_1 + x_2 + 2 \Theta \right] + 16g_3^2 \Lambda^2 \left[ x_1 + 0.5x_2 + \Theta \right]^2 \right]$$

\[(VI.3)\]

$$\frac{\partial u}{\partial x_2} = \frac{1}{B^2} \left[ 1.5g_1^2 \left[ \Theta - x_1 \right]^2 + 4g_2 g_3 x_1^2 \Lambda - 8g_1 g_3 \Lambda \left[ \Theta - x_1 \right] \left[ x_1 + 0.5x_2 + \Theta \right] + 16g_3^2 \Lambda^2 \left[ x_1 + 0.5x_2 + \Theta \right]^2 \right]$$

\[(VI.4)\]
\[ \frac{\partial u}{\partial \Lambda} = \frac{\mu g_3 \left[ x_1 + 0.5 x_2 + \theta \right]}{b^2} \left\{ c_1 \left[ \theta - x_1 \right] \left[ x_1 + 0.5 x_2 + \theta \right] + 2 \alpha_2 x_1^2 \right\} \]  
(VI.5)

\[ \frac{\partial u}{\partial \theta} = \frac{1}{b^2} \left[ g_1^2 \left[ \theta - x_1 \right]^2 - 2 \alpha_1 \alpha_2 x_1^2 + 8 \alpha_2 \alpha_3 x_1^2 \Lambda \right] - 4 \mu g_3 \alpha_3 \Lambda \left[ x_1 + 0.5 x_2 + \theta \right]^2 \]  
(VI.6)
Appendix VII. DERIVATIVES OF $\dot{\Lambda} = f_3$

From equation (5.18),

$$f_3(x_1, x_2, x_3, \Lambda, \Theta) = \Lambda \left[ \frac{\partial f_1}{\partial x_1} - \frac{\partial f_2}{\partial x_2} \right] + \Lambda^2 \frac{\partial f_2}{\partial x_1} - \frac{\partial f_1}{\partial x_2}. \quad (VII.1)$$

By definition,

$$\Psi_{ik} = \Psi_{ik}(x_1, x_2, x_3, \Theta) = \frac{\partial f_i}{\partial x_k} \text{ for } i, k = 1, 2. \quad (VII.2)$$

Therefore, using the chain rule for differentiation, we get

$$\left( \frac{\partial f_3}{\partial x_1} \right)_{x_2, x_3, \Lambda, \Theta} = \Lambda \left[ \frac{\partial \Psi_{11}}{\partial x_1} - \frac{\partial \Psi_{22}}{\partial x_1} \right] + \Lambda^2 \frac{\partial \Psi_{21}}{\partial x_1} - \frac{\partial \Psi_{12}}{\partial x_1}$$

or

$$\frac{\partial f_3}{\partial x_1} = \Lambda \left[ \frac{\partial^2 f_1}{\partial x_1^2} - \frac{\partial^2 f_2}{\partial x_1 \partial x_2} \right] + \Lambda^2 \frac{\partial^2 f_2}{\partial x_1^2} - \frac{\partial^2 f_1}{\partial x_1 \partial x_2}. \quad (VII.3)$$

Similarly,

$$\frac{\partial f_3}{\partial x_2} = \Lambda \left[ \frac{\partial^2 f_1}{\partial x_1 \partial x_2} - \frac{\partial^2 f_2}{\partial x_2^2} \right] + \Lambda^2 \frac{\partial^2 f_2}{\partial x_1 \partial x_2} - \frac{\partial^2 f_1}{\partial x_2^2}. \quad (VII.4)$$
\[ \frac{\lambda f_3}{\delta x_3} = \Lambda \left[ \frac{\partial^2 f_2}{\partial x_1 \partial x_3} - \frac{\partial^2 f_2}{\partial x_2 \partial x_3} \right] + \Lambda \frac{\partial^2 f_2}{\partial x_1 \partial x_3} - \frac{\partial^2 f_1}{\partial x_2 \partial x_3} \]  

(VII.5)

\[ \frac{\lambda f_3}{\lambda \Lambda} = \frac{\lambda f_1}{\lambda x_1} - \frac{\lambda f_2}{\lambda x_2} + 2 \lambda \frac{\lambda f_2}{\lambda x_1} \]  

(VII.6)

\[ \frac{\lambda f_3}{\lambda \theta} = \Lambda \left[ \frac{\partial^2 f_1}{\partial x_1 \partial \theta} - \frac{\partial^2 f_2}{\partial x_2 \partial \theta} \right] + \Lambda^2 \frac{\partial^2 f_2}{\partial x_1 \partial \theta} - \frac{\partial^2 f_1}{\partial x_2 \partial \theta} \]  

(VII.7)

The required first and second partial derivatives of \( f_1 \) and \( f_2 \) are written out in terms of \( x_1, x_2, x_3, \) and \( \theta \) in Appendix V.