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DYNAMIC OPTIMIZATION OF PLUG FLOW TUBULAR REACTORS WITH RECYCLE

By

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Submitted in partial fulfillment of the Requirements
for the degree of Doctor of Philosophy
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THESIS

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PRESENTED BY Guillermo E. Pareja

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ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. M. J. Reilly for his invaluable guidance.

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DEDICATION

To my dear wife for her
understanding and help.

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TABLE OF CONTENTS

		Page
ABSTRACT		i
LIST OF FIGURES		iv
CHAPTER 1	THE REACTOR-RECYCLE SYSTEM	
1-1	INTRODUCTION	1
1-2	PREVIOUS WORK	5
1-3	THE MATHEMATICAL MODEL	10
1-3.1	The Reactor-Recycle-Tank System	10
1-3.2	The Reactor-Recycle System	17
1-4	THE PLUG FLOW ASSUMPTION	19
CHAPTER 2	PERIODIC OPERATION OF REACTOR-RECYCLE SYSTEMS	
2-1	INTRODUCTION	22
2-2	PERIODIC RECYCLE ONE FEED STREAM	24
2-2.1	The Complementary Mode	28
2-2.11	Perturbation analysis for the complementary mode	28
2-2.12	Amplitude effect	35
2-2.13	Recycle effect	38
2-2.14	Frequency effect	40
2-2.15	Comments on the complementary mode	43
2-2.2	Complementary Mode Effects vs Recycle Effects	45
2-2.3	The Balanced Mode	49
2-2.31	Perturbation analysis for the balance mode	51
2-2.32	Comparison of the two modes	52
2-3	PERIODIC RECYCLE WITH MULTIPLE FEED STREAMS	56

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2-3.1	General Perturbation Analysis	58
2-3.2	Linear Systems	64
2-3.3	Nonlinear Systems	66
2-3.4	Numerical Solutions	71
2-3.5	Numerical Results	74
2-4	NON-ISOTHERMAL SYSTEMS	87
2-4.1	Periodic Recycle-Constant Feed Temperature	87
2-4.2	Periodic Feed Temperature-Constant Flow Rates	91
2-5	CONCLUSIONS	94
CHAPTER 3	OPTIMAL CONTROL OF REACTOR-RECYCLE SYSTEMS	
3-1	INTRDOUCTION	96
3-2	DESCRIPTION OF REACTOR-RECYCLE SYSTEM	98
3-3	THE START-UP PROBLEM	102
3-4	THE APPROXIMATION METHOD	106
3-5	SOLUTION OF THE APPROXIMATING PROBLEM	118
3-5.1	Steepest-Ascent Method	118
3-5.2	The Optimization Problem	118
3-5.3	The Variational Equations	122
3-5.4	The Adjoint Equations	126
3-5.5	Optimal Control Variation	130
3-5.6	Control Inequalities	132
3-5.7	The Inequality Constraints	133
3-5.8	Comments on the Steepest-Ascent Solution	135
3-6	SOLUTION OF THE ORIGINAL PROBLEM	138
3-6.1	The Optimization Problem	138

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3-6.2 The Variational Equations 141

3-6.3 The Adjoint Equations 141

3-6.4 Extension of Bryson's Method to Differential-Difference Equations 143

3-6.5 Comments on the Steepest-Ascent Solution 146

3-7 THE OPTIMAL SOLUTIONS 147

3-8 CONCLUSIONS 154

NOMENCLATURE 156

REFERENCES 160

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ABSTRACT

This thesis is devoted to the study of the dynamic optimization of plug flow tubular reactors with direct recycle. The periodic operation of the reactor-recycle system is studied. Also considered for these systems is the optimal start-up problem.

Recent literature has shown that a positive feedback control can be used to induce oscillations in continuous stirred tank reactors, and that these oscillations may improve the reactor performance. The feedback provided by the recycle line suggests that the tubular reactor-recycle system might be improved by periodic operation. It has also been reported that direct recycle can have a significant effect on product yield and selectivity. It may be expected that the periodic operation of tubular reactor-recycle systems can be used to promote selectively the yield of a desired reaction. In this thesis it is shown that the selectivity is enhanced by varying such easily manipulated variables as feed flow rate and recycle flow rate.

Perturbation techniques are used to estimate the magnitude and direction of the changes which result from periodic operation. There is excellent agreement between the analytical estimates and the results from the numerical solution of the describing equations.

When periodic processing gives a higher average pro-

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duct yield and selectivity than steady operation, both with and without recycle, then it is said that periodic operation improves the system's performance. The basis for comparing periodic and steady operation is that all three systems have the same reactor volume and the same time averaged throughput. The cost of generating the oscillations and separating the products is not included.

The results show that periodic operation can improve the performance of reactors with direct recycle. The examples show increases of 5-50% in product yield and selectivity obtained by varying the feed flow rate and the recycle flow rate. Correct choice of the reactant which is to have a periodic feed flow rate can lead to substantial increases in selectivity. This choice is dictated by the convexity of the reactor response curves, and by the reaction system.

The problem of how to optimally start a reactor with recycle is also considered. An approximate method for determining the optimal control of tubular reactors with recycle is presented. In this method, the time delay characteristic of recycle systems is approximated through a sequence of holding tanks. The number of holding tanks determines the degree of the approximation. The reaction is considered to take place in a zero-delay reactor. Thus the material and energy relationships for the reactor are preserved. The approximate system is used to obtain time-optimal and profit-optimal heating policies for the start-up of a nonlinear

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tubular reactor with direct recycle.

Optimal policies are determined for several degrees of approximation. The effect of these optimal controls for the approximate system on the exact equations is presented.

The holding tank approximation has the advantage that there is great flexibility in choosing a target set. It is possible to specify final conditions over one time delay. The approximation has the disadvantage that more than one problem must be solved, and that it is limited by the dimensionality of the problem. For complex reactions, where more than two equations are needed to describe the system, the dimensionality can become prohibiting.

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LIST OF FIGURES

Figure No.	DESCRIPTION	Page
CHAPTER 1		
(1-1)	REACTOR-RECYCLE-TANK SYSTEM	11
(1-2)	REACTOR-RECYCLE SYSTEM	11
CHAPTER 2		
(2-1)	REACTOR-RECYCLE SYSTEM	25
(2-2)	AMPLITUDE EFFECT	36
(2-3)	AMPLITUDE EFFECT	37
(2-4)	RECYCLE EFFECT-LINEAR SYSTEMS	39
(2-5)	FREQUENCY EFFECT-LINEAR SYSTEMS	41
(2-6)	RECYCLE EFFECT-NONLINEAR SYSTEMS	77
(2-7)	RECYCLE EFFECT-NONLINEAR SYSTEMS	80
(2-8)	REACTOR-RESPONSE CURVES	83
(2-9)	FREQUENCY EFFECT-NONLINEAR SYSTEMS	86
CHAPTER 3		
(3-1)	REACTOR-RECYCLE SYSTEM	99
(3-2)	APPROXIMATIONS FOR REACTOR-RECYCLE SYSTEM	111
(3-3)	MIXER CONCENTRATION DURING START-UP	115
(3-4)	EFFLUENT CONCENTRATION DURING START-UP	116
(3-5)	OPTIMAL HEATING POLICIES:MINIMUM TIME START-UP	148
(3-6)	MIXER CONDITIONS DURING MINIMUM TIME START-UP	150

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Figure No.	DESCRIPTION	Page
(3-7)	EFFLUENT CONDITIONS DURING MINIMUM TIME START-UP	151
(3-8)	OPTIMAL HEATING POLICIES: MAXIMUM-PROFIT START-UP	153

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CHAPTER 1

THE REACTOR-RECYCLE SYSTEM

1-1 INTRODUCTION

Recycling is frequently used in the chemical industry. Nagiev[1] presents an extensive survey of the industrial applications of recycle. Most often, the recycle system consists of a reactor connected to a separation unit. Nevertheless, it has recently been shown by Carberry[2] that direct recycle can have a significant effect on product yield and selectivity. Under direct recycle a fraction of the reactor effluent is returned directly and without concentration change to the reactor inlet.

Chemical reactors are usually designed on the basis of steady state values. However, it has recently been established, both theoretically and experimentally, that the periodic operation of chemical reactors is sometimes superior to the conventional steady state design[3-12]. Douglas and coworkers[3-10] have studied extensively the periodic behavior of continuous stirred tank reactors[6]. In one of their papers they demonstrate that a positive feedback control system can be used to improve the reactor performance. The feedback provided by the recycle line suggests that the tubular reactor-recycle system might be improved by periodic operation.

Most of the periodicity studies have been concerned

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with the effect on average conversion. Dorawala and Douglas[9] recently showed that periodic operation may also affect the selectivity in a multiple reaction system. As noted before, Carberry[2] has shown that direct recycle can have a significant effect on product yield and selectivity. It may then be expected that the periodic operation of tubular reactor-recycle systems can be used to promote the yield of a desired reaction, thus promoting the selectivity in a multiple reaction system. In this thesis it is shown that the selectivity can be enhanced by varying such easily manipulated variables as the recycle flow rate and the feed flow rate.

Sinusoidal oscillations in the recycle flow rate are considered. This type of periodic operation permits the use of perturbation techniques to solve the equations describing the system. The perturbation solutions provide estimates of the magnitude and direction of the changes in conversion and selectivity which result from periodic operation.

The analytical solutions resulting from the perturbation analysis show excellent agreement with the numerical solutions of the system's equations. This justifies using the perturbation estimates to identify cases which can be improved significantly by periodic operation. Non-sinusoidal periodic oscillations in the recycle flow rate may improve these cases even more.

If periodic processing gives a higher average product

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yield or selectivity than steady operation, both with and without recycle, then it is said that periodic operation improves the system's performance. The basis for comparing periodic and steady operation (with and without recycle) is that the three systems have the same reactor volume and the same time average feed flow rate. The cost of generating the oscillations and separating the products is not included.

The large increases in selectivity obtained by the periodic operation of reactors with direct recycle raises the question of how to control systems with direct recycle. Chapter 3 in the thesis addresses itself to this problem. It deals with the optimal start-up of reactors with recycle. Like the study of periodic operation, this chapter is devoted to how to best utilize the transient behavior of reactors with recycle.

A method to solve optimization problems for systems described by differential-difference equations, like those describing the tubular reactor-recycle system, is presented. In the method, the time delay which is characteristic of recycle systems is approximated through a sequence of holding tanks. Thus, the differential-difference equations are approximated by a set of ordinary differential equations. The number of holding tanks determines the degree of the approximation.

The approximate system is used to obtain time-optimal and profit-optimal heating policies for the start-up of a

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nonlinear tubular reactor with direct recycle.

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1-2 PREVIOUS WORK

Plug flow tubular reactors with recycle have been the object of some recent papers. Reilly and Schmitz[13] showed that the local stability of reactor-recycle systems may be readily determined upon calculation of the steady state solution. In a later paper[14] they analyzed the transient behavior near the steady state. Luus and Amundson[15] presented a different approach to the stability problem. Wand and Perlmutter[16] developed a graphical technique to handle tubular reactor sensitivity, and have extended this technique[17] to the problem of reactor-recycle stability. Pareja and Reilly[18] extended the stability analysis to reactor-recycle systems having heat exchangers and mixing tanks in the recycle line. Recently McGowin and Perlmutter[19] considered the effect of radial and axial mixing on the stability of reactor-recycle systems.

Douglas and his coworkers[3-10] have studied the periodic behavior of continuous stirred tank reactors (CSTR). They have shown that it is possible to produce a change in conversion when some of the system inputs are periodic. The magnitude and direction of the conversion shift is a function of the reaction system and of the chosen periodic input. They have also demonstrated that in order to produce a change in conversion, it is necessary for the reaction system to be nonlinear in some sense. This means that if

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the reactor is isothermal, the reaction must be second or higher order. In non-isothermal systems the reaction rate constants are nonlinear functions of the temperature. For the CSTR an easily manipulated variable, like the flow rate, produces a decrease in conversion.

The studies of periodic operation have been mostly concerned with the effect of periodicity on the time-averaged conversion. However, it is known that techniques for improving the yield and selectivity of complex reactions are usually more important than methods to improve the conversion. Recently Dorawala and Douglas[9] considered the effect of feed rate and feed temperature fluctuations on the behavior of a CSTR. They studied consecutive reactions of the form

$$nA \longrightarrow P \longrightarrow U$$

and parallel reactions of the form

$$2A \longrightarrow P$$

$$A \longrightarrow U$$

For the range of system parameters they considered only very small improvements are obtained for consecutive reactions (0.02% for 10% amplitude fluctuations in the feed flow rate). For the parallel reactions they found 0.3% improvements with 10% amplitude oscillations in the feed flow rate.

In this thesis examples are given of isothermal systems

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where the yield is improved 25%-30% by a periodic feed flow rate. For nonisothermal systems improvements of 50% were found.

Perturbation techniques are used to obtain estimates of the changes in yield and selectivity produced by periodic processing. Even though the treatment is limited to sinusoidal inputs, if some of the results show promises, it is possible to determine the optimal periodic input by a steepest-gradient technique such as the one presented in Chapter 3.

The interesting effects resulting from direct recycle reported in the literture[2,13-18] and found in this thesis provide the motivation for the study of the control of time-delayed systems. The time delay is characteristic of systems with recycle. Chapter 3 in the thesis presents an approach to controlsystems with delay. Under the method the time delay is replaced by a sequence of holding tanks. The number of tanks determines the degree of the approximation.

Chang Jen Wei[20] and Saludkvadze[21] used a similar approximation in the control of linear systems with delay. They assume that the minimum performance functional can be characterized by a finite number of parameters. It is then possible to apply the dynamic programming formalism to obtain the feedback control.

Krasovskii[22] proves that the approximation is valid

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for linear systems with quadratic performance criteria. Repin[23] demonstrates that the approximation suggested by Chang Jen Wei[20] and Saludkvadze[21] does converge to the original equations. The proof is limited to uncontrolled trajectories. However, no justification is given for the use of the method in nonlinear control problems.

Other approaches to the control of time-lag systems have appeared in the literature. Some of them like those of Kramer[24] and Koepcke[25] are limited to linear models. Under their approach the dimensionality is reduced by approximating the system by a finite algebraic difference equation.

Mackinnon[26] extended the work of Merriam[27] to systems with time delay. In this numerical procedure the first variation is used to obtain the necessary conditions for the optimum, and the second to obtain improvements in the control guesses. The computational difficulaties of this second variation method are magnified many fold by the increase in dimensionality.

Recently Ray[28] presented a numerical approach to determine the optimal control of linear time delayed systems which can be portraited by integral equations.

The approach to control the system in this thesis is not limited by nonlinear kinetics. However, the number of equations in the approximate system increases with the degree of the approximation. Hence for complex reactions,

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where more than two equations are needed to describe the system, the dimensionality of the approximate system can become prohibiting.

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1-3 THE MATHEMATICAL MODEL

The mathematical model of the reactor-recycle system, which is considered throughout the thesis, is developed in this section. In the next section the effects of some of the model assumptions are discussed. The equations are written for the case in which there is a single irreversible reaction taking place in the reactor. Reactions involving several components or even systems of simultaneous reactions may also be handled by the methods which follow.

The systems to be studied are depicted in Figure (1-1) and Figure (1-2). The subscripts f,0 and e refer respectiviely to the conditions of the feed, the reactor inlet and the reactor outlet. A fraction R_r of the effluent stream from the tubular reactor is returned through the recycle line to join the fresh feed at the reactor inlet. T_w represents the reactor wall temperature. It may be a function of time and position. In the examples presented later it is considered constant. In Figure (1-1), T_s is the temperature of the heating medium in the tank, and it is taken as constant. It is assumed that the recycle line is adiabatic, and that no reaction occurs within the mixing tank or within the recycle line.

1-3.1 The Reactor-Recycle-Tank System

Under the above assumptions, the mixing tank is described by the following dimensionless material and energy balances

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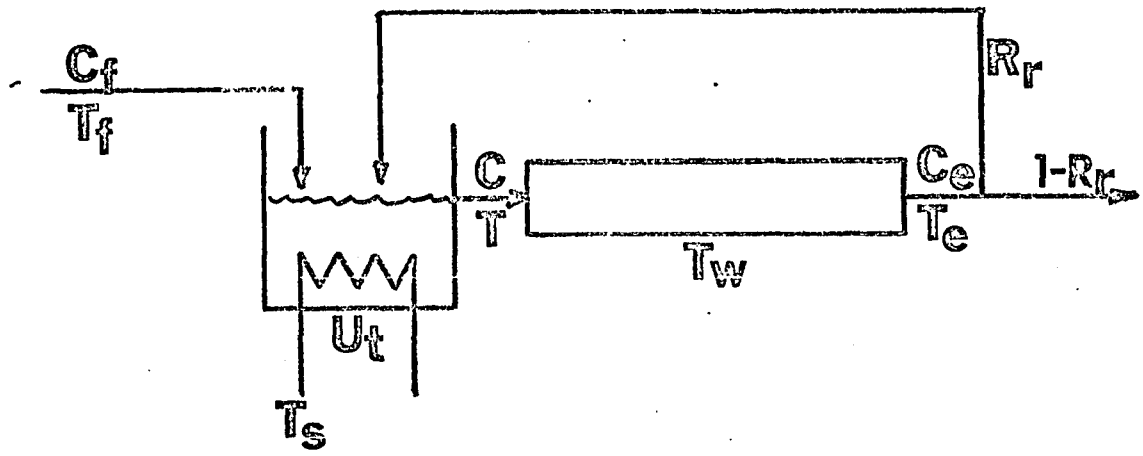
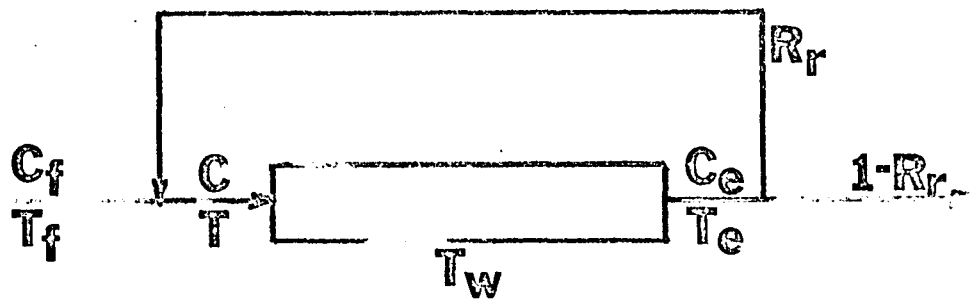


TANK-REACTOR-RECYCLE SYSTEM
FIG. (1-1)



REACTOR-RECYCLE SYSTEM
FIG. (1-2)

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$$\tau_t \frac{dC_o}{dt} = (1-R_r)\, C_f + R_r C_e\,(t-\tau_r) - C_o\,(t) \qquad (1\text{-}1)$$

$$\tau_t \frac{dT_o}{dt} = (1-R_r)\, T_f + R_r T_e\,(t-\tau_r) - T_o(t) + U_t(t)\,[T_s - T_o(t)] \qquad (1\text{-}2)$$

where τ_t is the time constant for the tank, τ_r is the transportation lag in the recycle line, $U_t(t)$ is the dimensionless heat transfer coefficient, and R_r is the ratio of the recycle flow rate to the total flow rate into the tank, i.e.,

$$R_r = \bar{R} \,/\, (\bar{F} + \bar{R}) \qquad (1\text{-}3)$$

where $\bar{F}$ = feed flow rate, and

$\bar{R}$ = recycle flow rate

It is now necessary to obtain a relationship for the reactor outlet conditions $C_e(t)$ and $T_e(t)$. When there is a single irreversible reaction taking place in the reactor, the dimensionless equations characterizing the tubular reactor are

$$\frac{\partial C}{\partial t} + v(t)\frac{\partial C}{\partial z} = \mathcal{R}(C,T) \qquad (1\text{-}4)$$

$$\frac{\partial T}{\partial t} + v(t)\frac{\partial T}{\partial z} = \mathcal{R}(C,T) + U_r\,(T_w - T) \qquad (1\text{-}5)$$

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In the above equations, it is assumed that plug flow exists in the reactor, there is no axial dispersion of heat or mass, radial gradients in temperature and concentration do not exist, and fluid properties are constant. The heat transfer coefficient U_r is taken to be constant, although this assumption may be easily relaxed.

It is convenient to define a state vector X, which is two dimensional in this case. Thus

$$x = \begin{bmatrix} C \\ T \end{bmatrix} \tag{1-6}$$

Equations (1-4) and (1-5) are summarized in vector form

$$\frac{\partial x}{\partial t} + v(t)\frac{\partial x}{\partial z} = \mu(x, t, z) \tag{1-7}$$

where the vector function μ is independent of time and distance whenever the wall temperature is constant.

In general, numerical integration is required because of the nonlinear nature of the reaction rate expression $\mathcal{R}(C,T)$. It is possible to integrate equations (1-4) and (1-5) by the method of characteristics[29]. The theory of partial differential equations shows that a first-order linear partial differential operator can be represented by a directional differential operator along a family of lines identified as the characteristics. Under this method the independent variables t and z are expressed in terms of two new independent variables σ and t_o according

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to

$$t = \sigma + t_o \tag{1-8}$$

$$z = \int_{t_o}^{t_o + \sigma} v(t)\, dt \tag{1-9}$$

These transformations correspond physically to studying the behavior of a fluid element as it flows through the reactor. The variable t_o may be interpreted as the time at which an element entered the reactor, and σ may be interpreted as the length of time this element takes upon traveling to the point z in the reactor.

Let τ denote the length of time which a fluid element requires to travel from the inlet to the outlet of the reactor. Then τ is a function of the inlet time t_o and is defined implicitly by

$$L = \int_{t_o}^{t_o + \tau} v(t)\, dt \tag{1-10}$$

where L is the reactor length. It is readily seen that

$$\frac{dt}{d\sigma} = 1 \tag{1-11}$$

and

$$\frac{dz}{d\sigma} = v(t_o + \sigma) = v(t) \tag{1-12}$$

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Consequently, equation (1-7) may be rewritten as

$$\frac{dx}{d\sigma} = \mu(x, \sigma, t_o) \tag{1-13}$$

and integrated numerically as a system of first order differential equations from the reactor inlet to the reactor outlet. It is clear that the state of this element at the reactor outlet at time $t = t_o + \tau(t_o)$ depends directly upon the state x_o of this element, at the reactor inlet at some earlier time $t = t_o$. This relationship may be denoted by

$$x_e\,[t_o + \tau(t_o)] = \Gamma[x_o\,(t_o),\ t_o] \tag{1-14}$$

where it is understood that equation (1-14) is evaluated by numerical integration of equation (1-13).

When the dimensionless velocity v(t) is constant, then the length of time which a plug spends in the reactor is independent of the time at which it enters. If in addition the wall temperature T_w is independent of time, then equation (1-14) has a simpler form

$$x_e\,(t_o + \tau) = \Gamma[x_o\,(t_o)] \tag{1-15}$$

or

$$\begin{aligned} C_e\,(t) &= \Gamma_1[C_o\,(t-\tau),\ T_o\,(t-\tau)] \\ T_e\,(t) &= \Gamma_2[C_o\,(t-\tau),\ T_o\,(t-\tau)] \end{aligned} \tag{1-16}$$

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Equations (1-16) and (1-17) can be introduced into equations (1-1) and (1-2). This yields the differential-difference equations describing the tank-reactor-recycle system.

$$\tau_t \frac{dC_o}{dt} = (1 - R_r)\, C_f + R_r\, {}_1[C_o(t - \tau - \tau_r),\ T_o(t - \tau - \tau_r)] - C_o(t) \qquad (1\text{-}18)$$

$$\tau_t \frac{dT_o}{dt} = (1 - R_r)\, T_f + R_r\, {}_2[C_o(t - \tau - \tau_r),\ T_o(t - \tau - \tau_r)] - T_o(t) + U_t(t)\,[T_s - T_o(t)] \qquad (1\text{-}19)$$

The initial functions for equations (1-18) and (1-19) can be obtained from the initial concentration and temperature profiles within the reactor and recycle line. The initial tank conditions must also be specified. Knowing the initial conditions in the recycle line is equivalent to knowing $C_e(t)$ and $T_e(t)$ for $0 \leq t \leq \tau_r$. From the initial state of the reactor we can calculate what the reactor output is from $t = 0$ to $t = \tau$. This reactor output will arrive at the tank from $t = \tau_r$ to $t = \tau + \tau_r$. Thus from the initial state in the recycle line and in the reactor, $C_e(t)$ and $T_e(t)$ can be found for $0 \leq t \leq \tau + \tau_r$. With these conditions equations (1-18) and (1-19) can be integrated from $t = 0$ to $t = \tau + \tau_r$. The temperature and concentration profiles from $t = 0$ to $t = \tau + \tau_r$ are then used as initial functions for the integration from $t = \tau + \tau_r$ to $t = 2(\tau + \tau_r)$.

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In this way the integration can be continued as long as desired.

1-3.2 The Reactor-Recycle System

The system described in this section is depicted in Figure (1-2). It only differs from the unit considered in the last section in the absence of the mixing tank. Even though this change does not modify the reactor, it does change the nature of the equations describing the system.

In addition to the equations which describe the plug-flow reactor, equations (1-13), (1-14), or (1-15), a complete model of the reactor-recycle system requires a description of the recycle segment. The model considers the case of direct recycle in which a fraction of the reactor effluent is returned to the inlet with negligible reaction and no heat loss. This recycle segment is described by

$$x_o(t) = (1 - R_r)\, x_f + R_r x_e\,(t - \gamma_r) \qquad (1\text{-}20)$$

It is assumed that the reactant feed conditions are constant and thus enter into this equation as parameters only. Equations (1-20) and (1-15) may be combined to form the difference equation

$$x_o(t) = (1 - R_r)\, x_f + R_r \Gamma[x_o\,(t - \gamma - \gamma_r)] \qquad (1\text{-}21)$$

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which relates the reactor effluent state at any time to its state at some earlier time.

When the tank volume is allowed to go to zero, the vector form of equations (1-16) and (1-17) reduce to equation (1-18). Elsgolt's[30] shows that the solution of the differential-difference equation tends, as $\tau_t \to 0$ to a stable root of the so called degenerate equation (with $\tau_t = 0$) and to that root which contains in its domain of influence the initial values.

Thus, the system without the tank can be considered a special case of the system with a tank preceding the reactor.

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1-4 THE PLUG FLOW ASSUMPTION

The assumptions of the ideal tubular flow reactor are discussed in the remaining part of this chapter. The effect of these assumptions on the rest of the work is considered.

The ideal flow reactor is built around three assumptions:

1) The velocity profile is flat.
2) There is no axial dispersion of heat or mass.
3) There are no radial gradients of heat or mass.

Even though each of the assumptions does not hold by itself, their effects cancel each other making the estimates obtained from the plug flow model valid in most instances.

The axial transport of matter and heat by longitudinal diffusion and conduction, respectively, is negligible as compared to convective transport. Whereas diffusion in the direction of flow is generally negligible, radial molecular diffusion may cause an appreciable reduction in dispersion because it provides for an exchange of material between different streamlines. Owing to turbulence, the radial transport of momentum and of matter is facilitated so that the velocity profile is flattened and radial mixing is improved.

Turner[31] reviews the considerable literature on flow

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through pipes and packed beds. He shows that only rarely does the ideal plug flow assumption fail to adequately describe the conversion in reactors of commercial importance. Tichacek[32] analyzes the effect of failures in the ideal plug flow assumptions on the selectivity in chemical reactor. Tichacek concludes that while the assumptions are usually adequate for commercial tubular reactors, they may lead to serious errors in calculations involving pilot and bench scale units. Horn[33] presents a method to find the effect of mixing on tubular reactor performance. In an example it is shown that for large Peclet numbers the plug flow assumption is valid. Kramer and Westerterp, in their book,[34] present an extensive discussion on the effect of longitudinal dispersion on tubular reactor performance.

Of special interest to this thesis is a paper on the dispersion of a solute in pulsating flow through a tube by Aris[35]. The conclusion is that, unless the amplitude of the fluctuations in the pressure gradient is larger than the mean pressure gradient, the effect of the periodic flow is likely to contribute rather less than 1% to the total dispersion.

The final conclusion is that the plug flow model is adequate in most instances to predict the reactor output. However, the results to be obtained later under periodic operation are based upon the ability to introduce variable conditions into the reactor, and on the assumption that

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these elements maintain their differences. Obviously, the axial diffusion and the turbulence tend to decrease the difference between adjacent fluid elements. Thus, the results obtained with the plug flow assumption represent an upper limit of the effect of periodically operating tubular reactors with recycle.

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CHAPTER 2

PERIODIC OPERATION OF REACTOR-RECYCLE SYSTEMS

2-1 INTRODUCTION

In this chapter the periodic operation of tubular reactors with recycle is studied. It is shown that considerable improvements in yield can be obtained by varying periodically the recycle flow rate. In contrast to systems without recycle, periodic operation of reactor-recycle systems affects the reactor performance when the reaction is first order and the reactor is isothermal.

The analysis considers sinusoidal oscillations in the recycle stream flow rate. This simple type of periodic operation permits the use of perturbation techniques to estimate the magnitude and the direction of the changes in conversion and selectivity which result from periodic operation.

When these estimates are compared with the results from numerical solution of the describing equations, excellent agreement is obtained. Thus the perturbation estimates can be used to identify cases which can be improved significantly by periodic operation. Recycle stream oscillations which are more complex than sinusoidal may improve these cases even more.

An improvement under periodic operation is taken to

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mean that the yield of a desired product has been increased or, in the case of multiple reactions, that the ratio of the product yield to the yield of a waste product has been increased. The yield and selectivity under periodic operation are compared with yield and selectivity under steady operation, both with and without recycle. The basis for comparison is that all three types of operation process the same average quantity of feed in the same size reactor. It is assumed that there are no specifications on reactor effluent concentration which constrain periodic operation and that the cost of generating oscillations is negligible.

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2-2 PERIODIC RECYCLE ONE FEED SYSTEM

The system under initial consideration is shown in Figure (2-1). The system contains a mixing tank with volume V_t followed by a plug-flow tubular reactor of volume V. The reactor's effluent stream is split into the recycle and the output streams. The recycle stream flows through the recycle line back to the mixing tank where it is mixed with the feed stream. The volumetric flow rate of the recycle stream is taken to be

$$R(t) = \bar{R}\ (1 + a_r \sin\omega t) \tag{2-1}$$

Since the volume in flow through the reactor is constant and since it is assumed that the density is constant throughout the system, the volumetric flow rate of the feed stream is complementary to the recycle flow

$$F(t) = \bar{F} - a_r\bar{R} \sin\omega t \tag{2-2}$$

To insure that both F(t) and R(t) are not negative, the amplitude of the recycle oscillations must satisfy

$$a_r \leq \begin{cases} 1 & \text{for } R_r \leq 0.5 \\ (1 - R_r)/R_r & \text{for } R_r \geq 0.5 \end{cases} \tag{2-3}$$

where R_r has been defined as

$$R_r = \frac{\bar{R}}{\bar{F} + \bar{R}} \tag{2-4}$$

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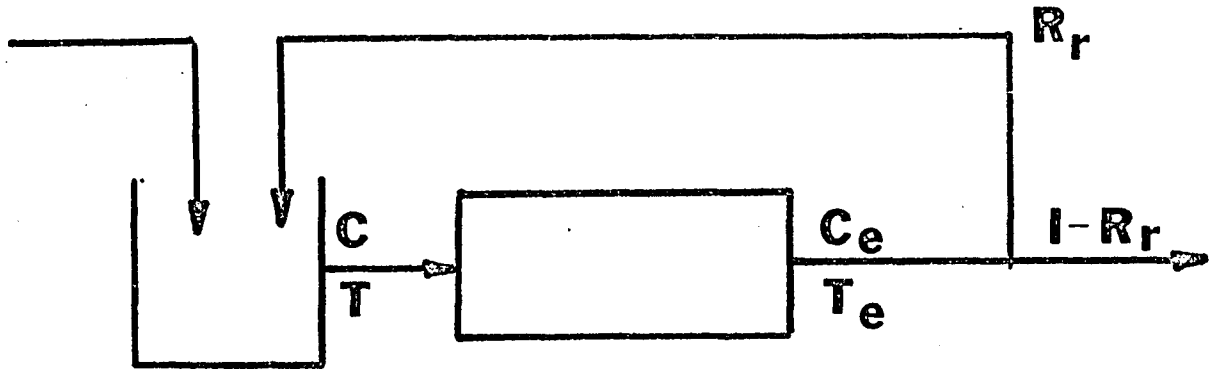

FIGURE (2-1) REACTOR- RECYCLE SYSTEM

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The residence times for the mixing tank and for the reactor depend upon the steady recycle ratio but are independent of time during periodic operation. They are given by

$$\tau_t = (1 - R_r)\, V_t/\bar{F} \tag{2-5}$$

$$\tau = (1 - R_r)\, V/\bar{F} \tag{2-6}$$

Under the assumption of negligible recycle line volume, the recycle transportation lag is zero. If this assumption is not valid, then the recycle transportation lag is generally a function of time because of the periodic recycle flow. The recycle lag for a fluid plug which enters the recycle line at time t_o is given by

$$\frac{(1-R_r)V_r}{R_r\,\bar{F}} = \int_{t_o}^{t_o+\tau_r\,(t_o)} (1 + a_r \sin\omega t)\, dt$$

In some cases, however, the term $(1 - R_r)\, V_r / R_r\, \bar{F}$ is an integer multiple of the period $2\pi/\omega$. In those cases, the recycle transportation lag is constant, and it can be shown that all results are identical to those for a zero recycle transportation lag. Thus the assumption of negligible recycle line volume does not seem unduly restrictive.

Some important features of the periodic operation of the reactor-recycle-tank system may be illustrated with a simple example. With this intent, consider a single, irreversible, first-order reaction

$$A \xrightarrow{k} P$$

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which occurs isothermally only within the reactor. For a plug-flow reactor, the effluent reactant concentration is given by

$$C_{A,e}(t) = e^{-k\tau} C_A (t - \tau) \tag{2-7}$$

where $C_A(t)$ is the reactant concentration in the mixing tank and hence in the reactor input stream. A material balance for the reactant around the mixing tank yields

$$V_t \frac{dC_A}{dt} = R(t)\, e^{-k\tau} C_A (t-\tau) + F(t) C_{A,f}(t) - (\bar{F}+\bar{R})\, C_A(t) \tag{2-8}$$

The concentration is made dimensionless by defining

$$C_A = \frac{\tilde{C}_A}{C_R}$$

where $\tilde{C}_A$ is the dimensional concentration and C_R is a reference concentration. For this linear system C_R will be chosen as $C_R = \langle C_{A,f} \rangle$. The flow averaged concentration $\langle C_{A,f} \rangle$ is defined by

$$\langle C_{A,f} \rangle = \frac{\omega/2\pi}{\bar{F}} \int_t^{t + 2\pi/\omega} F(t)\, C_{A,f}(t)\, dt$$

We wish to consider two modes of periodic operation

1) The <u>complementary</u> mode in which the reactant feed concentration is constant. Since the feed flow

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rate F(t) is complementary to the recycle flow rate, the molar reactant feed rate $F(t)C_{A,f}$ varies with time in the complementary mode.

2) The balanced mode in which any oscillations in the feed flow rate are balanced by oscillations in the reactant feed concentration. Thus the balanced mode provides for a constant molar reactant feed rate.

Some latter examples involving multiple feed streams, some of which are constant, may be interpreted as combining these two modes of operation.

2-2.1 The Complementary Mode

2-2.11 Perturbation analysis for the complementary mode

The reactant material balance, equation (1-8) may be rewritten as

$$\tau_t \frac{dC_A}{dt} = R_r (1 + a_r \sin\omega t)\, e^{-k\tau} C_A (t - \tau) + [1 - R_r (1 + a_r \sin\omega t)] C_{A,f} - C_A(t) \qquad (2\text{-}9)$$

Equation (2-9) is a linear differential-difference equation with periodic coefficients. Because this equation has a unique periodic solution for every sufficiently small a_r then, by the theorem on the analytical dependence of the solution on a parameter[30], the solution of equation (2-9) can be represented in the form

$$C_A(t) = C_A^{(o)}(t) + a_r C_A^{(1)}(t) + a_r^2 C_A^{(2)}(t) + \ldots \qquad (2\text{-}10)$$

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Substitution of this expression into equation (2-9) and subsequent collection of the coefficients of a_r yield the set of differential-difference equations

$$\tau_t \frac{dC_A^{(o)}}{dt} = R_r\, e^{-k\tau C_A^{(o)}(t-\tau)} - C_A^{(o)}(t) + (1 - R_r)\, C_{A,f} \qquad (2\text{-}11)$$

$$\tau_t \frac{dC_A^{(1)}}{dt} = R_r\, e^{-k\tau C_A^{(1)}(t-\tau)} - C_A^{(1)}(t) + R_r(e^{-k\tau C_A^{(o)}(t-\tau)} - C_{A,f}) \sin\omega t \qquad (2\text{-}12)$$

$$\tau_t \frac{dC_A^{(2)}}{dt} = R_r\, e^{-k\tau C_A^{(2)}(t-\tau)} - C_A^{(2)}(t) + R_r\, e^{-k\tau C_A^{(1)}(t-\tau)} \sin\omega t \qquad (2\text{-}13)$$

Our primary interest is in the asymptotic periodic solution of these equation. It is readily verified that those solutions are given by

$$C_A^{(o)} = C_{A,f}\,(1 - R_r)/(1 - R_r\, e^{-k\tau}) \qquad (2\text{-}14)$$

and

$$C_A^{(1)} = E_c\,(A \sin\omega t + B \cos\omega t) \qquad (2\text{-}15)$$

where

$$E_c = R_r\,(e^{-k\tau C_A^{(o)}} - C_{A,f}) = C_A^{(o)} - C_{A,f} \qquad (2\text{-}16)$$

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$$A = \frac{1 - \omega_c R_r e^{-k\tau}}{(1 - \omega_c R_r e^{-k\tau})^2 + (\omega\tau_t + \omega_s R_r e^{-k\tau})^2} \qquad (2\text{-}17)$$

$$B = \frac{\omega\tau_t + \omega_s R_r e^{-k\tau}}{(1 - \omega_c R_r e^{-k\tau})^2 + (\omega\tau_t + \omega_s R_r e^{-k\tau})^2} \qquad (2\text{-}18)$$

with $\omega_c = \cos\omega\tau$ and $\omega_s = \sin\omega\tau$.

We note that $C_A^{(o)}$ is the steady state solution for the case of constant recycle flow. The parameter E_c in equation (2-15) has the dimension of concentration and is termed the effective concentration for the complementary mode. We shall shortly see how a similar parameter E_B arises for the balanced mode. We note, however, that E_c is always negative and thus E_c should not be considered as an actual concentration.

If the reactant effluent concentration is represented in the series form

$$C_{A,e}(t) = C_{A,e}^{(o)} + a_r C_{A,e}^{(1)}(t) + a_r^2 C_{A,e}^{(2)}(t) + \ldots \qquad (2\text{-}19)$$

then, according to equation (2-7),

$$C_{A,e}^{(o)} = e^{-k\tau} C_A^{(o)} \qquad (2\text{-}20)$$

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and

$$C_{A,e}^{(1)}(t) = e^{-k\tau} E_c \ (A_e \sin\omega t + B_e \cos\omega t) \qquad (2\text{-}21)$$

where

$$A_e = A\omega_c + B\omega_s \qquad (2\text{-}22)$$

and

$$B_e = B\omega_c - A\omega_s \qquad (2\text{-}23)$$

We note that

i) A is always positive

ii) B may be either positive or negative

iii) A_e may have either sign

Upon substituting equation (2-15) into equation (2-13), one obtains

$$\tau_t \frac{dC_A^{(2)}}{dt} = R_r e^{-k\tau} C_A^{(2)} (t - \tau) - C_A^{(2)} (t) + \frac{R_r e^{-k\tau} E_c}{2} A_e + \psi_1 (t) \qquad (2\text{-}24)$$

where $\psi_1(t)$ is a linear combination of sin $(2\omega t)$ and cos $(2\omega t)$. The asymptotic solution to equation (2-14) is

$$C_A^{(2)} (t) = \frac{R_r e^{-k\tau}}{1 - R_r e^{-k\tau}} \frac{E_c A_c}{2} + \psi_2(t) \qquad (2\text{-}25)$$

where $\psi_2(t)$ is also a linear combination of sin $(2\omega t)$ and cos $(2\omega t)$. We see that equation (2-19) may be rewritten as

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$$C_{A,e}(t) = e^{-k\tau}[C_A^{(o)} + a_r E_c (A_e \sin\omega t + B_e \cos\omega t) + \frac{a_r^2}{2} \frac{R_r e^{-k\tau}}{1 - R_r e^{-k\tau}} E_c A_e + a_r^2 \psi_2(t) + \ldots] \quad (2\text{-}26)$$

The flow-averaged effluent concentration is defined as

$$\langle C_{A,e} \rangle = \frac{\omega/2\pi}{\bar{F}} \int_0^{2\pi/\omega} C_{A,e}(t) F(t) dt \quad (2\text{-}27)$$

Substitution of $C_{A,e}(t)$ from equation (2-26) and of $F(t)$ from equation (2-2) yields

$$\langle C_{A,e} \rangle = e^{-k\tau} [C_A^{(o)} - \frac{a_r^2}{2} \frac{R_r}{(1 - R_r)} \frac{(1 - e^{-k\tau})}{(1 - R_r e^{-k\tau})} E_c A_e] \quad (2\text{-}28)$$

Equation (2-28) may be further simplified through substitution of E_c for the complementary mode

$$\langle C_{A,e} \rangle = e^{-k\tau} C_A^{(o)} [1 + \frac{a_r^2}{2} \frac{R_r^2 (1 - e^{-k\tau})^2}{(1-R_r)^2 (1 - R_r e^{-k\tau})} A_e] \quad (2\text{-}29)$$

It can be seen that the flow-averaged effluent concentration is the sum of the steady state effluent concentration plus a correction term, which is proportional to the square of the amplitude of the recycle oscillations. The correction term is also proportional to A_e which, as observed above, can be either positive or negative, depending upon the frequency ω.

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Of particular interest is the relative magnitude of the periodic correction term. A_e has a maximum absolute value when

$$\tau_t = 0 \qquad (2\text{-}30)$$

and

$$\omega_s = \sin\omega\tau = 0 \qquad (2\text{-}31)$$

or

$$\omega\tau = n\pi, \text{ n integer} \qquad (2\text{-}32)$$

Equation (2-29) becomes

$$\langle C_{A,e} \rangle = e^{-k\tau} C_A^{(o)} \left[1 + \frac{a_r^2}{2} \frac{R_r^2}{(1-R_r)^2} \frac{(1 - e^{-k\tau})^2}{(1-Re^{-k\tau})\left(\frac{1}{\omega_c} - R, e^{-k\tau}\right)}\right] \qquad (2\text{-}33)$$

Since τ_t is the coefficient of the leading derivative, it is natural to ask if equation (2-30) is an allowable step. Elsgolt's[30] shows that the solution of the original differential-difference equation tends, as $\tau_t \longrightarrow 0$, to a stable root of the so called degenerate equation (with $\tau_t = 0$), and to that root which contains in its domain of influence the initial values. The material balance equation (2-9) has one stable and unique solution. Therefore, we can set τ_t to zero in the results of the perturbation analysis. Note with $\tau_t = 0$ equation (2-9) becomes

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$$0 = R_r\,(1+a_r \sin\omega t)\, e^{-k\tau} C_A(t-\tau) - C_A(t) + [1-R_r(1+a_r \sin\omega t)]\, C_{A,f} \qquad (2\text{-}34)$$

We want the correction term to be negative and have maximum absolute value in order to maximize the conversion. This is attained when

$$\omega_c = \cos\omega\tau = -1 \qquad (2\text{-}35)$$

This places a condition on the frequency since it is now required

$$\omega\tau = (2m+1)\,\pi,\ m \text{ integer} \qquad (2\text{-}36)$$

Under these conditions, it is easily seen that the correction term can become quite significant. For example, if $R_r = 0.75$ and $e^{-k\tau} = 1/9$ then

$$\langle C_{A,e}\rangle = e^{-k\tau}\, C_A^{(o)}\,(1 - 3.4\, a_r^2) \qquad (2\text{-}37)$$

Thus if $a_r^2 = 0.1$ the effluent reactant concentration is 34% lower for the case of periodic operation than for the nonoscillatory case. Equation (2-37) gives the average concentration of unreacted reactant at the reactor effluent. Hence, a lower value for $\langle C_{A,e}\rangle$ implies a higher average conversion.

The perturbation analysis shows that considerable im-

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provements in conversion can be obtained by varying periodically the recycle flow rate. It demonstrates that in systems with recycle it is not necessary to have a nonlinear reaction to produce a shift in the average conversion. It shows that the direction of the shift may be controlled by suitably choosing the frequency of the oscillations.

2-2.12 Amplitude effect

Figure (2-2) presents a comparison between the perturbation analysis solution, equation (2-33), and the numerical solution of equation (2-34). The method used to obtain the numerical solutions is presented later in section (2-3.4). The predictions of the perturbation analysis show excellent agreement with the computer results. The agreement is so good that the perturbation analysis solution can be used not only to make qualitative estimates, but also quantitative predictions of the shift in the average conversion. The analytical results can then be used to study the system parameters which have the greatest effect on this shift. As predicted Figure (2-2) shows that the shift or correction term varies with the square of the amplitude of the recycle oscillations.

In Figure (2-3) the results of the perturbation analysis, equation (2-37), are plotted as a function of the amplitude of the recycle oscillations. Also shown in the figure are the results of numerically solving equation (2-34) with the

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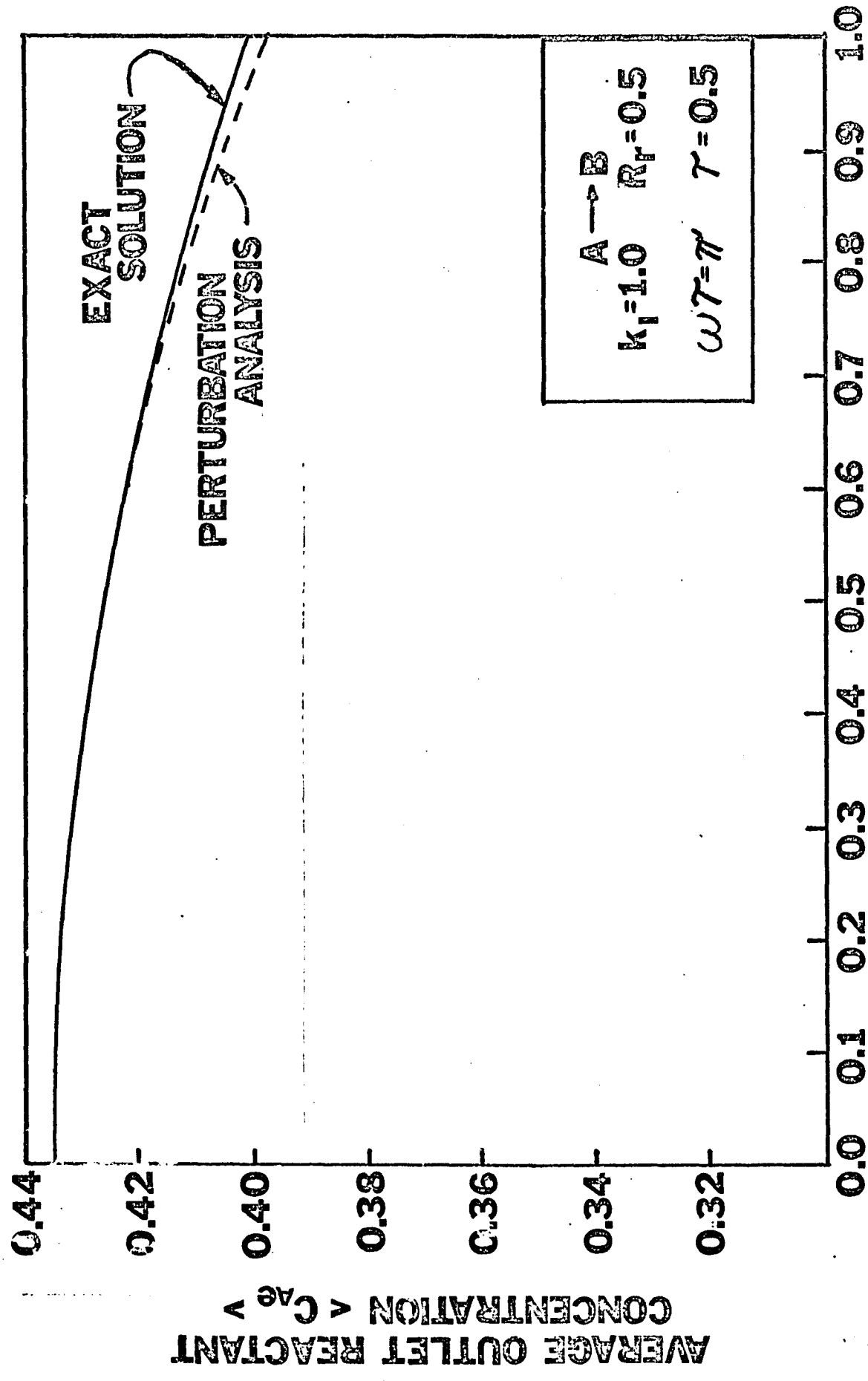

FIG. (2-2) AMPLITUDE EFFECT

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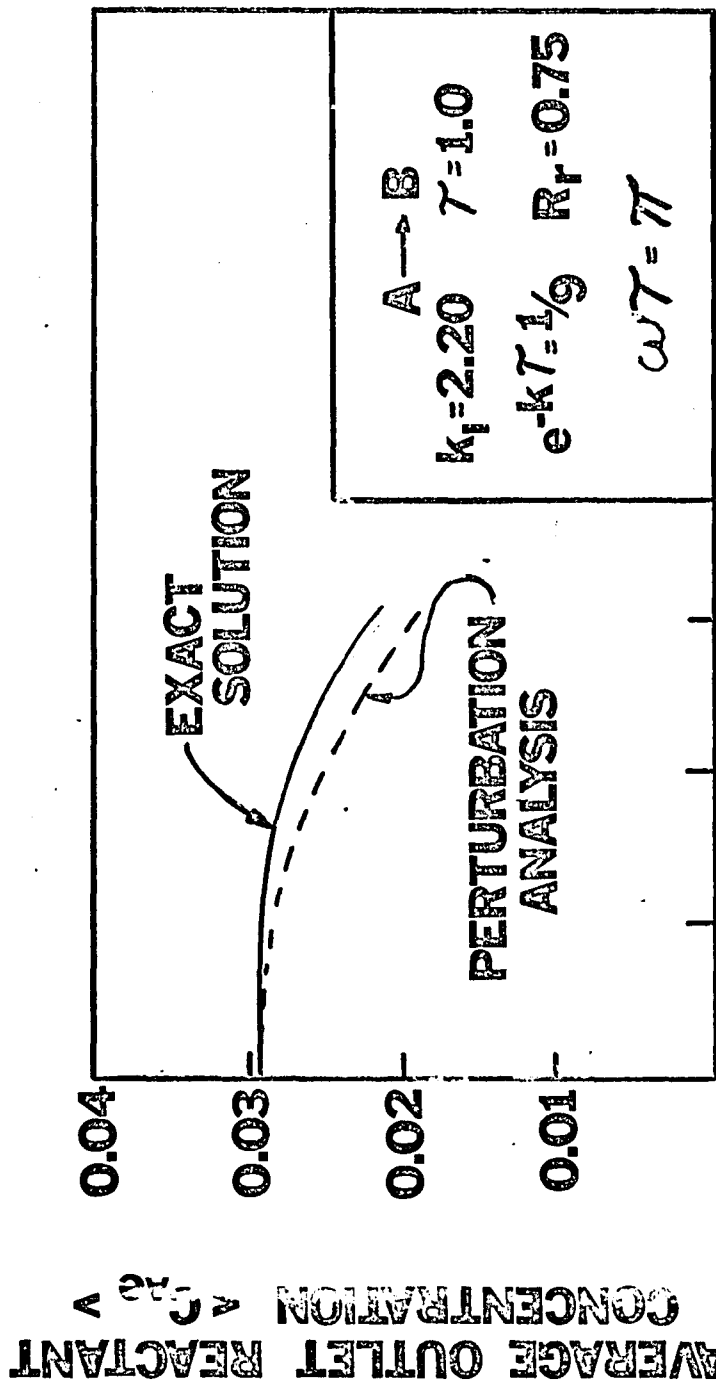

FIG. (2.3) AMPLITUDE EFFECT

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parameters used in equation (2-37), i.e., $R_r = 0.75$ and $e^{-k\tau} = 1/9$.

The maximum amplitude used is $a_r = 0.30$, since the amplitude of the oscillations is restricted to $a_r \leq 0.33$ when $R_r = 0.75$. Once again there is very good agreement between the analytical solution and the numerical solution. When comparing Figures (2-2) and (2-3), we note that the size of the shift in conversion, for a given amplitude, is larger in Figure (2-3) than in Figure (2-2). That is, as the steady state conversion increases so does the magnitude of the shift produced by the periodic manipulation of the recycle flow rate. This is predicted by the perturbation analysis, in equation (2-33), as $e^{-k\tau}$ decreases the shift in conversion increases.

2-2.13 Recycle effect

Figure (2-4) presents the flow-averaged outlet product concentration as a function of the recycle ratio for a first order isothermal reaction. Curves for periodic operation and for constant recycle are shown. The predictions of the perturbation analysis, equation (2-33), coincide within 0.1% with the computer results for periodic operation. In the figure, the recycle ratio is varied by increasing the average recycle flow rate while maintaining the average feed flow rate constant. Because the reactor throughput increases with the recycle ratio, the residence

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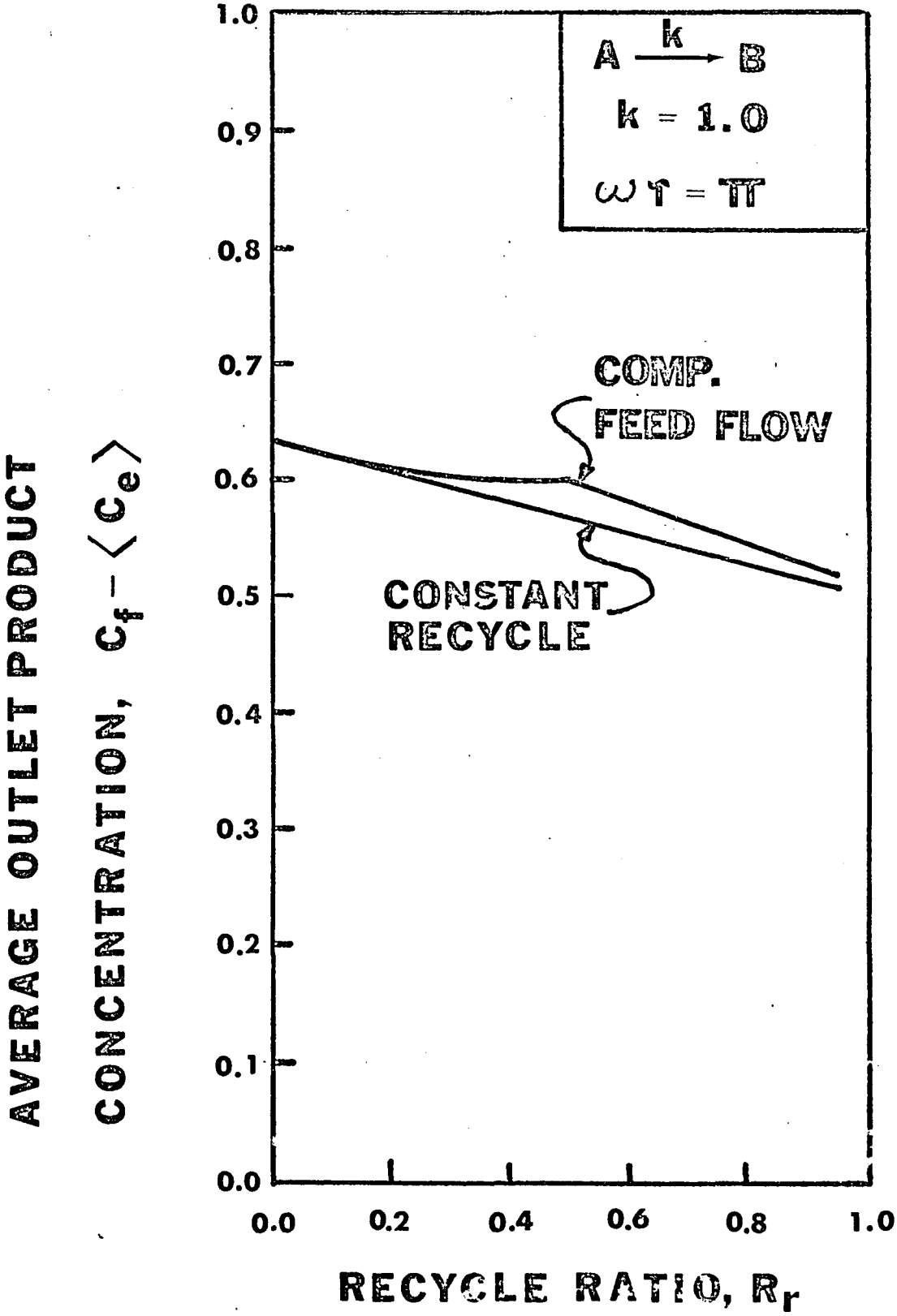

FIG.(2.4)EFFECT OF COMPLEMENTARY FEED FLOW

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time in the reactor decreases as the recycle ratio increases. The relationship is given by equation (2-6),

$$\tau = (1 - R_r)\, V/\bar{F}$$

The figure exhibits the magnitude of the shift in conversion achieved by periodic operation. The effect increases with the recycle ratio until $R_r = 0.5$ where it is a maximum. For larger recycle ratios the shift is reduced because of the smaller allowable maximum oscillation amplitude. The amplitude of the recycle oscillations must satisfy inequalities (2-3). Thus, the amplitude of recycle oscillations in Figure (2-4) is

$$a_r = 1.0 \text{ for } R_r \leq 0.5$$
$$a_r = (1 - R_r)/R_r \text{ for } R_r \geq 0.5$$

2-2.14 Frequency effect

Figure (2-5) is a plot of the flow-averaged reactant concentration versus frequency for a linear isothermal system. The figure gives the results of the numerical solution of equation (2-34). The concentration is shown to be a maximum for $\omega_c = -1$ and a minimum for $\omega_c = 1$ as predicted by the perturbation analysis, equation (2-29) with $\tau_t = 0$, i.e.,

$$\langle C_{A,e} \rangle = e^{-k\tau}\, C_A^{(o)} \left[1 + \frac{a_r^2}{2} \frac{(R_r)^2}{(1-R_r)^2} \frac{(1-e^{-k\tau})^2}{(1-R_r e^{-k\tau})} \frac{(\omega_c - R_r e^{-k\tau})}{(R_r e^{-k\tau} - \omega_c)^2 + \omega_s^2}\right] \tag{2-38}$$

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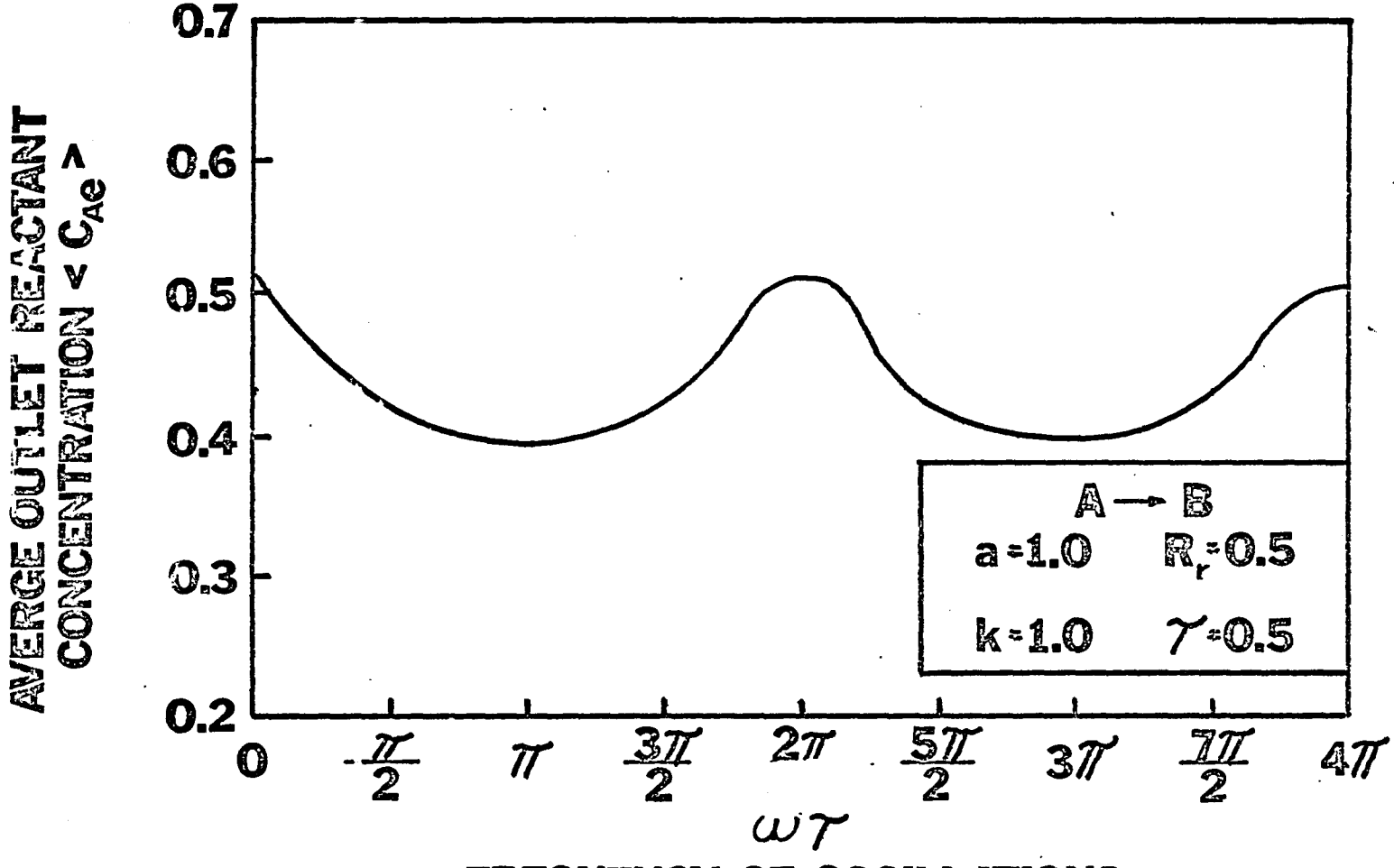

FREQUENCY OF OSCILLATIONS
FIG (2-5) FREQUENCY EFFECT

At frequencies different from $n\pi$ the conversion lies between the extremes obtained with $\omega_c = \pm 1$. All the peaks in the curve are round, and slight variations in the frequency do not modify the average very much. However, it is possible to reverse the direction of the shift in conversion completely by going from $\omega\tau = n\pi$ to $\omega\tau = (n + 1)\pi$. It is to be noted that there is a shift at very low frequencies. This low frequency effect corresponds to the result of mixing the outputs of steady state systems with different recycle ratios. The zero frequency effect can be estimated by taking the limit as $\omega\tau \to 0$ in equation (2-38), the result is

$$\langle C_{A,e} \rangle = e^{-k\tau} C_A^{(o)} \left[1 + \frac{a_r^2}{2} \frac{R_r^2}{(1 - R_r)^2} \frac{(1 - e^{-k\tau})^2}{(1 - R_r e^{-k\tau})^2} \right] \quad (2\text{-}39)$$

Equation (2-39) predicts a positive correction term for low frequencies. Hence, the average reactant outlet concentration is higher for low frequency oscillations than under steady conditions. Thus, low frequency oscillations reduce the average conversion.

For $R_r = 0.5$, $a_r = 1.0$, $k = 1.0$ and $\tau = 0.5$, the parameters used in Figure (2-5), equation (2-39) becomes

$$\langle C_{A,e} \rangle = e^{-k\tau} C_A^{(o)} \quad (1 + 0.16) \quad (2\text{-}40)$$

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Equation (2-40) predicts a 16% increase in the average reactant effluent concentration. Figure (2-5) which presents the results of the numerical solution shows an 18% shift for low frequencies.

2-2.15 Comments on the complementary mode

From this simple and interesting example, a considerable amount of insight into the nature of periodic phenomena on systems with recycle can be obtained. Note first, that even though the feed and recycle flow rates are periodic, they are combined in such a way as to provide a constant flow into the reactor. Hence, the reactor is subjected to an input of constant flow rate and oscillating concentration. Because the reaction chosen for this example is isothermal and linear in the concentration, oscillations in the reactor input concentration do not change the time average value of the reactor outlet concentration. Consequently, the shift in the flow averaged value of the system effluent concentration is not produced in the reactor. It comes from the oscillations in the flow rate leaving the system coupled with the oscillations in the reactor outlet concentration. It is this product of flow rate and concentration that produces the change. The coupling is optimal when $\tau_t = 0$ and $\omega_c = -1$. Consider what these values means in terms of the reactor outlet concentration and the effluent flow rate. The reactant reactor outlet concentration is given by equation (2-26), i.e.,

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$$C_{A,e}(t) = e^{-k\tau}\left[C_A^{(o)} + a_r E_c (A_e \sin\omega t + B_e \cos\omega t) + \frac{a_r^2}{2}\frac{R_r e^{-k\tau}}{(1-R_r e^{-k\tau})} E_c A_e + a_r^2 \psi_2 (t)\right] \quad (2\text{-}41)$$

with $\tau_t = 0$ and $\omega_s = 0$ equation (2-41) becomes

$$C_{A,e}(t) = e^{-k\tau} C_A^{(o)} + \frac{a_r^2}{2} e^{-k\tau} E_c A_e \frac{R_r e^{-k\tau}}{(1-R_r e^{-k\tau})} + a_r e^{-k\tau} E_c A_e \sin\omega t + a_r^2 e^{-k\tau} \psi_2 (t) \quad (2\text{-}42)$$

and

$$E_c A_e = R_r (e^{-k\tau} C_A^{(o)} - C_{A,f}) \frac{\omega_c}{(1-\omega_c R_r e^{-k\tau})} \quad (2\text{-}43)$$

we note that

when $\omega_c = -1$	$E_c A_e > 0$
when $\omega_c = 1$	$E_c A_e < 0$

Thus at the optimum ($\omega_c = -1$) the constant terms in equation (2-42) are positive, and the coefficient of $\sin\omega t$ is greater than zero. At the same time the effluent flow rate is given by equation (2-2)

$$F(t) = \bar{F} - a_r \bar{R} \sin\omega t$$

Consequently at the optimum ($\omega_c = -1$) a maximum in the

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amount withdrawn, F(t), corresponds to a minimum in the reactant concentration, $C_{A,e}(t)$, i.e., maximum instantaneous conversion. We are withdrawing more when the conversion is higher. The recycle flow rate is given by

$$R(t) = \bar{R}\ (1 + a_r \sin\omega t)$$

Hence, at the optimum, whenever the reactant outlet concentration, $C_{A,e}(t)$, is a maximum, the amount recycled is also a maximum, and we recycle most of the unconverted reactant.

2-2.2 Complementary Mode Effects vs Recycle Effects

In the last few sections we obtained a perturbation solution for a linear system operating in the complementary mode. The question arises about possible extensions of the complementary mode to other recycle systems. Consider then some of the effects of the complementary mode of operation as they relate to some of the reasons for recycling.

According to equation (2-10), the reactant concentration at the reactor inlet can be represented in the form

$$C_A(t) = C_A^{(o)} + a_r C_A^{(1)}(t) + a_r^2 C_A^{(2)}(t) + \ldots$$

For a linear isothermal reaction $C_A^{(o)}$, $C_A^{(1)}$ and $C_A^{(2)}$ are given by equations (2-14), (2-15) and (2-25) respectively. Since the flow rate into the reactor is constant, the flow average reactant concentration at the reactor

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inlet is given by

$$\langle C_A \rangle = \langle C_A^{(o)} \rangle + a_r \langle C_A^{(1)} \rangle + a_r^2 \langle C_A^{(1)} \rangle \quad (2\text{-}45)$$

with

$$\langle C_A^{(o)} \rangle = C_A^{(o)} = \frac{(1-R_r)\, C_{A,f}}{(1-R_r e^{-k\tau})}$$

$$\langle C_A^{(1)} \rangle = 0$$

and

$$\langle C_A^{(2)} \rangle = \frac{R_r e^{-k\tau}}{(1-R_r e^{-k\tau})} \frac{E_c A_e}{2} \quad (2\text{-}46)$$

thus

$$\langle C_A \rangle = C_A^{(o)} + \frac{a_r^2}{2} \frac{R_r e^{-k\tau}}{(1-R_r e^{-k\tau})} \frac{E_c A_e}{2} \quad (2\text{-}47)$$

At the same time the flow averaged effluent concentration is given by equation (2-28), i.e.,

$$\langle C_{A,e} \rangle = e^{-k} \left[C_A^{(o)} - \frac{a_r^2}{2} \frac{R_r}{(1-R_r)} \frac{(1-e^{-k\tau})}{(1-R_r e^{-k\tau})} E_c A_e \right] \quad (2\text{-}48)$$

We note that

the shift in $\langle C_A \rangle$ is proportional to $E_c A_e$

while the shift in $\langle C_{A,e} \rangle$ is proportional to $-E_c A_e$

For periodic operation to produce an increase in the average conversion, $-E_c A_e$ must be less than zero, which implies $E_c A_e > 0$ and $\langle C_A \rangle > C_A^{(o)}$. Thus when the conversion

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is improved, the average reactant input concentration is higher under periodic operation than under steady conditions. This increase in the average input concentration goes against one of the very reasons for recycling, i.e., recycle in isothermal systems is used to reduce the reactant concentration in order to avoid undesired side reactions.

Carberry[2] has shown that a plug flow tubular reactor (PFR) with partial effluent recycle simulates a degree of mixing intermediate between the perfect mixing of a continuous stirred tank reactor (CSTR) and the no mixing of a PFR. At a recycle ratio R_r, of zero, PFR performance prevails while CSTR behavior is exactly duplicated at $R_r > 25$. Carberry[2] presents results for consecutive, simultaneous, and mixed Van de Vusse schemes[36]. While the overall integral yield assumes the expected intermediate level for consecutive and simultaneous reactions, in the Van de Vusse kinetic scheme, for certain rate coefficient ratios, the reactor-recycle system proves to be superior.

The reaction kinetic scheme analyzed by Van de Vusse is

$$A \xrightarrow{k_1} P \xrightarrow{k_2} U_1$$

$$2A \xrightarrow{k_3} U_2$$

where P is the desired product.

Overall yield is defined as

> yield is the ratio between the amount of a desired product P obtained and the amount of key reactant A converted

and overall integral selectivity is defined as

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selectivity is the ratio between the amount of a desired product P and that of some undesired product U. Selectivity is then the ratio of the yield of a product to that of a by-product

Whenever we refer to yield and selectivity in this thesis, we understand the overall integral values defined above.

Thus direct recycle is especially applicable as a tool to obtain a yield higher than that resulting from the conventional no recycle reactors. However we have that periodic operation increases the average reactant concentration at the reactor inlet. This increase can be expected to have an adverse effect in the selectivity of most reaction systems. Hence, what is needed is a system where we can selectively use the effects of periodic operation and affect only or mainly some of the reactions.

Consider the case where there are two reactants A and B and two products P and U. Assume that the feed flow rate of A is constant

$$F_A(t) = \bar{F}_A$$

while the feed flow rate of B is periodic and complements the recycle oscillations

$$F_B(t) = \bar{F}_B - a_r \bar{R} \sin\omega t$$

$$R(t) = \bar{R}(1 + a_r \sin\omega t)$$

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Hence, the total reactor throughput, TP, is independent of time

$$TP = \bar{F}_A + \bar{F}_B + \bar{R}$$

We note that reactant B is under conditions similar to those existing in complementary feed flow, i.e., a periodic feed and a periodic recycle. However, reactant A has a constant feed input while the recycle is periodic. We will show that this combination of a periodic feed with a constant feed can be used to selectively promote the reactions in which reactant B participates.

In order to understand this multiple feed system let us analyze a linear system under the conditions experienced by reactant A. Thus consider the balanced feed mode of operation.

2-2.3 The Balanced Mode

Periodic recycle with a balanced feed mode of operation has been defined as the mode in which the recycle is periodic and the oscillations in the feed flow rate are balanced by oscillations in the reactant feed concentration. The oscillations in the reactant feed concentration balance the oscillations in the feed flow rate so as to provide for a constant molar feed rate.

We do not claim the balanced mode as a practical way of operating the reactor-recycle system. Its main usefulness

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is that it will be used together with the complementary mode to explain some of the effects found in systems with multiple feeds.

In the previous example reactant A had a constant molar feed rate, the recycle flow rate was periodic, and the reactor throughput was constant. These are exactly the conditions we defined as the balanced mode.

To determine the effects of this mode of operation, consider a single, irreversible, first-order reaction

$$A \longrightarrow P$$

which occurs isothermally only within the reactor. The recycle flow rate is taken to be

$$R(t) = \bar{R}(1 + a_r \sin\omega t) \qquad (2\text{-}49)$$

and the feed flow rate is complementary to the recycle flow

$$F(t) = \bar{F} - \bar{R}\, a_r \sin\omega t \qquad (2\text{-}50)$$

The reactant concentration is made to vary in such a way as to maintain a constant molar feed rate, i.e.,

$$F(t)\, C_{A,f}(t) = \text{constant} = \bar{F} \langle C_{A,f} \rangle \qquad (2\text{-}51)$$

A material balance for the reactant around the tank yields

$$V_t \frac{dC_A}{dt} = \bar{F} \langle C_{A,f} \rangle + R(t)\, C_{A,e}(t) - (\bar{F} + \bar{R})\, C_A(t) \qquad (2\text{-}52)$$

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with

$$C_{A,e}(t) = e^{-k\tau} C_A (t - \tau)$$

we may rewrite (2-52) as

$$\tau_t \frac{dC_A}{dt} = (1 - R_r) \langle C_{A,f} \rangle - C_A(t) + R_r (1 + a_r \sin \omega t) e^{-k\tau} C_A (t - \tau) \quad (2\text{-}53)$$

2-2.31 Perturbation analysis for the balanced mode

Equation (2-53) is a linear differential-difference equation with periodic coefficients. As for the complementary mode, it is possible to represent the solution of equation (2-53) in the form

$$C_A(t) = C_A^{(o)}(t) + a_r C_A^{(1)}(t) + a_r^2 C_A^{(1)}(t) + \ldots$$

Substitution of this expression into equation (2-53) and subsequent collection of the terms with equal powers of a_r yields the following set of differential-difference equations

$$\tau_t \frac{dC_A^{(o)}}{dt} = (1 - R_r) \langle C_{A,f} \rangle - C_A^{(o)}(t) + R_r e^{-k\tau} C_A^{(o)} (t - \tau) \quad (2\text{-}54)$$

$$\tau_t \frac{dC_A^{(1)}}{dt} = R_r e^{-k\tau} C_A^{(1)} (t - \tau) - C_A^{(1)}(t) + R_r e^{-k\tau} C_A^{(o)} (t - \tau) \sin \omega t \quad (2\text{-}55)$$

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and

$$\tau_t \frac{dC_A^{(2)}}{dt} = R_r e^{-k\tau} C_A^{(2)}(t-\tau) - C_A^{(2)}(t) + R_r e^{-k\tau} C_A^{(1)}(t-\tau) \sin \omega t \qquad (2\text{-}56)$$

The asymptotic solutions of these equations are

$$C_A^{(o)} = \frac{(1-R_r)\langle C_{A,f}\rangle}{(1 - R_r e^{-k\tau})} \qquad (2\text{-}57)$$

$$C_A^{(1)} = E_B (a \sin \omega t + B \cos \omega t) \qquad (2\text{-}58)$$

and

$$C_A^{(2)} = \frac{R_r e^{-k\tau}}{(1-R_r e^{-k\tau})} \frac{E_B A_e}{2} + \psi_3(t) \qquad (2\text{-}59)$$

where

$$E_B = R_r e^{-k\tau} C_A^{(o)} \qquad (2\text{-}60)$$

A and B are identical to those obtained for the complementary mode and are given by equations (2-17) and (2-18). $\psi_3(t)$ is a linear combination of sin $(2\omega t)$ and cos $(2\omega t)$.

The flow-averaged effluent concentration is defined as

$$\langle C_{A,e}\rangle = \frac{\omega/2\pi}{\bar{F}} \int_t^{t + 2\pi/\omega} C_{A,e}(t)\, F(t)\, dt$$

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Following the sequence of substitutions used for the complementary mode gives the average as

$$\langle C_{A,e} \rangle = e^{-k\tau}\left[C_A(o) - \frac{a_r^2}{2}\frac{R_r}{(1-R_r)}\frac{(1-e^{-k\tau})}{(1-R_r e^{-k\tau})} E_B A_e\right] \qquad (2\text{-}61)$$

2-2.32 Comparison of the two modes

For comparison purposes let us rewrite the result obtained for the complementary mode, equation (2-28), i.e.,

$$\langle C_{A,e} \rangle = e^{-k\tau}\left[C_A(o) - \frac{a_r^2}{2}\frac{R_r}{(1-R_r)}\frac{(1-e^{-k\tau})}{(1-R_r e^{-k\tau})} E_c A_e\right] \qquad (2\text{-}62)$$

We note that when the molar feed rate is not constant, the only difference in the form of the flow average effluent concentration is that

$$E_c = R_r\left(e^{-k\tau} C_A(o) - C_{A,f}\right) \qquad (2\text{-}63)$$

replaces

$$E_B = R_r e^{-k\tau} C_A(o) \qquad (2\text{-}64)$$

Since $e^{-k\tau} C_A(o)$ is just the effluent reactant concentration for steady conditions, the following inequality holds

$$e^{-k\tau} C_A(o) < C_{A,f}$$

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Thus E_c is negative while E_B is positive, and the two modes of operation give opposing results.

This is a very significant result, because it indicates that in a reaction system where some reactant B is in the complementary mode while the other reactant A is in the balanced mode, then the reactions in which B participates are promoted while the reactions in which A participates are slowed down. Thus the combination of the two modes of operation can be used to selectively improve the yield of some reactions in a multiple reaction system.

To obtain some feel for the magnitude of the correction, term in the balanced mode, set $\omega_c = -1$, $R_r = 0.75$ and $e^{-k\tau} = 1/9$ in equation (2-61). These same parameters when used in the complementary mode, equation (2-33), gave a 34% shift in the average conversion for $a_r^2 = 1.0$. With these parameters equation (2-61) becomes

$$\langle c_{A,e} \rangle = e^{-k\tau} c_A(o) (1 + 0.1\, a_r^2) \qquad (2\text{-}65)$$

For $a_r^2 = 1.0$ the correction term is 10% of the steady solution. That is, the unreacted reactant concentration is 10% higher than at steady state, while in the complementary mode the unreacted reactant concentration is 34% lower than the steady state value. Note that the shift in the balanced mode is proportional to the concentration of unreacted reactant $e^{-k\tau} c_A(o)$, hence as the steady conversion increases the shift decreases. While in the complementary

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mode the shift is directly proportional to $C_{A,f}-e^{-k\tau}C_A^{(o)}$, which is proportional to the steady conversion, hence as the steady conversion increases the shift caused by the complementary mode increases.

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2-3 PERIODIC RECYCLE WITH MULTIPLE FEED STREAMS

In this section the results obtained for the complementary mode and for the balanced mode are combined to increase the selectivity in a multiple reaction system. The analysis presented is limited to systems with two reactants, A and B, the extension of the results to larger systems is immediate.

A material balance for reactants A and B around the tank yields

$$V_t \frac{dC_A}{dt} = F_A(t)\, C_{A,f} + R(t)\, C_{A,e}(t) - [F_A(t) + F_B(t) + R(t)]\, C_A(t) \qquad (2\text{-}66)$$

$$V_t \frac{dC_B}{dt} = F_B(t)\, C_{B,f} + R(t)\, C_{B,e}(t) - [F_A(t) + F_B(t) + R(t)]\, C_B(t) \qquad (2\text{-}67)$$

Reactant A has a constant feed flow rate, while reactant B has a periodic feed flow rate which complements the recycle oscillations. The reactants feed concentrations are constant. Thus,

$$F_A(t) = \bar{F}_A \qquad (2\text{-}68)$$

$$F_B(t) = \bar{F}_B - a_r \bar{R} \sin \omega t \qquad (2\text{-}69)$$

$$R(t) = \bar{R}\,(1 + a_r \sin \omega t) \qquad (2\text{-}70)$$

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The reactor throughput, TP, is constant

$$TP = \bar{F}_A + \bar{F}_B + \bar{R} = F_A(t) + F_B(t) + R(t) \qquad (2\text{-}71)$$

with

$$R_r = \frac{\bar{R}}{TP} \qquad \gamma_t = \frac{V_t}{TP} \qquad (2\text{-}72)$$

Equations (2-66) and (2-67) may be rewritten as

$$\gamma_t \frac{dC_A}{dt} = \frac{\bar{F}_A}{TP} C_{A,f} + R_r (1 + a_r \sin \omega t) C_{A,e}(t) - C_A(t) \qquad (2\text{-}73)$$

$$\gamma_t \frac{dC_B}{dt} = \frac{\bar{F}_B}{TP} (1 - a_r \frac{\bar{R}}{\bar{F}_B} \sin \omega t) C_{B,f} + R_r (1 + a_r \sin \omega t) C_{B,e}(t) - C_B(t) \qquad (2\text{-}74)$$

It is clear that reactant B is under conditions similar to those existing in the complementary mode; there is a periodic recycle and it has a feed flow rate which complements the recycle. On the other hand reactant A is under the conditions defined as the balanced mode. It has a constant molar feed rate, while the recycle flow rate is periodic and the reactor throughput is constant. Thus what is left is to analyze the system when both modes are present.

In the case where reactants A and B participate in separate and independent linear reactions such as

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$$A \xrightarrow{k_1} U \qquad (2\text{-}75)$$

$$B \xrightarrow{k_2} P \qquad (2\text{-}76)$$

then the results obtained so far are directly applicable, i.e., for $e^{-k_1\tau} = e^{-k_2\tau} = 1/9$ and $R_r = 0.75$, it is possible to increase the conversion of A to P by 34%, as shown by equation (2-37), while decreasing the conversion of A to U by 10%, as shown by equation (2-65). More realistic conditions are when there is coupling between the reactants and the reaction rates depend upon both reactants.

2-3.1 General Perturbation Analysis

In order to predict the direction of the shift in yield and selectivity in nonlinear coupled systems, let us carry out a perturbation analysis for a system described by equations (2-73) and (2-74). We can represent the solution of these equations in the form

$$C_A(t) = C_A^{(o)}(t) + a_r C_A^{(o)}(t) + a_r^2 C_A^{(1)}(t) + \ldots \qquad (2\text{-}77)$$

$$C_B(t) = C_B^{(o)}(t) + a_r C_B^{(1)}(t) + a_r^2 C_B^{(2)}(t) + \ldots \qquad (2\text{-}78)$$

The reactor outlet conditions can be approximated by a Taylor series expansion about $C_{A,e}^{(o)}$ and $C_{B,e}^{(o)}$, the steady state values. Thus

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$$C_{A,e}(t) = C_{A,e}^{(o)} + [a_r C_A^{(1)}(t-\gamma) + a_r^2 C_A^{(2)}(t-\gamma)]\frac{\partial C_{A,e}}{\partial C_A}$$

$$+ [a_r C_B^{(1)}(t-\gamma) + a_r^2 C_B^{(2)}(t-\gamma)]\frac{\partial C_{A,e}}{\partial C_B}$$

$$+ \tfrac{1}{2}[a_r^2 C_A^{(1)}(t-\gamma)\, C_A^{(1)}(t-\gamma)\frac{\partial^2 C_{A,e}}{\partial C_A^2}$$

$$+ a_r^2 C_B^{(1)}(t-\gamma)\, C_B^{(1)}(t-\gamma)\frac{\partial^2 C_{A,e}}{\partial C_B^2}$$

$$+ 2 a_r^2 C_A^{(1)}(t-\gamma)\, C_B^{(1)}(t-\gamma)\frac{\partial^2 C_{A,e}}{\partial C_A \partial C_B}] \qquad (2\text{-}79)$$

$$+ \text{terms of third and higher order in } a_r$$

and

$$C_{B,e}(t) = C_{B,e}^{(o)}(t) + [a_r C_B^{(1)}(t-\gamma) + a_r^2 C_B^{(2)}(t-\gamma)]\frac{\partial C_{B,e}}{\partial C_B}$$

$$+ [a_r C_A^{(1)}(t-\gamma) + a_r^2 C_A^{(2)}(t-\gamma)]\frac{\partial C_{B,e}}{\partial C_A}$$

$$+ \tfrac{1}{2}[a_r^2 C_B^{(1)}(t-\gamma)\, C_B^{(1)}(t-\gamma)\frac{\partial^2 C_{B,e}}{\partial C_B^2}$$

$$+ a_r^2 C_A^{(1)}(t-\gamma)\, C_A^{(1)}(t-\gamma)\frac{\partial^2 C_{B,e}}{\partial C_A^2}$$

$$+ 2 a_r^2 C_A^{(1)}(t-\gamma)\, C_B^{(1)}(t-\gamma)\frac{\partial^2 C_{B,e}}{\partial C_A \partial C_B}] \qquad (2\text{-}80)$$

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The partial derivatives are evaluated at the steady state.

Differential equations for $C_A^{(o)}$, $C_A^{(1)}$ and $C_A^{(2)}$ are obtained by substituting (2-79) and (2-77) into equation (2-73) and equating powers of a_r. The same procedure is followed to obtain equation for $C_B^{(o)}$, $C_B^{(1)}$ and $C_B^{(2)}$. In order to simplify the presentation use will be made of vector notation. Let

$$X = \begin{bmatrix} C_A \\ C_B \end{bmatrix} \tag{2-81}$$

$$\bar{F} = \begin{bmatrix} \bar{F}_A \\ \bar{F}_B \end{bmatrix} \tag{2-82}$$

and

$$E = R_r \begin{bmatrix} C_{A,e}^{(o)} \\ C_{B,e}^{(o)} - C_{B,f} \end{bmatrix} \tag{2-83}$$

With these nomenclature the equations satisfied by $X^{(o)}$, $X^{(1)}$ and $X^{(2)}$ are

$$\tau_t \frac{dX^{(o)}}{dt} = \frac{1}{TF} \begin{bmatrix} \bar{F}_A & C_{A,f} \\ \bar{F}_B & C_{B,f} \end{bmatrix} + R_r X_e^{(o)}(t) - X^{(o)}(t) \tag{2-84}$$

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$$\tau_t \frac{dX^{(1)}}{dt} = E \sin\omega t - X^{(1)}(t) + R_r J X^{(1)}(t - \tau) \qquad (2\text{-}85)$$

$$\tau_t \frac{d X^{(2)}}{dt} = R_r J X^{(2)}(t - \tau) - X^{(2)}(t) + R_r J X^{(1)}(t - \tau) \sin\omega t + \tfrac{1}{2} R_r X^{(1)}(t - \tau)' H_V X^{(1)}(t - \tau) \qquad (2\text{-}86)$$

where J is the jacobian matrix for the reactor, i.e.,

$$J = \begin{bmatrix} \frac{\partial C_{A,e}}{\partial C_A} & \frac{\partial C_{A,e}}{\partial C_B} \\ \frac{\partial C_{B,e}}{\partial C_A} & \frac{\partial C_{B,e}}{\partial C_B} \end{bmatrix} \qquad (2\text{-}87)$$

and H_V is a matrix whose elements are vectors

$$H_V = \begin{bmatrix} \begin{bmatrix} \frac{\partial^2 C_{A,e}}{\partial C_A^2} \\ \frac{\partial^2 C_{B,e}}{\partial C_A^2} \end{bmatrix} & \begin{bmatrix} \frac{\partial^2 C_{A,e}}{\partial C_A \partial C_B} \\ \frac{\partial^2 C_{B,e}}{\partial C_A \partial C_B} \end{bmatrix} \\ \begin{bmatrix} \frac{\partial^2 C_{A,e}}{\partial C_A \partial C_B} \\ \frac{\partial^2 C_{B,e}}{\partial C_A \partial C_B} \end{bmatrix} & \begin{bmatrix} \frac{\partial^2 C_{A,e}}{\partial C_B^2} \\ \frac{\partial^2 C_{A,e}}{\partial C_B^2} \end{bmatrix} \end{bmatrix} \qquad (2\text{-}88)$$

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The asymptotic solutions for large values of time are

$$X^{(o)}(t) = \text{steady state solution} \qquad (2\text{-}89)$$

$$X^{(1)}(t) = (A \sin \omega t + B \cos \omega t)\, E \qquad (2\text{-}90)$$

$$X^{(2)}(t) = \bar{X}^{(2)} + \Psi(t) \qquad (2\text{-}91)$$

where $\Psi(t)$ is a linear combination of $\sin 2\omega t$ and $\cos 2\omega t$.

A and B are matrices given by

$$A = -[(\omega \tau_t I + \omega_s R_r J)^2 + (\omega_c R_r J - I)^2]^{-1} (\omega_c R_r J - I) \qquad (2\text{-}92)$$

$$B = [(\omega \tau_t I + \omega_s R_r J)^2 + (\omega_c R_r J - I)^2]^{-1} (\omega \tau_t I + \omega_s R_r J) \qquad (2\text{-}93)$$

In arriving at (2-92) and (2-93) use was made of the following equality

$$(\omega \tau_t I + \omega_s R_r J)(\omega_c R_r J - I) = (\omega_c R_r J - I)(\omega \tau_t I + \omega_s R_r J) \qquad (2\text{-}94)$$

that is, the above matrices commute.

$\bar{X}^{(2)}$ is a constant given by

$$\bar{X}^{(2)} = (I - R_r J)^{-1} \left[\frac{R_r}{2} J A_e E + \frac{R_r}{4} ((A_e + B_e)E)' H_v (A_e + B_e)E \right] \qquad (2\text{-}95)$$

where A_e and B_e are defined as in equations (2-22) and (2-23), that is

$$A_e = A \omega_c + B \omega_s$$

$$B_e = B \omega_c - A \omega_s$$

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A and B are now the matrices of equations (2-92) and (2-93). Note that the elements of A_e and B_e may be either positive or negative.

Equations (2-80) and (2-81) which give the reactor outlet conditions can then be rewritten as

$$X_e(t) = X_e^{(o)} + J\,[a_r X^{(1)}(t-\tau) + a_r^2\, X^{(2)}\,(t-\tau)]$$
$$+ \frac{a_r^2}{2}[X^{(1)}(t-\tau)'\, H_v\, X^{(1)}\,(t-\tau)]$$
$$= X_e^{(o)} + J\,[a_r(A_e \sin\omega t + B_e \cos\omega t)E \qquad (2\text{-}96)$$
$$+ a_r^2 \bar{X}^{(2)} + a_r^2\, \psi(t)] + \frac{a_r^2}{2}[((A_e \sin\omega t$$
$$+ B_e \sin\omega t)E)'\, H_v\, (A_e \sin\omega t + B_e \cos\omega t)E]$$

The flow average outlet conditions are defined by

$$\langle X_e \rangle\,(\bar{F}_A + \bar{F}_B) = \frac{\omega}{2\pi} \int_t^{t + 2\pi/\omega} X_e(t)\,(F_A(t) + F_B(t))\,dt \qquad (2\text{-}97)$$

Substituting equations (2-68), (2-69) and (2-96) into equation (2-97) yields the average as

$$\langle X_e \rangle = X_e^{(o)} + a_r^2\, J\, \bar{X}^{(2)}$$
$$- \frac{a_r^2}{2}\,\frac{\bar{n}_r}{(1-R_r)}\, J\, A_e E$$
$$+ \frac{a_r^2}{4}\,((A_e + B_e)E)'\, H_v\, (A_e + B_e)E$$

(2-98)

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These results are a direct extension of those obtained in the complementary and balanced modes. The new terms which depend upon the cross derivatives, like $\partial C_{A,e}/\partial C_B$ are due to the mutual interdependance of the reaction rates. Whenever the reaction rate of A is independent of that of B, and vice versa, then these terms are equal to zero. The second order derivatives reflect the effects produced when the reaction rate expressions are nonlinear.

2-3.2 Linear Systems

From the general result for two reactants, equation (2-98), we can derive predictions for a linear system. The case when the reactions are linear and independent has already been considered in reactions (2-75) and (2-76). We now study the effects of periodic operation when the reactions are linear but coupled. For example, the set of reactions

$$A \xrightarrow{k_1} U \qquad (2\text{-}99)$$

$$A + B \xrightarrow{k_2} \qquad (2\text{-}100)$$

with reaction rate expressions given by

$$\mathcal{R}_A = -k_1 C_A - k_2 C_B \qquad (2\text{-}101)$$

$$\mathcal{R}_B = -k_2' C_B \qquad (2\text{-}102)$$

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where

$$k_2' = k_2 C_A$$

when $C_A >> C_B$ then k_2' can be considered constant and the system is approximately linear but coupled. Thus, assuming that the reactor is described by a set of linear equations, then we have

$$H_v = 0 \tag{2-103}$$

Equation (2-98) can then be written as

$$\langle X_e \rangle = X_e^{(o)} - \frac{a_r^2}{2} K_p A_e E \tag{2-104}$$

where K_p is a 2 x 2 matrix given by

$$K_p = J \left[I - R_r J \right]^{-1} R_r J$$

$$= \frac{R_r}{(1-R_r)} J \tag{2-105}$$

Note that the shift in the average outlet conditions is directly proportional to E, which is defined in equation (2-83) as

$$E = R_r \begin{bmatrix} C_{A,e}^{(o)} \\ C_{B,e}^{(o)} - C_{B,f} \end{bmatrix} \tag{2-106}$$

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If the feed flow rate of A was periodic rather than constant and the feed flow rate of B was constant rather than periodic, then E would be given by

$$E = R_r \begin{bmatrix} C_{A,e}^{(o)} - C_{A,f} \\ \\ C_{B,e}^{(o)} \end{bmatrix} \qquad (2\text{-}107)$$

equation (2-104) would remain otherwise unchanged. The components of E in equation (2-107) have opposite signs to those in equation (2-105). Hence, the direction of the shift in each of the average outlet conditions can be reversed by reversing the roles of the feed flow rates. Consequently, the direction of each of the shifts can be chosen by specifying the reactant with the periodic feed flow rate and the reactant with the constant feed flow rate.

The shifts are also proportional to A_e the elements of which, as observed before, can be either positive or negative, depending upon the frequency ω.

2-3.3 Nonlinear Systems

In this section it is shown that the yield of nonlinear reactor-recycle systems can sometimes be improved by periodic operation.

Equation (2-98) gives the results of the general perturbation analysis for a periodic reactor-recycle system.

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It is possible to divide the terms in equation (2-98) into those common to linear and nonlinear systems and those that are specific to nonlinear systems. Since it has been shown that the selectivity of linear systems can be improved by periodic processing, it is not necessary to consider the terms common to linear and nonlinear systems. We can concentrate on the terms characteristic of nonlinear systems.

The effects of the nonlinear reaction rates are represented by the terms which depend on H_v. If the reaction rates are linear H_v is equal to zero. Let us analyze the terms involving H_v, these terms are of the form

$$((A_e + B_e)E)' \; H_v \; (A_e + B_e)E \tag{2-108}$$

Denoting the components of $(A_e + B_e)E$ as V_1 and V_2, expression (2-108) can be rewritten as

$$\left[\begin{array}{l} V_1^2 \dfrac{\partial^2 C_{A,e}}{\partial C_A^2} + 2V_1V_2 \dfrac{\partial^2 C_{A,e}}{\partial C_A \partial C_B} + V_2^2 \dfrac{\partial^2 C_{A,e}}{\partial C_B^2} \\ \\ V_1^2 \dfrac{\partial^2 C_{B,e}}{\partial C_A^2} + 2V_1V_2 \dfrac{\partial^2 C_{B,e}}{\partial C_A \partial C_B} + V_2^2 \dfrac{\partial^2 C_{B,e}}{\partial C_B^2} \end{array} \right] \tag{2-109}$$

assume that reactant B participates in the reaction giving the desired product P, and that B does not react to form the wasted by-product U. Then we want the second component in (2-109) to be, a) negative, and b) to have the largest

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absolute value. These conditions would lead to a reduction in $\langle C_{B,e} \rangle$ which, as assumed, implies an increase in the amount of P formed. The second component of (2-109) should have an absolute value larger than the first component, so that the reduction in $\langle C_{B,e} \rangle$ is larger than the reduction in $\langle C_{A,e} \rangle$ thus affecting more the formation of the product P, than that of the by-product U.

If V_1 and V_2 are of the same order of magnitude then conditions a) and b) are equivalent to

$$\frac{\partial^2 C_{B,e}}{\partial C_A^2} \pm 2 \frac{\partial^2 C_{B,e}}{\partial C_A \partial C_B} + \frac{\partial^2 C_{B,e}}{\partial C_B^2} < 0 \qquad (2\text{-}110)$$

and

$$\left| \frac{\partial^2 C_{B,e}}{\partial C_A^2} \pm 2 \frac{\partial^2 C_{B,e}}{\partial C_A \partial C_B} + \frac{\partial^2 C_{B,e}}{\partial C_B^2} \right| > \qquad (2\text{-}111)$$

$$\left| \frac{\partial^2 C_{A,e}}{\partial C_A^2} \pm 2 \frac{\partial^2 C_{A,e}}{\partial C_A \partial C_B} + \frac{\partial^2 C_{A,e}}{\partial C_B^2} \right|$$

The plus and minus signs are needed because the product $V_1 V_2$ can be either positive or negative depending on the frequency and the given steady state.

If $|V_1| >> |V_2|$, then conditions a) and b) reduce to

$$\frac{\partial^2 C_{B,e}}{\partial C_A^2} < 0 \qquad (2\text{-}112)$$

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and

$$\left| \frac{\partial^2 C_{B,e}}{\partial C_A^2} \right| > \left| \frac{\partial^2 C_{A,e}}{\partial C_A^2} \right| \qquad (2\text{-}113)$$

If $|V_2| \gg |V_1|$, then conditions a) and b) are equivalent to

$$\frac{\partial^2 C_{B,e}}{\partial C_B^2} < 0 \qquad (2\text{-}114)$$

and

$$\left| \frac{\partial^2 C_{B,e}}{\partial C_B^2} \right| > \left| \frac{\partial^2 C_{A,e}}{\partial C_B^2} \right| \qquad (2\text{-}115)$$

Inequalities (2-110) through (2-115) are conditions on the convexity of the reactor response surfaces. The reactor response can be characterized by curves of $C_{A,e}$ vs C_B and C_A and curves of $C_{B,e}$ vs C_B and C_A, these curves constitute the reactor response surfaces. If

$$\frac{\partial^2 C_{B,e}}{\partial C_B^2} < 0 \qquad (2\text{-}116)$$

then the curve of $C_{B,e}$ vs C_B is convex. Conditions (2-110), (2-112) and (2-114) imply that the reactor response curves of $C_{B,e}$ vs C_A and C_B should be convex. Inequalities (2-111)

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(2-112) and (2-115) specify that the reactor response curves of $C_{B,e}$ (2-112) and (2-115) specify that the reactor response curv $_{A,e}$. not surprising, since it merely says that we would want reactant B, which produces P, to be more sensitive to input oscillations than reactant A.

It should be pointed out that reactions with reaction rate expressions of the form

$$\mathcal{R}_A = - k C_A^n \qquad (2\text{-}117)$$

have a convex reactor response curve. When the rate equation is given by equation (2-117), then

$$\frac{dC_{A,e}}{dC_A} = \left(\frac{C_{A,e}}{C_A}\right)^n \qquad (2\text{-}118)$$

and

$$\frac{d^2C_{A,e}}{dC_A^2} = \frac{n}{C_A}\left(\frac{C_{A,e}}{C_A}\right)^n\left[\left(\frac{C_{A,e}}{C_A}\right)^{n-1} - 1\right] < 0 \qquad (2\text{-}119)$$

Thus, the $C_{A,e}$ vs C_A curve is convex, and the convexity increases with n, the reaction order.

Amplitude effect-From equation (2-98) it can be seen that the shifts in the average outlet conditions is proportional to the square of the amplitude of the recycle oscillations. The same results was obtained for linear systems.

Recycle ratio effect-According to (2-98) the shifts

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in the averages increase with the recycle ratio R_r.

Frequency effect - The frequency dependency of nonlinear systems appears quite complex, since V_1^2, V_2^2 and V_1V_2 the coefficients of the second derivatives are complex functions of ω_c^2 and ω_s^2. However, we should have local maxima for $\omega_c = -1$.

2-3.4 Numerical Solutions

The mathematical model for the reactor-recycle-tank system and for the reactor-recycle system were developed in Chapter 1 sections 1-3.1 and 1-3.2, respectively. In sections 1-3.1 it was mentioned how the solution of differential-difference equations can be obtained a time delay at a time, i.e., with the initial functions specified over $-\tau \leq t \leq 0$, the system equations can be integrated to find solutions for $0 \leq t \leq \tau$. These solutions are then used to integrate the system equations for $\tau \leq t \leq 2\tau$, and so on. In this section we will discuss how to obtain the solutions of the difference equations which describe a periodically operated reactor-recycle system.

The equations describing the tubular reactor are

$$\frac{\partial x}{\partial t} + v(t) \frac{\partial x}{\partial z} = \mathcal{R}(x) \qquad (2\text{-}120)$$

Solution of this set of equations requires knowing the reactor inlet conditions. These are given by

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$$X_o(t) = [1-R_r(t)]\, X_f + R_r(t)\, X_e(t-\tau_r) \qquad (2\text{-}121)$$

where (2-121) denotes the mixing of the feed and recycle streams at the reactor inlet. As it was shown in section 1-3.1 equation (2-120) can be integrated as a set of ordinary differential equations along the characteristic lines.

$$\frac{dX}{d\sigma} = \mathcal{R}(X) \qquad (2\text{-}122)$$

where

$$t = \sigma + t_o$$

and

$$z = \int_{t_o}^{t_o + \sigma} v(t)\, dt$$

This is equivalent to following an element of fluid as it travels along the reactor.

Hence, if we specify $\varphi(t)$ as the initial reactor outlet conditions, i.e.,

$$X(t) = \varphi(t) \qquad , \quad -(\tau + \tau_r) \leq t \leq 0$$

and with

$$R_r(t) = R_r(1 + a_r \sin \omega t)$$

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then the reactor inlet conditions can be calculated with equation (2-121), from t = 0 to t = $\tau + \tau_r$. Equation (2-122) can then be integrated along the characteristic lines from 0 to τ. Note that, if we denote the time increments as Δt, then the tubular reactor equations (2-122) must be integrated from 0 to τ every Δt times units. Hence if $N\Delta t=(\tau+\tau_r)$, N integrations are required to obtain the reactor outlet conditions from t = 0 to t = $\tau + \tau_r$. The size, $\Delta\sigma$, of the integration steps along the characteristic lines is independent of Δt the time steps. In this thesis they were both 0.01.

The reactor outlet conditions from t = 0 to t = $\tau + \tau_r$ are saved to calculate reactor inlet conditions through equation (2-121). With these inlet conditions the reactor equations can be integrated again. In this way the solutions can be obtained for any desired time interval.

To obtain the flow averaged quantities the integral

$$\langle X_e \rangle = \frac{\omega/2\pi}{\bar{F}} \int_{t}^{t + 2\pi/\omega} F(t)\, X_e(t)\, dt \qquad (2\text{-}123)$$

is approximated by

$$\langle X_e \rangle = \sum_{i=0}^{N} \frac{F(i\Delta t)\, X_e\,(i\Delta t)}{\bar{F}} \cdot \frac{\omega}{2\pi} \qquad (2\text{-}124)$$

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where

$$N = \frac{2\pi}{\omega} \Delta t$$

In the numerical calculations, the steady state conditions for constant recycle were used as initial functions, i.e.,

$$X(t) = \begin{bmatrix} C_{A,e}^{(o)} \\ C_{B,e}^{(o)} \end{bmatrix} \quad \cdots (\tau + \tau_r) \leq t \leq 0$$

After five to seven passes around the unit the averages remain unchanged. A pass is defined as the time it takes an element of fluid to go around the unit, that is, the total transportation lag. The same average values are achieved when the initial functions differ from the steady state, but it takes longer to converge. This method, when applied to a system with multiple steady states, yields only stable solutions, because the unit does not have any tendency to converge to an unstable steady state.

2-3.5 Numerical Results

To be specific consider the following reaction system

$$2A \xrightarrow{k_1'} U \qquad (2\text{-}120)$$

$$A + 2B \xrightarrow{k_2'} P \qquad (2\text{-}121)$$

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with reaction rates given by

$$\mathcal{R}_A = -k_1 C_A^2 - k_2 C_A C_B^2$$
$$\mathcal{R}_B = 2 k_2 C_A C_B^2$$
$$\mathcal{R}_U = k_1 C_A^2 / 2 \qquad (2\text{-}122)$$
$$\mathcal{R}_P = -\mathcal{R}_B / 2 = k_2 C_A C_B^2$$

Since we are dealing with dimensionless concentrations defined as

$$C_A = \frac{\tilde{C}_A}{C_R} \quad ; C_B = \frac{\tilde{C}_B}{C_R} \qquad (2\text{-}123)$$

where $\tilde{C}_A$, $\tilde{C}_B$ are the dimensional concentrations and C_R is the reference concentration. Then the reaction rate constants k_1 and k_2 are related to the constants used in equation (2-122) by

$$k_1 = k_1' C_R^2$$
$$k_2 = k_2' C_R^3 \qquad (2\text{-}124)$$

In this reaction system P is the desired product and U is a wasted by-product. The second reaction (2-121) calls for a plug flow tubular reactor where the concentrations are high favoring the production of P. However, to reduce the formation of the by-product U the concentration of A should be kept at a minimum, thus a continuous stirred

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tank reactor should be used. These two objectives are best accomplished in a plug flow tubular reactor with recycle, where the feed of A is kept constant while that of B is allowed to oscillate. The mass recycled keeps the concentration of A low and the periodic feed of B raises the average input concentration of B.

For $\gamma_t = 0$, $\bar{F}_A = \bar{F}_B$, $C_{A,f} = C_{B,f} = 2.0$, $k_1 = 2.0$ and $k_2 = 1.0$, Figure (2-6) presents a plot of yield and conversion as a function of recycle ratio. For this reaction system the yield, selectivity and conversion are defined as

$$Y = \text{Yield} = \frac{< C_{P,e} >}{\frac{\bar{F}_A}{\bar{F}_A + \bar{F}_B} C_{A,f} - < C_{A,e} >} \qquad (2\text{-}125)$$

$$S = \text{Selectivity} = \frac{< C_{P,e} >}{< C_{U,e} >} \qquad (2\text{-}126)$$

$$CONV = \text{Conversion} = 1 - \frac{< C_{A,e} >}{\frac{\bar{F}_A}{\bar{F}_A + \bar{F}_B} C_{A,f}} \qquad (2\text{-}127)$$

with the parameter values specified above, we have

$$Y = \frac{< C_{P,e} >}{1 - < C_{A,e} >}$$

$$S = \frac{< C_{P,e} >}{< C_{U,e} >} = \frac{Y}{1 - Y}$$

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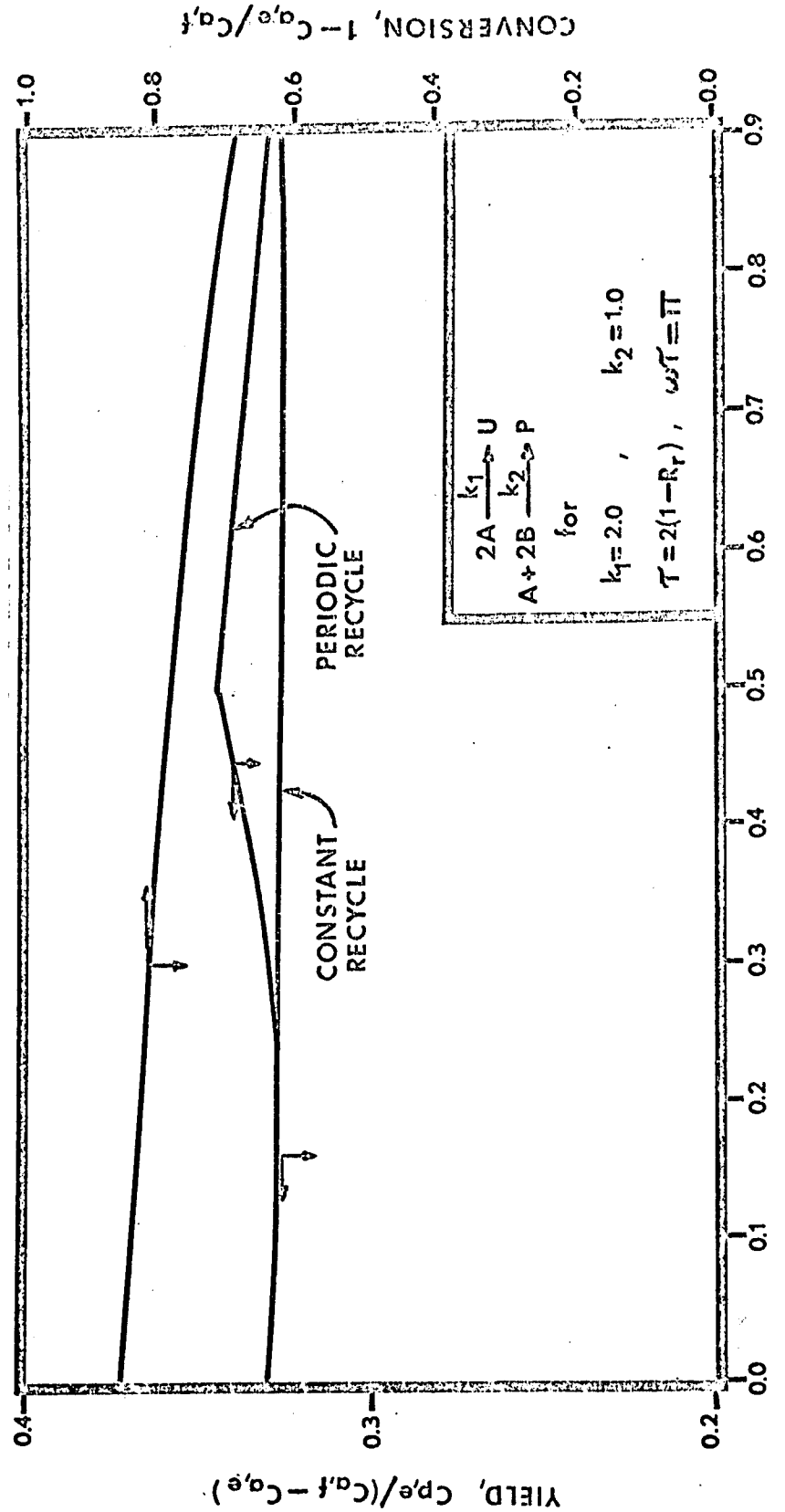

FIGURE (2-6) EFFECT OF RECYCLE

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$$CONV = 1 - \langle C_{A,e} \rangle$$

Yield curves for periodic recycle flow rate and constant recycle flow rate are shown. Only one conversion curve is shown because the average conversion for periodic recycle is always within 0.01% of the conversion for steady operation. The yield is shown to increase with recycle ratio until $R_r = 0.5$ where it is a maximum. For higher recycle ratios the yield decreases because the amplitude of the oscillations decreases.

The amplitude of the recycle flow rate oscillations is constrained by

$$a_r \leq 1.0$$

$$a_r \leq \frac{\overline{F}_B}{\overline{R}} = \frac{\frac{\overline{F}_B}{\overline{F}_A}(1-R_r)}{R_r\left(1 + \frac{\overline{F}_B}{\overline{F}_A}\right)} \qquad (2\text{-}128)$$

These constraints are necessary to assure positive feed and recycle flow rates, with $\overline{F}_A = \overline{F}_B$ equation (2-128) becomes

$$a_r \leq \frac{(1-R_r)}{2R_r} \qquad (2\text{-}129)$$

$$a_r \leq 1.0$$

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The amplitude of the oscillations used in Figures (2-6) and (2-7) is

$$a_r = 0.5 \text{ for } R_r \leq 0.5$$
$$a_r = \frac{(1-R_r)}{2R_r} \text{ for } R_r \geq 0.5 \qquad (2\text{-}130)$$

Figure (2-7) presents similar curves for $k_1 = 4.0$, the rest of the parameters are the same as in Figure (2-6).

We note that in Figure (2-6) no recycle gives a higher yield than constant recycle, while in Figure (2-7) constant recycle produces a higher yield than no recycle. However, in both cases the periodically operated system gives the best performance of the three.

Let us analyze what the effect of the nonlinear terms is on Figure (2-6). The Jacobian matrix can be determined by integrating the following matrix equation from 0 to τ.

$$\frac{dM}{dz} = \begin{bmatrix} \frac{\partial R_A}{\partial C_A} & \frac{\partial R_A}{\partial C_B} \\ \frac{\partial R_B}{\partial C_B} & \frac{\partial R_B}{\partial C_B} \end{bmatrix} M \qquad (2\text{-}131)$$

where

$$M = \begin{bmatrix} \frac{\partial C_A}{\partial C_{A,o}} & \frac{\partial C_A}{\partial C_{B,o}} \\ \frac{\partial C_B}{\partial C_{A,o}} & \frac{\partial C_B}{\partial C_{B,o}} \end{bmatrix} \qquad (2\text{-}132)$$

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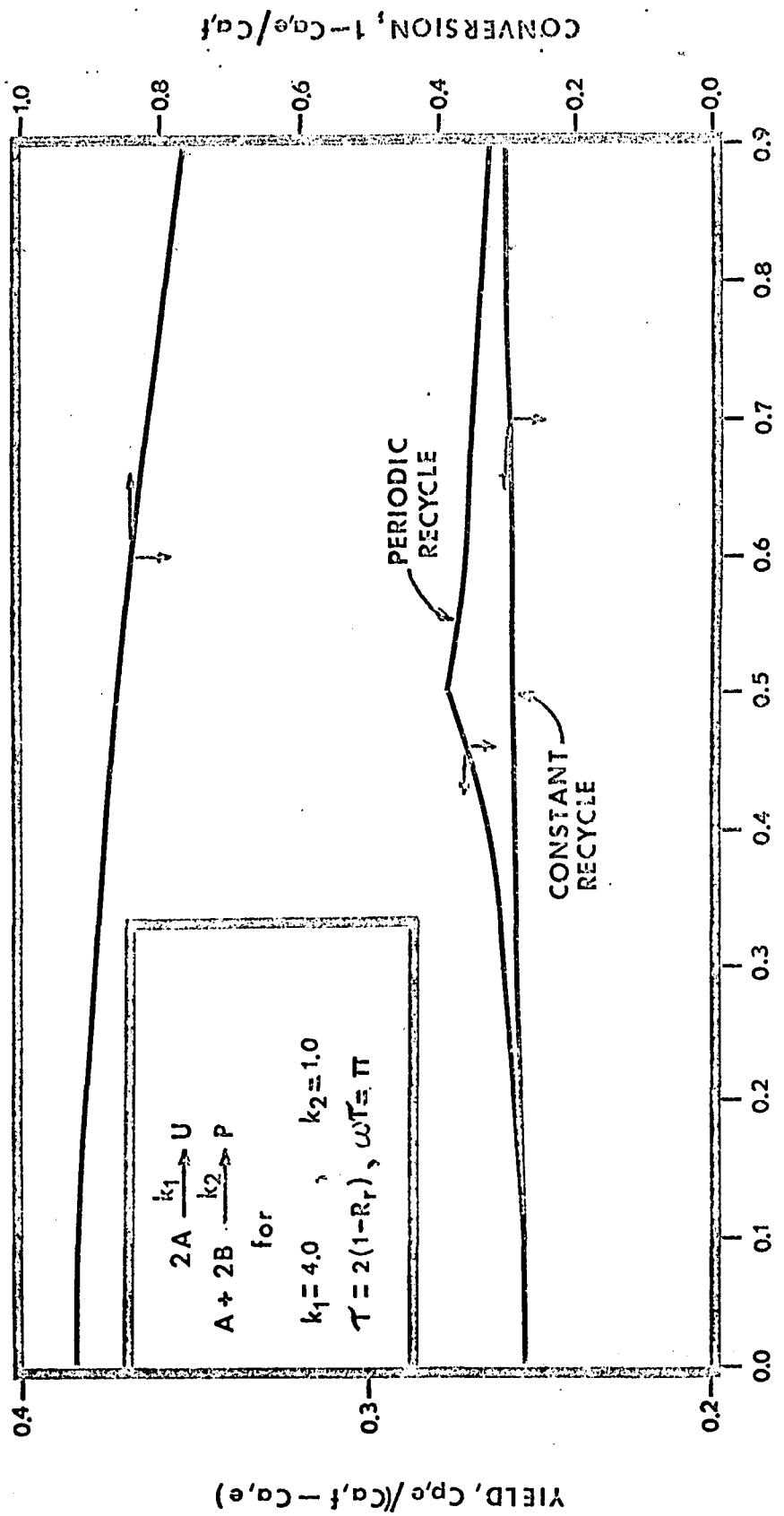

FIGURE (2-7) EFFECT OF RECYCLE

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with inital conditions

$$M(0) = I \tag{2-133}$$

The subscript o indicates a condition evaluated at the reactor inlet.

For $k_1 = 2.0$ and $k_2 = 1.0$ the Jacobian matrix for this system is

$$J = \begin{bmatrix} 0.208 & -0.117 \\ -0.208 & 0.485 \end{bmatrix} \tag{2-134}$$

V_1 and V_2 the components of $(A_e + B_e)E$ are given by

$$\begin{aligned} V_1 &= 0.47 \\ V_2 &= -0.23 \end{aligned} \tag{2-135}$$

In obtaining (2-135), the frequency was specified so that $\omega_c = -1$ and τ_t was set to zero.

From the analysis in the last section, section 2-3.3, it is known that when

$$|V_1| > |V_2|$$

it is desirable to have

$$\frac{\partial^2 C_{B,e}}{\partial C_A^2} < 0 \tag{2-136}$$

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and

$$\left| \frac{\partial^2 C_{B,e}}{\partial C_A^2} \right| > \left| \frac{\partial^2 C_{A,e}}{\partial C_A^2} \right| \qquad (2\text{-}137)$$

Figure (2-8) presents curves of the concentration of B at the reactor outlet, $C_{B,e}$, versus the concentration of A at the reactor inlet, C_A, for several values of the concentration of B at the reactor inlet. The curves shown are concave, i.e.,

$$\frac{\partial^2 C_{B,e}}{\partial C_A^2} > 0 \qquad (2\text{-}138)$$

Thus in this system convexity does not help the yield improvement produced by periodic operation.

Knowing the Jacobian matrix, it is possible to find what the perturbation analysis predictions are. The perturbation solutions for linear coupled systems are given by equation (2-104). For the parameter values used in Figure (2-6) with $\Pi_r = 0.5$, equation (2-104) predicts

$$\langle X_e \rangle = X_e(o) + \begin{bmatrix} 0.031 \\ -0.04 \end{bmatrix}$$

or

$$\langle C_{A,e} \rangle = 0.215 + 0.031 = 0.245$$

$$\langle C_{B,e} \rangle = 0.491 - 0.04 = 0.451 ,$$

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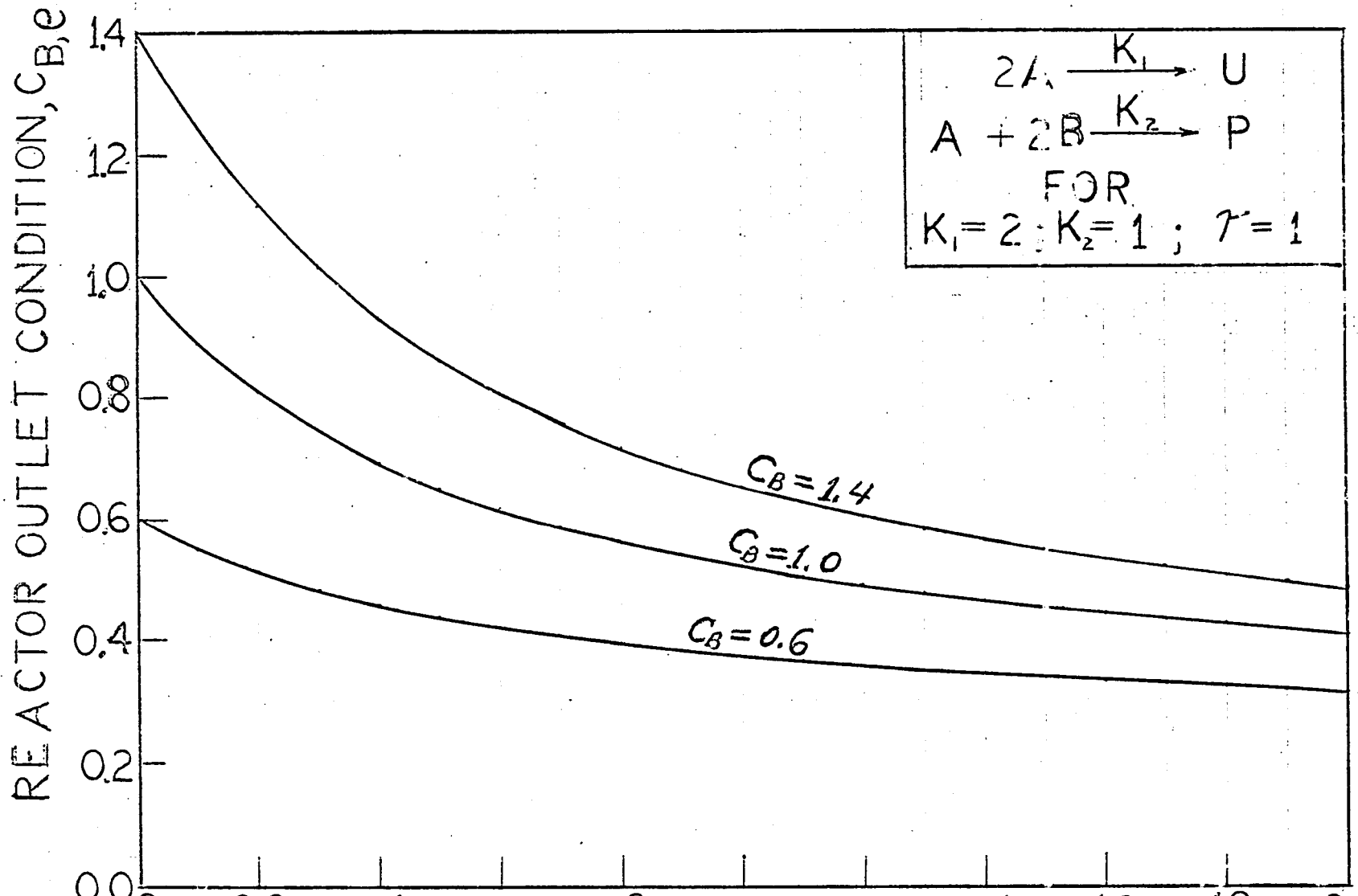

FIGURE (2-8) REACTOR RESPOSE CURVES

which is equivalent to

$$\text{yield} = 0.364$$

$$\text{conversion} = 0.754$$

The average values for periodic and steady operation are

	CONSTANT RECYCLE	PERIODIC OPERATION	PERTURBATION ANALYSIS
$\langle C_{A,e} \rangle$	0.215	0.220	0.246
$\langle C_{B,e} \rangle$	0.491	0.464	0.451

We note that the perturbation analysis predicts larger changes than those which actually take place. Nevertheless, the direction and order of magnitude of the predictions are correct.

It should be pointed out that the eigenvalues of

$$J_1 = R_r J$$

are

$$\lambda_1 = 0.340 \qquad (2\text{-}139)$$

$$\lambda_2 = 0.335$$

that is, the eigenvalues are real and have an absolute value less than unity. These are the conditions given by Reilly and Schmitz[13] for a steady state to be stable and nonoscillatroy.

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Figure (2-9) presents plots of yield and selectivity versus frequency for reaction system (2-120), (2-121). We see from this figure, that there is a zero frequency effect for nonlinear systems just as we found in the linear example. In the same way the shift in the averages is the largest for $\omega\tau = n\pi$. The improvements being obtained when $\omega\tau = \pi, 3\pi$ i.e., $\omega_c = -1$. However this nonlinear system presents large changes in the averages when $2\pi < \omega\tau < 3\pi$ in this it differs from the linear case. The differences may be produced by high order harmonics coming to play at the higher frequencies.

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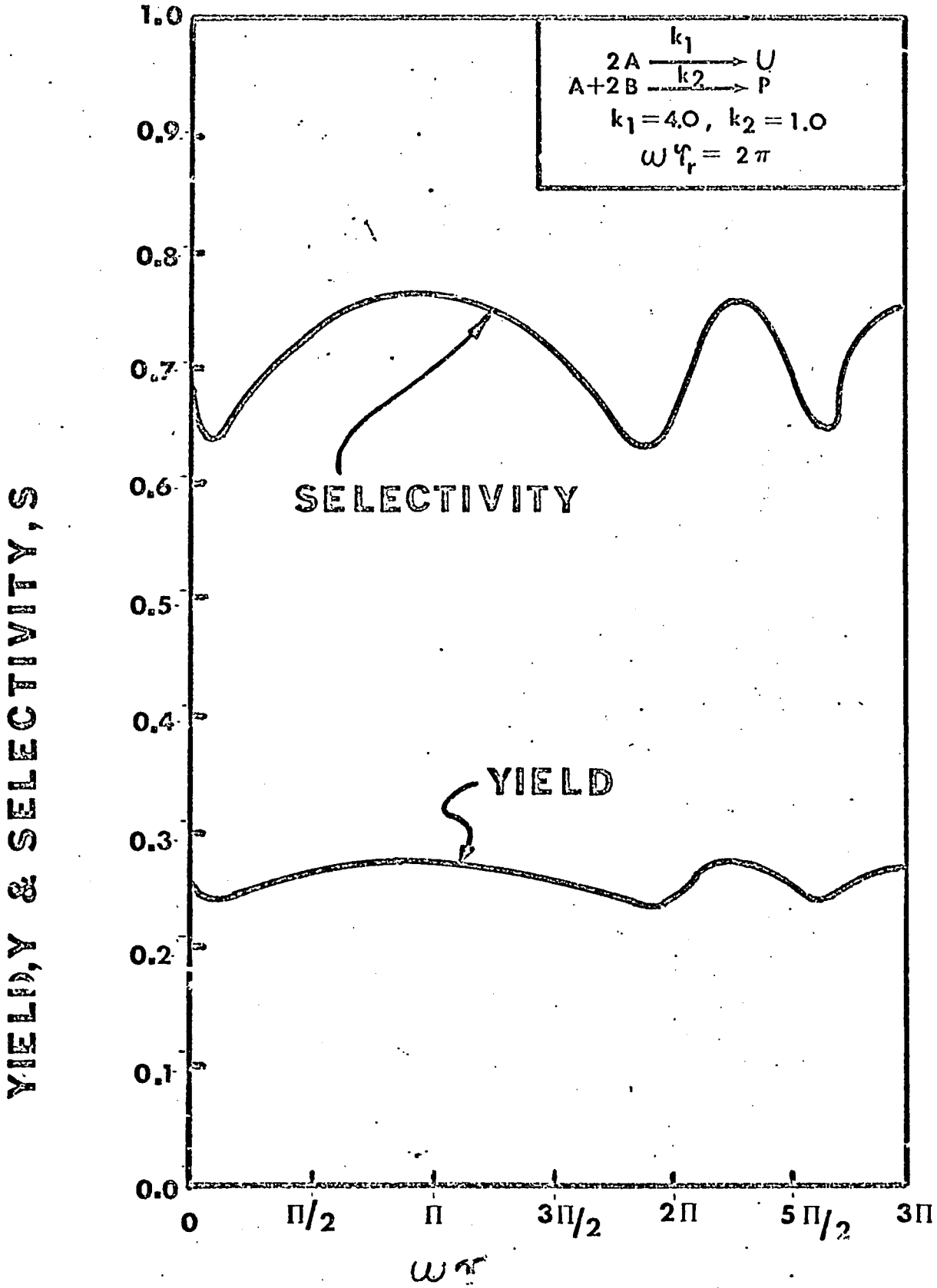

FIG.(2-9) FREQUENCY EFFECT

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2-4 NON-ISOTHERMAL SYSTEMS

2-4.1 Periodic Recycle-Constant Feed Temperature

In this section we will consider non-isothermal systems where the feed temperature is constant and the recycle flow rate is periodic. In the next section, 2-4.2, the case where all the flows are constant and the periodicity is produced by a variable feed temperature is considered. In the examples studied considerable improvements are obtained with periodic operation.

In non-isothermal systems in addition to the material balance an energy balance must be considered. For a system with two reactants A and B, the material balance equations are (2-73) and (2-74), and the energy balance around the tank is

$$V_t \frac{dT}{dt} = F_A(t)\, T_{A,f} + F_B(t)\, T_{B,f} + R(t) T_e - (F_A(t) + F_B(t) + R(t))\, T(t) \qquad (2\text{-}140)$$

In addition to equations (2-73), (2-74) and (2-140), the dimensionless equations describing the tubular reactor are

$$\frac{\partial C_A}{\partial t} + v(t) \frac{\partial C_A}{\partial z} = \mathcal{R}_A (C_A, C_B, T) \qquad (2\text{-}141)$$

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$$\frac{\partial C_B}{\partial t} + v(t) \frac{\partial C_B}{\partial z} = \mathcal{R}_B (C_A, C_B, T) \qquad (2\text{-}142)$$

$$\frac{\partial T}{\partial t} + v(t) \frac{\partial T}{\partial z} = -\mathcal{R}_A - \mathcal{R}_B - U_r(T - T_\infty) \qquad (2\text{-}143)$$

Consider the reaction system

$$\begin{aligned} A &\xrightarrow{k_1} U \\ A + B &\xrightarrow{k_2} P \end{aligned} \qquad (2\text{-}144)$$

with reaction rate expressions given by

$$\mathcal{R}_A = - k_1 C_A - k_2 C_A C_B \qquad (2\text{-}145)$$

$$\mathcal{R}_B = - k_2 C_A C_B \qquad (2\text{-}146)$$

with

$$\begin{aligned} k_1 &= e^{9.2-15/T} \\ k_2 &= e^{18-24/T} \end{aligned} \qquad (2\text{-}147)$$

and

$$\frac{\Delta H_1}{\Delta H_2} = 0.5 \qquad (2\text{-}148)$$

then the second reaction has the larger activation energy and is promoted by high temperatures. For highly exothermic reactions, it is important to know the shape of the T_c vs T

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curve. This curve depends upon the inlet concentrations. The reader is referred to papers by Reilly and Schmitz[13], Luus and Amundson[15] and Pareja and Reilly[18] where typical T_e vs T curves are presented for different parameters. In general the T_e vs T is S shaped or convex. In a concave part of this curve, oscillations in the input temperature favor the reaction which is most temperature dependent. Thus, since the product of the first reaction is supposed to be a wasted species and that of the second a wanted product, then when operating in the concave part of the curve oscillations in the feed flow rate of B will better the performance. Let

$$F_A(t) = \bar{F}_A \tag{2-149}$$

$$F_B(t) = \bar{F}_B - a_r R \sin\omega t \tag{2-150}$$

$$R(t) = \bar{R}(1+a_r \sin\omega t) \tag{2-151}$$

$$T_{A,f} = \bar{T}_{A,f} \tag{2-152}$$

$$T_{B,f}(t) = \bar{T}_{B,f} \tag{2-153}$$

For $t_t = 0$, $\omega_c = -1$, $a_r = 0.5$, $T_W = 1.0$, $\bar{T}_{A,f} = 1.1$, $\bar{T}_{B,f} = 1.1$, $R_r = 0.5$, $C_{A,f} = C_{B,f} = 2.0$, and $a_r = 0.5$ the average output conditions for system (2-144) are

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	NO RECYCLE	CONSTANT RECYCLE	PERIODIC OPERATION
$< T_e >$	1.058	1.060	1.10
$<C_{A,e}>$	0.954	0.961	0.92
$<C_{B,e}>$	0.972	0.977	0.95
Y	0.612	0.592	0.675

We note that for this system

$$S = Y/(1-Y)$$

This steady state lies in the concave part of the T_e vs T curve. The selectivity under periodic operation is 50% better than for constant recycle, and 30% better than for no recycle.

For this same reaction and operating conditions but with rate constants

$$k_1 = e^{9.8 - 15/T}$$
$$k_2 = e^{18.6 - 24/T} \qquad (2\text{-}154)$$

The average output are

	NO RECYCLE	CONSTANT RECYCLE	PERIODIC OPERATION
$< T_e >$	1.092	1.513	1.520
$<C_{A,e}>$	0.890	0.[illegible]	0.002
$<C_{B,e}>$	0.930	0.170	0.149
Y	0.635	0.83	0.85

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In this case the mixture is ignited by the fluid feedback through the recycle line and almost complete conversion of A is obtained. The system is operating in a steady state on the last part of the T_e vs T curve where it is very flat. Under these conditions temperature variations are of little consequence. Then the improvements brought by periodic operation is, in this case, mainly a concentration effect similar to that obtained for isothermal systems.

These two examples show that by properly choosing one of the feed flow rates as forcing agent a nonisothermal system may be improved.

2-4.2 Periodic Feed Temperature-Constant Flow Rates

Consider the following reaction

$$A \xrightarrow{k} P$$

taking place adiabatically in the reactor, with rate expression given by

$$\mathcal{R}_A = - k C_A \qquad (2\text{-}155)$$

where

$$k = k_o \, e^{-E_r/T}$$

For

$$k = e^{4-15/T} \qquad (2\text{-}156)$$

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and

$$T_f = 2.4\ (1 + 0.2 \sin\omega t) \qquad (2\text{-}157)$$

with $\tau_t = 0, \omega_c = 1, R_r = 0.5$ and $C_{A,f} = 1.0$ the flow-averaged outlet conditions are

	NO RECYCLE	CONSTANT RECYCLE	PERIODIC FEED TEMP
$< T_e >$	2.65	2.676	2.70
$<C_{A,e}>$	0.75	0.724	0.70

The criteria to determine whether or not to use a periodic feed temperature in complex reaction networks is; if as the temperature increases the desired reaction becomes dominant, and if the heats of reaction are of the same order of magnitude, then a variable feed temperature raises the average temperature and this promotes the formation of the desired product. We note that the complementary mode of periodic operation raises the average input concentration in linear systems. The following set of parallel reactions further illustrates the idea.

Consider

$$\begin{aligned} A &\xrightarrow{k_1} U \\ A &\xrightarrow{k_2} P \end{aligned} \qquad (2\text{-}158)$$

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where

$$k_1 = e^{3-10/T} \qquad (2\text{-}159)$$

$$k_2 = e^{25.3 - 75/T} \qquad (2\text{-}160)$$

and

$$\mathcal{R}_A = -k_1 C_A - k_2 C_A$$

The second reaction is more temperature sensitive than the first one. For

$$T_f = 2.2\ (1+0.3 \sin \omega t) \qquad (2\text{-}161)$$

with $\tau_t = 0, \omega_c = 1, R_r = 0.5$ and $C_{A,f} = 1.0$ the flow average outlet conditions are

	NO RECYCLE	CONSTANT RECYCLE	PERIODIC FEED TEMP.
$< T_e >$	2.711	2.763	2.950
$<C_{A,e}>$	0.489	0.437	0.253
$<C_{U,e}>$	0.493	0.511	0.439
$<C_{T,e}>$	0.018	0.052	0.308

It can be seen that the yield and selectivity for a periodic feed temperature are superior to those resulting when the feed temperature is constant and equal to the mean.

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2-5 CONCLUSIONS

The results show how a periodic recycle flow rate can be used to improve the performance of reactors with recycle. In constrast with systems without recycle, periodic operation of reactor-recycle systems affects the reactor performance when the reaction is first order and the reactor is isothermal. The direction of the shifts in the average conversion and yield produced by periodic operation may be controlled by suitably choosing the frequency of the oscillations.

The perturbation techniques of nonlinear mechanics proved very well suited for the analysis of periodic processing. Excellent agreement was obtained between the numerical solutions and the solutions from the perturbation analysis. Thus, it was possible to use the perturbation estimates to identify cases which can be improved significantly by periodic operation.

It was shown that the yield, in multiple reaction systems, can be improved by periodically varying the feed flow rate of one of the reactants. Reactions in which one one of the reactants is in the complementary mode are promoted over reactions in which the reactants are in the balanced mode of operation.

The magnitude of the improvements, up to 50%, warrant further research into the practical implementation of those oscillators. For a realistic process the cost of producing

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the oscillations must be considered together with product separation costs and product specifications.

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CHAPTER 3

OPTIMAL CONTROL OF REACTOR-RECYCLE SYSTEMS

3-1 INTRODUCTION

In the last chapter we demonstrated how the performance of a reactor-recycle system can be improved by the periodic manipulation of the recycle flow rate. That is, Chapter 2 was concerned with how to utilize the transient behavior, which exists during periodic operation, to improve the performance of the reactor-recycle system. This chapter is concerned with the optimal start-up of a reactor-recycle system. Once the unit has been started, it can be operated in either an oscillatory or nonoscillatory fashion. Thus, this chapter deals with the transient behavior of reactor-recycle systems during start-up.

A method to solve extremal problems for reactor-recycle systems is presented. The method is applicable to systems described by differential-difference equations. The time delay is approximated by means of a sequence of holding tanks. The number of holding tanks determines the degree of the approximation. The approximate system is used to obtain time-optimal and profit-optimal heating policies for the start-up of a nonlinear tubular reactor with direct recycle.

Optimal policies are determined for several degrees of approximation. The effects upon the exact equations of

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these optimal controls for the auxiliary system are presented.

Although the approximation is new for the control of nonlinear reactor-recycle systems, its applicablity to less complicated problems has been established.

Jen Wei[20] and Saludkvadze[21] used a similar approximation in the control of linear systems with delay. Krasonskii[22] proved that the approximation converges for linear systems with quadratic performance criteria. Repin[23] showed the approximation to converge for nonlinear uncontrolled systems.

Other approaches to the control of time-lag systems have appeared in the literature. Some of them like those of Kramers',[24] Koepcke,[25] Koppel[37] and Ray[28] are limited to linear models. McKinnon[26] extended the work of Merriam[27] to systems with time delay. The computational difficulties of this second variation method are magnified many fold by the time delay. Recently Seinfeld[38] used a steepest-ascent method for computing the optimal control of a continuous stirred tank reactor (CSTR) with an exothermic reaction in which a transportation lag occurs in the control loop.

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3-2 DESCRIPTION OF THE REACTOR-RECYCLE SYSTEM

A sketch of the system is shown in Figure (3-1). The reactant feed stream, with temperature T_f and reactant concentration C_f, is combined in the mixing tank with a fraction R_r of the reactor effluent stream, which is denoted by the subscript e. The output from the mixing tank enters directly the plug flow tubular reactor, which is taken to be adiabatic. The mixing tank, however, contains a heat exchanger, which provides for controllable heat inputs to the system.

A single exothermic reaction

$$A \xrightarrow{k} P$$

at constant pressure is considered. In the numerical examples to follow we take

$$k = 10^{11}\, e^{-75/T}$$

The reaction is assumed to occur only within the tubular reactor and not within the mixing tank or the recycle line. These assumptions simplify the numerical computations and permit a clearer discussion of the approximation method. The method remains applicable, however, without these assumptions as long as the reactor-recycle system is described by differential-difference equations.

For an exothermic reaction, the recycle stream in the case of sustained operation may be used to preheat the re-

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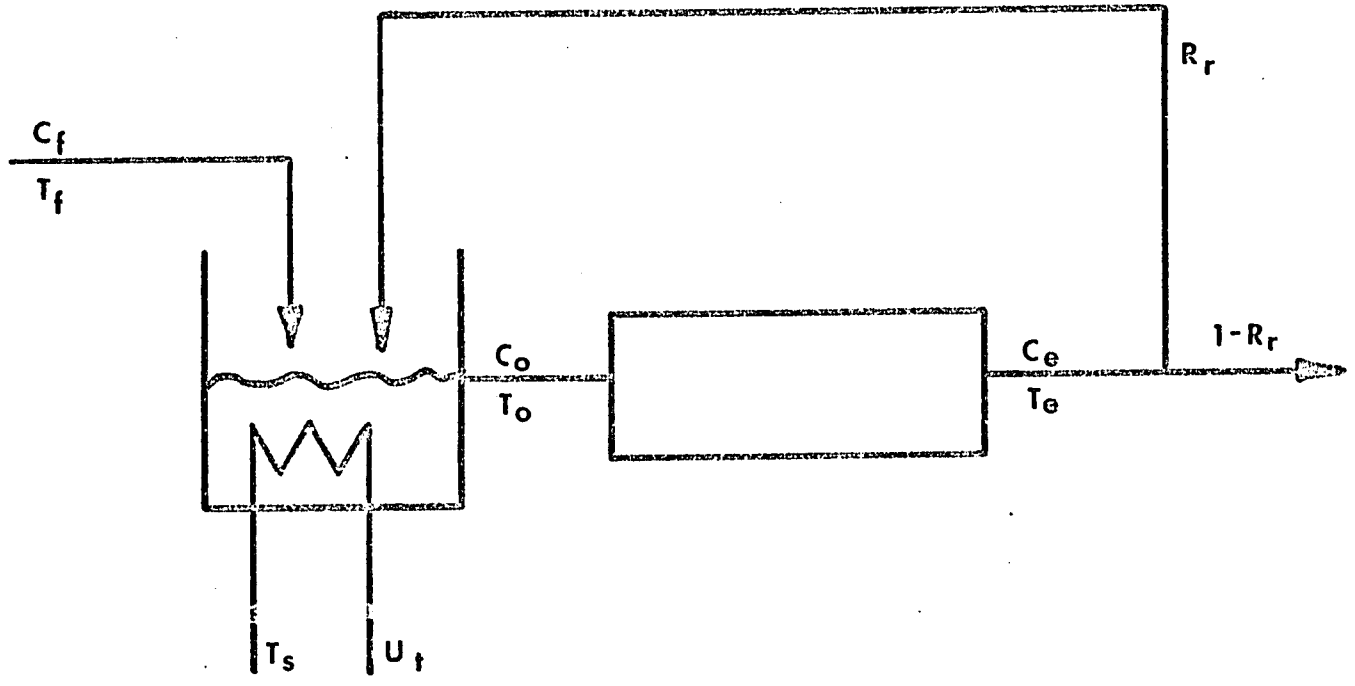

Figure(3-1)Reactor Recycle System

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actant mixture to a temperature sufficiently high to maintain the desired rate. In the case of start-up, the recycle stream is initially too cold to heat up the reaction mixture. If cold reactants are fed to the reactor, there is a minor extent of reaction, and insufficient heat is generated to raise significantly the temperature of the reactor effluent stream. Hence, it is necessary to use the tank exchanger to ignite the reaction. After the start-up period, the recycle stream sustains the ignited state of the system. The tank heat exchanger may be used to control for disturbances during sustained operation.

The above considerations suggest the adequacy of simple on-off operation of the heat exchanger. Thus the heat input to the tank is proportional to $U_t\ (T_s - T_o)$, where $U_t = 0$ during periods of no heating. For convenience, U_t may be taken to be unity during heating periods.

The dimensionless equations which describe the mixing tank have the following form

$$\tau_t \frac{dC_o}{dt} = (1-R_r)\ C_f + R_r\ C_e\ (t-\tau_r) - C_o(t) \qquad (3\text{-}1)$$

and

$$\tau_t \frac{dT_o}{dt} = (1-R_r)\ T_f + R_r T_e\ (t-\tau_r) - T_o(t) + U_t(t)[T_s - T_o(t)] \qquad (3\text{-}2)$$

where τ_t is the time constant for the tank, τ_r is the transportation lag in the recycle line, and $U_t(t)$ is the

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on-off control variable.

Because of the plug flow assumption, the reactor outlet conditions, $C_e(t)$ and $T_e(t)$ of a given fluid element, can be determined from the reactor inlet conditions of this same element at a previous time. Thus the following functional relationships can be written

$$C_e(t) = \Gamma_1[C_o(t-\tau),\ T_o(t-\tau)] \qquad (3\text{-}3)$$

$$T_e(t) = \Gamma_2[C_o(t-\tau),\ T_o(t-\tau)] \qquad (3\text{-}4)$$

Equations (3-3) and (3-4) may be substituted for C_e and T_e in equations (3-1) and (3-2). These yield the following system of differential-difference equations.

$$\tau_t \frac{dC_o}{dt} = (1-R_r)\ C_f + R_r\Gamma_1[C_o(t-\tau'),\ T_o(t-\tau')] - C_o(t) \qquad (3\text{-}5)$$

$$\tau_t \frac{dT_o}{dt} = (1-R_r)\ T_f + R_r\Gamma_2[C_o(t-\tau'),\ T_o(t-\tau')] - T_o(t) + U_t(t)\ [T_s - T_o(t)] \qquad (3\text{-}6)$$

where $\tau' = \tau_r + \tau$ is the total transportation lag in the system.

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3-3 THE START-UP PROBLEM

In the start-up problem under consideration, it is assumed that the system is initially at a uniform temperature and is filled with a fluid devoid of the reacting species. This is equaivalent to the statement that the mixing tank ouput prior to start-up had a uniform temerature and zero reactant concentration over a time interval of duration equal to the total transportation lag. For the numerical examples, the initial conditions for the tank are

$$C_o(t) = 0.0 \text{ and } T_o(t) = 2.65 \text{ for } -\gamma' \leq t \leq 0 \quad (3\text{-}7)$$

The start-up period ends once the system reaches the target set, which ensures self-sustaining operation. That is, in the absence of major disturbances, the system will remain at or near the desired steady state without external heating (i.e., $U_t = 0$). In systems with time delay, the target set must be defined over a time interval of duration equal to the transportation lag. A shorter interval cannot ensure that the system will remain within the desired limits after start-up.

For example, if the recycle ratio is 0.5, if the reactant feed concentration is 1, and if the feed temperature is 2.35, then the system has multiple steady states for $U_t = 0$. The desired steady state is the one with the highest conversion, for which the reactor input and effluent condition are

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$$C_{os} = 0.51 \qquad C_{es} = 0.02$$
$$\text{and} \tag{3-8}$$
$$T_{os} = 2.84 \qquad T_{es} = 3.33$$

If one evaluates equations (3-3) and (3-4) for any value of C_o and T_o within the limits

$$0.50 \leq C_o \leq 0.52$$
$$2.82 \leq T_o \leq 2.86$$

one finds that the reactor effluent is bounded by

$$0.0 \leq C_e \leq 0.03 \tag{3-9}$$
$$3.32 \leq T_e \leq 3.35$$

If that effluent is recycled to the mixing tank and combined with the feed, the resulting tank output must lie within the above limits for C_o and T_o. Therefore, self-sustaining operation is assumed if the target set is defined as

$$0.50 \leq C_o(t) \leq 0.52 \qquad \text{for } t_f - \tau' \leq t \leq t_f \tag{3-10}$$
$$2.82 \leq T_o(t) \leq 2.86$$

where t_f marks the end of the start-up period.

Two different performance criteria are considered in this study. The first one is time optimal, i.e., the control must be chosen so as to drive the system to the target set, equation (3-10) in minimum time. Thus

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$$\phi_1 = \int_0^{t_f} \theta_1 \, dt = -\int_0^{t_f} dt \qquad (3\text{-}11)$$

where t_f is free. This objective is meaningful for systems where the total transportation lag is of hours or longer. In the system under consideration, with the heat transfer coefficient as controller, the minimum time needed to reach steady state is of the order of four times the transportation lag.

The other performance criterion is

$$\phi_2 = \int_0^{t_f} \theta_2 \, dt = \int_0^{t_f} [(1-C_e) - P_u \, U_t(t)] \, dt \qquad (3\text{-}12)$$

where t_f is fixed. This is a dimensionless profit function, in which $(1-C_e)$ is the concentration of product in the effluent stream, and P_u is the ratio of control cost to product value. Equation (3-12), imposes a cost on the duration of heating, a price is paid whenever steam is supplied.

In vector notation the Hamiltonians for the two performance criteria can be written as

$$H_j = -\theta_j + \frac{P(t)'}{\tau_t} \left\{ (1-R_r) \, x_F + R_r \Gamma[x(t-\tau')] - x(t) + [0, U_t(T_s - T)]' \right\} \qquad (3\text{-}13)$$

where P(t) is the adjoint variable, and $x = (C,T)'$, $j = 1,2$.

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Because the Hamiltonian is in each case, j = 1,2, a linear function of the control U_t, the optimal control must be either bang-bang or singular. In the examples considered the control was found to be nonsingular. The equations satisfied by the adjoint variables together with their boundary conditions are presented in section 3-5.4, where the numerical solution is discussed.

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3-4 THE APPROXIMATION METHOD

The general form, in vector nontation, of the differential-difference equations (3-5) and (3-6) for the reactor-recycle system is

$$\dot{x}(t) = f(x(t),\ x(t-\tau')) \qquad (3\text{-}14)$$

The approximation method is based upon defining a set of vector functions $y_i(t)$ which approximate x at a set of points $t = \frac{i\tau'}{N}$ in the interval $t-\tau'$ and t. If each function is generated by an ordinary differential equation, then the differential-difference equation (3-14) is approximated by a larger number of ordinary differential equations since $x(t-\tau')$ in equation (3-14) may be replaced by the function $y_N(t)$ which approximates it. For example, it is quite small, then it is reasonable to expect that

$$\dot{x}(t-\tau') = (x(t) - x(t-\tau'))/\tau'$$

If the functions $y_o(t)$ and $y_1(t)$ are defined by

$$\dot{y}_o(t) = f(y_o(t),\ y_1(t))$$

$$\dot{y}_1(t) = (y_o(t) - y_1(t))/\tau'$$

with initial conditions

$$y_o(0) = x(0) \text{ and } y_1(0) = x(-\tau')$$

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then we would expect that

$$y_o(t) \simeq x(t), \text{ and}$$
$$y_1(t) \simeq x(t-\tau').$$

The validity of the above approximation is limited to all small values of the time delay τ' and to small values of time t. These limits may be extended by increasing the number of points at which x is approximated. This requires an increase in the number of approximating functions $y_i(t)$, which are defined by

$$\dot{y}_o(t) = f(y_o(t), y_N(t))$$

and

$$\dot{y}_i(t) = N(y_{i-1}(t) - y_i(t))/\tau' \qquad i = 1,\ldots,N$$

with initial conditions

$$y_i(0) = x(-i\tau'/N)$$

We note that $y_j(t)$ is the approximating function for $x(t-i\tau'/N)$.

For the reactor-recycle problem under consideration, the approximating system can be written

$$\tau_t \dot{y}_o(t) = (1-R_r)y_f + R_r\Gamma[y_N(t)] - y_o(t) + U_t(t)\,[0, T_s - y_{2,o}(t)]' \qquad (3\text{-}15)$$

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$$y_i(t) = \frac{N}{\tau} (y_{i-1}(t) - y_i(t)) \qquad (3\text{-}16)$$
$$i = 1,\ldots,N$$

where $y_{2,o}$ is the approximating function to T_o, and N is the degree of approximation.

The start-up problem is now one of determining the optimal control policy for the approximating system. In general, the optimal control problem for ordinary differential equations is much simpler than that for differential-difference equations. The optimal start-up policy, which is denoted by $U_t^*(t; N)$ is dependent upon the degree of approximation. One cannot tell a priori how large N must be in order to obtain a satisfactory approximation to the optimal policy for the original system. The computations for the reactor-recycle start-up problem indicate that very good results are obtained for N = 4. The initial conditions for equations (3-15) and (3-16) are

$$y_i(0) = \begin{bmatrix} 0.0 \\ 2.65 \end{bmatrix} \qquad (3\text{-}17)$$
$$i = 0,1,2,\ldots,N$$

and the target is defined by

$$\begin{bmatrix} 0.50 \\ 2.82 \end{bmatrix} \leq y_i(t_f) \leq \begin{bmatrix} 0.52 \\ 2.86 \end{bmatrix} \qquad (3\text{-}18)$$
$$i = 0,1,2,\ldots N$$

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No modification is needed for the time optimal criterion. While the profit function criterion, given by equation (3-12), must be written with the appropriate variables, i.e.,

$$\phi_2 = \int_0^{t_f} \theta_2(U_t;N)\,dt = \int_0^{t_f} \left\{ 1 - \Gamma_1[y_N(t)] - P_u U_t(t;\ N) \right\} dt \qquad (3\text{-}19)$$

The auxiliary problem is to transfer the system described by equations (3-15) and (3-16), from (3-17) to the target set specified by equation (3-18) in an optimal fashion, i.e., either in minimum time or maximizing the profit given by equation (3-19).

The Hamiltonians for the two performance criteria ar given by

$$H_j = Q_j + \frac{Q_o(t)'}{\gamma_t} \quad (1-R_r)\, y_f + R_r\,[y_N(t)] \; - y_o(t)$$

$$+U_t(t;\ N) \quad [T_s - y_{2,0}(t)]$$

$$+ \sum_{i=1}^{N} Q_i(t)' \,[y_{i-1}(t) - y_i(t)] \frac{N}{\gamma_i} \qquad (3\text{-}20)$$

$j = 1,2$

where Q_j, $j = 0,N$ are the adjoint variables for the approximating problem. The equations satisfied by the adjoint variables are given in section 3-6.3. The H_j's are linear functions of the control. As is the case for the

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exact equations, the optimal control is either bang-bang or singular.

Before going ahead with the solution of the optimization problem, a few things should be pointed out about the approximation. Figure (3-2a) presents a graphical representation of equations (3-15) and (3-16). The mixer output is sent to a series of holding tanks which are approximating the transportation lag. The output of this tank sequence goes through an input-output element or transformation before effluent and recycle streams are withdrawn. This transformation is the tubular reactor equation, i.e., whatever the tank outlet conditions are, they are used as initial conditions for the integration of the plug flow reactor equations. It is not necessary to consider any further delay in the reactor, since it has already been approximated by the series of tanks.

Figure (3-2b) presents a graphical representation of the usual approximation to a tubular reactor, i.e., in which the tubular reactor is replaced by a sequence of perfectly mixed reactors. The equations characterizing this situation are

$$\tau_t \dot{Z}_o(t) = (1-R_r)Z_f + R_r Z_N(t) - Z_o(t) \qquad (3\text{-}21)$$

$$\dot{Z}_1(t) = \frac{n}{\tau}\left[Z_{i-1}(t) - Z_i(t)\right] - r\left[Z_i(t)\right] \qquad (3\text{-}22)$$

$$i = 1,2,\ldots,n$$

and

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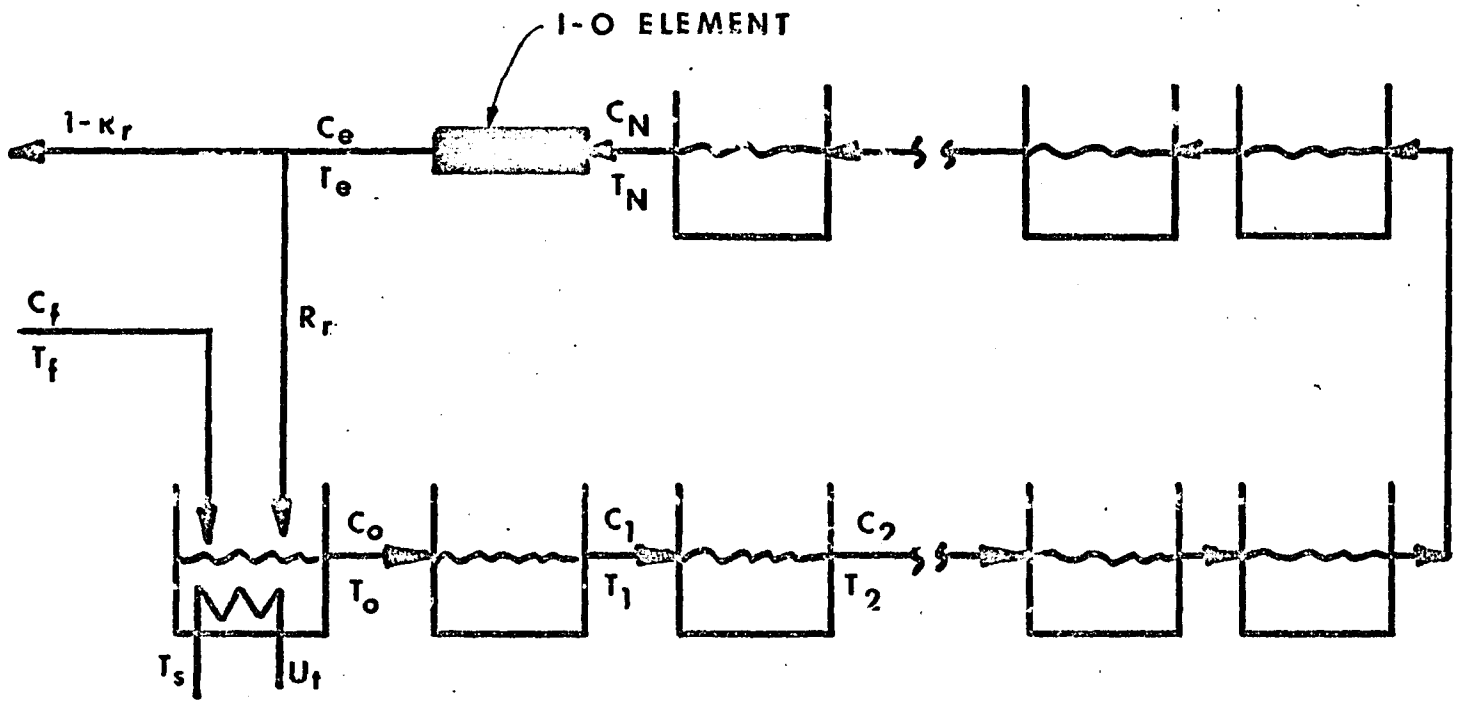
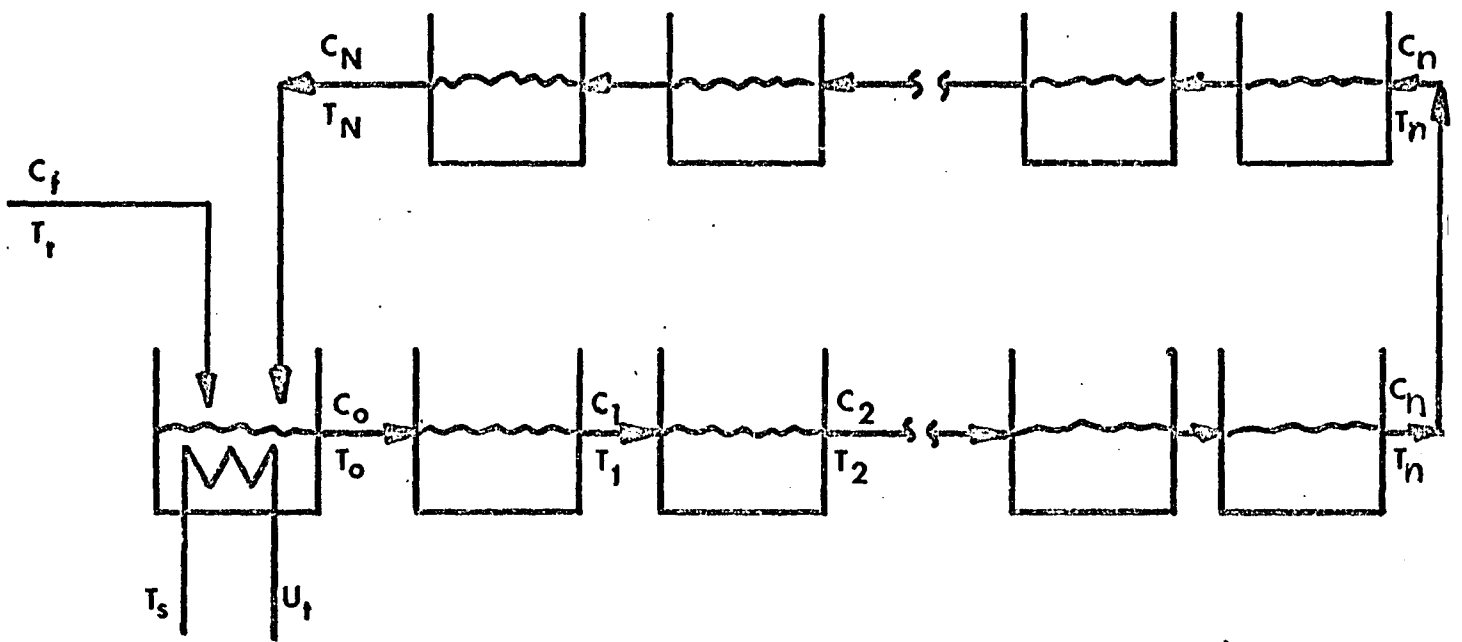


(a) Holding Tank Approximation

(no reaction in tanks)



(b) CSTR Approximation (reaction in tanks)

Figure (3-2) Approximations for Reactor-Recycle System

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$$\dot{Z}_i(t) = \frac{(N-n)}{\tau_r}\left[Z_{i-1}(t) - Z_i(t)\right] \qquad (3\text{-}23)$$

$$i = n+1,\ n+2,\ \ldots,N$$

where $r\left[Z_i(t)\right]$ is the reaction rate. When $\tau_r = 0$, set $n = N$ and equation (3-23) does not have to considered. The differences between the approximations are now discussed. The approximation used in this paper is referred to as the holding tank approximation, and that depicted in Figure (3-2b) is labeled the CSTR approximation.

a) Both methods approximate the delay in the same way. That is, the delay is replaced by a sequence of holding tanks in both approximations. When there is no reaction taking place in the reactor the two approximations are identical. However, when there is a reaction taking place in the reactor, the holding tank approximation uses the exact tubular reactor equations.

b) The holding tank approximation has the same steady state solutions as the original equations. This is not the case for the CSTR approximation.

c) For a given set of inputs conditions the plug flow tubular reactor has a unique set of outlet conditions. This is not necessarily the situation with the CSTR approximation. For

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non-isothermal reactions each of the CSTR's may have multiple solutions leading to a profile which is not unique, and to spurious solutions to the problem. Aris[39] reports a case in which the CSTR approximation gave rise to seven different outlet conditions.

d) For large enough N, Rapin[23] proved that the steady state solutions of the holding tank system have the same stability as those of the original problem. The CSTR approximation can be expected to have different stability regions, since it has extraneous solutions.

e) Krasovskii[22] showed, for a linear system with a quadratic performance criterion, that the solutions of the auxiliary problem converge to the solutions of the original problem, and that the trajectories of the original system generated by the control law found from the solution of the approximate problem are close to the optimal trajectories. For Krasovskii's theorem to be applicable to the reactor-recycle system the reaction must be linear or a linear approximation must be used. A convergence proof for the uncontrolled trajectories of the auxiliary system is given by Rapin[23]. No such evidence exists for the CSTR approximation, even though

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it is reasonable to expect convergence in certain instances.

f) The degree of approximation necessary to obtain a good representation of the system is smaller for the auxiliary system than for the CSTR approximations. The CSTR approximation is known to be accurate only for large N's, i.e., $N > 20$, while the results of this work indicate good modeling with $N = 5$ for the holding tank approximation. Figures (3-4) and (3-5) show for a single linear isothermal reaction the results of approximating the system by the two methods. Conditions in the figures are those of start-up. The parameters chosen ($\tau_r = 0$) favor the CSTR model, because when $\tau_r = 0$ no holding tanks are needed to approximate the delay in the recycle line. Hence, $n = N$ and the degree of the approximation is equal to the number of CSTR's approximating the tubular reactor. The figures demonstrate the holding tank approximation to be superior to the CSTR approximation. They also show that a small degree of approximation, like $N = 5$, is enough to get a good facsimile of the original system.

g) It must be said in favor of the CSTR approxi-

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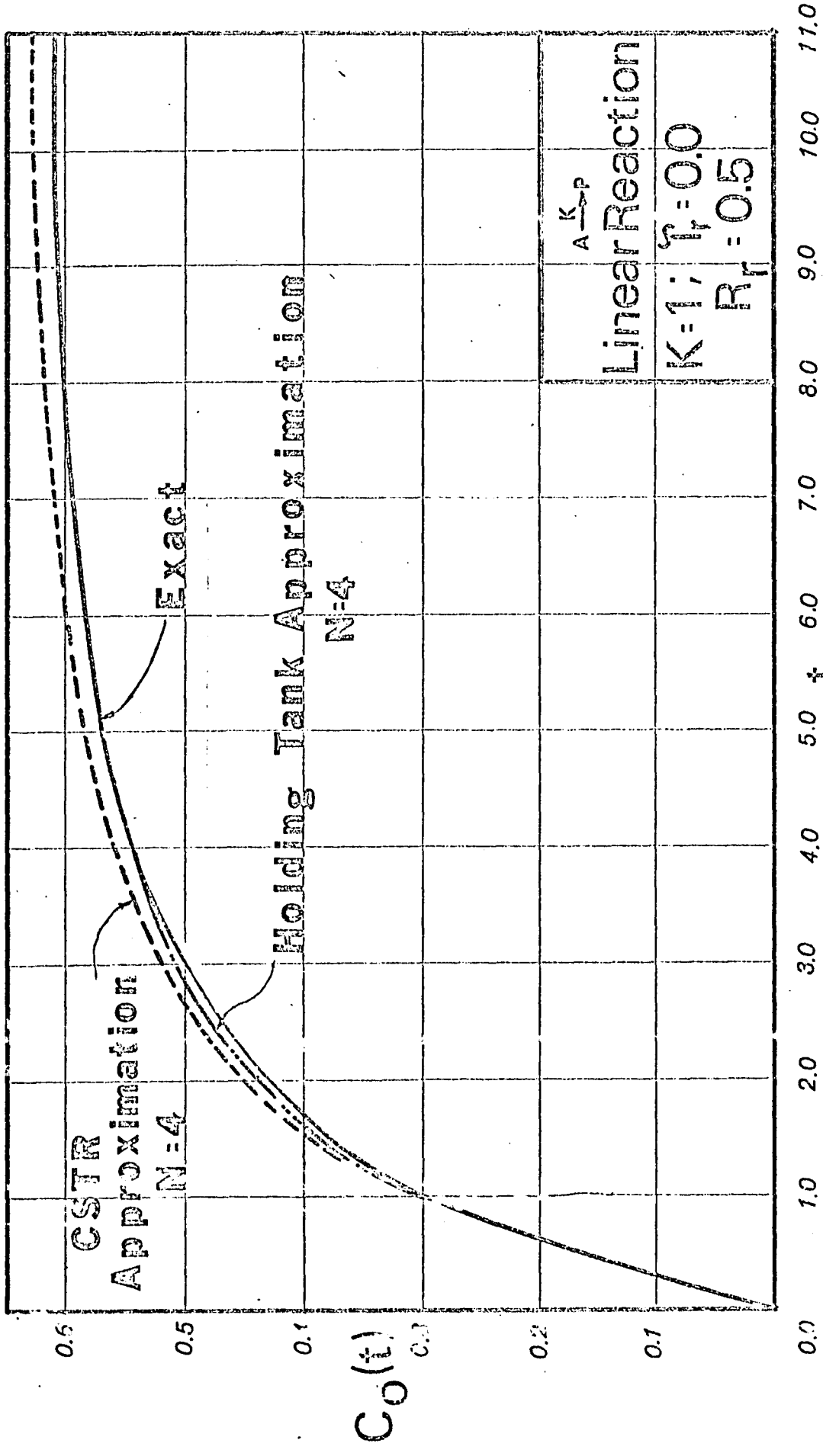

Figure(3-3)Mixer Concentration During Start Up

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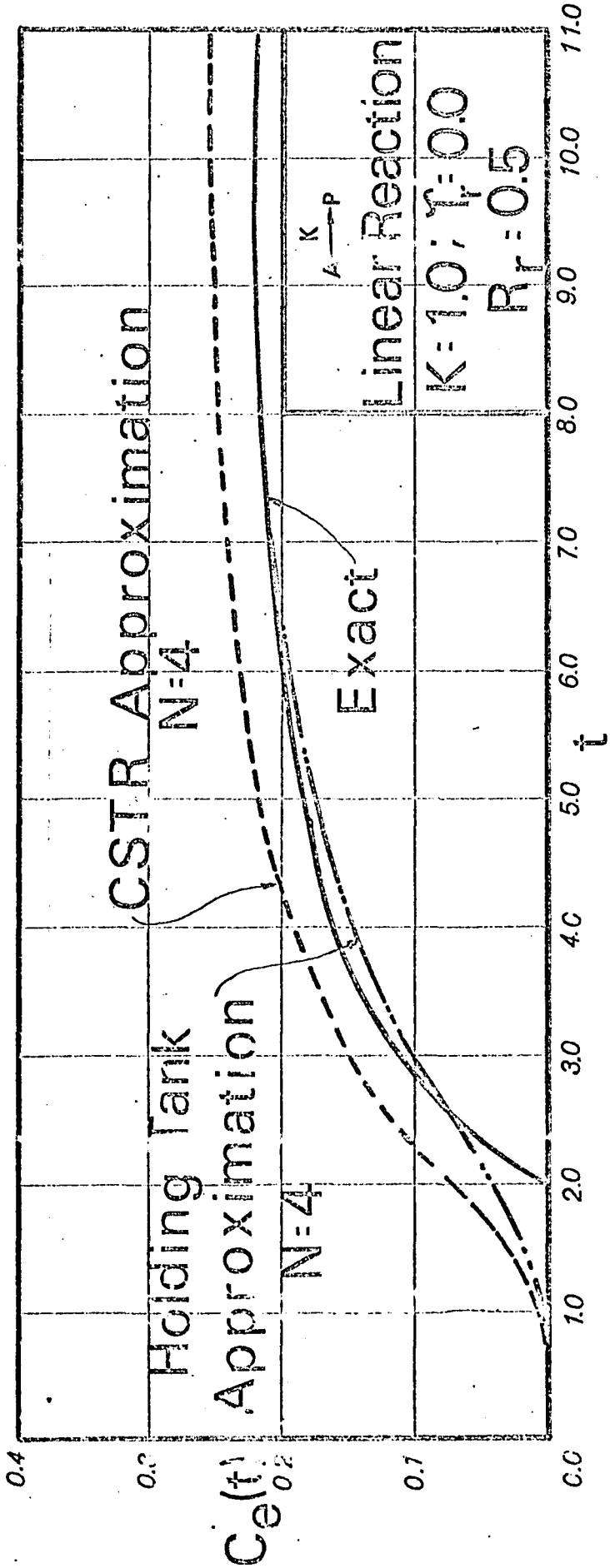

Figure(3-4)Effluent Concentration During Start Up

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mation that it has a physical interpretation which gives insight as to the effects of diffusion on the system.

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3-5 SOLUTION OF THE APPROXIMATING PROBLEM

The steepest-ascent method for solving optimum programming problems developed by Bryson and Denham[40] is used. A few modifications in the method are needed to allow for inequality constraints. These are given in section 3-5.7.

3-5.1 Steepest-Ascent Method

In the steepest-ascent method the linearized variational equations are used to determine the sensitivity of the performance criterion and of any required constraints to control adjustments at each point in time. Control is modified to provide improvement in the performance criterion within the constraints. The magnitude of the control adjustments are limited at each iteration to hold response changes within a sufficiently small neighborhood of the previous or nominal trajectory. This assures that the linearized equations are sufficiently accurate and superposition of the effects of control and state changes is valid.

Thus, the method uses information from the system response characteristics about a nominal trajectory to generate an improved response trajectory. This new trajectory is treated as a revised nominal trajectory, and the process is repeated until terminal conditions are satisfied or improvements are negligible.

3-5.2 The Optimization Problem

In order to apply the steepest-ascent algorithm to

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our problem, it is necessary to introduce a new variable $Y_{1,N+1}$, and an additional differential equation.

$$\dot{Y}_{1,N+1} = \Theta_i \tag{3-24}$$

where i is either one or two depending on the problem being solved. For the time optimal problem

$$\dot{Y}_{1,N+1} = \Theta_1 = -1 \tag{3-25}$$

with boundary condition

$$Y_{1,N+1}\ (0) = 0 \tag{3-26}$$

Hence

$$Y_{1,N+1}\ (t_f) = -\int_0^{t_f} dt = \phi_1 \tag{3-27}$$

The problem then becomes to determine $U_t\ (t;N)$ in the interval $0 \leq t \leq t_f$ so as to maximize

$$\phi = Y_{1,N+1}\ (t_f) \tag{3-28}$$

subject to the constraints

$$\tau_t \dot{Y}_o = (1-R_r)\ Y_f + R_r \Gamma[Y_N(t)] - Y_o\ (t) \tag{3-29}$$
$$+ [0,\ U_t\ (t;N)] \cdot (T_s - Y_{2,o})$$

$$\dot{Y}_i = \frac{N}{\tau} [Y_{i-1}\ (t) - Y_i\ (t)] \tag{3-30}$$

$$i = 1,2,\ldots\ldots,N$$

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with

$$Y_i(0) = \begin{bmatrix} 0.0 \\ \\ 2.65 \end{bmatrix} \qquad (3\text{-}31)$$

$$i = 0,1,2,.....N$$

and

$$\begin{bmatrix} 0.50 \\ \\ 2.82 \end{bmatrix} \leq Y_i\ (t_f) \leq \begin{bmatrix} 0.52 \\ \\ 2.86 \end{bmatrix} \qquad (3\text{-}32)$$

$$i = 0,1,2.....N$$

There is also a constraint on the magnitude of the control effort,

$$0 \leq U_t\ (t;N) \leq 1$$

The dimensionless stream temperature T_s is 3.4.

A stopping condition is needed to determine the final time t_f in each iteration. In the time optimal problem the stopping condition is

$$\Omega = \sum_{i=0}^{N} [(Y_{1,i}-0.51) + (Y_{2,i}-2.84)] = 0$$

or

$$\Omega = \sum_{i=0}^{N} (Y_{1,i}+Y_{2,i})-(N+1)(0.51+2.84) = 0 \qquad (3\text{-}33)$$

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where $Y_{1,i}$ is the approximating function for C $(t - i\tau'/N)$ and $Y_{2,i}$ is the approximating function for T $(t - i\tau'/N)$.

A stopping condition is necessary because for a given nominal control the system might not satisfy inequalities (3-32). Thus a way to stop the integration is needed. The integration is stopped when the sum of the approximating functions is equal to (N+1) times the final steady state value. Since it is the total sum which is compared, it is not necessary for the system to reach steady state at each iteration. The stopping condition is imposed on both the concentration and the temperature, because either one of them separately would be too restrictive, i.e., the integration would be stopped too soon. For example if in the optimal solution the temperature oscillates about the final steady state value while the concentration coasts to its final steady state value. Then whenever the integration is stopped the first time the temperature is equal to the steady state value, the concentration is different from its final value and the constraints can never be satisfied.

In the profit optimal problem the final time is constant, $t_f = 5$

The steepest-ascent method was developed for problems with equality constraints. The method will be presented for these type problems. The modifications necessary to handle inequality constraints like equation (3-32) will be presented later in section (3-5.7). The additions

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needed to accomodate control inequalities are given in section (3-5.6). Thus, consider the following set of equality constraints

$$\Psi_i(t_f) = Y_i(t_f) - \begin{bmatrix} 0.51 \\ 2.84 \end{bmatrix} = \begin{bmatrix} 0.0 \\ 0.0 \end{bmatrix} \qquad (3\text{-}34)$$

$$i = 0,1,2,\ldots\ldots N$$

and

$$\Psi = [\Psi_0, \Psi_1, \Psi_2, \ldots\ldots, \Psi_N]'$$

That is, the target set is now, equation (3-34), one point in space rather than the rectangle specified by equation (3-32).

3-5.3 The Variational Equations

The method proceeds by guessing some reasonable control, $U_t\ (t;N)_*$, and using it with the initial conditions (3-31) and the differential equations (3-29) and (3-30) to calculate, numerically, the state variables $Y(t)_*$ until the stopping condition is satisfied. In general, this nominal trajectory will not satisfy the terminal conditions $\Psi = 0$, or yield the maximum possible value of the performance criterion $\emptyset$.

To find out how to improve on the nominal control, consider small perturbations δU_t about the nominal control, where

$$\delta U_t = U_t - (U_t)_*$$

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These perturbations will cause perturbations in the state variable $\delta Y(t)$,

$$\delta Y(t) = Y(t) - Y(t)_*$$

where

$$Y = [Y_o, Y_1, \ldots\ldots, Y_N]'$$

and

$$\dot{Y} = f_a[Y(t), U_t(t;N)]$$

where the subscript a refers to the approximate function is

$$f_a = \begin{bmatrix} \frac{1}{\tau_t}\left[(1-R_r)\, Y_f + R_r \left[Y_N(t)\right] - Y_o(t) + \left[0, U_t(t;N)\right]'\,(T_s - Y_{2,o})\right] \\ \frac{N}{\tau'}\left[Y_o(t) - Y_1(t)\right] \\ \vdots \\ \frac{N}{\tau'}\left[Y_{N-1}(t) - Y_N(t)\right] \end{bmatrix}$$

θ_i

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The effects of small changes in U_t and Y are described by the linear differential equation for $\delta Y(t)$,

$$\frac{d}{dt}(\delta Y) = J_Y[f_a]\,\delta Y + \nabla_U[f_a]\,\delta U_t \qquad (3\text{-}35)$$

where $J_Y[f_a]$ and $\nabla_U[f_a]$ are matrices of partial derivatives with respect to the state and control respectively. $J_y[f_a]$ is a $(2(N+1)+1) \times (2(N+1)+1)$ matrix given by

$$J_Y[f_a] = \begin{bmatrix} \frac{1}{\tau_t}\begin{bmatrix} -1 & 0 \\ C & -1+U_t \end{bmatrix} & 0_2 & 0_2 & \frac{R_r}{\tau_t} J_{Y_N}[\Gamma(Y_N)] & 0 \\ \begin{bmatrix} N/\tau' & 0 \\ 0 & N/\tau' \end{bmatrix}\begin{bmatrix} -N/\tau' & 0 \\ 0 & -N/\tau' \end{bmatrix} & & 0_2 & 0_2 & 0 \\ 0_2 & 0_2 & 0_2 & 0_2 & \vdots \\ \vdots & \vdots & \vdots & \vdots & \\ 0_2 & 0_2 & \begin{bmatrix} N/\tau' & 0 \\ 0 & N/\tau' \end{bmatrix}\begin{bmatrix} -N/\tau' & 0 \\ 0 & -N/\tau' \end{bmatrix} & & 0 \\ & & Y\,\theta_1 & & \end{bmatrix}$$

where 0_2 is a 2 x 2 zero matrix, and

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$$J_{Y_N}[\Gamma(Y_N)] = \begin{bmatrix} \frac{\partial \Gamma_1}{\partial Y_{1,N}} & \frac{\partial \Gamma_1}{\partial Y_{2,N}} \\ \frac{\partial \Gamma_2}{\partial Y_{1,N}} & \frac{\partial \Gamma_2}{\partial Y_{2,N}} \end{bmatrix} \qquad (3\text{-}37)$$

Equation (3-37) is the Jacobian matrix for the tubular reactor in terms of the approximating functions. $\nabla_Y \theta_i$ is given by

$$\nabla_Y \theta_i = [0,0,\ldots\ldots\ldots\ldots\ldots\ldots 0,0] \qquad (3\text{-}38)$$

$$\nabla_Y \theta_2 = [0,0,\ldots\ldots,0,(1-U_t)\left(-\frac{\partial \Gamma_1}{\partial Y_{1,N}} - \frac{\partial \Gamma_1}{\partial Y_{2,N}}\right),0] \qquad (3\text{-}39)$$

In equation (3-35) $\nabla_U[f_a]$ is defined as

$$\nabla_U[f_a] = \begin{bmatrix} 0 \\ \frac{1}{\tau_t}(T_s - Y_{2,o}) \\ 0 \\ \vdots \\ 0 \\ U^{\theta_i} \end{bmatrix}_* \qquad (3\text{-}40)$$

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where

$$\nabla_U \theta_1 = 0 \tag{3-41}$$

$$\nabla_U \theta_2 = -(1 - \Gamma_1(Y_N)) \tag{3-42}$$

$\nabla_U[f_a]$ is a (2(N+1)+1) X 1 matrix because there is only one control, U_t.

The subscript * indicates that the quantities are evaluated along the nominal path.

3-5.4 The Adjoint Equations

Consider also the matrix adjoint set

$$\dot{Q} = J_Y[f_a]' \, Q \tag{3-43}$$

or in terms of the components of Q, equation (3-43) can be written as

$$\dot{Q}_o(t) = \frac{Q_o(t)}{\tau_t} - \frac{N}{\tau'} Q_1(t) + [0, U_t(t-N)]' \frac{Q_o(t)}{\tau_t}$$

$$\dot{Q}_i(t) = \frac{N}{\tau'} [Q_{i+1}(t) - Q_i(t)] \qquad i = 1,2,\ldots,N-1 \tag{3-44}$$

$$\dot{Q}_N(t) = \frac{N}{\tau'} Q_N(t) - \frac{R_r}{\tau_t} J_{Y_N}[\Gamma(Y_N)]' Q_o(t) - (1-U_t) \nabla \Gamma_1(Y_N)'$$

$$\dot{Q}_{1,N+1}(t0 = 0$$

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The last term in the equation for Q_N appears only in the profit optimal problem.

Equation (3-44) gives the differential equations satisfied by the adjoint variables used in the Hamiltonian, equation (3-20). The proper boundary conditions for this set of equations depends on what sensitivity function is being calcuated. They will be shown to be given by equations (3-47), (3-55) and (3-61).

According to equations (3-35) and (3-43), we have that

$$\frac{d}{dt}(Q'\delta Y) = Q'J_Y[f_a]\,\delta Y + Q'\nabla_U[f_a]\,\delta U_t \qquad (3\text{-}45)$$

$$-Q'J_Y[f_a]\,\delta Y = Q'\nabla_U[f_a]\,\delta U_t$$

Hence

$$Q'(t_f)\,\delta Y(t_f) = \int_0^{t_f} Q'\nabla_U[f_a]\,\delta U_t\,dt \qquad (3\text{-}46)$$

$$+ Q'(0)\,\delta Y(0)$$

It is possible to arbitrarily assign $Q(t_f)$ as

$$Q_\psi(t_f)' = J_Y[\psi] \qquad (3\text{-}47)$$

where the subscript ψ in Q is used merely to indicate that this is the sensitivity function relating $\delta\psi$ to δY and δU_t. $J_Y[\psi]$ is the Jacobian of ψ with respect to Y, in this case it is equal to

$$J_Y[\psi] = [1,1,\ldots\ldots,1]' \qquad (3\text{-}48$$

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Making use of equation (3-46) and boundary conditions (3-47), it is apparent that the change in Ψ at t_f, denoted is given by

$$\delta\Psi = J_Y[\Psi]\,\delta Y(t_f) = Q_\Psi(t_f)\cdot\delta Y(t_f)$$

$$\delta\Psi = \int_0^{t_f} Q_\Psi \cdot \nabla_U[f_a]\,\delta U_t\,dt \qquad (3\text{-}49)$$

Since the initial conditions are specifed $\delta Y(0) = 0$.

It is possible to assign the terminal conditions (3-47) to Q, since Q is introduced into the problem for our convenience. The change given by equation (3-49) is obtained assuming t_f is fixed. Since the computational integration procedure is stopped by either the target set or a fixed time, the final time t_f can change on each iterations, the change is denoted by dt_f. The total change is then given by

$$d\Psi = \delta\Psi + \dot{\Psi}\,dt_f \qquad (3\text{-}50)$$

From equation (3-34), $\dot{\Psi}$ is equal to

$$\dot{\Psi}_i = \dot{Y}_i \qquad (3\text{-}51)$$

A similar analysis readily provides sensitivity functions relating an arbitrary function at $t = t_f$ to changes in the control and initial state. Thus,

$$d\phi = \delta\phi + \dot{\phi}\,dt_f \qquad (3\text{-}52)$$

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where

$$\dot{\phi} = \dot{Y}_{1,N+1} \tag{3-53}$$

and

$$\delta \phi = \int_0^{t_f} Q_\phi' \nabla_U [f_a] \delta U_t \, dt \tag{3-54}$$

Q_ϕ is obtained by integrating the adjoint equations (3-43) with boundary conditions

$$Q_\phi (t_f)' = \nabla_Y \phi \tag{3-55}$$

In the time optimal problem

$$Q_\phi (t_f) = [0, \ldots\ldots\ldots 0]' \tag{3-56}$$

In the profit optimal problem

$$Q_\phi (t_f) = [0, \ldots, \nabla_{Y_N} [\Gamma(Y_N)]]' \tag{3-57}$$

The change in the stopping condition Ω is given by

$$d\Omega = \delta \Omega + \dot{\Omega} \, dt_f \tag{3-58}$$

where

$$\dot{\Omega} = \sum_{i=0}^{N} (\dot{Y}_{1,N} + \dot{Y}_{2,N}) \tag{3-59}$$

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and

$$\delta \Omega = \int_0^{t_f} \phi_\Omega' \nabla_U [f_a] \delta U_t \, dt \qquad (3\text{-}60)$$

Q_Ω is obtained by integrating the adjoint equations (3-43) with boundary conditions

$$Q_\Omega(t_f)' = \nabla_Y \Omega \qquad (3\text{-}61)$$

that is

$$Q_\Omega(t_f) = [1,1,\ldots,1]' \qquad (3\text{-}62)$$

It is now apparent that Q_ϕ, Q_ψ, and Q_Ω can be interpreted as influence, or sensitivity functions, since they define changes in the functions ϕ, Ψ and Ω at $t = t_f$ in terms of $\delta Y(0)$ and $\delta U_t(t)$. Note also that the adjoint equations (3-43) must be integrated backward since the boundary conditions are given at the terminal point.

3-5.5 Optimal Control Variation

For steepest-ascent we wish to find the δU_t that maximizes $d\phi$ in equation (3-52) for a given value of the integral

$$(dS)^2 = \int_0^{t_f} \delta U_t \, W(t) \, \delta U_t \, dt \qquad (3\text{-}63)$$

given values of $d\Psi$ in equation (3-50) and $d\Omega = 0$ in equation (3-58). The values of $d\Psi$ are chosen to bring

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the nominal solution closer to the desired terminal constraint, $\Psi = 0$, the values chosen in our problem, are given in the next section, section 3-5.6. Since $\Omega = 0$ is used as the stopping condition, $d\Omega = 0$ on each iteration. Choice of dS is made to insure that the perturbations δU_t will be small enough for the linearization leading to the variational equations to be reasonable. W(t) is an arbitrary weighting function chosen to improve convergence of the steepest-ascent procedure. In some problems it might be desirable to subdue δU_t in sensitive regions. After several trials

$$W(t) = 1.0 \tag{3-64}$$

$$(dS)^2 = 0.1 \tag{3-65}$$

were found to give satisfactory convergence.

The derivation of the proper choice of δU_t is given by Bryson and Denham; it is also discussed in several text books[40-41]. The result is

$$\delta U_t = \pm W^{-1}\nabla_U[f_a]\left[Q_{\phi\Omega} - Q_{\Psi\Omega} I_{\Psi\Psi}^{-1} I_{\Psi\phi}\right] \left[\frac{(dS)^2 - dB' I_{\Psi\Psi}^{-1} dB}{I_{\phi\phi} - I_{\Psi\phi}' I_{\Psi\Psi}^{-1} I_{\Psi\phi}}\right]^{\frac{1}{2}} + W^{-1}\nabla_U[f_a] Q_{\Psi\Omega} I_{\Psi\Psi}^{-1} dB \tag{3-66}$$

where

$$dB = d\Psi - Q_{\Psi\Omega}(0)\,\delta Y(0)$$

$$Q_{\phi\Omega} = Q_\phi - \frac{\dot{\phi}}{\dot{\Omega}} Q_\Omega$$

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$$Q_{\psi\Omega} = Q_{\psi} - \frac{\dot{\psi}}{\dot{\Omega}} Q_{\Omega}$$

$$I_{\psi\psi} = \int_0^{t_f} Q_{\psi\Omega} \cdot \nabla_U[f_a]\, W^{-1} \nabla_U[f_a] \cdot Q_{\psi\Omega}\, dt$$

$$I_{\psi\phi} = \int_0^{t_f} Q_{\psi\Omega} \cdot \nabla_U[f_a]\, W^{-1} \nabla_U[f_a] \cdot Q_{\phi\Omega}\, dt$$

$$I_{\phi\phi} = \int_0^{t_f} Q_{\phi\Omega} \cdot \nabla_U[f_a]\, W^{-1} \nabla_U[f_a] \cdot Q_{\phi\Omega}\, dt$$

The plus sign is used in (3-66) if ϕ is to be increased and the minus sign if ϕ is to be decreased. The first term in equation (3-66) defines the component of δU_t used to satisfy the constraints of $d\psi$, and the second term indicates how the remaining control effort is best used to improve ϕ.

3-5.6 Control Inequalities

The development of δU_t has not considered the fact that $U_t(t;N)$ is constrained. The constraints are taken into account by setting

$$\begin{aligned} U_t &= 0 && \text{when} && U_t \leq 0 \\ U_t &= U_t && " && 0 \leq U_t \leq 1 \\ U_t &= 1 && " && 1 \leq U_t \end{aligned} \qquad (3\text{-}68)$$

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The definition of δU_t, equation (3-66), must be modified to bring the solution within the allowable constraints. Define a new control increment $\delta\alpha$ by

$$\begin{aligned} \delta\alpha &= 0 && \text{when} && U_t < 0 \\ \delta\alpha &= H_e(\ U_t) && && U_t = 0 \\ \delta\alpha &= \delta\ U_t && && 0 < U_t < 1 \\ \delta\alpha &= H_e(-\delta\ U_t) && && U_t = 1 \\ \delta\alpha &= 0 && && U_t > 1 \end{aligned} \qquad (3\text{-}69)$$

where H_e is the Heavisdic unit step function, i.e.,

$$\begin{aligned} H_e\ (\delta U_t) &= 0 && \text{for} && \delta U_t < 0 \\ H_e\ (\delta U_t) &= 1 && && \delta U_t > 0 \end{aligned} \qquad (3\text{-}70)$$

Equation (3-69) determines whether or not the gradient direction leads into or out of the interval $0 \leq U_t(t;N) \leq 1$

Hence a new control variable point is obtained as

$$U_t\ (\text{New}) = U_t\ (\text{Old}) + \delta\alpha \qquad (3\text{-}71)$$

3-5.7 The Inequality Constraints

The method has been presented for a problem with a set of equality constraints, equation (3-34). There are two reasons for considering a set of inequality constraints, equation (3-32) rather than the more restrictive equalities. 1) Once the system is within the bounds specified by the inequalities, it will remain within these bounds for $t \geq tf$; no additional control effort is needed after this point.

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Thus, the system is self-sustaining, and the start-up period has been completed. 2) The control found to be the solution for one degree of approximation is used as nominal control, to start the search, for a system with a higher degree of approximation, a larger N. The solutions for these approximating problems are intermediate steps to the final solution, the optimal control for the original system. Hence, exact answers to the approximating problems are not needed.

To adapt the method to problems with inequality constraints, the boundary conditions for Q_ψ must be redefined and $d\psi$ must be properly chosen. Define

$$\begin{aligned} d\psi_i &= 0 \\ \dot{\psi}_i &= 0 \\ Q_\psi(t_f) &= 0 \end{aligned} \qquad \text{when } \begin{bmatrix} 0.50 \\ 2.82 \end{bmatrix} \leq Y_i(t_f) \leq \begin{bmatrix} 0.52 \\ 2.86 \end{bmatrix} \quad (3\text{-}72)$$

$$i = 0, 1, \ldots\ldots, N$$

That is when the system is within the bounds, all subscripted terms disappear, and no improvement upon is tried at that iteration. Whenever the system exceeds one of the bounds $d\psi$ is chosen to bring the system closer to this bound, i.e., when

$$Y_i(t_f) \geq \begin{bmatrix} 0.52 \\ 2.86 \end{bmatrix} \quad \text{or} \quad Y_i(t_f) \leq \begin{bmatrix} 0.50 \\ 2.82 \end{bmatrix}$$

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define

$$d\Psi_i = Y_i(t_f) - \begin{bmatrix} 0.51 \\ 2.84 \end{bmatrix}$$

$$\dot{\Psi}_i = \dot{Y}_i \qquad (3\text{-}73)$$

$$Q_\Psi(t_f) = J_Y[\Psi]$$

where $J_Y[\Psi]$ is defined by equation (3-48).

3-5.8 Comments On The Steepest-Ascent Solution

An important distinction separates the Bryson-Denham method from the commonly referred steepest-ascent procedure. In steepest-ascent methods the control adjustment is made proportional to the gradient magnitude; this is not the case in Bryson s method. On each iteration a fixed amount of integrated control effort change, limited to $(dS)^2$, is made in the gradient direction. Thus the solution procedure does not depend on magnitude of the gradient, and convergence does not slow down in the neighborhood of the optimum.

The method is very flexible and can be applied to a great many problems. Because of its very flexibility, there are a number of adjustable parameters, like dS, W and $d\Psi$, which must be chosen. Only after several trials parameter values that help convergence can be found. The values used in our problem worked; they are not claimed to be the optimal ones.

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To start the search, the optimal control for one degree of approximation is used as nominal control for the system with a higher degree of approximation, i.e., a larger N. This procedure reduces the number of iterations needed to reach the optimum. When N=0, between eight and ten iterations are used before the switching regions are established. With the optimal control for N=0 as starting function, N=1 only requires around five iterations. For N>5, the starting control is the optimal control, and two or three iterations show this.

The number of integrations in each iterations increases rapidly with N, the degree of approximation. The total number of integrations per step is $6(N + 1) + 2$. But even more time consuming than the number of equations is the integration of the reactor equations. At each step in the integration of the tank equations, the conditions at the reactor outlet are required. Thus, the reactor equations must be integrated from o to τ for each step in the tank integration. In addition, the Jacobian matrix for the reactor is needed in the evaluation of the adjoints. This requires the integration of a set of four nonlinear equations from o to τ. The net result is that except for very large N, the computer time per iteration is almost independent of the degree of approximation.

Because of the complications arising from the discontinuity of the derivatives at the switching points,

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the gradient method is only used as a means for roughly estimating the switching points. Actual simulation of the system is then used, to accurately determine where the optimal switching points are.

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3-6 SOLUTION OF THE ORIGINAL PROBLEM

A steepest-ascent technique is used to confirm that the optimal control found via the approximating problem is at least a local optimum of the original system. It is shown that Bryson and Denham s method is applicable to differential-difference equations.

3-6.1 The Optimization Problem

As in the approximate problem, we define an additional variable X_3 with

$$\dot{X}_3 = \theta_i \tag{3-74}$$

θ_i is either one or two depending on the problem being solved. The initial condition is

$$X_3(0) = 0 \tag{3-75}$$

Hence

$$X_3(t_f) = \int_0^{t_f} \theta_i dt = \phi_i \tag{3-76}$$

The problem is to determine $U_t(t)$ in the interval

$0 \leq t \leq t_f$ so as to maximize

$$X_3(t_f) \tag{3-77}$$

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Subject to the constraints

$$\gamma_t \dot{X}(t) = (1-R_r)\, X_f + R_r \left[[X(t-\gamma')] - X(t) \right] + [0, U_t(t)]' \, (T_s - T) \qquad (3\text{-}78)$$

with

$$X(\sigma) = \begin{bmatrix} 0.0 \\ 2.65 \end{bmatrix} \qquad -\gamma' \leq \sigma \leq 0 \qquad (3\text{-}79)$$

and

$$\begin{bmatrix} 0.50 \\ 2.82 \end{bmatrix} \leq X(t_f) \leq \begin{bmatrix} 0.52 \\ 2.86 \end{bmatrix} \qquad (3\text{-}80)$$

where $X = (C, T)$

Note that the target set, equation (3-80), is defined only at $t = t_f$. While the target set for the approximate system is specified for $Y_i(t_f)$, $i = 0,1,.....N$. This is equivalent to specifying a target set for the original system for a period of time equal to the total delay in the system.

The control effort is also bounded

$$0 \leq U_t(t) \leq 1 \qquad (3\text{-}81)$$

and

$$T_s = 3.4$$

3-6.2 The Variational Equations

Set

$$X = (C, T, X_3) \qquad (3\text{-}82)$$

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and

$$\dot{X} = f_e\, X(t),[X(t-\tau'),\ U_t(t)] \qquad (3\text{-}83)$$

Then, the effects of small changes in U_t and X are described by the linear differential-difference equation for $\delta X(t)$.

$$\frac{d}{dt}(\delta X) = J_X[f_e]\,\delta X(t) + J_{X(t-\tau')}[f_e]\,\delta X(t-\tau') + \nabla_U[f_e]\,\delta U_t \qquad (3\text{-}84)$$

where

$$J_X[f_e] = \begin{bmatrix} -\frac{1}{\tau_t} & 0 & 0 \\ 0 & -\frac{1}{\tau_t}(1+U_t) & 0 \\ 0 & 0 & 0 \end{bmatrix}_* \qquad (3\text{-}85)$$

For the profit optimal problem

$$J_{X(t-\tau')}[f_e] = \begin{bmatrix} \frac{R_r}{\tau_t} & \begin{bmatrix} \frac{\partial C_e}{\partial C_o} & \frac{\partial C_e}{\partial T_o} \\ \frac{\partial T_e}{\partial C_o} & \frac{\partial T_e}{\partial T_o} \end{bmatrix} & 0 \\ (1-U_t) & \begin{bmatrix} \frac{\partial C_e}{\partial C_o} & -\frac{\partial C_e}{\partial T_o} \end{bmatrix} & 0 \end{bmatrix}_* \qquad (3\text{-}86)$$

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and

$$\nabla_U[f_e] = \left[\begin{array}{c} 0 \\ \frac{1}{\tau_t}(T_S - T) \\ -(1-C_e) \end{array}\right]_* \qquad (3\text{-}87)$$

In the time optimal problem

$$J_{X(t-\tau')}[f_e] = \left[\begin{array}{ccc} \frac{R_r}{\tau_t}\left[\begin{array}{cc} \frac{\partial C_e}{t_o} & \frac{\partial C_e}{T_o} \\ \frac{\partial T_e}{\partial C_o} & \frac{\partial T_e}{\partial T_o} \end{array}\right] & \begin{array}{c} 0 \\ 0 \end{array} \\ \begin{array}{cc} 0 & 0 \end{array} & 0 \end{array}\right]_* \qquad (3\text{-}88)$$

and

$$\nabla_U[f_e] = \left[\begin{array}{c} 0 \\ \frac{1}{\tau_t}(T_S - T) \\ 0 \end{array}\right]_* \qquad (3\text{-}89)$$

3-6.3 The Adjoint Equations

The differential-difference equations adjoint to equation (3-84) are

For $0 \leq t \leq t - \tau'$ (3-90)

$$\dot{\underline{P}}(t) = -J_{X(t)}[f_e]\,\underline{P}(t) - J_{X(t-\tau')}[f_e]\,P(\sigma)\Big|_{\sigma=t+\tau'}$$

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That is with $P = (\underline{P}_1, \underline{P}_2)$

$$\dot{P}(t) = \frac{P(t)}{\tau_t} + (0, U_t(t))' \frac{P(t)}{\tau_t} \frac{R_T}{\tau_t} J[\Gamma]' P(\sigma)\Big|_{\sigma=t+\tau'} + [1-U(\sigma)]'[\nabla C_e] P(\sigma)\Big|_{\sigma=t+\tau'} \tag{3-91}$$

$$\dot{P}_3(t) = 0 \tag{3-92}$$

where

$$\nabla C_e = \left[\frac{\partial C_e}{\partial C_o} \quad \frac{\partial C_e}{\partial T_o}\right] \tag{3-93}$$

$$J[\Gamma] = \begin{bmatrix} \frac{\partial C_e}{\partial C_o} & \frac{\partial C_e}{\partial T_o} \\ \frac{\partial T_e}{\partial C_o} & \frac{\partial T_e}{\partial T_o} \end{bmatrix} \tag{3-94}$$

The last term in equation (3-91) appears only in the profit optimal problem.

For $t_f - \tau' \leq t \leq t_f$

$$\dot{P}(t) = - J_{V(+)}[f_e]\, P(t) \tag{3-95}$$

or

$$\dot{P}(t) = \frac{P(t)}{\tau_t} + (0, U_t(t))' \frac{P(t)}{\tau_t} \tag{3-96}$$

$$\dot{P}_3(t) = 0 \tag{3-97}$$

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Note equation (3-91) is a differential-difference equation with advance argument $P(t+\tau')$, while equation (3-96) is an ordinary differential equation.

Once the boundary conditions for equation (3-96) are specified, then the solutions of equation (3-96) serve as initial functions for equation (3-91). Thus, it is only necessary to specify boundary conditions at one point in time, $t = t_f$. It will be shown next that, as in the approximate problem, the boundary conditions are given by

$$\begin{aligned} P_{\Psi}(t_f)' &= J_X[\Psi] \\ P_{\phi}(t_f)' &= \nabla_X \phi \\ P_{\Omega}(t_f)' &= \nabla_X \Omega \end{aligned} \tag{3-98}$$

3-6.4 Extension of Bryson's Method to Differential-Difference Equations

Key in the development of Bryson-Denham's method are the equations relating $d\Psi$, $d\phi$ and $d\Omega$ to δX and δU_t. In the approximate problem these changes were related by using the fact that

$$\frac{d}{dt}(Q'\delta Y) = \nabla_U[f_e]\delta U_t$$

A similar identity does not hold for differential-difference equations, i.e.,

$$\frac{d}{dt}(P'\delta X) \neq \nabla_U[f_e]\delta U_t \tag{3-99}$$

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Substituting we get

$$\frac{d}{dt}(\underline{P}'\delta X) = \nabla_U[f_e]\delta U_t + \underline{P}(t)' J_{X(t-\tau')}[f_e]\delta X(t-\tau') - \underline{P}(t)' J_{X(t-\tau')}[f_e]\delta X(t)$$

Even though the differential form of equation (3-99) is not valid, its integrated form is an identity even for differential-difference equation, i.e.,

$$\underline{P}(t)'\delta X(t)\Big|_0^{t_f} = \int_0^{t_f} P'\nabla_U[f_e]\delta U_t dt \qquad (3\text{-}100)$$

Once equation (3-100) has been established, the rest of the equations in the Bryson-Denham method can be applied. As shown next equation (3-100) holds

$$\int_0^{t_f} \frac{d}{dt}(\underline{P}'\delta X) = \int_0^{t_f} \underline{P}'\delta\dot{X}\,dt + \int_0^{t_f} \dot{\underline{P}}'\delta X\,dt$$

$$= \int_0^{t_f}\Big\{\underline{P}' J_X[f_e]\delta X(t) + \underline{P}' J_{X(t-\tau')}[f_e]\delta X(t-\tau') + \underline{P}\nabla_U[f_e]\delta U_t\Big\}dt - \int_0^{t_f} \underline{P}' J_X[f_e]\delta X(t)\,dt \qquad (3\text{-}101)$$

$$- \int_0^{t_f-\tau'} \underline{P}(\sigma) J_{X(\sigma-\tau')}[f_e]\Big|_{\sigma=t+\tau'}\delta X(t)\,dt$$

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Hence

$$\int_0^{t_f} \frac{d}{dt}\,(\underline{P}'\delta X)dt = \int_0^{t_f} \underline{P}'\nabla_U[f_e]\,\delta U_t dt$$

$$+ \int_0^{t_f} \underline{P}(t)'\, J_{X(t-\gamma')}[f_e]\,\delta X(t-\gamma')\,dt \qquad (3\text{-}102)$$

$$- \int_0^{t_f-\gamma'} \underline{P}(\sigma)'\, J_{X(\sigma-\gamma')}[f_e]\,\Big|_{\sigma=t+\gamma'} \delta X(t)\,dt$$

Consider the last two integrals in equation (3-102). Since

$$X(t-\gamma') = 0, \quad -\gamma' \le t \le 0.$$

Then

$$\int_0^{t_f} P(t)'\, J_{X(t-\gamma')}[f_e]\,\delta X(t-\gamma')dt = \int_{\gamma}^{t_f} P(t)'\, J_{X(t-\gamma')}[f_e]\,\delta X(t-\gamma')dt$$

Let $\theta = t - \gamma'$

$$\int_{\gamma}^{t_f} P(t)'\, J_{X(t-\gamma')}[f_e]\,\delta X(t-\gamma')dt = \int_0^{t_f-\gamma'} P(\theta+\gamma')\, J_{X(\theta)}[f_e]\,\delta X(\theta)d\theta \qquad (3\text{-}103)$$

Hence, the last two integrals in equation (3-102) cancel each other, and

$$\int_0^{t_f} \frac{d}{dt}\,(P'\delta X)\,dt = \int_0^{t_f} \underline{P}(t)'\nabla_U[f_e]\,\delta U_t dt$$

which is the equation that needed verification.

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3-6.5 Comments on the Steepest-Ascent Solution

The method is limited by the forms of the target set that can be used. Equation (3-10) gives the target set as two functions which bound the trajectory from $t = t_f - \gamma'$ up to $t = t_f$. This kind of target set can not be incorporated into the method, and without it there is no assurance that the system remains at the steady state after t_f. One way to obviate this difficulty is by stopping the integration one time delay after the target set is satisfied. In this way it is know that $X(t_f - \gamma')$ is in the target set, and the algorithm forces $X(t_f)$ to satisfy the terminal constraints. The difficulty is not very serious here because the optimal control is already know, and what is wanted is verification. In all the cases considered the optimal control found via the auxiliary problem is confirmed to give at least a local optimum in the original problem.

Ray[28] solves the problem of the target set by leaving $X(t_f)$ free, designing the objective function to drive $X(t_f)$ to the desired values, and choosing t_f sufficiently larger than the time to first reach the desired steady state. In this way, the memory effects have disappeared at $t = t_f$. This approach has the disadvantage that it lengthens the trajectories and thus increases the computation time for each iteration.

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3-7 THE OPTIMAL SOLUTIONS

The time optimal controls for several degrees of approximation are given in Figure (3-5).

According to Figure (3-5) the optimal controls have the same form for the different degrees of approximations; there always is a time interval of no control action, followed by a period of heating, and a segment where the system is allowed to coast down to the steady state. The final time in the last interval represents the minimum time necessary for all the trajectories to reach the target set. After this point no more heat is needed to maintain the system at the desired steady state.

The question of how good an approximation is obtained by setting the transportation lag equal to zero and solving for the optimal policy of the system without lag is answered by the holding tank approximation for N = 0. The optimal control for this case grossly underestimates the control effort needed to achieve the desired steady state. When the optimal control for N = 0 is used in conjunction with the exact equations, the system converges to the low conversion steady state. Thus, it fails to realize the problem objectives. However, for this problem, the optimal control for N = 0 has the same structure as the optimal control for higher degrees of approximation. Consequently, the results of setting the time delay to zero prove useful as an initial guide for obtaining the final solution.

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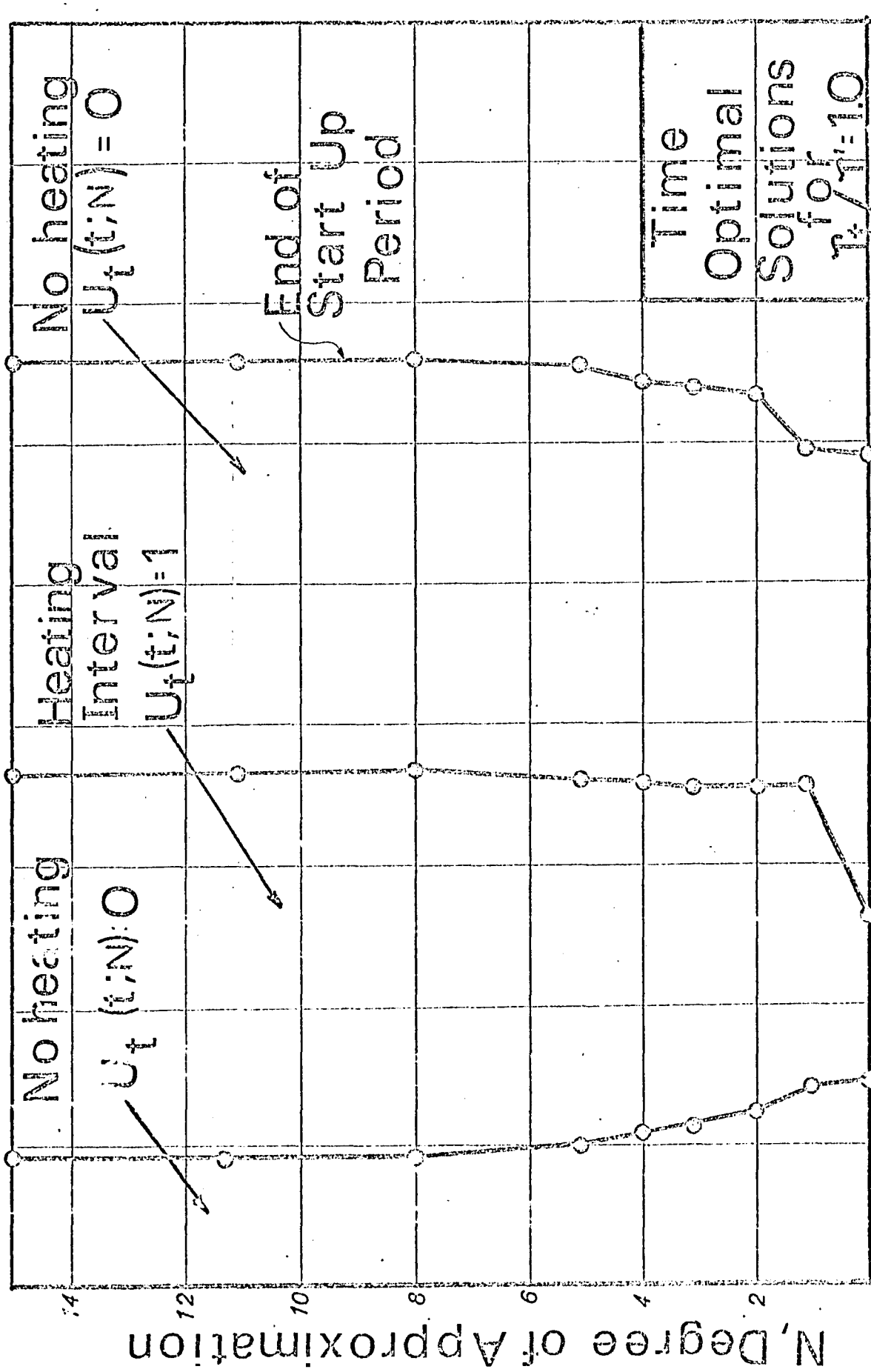

Figure(3-5)Optimal Heating Policies: Minimum Time Start Up

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The time-optimal control is the same for N = 8, 11 and 15. This control is also verified to give at least a local optimum in the original problem. Figure (3-6) shows the tank temperature and concentration as a function of time. These trajectories are obtained by integrating the exact equations with the optimal control as heating policy. The figure shows that the concentration is allowed to build up before the heating is started.

In determining the optimal switching points, the optimal solution is compared with adjacent trajectories. From this search, it is found that when the optimal amount of heat supplied is slightly reduced, the system converges to the low conversion steady state and not to the target set. The reduction can be caused by a small delay in the switch-on time or an early switch-off. On the other hand, when the quantity of heat is greater than at the optimum, the system is driven to the target set, but it takes longer for the trajectories to remain within the given bounds.

Figure (3-7) shows the reactor outlet temperature and concentration as a function of time for the exact equations with the time optimal control as heating policy.

Since the optimal controls for $N \leq 5$ provide less heat than the optimal control for the exact equations, these controls when used on the exact equations drive the system to the low conversion steady state. In other sit-

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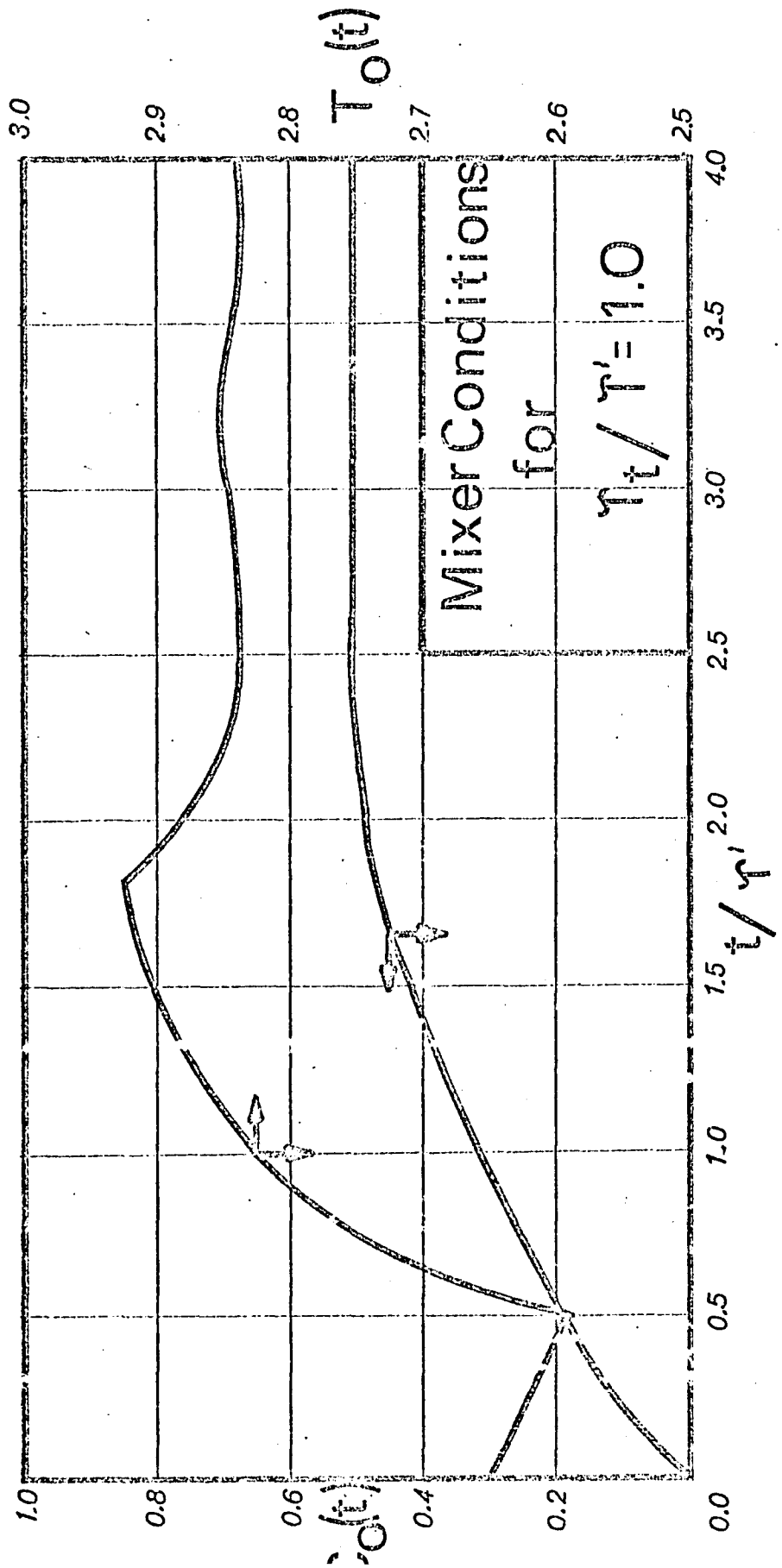

Figure (3-6) Mixer Conditions During Minimum Time Start Up

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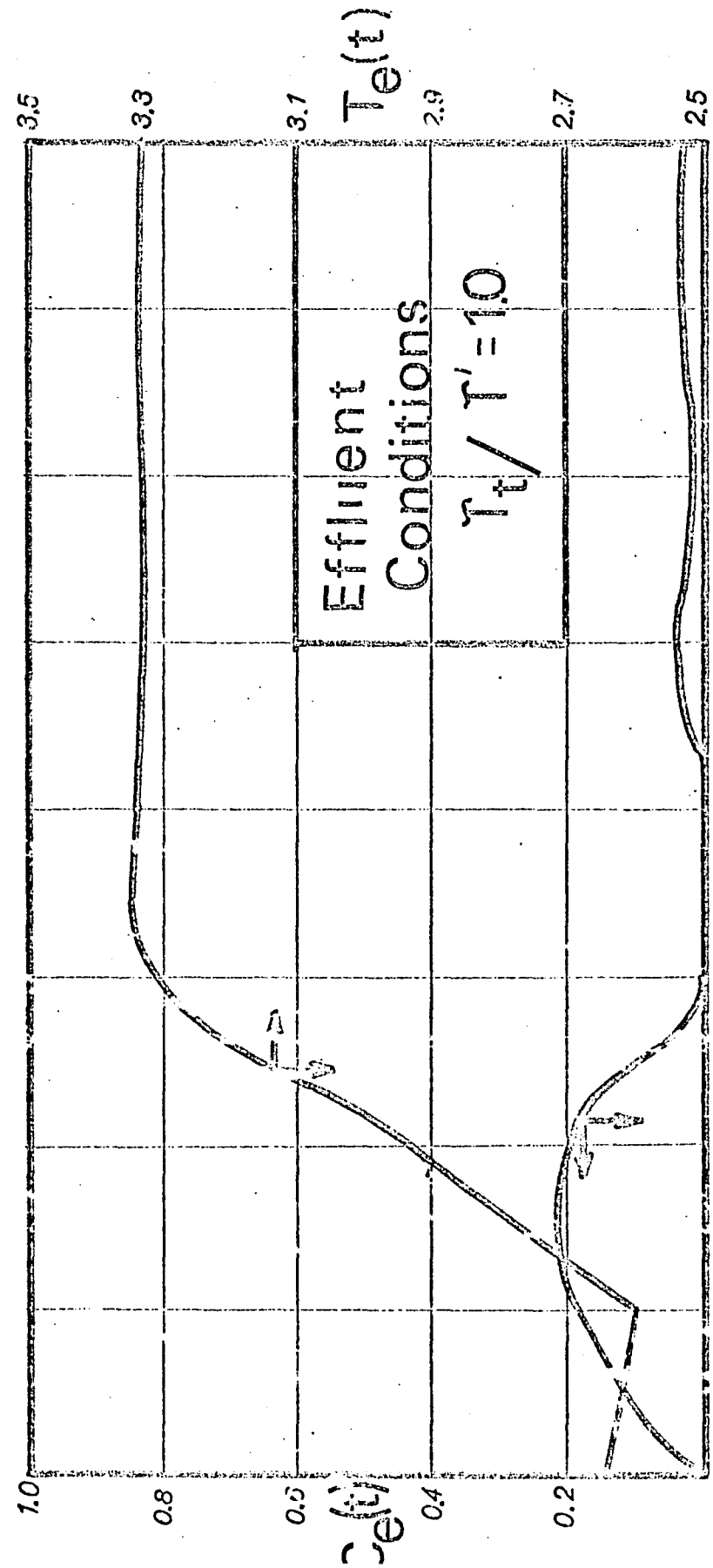

Figure (3-7) Effluent Conditions During Minimum Time Start Up

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uations, where there are no multiple steady states, and when the region of asymptotic stability of the desired steady state is larger than in this problem, the optimal control for the auxiliary problem can be expected to provide a suboptimal policy for the original system. This is shown by the similar control structures.

Figure (3-8) gives the optimal controls for several cost ratios. The solutions illustrate how the optimal control changes when the product price is larger, equal and smaller than the control cost.

The profit-optimal solution is the same for $P_U = 1.0$ and $P_U = 2.0$. This indicates that the heating period provided by these optimal controls is the minimum necessary to reach the target set within the allocated time.

Note the profit-optimal control for $P_U = 1.0$ is the same as the time-optimal control for this problem. Thus, for this control cost, the profit is maximized by reaching the target-set in minimum time.

Figure (3-8) shows that the length of the heating period increases as the control cost decreases. This additional heat is applied early so as to obtain rapid ignition. For very small control cost, the determining factor is the target set. Even if the control is free, its use is limited. Otherwise, the target set is not met within the specified time.

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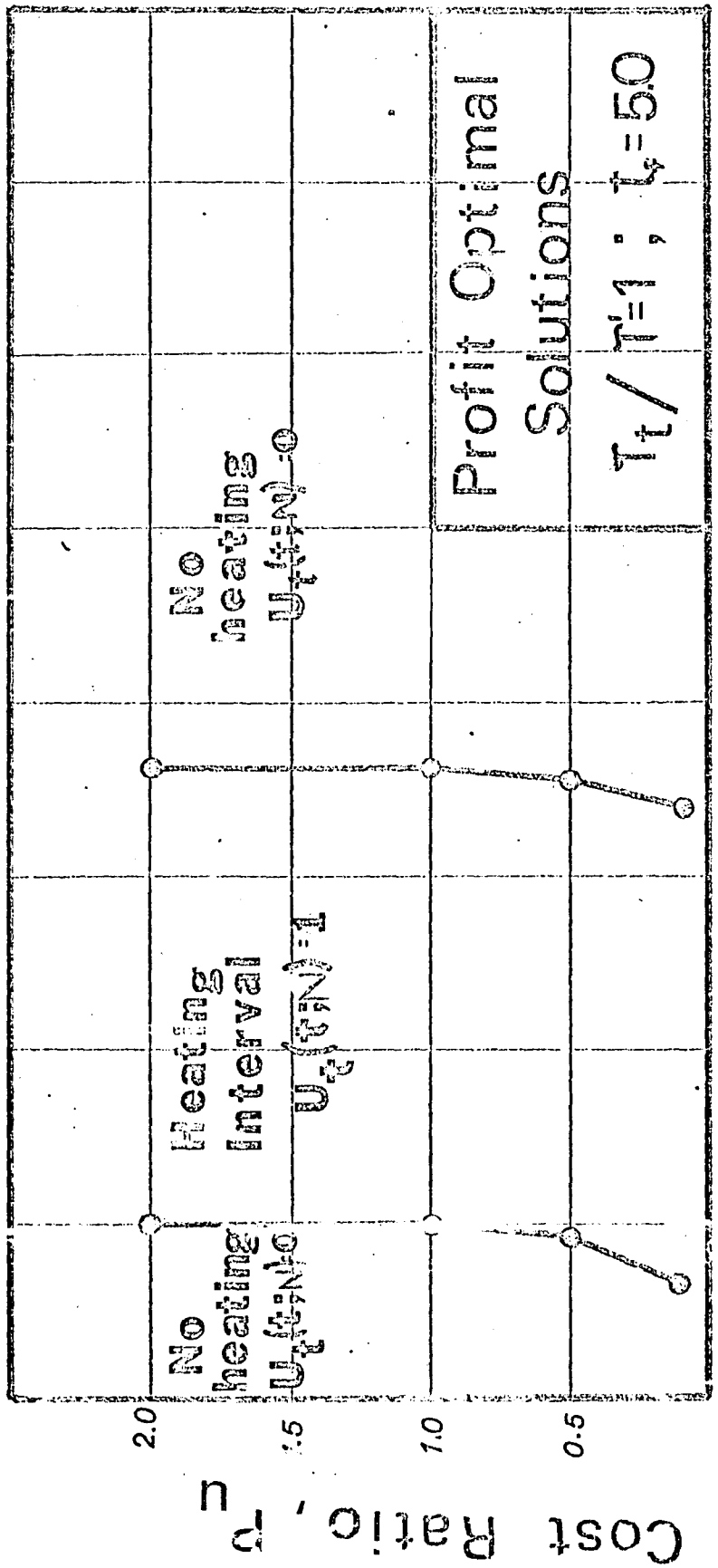

Figure (3-8) Optimal Heating Policies: Maximum Profit Start Up

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3-8 CONCLUSIONS

It can be concluded that, the use of the holding tank approximation in solving extremal problems for reactor-recycle systems has the advantage that there is great flexibility in choosing a target set. It is possible to specify what the trajectory should be over one time delay.

The holding tank approximation has the obvious disadvantages of the dimensionality of the problem, and of the number of problems which must be solved. For complex reactions, where more than two equations are needed to describe the system, the dimensionality can become prohibiting.

The determination of the optimal solution from the exact equations has the advantage that only one problem has to be considered, and that no dimensionality limitations are encountered. However, this direct approach is severely limited by the specification of the target set. There is no way of adequately forcing the system to satisfy some condition for one time delay. Without this specification, there is no assurance that the system remains at the desired steady state.

The correct choice of method depends on the particular problem. Nevertheless, the approach used in this study is probably widely applicable. It essentially consists of solving the easiest problem, with smaller N, first. With the information provided by this case, the more diffi-

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cult problems can be attacked. Even though the complexity of the problem increases with N, so does the available information.

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NOMENCLATURE

a_r	amplitude recycle oscillations
A	constant defined by equation (2-17)
A_e	constant defined by equation (2-22)
B	constant defined by equation (2-18)
B_e	constant defined by equation (2-23)
C	dimensionless concentration, $\tilde{C}/C_R$
$(dS)^2$	parameter defined by equation (3-63)
E	effective concentration defined by equation (2-83)
E_B	effective concentration defined by equation (2-60)
E_c	effective concentration defined by equation (2-16)
F(t)	feed flow rate
f	function
H	Hamiltonian
H_v	matrix defined by equation (2-88)
H_e	heaviside expansion
ΔH	heat of reaction
I	identity matrix
$I_{\psi\psi}$	matrix defined by equation (3-66)
$I_{\psi\phi}$	matrix defined by equation (3-66)
$I_{\phi\phi}$	matrix defined by equation (3-66)
J	Jacobian matrix
k	reaction rate constant
K_p	matrix defined by equation (2-105)
L	reactor length
M	integer

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n	integer
N	integer, degree of approximation
P	adjoint variable for exact system
Q	adjoint variable for approximate system
R(t)	recycle flow rate
R_r	recycle ratio, defined by equation (2-4)
$\mathcal{R}$	reaction rate
t	time
T	dimensionless temperature, $\tilde{T}\rho C_p/(-\Delta H)\,\tilde{C}_R$
T_S	dimensionless steam temperature, $\tilde{T}_S\rho C_p/(-\Delta H)\,\tilde{C}_R$
TP	throughput, defined by equation (2-71)
t_f	final time
U	heat transfer coefficient
U_r	dimensionless reactor heat transfer coefficient $4U/D\rho C_p$
U_t	dimensionless tank heat transfer coefficient $U\tau_c/\rho C_p$
V_t	volume tank
V	volume reactor
V_1	first component, $(A_e + B_e)E$
V_2	second component, $(A_e + B_e)E$
v(t)	fluid velocity in the reactor
X	state vector
X	expanded state vector, (X_1, X_2, X_3)
y_i	state vector for holding tank approximation
Y	expanded state vector for the holding tank approximation, $(Y_o, Y_1, \ldots\ldots Y_N, Y_{N+1})$
z	distance along the reactor
Z	state vector for the CSTR approximation

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Greek Letters

$\langle\ \rangle$ flow averaged quantity

ω frequency

ω_c defined as $\cos\omega\tau$

ω_s defined as $\sin\omega\tau$

τ_t tank time constant

τ time delay in the reactor

τ_r time delay in the recycle line

τ' total time delay, $\tau+\tau_r$

σ dummy variable

Γ functional relationship, defined by equation (3-3)

∇ gradient

Ψ matrix of constraints, defined by equation (3-34)

δ small change in variable

θ integrand performance index

ϕ performance index

Ω stopping condition

$\delta\alpha$ optimal control increment, defined by equation (3-69)

Subscripts

A reactant A

B reactant B

e reactor outlet

f feed

o reactor inlet

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P desired product P

R reference

r recycle

S steady state

W reactor wall

* nominal path

Superscripts

. differentiation with respect to time

' transpose

- time averaged

~ dimensional quantity

* optimal quantity

(0) zero order approximation in perturbation analysis

(1) first order approximation in perturbation analysis

(2) second order approximation in perturbation analysis

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