This is to certify that the

thesis entitled

ANALYSIS OF PERIODIC REACTOR OPERATION
A CASE STUDY

presented by

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has been accepted towards fulfillment
of the requirements for

M.S. degree in Chemical Eng.

Antonio L. DeVera

Major professor

Date 2/1/83

ANALYSIS OF PERIODIC REACTOR OPERATION
A CASE STUDY

By

Eden Yee Tang T. Dionne

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1983

ABSTRACT

ANALYSIS OF PERIODIC REACTOR OPERATION

A CASE STUDY

By

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The Van de Vusse reaction scheme, represented as

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

$$A + A \xrightarrow{k_3} D$$

is considered as a case study for investigating the effects of periodically controlling the volumetric rate of throughput to an isothermal CSTR and PFR. It is shown that a selectivity shift to an enhanced production of the intermediate product B is encountered when large fluctuations of the cycling frequency is implemented in the CSTR. An adverse effect to the yield of B is obtained for the periodic control of the volumetric flow rate in a PFR. The effects of large cycling frequencies can not be surmised for a PFR operating under a periodic control of the volumetric flow rate because the physics describing the flow and mixing patterns are no longer similar to the plug flow behavior.

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NOTATIONS--CHAPTER 1

A_{ref}	Reference concentration for species A
H	Hamiltonian
J	Objective function
k_1, k_2, k_3	Kinetic constants
K_1^o	$\tau_s^o k_1$
K_2	k_2/k_1
K_3^o	$\tau_s^o k_3 A_{ref}$
$\bar{\bar{K}}_1$	$k_3 A_{ref}/k_1$
$\bar{\bar{K}}_2$	k_2/k_1 or K_2
P_1, P_2	Periodic functions in the S-D perturbation method
T^o	Optimal cycle time $= \frac{2\pi}{\Lambda}$
x_1, x_2	A/A_{ref}, B/A_{ref} - dimensionless concentration
x_3	V/Vref - dimensionless reaction volume
$x_{1_s}^o$, $x_{2_s}^o$, $x_{3_s}^o$	Dimensionless optimal steady state concentration and reaction volume
u_1	Dimensionless residence time
u_2	Dimensionless reactant feed concentration
$u_{1_s}^o$, $u_{2_s}^o$	Dimensionless optimal steady state residence time and reactant feed concentration

Greek Symbols

ϵ	Perturbation amplitude

$\lambda_{1_s}^{\circ}, \lambda_{2_s}^{\circ}, \lambda_{3_s}^{\circ}$	Multipliers evaluated at the optimal steady state
Λ	$\omega\tau_s^{\circ}$, dimensionless cycling frequency
η_1, η_2	Defined in table 2.
τ_s°	Optimal steady state resifence time
θ	$\frac{t}{\tau_s^{\circ}}$, dimensionless lime ($\equiv$ t)
ω	Cycling frequency

NOTATIONS--CHAPTER 2

A_c	Denotes the change in conversion of reactant A
E	Enhancement of the yield of the intermediate product B in the Van de Vusse kinetic scheme.
J	Objective function
K	K_3/K_1
K_i	Dimensionless reaction rate constants
$\underline{P}^i$	Periodic terms in the asymptotic sequences for the perturbation solutions to x_j
r	Independent variable in the application of the method of characteristics
s	Independent variable in the application of the method of characteristics
T	One cycle time
u	Control variable
$\bar{v}$	Dimensionless fluid velocity
$\bar{v}$	Periodic terms in the asymptotic sequence for the perturbation solution to $\bar{v}$
x_1	Dimensionless concentration for reactant (A) in the Van de Vusse kinetic scheme
x_2	Dimensionless concentration for the intermediate product B in the Van de Vusse kinetic scheme
$\tilde{x}$	x as a function of r and s

Superscripts

o	Denotes the optimum state

Subscripts

s	Denotes the steady state
∞	Approaching infinity

Greek Symbols

α_0	K/(K+1)
β_{ij}	Defined in Appendix H
ϵ	Perturbation amplitude
θ	Dimensionless time
Λ	Dimensionless cycling freqency
ξ	Dimensionless reactor distance
τ	Dimensionless reaction residence time
Ω_1	$\left(\frac{K_1^\circ \alpha_0 \Lambda}{2K}\right)\left(\frac{1}{2}K_1^\circ - 1\right)$
Ω_{2i}	$\frac{(K_1^\circ)^2\Lambda}{2K}\sum_{i=1}^{\infty}\frac{\alpha_0^i}{R_7}\left(e^{-R_7} + \frac{e^{-R_7}-1}{R_7}\right)$; $R_7 = iK_1^\circ$
Ω_{3i}	$\frac{(K_1^\circ)^2\alpha_0\Lambda}{2K}\sum_{i=0}^{\infty}\frac{\alpha_0^{R_8}}{R_8}\left(e^{-R_8} + \frac{e^{-R_8}-1}{R_8}\right)$; $R_8 = (i+1)K_1^\circ$
Ω_{4i}	$\sum_{i=0}^{\infty}(1+i)\alpha_0^i\left[\Omega_{5i}-\Omega_{6i}+\Omega_{7i}+\Omega_{8i}-\Omega_{9i}+\Omega_{10i}\right]$
Ω_{5i}	$\frac{\Lambda^2+(K_1^\circ)^2}{2(K_3^\circ)^2}\left[\frac{e^{-R_8}}{R_8}\left(1+\frac{2}{R_8}+\frac{2}{R_8^2}\right)-\frac{2}{R_8^3}\right]$
Ω_{6i}	$\frac{\alpha_0\Lambda^2}{K_3^\circ K}\left[\frac{e^{-R_8}}{R_8}\left(1+\frac{1}{R_8}\right)-\frac{1}{R_8^2}\right]$
Ω_{7i}	$\frac{\alpha_0^2\Lambda^2}{2(K_3^\circ)^2}\left[\frac{e^{-R_8}-1}{R_8}\right]$

Ω_{8i} $$\frac{\alpha_0\Lambda^2}{K_3^\circ K}\left[\frac{e^{-R_9}}{R_9}\left(1+\frac{1}{R_9}\right)-\frac{1}{R_9^2}\right] \quad ; \quad R_9=(i+2)K_1^\circ$$

Ω_{9i} $$\frac{\alpha_0^2\Lambda^2}{(K_3^\circ)^2}\left[\frac{e^{-R_9}-1}{R_9}\right]$$

Ω_{10i} $$\frac{\alpha_0^2\Lambda^2}{2(K_3^\circ)^2}\left[\frac{e^{-R_9}-1}{R_9}\right]$$

CHAPTER 1

SINE-WAVE CONTROL OF INPUT VOLUMETRIC FLOW RATE IN AN ISOTHERMAL CSTR WITH A VAN DE VUSSE KINETICS

INTRODUCTION

Numerous investigations [1-12], both theoretical and experimental studies, have shown that forced periodic operation of chemical reactors in some cases lead to improved conversion, enhanced selectivity, improved selectivity, and reduced parametric sensitivity. Recently, Skerik and DeVera [12] applied periodic control modes to an isothermal CSTR with a selectivity reaction system that is described by a Van de Vusse kinetic scheme [13] ,i.e.,

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

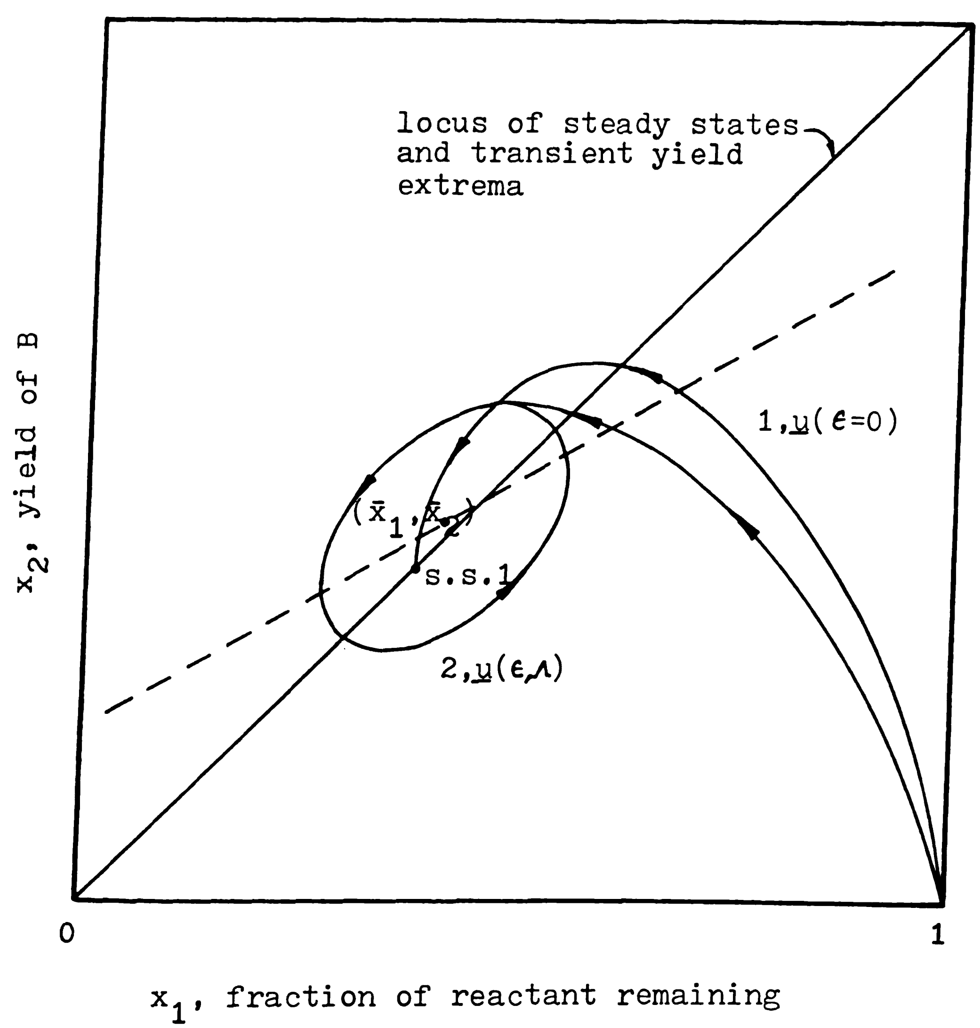
$$A + A \xrightarrow{k_3} D$$

This scheme exhibits interesting selectivity aspects. First, from a reactor selection point of view, Gillespie and Carberry [14] and DeVera and Varma [15] have demostrated that a level of macromixing, simulated by a PFR with recycle, in some cases provides a maximum yield of B greater than can be realized with the CSTR or the PFR modes of flow. Lee [16] treated a similar partial mixing model of the steady state tubular reactor and have shown that when the recycle is fed within the reactor length instead of the exit, the yield of B is further enhanced. Second, from a periodic process viewpoint, Riddlehoover and Seagrave [17] and Lund and Seagrave [18] have demonstrated that via simulated intermediate levels of mixing, a superior yield of the desired product B compared to the CSTR and PFR can be obtained.

In the dynamic but not periodic mode, the intermediate B exhibits an absolute maximum concentration even though it is already above the steady state it is approaching [19]. Hence periodic operation provides an inviting method to capitalize on this phenomena. The objective is to determine a control mode, certainly a periodic one, that will maintain the reactor in a dynamic mode which is characterized by a stable limit cycle. Such limit cycle should provide a time-average yield of B greater than the corresponding optimal steady state yield. In the phase plane formalism, we require an (x_1,x_2) trajectory similar to trajectory 2 as depicted schematically in figure 1. Trajectory 2 is characterized by an unknown control vector $\underline{u}$ which is a function of a perturbation amplitude ϵ and a cycling frequency Λ. Trajectory 1 is an unperturbed transient state which exhibits a transient maximum yield. Now, Skeirik and DeVera [12] demonstrated that, when the isothermal CSTR was subjected under the bang-bang and sine-wave control modes of the reactant feed concentration, the time-average yield of B, regardless of process parameters, is always less than the corresponding steady state (optimal and non-optimal). However, the sine-wave control mode led to an enhancement of conversion, regardless of the magnitude of the perturbation amplitude and cycling frequency. By applying the second variation in the frequency domain method [20], a similar conclusion to the latter can

FIGURE 1. Phase plane plot of a periodic controlled isothermal CSTR with a Van de Vusse kinetics. $\bar{x}_2$ and $1-\bar{x}_1$ are time-average yield and conversion, respectively.

FIGURE 1.


locus of steady states
and transient yield
extrema
$1, \underline{u}(\epsilon=0)$
$(\bar{x}_1, \bar{x}_2)$
s.s.1
$2, \underline{u}(\epsilon, \Lambda)$
x_2, yield of B
0
1
x_1, fraction of reactant remaining

be obtained, as in Sinčić and Bailey [10] calculations for the second order kinetics. Figure 2 dipictes schematically some of Skeirik and DeVera's [12] results. The shaded area represents the region of the time-average x_2 and x_1. Moreover, the limit cycle which has a perturbation amplitude at its maximum, (i.e., $\epsilon=1$) envelopes the transient maximum yield. Although a negative enhancement of the yield was observed for both bang-bang and sine-wave controls, a difference in these two control modes was observed: a square-wave control mode is more effective in shifting the product distribution than a sine-wave control mode, and in almost every case, the effect of the cycling mode increases as the oscillation increases.

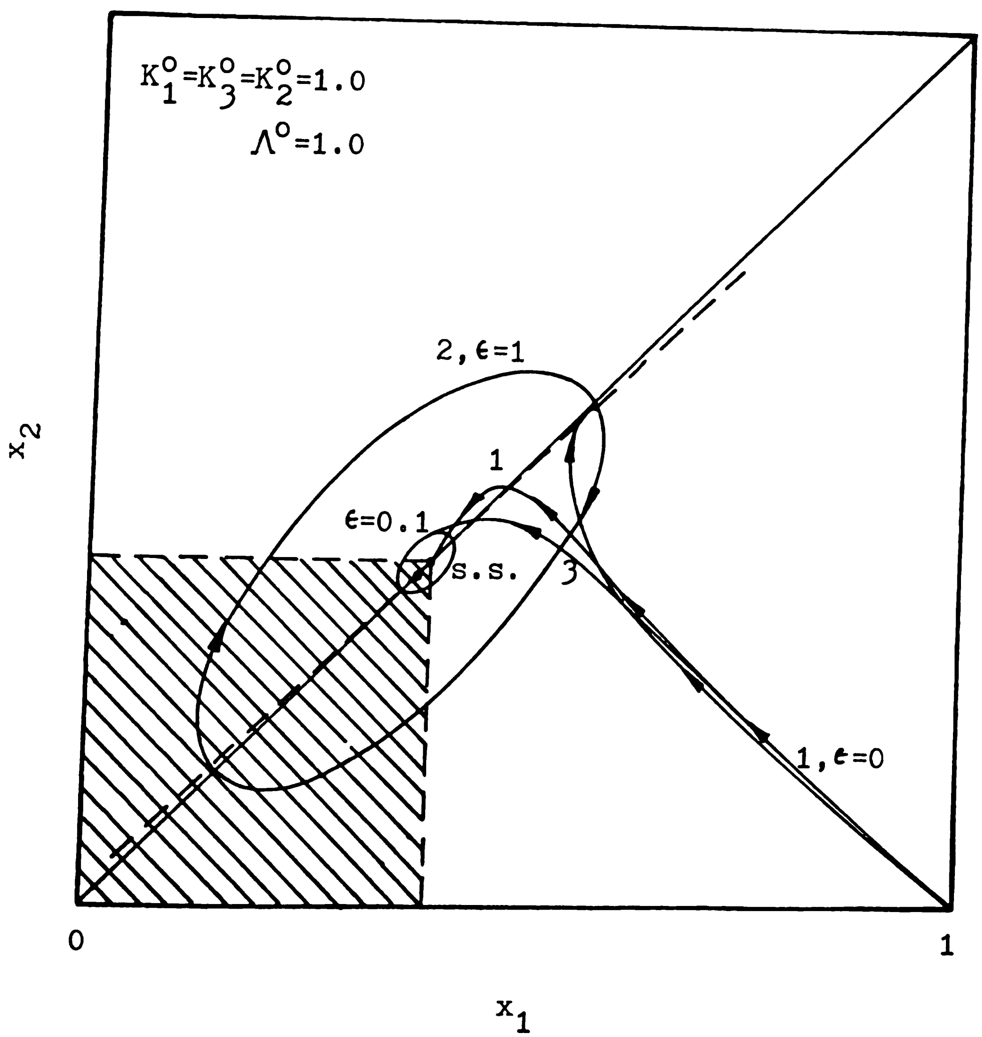
In this work, we present an approximation to the global dynamics of an isothermal CSTR which is subjected under a sinusoidal control of the volumetric throughput. From the approximate solution, we conduct a sensitivity analysis and derive a predictive equation for the objective function. Here, the objective function is the maximum yield of the intermediate product in a periodically controlled isothermal CSTR. Finally, we compare the yield enhancement values obtained from a perturbation method [11] and the enhancement prediction from the second variational in the frequency domain method [10,20,21].

BASIC EQUATIONS

The isothermal CSTR material balance for component A

FIGURE 2. Phase plane plot of a sine-wave control of the reactant feed concentration in an isothermal CSTR with a Van de Vusse kinetics.

FIGURE 2.



(species 1) and B (species 2) in the Van de Vusse kinetic scheme are expressed as

$$\frac{dx_1}{d\theta}=\frac{u_1u_2}{x_3}-\frac{x_1}{x_3}-(K_1^\circ x_1+K_3^\circ x_1^2)-\frac{x_1}{x_3}(u_1-1)\equiv f_1 \quad (1.1)$$

$$\frac{dx_2}{d\theta}=-\frac{x_2}{x_3}-(K_1^\circ K_2 x_2-K_1^\circ x_1)-\frac{x_2}{x_3}(u_1-1)\equiv f_2 \quad (1.2)$$

$$\frac{dx_3}{d\theta}=u_1-1\equiv f_3 \quad (1.3)$$

with initial conditions

$$\theta = 0: x_1=x_1(0)=1;\ x_2=0;\ x_3=1 \quad (1.4)$$

Equations (1.1-1.3) consider a constant output volumetric flow rate and negligible composition variation of the reaction solution density. The time derivative of x_3 ($\equiv$ dimensionless dynamic reaction volume) accounts for the changes in the reaction volume due to the controlled volumetric throughput. For the periodic process, the following integral constraints are imposed as a basis of comparison with an optimal steady state condition.

$$\frac{1}{T^\circ}\oint u_1u_2\,d\theta=u_{1s}^\circ u_{2s}^\circ \quad ; \quad T^\circ=\frac{2\pi}{\Lambda} \quad (2.1)$$

$$\frac{1}{T^\circ}\oint u_1\,d\theta=u_{1s}^\circ \quad (2.2)$$

Eqn. (2.1) requires the values of u_1 and u_2 should be chosen such that the amount of reactant input is equal to the optimal steady state. Eqn. (2.2) requires the residence time for both periodic and time-invariant processes should be the same. When $u_2=u_{2_s}^o=1$, equations (2.1) and (2.2) collapse to

$$\frac{1}{T^\circ}\oint u_1\,d\theta=u_{1s}^\circ=1 \quad (2.3)$$

Here, we chose

$$u_1 = 1 + \epsilon \sin \Lambda^{\circ} \theta \tag{2.4}$$

OPTIMAL STEADY STATE

The objective function for the time invariant process is the yield maximization of the intermediate product with respect to residence time and amount of reactant entering the reactor; thus

$$\text{objective function} = J^{o} = x^{o}_{2_s} \tag{3.1}$$

$x^{o}_{2_s}$ is obtained from

$$H_x (\underline{x}^{o}_{s}, \underline{u}^{o}_{s}, \underline{\lambda}^{o}_{s}) = 0 \tag{3.2}$$

$$H_u (\underline{x}^{o}_{s}, \underline{u}^{o}_{s}, \underline{\lambda}^{o}_{s}) = 0 \tag{3.3}$$

$$\underline{f} (\underline{x}^{o}_{s}, \underline{u}^{o}_{s}, \underline{\lambda}^{o}_{s}) = 0 \tag{3.4}$$

where H Hamiltonian $= x_2 + \underline{\lambda}^T \underline{f} (\underline{x}, \underline{u}, \underline{\lambda})$ (3.5)

Hence,

$$x^{o}_{1_s} = \bar{K}_2 \left[\sqrt{1 + \bar{K}_1} + \sqrt{\bar{K}_2} \right]^{-1} \tag{3.6}$$

$$x^{o}_{2_s} = K^{o}_1 x^{o}_{1_s} (1 + K^{o}_1 K_2)^{-1} \tag{3.7}$$

$$x^{o}_{3_s} = 1 \tag{3.8}$$

$$\tau^{o}_{s} = \left[k_2 + (k_1 - k_2) x^{o}_{1_s} \right]^{-1} \tag{3.9}$$

$$\lambda^{o}_{1_s} = K^{o}_1 x^{o}_{1_s} (1 + K^{o}_1 K_2)^{-2} (1 - x^{o}_{1_s})^{-1} \tag{3.10}$$

$$\lambda^{o}_{2_s} = (1 + K^{o}_1 K_2)^{-1} \tag{3.11}$$

$$\lambda^{o}_{3_s} = 0 \tag{3.12}$$

A similar conclusion can be found in [22, 23].

PERTURBATION SOLUTION: PERIODIC PROCESS

The time-average yield of B at the limit cycle is

$$\bar{x}_2 = \frac{1}{T^o}\oint x_2(\underset{\sim}{x},\underset{\sim}{u})\,d\theta_\infty \qquad (4.1)$$

and thus, $J_\infty = \underset{\substack{\underset{\sim}{x}\in X \\ \underset{\sim}{u}\in U}}{\mathrm{Max}}\ \bar{x}_2$ (4.2)

When the perturbation method developed by Skeirik and DeVera [12] is applied to equations (1.1) and (2.4), the following set of moderately nonlinear and non-autonomous differential equations is obtained:

$$\frac{dF}{d\theta} = 1 - K_3^o F^2 - (1+K_1^o)F \qquad (5.1)$$

$$\frac{dP_1}{d\theta} = \frac{\cos\Lambda^o\theta}{\Lambda^o}\cdot\frac{dF}{d\theta} - (1+K_1^o)P_1 - \frac{1}{\Lambda^o}(\Lambda^o\sin\Lambda^o\theta - K_1^o\cos\Lambda^o\theta)F$$
$$+\sin\Lambda^o\theta - 2K_3^o F P_1 + \frac{K_3}{\Lambda^o}\cos\Lambda^o\theta\cdot F^2 \qquad (5.2)$$

$$\frac{dP_2}{d\theta} = \frac{\cos\Lambda^o\theta}{\Lambda^o}\cdot\frac{dP_1}{d\theta} - (1+K_1^o)P_2 + \frac{\Lambda^o\sin(\Lambda^o\theta) - K_1^o\cos\Lambda^o\theta}{\Lambda^o}\cdot P_1$$
$$-K_3^o(2FP_2 + P_1^2) + \frac{2K_3^o}{\Lambda^o}(\cos\Lambda^o\theta)FP_1 \qquad (5.3)$$

where P_1 and P_2 are periodic functions while F satisfies

$$\dot{x}_1 = f_1(\underset{\sim}{x}, u_{1_s}^o) \quad , \quad F(0) = x_1(0) \qquad (5.4)$$

The closed form solution to equations (5.1 - 3) is given in Appendix A and has a structure described by

$$x_1 = F(\theta) + \epsilon P_1(\theta) + \epsilon^2 P_2(\theta) \qquad (5.5)$$

Eqn. (5.5) is valid only for values of $\frac{\epsilon}{\Lambda} < 1$. Hence the sensitivity of x_1 strongly depends on this ratio. Moreover, for $\frac{\epsilon}{\Lambda}>1$, the reaction volume assumes negative values and thus the model loses its physics.

The time-average conversion is

$$1-\bar{x}_1 = 1-x_{1_s}^{\circ} - \frac{\epsilon^2}{T^{\circ}}\oint P_2 \, d\theta_{\infty} \tag{5.6}$$

As in [12], only the second order term contributes to $\bar{x}_1$ and F reduces to $x_{1_s}^{o}$. Once the global dynamics for x_1 is known, the solution to x_2 is readily obtained by substituting eqn. (5.5) into eqn. (1.2). Such results lead to a closed form solution structure similar to eqn. (5.5). Thus, the enhancement is calculated and is presented in table 1. A sensitivity analysis of the forced periodic CSTR is also presented here using the second variation of the objective function in the frequancy domain. The latter technique was initially developed by Guardabassi and colleagues [20] and was extended by Sinčič and Bailey [21] for variable time delay process. The second variation of the objective function is

$$\frac{1}{2}\delta^2 J = \frac{\epsilon^2}{2}\pi(\Lambda) \tag{5.7}$$

where $\pi(\Lambda) \equiv \underline{\underline{G}}^T(-j\Lambda)\underline{\underline{P}}\,\underline{\underline{G}}(j\Lambda) + \underline{\underline{Q}}^T\underline{\underline{G}}(j\Lambda) + \underline{\underline{G}}^T(-j\Lambda)\,\underline{\underline{Q}} + \underline{\underline{R}}\,, \quad j^2=-1$ (5.8)

$$\underline{\underline{G}}(s) \equiv [s\underline{\underline{I}} - \underline{\underline{A}}]^{-1}\underline{\underline{B}}$$

$$\underline{\underline{A}} \equiv [f_x(\underline{x}_s^{\circ}, \underline{u}_s^{\circ})]$$

$$\underline{\underline{B}} \equiv [f_u(\underline{x}_s^{o}, \underline{u}_s^{\circ})]$$

$$\underline{\underline{P}} \equiv [H_{xx}(\underline{x}_s^{\circ}, \underline{u}_s^{\circ}, \underline{\lambda}_s^{\circ})]$$

$$\underline{\underline{Q}} \equiv [H_{xu}(\underline{x}_s^{\circ}, \underline{u}_s^{\circ}, \underline{\lambda}_s^{\circ})]$$

$$\underline{\underline{R}} \equiv [H_{uu}(\underline{x}_s^{\circ}, \underline{u}_s^{\circ}, \underline{\lambda}_s^{\circ})] = 0$$

and H is the Hamiltonian defined earlier.

The value of $\pi(\Lambda)$ is presented in table 1.

TABLE 1. Yield enhancement

TABLE 1.

$$\bar{x}_2 - x^{\circ}_{2_s} = \frac{\epsilon^2}{2} E$$

where

$$E \equiv \frac{1}{(1+\hat{K}_2)^2 + 4\Lambda^2}\left\{\frac{1-x^{\circ}_{1_s}}{\Lambda(\eta_1^2+\Lambda^2)}\cdot\frac{\eta_1 K_1^{\circ}}{(\eta_1^2+4\Lambda^2)}\left[\frac{1-x^{\circ}_{1_s}}{\Lambda(\eta_1^2+\Lambda^2)}\left[\Lambda^2(1+\eta_1)^2+(\eta_1-\Lambda^2)^2\right] + \frac{1-x^{\circ}_{1_s}}{\Lambda^2} - \left[\eta_1-\Lambda^2+(1+\eta_1)\Lambda\right]\right] - \frac{1-x^{\circ}_{1_s}}{\Lambda(\eta_1^2+\Lambda^2)}\cdot\frac{K_1^{\circ}}{(\eta_2^2+\Lambda^2)}\left[\eta_1-\Lambda^2+(\eta_1+1)\Lambda\hat{K}_2^{\circ}\right]\right.$$

$$\left. - \frac{x^{\circ}_{2_s}(\hat{K}_2^{\circ}\Lambda+\eta_2+\Lambda^2)}{(\Lambda^2+\eta_2^2)\Lambda}\right\}\left\{\frac{4\Lambda^2}{1+\hat{K}_2^{\circ}} + 1 + \hat{K}_2^{\circ}\right\} + \frac{4\Lambda^2 K_1^{\circ}}{\eta_1(1+\hat{K}_2^{\circ})(\eta_1^2+4\Lambda^2)}\cdot\frac{1-x^{\circ}_{1_s}}{\Lambda(\eta_1^2+\Lambda^2)}\left\{\frac{1-x^{\circ}_{1_s}}{\Lambda(\eta_1^2+\Lambda^2)}\left[\Lambda^2(1+\eta_1)^2+(\eta_1-\Lambda^2)^2\right] + \frac{1-x^{\circ}_{1_s}}{\Lambda^2} - \left[\eta_1-\Lambda^2+(1+\eta_1)\Lambda\right]\right\}$$

$$\eta_1 \equiv 1 + K_1^{\circ} + 2K_3^{\circ} x^{\circ}_{1_s} \quad ; \quad \eta_2 \equiv 1 + K_1^{\circ} K_2$$

$\pi(\Lambda)$ term in the second variation:

$$\pi(\Lambda) \equiv \left\{-K_3^{\circ}\lambda^{\circ}_{1_s}(1+\Lambda^2)(1-x^{\circ}_{1_s})^2(\Lambda^2+\eta_2^2) + \lambda^{\circ}_{1_s}(1-x^{\circ}_{1_s})(\Lambda^2+\eta_2^2)(\Lambda^2+\eta_1) - K_1^{\circ}\lambda^{\circ}_{2_s}(1-x^{\circ}_{1_s})\left[(\eta_1+\eta_2-1)\Lambda^2+\eta_1\eta_2\right] - \lambda^{\circ}_{2_s}x^{\circ}_{2_s}(\Lambda^2+\eta_1^2)(\Lambda^2+\eta_2)\right.$$

$$\left. + \left[\lambda^{\circ}_{1_s}(1-x^{\circ}_{1_s}) - \lambda^{\circ}_{2_s}\right](\Lambda^2+\eta_2^2)(\Lambda^2+\eta_1^2)\right\}\left\{\Lambda^2(\Lambda^2+\eta_1^2)(\Lambda^2+\eta_2^2)\right\}^{-2} + \frac{\lambda^{\circ}_{1_s}(1-x^{\circ}_{1_s})\left[-\Lambda^4+(\eta_1^2-2\eta_1-\eta_2+2\eta_1\eta_2)\Lambda^2+\eta_1^2\eta_2\right]}{\Lambda^2(\eta_1^2+\Lambda^2)^2(\eta_2^2+\Lambda^2)}$$

$$- \frac{K_1^{\circ}\lambda^{\circ}_{2_s}(1-x^{\circ}_{1_s})\left[1-2\eta_1-2\eta_2\right]\Lambda^4 - (\eta_1^2+4\eta_1\eta_2-2\eta_1^2\eta_2-2\eta_1\eta_2^2+\eta_2^2)\Lambda^2+\eta_1^2\eta_2^2}{\Lambda^2\left[(\eta_1^2+\Lambda^2)(\eta_2^2+\Lambda^2)\right]^2} + \frac{\lambda^{\circ}_{2_s}x^{\circ}_{2_s}\left[\Lambda^4+(2\eta_2-\eta_2^2+\eta_1-2\eta_1\eta_2)\Lambda^2-\eta_1\eta_2^2-\eta_2^2\eta_1\right]}{\Lambda^2(\eta_1^2+\Lambda^2)(\eta_2^2+\Lambda^2)^2}$$

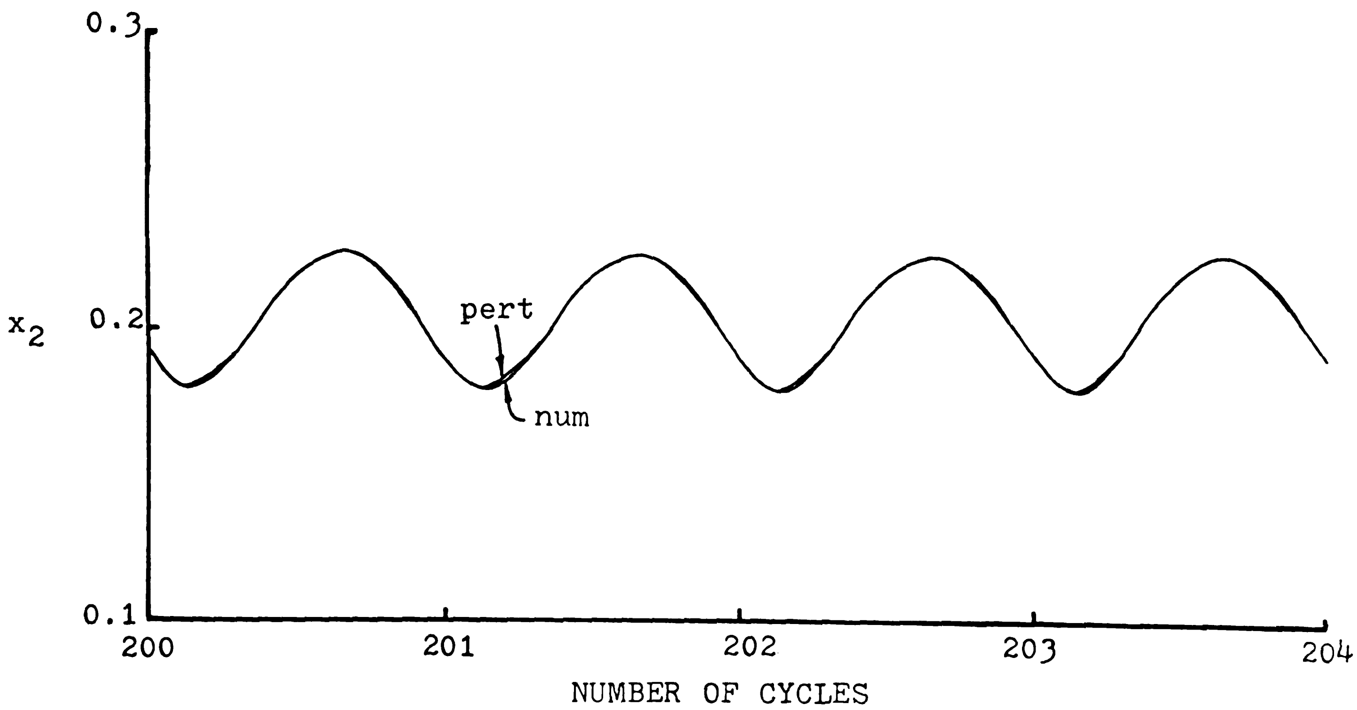
$$+ \frac{\left[\lambda^{\circ}_{1_s}(1-x^{\circ}_{1_s}) - \lambda^{\circ}_{2_s}x^{\circ}_{2_s}\right](\eta_1\eta_2-\Lambda^2)}{\Lambda^2(\eta_1^2+\Lambda^2)(\eta_2^2+\Lambda^2)}$$

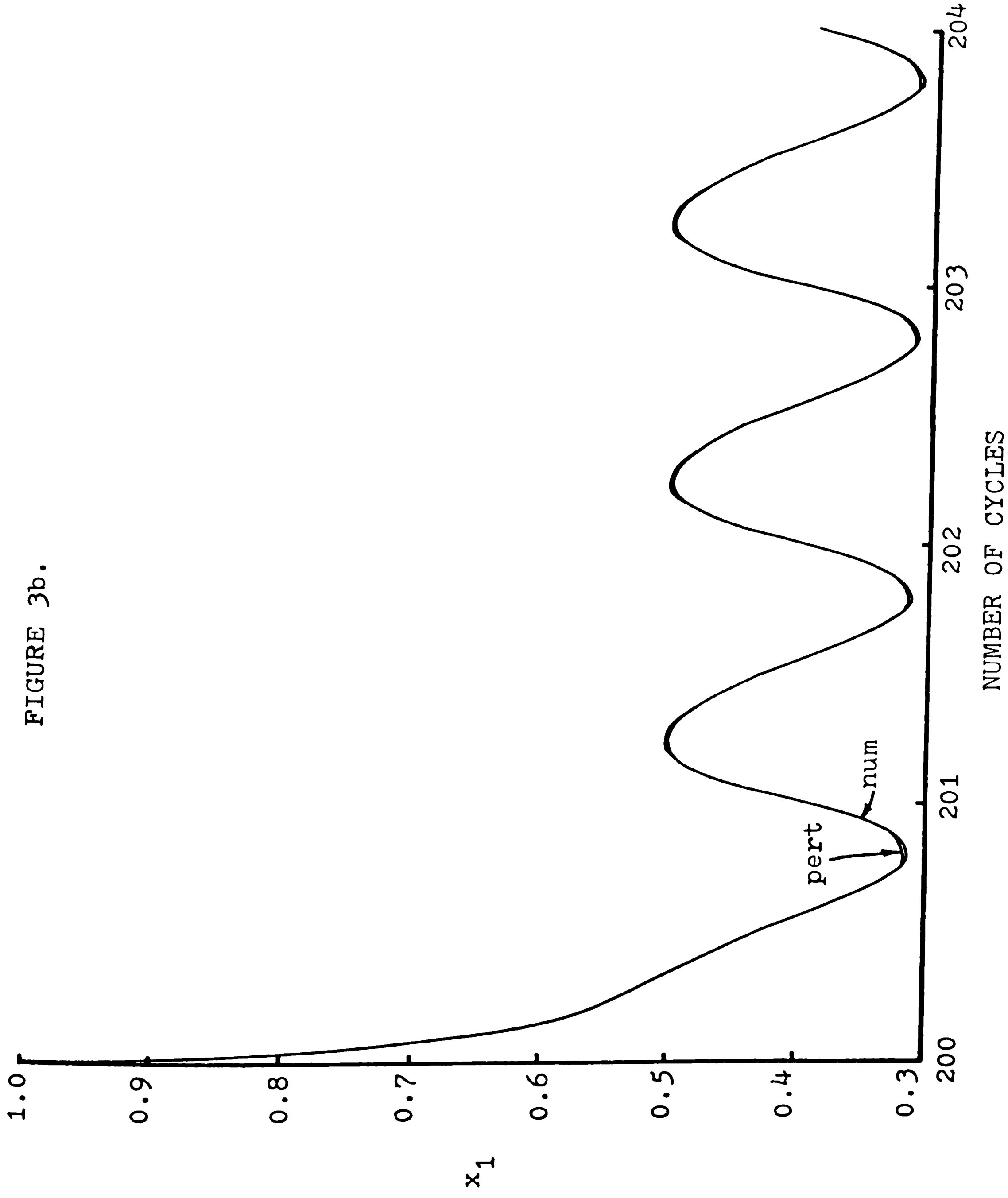
DISCUSSION

The perturbation method developed by Skeirik and DeVera [12] for the sine-wave control of the reactant feed concentration was numerically verified. They have concluded, that, regardless of the process parameters and frequency of cycling, their perturbation method is a very reliable approximation to the global dynamics, even up to a perturbation amplitude close to unity and any magnitude of the cycling frequency. However, in applying the Skeirik-DeVera (or S-D) perturbation method to our present work, we found that the $\frac{\epsilon}{\Lambda}$ ratio characterizes the error sensitivity from the numerical simulation (vis IMSL's DGEAR implementation). Figures 3 and 4 illustrate the comparison of the dynamic profile using the S-D solution and the numerical simulation. Figures 5a-5i exhibit the percent deviation of the S-D perturbation solution from the numerical simulation. The process parameters chosen are not necessarily those that pertain to an optimal steady state yield, since the S-D perturbation solution generally holds for any process parameters. It is clear from such plots that the deviation is strongly influenced by the $\frac{\epsilon}{\Lambda}$ close to unity, regardless of the ϵ value, and the deviation is very small when $\frac{\epsilon}{\Lambda}$ is near zero. Furthermore, the deviation for x_2 at the limit cycle is slightly less than the deviation for x_1 with almost any process parameters. For $\frac{\epsilon}{\Lambda}$ value close to 1/2, the deviation is in the vicinity of 3 to 4 percent absolute when K_1^o is moderately large but the deviation tend to approach a maximum of 13 percent absolute for

FIGURE 3(a-b). Perturbation solution versus numerical solution with $k_1=k_2=k_3A_{ref}=\tau=1.,\Lambda=2.$ $\epsilon=0.5$

FIGURE 3a.





1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
x_1
200
201
202
203
204
NUMBER OF CYCLES
pert
num

FIGURE 3b.

FIGURE 4(a-b). Perturbation solution versus numerical solution with $K_1=1, K_2=\hat{K}_2=5$, $\Lambda=0.5$, $\epsilon=0.25$

FIGURE 4a.

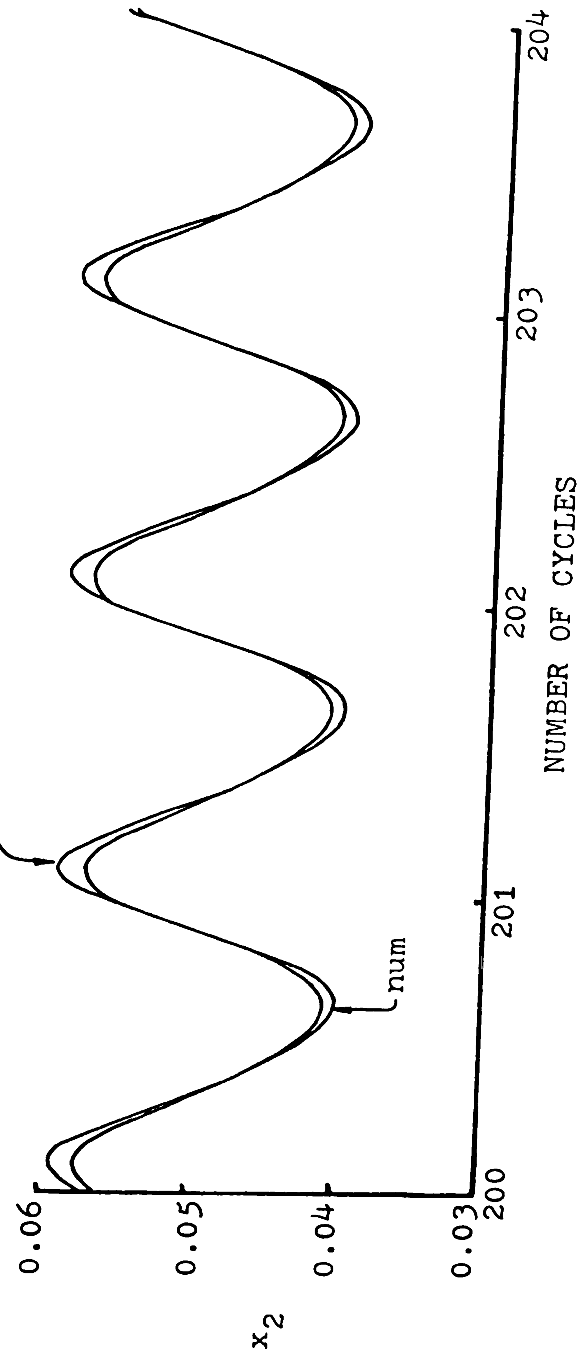

pert
num
0.06
0.05
0.04
0.03
x_2
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 4b.

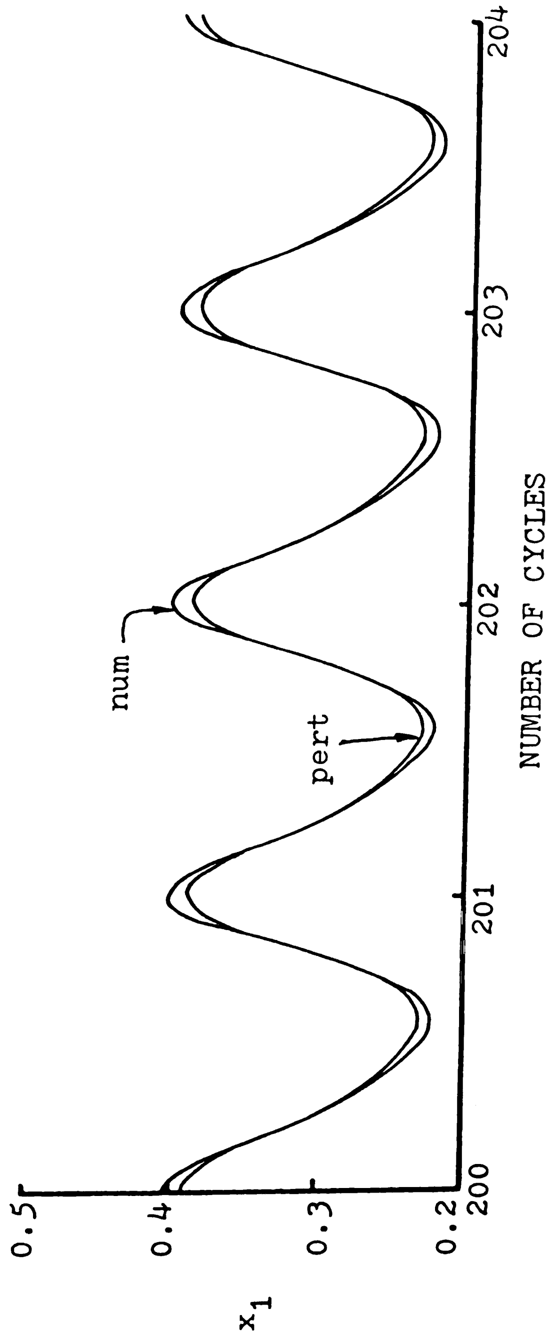


FIGURE 5. Deviation of perturbation solution from numerical simulation for

(a) $K_1=1$, $K_2=\hat{K}_2=5$, $\Lambda=0.5$, $\epsilon=0.25$

(b) $K_1=4.928$, $K_2=24.642$, $\hat{K}_2=0.493$, $\Lambda=10.$, $\epsilon=0.1$

(c) $K_1=K_2=\hat{K}_2=1$, $\Lambda=10$, $\epsilon=0.8$

(d) $K_1=K_2=\hat{K}_2=1$, $\Lambda=10$, $\epsilon=0.5$

(e) $K_1=20$, $K_2=2$, $\hat{K}_2=30$, $\Lambda=1$, $\epsilon=0.5$

(f) $K_1=20$, $K_2=2$, $\hat{K}_2=30$, $\Lambda=1$, $\epsilon=0.8$

(g) $K_1=20$, $K_2=2$, $\hat{K}_2=30$, $\Lambda=1$, $\epsilon=0.1$

(h) $K_1=1$, $K_2=\hat{K}_2=5$, $\Lambda=0.5$, $\epsilon=0.025$

(i) $K_1=1$, $K_2=\hat{K}_2=5$, $\Lambda=0.05$, $\epsilon=0.0495$

FIGURE 5a.

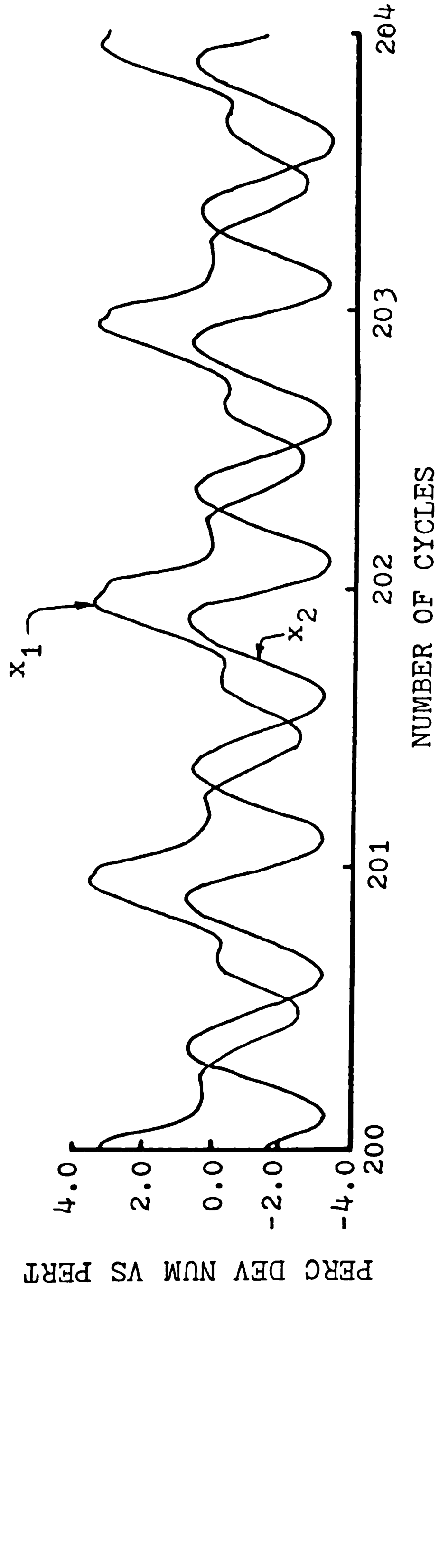

PERC DEV NUM VS PERT
4.0
2.0
0.0
-2.0
-4.0
200
201
202
203
204
NUMBER OF CYCLES
x_1
x_2

FIGURE 5b.

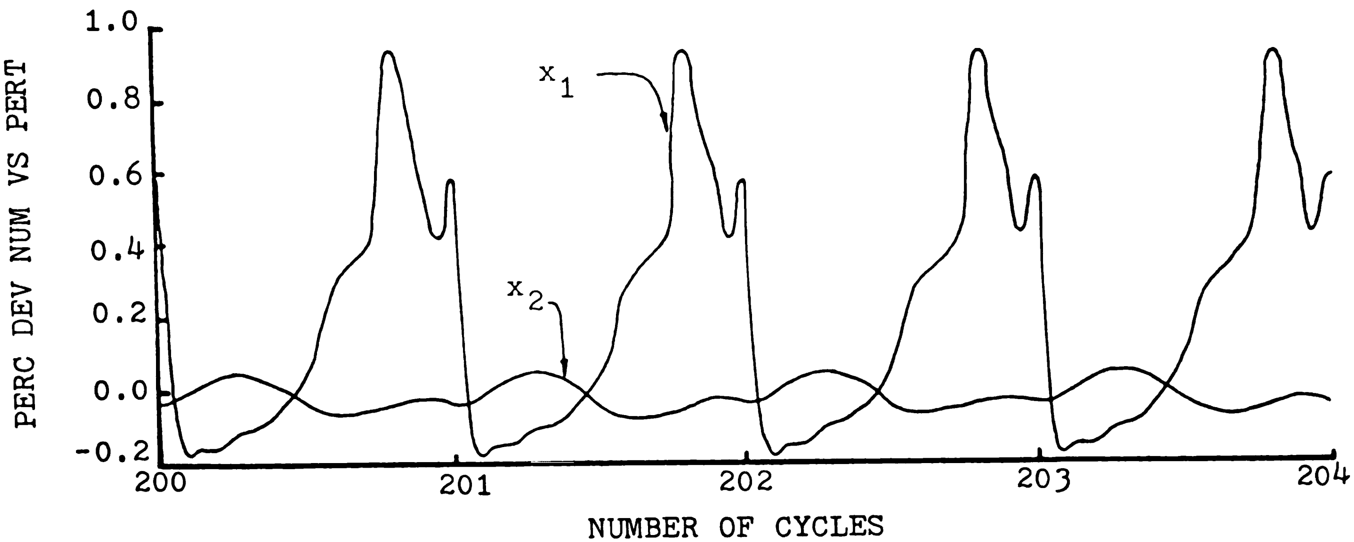

1.0
0.8
0.6
0.4
0.2
0.0
-0.2
PERC DEV NUM VS PERT
200
201
202
203
204
NUMBER OF CYCLES
x1
x2

FIGURE 5c.

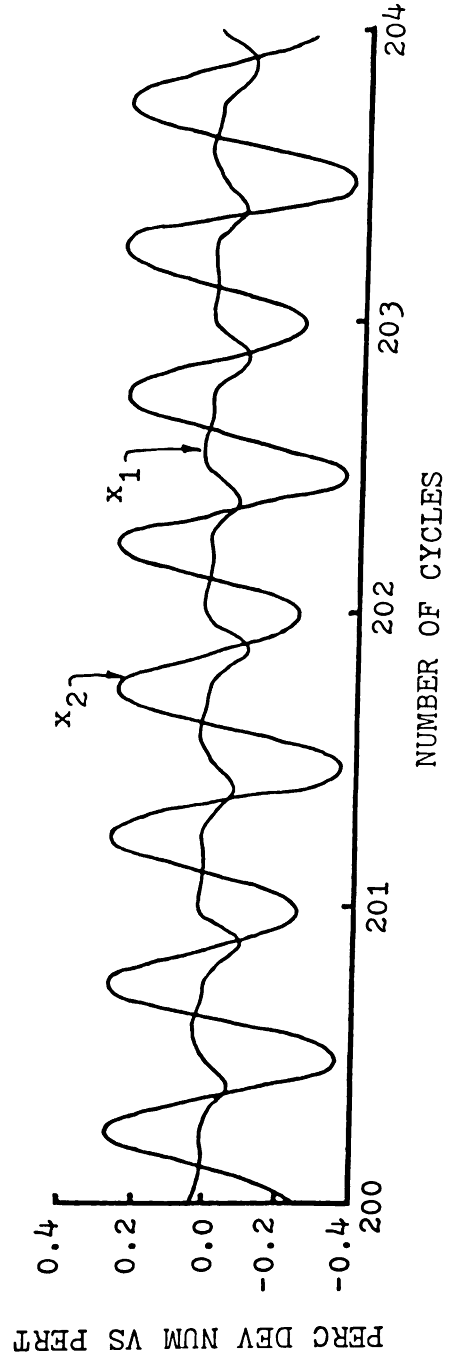

PERC DEV NUM VS PERT
0.4
0.2
0.0
-0.2
-0.4
200
201
202
203
204
NUMBER OF CYCLES
x_1
x_2

FIGURE 5d.

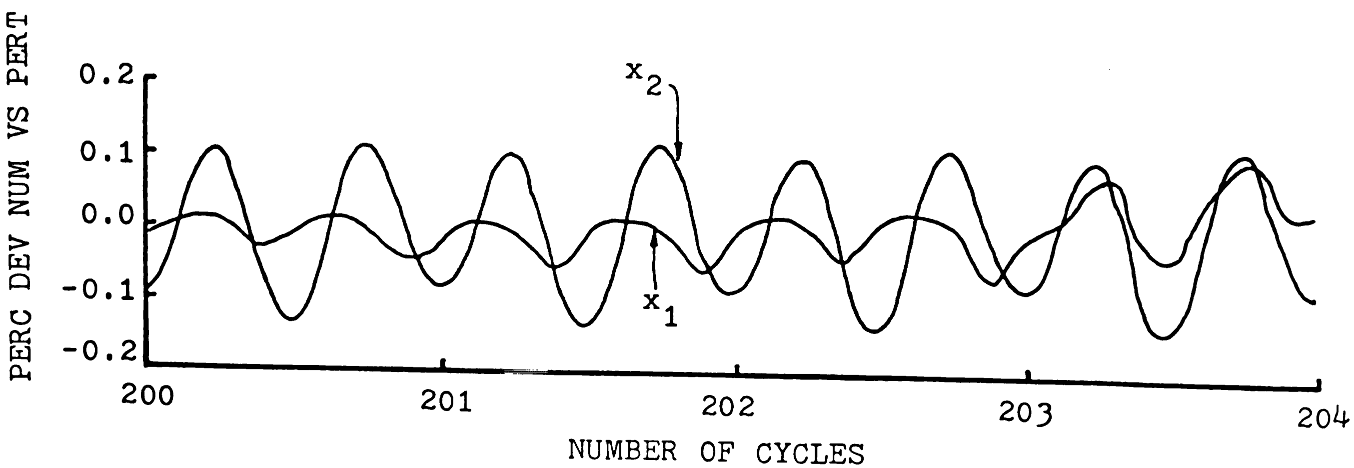

PERC DEV NUM VS PERT
0.2
0.1
0.0
-0.1
-0.2
x_2
x_1
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 5e.

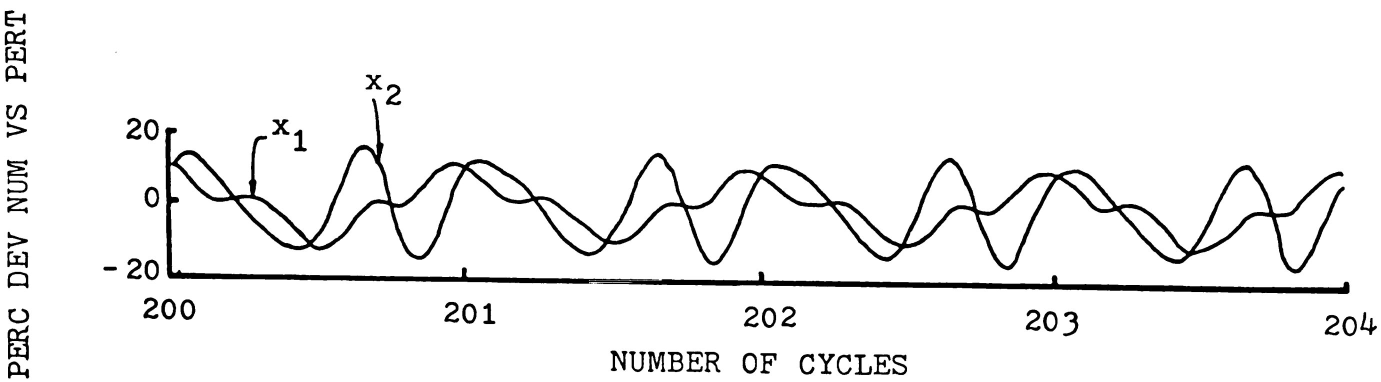
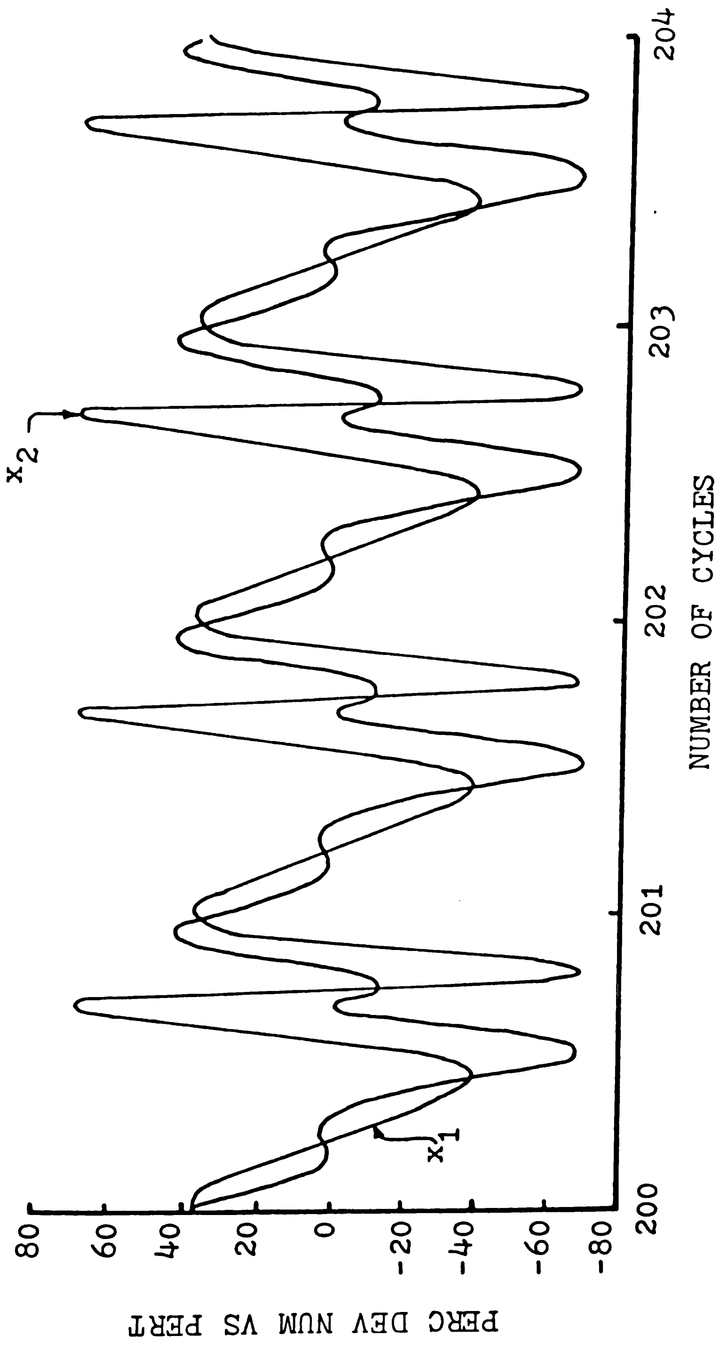
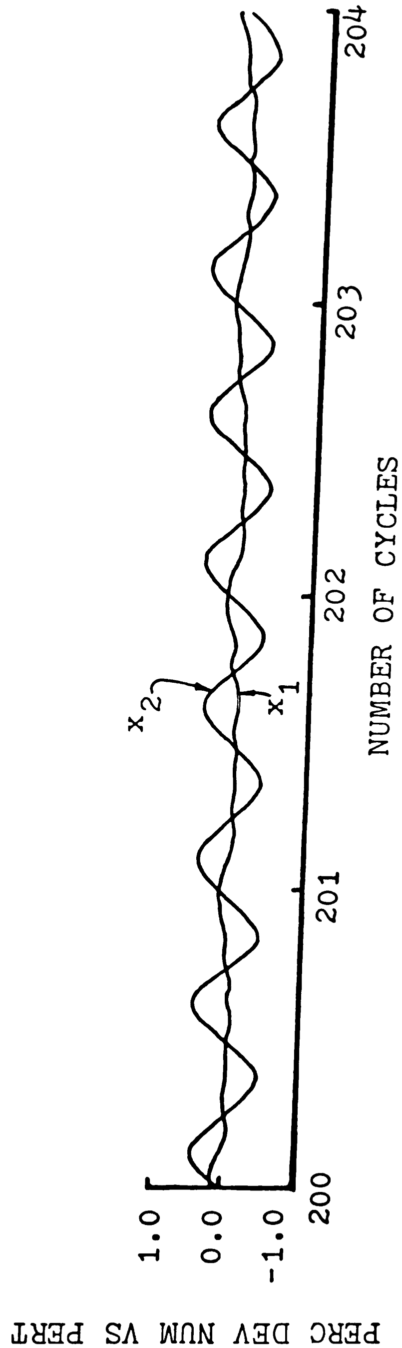

PERC DEV NUM VS PERT
20
0
-20
200
201
202
203
204
NUMBER OF CYCLES
x_1
x_2

FIGURE 5f.


PERC DEV NUM VS PERT
80
60
40
20
0
-20
-40
-60
-80
200
201
202
203
204
NUMBER OF CYCLES
x_1
x_2



PERC DEV NUM VS PERT
1.0
0.0
-1.0
200
201
202
203
204
x_2
x_1
NUMBER OF CYCLES

FIGURE 5g.

FIGURE 5h.

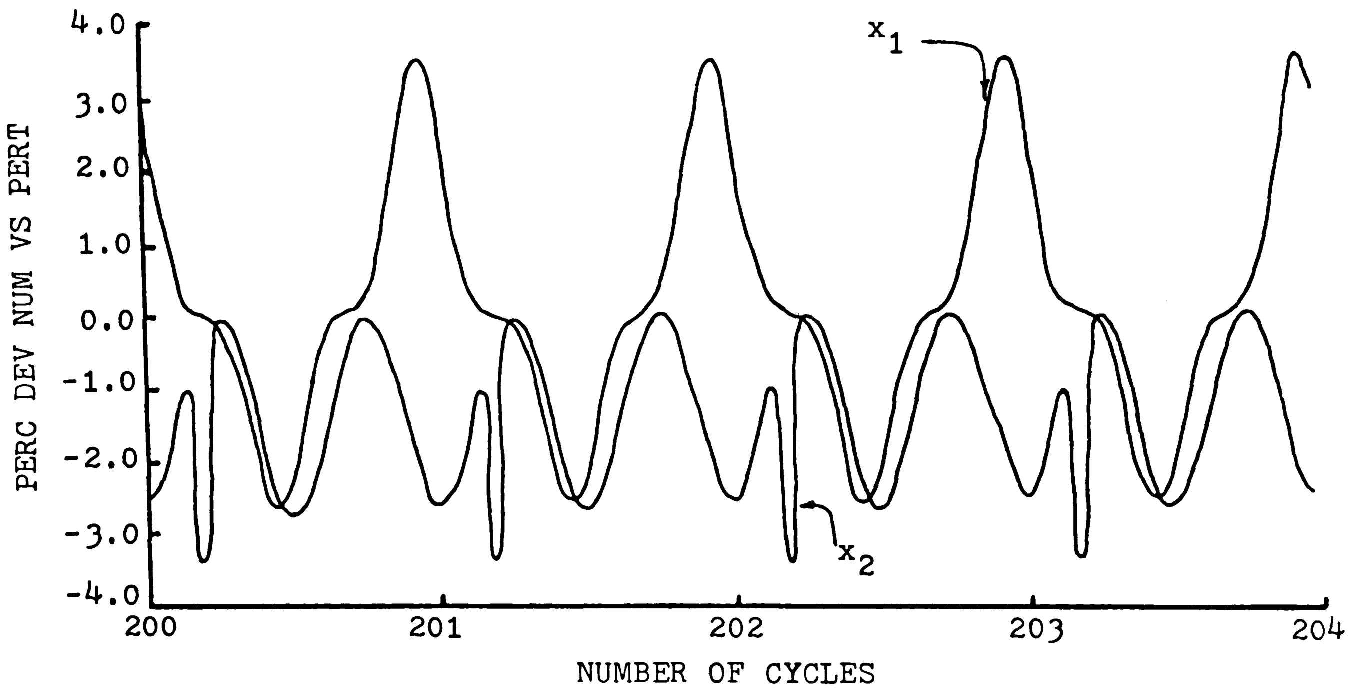
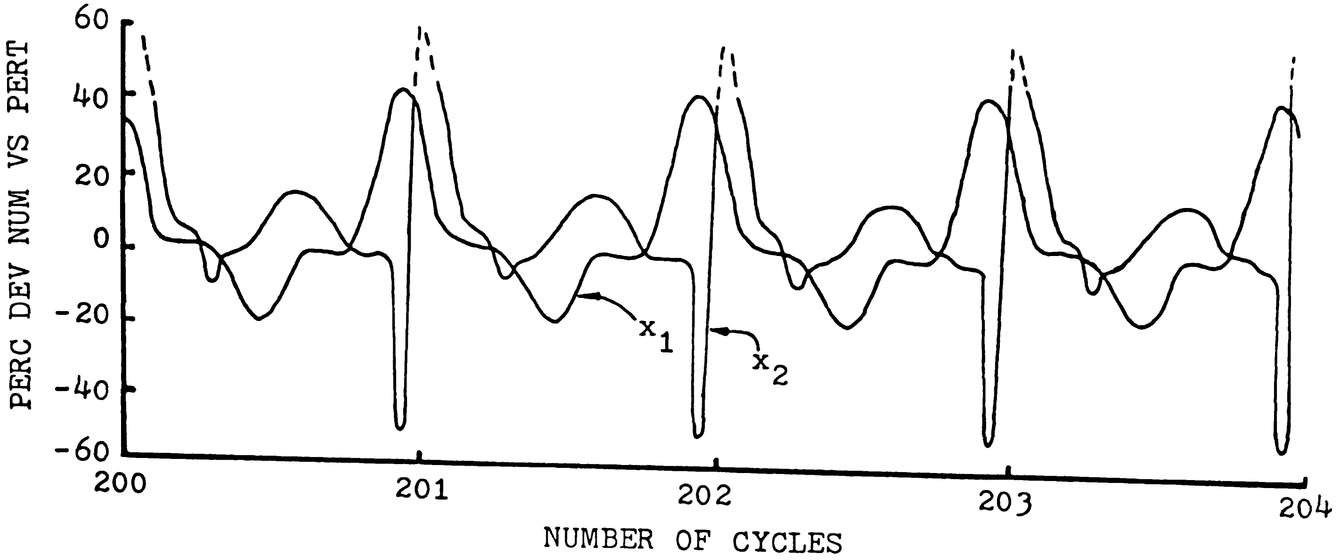

PERC DEV NUM VS PERT
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
200
201
202
203
204
NUMBER OF CYCLES
x_1
x_2

FIGURE 5i.


PERC DEV NUM VS PERT
60
40
20
0
-20
-40
-60
200
201
202
203
204
NUMBER OF CYCLES
x_1
x_2

very large values of K_1^o.

Figures 6(a) and 6(b) show a limit cycle in the x_2-x_1 phase plane and a trajectory relative to a time-invariant process at the optimal steady state. The trajectory in figures 6(a) and 6(b) which starts at $x_1 = 1.0$ corresponds to the dynamics of the system at zero perturbation amplitude. Unlike in the reactant feed concentration cycling, the limit cycle trajectory which oscillates about the optimal steady state, has x_1-x_2 boundaries less than those encountered for the unperturbed transient maximum. Further, the limit cycle patterns for various cycling frequencies are somewhat skewed. (Figure 6(a)) compared to the more regular pattern found for the system with amplitude variation (Figure 6(b)). An increase of the cycling frequency produces a more profound effect of shifting the trend of selectivity enhancement than an increase in the magnitude of the perturbation amplitude. In almost all kinetic and optimal steady state process parameters, increasing further the cycling frequency will change a negative selectivity enhancement to positive. However, an increase in the magnitude of the perturbation amplitude only augments the selectivity enhancement, so that an already positive enhancement at some large cycling frequency is further improved

Recently, Sinčić and Bailey [10] and Watanabe et al [11] have extended Guardabassi's technique [20] for local optimal periodic operation of an isothermal CSTR. (For brevity, such technique is referred to as the pi-criterion.)

FIGURE 6a. x_2-x_1 phase plane for $K_1=K_2=\hat{K}_2=1$, $\Lambda=1$, with varying ϵ.

FIGURE 6a.

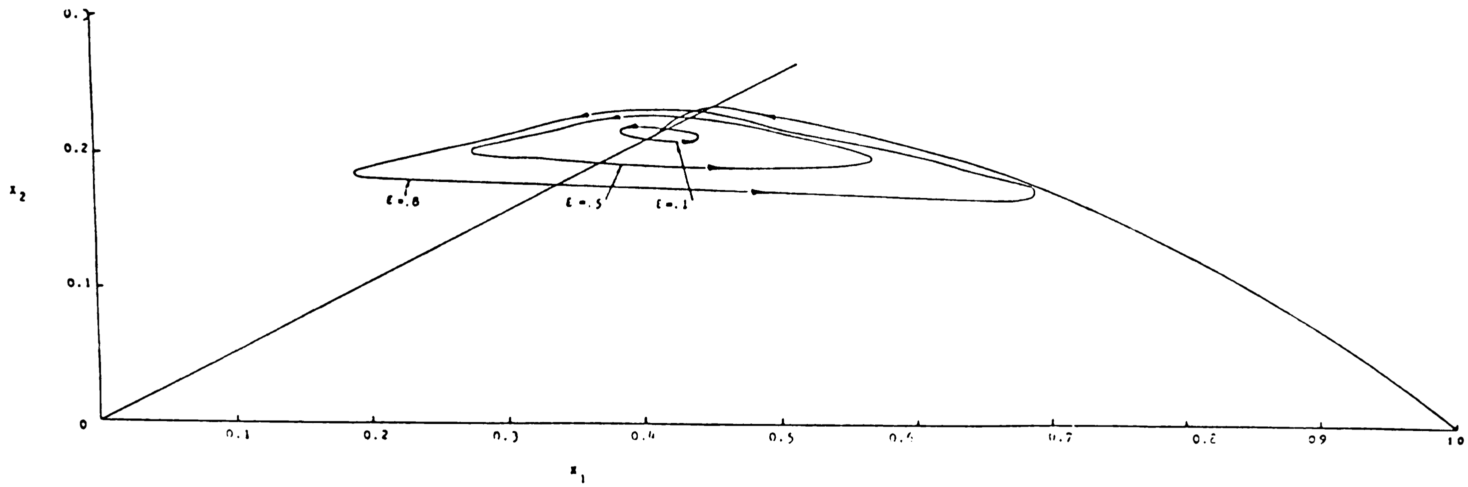
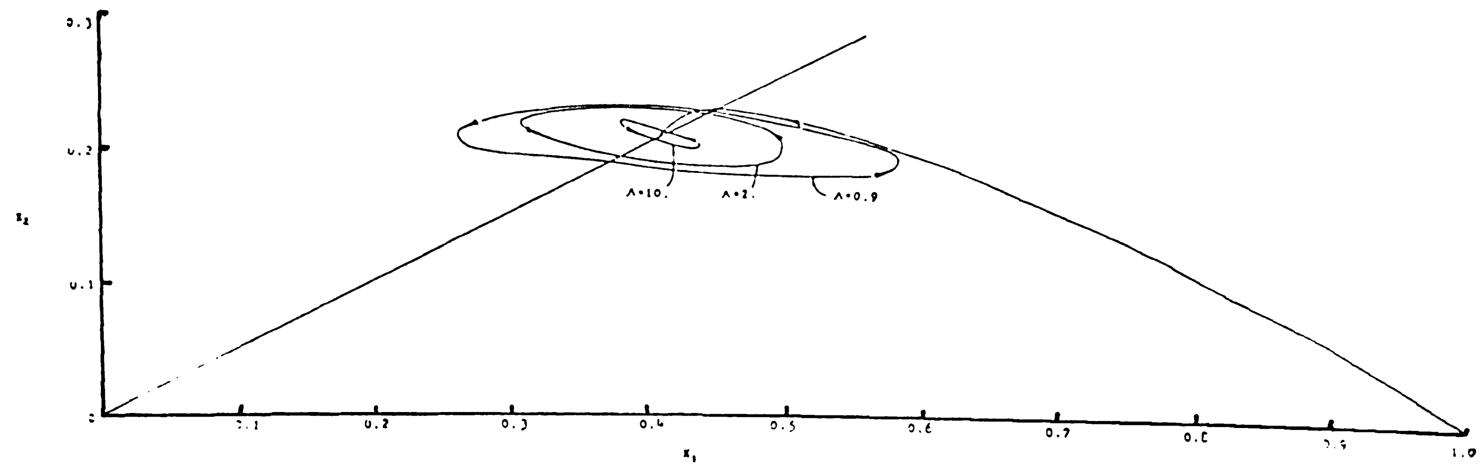


FIGURE 6b. x_2-x_1 phase plane for $K_1=K_2=\hat{K}_2=1$, $\epsilon=0.5$, with varying Λ.

FIGURE 6b.



The pi-criterion, which uses a variational approach to the objective function is limited by very small magnitudes of the perturbation amplitude. Such restriction is required in order to linearize the system dynamics with respect to an optimal steady state, otherwise the second variation would be difficult to evaluate. Characteristically, the pi-criterion is generally useful in predicting only a locally improper or proper optimal periodic process without excessive calculations. Here, the pi-criterion is applied to the present case and examine, as a function of $\frac{\epsilon}{\Lambda}$, the extent of its deviation from the enhancement predicted by the S-D perturbation solution. For comparison, $\frac{\epsilon}{\Lambda}=0.005$ and 0.01 were chosen, since such values yield very small deviation of the S-D perturbation solution from numerical simulation. These results are presented in Figures 7(a) and 7(b). In the perturbation method, both $\frac{\epsilon}{\Lambda}$ values yield a similar selectivity enhancement trend, i.e., negative to positive with increasing values of the cycling frequency and perturbation amplitude. However, in contrast to the perturbation method, the pi-criterion predicts a selectivity enhancement trend of proceeding from negative to positive and finally back to negative enhancement with increasing values of cycling frequency and perturbation amplitude. It appears that the predictability of the pi-criterion fails at Λ somewhere between 0.01 and 0.03. Nevertheless, even at such small amplitudes, the shift in selectivity enhancement is consistent with the perturbation method. However, for perturbation amplitude

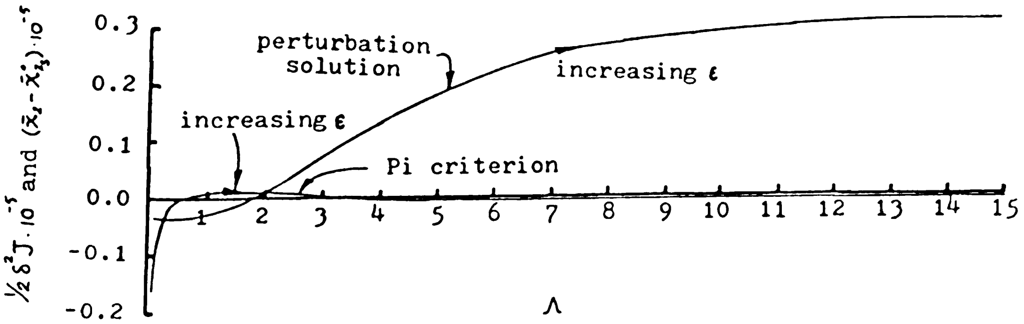
FIGURE 7. Comparison between perturbation solution and Pi-criterion method with $k_1=k_2=k_3A_{ref}=1$,

(a) $\epsilon/\Lambda=0.005$

(b) $\epsilon/\Lambda=0.01$

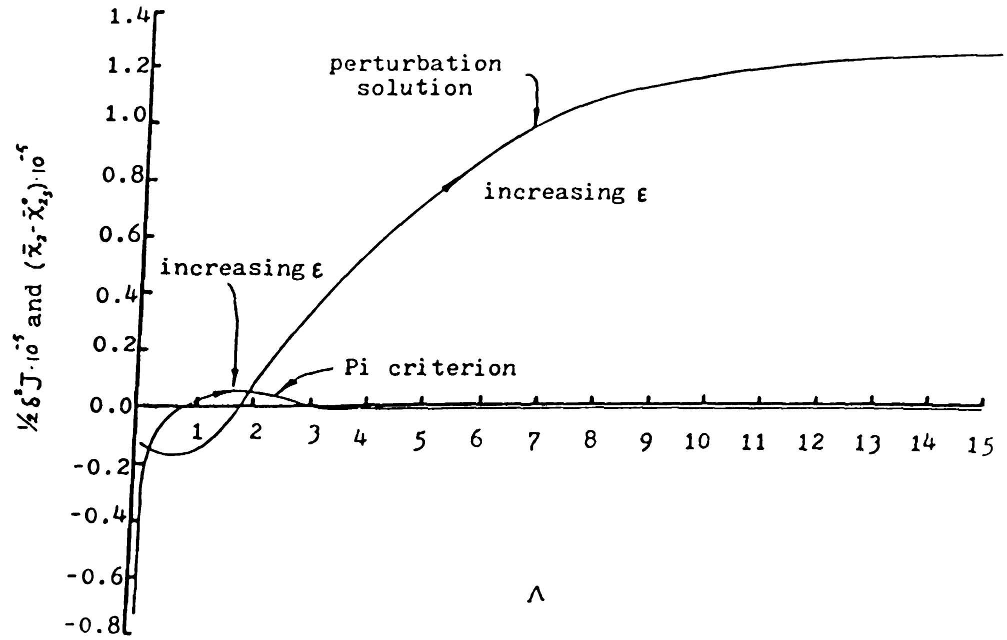
FIGURE 7.

(a)



$\frac{1}{2}\delta^2 J \cdot 10^{-5}$ and $(\bar{x}_2 - \bar{x}_{2s}^{\circ}) \cdot 10^{-5}$
0.3
0.2
0.1
0.0
-0.1
-0.2
perturbation solution
increasing ε
increasing ε
Pi criterion
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Λ

(b)



$\frac{1}{2}\delta^2 J \cdot 10^{-5}$ and $(\bar{x}_2 - \bar{x}_{2s}^{\circ}) \cdot 10^{-5}$
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
perturbation solution
increasing ε
increasing ε
Pi criterion
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Λ

greater than 0.03 (with $\frac{\epsilon}{\Lambda}$=0.005 to 0.01), the selectivity enhancement results from the pi-criterion is less to be confided. Furthermore, the ϵ and Λ values at which the switch from negative to positive enhancement occurs, lies ahead of the ϵ-Λ values obtained from the S-D perturbation method.

Finally, when the pi-criterion is applied to the case presented by Skeirik and DeVera [12] , the selectivity enhancement trend was correctly predicted for all values of cycling frequencies and for small to moderately large values of the perturbation amplitude. These results are presented in table 2.

CONCLUSION

In general, for an isothermal CSTR subjected under a sinusoidal control of the volumetric throughput, the yield of the intermediate product in the Van de Vusse kinetic scheme is improved via implementation of large magnitude of the cycling frequency. The magnitude of the yield enhancement is further improved by imposing large magnitudes of the perturbation amplitude. Regardless of the size of the perturbation amplitude, negative yield enhancement results from small cycling frequency.

The application of the S-D perturbation method yields a good approximation to the global dynamics, and hence the calculated trend of yield enhancement is reliable. The perturbation solution is sensitive to $\frac{\epsilon}{\Lambda}$ such that large deviations from the numerical simulation is encountered when $\frac{\epsilon}{\Lambda}$ is

TABLE 2. Yield enhancement as predicted by the pi-criterion and S-D perturbation method.

TABLE 2.

Λ	ϵ	B enhancement pert. method	B enhancement Pi-criterion
0.2	0.025	-0.0019219	-0.00068700
	0.075	-0.0172934	-0.00061838
1.0	0.100	-0.0001263	-0.00009820
	0.25	-0.0007828	-0.00061380
	0.75	-0.0070416	-0.00552420
5.0	0.25	-0.0001678	-0.00016740
	0.75	-0.0015057	-0.00150660

close to unity.

CHAPTER 2

SINE-WAVE CONTROL OF INPUT VOLUMETRIC FLOW RATE IN AN ISOTHERMAL PFR WITH A VAN DE VUSSE KINETICS

INTRODUCTION

The study of periodic operation in tubular reactors with plug flow model has not been as thoroughly investigated as its counterpart, i.e., continuous stirred tank reactor. Mainly, the reason is the lack of sufficient theory for assessing whether or not a certain periodic control policy is a locally proper optimal. Moreover, the specific case of a persistent disturbance in the volumetric flow rate, imposes a difficult description of the flow field, especially for cases where the disturbances are substantial. The first chapter has set forth two techniques which in some ways had advanced our understanding of periodic reactor operation involving a lumped parameter system, e.g. an isothermal CSTR with a mildly nonlinear kinetics. The techniques discussed there had to utilize some approximation. The Skeirik-DeVera (S-D) perturbation method assumes that when a transient state is disturbed because of an advertent control of the input stream, the response to such a controlled disturbance should produce a state dynamics that can be characterized by the nature of the disturbance. Such assumption led them to assume the structure of the closed form solution which entails a perturbation over an unperturbed transient state. The success of the S-D perturbation method lies on the determination of a closed form solution for the unperturbed dynamics of the yield of the intermediate product in a Van de Vusse reaction scheme. The zero order correction solution (or the unperturbed dynamic solution) along with the structure of the initial value are important in obtaining the periodic terms in the perturbation solution. Hence, the S-D perturbation solution can be extended to any control mode of an isothermal CSTR with a quadratic nonlinearity in the kinetic rate expression.

The second method due to Guardabassi [1] is a variational approach requiring limitations on the magnitude of the perturbation amplitude. It was shown in Chapter 1 the extent of applicability of Guardabassi's variational method. Indeed the variational approach is restrained by very small variations in the amplitude (i.e. only local fluctuations), regardless of the cycling frequency. While the same restrictions appeared to be innocuous for the S-D perturbation method, the variational method, unlike the S-D perturbation method, can be used for a host of different periodic control of CSTR's, including periodic heating and cooling rates, and CSTR's with kinetic rate expressions other than a quadratic nonlinearity, e.g. Langmuir-Hinshelwood type.

The sets of research on distributed parameter systems, for which the dynamics of a tubular reactor is a subset are classified into two categories, viz (i) model systems that involve a linear operator with a nonlinear nonhomogeneous part and (ii) model systems described by a nonlinear operator, e.g. a tubular reactor where the flow field is characterized by a nonlinear hyperbolic partial differential operator. Much of the mathematical analysis and actual control simulation have been done on the first category. Such topics include state-space approximation of fixed-bed reactor dynamics using collocation techniques [2]; approximate linear dynamics of packed tubular reactors [3]; analysis of the thermal and concentration traveling waves within a fixed bed chemical reactor that yields optimal control policies [4]; experimental measurements of the temperature response of a fixed bed reactor to sinusoidal disturbances in the feed concentration, temperature and flow rate [5]; and, simulation and control of a packed-bed tubular reactor which exhibits the existence of hot spots [8].

In other areas typical of the first category, the usual concern involves the establishment of criteria and computational schemes of control and optimal control (non-periodic control). For instance, Chang and Bankoff [6] has extended Sirazetdinov's formulation [7] of determining the necessary conditions for optimization. They have included general objective functionals and boundary conditions such as the recycle of an unconverted reactant with an appropriate time delay for separation and a free choice of final time. Chang and Bankoff's technique underlies a variational approach which provides conditions (usually in terms of boundary and final conditions of an adjoint partial differntial equation) for the maximum of an objective functional. The computational scheme that arose from their analysis involves the simultaneous solution to an adjoint variable using the method of characteristics, and the gradient method for establishing the minimal or maximal of the objective function. This approach is different from a periodic operation, because the nature of the latter problem is concerned with determining the optimal control such that when a new optimal steady state is obtained, an objective functional is satisfied. Chang and Bankoff [6] has also provided a review of optimal control in distributed parameter systems. Along the same goal as the works earlier mentioned, Koppel and Shih [9] has derived a strong minimum principle by converting a vector of linear hyperbolic partial differential equation to a vector of ordinary differential equation and then defining a performance index along a ground characteristic (i.e., t-z plane). Unlike the rest, they accounted for the time fluctuation of the fluid velocity over a certain steady state velocity, i.e. plug flow. In an earlier paper, Koppel [10] treated a similar differential operator but he aimed at comparing the exact solution and the solution from a linearized dynamics of an isothermal tubular reactor with an nth order irreversible reaction. Finally, for a completely periodic operation, Fjeld and Kristiansen [11] applied a variational method to establish conditions for local optimality of distributed parameter systems with a linear space-time differential operator matrix e.g. transient plug flow and axial dispersion tubular reactors. The search for the optimal periodic control involves the solution to the process equations and the associated adjoint differential equations.

The thrust of this work is twofold, viz, to find an appropriate model description of an isothermal plug flow tubular reactor under periodic perturbations of the volumetric flow rate and to compare the yield enhancement of periodically forced plug flow tubular and continuous flow stirred tank reactors. In this work, the local optimality of an isothermal tubular reactor which is subjected under a forced periodic volumetric throughput is determined by employing a perturbation method developed earlier by Skerik-DeVera [12]. It will be illustrated in the ensuing discussions that the Skerik-DeVera perturbation method provides a very reliable approximation of the state variable response for small perturbation amplitudes and cycling frequencies. Such results can be rationalized by comparing the equivalent lumped parameter system (expressed in terms of a ground characteristic variable, s) and the process dynamics equation of an isothermal CSTR.

BASIC EQUATIONS AND THE PERTURBATION MODEL

Consider a one-dimensional model of the plug flow tubular reactor. The material conservation equations for the tubular reactor with a homogeneous Van de Vusse reaction scheme is expressed as for species A,

$$\frac{\partial \chi_1}{\partial \theta} + \frac{\partial}{\partial \xi}\left(\bar{v}\chi_1\right) = -K_1^\circ \chi_1 - K_3^\circ \chi_1^2 \equiv h_1 \tag{1.1}$$

for species B,

$$\frac{\partial \chi_2}{\partial \theta} + \frac{\partial}{\partial \xi}\left(\bar{v}\chi_2\right) = K_1^\circ \chi_1 - K_2^\circ \chi_2 \equiv h_2 \tag{1.2}$$

The mean fluid velocity which is associated in the material conservation equations has space and time dependencies caused by the continuous flow disturbance at the reactor entrance. The flow disturbance is treated as small enough so as to maintain the plug flow behavior and avoid the formation of eddies which would transform the prescribed mass conservation equations to one containing dispersive effects.

The velocity field is obtained by a momentum conservation which assumes that pressure, viscous and gravity effects are insignificant, hence

$$\frac{\partial \bar{v}}{\partial \theta} + \bar{v}\frac{\partial \bar{v}}{\partial \xi} = 0 \tag{2.1}$$

Perhaps, a rather general and yet simpler description of the velocity field is due to Burger's equation [13, 14]. But the simplified model given by equation (2.1) would temporarily suffice since the present investigation is solely concerned with local fluctuations to an already established velocity, i.e. plug flow velocity at the steady state. These local fluctuations arise because the input volumetric flow rate is continuously perturbed by some periodic control. Here, the local fluctuations, unlike in Koppel's work [9, 10], would assume not only time but also spatial dependency. Such formulation will be discussed later. Actually equation (2.1) is a subclass of Burger's equation and thus the solution contains a limiting function whose properties, in general, contains shock-discontinuities. The limiting function is derived from the solution to Burger's equation at the asymptotic limit of vanishing reaction mixture viscosity. There is a number of both analytical and numerical investigations of Burger's turbulence and a most recent review is found in [15]. A very important contribution to the analysis of Burger's turbulence is the description of formation and decay of weak shock waves in a compressible flow [16, 17]. Here, the existence of these weak shock waves will be disregarded in spite of the continuous change in the mean velocity at the reactor entrance. Such assumption is tenacious only at very small magnitudes of the perturbation amplitude and the cycling frequency (or quasi-steady state). Hence, the velocity field which is regular and smooth can be represented as

$$\bar{V} = 1 + \epsilon \bar{V}_1 + \epsilon^2 \bar{V}_2 \qquad (2.2)$$

and where $\bar{v}_1$ and $\bar{v}_2$ are fluctuation functions obtained from the solution of equation (2.1), and where ϵ (<<< 1) denotes the perturbation amplitude.

Finally, the reactor is initially void of reactants and some inerts are already flowing inside the reactor at a mean velocity corresponding to an optimal steady state residence time.

PERTURBATION SOLUTION AND OPTIMAL PERIODIC PROCESS

The objective function which seeks for the optimal yield of the intermediate product via a periodic control of the input volumetric flow rate is expressed as

$$J = \frac{1}{T^\circ} \oint x_2(1,\theta)\, d\theta \tag{3}$$

where T° is a dimensionless cycle time relative to an optimal steady state residence time. The optimal function x_2 is subject to the following:

$$\frac{\partial \underline{x}}{\partial \theta} = \underline{f}\left(\underline{x}, \frac{\partial}{\partial \xi}(\bar{v}\underline{x}), \underline{h}(\underline{x})\right) \tag{4}$$

$$\frac{\partial \bar{v}}{\partial \theta} = -\bar{v}\frac{\partial \bar{v}}{\partial \xi} \tag{5}$$

$$\underline{x}(0,\theta) = \begin{cases} 1 & \text{for } x_1 \\ 0 & \text{for } x_2 \end{cases} \tag{6}$$

$$\underline{x}(\xi,0) = 0 \tag{7}$$

$$\bar{v}(\xi,0) = 1 \tag{8}$$

$$\bar{v}(0,\theta) = u(\theta;\epsilon) = u_s^\circ + \delta u$$
$$= \text{a control variable} \tag{9}$$

$$\frac{1}{T^{\circ}}\oint \bar{v}(0,\theta)\,d\theta = 1 \qquad (10)$$

Here the yield enhancement is defined relative to an optimal steady state (J_s°) i.e.,

$$E = J - J_s^{\circ} \qquad (11)$$

The optimal steady state can be found in [18, 19].

Now, in the region $\theta \ggg \xi$, the velocity field according to the perturbation model is expressed as

$$\bar{v} = 1 + \epsilon \sin\Lambda(\theta-\xi) + \epsilon^2 \frac{\Lambda}{2}\xi \sin 2\Lambda(\theta-\xi) \quad , \quad \theta \ggg \xi \qquad (12)$$

for $\delta u = \epsilon \sin\Lambda\theta$. Since the limit cycle exists in the same region $\theta \ggg \xi$, the asymptotic sequence

$$\underline{x} = \underline{x}_s^{\circ} + \epsilon\, \underline{P}^1(\theta,\xi) + \epsilon^2 \underline{P}^2(\theta,\xi) \quad , \quad \theta \ggg \xi \qquad (13)$$

can be assumed. $\underline{P}^1$ and $\underline{P}^2$ are periodic functions obtained from the solution to equation (4) and, in the region $\theta \ggg \xi$ has initial (or boundary) conditions given by $\underline{P}^1(s=0) = \underline{P}^2(s=0) = 0$. s is a ground characteristic variable. The development of these initial conditions assumes that the zero order term at $\xi=0$ has the same value as $\underline{x}(0,\theta)$. A discussion of the initial conditions is found in Appendices I and J. Furthermore, here, the second order term is accounted because

$$\frac{1}{T^{\circ}}\oint \underline{P}^1(\theta_\infty,\xi)\,d\theta_\infty = 0 \quad , \quad \theta \ggg \xi \qquad (14)$$

Hence, the first order terms do not contribute any information about the yield enhancement. Such is typical of the S-D perturbation method [12].

In the $\theta >\!>\!> \xi$ region, $\underline{P}^1$ and $\underline{P}^2$ satisfies the following set of ordinary differential equations along a ground characteristic s.

$$\frac{dP_1^1}{ds} + K_1^\circ\left[1 + \frac{2\alpha_0 e^{-K_1^\circ s}}{1-\alpha_0 e^{-K_1^\circ s}}\right]P_1^1 = \frac{\alpha_0 e^{-K_1^\circ s}}{K(1-\alpha_0 e^{-K_1^\circ s})}\left[\Lambda\cos\Lambda r + \frac{K_1^\circ \sin\Lambda r}{1-\alpha_0 e^{-K_1^\circ s}}\right] \tag{15}$$

$$\frac{dP_1^2}{ds} + K_1^\circ(1+2K\tilde{\chi}_{1s}^\circ)P_1^2 = -\bar{v}_1(s;r)\left[\frac{\partial P_1^1}{\partial \xi}\right]_{s;r} - P_1^1\left[\frac{\partial \bar{v}_1}{\partial \xi}\right]_{s;r} - \bar{v}_2(s;r)\left[\frac{d\chi_{1s}^\circ}{d\xi}\right]_{s;r}$$
$$- \tilde{\chi}_{1s}^\circ\left[\frac{\partial \bar{v}_2}{\partial \xi}\right]_{s;r} - K_3^\circ(P_1^1)^2 \tag{16}$$

$$\frac{dP_2^1}{ds} + K_2^\circ P_2^1 = K_1^\circ P_1^1 - \left[\frac{d\chi_{2s}^\circ}{d\xi}\right]_{s;r}\sin\Lambda r + \Lambda\cos\Lambda r\cdot\tilde{\chi}_{2s}^\circ \tag{17}$$

$$\frac{dP_2^2}{ds} + K_2^\circ P_2^2 = -\sin\Lambda r\left[\frac{\partial P_2^1}{\partial \xi}\right]_{s;r} - \frac{\Lambda s}{2}\sin 2\Lambda r\left[\frac{d\chi_{2s}^\circ}{d\xi}\right]_{s;r} + \Lambda P_2^1\cos\Lambda r$$
$$-\left[\frac{\Lambda}{2}\sin 2\Lambda r - s\Lambda^2\cos 2\Lambda r\right]\tilde{\chi}_{2s}^\circ + K_1^\circ P_1^2 \tag{18}$$

where $\underline{x}_s^{\circ}$ = optimal steady state concentration profile.

$\tilde{\underline{x}}_s^{\circ} = x_s^{\circ}(\rho ; r)$

$\rho = \xi$ and $r = \theta - \xi$

$\alpha_0 = \dfrac{K}{1+K}$

The solution to equations (15) to (18) is found in Appendix G. Thus, the average conversion and yield is expressed as

$$1-\bar{x}_1 = 1 - \frac{e^{-K_1^{\circ}}}{1-\alpha_0 e^{-K_1^{\circ}}}\left[\frac{\alpha_0}{K} + \frac{\epsilon^2}{1-\alpha_0 e^{-K_1^{\circ}}}\left[\Omega_1 - \Omega_{2i} - \Omega_{3i} + K_3^{\circ}\alpha_0^2\Omega_{4i}\right]\right] \tag{19}$$

$$\bar{x}_2 = \frac{K_1^{\circ}}{K} e^{-K_2^{\circ}} \sum_{j=0}^{\infty} \alpha_0^{1+j} \begin{cases} 1 & , \text{if } K_2^{\circ} = K_1^{\circ}(1+j) \\ \dfrac{e^{K_2^{\circ} - K_1^{\circ}(1+j)} - 1}{K_2^{\circ} - K_1^{\circ}(1+j)} & , \text{otherwise} \end{cases}$$

$$+ \epsilon^2 e^{-K_2^{\circ}}\left[\beta_{1j} + \beta_{2j} + K_1^{\circ}\left[\beta_{3j} + \sum_{k=4}^{13}(\beta_{ij})_k\right]\right] \tag{20}$$

where the Ω's are defined in the notation section and the β's are defined in Appendix H.

DISCUSSION

The periodic cycling of the input volumetric flow rate in an isothermal tubular reactor would certainly create fluctuations in the flow field within the tubular reactor. In what manner can the fluid velocity inside the reactor be mathematically described is a matter of how much refinement is needed to adequately model the flow field. If only small perturbations from an optimal steady state is desired perhaps a simple perturbation model as described earlier would suffice. Clearly, the enhancement is a function of the nature of the flow field. Even in an already optimal steady state regime, the differences in the steady state flow patterns or the steady state flow models have created different maximum yield [18, 19, 20]. Among different steady state flow patterns that were investigated, the optimal yield corresponds to an absolute maximum.

In this work, the velocity fluctuation is regarded as smooth, regular and when random shock-discontinuities could be present, is eliminated by assuming quasi-steady state. The description of the quasi-steady state fluid velocity is afforded by the limiting Burger's differential equation (i.e., $\mu \to 0$). A decomposition of the fluid velocity into two fluctuating functions in terms of time and spatial coordinate is necessary because the time-average of the periodic functions $\underline{P}^1$ do not produce information regarding the yield enhancement. Such result is typical of the S-D perturbation method. Hence, in retrospect the present work would assess a properly local optimal yield in an isothermal tubular reactor whereby the flow field response to a periodic disturbance in the reactor is described by equation (12).

The sensitivity of the perturbation solution was tested against the numerical simulation of the hyperbolic differential equations as suggested by Acrivos [21]. The numerical solution to the material conservation equations employed the perturbation equation for $\bar{v}$. This was implemented here because of the good matching between the perturbation solution for $\bar{v}$ and the numerical implementation of equation (2.1). Hence, the numerical solution to the conservation equation is partly simplified. For the parameters that were used in the calculations (e.g. small Λ and small ϵ), the percent deviation between perturbation and numerical was generally small (for example Figures 1a-1d). The absolute maximum percent deviation is 0.02 at ϵ =0.1 and Λ =0.1. Usually the sensitivity is largely influenced by the magnitude of ϵ . Hence, in subsequent calculations for the material balance equations, particularly small values of ϵ were chosen. The requirement of small values of Λ is imposed, not from a standpoint of numerical matching of solution, but from a standpoint of the required physics. However, the magnitude of Λ somehow affects the matching between the numerical simulation and the perturbation solution. Although the percent deviation is yet small for the same value of ϵ , an increase in the cycling frequency leads to increase in the

FIGURE 1. Velocity profile at $\xi=1.0$

(a) $\epsilon=\Lambda=0.05$

(b) $\epsilon=0.01$, $\Lambda=0.1$

FIGURE 1.

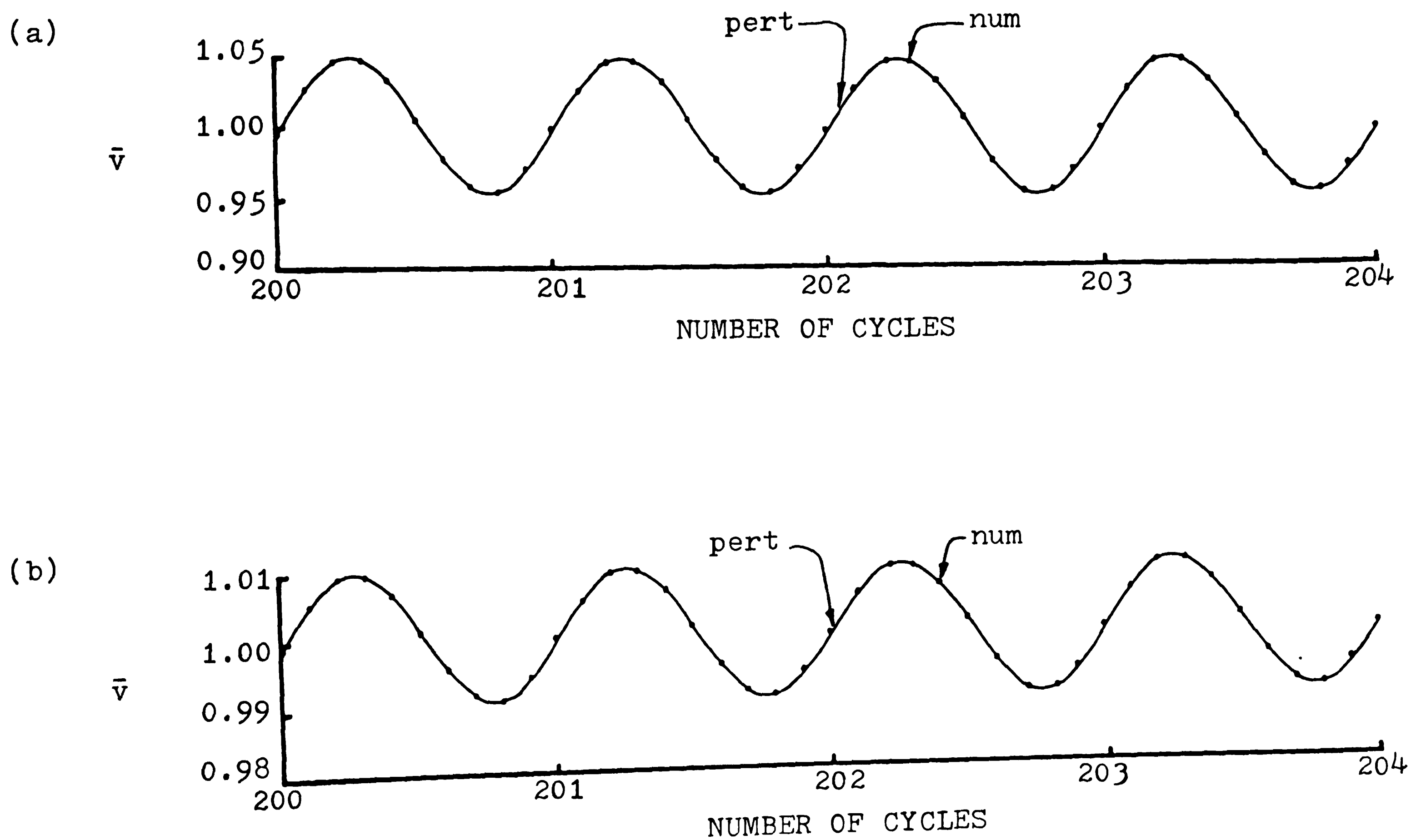

(a)
pert
num
1.05
1.00
$\bar{v}$
0.95
0.90
200
201
202
203
204
NUMBER OF CYCLES
(b)
pert
num
1.01
1.00
$\bar{v}$
0.99
0.98
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 1. Deviation of perturbation solution from numerical simulation for the velocity profile at $\xi = 1.0$

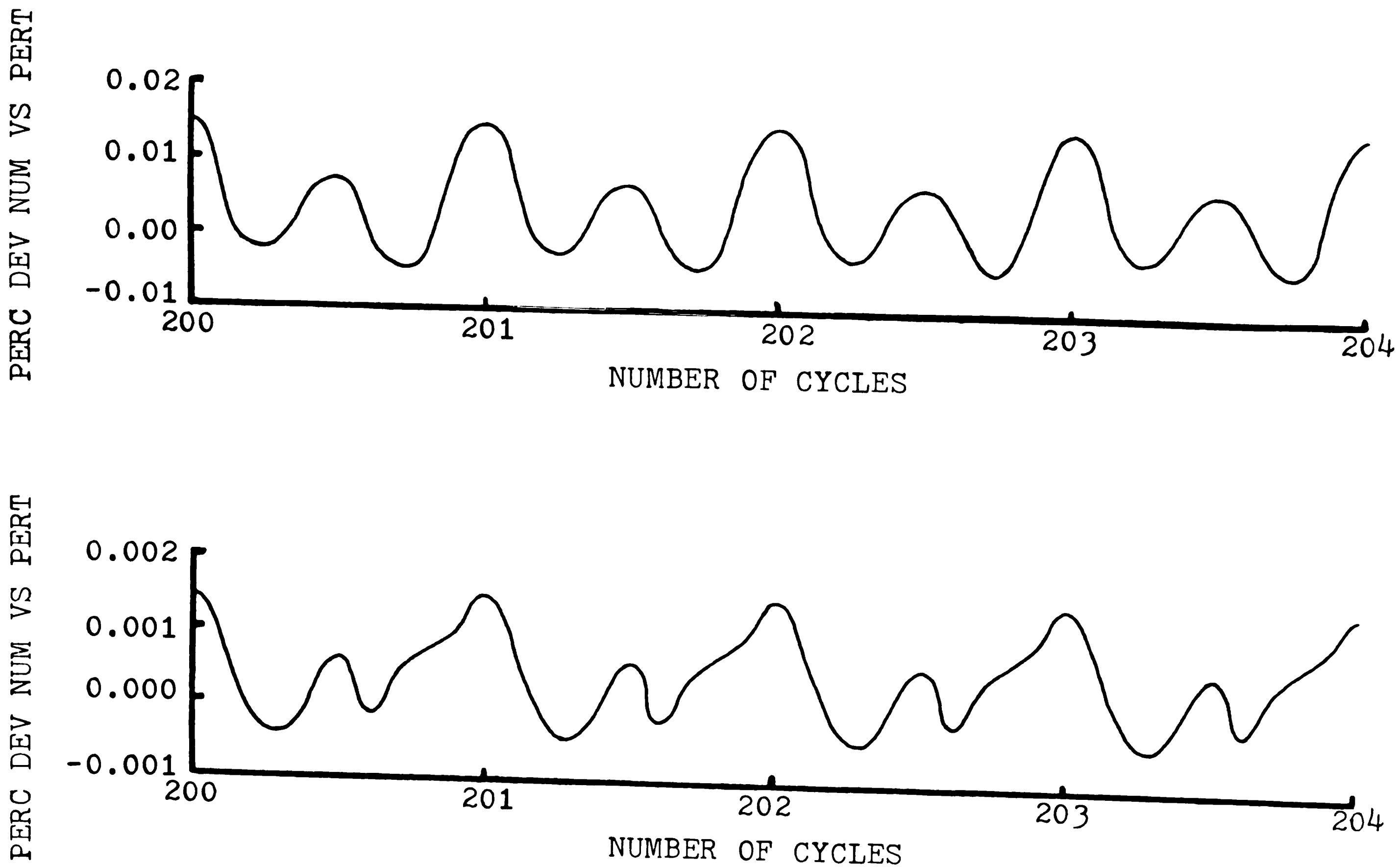
(c) $\epsilon = \Lambda = 0.05$

(d) $\epsilon = 0.01$, $\Lambda = 0.1$

FIGURE 1.

(c)

(d)


PERC DEV NUM VS PERT
0.02
0.01
0.00
-0.01
200
201
202
203
204
NUMBER OF CYCLES
PERC DEV NUM VS PERT
0.002
0.001
0.000
-0.001
200
201
202
203
204
NUMBER OF CYCLES

percent deviation (for example Figures 2a-2x and Figures 3a-3h). Furthermore, the large Λ has percent deviation propagating along ξ as compared to a more uniform percent deviation along ξ for smaller values.

In the $x_1(\theta\,;\xi) - x_2(\theta\,;\xi)$ phase plane (Figures 4a-4i), the size of the limit cycle increases from the reactor entrance to the exit. Such is caused by the fluctuations in the fluid velocity along the reactor. Finally, the importance of these effects render the yield enhancement to achieve negative values but achieve positive values for conversion enhancement (Tables 1 and 2). It appears that increasing Λ creates a larger negative yield enhancement and increasing conversion enhancement (Table 2). Hence increasing Λ would tend to shift, in a way, the reaction to the side reaction ($A+A \rightarrow D$), and thus favoring a higher yield for species D.

CONCLUSION

When an isothermal tubular reactor is allowed to undergo a quasi-steady state periodic control of the input volumetric flow rate, the time-average yield of B is less than the corresponding optimal steady state yield with plug flow behavior of the fluid. It appears that implementation of larger frequencies would shift the direction of enhanced selectivity to the side reaction.

Finally, the result presented here is not general for all classes of forced input volumetric flow rate oscillation.

FIGURE 2. Behavior of Van de Vusse system for $K_1=K_2=K_3=0.515$, $\epsilon=0.01$, $\Lambda=0.05$ at

(a-b) $\xi=0.2$

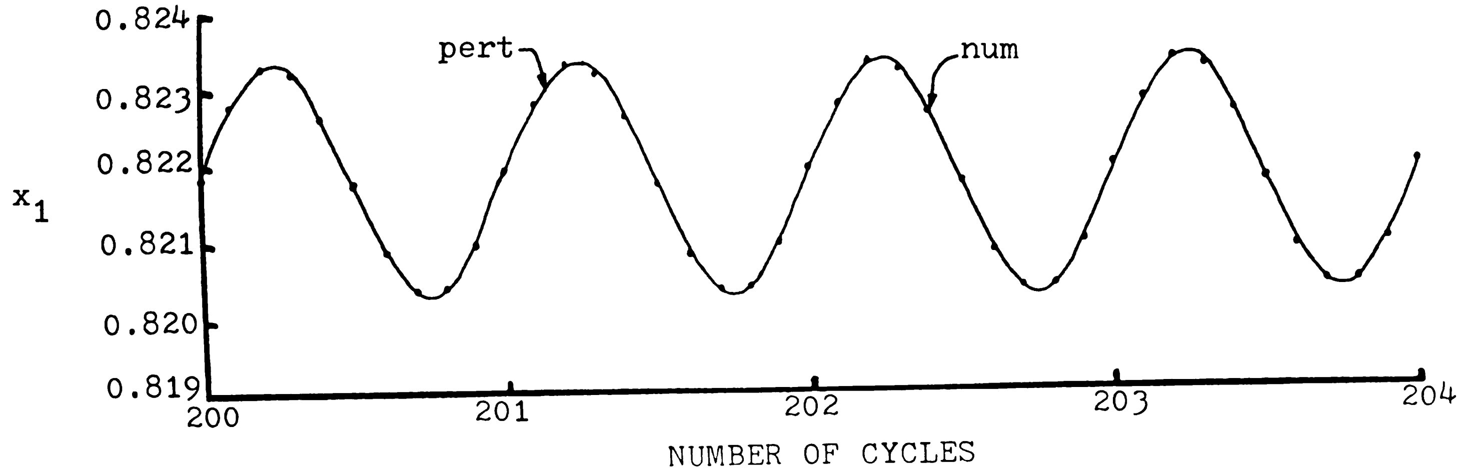
(c-d) $\xi=0.5$

(e-f) $\xi=0.75$

(g-h) $\xi=1.0$

FIGURE 2.

(a)


0.824
0.823
0.822
0.821
0.820
0.819
x_1
pert
num
200
201
202
203
204
NUMBER OF CYCLES

(b)

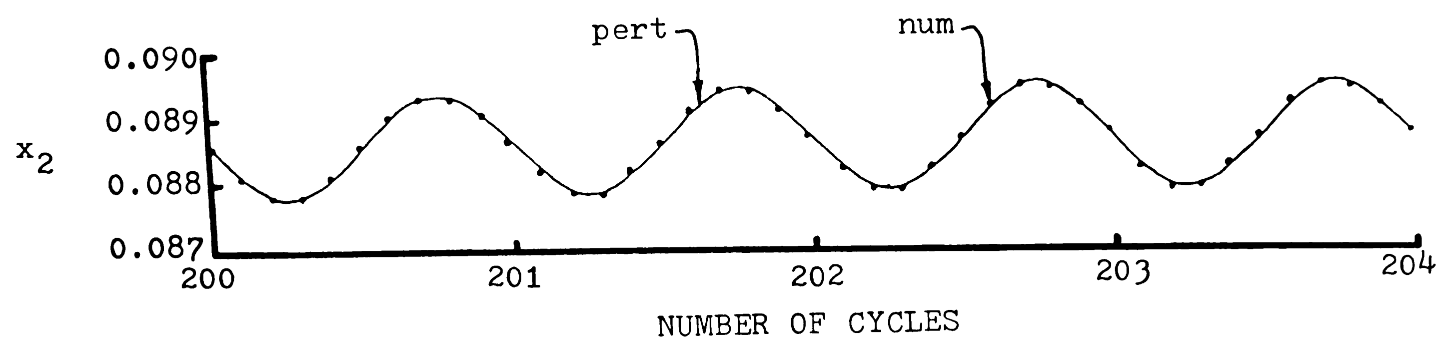

0.090
0.089
0.088
0.087
x_2
pert
num
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 2.

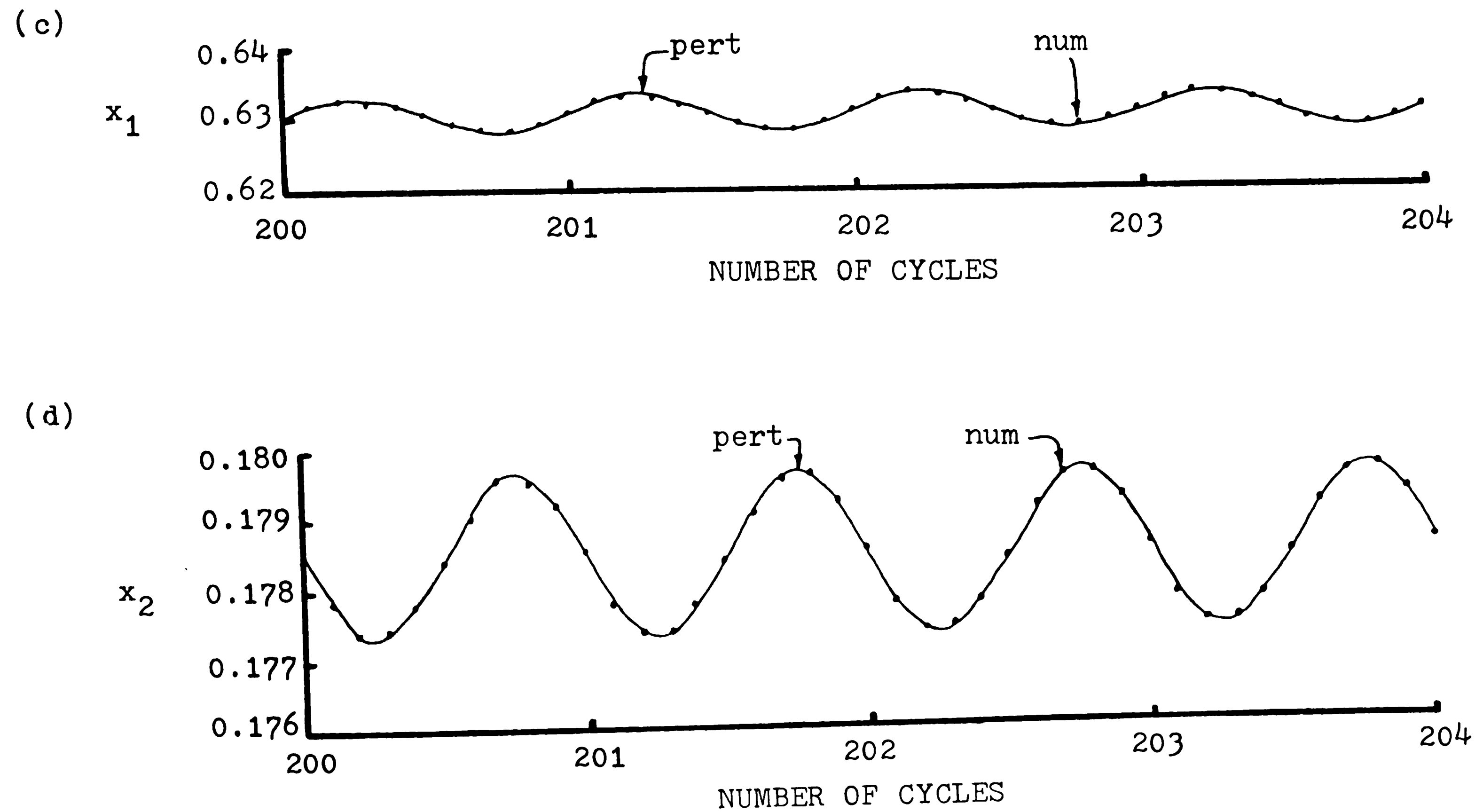

(c)
x1
0.64
0.63
0.62
pert
num
200
201
202
203
204
NUMBER OF CYCLES
(d)
x2
0.180
0.179
0.178
0.177
0.176
pert
num
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 2.

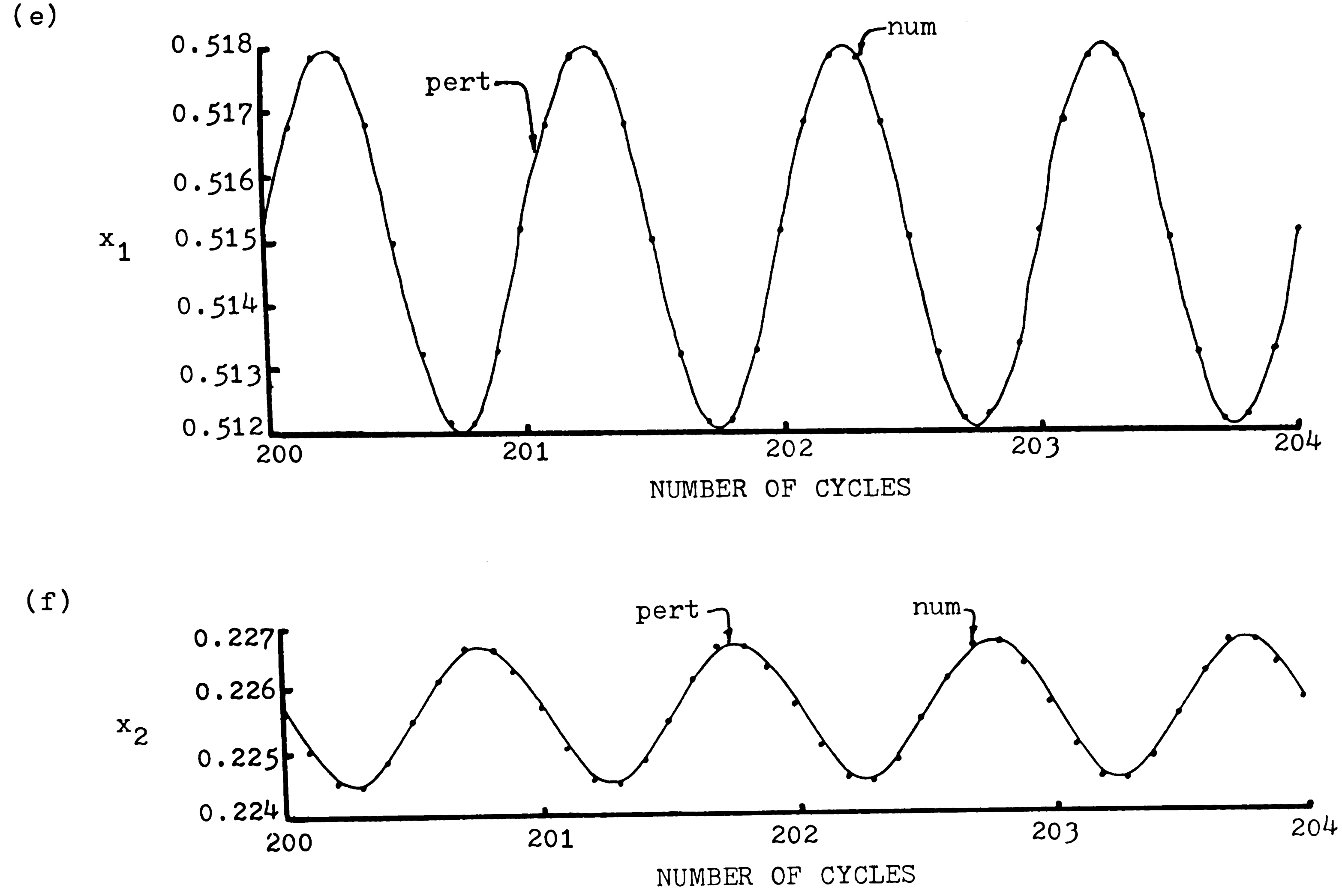
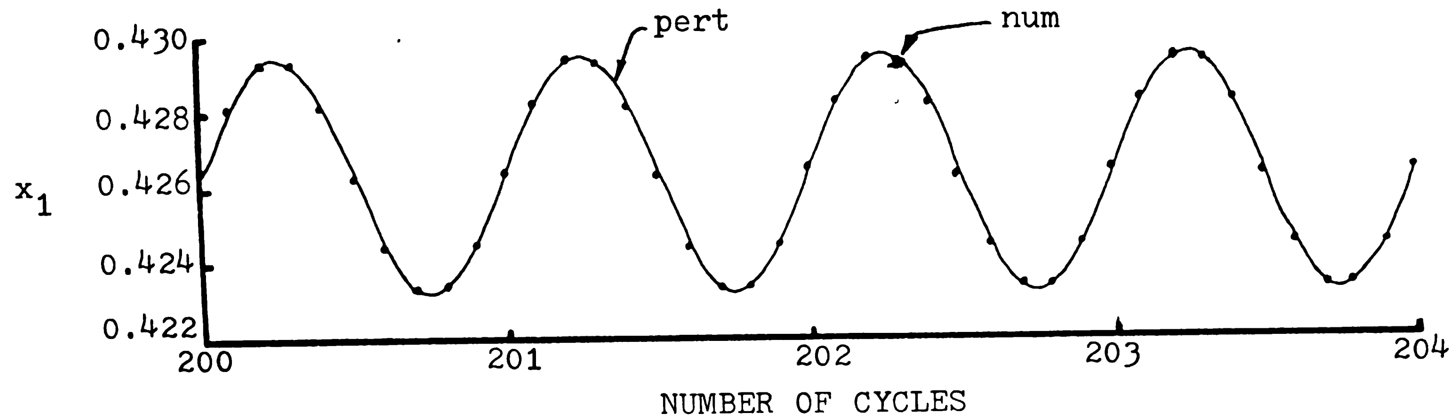

(e)
x_1
0.518
0.517
0.516
0.515
0.514
0.513
0.512
pert
num
200
201
202
203
204
NUMBER OF CYCLES
(f)
x_2
0.227
0.226
0.225
0.224
pert
num
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 2.

(g)


pert
num
0.430
0.428
0.426
0.424
0.422
x_1
200
201
202
203
204
NUMBER OF CYCLES

(h)

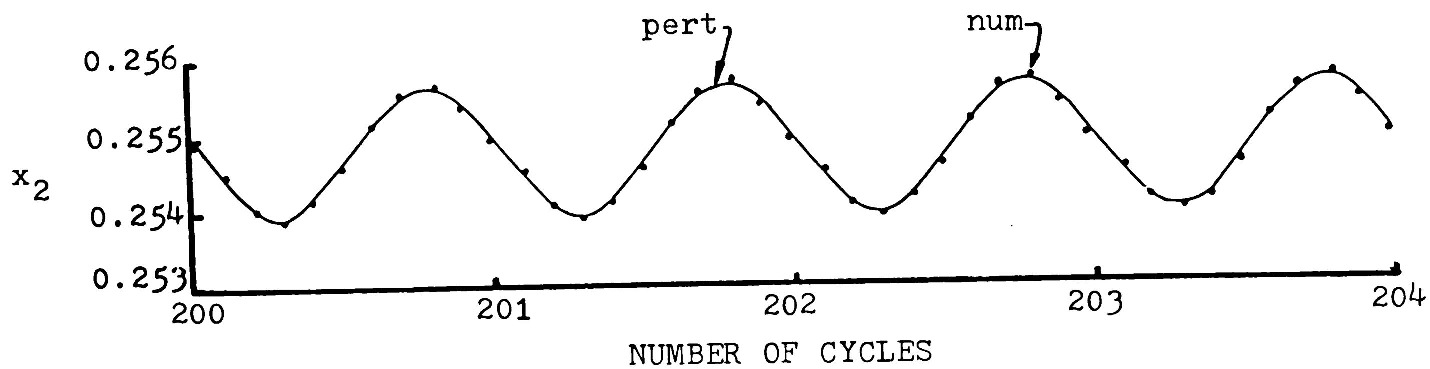

pert
num
0.256
0.255
0.254
0.253
x_2
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 2. Behavior of Van de Vusse system for $K_1=K_2=K_3=0.515$, $\epsilon=0.01$, $\Lambda=0.2$ at

(i-j) $\zeta = 0.2$

(k-l) $\zeta = 0.5$

(m-n) $\zeta = 0.75$

(o-p) $\zeta = 1.0$

FIGURE 2.

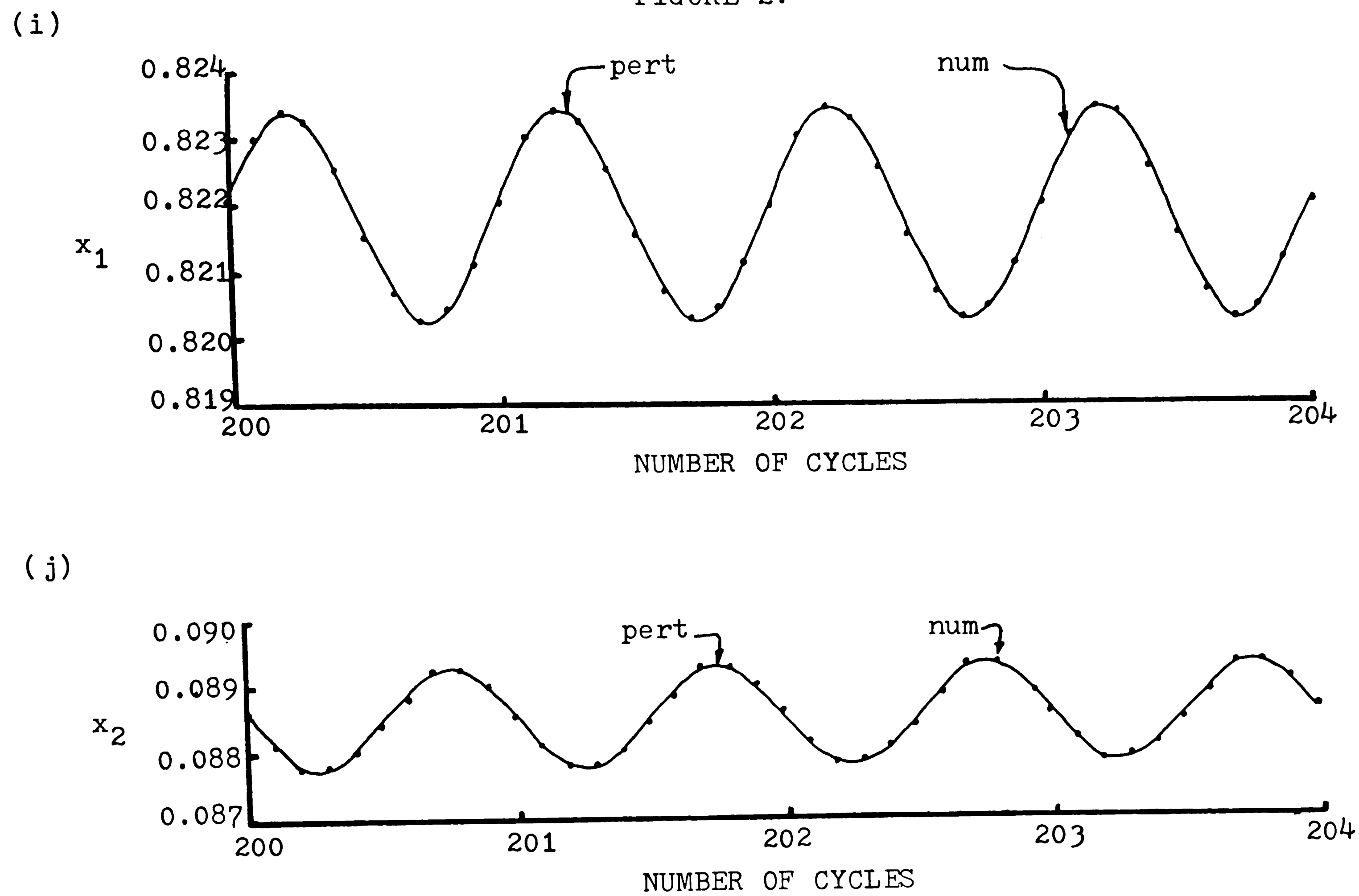

(i)
x_1
0.824
0.823
0.822
0.821
0.820
0.819
200
201
202
203
204
NUMBER OF CYCLES
pert
num
(j)
x_2
0.090
0.089
0.088
0.087
200
201
202
203
204
NUMBER OF CYCLES
pert
num

FIGURE 2.

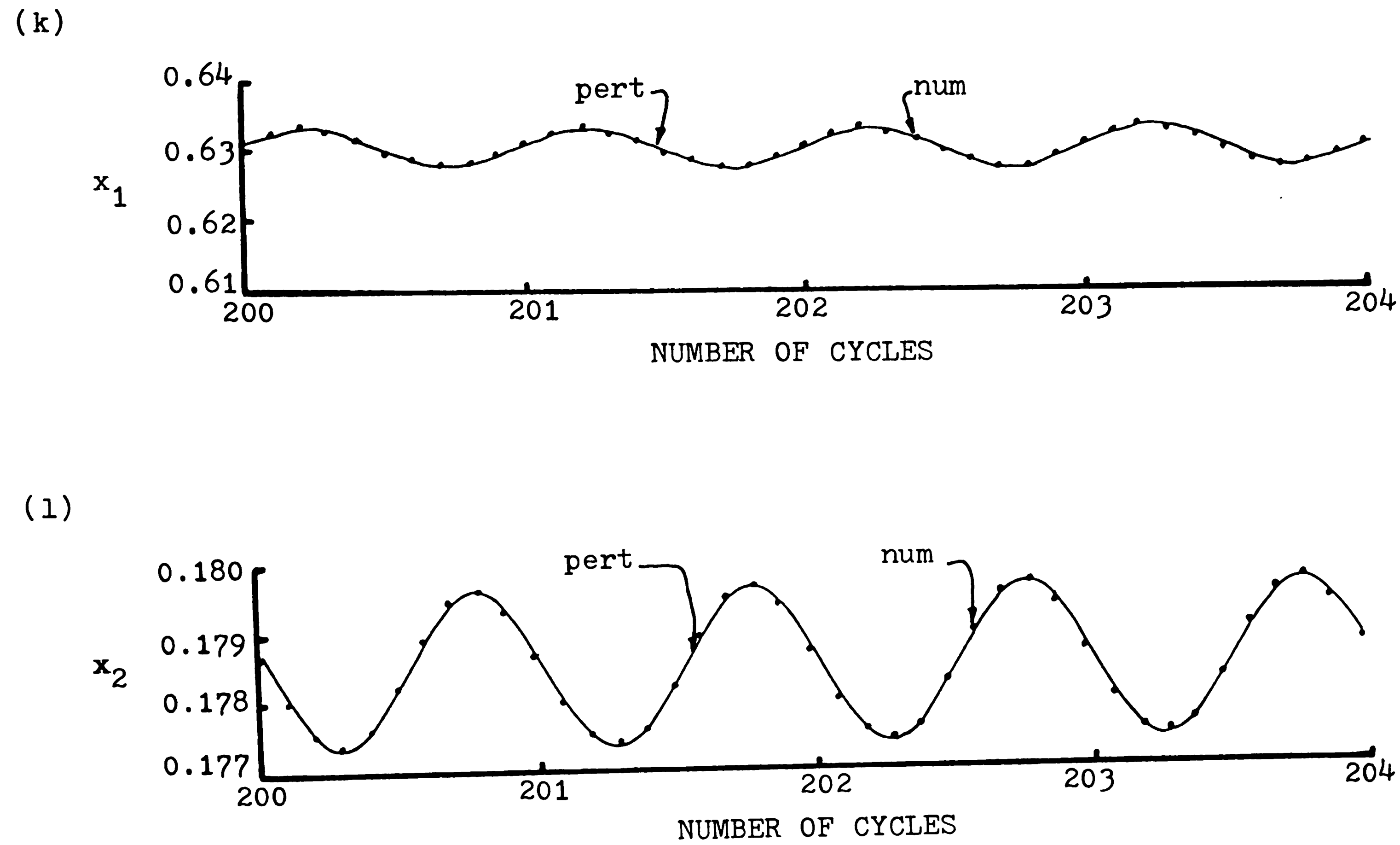

(k)
0.64
0.63
0.62
0.61
x_1
pert
num
200
201
202
203
204
NUMBER OF CYCLES
(l)
0.180
0.179
0.178
0.177
x_2
pert
num
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 2.

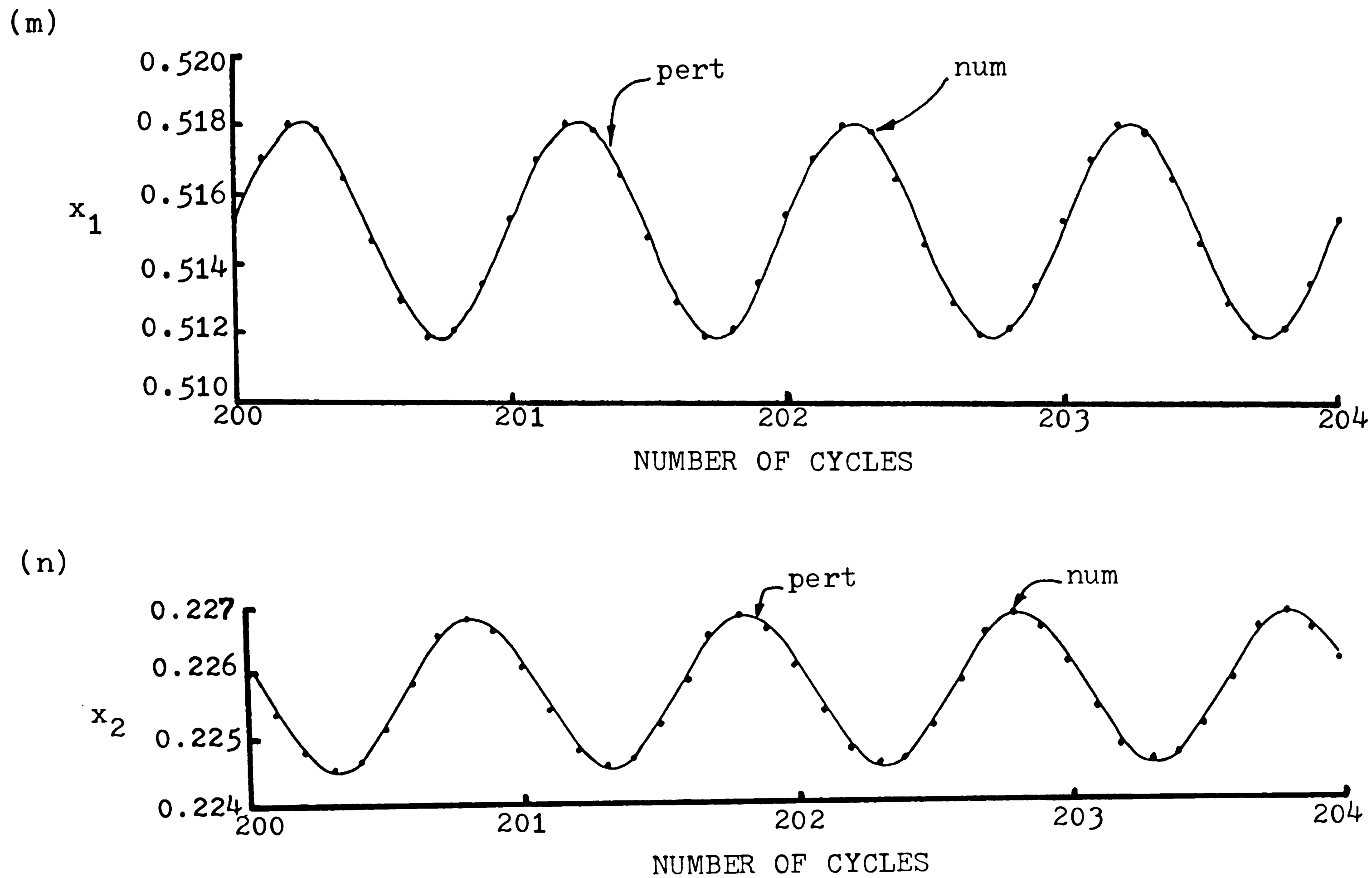

(m)
0.520
0.518
0.516
0.514
0.512
0.510
x_1
pert
num
200
201
202
203
204
NUMBER OF CYCLES
(n)
0.227
0.226
0.225
0.224
x_2
pert
num
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 2.

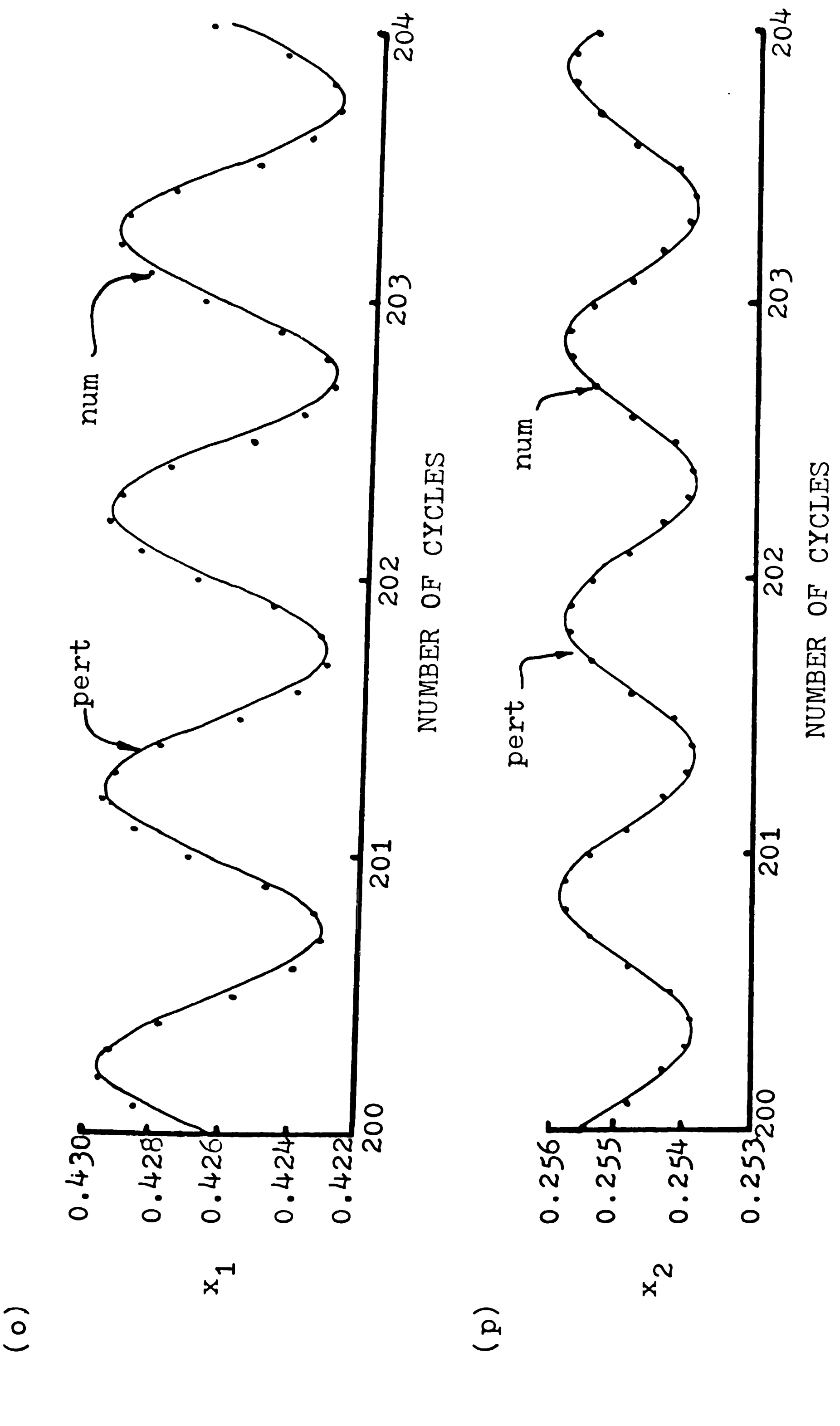

(o)
x_1
0.430
0.428
0.426
0.424
0.422
200
201
202
203
204
NUMBER OF CYCLES
pert
num
(p)
x_2
0.256
0.255
0.254
0.253
200
201
202
203
204
NUMBER OF CYCLES
pert
num

FIGURE 2. Behavior of Van de Vusse system for $K_1=K_2=K_3=0.515$, $\epsilon=0.05$, $\Lambda=0.2$ at

(q-r) $\xi = 0.2$

(s-t) $\xi = 0.5$

(u-v) $\xi = 0.75$

(w-x) $\xi = 1.0$

FIGURE 2.

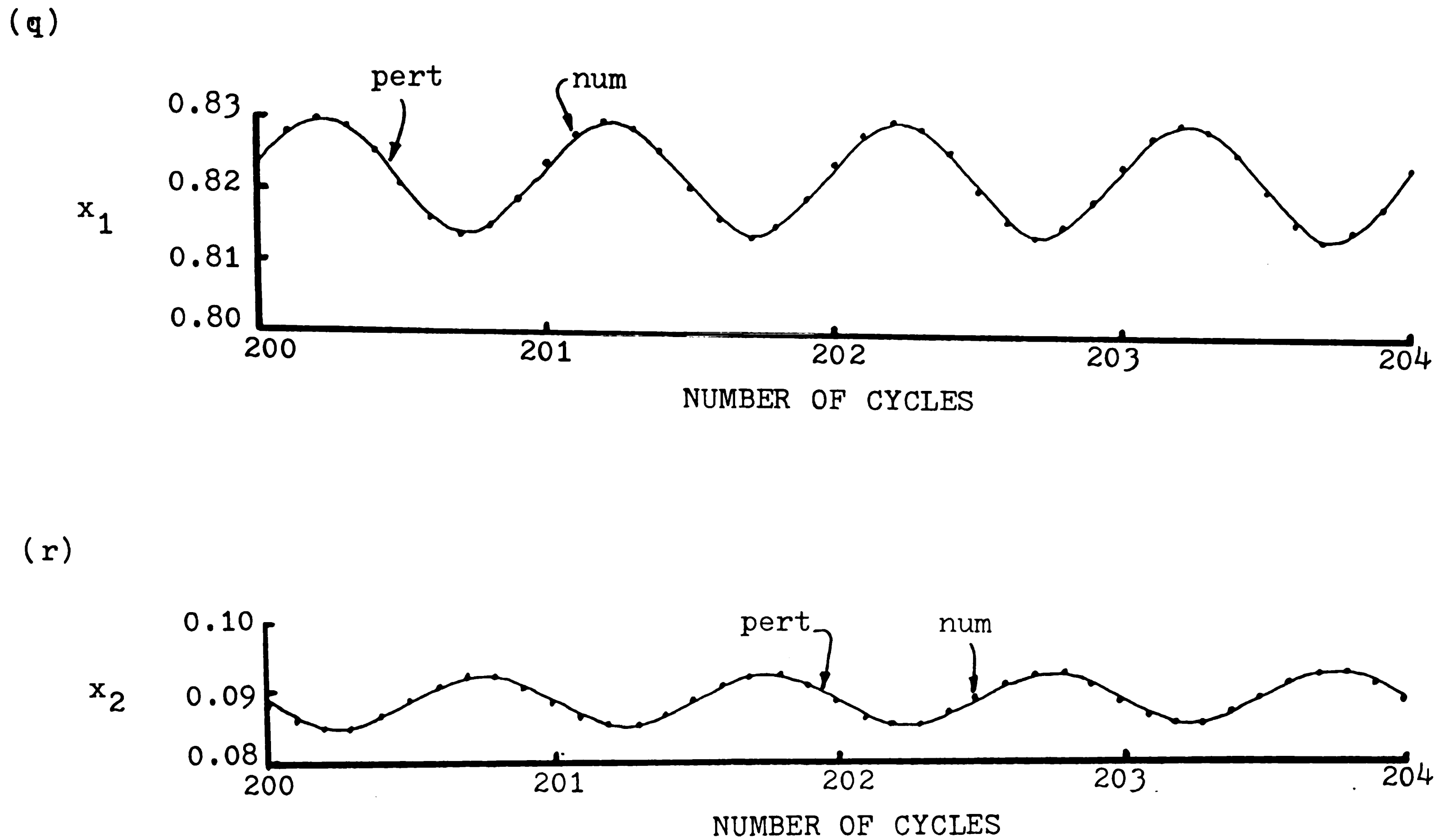

(q)
pert
num
0.83
0.82
0.81
0.80
x_1
200
201
202
203
204
NUMBER OF CYCLES
(r)
pert
num
0.10
0.09
0.08
x_2
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 2.

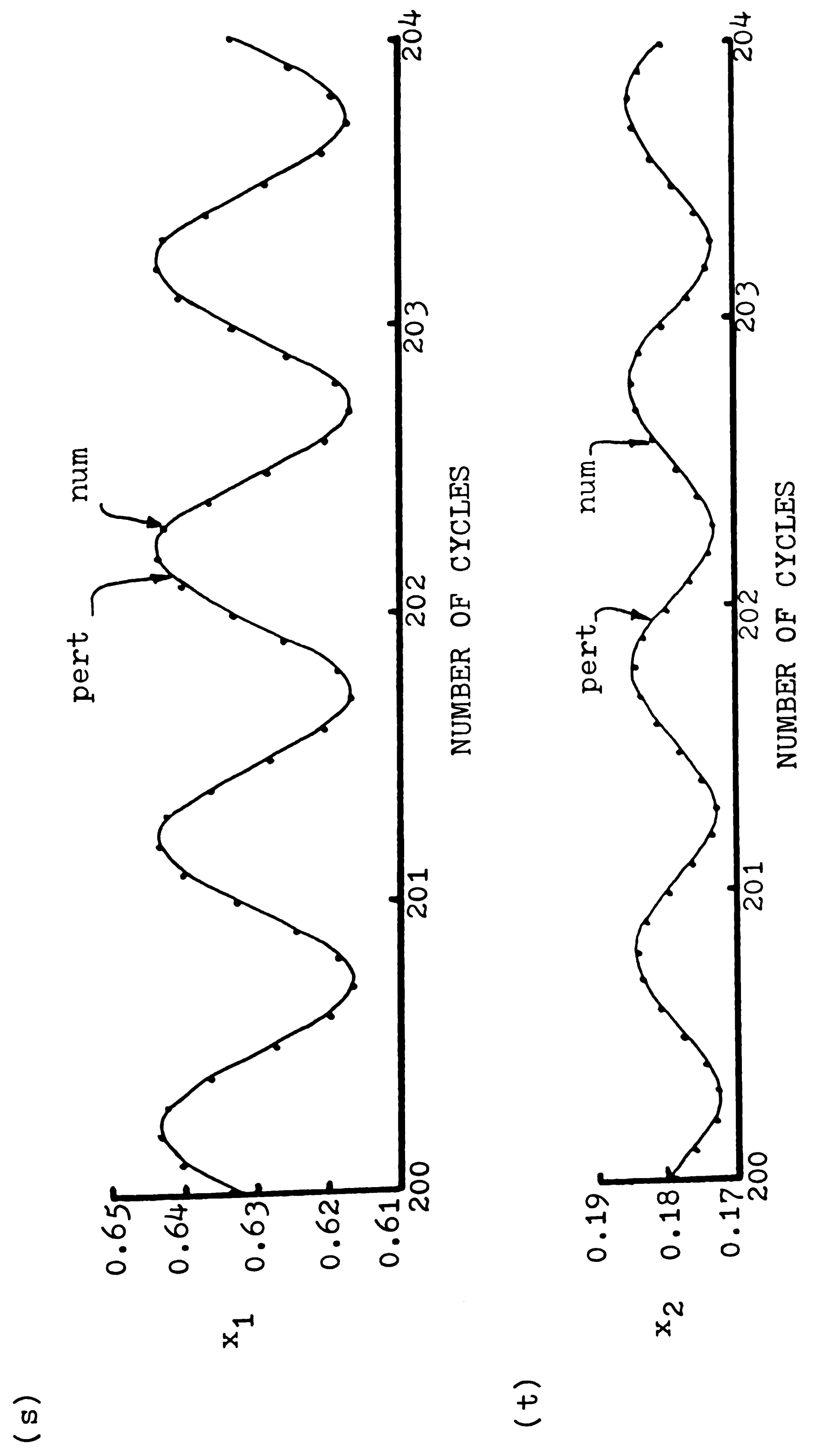

(s)
x_1
0.65
0.64
0.63
0.62
0.61
200
201
202
203
204
pert
num
NUMBER OF CYCLES
(t)
x_2
0.19
0.18
0.17
200
201
202
203
204
pert
num
NUMBER OF CYCLES

FIGURE 2.

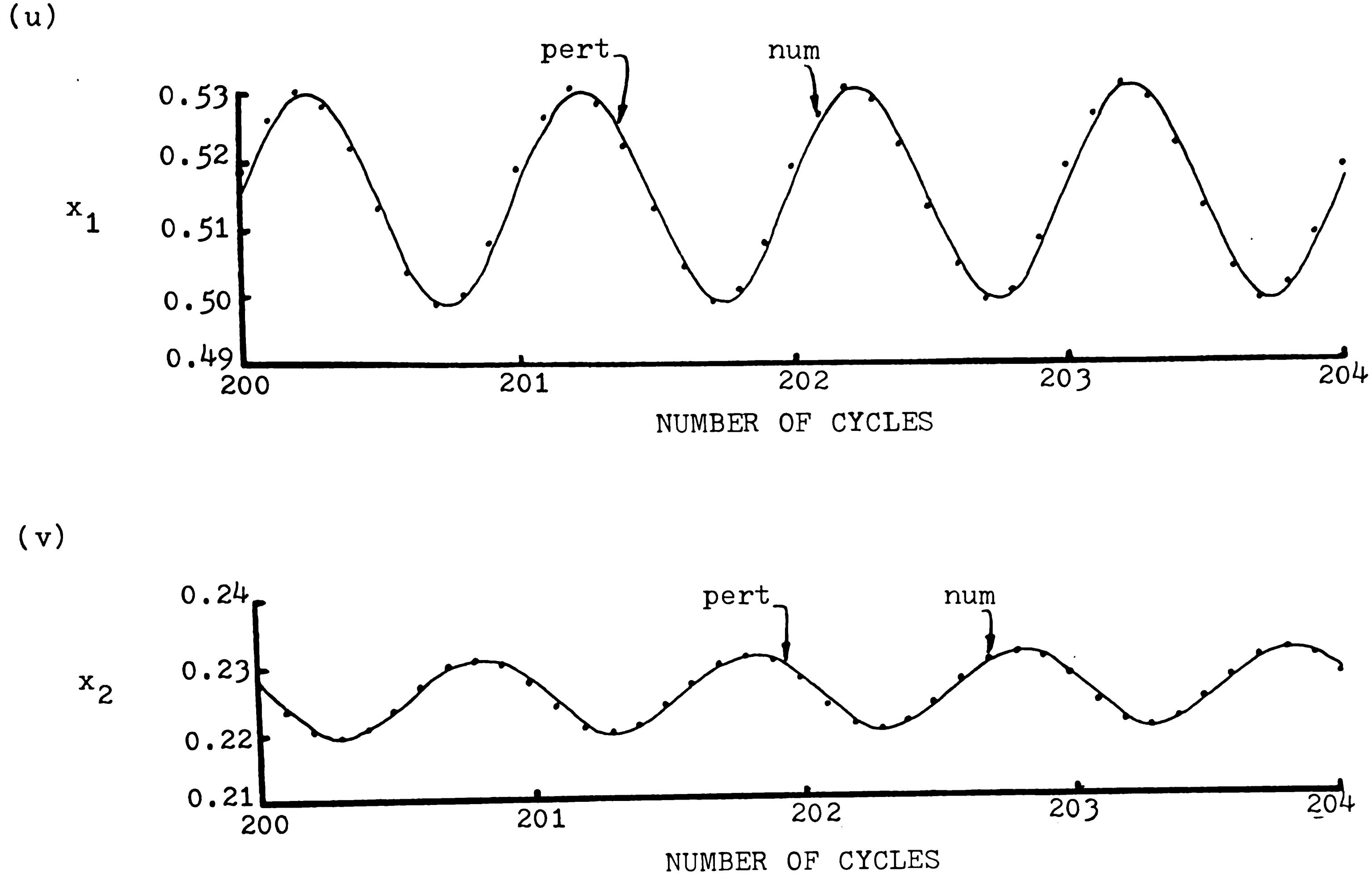

(u)
pert
num
0.53
0.52
0.51
0.50
0.49
x1
200
201
202
203
204
NUMBER OF CYCLES
(v)
pert
num
0.24
0.23
0.22
0.21
x2
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 2.

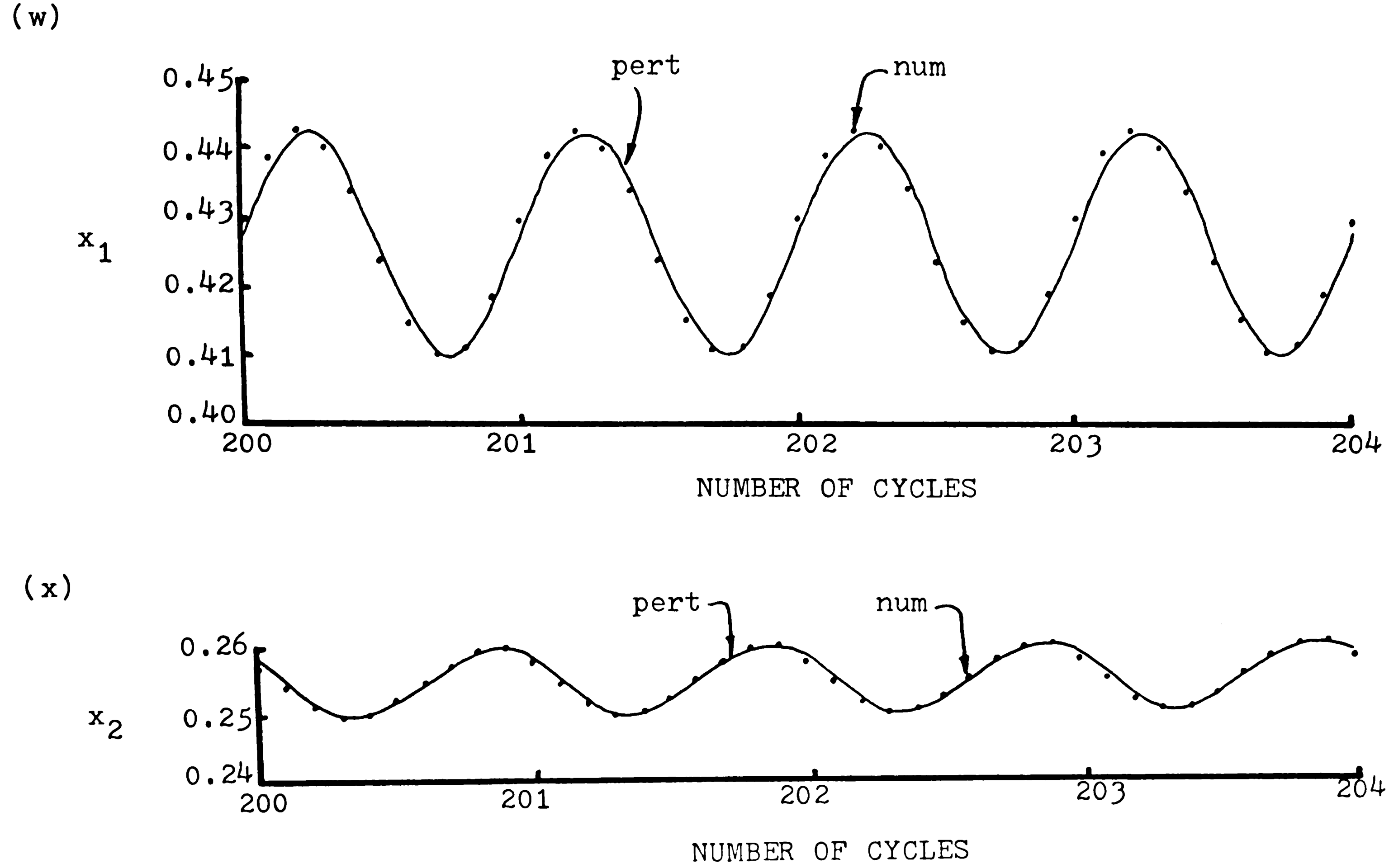

(w)
x_1
0.45
0.44
0.43
0.42
0.41
0.40
200
201
202
203
204
NUMBER OF CYCLES
pert
num
(x)
x_2
0.26
0.25
0.24
200
201
202
203
204
NUMBER OF CYCLES
pert
num

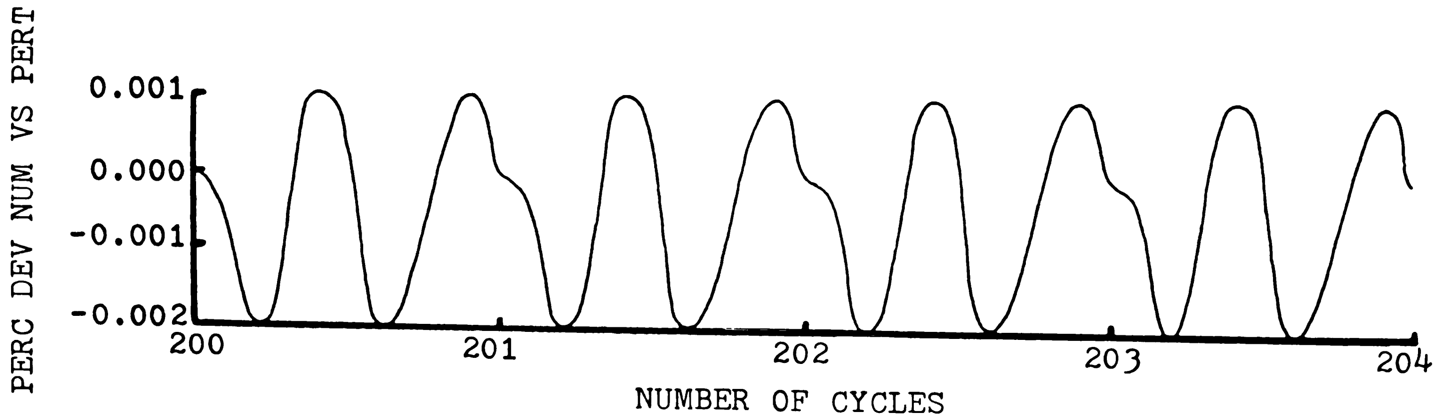
FIGURE 3. Deviation of perturbation solution from numerical simulation at ζ=0.5, ϵ=0.01, Λ=0.05.

(a) for the velocity profile.

(b) for Van de Vusse system with $K_1=K_2=K_3=0.515$.

FIGURE 3.

(a)


PERC DEV NUM VS PERT
0.001
0.000
-0.001
-0.002
200
201
202
203
204
NUMBER OF CYCLES

(b)

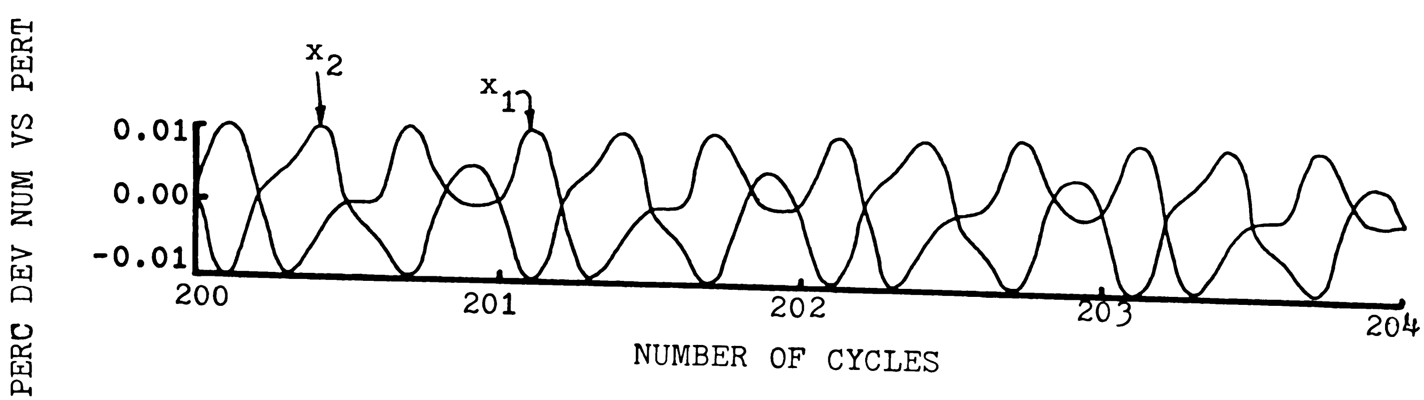

PERC DEV NUM VS PERT
x_2
x_1
0.01
0.00
-0.01
200
201
202
203
204
NUMBER OF CYCLES

FIGURE 3. Deviation of perturbation solution from numerical simulation at ξ=1.0, ϵ=0.01, Λ=0.05.

(c) for the velocity profile

(d) for Van de Vusse system with K_1=K_2=K_3=0.515

FIGURE 3.

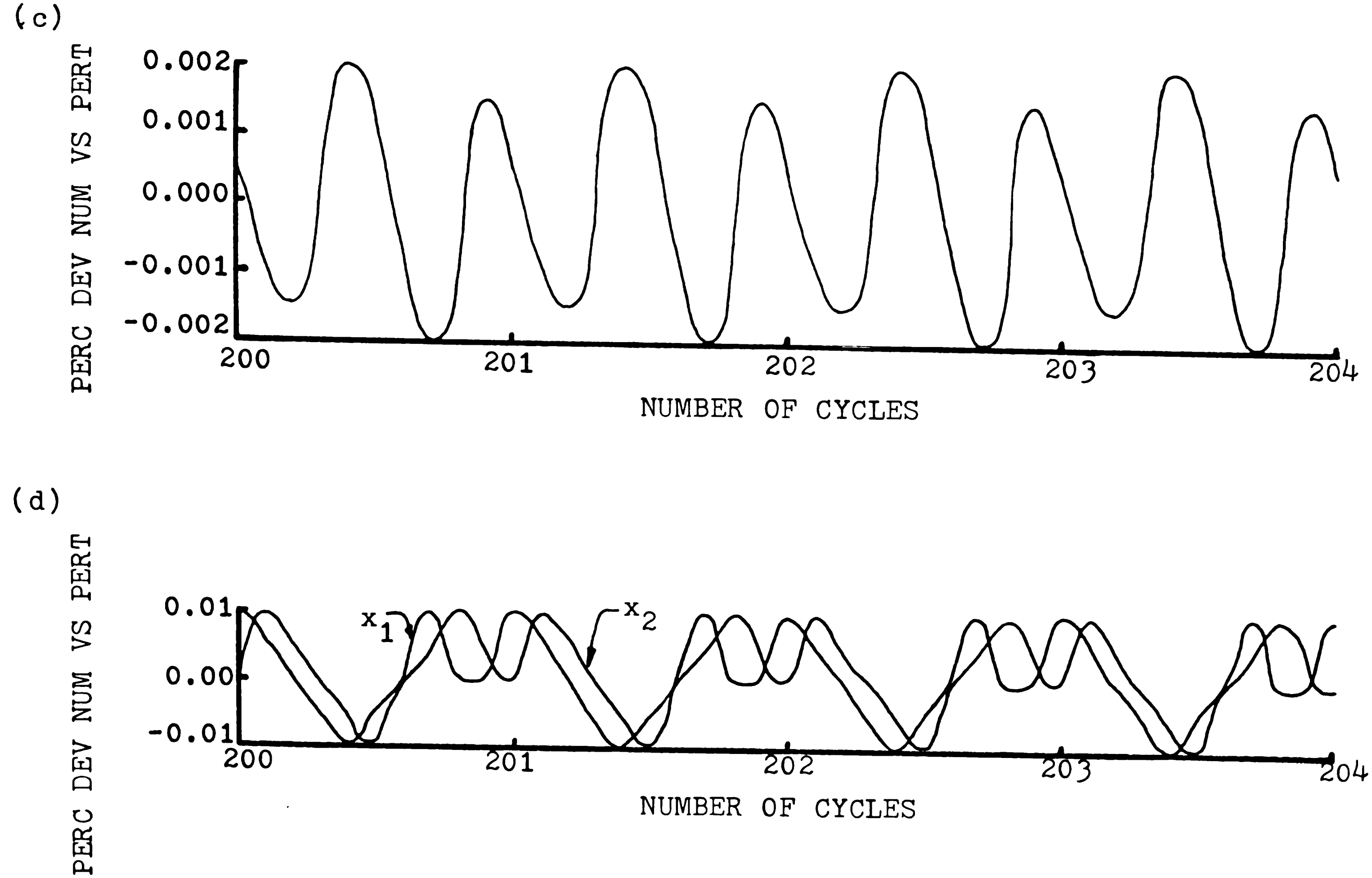

(c)
PERC DEV NUM VS PERT
0.002
0.001
0.000
-0.001
-0.002
200
201
202
203
204
NUMBER OF CYCLES
(d)
PERC DEV NUM VS PERT
0.01
0.00
-0.01
x_1
x_2
200
201
202
203
204
NUMBER OF CYCLES

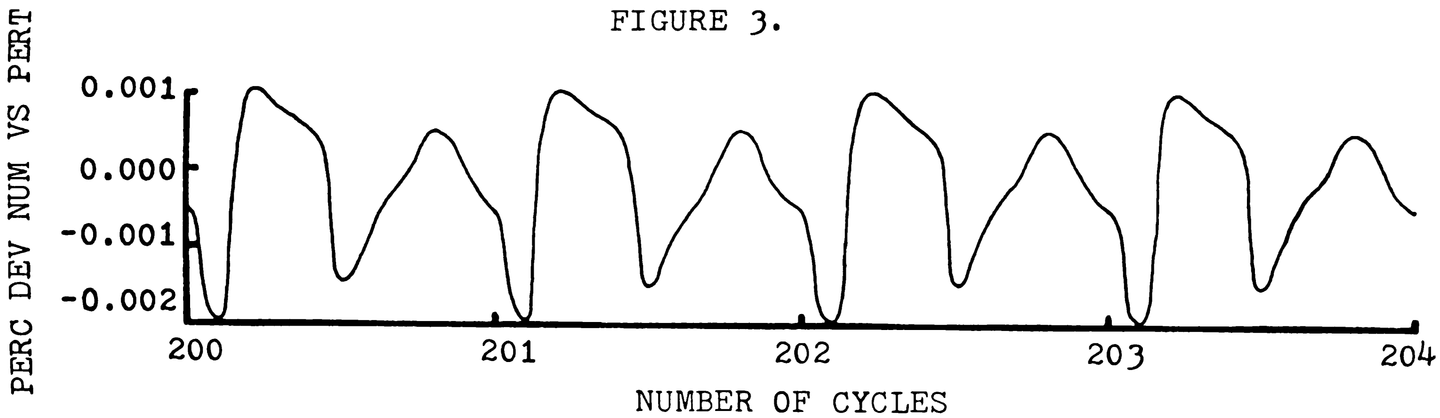
FIGURE 3. Deviation of perturbation solution from numerical simulation at ξ=0.5, ϵ=0.01, Λ=0.2.

(e) for the velocity profile.

(f) for Van de Vusse system with $K_1=K_2=K_3=0.515$.

FIGURE 3.

(e)


PERC DEV NUM VS PERT
0.001
0.000
-0.001
-0.002
200
201
202
203
204
NUMBER OF CYCLES

(f)

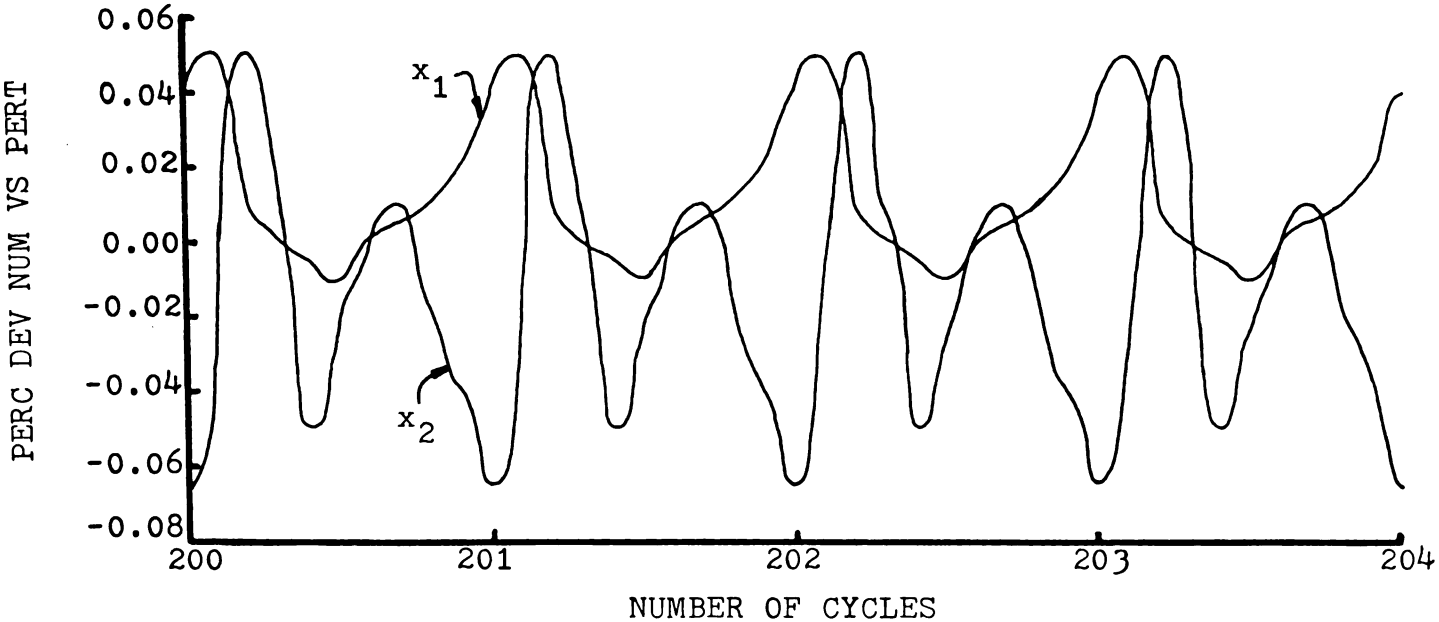

PERC DEV NUM VS PERT
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
x_1
x_2
200
201
202
203
204
NUMBER OF CYCLES

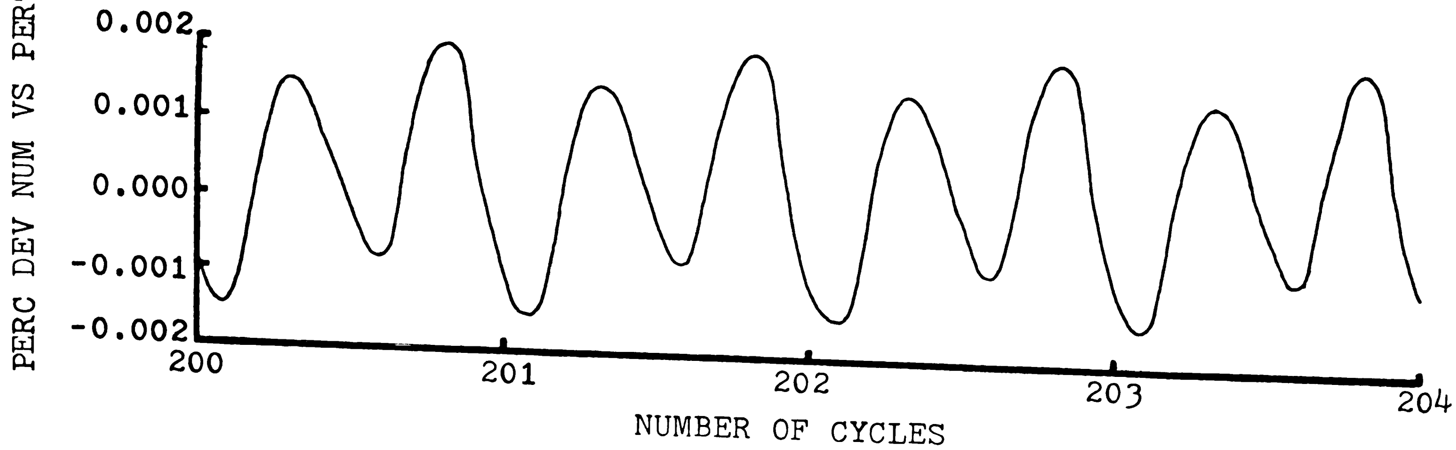
FIGURE 3. Deviation of perturbation solution from numerical simulation at $\xi=1.0$, $\epsilon=0.01$, $\Lambda=0.2$.

(g) for the velocity profile.

(h) for Van de Vusse system with $K_1=K_2=K_3=0.515$.

FIGURE 3.

(g)


PERC DEV NUM VS PERT
0.002
0.001
0.000
-0.001
-0.002
200
201
202
203
204
NUMBER OF CYCLES

(h)

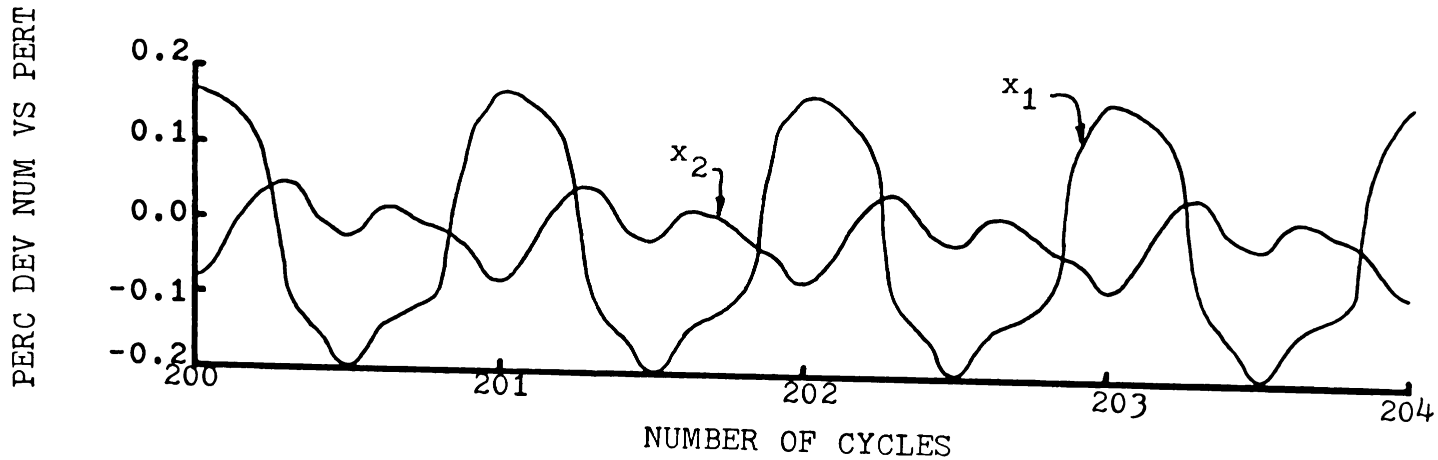

PERC DEV NUM VS PERT
0.2
0.1
0.0
-0.1
-0.2
200
201
202
203
204
x1
x2
NUMBER OF CYCLES

FIGURE 4. x_2-x_1 phase plane for $K_1=K_2=K_3=0.515$, $\epsilon=\Lambda=0.1$ at

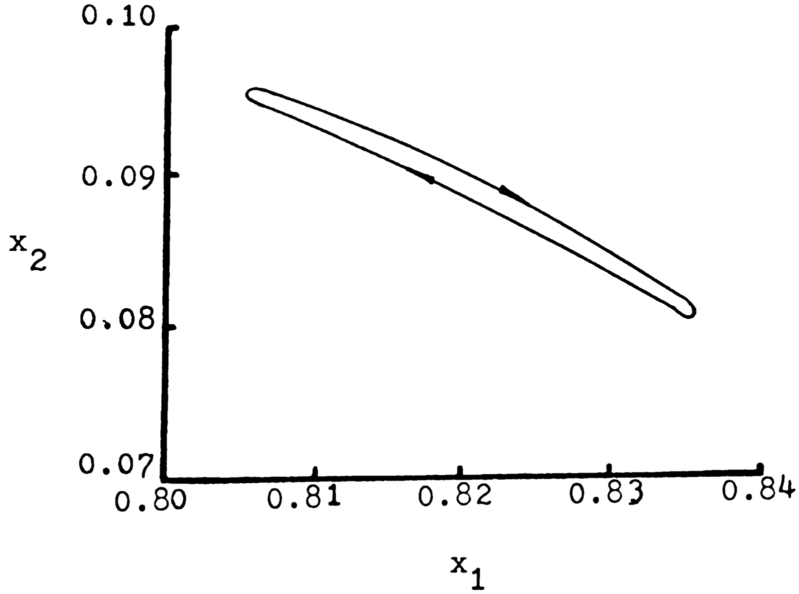
(a) $\xi=0.2$

(b) $\xi=0.75$

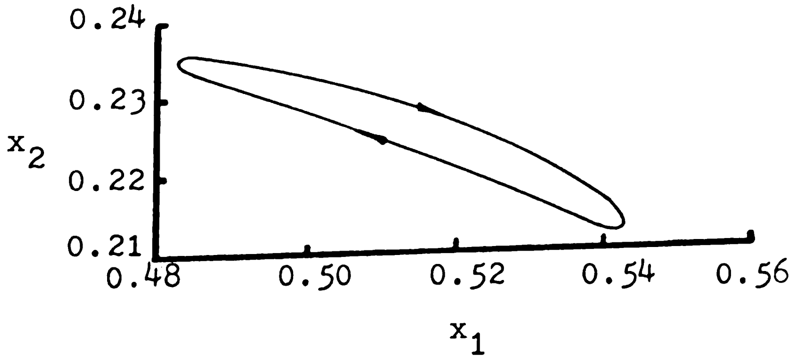
(c) $\xi=1.0$

FIGURE 4.

(a)


0.10
0.09
0.08
0.07
x2
0.80
0.81
0.82
0.83
0.84
x1

(b)


0.24
0.23
0.22
0.21
x2
0.48
0.50
0.52
0.54
0.56
x1

(c)

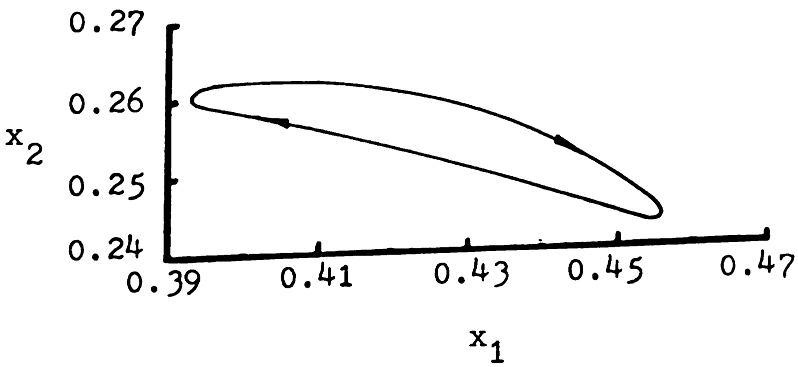

0.27
0.26
0.25
0.24
x2
0.39
0.41
0.43
0.45
0.47
x1

FIGURE 4. x_2-x_1 phase plane for $K_1=K_2=K_3=0.515$, $\epsilon=0.01$, $\Lambda=0.05$ at

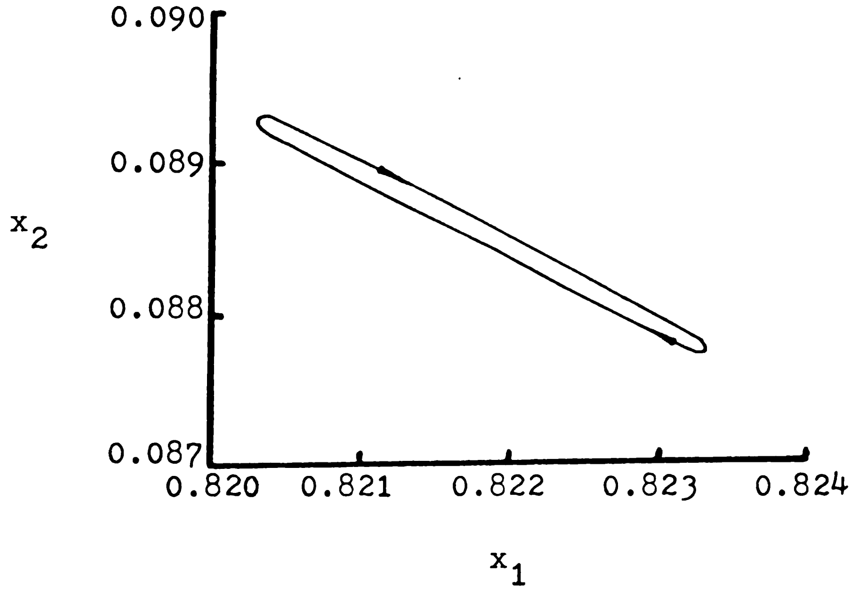
(d) $\xi=0.2$

(e) $\xi=0.75$

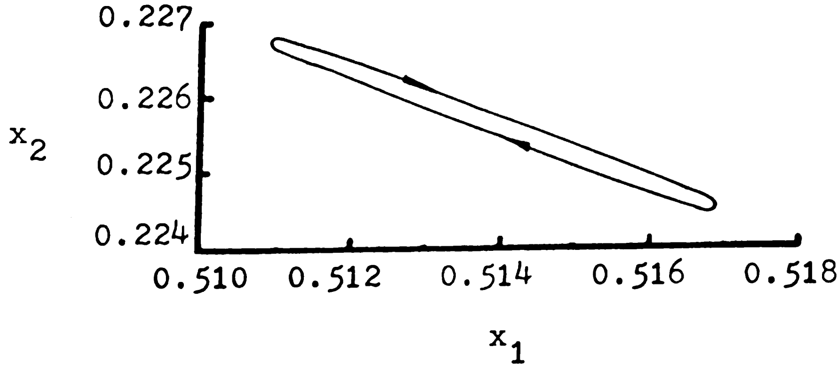
(f) $\xi=1.0$

FIGURE 4.

(d)


0.090
0.089
0.088
0.087
x_2
0.820
0.821
0.822
0.823
0.824
x_1

(e)


0.227
0.226
0.225
0.224
x_2
0.510
0.512
0.514
0.516
0.518
x_1

(f)

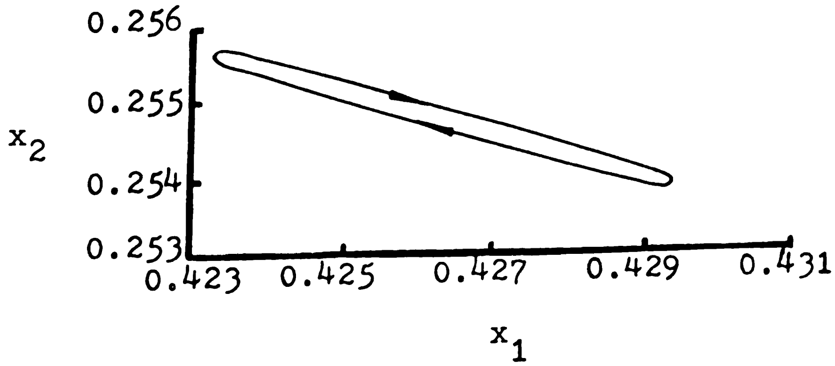

0.256
0.255
0.254
0.253
x_2
0.423
0.425
0.427
0.429
0.431
x_1

FIGURE 4. x_2-x_1 phase plane for $K_1=K_2=K_3=0.515$, $\epsilon=0.01$, $\Lambda=0.2$ at

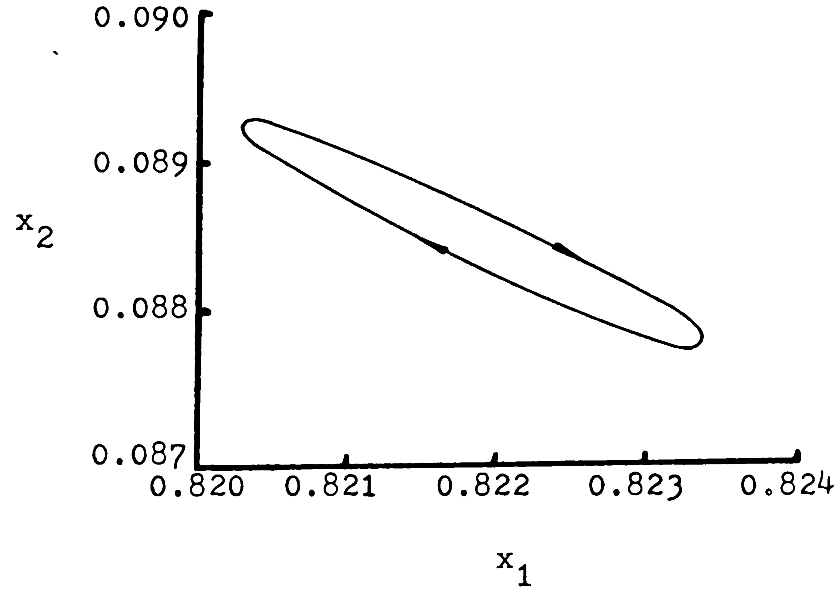
(g) $\xi=0.2$

(h) $\xi=0.75$

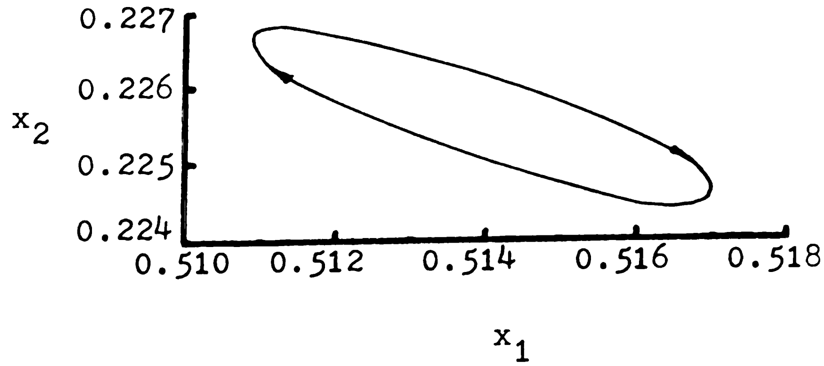
(i) $\xi=1.0$

FIGURE 4.

(g)


0.090
0.089
0.088
0.087
x2
0.820 0.821 0.822 0.823 0.824
x1

(h)


0.227
0.226
0.225
0.224
x2
0.510 0.512 0.514 0.516 0.518
x1

(i)

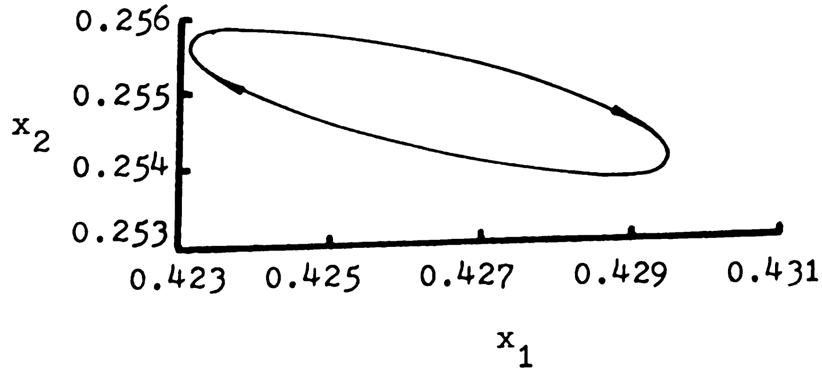

0.256
0.255
0.254
0.253
x2
0.423 0.425 0.427 0.429 0.431
x1

TABLE 1. Percent yield and conversion enhancement with varying reaction rate constants.

TABLE 1.

k_1	k_2A_{ref}	k_3	τ°	ϵ	Λ	$x^o_{2_s}$	$x^o_{1_s}$	$\%E_{x_2}\cdot 10^4$	$\%A_c\cdot 10^{4*}$
1.	1.	1.	0.8310	0.01	0.1	0.27846	0.27846	-2.2085	1.878
1.	1	2.	0.5694	0.01	0.1	0.19728	0.39455	-2.2608	1.952
1.	2.	1.	0.7450	0.01	0.1	0.23153	0.23153	-2.0343	1.546
2.	1.	1.	0.6285	0.01	0.1	0.41906	0.20953	-2.1834	1.670
2.	2.	1.	0.5862	0.01	0.1	0.36630	0.18315	-2.0339	1.381
12.	3.	3.	0.1470	0.01	0.01	0.56838	0.14209	-2.0128	0.651
3.	12.	1.	0.3838	0.01	0.01	0.25400	0.08466	-1.4765	2.658

*A_c denotes the change in the conversion of the reactant A.

TABLE 2. Percent yield and conversion enhancement with varying Λ .

TABLE 2.

k_1	k_2A_{ref}	k_3	τ°	ϵ	Λ	$x^o_{2_s}$	$x^o_{1_s}$	$\%E_{x_2}\,10^4$	$\%A_c\,10^4$ *
1.	1.	2.	0.5694	0.01	0.2	0.19728	0.39455	-2.2659	1.9617
1.	1.	2.	0.5694	0.01	0.1	0.19728	0.39455	-2.2608	1.9516
1.	1.	2.	0.5694	0.01	0.05	0.19728	0.39455	-2.2608	1.9465
1.	1.	2.	0.5694	0.01	0.01	0.19728	0.39455	-2.2608	1.9465
1.	1.	2.	0.5694	0.01	0.001	0.19728	0.39455	-2.2608	1.9465

* A_c denotes the change in the conversion of the reactant A.

Once the value of Λ is allowed to assume larger magnitudes, another flow model which would allow the formation of shock-discontinuity should be built into the flow model, even if internal mixing can be neglected. The latter is obviously more complex to handle because the material conservation equation would have to include dispersion effects superimposed on convective material flow.

The S-D perturbation method proved to be very reliable even for problems involving a hyperbolic partial differential equation which does not, along with the boundary and initial conditions, induce the presence of shock-discontinuity. A similar conclusion was obtained for the isothermal CSTR which is subjected under the same periodic control of the input volumetric flow rate [22].

APPENDICES

APPENDIX A

DERIVATION OF THE CLOSED FORM SOLUTION FOR REACTANT A (A PERTURBATION SOLUTION)

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The material balance for reactant A (species 1) in the Van de Vusse kinetic scheme

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad , \quad A + A \xrightarrow{k_3} D$$

has a form of

$$q_f A_f - \bar{q} A - (k_1 A + k_3 A^2) V = A \frac{dV}{dt} + V \frac{dA}{dt} \qquad \text{(A-1.1)}$$

with the initial condition $A(0)=A_{ref}$.

where

t=time

q_f= the feed volumetric flow rate which is subjected to perturbation.

$\bar{q}$=the outlet volumetric flow rate which is controlled at a fixed rate.

V=the reactor volume

A=concentration of species 1.

k_1, k_3=reaction rate constants.

Assuming the reaction solution density is independent of composition, the following expression is true,

$$q_f - \bar{q} = \frac{dV}{dt} \qquad \text{(A-1.2)}$$

integrating equation (A-1.2) from initial points t=0 and $V=\bar{V}$ yields

$$V=\bar{V}+\int_0^t (q_f-\bar{q})\,dt \tag{A-1.3}$$

For a sinusoidal perturbation of the inlet volumetric flow rate, we specify

$$q_f=\bar{q}\,(1+\epsilon\sin\omega t) \tag{A-1.4}$$

where

ϵ=perturbation amplitude

ω=cyclic frequency.

Combining equations (A-1.3) and (A-1.4) gives the following result:

$$V=\bar{V}-\frac{\bar{q}\,\epsilon}{\omega}\cos\omega t \tag{A-1.5}$$

or,

$$\frac{dV}{dt}=\bar{q}\,\epsilon\sin\omega t \tag{A-1.6}$$

Upon substituting equations (A-1.4), (A-1.5), (A-1.6) to equation (A-1.1) and introducing the following dimensionless variables:

$$\bar{\tau}=\frac{\bar{V}}{\bar{q}}\ ;\ \Lambda=\bar{\tau}\omega\ ;\ \theta=\frac{t}{\bar{\tau}}\ ;\ K_1=\bar{\tau}k_1\ ;\ K_3=k_3A_{ref}\bar{\tau}\ ;\ x_1=\frac{A}{A_{ref}} \tag{A-1.7}$$

with some rearrangements, the dimensionless material balance equation for species 1 is expressed as

$$\frac{dx_1}{d\theta}\left(1-\frac{\epsilon}{\Lambda}\cos\Lambda\theta\right)+x_1\left[(1+K_1)+(\Lambda\sin\Lambda\theta-K_1\cos\Lambda\theta)\frac{\epsilon}{\Lambda}\right]$$
$$=1+\epsilon\sin\Lambda\theta-K_3x_1^2\left(1-\frac{\epsilon}{\Lambda}\cos\Lambda\theta\right) \tag{A-2.1}$$

with initial condition $x_1(0)=1$.

An analytic solution to (A-2.1) is obviously not possible. In order to develop an approximate one, the solution is assumed to be composed of a non-periodic term and a sum of periodic terms:

$$x_1(\theta)=F(\theta)+\epsilon P_1(\theta)+\epsilon^2 P_2(\theta) \tag{A-2.2}$$

This requires that ϵ be small enough so that terms of the order ϵ^3 can be neglected.

Substituting equation (A-2.2) into equation (A-2.1) and collecting terms of same order in ϵ yields the following three differential equations:

$$\frac{dF}{d\theta}=1-K_3F^2-(1+K_1)F \tag{A-3.1}$$

$$\frac{dP_1}{d\theta}-\frac{1}{\Lambda}\cos\Lambda\theta\frac{dF}{d\theta}+(1+K_1)P_1+\frac{1}{\Lambda}(\Lambda\sin\Lambda\theta-K_1\cos\Lambda\theta)F$$
$$=\sin\Lambda\theta-2K_3FP_1+\frac{K_3}{\Lambda}\cos\Lambda\theta F^2 \tag{A-3.2}$$

$$\frac{dP_2}{d\theta}-\frac{1}{\Lambda}\cos\Lambda\theta\frac{dP_1}{d\theta}+(1+K_1)P_2+\frac{1}{\Lambda}(\Lambda\sin\Lambda\theta-K_1\cos\Lambda\theta)P_1$$
$$=-K_3(2FP_2+P_1^2)+2K_3\frac{\cos\Lambda\theta}{\Lambda}FP_1 \tag{A-3.3}$$

with the initial conditions

$F(0)=1$ and $P_1(0)=P_2(0)=0$.

<u>Solution to $F(\theta)$</u>

Equation (A-3.1) can be rewritten as

$$\frac{dF}{d\theta} = -K_3\left(F^2 + \frac{1+K_1}{K_3}F - \frac{1}{K_3}\right) = -K_3(F-F_+)(F-F_-) \tag{A-4.1}$$

where $F_\pm$ are readily obtained, thus

$$F_\pm = \frac{-(1+K_1) \pm \sqrt{(1+K_1)^2 + 4K_3}}{2K_3} \tag{A-4.2}$$

Integrate equation (A-4.1) by partial fraction from 0 to θ yields

$$\frac{1}{F_+ - F_-}\left[\ln\frac{F(\theta) - F_+}{F(0) - F_+} - \ln\frac{F(\theta) - F_-}{F(0) - F_-}\right] = -K_3\theta \tag{A-4.3}$$

define

$$\alpha = \frac{F(0) - F_+}{F(0) - F_-} \tag{A-4.4}$$

and substituting equation (A-4.2) for F_+ and F_- into equation (A-4.3) gives

$$F(\theta) = F_+ + \frac{\sqrt{(1+K_1)^2 + 4K_3}\ \cdot \alpha \exp\left[-\sqrt{(1+K_1)^2 + 4K_3}\ \theta\right]}{K_3\left(1 - \alpha \cdot \exp\left[-\sqrt{(1+K_1)^2 + 4K_3}\ \theta\right]\right)} \tag{A-4.5}$$

Notice that F_+ is indeed the steady state solution that satisfies

$$0 = 1 - (1+K_1) f_{ss} - K_3 f_{ss}^2 \tag{A-4.6}$$

For convenience, we let

$$C_3 = \sqrt{(1+K_1)^2 + 4K_3} \qquad \text{and} \qquad \bar{C}_2 = 2K_3 \tag{A-4.7}$$

hence equation (A-4.5) simpifies to

$$F(\theta)=f_{ss}+\frac{2C_3\alpha\exp(-C_3\theta)}{\bar{C}_2\left[1-\alpha\exp(-C_3\theta)\right]} \tag{A-4.8}$$

Furthermore, using the binomial series and a little rearrangement, equation (A-4.8) can be equivalently written as

$$F(\theta)= f_{ss}+\frac{2C_3}{\bar{C}_2}\sum_{j=0}^{\infty}\alpha^{1+j}e^{-C_3(1+j)\theta} \tag{A-4.9}$$

Solution to $P_1(\theta)$

Equation (A-3.2) is rearranged and rewritten as

$$\frac{dP_1}{d\theta}+\left[(1+K_1)+2K_3F\right]P_1$$

$$=\frac{1}{\Lambda}(\cos\Lambda\theta+\Lambda\sin\Lambda\theta)-\frac{1}{\Lambda}(\cos\Lambda\theta+\Lambda\sin\Lambda\theta)F \tag{A-5.1}$$

the integrating factor needed to solve the above equation is found to be

$$I=e^{C_3\theta}-2\alpha+\alpha^2e^{-C_3\theta} \tag{A-5.2}$$

substituting equation (A-5.2) into equation (A-5.1) and carrying out the integration, we obtain along with the following definition of terms,

$$\psi_1=\frac{2\alpha}{\Lambda}\left(1+\frac{1+K_1}{2K_3}\right) \tag{A-5.3.1}$$

$$\psi_2=\frac{\alpha^2}{\Lambda}\left[1+\frac{1+K_1+C_3}{2K_3}\right]\frac{1}{\Lambda^2+C_3^2} \tag{A-5.3.2}$$

$$\psi_3 = \frac{1-f_{ss}}{\Lambda(\Lambda^2+C_3^2)} \qquad \text{(A-5.3.3)}$$

solution to $P_1(\theta)$ is found to be

$$P_1(\theta) = -\frac{\psi_1 e^{-C_3\theta}\left(\frac{\sin\Lambda\theta}{\Lambda} - \cos\Lambda\theta\right)}{(1-\alpha e^{-C_3\theta})^2} + \frac{\psi_2\left[\Lambda(1-C_3)\sin\Lambda\theta - (C_3+\Lambda^2)\cos\Lambda\theta\right]}{(1-\alpha e^{-C_3\theta})^2}$$

$$+ \frac{\psi_3\left[(C_3-\Lambda^2)\cos\Lambda\theta + \Lambda(1+C_3)\sin\Lambda\theta\right]}{(C_3^2+\Lambda^2)(1-\alpha e^{-C_3\theta})^2} + \frac{e^{-C_3\theta}}{(1-\alpha e^{-C_3\theta})^2} C(P_1(0)) \qquad \text{(A-5.4)}$$

where $C(P_1(0))$ is the constant of integration evaluated at $P_1(0)=0$, thus

$$C(P_1(0)) = -\psi_1 + (C_3+\Lambda^2)\psi_2 - (C_3-\Lambda^2)\psi_3 \qquad \text{(A-5.5)}$$

<u>Solution to $P_2(\theta)$</u>

The process of solving equation (A-3.3) is similar to the solution of equation (A-3.2). (A-3.3) is equivalently written as

$$\frac{dP_2}{d\theta} + (1+K_1+2K_3F)P_2$$
$$= -K_2P_1^2 + 2K_3\frac{\cos\Lambda\theta}{\Lambda}FP_1 - \frac{\Lambda\sin\Lambda\theta - K_1\cos\Lambda\theta}{\Lambda}P_1 + \frac{\cos\Lambda\theta}{\Lambda}\cdot\frac{dP_1}{d\theta} \qquad \text{(A-6.1)}$$

by comparing euqation (A-6.1) with (A-5.1), it is clear that the integrating factor for solving equation (A-6.1) is similar to equation (A-5.1). The integration can be readily performed. The procedure is straight forward but quite lengthy. Hence, the solution to $P_2(\theta)$ is expressed as

$$
\begin{aligned}
P_2(\theta) = \frac{1}{(1-\alpha e^{-C_3\theta})^2} \cdot \Bigg\{ & C(P_2(0))\, e^{-C_3\theta} \\
& + K_2 \Bigg\{ \gamma_1 \left[\frac{e^{-2C_3\theta}\sin\Lambda\theta}{C_3^2+4\Lambda^2}\left(C_3\sin\Lambda\theta + 2\Lambda\cos\Lambda\theta\right) + \frac{2\Lambda^2 e^{-2C_3\theta}}{C_3(C_3^2+4\Lambda^2)} \right] \\
& \quad + \gamma_2 \left[\frac{e^{-4C_3\theta}\sin\Lambda\theta}{9C_3^2+4\Lambda^2}\left(3C_3\sin\Lambda\theta + 2\Lambda\cos\Lambda\theta\right) + \frac{2\Lambda^2 e^{-4C_3\theta}}{3C_3(9C_3^2+4\Lambda^2)} \right] \\
& \quad - \gamma_3 \frac{e^{-3C_3\theta}}{4C_3^2+4\Lambda^2}\left[\sin\Lambda\theta\left(2C_3\sin\Lambda\theta + 2\Lambda\cos\Lambda\theta\right) + \frac{\Lambda^2}{C_3} \right] \\
& \quad + \gamma_4 \left(\frac{\theta}{2} - \frac{\sin 2\Lambda\theta}{4\Lambda} \right) e^{-C_3\theta} \\
& \quad - \frac{\gamma_5}{C_3^2+4\Lambda^2}\left(C_3\sin^2\Lambda\theta - \Lambda\sin 2\Lambda\theta + \frac{2\Lambda^2}{C_3} \right) \\
& \quad + 2\sum_{j=1}^{\infty}\alpha^j \Bigg[\frac{\gamma_1 e^{-C_3(2+j)\theta}}{C_3^2(j+1)^2+4\Lambda^2}\left[C_3(1+j)\sin^2\Lambda\theta + \Lambda\sin 2\Lambda\theta + \frac{2\Lambda^2}{C_3(1+j)} \right] \\
& \qquad + \frac{\gamma_2 e^{-C_3(4+j)\theta}}{C_3^2(3+j)^2+4\Lambda^2}\left[C_3(3+j)\sin^2\Lambda\theta + \Lambda\sin 2\Lambda\theta + \frac{2\Lambda^2}{C_3(3+j)} \right] \\
& \qquad - \frac{\gamma_3 e^{-C_3(3+j)\theta}}{C_3^2(2+j)^2+4\Lambda^2}\left[C_3(2+j)\sin^2\Lambda\theta + \Lambda\sin 2\Lambda\theta + \frac{2\Lambda^2}{C_3(2+j)} \right] \\
& \qquad - \frac{\gamma_4 e^{-C_3(1+j)\theta}}{C_3^2 j^2+4\Lambda^2}\left[C_3 j\sin^2\Lambda\theta + \Lambda\sin 2\Lambda\theta + \frac{2\Lambda^2}{C_3 j} \right] \\
& \qquad + \gamma_5 \begin{cases} \dfrac{e^{-C_3 j\theta}}{C_3^2(j-1)^2+4\Lambda^2}\left[C_3(j-1)\sin^2\Lambda\theta + \Lambda\sin 2\Lambda\theta + \dfrac{2\Lambda^2}{C_3(j-1)} \right], & \text{if } j \neq 1 \\[2ex] \left(\dfrac{\sin 2\Lambda\theta}{4\Lambda} - \dfrac{\theta}{2} \right) e^{-C_3\theta}, & \text{otherwise} \end{cases} \Bigg]
\end{aligned}
$$

$$+\sum_{j=}^{\infty}\sum_{l=1}^{\infty}\alpha^{j+l}\left[\frac{\gamma_1 e^{-c_3(j+l+2)\theta}}{c_3^2(j+l+1)^2+4\Lambda^2}\left[c_3(j+l+1)\sin^2\Lambda\theta+\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(j+l+1)}\right]\right.$$

$$+\frac{\gamma_2 e^{-c_3(j+l+4)\theta}}{c_3^2(j+l+3)^2+4\Lambda^2}\left[c_3(j+l+3)\sin^2\Lambda\theta+\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(j+l+3)}\right]$$

$$-\frac{\gamma_3 e^{-c_3(j+l+3)\theta}}{c_3^2(j+l+2)^2+4\Lambda^2}\left[c_3(j+l+2)\sin^2\Lambda\theta+\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(j+l+2)}\right]$$

$$-\frac{\gamma_4 e^{-c_3(j+l+1)\theta}}{c_3^2(j+l)^2+4\Lambda^2}\left[c_3(j+l)\sin^2\Lambda\theta+\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(j+l)}\right]$$

$$\left.-\frac{\gamma_5 e^{-c_3(j+l)\theta}}{c_3^2(j+l-1)^2+4\Lambda^2}\left[c_3(j+l-1)\sin^2\Lambda\theta+\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(j+l-1)}\right]\right]$$

$$-\frac{\gamma_6 e^{-4c_3\theta}}{9c_3^2+4\Lambda^2}\left(3c_3\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{3c_3}\right)$$

$$+\frac{\gamma_7 e^{-3c_3\theta}}{4c_3^2+4\Lambda^2}\left(2\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{\Lambda}{c_3}\right)$$

$$-\frac{\gamma_8 e^{-2c_3\theta}}{c_3^2+4\Lambda^2}\left(c_3\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3}\right)$$

$$-\gamma_9 e^{-c_3\theta}\left(\frac{\theta}{2}+\frac{\sin 2\Lambda\theta}{4\Lambda}\right)$$

$$-\frac{\gamma_{10}}{c_3^2+4\Lambda^2}\left(c_3\cos^2\Lambda\theta+\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3}\right)$$

$$+2\sum_{j=1}^{\infty}\alpha^{j}\left[\frac{\gamma_6 e^{-c_3(4+j)\theta}}{c_3^2(3+j)^2+4\Lambda^2}\left[c_3(3+j)\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(3+j)}\right]\right.$$

$$-\frac{\gamma_7 e^{-c_3(3+j)\theta}}{c_3^2(j+2)^2+4\Lambda^2}\left[c_3(2+j)\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(2+j)}\right]$$

$$+\frac{\gamma_8 e^{-c_3(2+j)\theta}}{c_3^2(1+j)^2+4\Lambda^2}\left[c_3(1+j)\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(1+j)}\right]$$

$$+\frac{\gamma_9 e^{-c_3(1+j)\theta}}{c_3^2 j^2+4\Lambda^2}\left[c_3 j\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3 j}\right]$$

$$+\gamma_{10}\left\{\begin{array}{ll}\dfrac{e^{-c_3 j\theta}}{c_3^2(j-1)^2+4\Lambda^2}\left[c_3(j-1)\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\dfrac{2\Lambda^2}{c_3(j-1)}\right], & \text{if } j\neq 1\\ \left(-\dfrac{\theta}{2}-\dfrac{\sin 2\Lambda\theta}{4\Lambda}\right)e^{-c_3\theta}, & \text{otherwise}\end{array}\right]$$

$$+\sum_{j=1}^{\infty}\sum_{\ell=1}^{\infty}\alpha^{j+\ell}\Bigg[\frac{\gamma_6 e^{-c_3(j+\ell+4)\theta}}{c_3^2(3+j+\ell)^2+4\Lambda^2}\left[c_3(j+\ell+3)\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(j+\ell+3)}\right]$$

$$-\frac{\gamma_7 e^{-c_3(j+\ell+3)\theta}}{c_3^2(j+\ell+2)^2+4\Lambda^2}\left[c_3(j+\ell+2)\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(j+\ell+2)}\right]$$

$$+\frac{\gamma_8 e^{-c_3(j+\ell+2)\theta}}{c_3^2(j+\ell+1)^2+4\Lambda^2}\left[c_3(j+\ell+1)\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(j+\ell+1)}\right]$$

$$+\frac{\gamma_9 e^{-c_3(j+\ell+1)\theta}}{c_3^2(j+\ell)^2+4\Lambda^2}\left[c_3(j+\ell)\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(j+\ell)}\right]$$

$$+\frac{\gamma_{10} e^{-c_3(j+\ell)\theta}}{c_3^2(j+\ell-1)^2+4\Lambda^2}\left[c_3(j+\ell-1)\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{c_3(j+\ell-1)}\right]$$

$$-\frac{\gamma_{11} e^{-4c_3\theta}}{9c_3^2+4\Lambda^2}\left(3c_3\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right)+\frac{\gamma_{12} e^{-3c_3\theta}}{4c_3^2+4\Lambda^2}\left(2c_3\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right)$$

$$-\frac{\gamma_{13} e^{-2c_3\theta}}{c_3^2+4\Lambda^2}\left(c_3\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right)+\frac{\gamma_{14} e^{-c_3\theta}\cos 2\Lambda\theta}{2\Lambda}$$

$$-\frac{\gamma_{15}}{c_3^2+4\Lambda^2}\left(c_3\sin 2\Lambda\theta-2\Lambda\cos 2\Lambda\theta\right).$$

$$+2\sum_{j=1}^{\infty}\alpha^{j}\Bigg[-\frac{\gamma_{11} e^{-c_3(j+4)\theta}}{c_3^2(3+j)^2+4\Lambda^2}\left[c_3(j+3)\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right]$$

$$+\frac{\gamma_{12} e^{-c_3(j+3)\theta}}{c_3^2(j+2)^2+4\Lambda^2}\left[c_3(j+2)\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right]$$

$$+\frac{\gamma_{13}e^{-c_3(2+j)\theta}}{c_3^2(1+j)^2+4\Lambda^2}\left[c_3(1+j)\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right]$$

$$+\frac{\gamma_{14}e^{-c_3(1+j)\theta}}{c_3^2j^2+4\Lambda^2}\left[c_3j\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right]$$

$$\left.+\gamma_{15}\begin{cases}\dfrac{e^{-c_3j\theta}}{c_3^2(j-1)^2+4\Lambda^2}\left[c_3(j-1)\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right], & \text{if } j\neq 1\\[2ex] e^{-c_3\theta}\dfrac{\cos 2\Lambda\theta}{2\Lambda}\,; & \text{otherwise}\end{cases}\right]$$

$$+\sum_{j=1}^{\infty}\sum_{l=1}^{\infty}\alpha^{j+l}\left[-\frac{\gamma_{11}e^{-c_3(j+l+4)\theta}}{c_3^2(j+l+3)^2+4\Lambda^2}\left[c_3(j+l+3)\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right]\right.$$

$$+\frac{\gamma_{12}e^{-c_3(j+l+3)\theta}}{c_3^2(j+l+2)^2+4\Lambda^2}\left[c_3(j+l+2)\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right]$$

$$+\frac{\gamma_{13}e^{-c_3(2+j+l)\theta}}{c_3^2(j+l+1)^2+4\Lambda^2}\left[c_3(j+l+1)\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right]$$

$$+\frac{\gamma_{14}e^{-c_3(j+l+1)\theta}}{c_3^2(j+l)^2+4\Lambda^2}\left[c_3(j+l)\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right]$$

$$\left.+\frac{\gamma_{15}e^{-c_3(j+l)\theta}}{c_3^2(j+l-1)^2+4\Lambda^2}\left[c_3(j+l-1)\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta\right]\right]$$

$$+2C(P_1(0))\left[\frac{\gamma_{16}e^{-3c_3\theta}}{4c_3^2+\Lambda^2}(2c_3\sin 2\Lambda\theta+\Lambda\cos\Lambda\theta)-\frac{\psi_1e^{-2c_3\theta}}{\Lambda(c_3^2+\Lambda^2)}(c_3\sin\Lambda\theta+\Lambda\cos\Lambda\theta)\right.$$

$$+\frac{\gamma_{17}e^{-c_3\theta}\cos\Lambda\theta}{\Lambda}$$

$$+2\sum_{j=1}^{\infty}\alpha^j\left[\frac{\gamma_{16}e^{-c_3(3+j)\theta}}{c_3^2(2+j)^2+\Lambda^2}\left[c_3(2+j)\sin\Lambda\theta+\Lambda\cos\Lambda\theta\right]\right.$$

$$-\frac{\psi_1e^{-c_3(2+j)\theta}}{\Lambda\left[c_3^2(j+1)^2+\Lambda^2\right]}\left[c_3(j+1)\sin\Lambda\theta+\Lambda\cos\Lambda\theta\right]$$

$$\left.\left.+\frac{\gamma_{17}e^{-c_3(1+j)\theta}}{c_3^2j^2+\Lambda^2}\left[c_3j\sin\Lambda\theta+\Lambda\cos\Lambda\theta\right]\right]\right]$$

$$+\sum_{j=1}^{\infty}\sum_{l=1}^{\infty}\alpha^{j+l}\left[\frac{\gamma_{16}e^{-C_3(j+l+3)\theta}}{C_3^2(j+l+2)^2+\Lambda^2}\left[C_3(j+l+2)\sin\Lambda\theta+\Lambda\cos\Lambda\theta\right]\right.$$

$$-\frac{\psi_1 e^{-C_3(j+l+2)\theta}}{\Lambda\left[C_3^2(j+l+1)^2+\Lambda^2\right]}\left[C_3(j+l+1)\sin\Lambda\theta+\Lambda\cos\Lambda\theta\right]$$

$$\left.+\frac{\gamma_{17}e^{-C_3(j+l+1)\theta}}{C_3^2(j+l)^2+\Lambda^2}\left[C_3(j+l)\sin\Lambda\theta+\Lambda\cos\Lambda\theta\right]\right]$$

$$-\frac{\gamma_{18}e^{-3C_3\theta}}{4C_3^2+\Lambda^2}\left(2C_3\cos\Lambda\theta-\Lambda\sin\Lambda\theta\right)+\frac{\psi_1 e^{-2C_3\theta}}{(C_3^2+\Lambda^2)}\left(C_3\cos\Lambda\theta-\Lambda\sin\Lambda\theta\right)$$

$$+\frac{\psi_1 e^{-2C_3\theta}}{(C_3^2+\Lambda^2)}\left(C_3\cos\Lambda\theta-\Lambda\sin\Lambda\theta\right)-\frac{\gamma_{19}e^{-C_3\theta}}{\Lambda}\sin\Lambda\theta$$

$$+2\sum_{j=1}^{\infty}\alpha^{j}\left[-\frac{\gamma_{18}e^{-C_3(3+j)\theta}}{C_3^2(2+j)^2+\Lambda^2}\left[C_3(2+j)\cos\Lambda\theta-\Lambda\sin\Lambda\theta\right]\right.$$

$$+\frac{\psi_1 e^{-C_3(j+2)\theta}}{C_3^2(1+j)^2+\Lambda^2}\left[C_3(1+j)\cos\Lambda\theta-\Lambda\sin\Lambda\theta\right]$$

$$\left.+\frac{\gamma_{19}e^{-C_3(j+1)\theta}}{C_3^2 j^2+\Lambda^2}\left(C_3 j\cos\Lambda\theta-\Lambda\sin\Lambda\theta\right)\right]$$

$$+\sum_{j=1}^{\infty}\sum_{l=1}^{\infty}\alpha^{j+l}\left[-\frac{\gamma_{18}e^{-C_3(l+j+3)\theta}}{C_3^2(l+j+2)^2+\Lambda^2}\left[C_3(l+j+2)\cos\Lambda\theta-\Lambda\sin\Lambda\theta\right]\right.$$

$$+\frac{\psi_1 e^{-C_3(j+l+2)\theta}}{C_3^2(j+l+1)^2+\Lambda^2}\left[C_3(j+l+1)\cos\Lambda\theta-\Lambda\sin\Lambda\theta\right]$$

$$\left.\left.+\frac{\gamma_{19}e^{-C_3(j+l+1)\theta}}{C_3^2(j+l)^2+\Lambda^2}\left[C_3(j+l)\cos\Lambda\theta-\Lambda\sin\Lambda\theta\right]\right]\right]$$

$$\left.+\left[C(P_1(0))\right]^2\left[\frac{e^{-2C_3\theta}}{C_3}+2\sum_{j=1}^{\infty}\alpha^{j}\frac{e^{-C_3(j+2)\theta}}{C_3(j+1)}+\sum_{j=1}^{\infty}\sum_{l=1}^{\infty}\alpha^{j+l}\frac{e^{-C_3(j+l+2)\theta}}{C_3(j+l+1)}\right]\right\}$$

$$+\frac{1}{2}\left[\frac{\psi_2(1-2C_3-\Lambda^2)e^{-2C_3\theta}}{C_3^2+4\Lambda^2}\left(C_3\sin2\Lambda\theta+2\Lambda\cos2\Lambda\theta\right)-\frac{\psi_3(1+2C_3-\Lambda^2)(C_3\sin2\Lambda\theta-2\Lambda\cos2\Lambda\theta)}{C_3^2+4\Lambda^2}\right.$$

$$\left.+\left(\psi_1-\frac{\psi_1}{\Lambda^2}\right)\frac{\cos2\Lambda\theta}{2\Lambda}e^{-C_3\theta}\right]$$

$$+\frac{1-f_{ss}}{2\Lambda}\left[\frac{C_3\sin 2\Lambda\theta-2\Lambda\cos 2\Lambda\theta}{C_3^2+4\Lambda^2}+\frac{\alpha e^{-C_3\theta}}{\Lambda}\cos 2\Lambda\theta-\frac{\alpha^2 e^{-2C_3\theta}}{C_3^2+4\Lambda^2}(C_3\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta)\right]$$

$$+\frac{C_3\alpha}{\bar{C}_2\Lambda}\left[\frac{e^{-C_3\theta}\cos 2\Lambda\theta}{2\Lambda}-\frac{\alpha e^{-2C_3\theta}}{C_3^2+4\Lambda^2}(C_3\sin 2\Lambda\theta+2\Lambda\cos 2\Lambda\theta)\right]$$

$$-\frac{1}{\Lambda}\left[\psi_1\left(\frac{\theta}{2}+\frac{\sin 2\Lambda\theta}{4\Lambda}\right)e^{-C_3\theta}+\frac{\psi_2(C_3+\Lambda^2)e^{-2C_3\theta}}{C_3^2+4\Lambda^2}\left(C_3\cos^2\Lambda\theta+\Lambda\sin 2\Lambda\theta-\frac{2\Lambda^2}{C_3}\right)\right.$$

$$\left.+\frac{\psi_1(C_3-\Lambda^2)}{C_3^2+4\Lambda^2}\left(C_3\cos^2\Lambda\theta+\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{C_3}\right)\right]$$

$$+\frac{1-f_{ss}}{\Lambda^2}\left[\frac{C_3\cos^2\Lambda\theta+\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{C_3}}{C_3^2+4\Lambda^2}-2\alpha\left(\frac{\theta}{2}+\frac{\sin 2\Lambda\theta}{4\Lambda}\right)e^{-C_3\theta}\right.$$

$$\left.-\frac{\alpha^2 e^{-2C_3\theta}}{C_3^2+4\Lambda^2}\left(C_3\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{C_3}\right)\right]$$

$$-\frac{2\alpha C_3}{\bar{C}_2\Lambda^2}\left[\left(\frac{\theta}{2}+\frac{\sin 2\Lambda\theta}{4\Lambda}\right)e^{-C_3\theta}+\frac{\alpha e^{-2C_3\theta}}{C_3^2+4\Lambda^2}\left(C_3\cos^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{C_3}\right)\right]$$

$$+\frac{\psi_1}{\Lambda}\left(\frac{\theta}{2}-\frac{\sin 2\Lambda\theta}{4\Lambda}\right)e^{-C_3\theta}+\frac{\Lambda\psi_2(1-C_3)e^{-2C_3\theta}}{C_3^2+4\Lambda^2}\left(C_3\sin^2\Lambda\theta+\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{C_3}\right)$$

$$-\frac{\psi_2(1+C_3)\Lambda}{C_3^2+4\Lambda^2}\left(C_3\sin^2\Lambda\theta-\Lambda\sin 2\Lambda\theta+\frac{2\Lambda^2}{C_3}\right)$$

$$\left.-C(P_1(0))\left(\frac{\sin\Lambda\theta}{\Lambda^2}-\frac{\cos\Lambda\theta}{\Lambda}\right)e^{-C_3\theta}\right\} \qquad \text{(A-6.2)}$$

where $C(P_2(0))$ is the constant of integration which has the following form:

$$C(P_2(0))=K_2\left\{-\frac{2\gamma_1\Lambda^2}{C_3(C_3^2+4\Lambda^2)}-\frac{2\gamma_2\Lambda^2}{3C_3(9C_3^2+4\Lambda^2)}+\frac{\gamma_3\Lambda^2}{C_3(4C_3^2+4\Lambda^2)}+\frac{2\gamma_5\Lambda^2}{C_3(C_3^2+4\Lambda^2)}\right.$$

$$+2\sum_{j=1}^{\infty}\alpha^j\left[-\frac{2\gamma_1\Lambda^2}{[C_3^2(j+1)^2+4\Lambda^2]C_3(1+j)}-\frac{2\gamma_2\Lambda^2}{[C_3^2(j+3)^2+4\Lambda^2]C_3(3+j)}+\frac{2\gamma_3\Lambda^2}{[C_3^2(j+2)^2+4\Lambda^2]C_3(2+j)}\right.$$

$$+\frac{2\gamma_4\Lambda^2}{(C_3^2 j^2+4\Lambda^2)C_3 j}-\gamma_5\begin{cases}\dfrac{2\Lambda^2}{[C_3^2(j-1)^2+4\Lambda^2]\,C_3(j-1)}, & \text{if } j\neq 1\\[2ex] 0, & \text{otherwise}\end{cases}\Bigg]$$

$$+\sum_{j=1}^{\infty}\sum_{\ell=1}^{\infty}\alpha^{j+\ell}\Bigg[-\frac{2\gamma_1\Lambda^2}{C_3(j+\ell+1)[C_3^2(j+\ell+1)^2+4\Lambda^2]}-\frac{2\gamma_2\Lambda^2}{C_3(j+\ell+3)[C_3^2(j+\ell+3)^2+4\Lambda^2]}$$

$$+\frac{2\gamma_3\Lambda^2}{C_3(j+\ell+2)[C_3^2(j+\ell+2)^2+4\Lambda^2]}+\frac{2\gamma_4\Lambda^2}{C_3(j+\ell)[C_3^2(j+\ell)^2+4\Lambda^2]}$$

$$-\frac{2\gamma_5\Lambda^2}{C_3(j+\ell-1)[C_3^2(j+\ell-1)^2+4\Lambda^2]}\Bigg]$$

$$-\frac{\gamma_6}{9C_3^2+4\Lambda^2}\left(3C_3+\frac{2\Lambda^2}{3C_3}\right)+\frac{\gamma_7}{4C_3^2+4\Lambda^2}\left(2C_3-\frac{\Lambda^2}{C_3}\right)-\frac{\gamma_8-\gamma_{10}}{C_3^2+4\Lambda^2}\left(C_3+\frac{2\Lambda^2}{C_3}\right)$$

$$+2\sum_{j=1}^{\infty}\alpha^{j}\Bigg[-\frac{\gamma_6}{C_3^2(3+j)^2+4\Lambda^2}\left[C_3(3+j)+\frac{2\Lambda^2}{C_3(3+j)}\right]+\frac{\gamma_7}{C_3^2(j+2)^2+4\Lambda^2}\left[C_3(j+2)+\frac{2\Lambda^2}{C_3(2+j)}\right]$$

$$-\frac{\gamma_8}{C_3^2(1+j)^2+4\Lambda^2}\left[C_3(1+j)+\frac{2\Lambda^2}{C_3(1+j)}\right]-\frac{\gamma_9}{C_3^2 j^2+4\Lambda^2}\left(C_3 j+\frac{2\Lambda^2}{C_3 j}\right)$$

$$-\gamma_{10}\begin{cases}\dfrac{1}{C_3^2(j-1)^2+4\Lambda^2}\left[C_3(j-1)+\dfrac{2\Lambda^2}{C_3(j-1)}\right], & \text{if } j\neq 1\\[2ex] 0, & \text{otherwise}\end{cases}\Bigg]$$

$$+\sum_{j=1}^{\infty}\sum_{\ell=1}^{\infty}\alpha^{j+\ell}\Bigg[-\frac{\gamma_6}{C_3^2(j+\ell+3)^2+4\Lambda^2}\left[C_3(j+\ell+3)+\frac{2\Lambda^2}{C_3(j+\ell+3)}\right]-\frac{\gamma_7}{C_3^2(j+\ell+2)^2+4\Lambda^2}\left[C_3(j+\ell+2)+\frac{2\Lambda^2}{C_3(j+\ell+2)}\right]$$

$$-\frac{\gamma_8}{C_3^2(j+\ell+1)^2+4\Lambda^2}\left[C_3(j+\ell+1)+\frac{2\Lambda^2}{C_3(j+\ell+1)}\right]-\frac{\gamma_9}{C_3^2(j+\ell)^2+4\Lambda^2}\left[C_3(j+\ell)+\frac{2\Lambda^2}{C_3(j+\ell)}\right]$$

$$-\frac{\gamma_{10}}{C_3^2(j+\ell-1)^2+4\Lambda^2}\left[C_3(j+\ell-1)+\frac{2\Lambda^2}{C_3(j+\ell-1)}\right]\Bigg]$$

$$+\frac{2\gamma_{11}\Lambda}{9C_3^2+4\Lambda^2}-\frac{2\gamma_{12}\Lambda}{4C_3^2+4\Lambda^2}-\frac{2\Lambda(\gamma_{13}+\gamma_{15})}{C_3^2+4\Lambda^2}-\frac{\gamma_{14}}{2\Lambda}$$

$$+2\sum_{j=1}^{\infty}\alpha^{j}\left[\frac{2\gamma_{11}\Lambda}{C_3^2(3+j)^2+4\Lambda^2}-\frac{2\gamma_{12}\Lambda}{C_3^2(j+2)^2+4\Lambda^2}-\frac{2\gamma_{13}\Lambda}{C_3^2(1+j)^2+4\Lambda^2}-\frac{2\gamma_{14}\Lambda}{C_3^2 j^2+4\Lambda^2}\right.$$

$$\left.-\gamma_{15}\begin{cases}\dfrac{2\Lambda}{C_3^2(j-1)^2+4\Lambda^2}, & \text{if } j\neq 1\\[2ex] \dfrac{1}{2\Lambda}, & \text{otherwise}\end{cases}\right]$$

$$+\sum_{j=1}^{\infty}\sum_{l=1}^{\infty}\alpha^{j+l}\left[\frac{2\gamma_{11}\Lambda}{C_3^2(j+l+3)^2+4\Lambda^2}-\frac{2\gamma_{12}\Lambda}{C_3^2(j+l+2)^2+4\Lambda^2}-\frac{2\gamma_{13}\Lambda}{C_3^2(j+l+1)+4\Lambda^2}-\frac{2\gamma_{14}\Lambda}{C_3^2(j+l)^2+4\Lambda^2}-\frac{2\gamma_{15}\Lambda}{C_3^2(j+l-1)^2+4\Lambda^2}\right]$$

$$+2C(P_1(0))\left[-\frac{\gamma_{16}\Lambda}{4C_3^2+\Lambda^2}-\frac{\psi_1}{C_3^2+\Lambda^2}-\frac{\gamma_{17}}{\Lambda}\right.$$

$$+2\sum_{j=1}^{\infty}\alpha^{j}\left[-\frac{\gamma_{16}\Lambda}{C_3^2(2+j)^2+\Lambda^2}-\frac{\psi_1}{C_3^2(j+1)^2+\Lambda^2}-\frac{\gamma_{17}\Lambda}{C_3^2 j^2+\Lambda^2}\right]$$

$$+\sum_{j=1}^{\infty}\sum_{l=1}^{\infty}\alpha^{j+l}\left[-\frac{\gamma_{16}\Lambda}{C_3^2(j+l+2)^2+\Lambda^2}+\frac{\psi_1}{C_3^2(j+l+1)^2+\Lambda^2}-\frac{\gamma_{17}\Lambda}{C_3^2(j+l)^2+\Lambda^2}\right]$$

$$+\frac{2\gamma_{18}C_3}{4C_3^2+\Lambda^2}-\frac{\psi_1 C_3}{C_3^2+\Lambda^2}$$

$$+2\sum_{j=1}^{\infty}\alpha^{j}\left[\frac{\gamma_{18}C_3(2+j)}{C_3^2(2+j)^2+\Lambda^2}-\frac{\psi_1 C_3(1+j)}{C_3^2(1+j)^2+\Lambda^2}-\frac{\gamma_{19}C_3 j}{C_3^2 j^2+\Lambda^2}\right]$$

$$\left.+\sum_{j=1}^{\infty}\sum_{l=1}^{\infty}\alpha^{j+l}\left[\frac{\gamma_{18}C_3(l+j+2)}{C_3^2(l+j+2)^2+\Lambda^2}-\frac{\psi_1 C_3(j+l+1)}{C_3^2(j+l+1)^2+\Lambda^2}-\frac{\gamma_{19}C_3(j+l)}{C_3^2(j+l)^2+\Lambda^2}\right]\right]$$

$$\left.-\left[C(P_1(0))\right]^2\left[\frac{1}{C_3}+2\sum_{j=1}^{\infty}\frac{\alpha^{j}}{C_3(j+1)}+\sum_{j=1}^{\infty}\sum_{l=1}^{\infty}\frac{\alpha^{j+l}}{C_3(j+l+1)}\right]\right\}$$

$$+\frac{1}{2}\left[\frac{2\psi_2\Lambda(1-2C_3-\Lambda^2)}{C_3^2+4\Lambda^2}+\frac{2\psi_3\Lambda(1+2C_3-\Lambda^2)}{C_3^2+4\Lambda^2}-\frac{1}{2\Lambda}\left(\psi_1-\frac{\psi_1}{\Lambda^2}\right)\right]$$

$$-\frac{1-f_{ss}}{2\Lambda}\left[\frac{2\Lambda}{C_3^2+4\Lambda^2}-\frac{\alpha}{\Lambda}+\frac{2\Lambda\alpha^2}{C_3^2+4\Lambda^2}\right]+\frac{C_3\alpha}{\bar{C}_2\Lambda}\left(\frac{1}{\Lambda}-\frac{2\alpha\Lambda}{C_3^2+4\Lambda^2}\right)-\frac{1}{\Lambda}\left[\frac{\psi_2(C_3+\Lambda^2)(C_3^2+2\Lambda^2)(\psi_2-\psi_3)}{(C_3^2+4\Lambda^2)C_3}\right]$$

$$+\frac{(1-f_{ss})(C_3^2+2\Lambda^2)(1-\alpha^2)}{\Lambda^2 C_3(C_3^2+4\Lambda^2)}-\frac{2\alpha(C_3^2+2\Lambda^2)}{\bar{C}_2\Lambda(C_3^2+4\Lambda^2)}+\frac{2\Lambda^3\psi_2(1-C_3)-2\Lambda^3\psi_3(1+C_3)}{C_3(C_3^2+4\Lambda^2)}+\frac{C(P_1(0))}{\Lambda}\qquad\text{(A-6.2)}$$

Other terms, such as γ_i, $(i=1,19)$ appear in the $P_2(\theta)$ solution are defined as

$$\gamma_1 = \frac{\psi_1^2}{\Lambda^2} + 2\psi_2\psi_3\Lambda^2(1-C_3^2) \qquad \text{(A-6.4.1)}$$

$$\gamma_2 = \psi_2^2\Lambda^2(1-C_3)^2 \qquad \text{(A-6.4.2)}$$

$$\gamma_3 = 2\psi_1\psi_2(1-C_3) \qquad \text{(A-6.4.3)}$$

$$\gamma_4 = 2\psi_1\psi_3(1+C_3) \qquad \text{(A-6.4.4)}$$

$$\gamma_5 = \psi_3^2\Lambda^2(1+C_3)^2 \qquad \text{(A-6.4.5)}$$

$$\gamma_6 = \psi_2^2(C_3+\Lambda^2)^2 \qquad \text{(A-6.4.6)}$$

$$\gamma_7 = 2\psi_1\psi_2(C_3+\Lambda^2) \qquad \text{(A-6.4.7)}$$

$$\gamma_8 = \psi_1^2 - 2\psi_2\psi_3(C_3^2-\Lambda^4) \qquad \text{(A-6.4.8)}$$

$$\gamma_9 = 2\psi_1\psi_3(C_3-\Lambda^2) \qquad \text{(A-6.4.9)}$$

$$\gamma_{10} = \psi_3^2(C_3-\Lambda^2)^2 \qquad \text{(A-6.4.10)}$$

$$\gamma_{11} = \psi_2^2\Lambda(1-C_3)(C_3+\Lambda^2) \qquad \text{(A-6.4.11)}$$

$$\gamma_{12} = \psi_1\psi_2\left(2\Lambda + \frac{C_3}{\Lambda} - C_3\Lambda\right) \qquad \text{(A-6.4.12)}$$

$$\gamma_{13} = \psi_2\psi_3\Lambda(1-C_3)(C_3-\Lambda^2) - \frac{\psi_1^2}{\Lambda} - \psi_2\psi_3\Lambda(1+C_3)(C_3+\Lambda^2) \qquad \text{(A-6.4.13)}$$

$$\gamma_{14} = -\psi_1\psi_3\left(\frac{C_3}{\Lambda} - 2\Lambda - C_3\Lambda\right) \qquad \text{(A-6.4.14)}$$

$$\gamma_{15} = \psi_3^2\Lambda(1+C_3)(C_3-\Lambda^2) \qquad \text{(A-6.4.15)}$$

$$\gamma_{16} = \psi_2\Lambda(1-C_3) \qquad \text{(A-6.4.16)}$$

$$\gamma_{17} = \psi_3\Lambda(1+C_3) \qquad \text{(A-6.4.17)}$$

$$\gamma_{18} = \psi_2 (C_3 + \Lambda^2) \tag{A-6.4.18}$$

$$\gamma_{19} = \psi_3 (C_3 - \Lambda^2) \tag{A-6.4.19}$$

Substituting the solution to $F(\theta)$, $P_1(\theta)$ and $P_2(\theta)$ into equation (A-2.2) gives the approximate global solution to x_1 as a function of θ.

APPENDIX B

THE INITIAL CONDITIONS FOR THE PERTURBATION CALCULATION

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THE INITIAL CONDITIONS FOR THE PERTURBATION CALCULATION

In order to obtain the initial conditions for F, P_1 and P_2, we evaluate equations (A-2.1), (A-2.2), derivative of equations (A-2.2), (A-3.1), (A-3.2) and (A-3.3) at $\theta=0$. However these six equations consist of a total of seven unknowns, viz., $F(0)$, $F'(0)$, $P_1(0)$, $P_1'(0)$, $P_2(0)$, $P_2'(0)$ and $x_1'(0)$ which make the problem not well posed. So an "ad hoc" assumption is then attempted by imposing $x_1(0)=F(0)$ and $P_1(0)=P_2(0)=0$, and thus achieve self-consistency of the problem. Of course, the validity of this assumption needs to be verified by comparing the perturbation solution based on these initial conditions against the full numerical solution. As shown in figures 3, 4 and 5, the results are very satisfactory and the error is large only at the initial transients because if the initial conditions are important the error could propagate in the limit cycle. Such were not observed in the present work. But as clearly seen in the perturbation solution at θ_∞, the initial conditions vanish.

APPENDIX C

ASYMPTOTIC SOLUTION TO x_1 AND x_2 AT θ_∞

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ASYMPTOTIC SOLUTION TO x_1 AND x_2 AT θ_∞

The objective function in the present work is the optimization of the yield of the intermediate product B (species 2) in the Van de Vusse kinetic scheme. The component B material balance is

$$q_f B_f - \bar{q} B - (k_2 B - k_1 A) V = B \frac{dV}{dt} + V \frac{dB}{dt} \qquad \text{(C-1.1)}$$

assuming there is no product B in the inlet stream, then, B(0)=0.

Introducing the dimensionless variables

$$x_2 = \frac{B}{A_{ref}} \quad , \quad \hat{K}_2 = \bar{\tau} k_2 \qquad \text{(C-1.2)}$$

(where $\hat{K}_2 = K_1 K_2$ and $K_2 = k_2/k_1$), and substituting (A-1.4), (A-1.5), (A-1.6), (A-1.7), (C-1.2) into (C-1.1) yields the dimensionless material balance for species 2 (or B):

$$\left(1 - \frac{\epsilon}{\Lambda}\cos\Lambda\theta\right)\frac{dx_2}{d\theta} = -(1+\epsilon\sin\Lambda\theta)\,x_2 - (\hat{K}_2 x_2 - K_1 x_1)\left(1 - \frac{\epsilon}{\Lambda}\cos\Lambda\theta\right) \qquad \text{(C-2.1)}$$

The global solution to (C-2.1) is not necessary for calculation the average yield of B at the limit cycle. Therefore, an asymptotic solution for B is sufficient.

It is clear from (C-2.1) that the asymptotic solution to A(species 1) is required. Referring to Appendix A, and substituting $F(\theta)$, $P_1(\theta)$, $P_2(\theta)$ into (A-2.2) and then evaluating the resulting equation at $\theta = \theta_\infty$ yields the following expression (θ_∞ denoting large reaction time).

$$X_1(\theta_\infty) = F(\theta_\infty) + \epsilon P_1(\theta_\infty) + \epsilon^2 P_2(\theta_\infty) \tag{C-3.1}$$

where,

$$F(\theta_\infty) = f_{ss} \tag{C-3.2}$$

$$P_1(\theta_\infty) = \frac{(1-f_{ss})\left[(C_3-\Lambda^2)\cos\Lambda\theta_\infty + \Lambda(1+C_3)\sin\Lambda\theta_\infty\right]}{\Lambda(C_3^2+\Lambda^2)} \tag{C-3.3}$$

$$\begin{aligned}
P_2(\theta_\infty) = \frac{1}{C_3^2+4\Lambda^2}\Big[& \gamma_5\left(C_3\sin^2\Lambda\theta_\infty - \Lambda\sin 2\Lambda\theta_\infty + \frac{2\Lambda^2}{C_3}\right) \\
& + \gamma_{10}\left(C_3\cos^2\Lambda\theta_\infty + \Lambda\sin 2\Lambda\theta_\infty + \frac{2\Lambda^2}{C_3}\right) + \gamma_{15}\left(C_3\sin 2\Lambda\theta_\infty - 2\Lambda\cos 2\Lambda\theta_\infty\right) \\
& - \frac{\psi_3}{2}(1+2C_3-\Lambda^2)(C_3\sin 2\Lambda\theta_\infty - 2\Lambda\cos 2\Lambda\theta_\infty) \\
& + \frac{1+f_{ss}}{2\Lambda}(C_3\sin 2\Lambda\theta_\infty - 2\Lambda\cos 2\Lambda\theta_\infty) \\
& - \frac{\psi_3(C_3-\Lambda^2)}{\Lambda}\left(C_3\cos^2\Lambda\theta_\infty + \Lambda\sin 2\Lambda\theta_\infty + \frac{2\Lambda^2}{C_3}\right) \\
& + \frac{1-f_{ss}}{\Lambda^2}\left(C_3\cos^2\Lambda\theta_\infty + \Lambda\sin 2\Lambda\theta_\infty + \frac{2\Lambda^2}{C_3}\right)\Big]
\end{aligned} \tag{C-3.4}$$

Since equation (C-2.1) is structurally similar to equation (A-2.1), an analytic solution is again not possible. In order to obtain an approximate solution, the following asymptotic sequence is assumed:

$$X_2(\theta_\infty) = b_0(\theta_\infty) + \epsilon b_1(\theta_\infty) + \epsilon^2 b_2(\theta_\infty) \tag{C-4.1}$$

where b_0=non-periodic term

b_1 and b_2 = periodic terms

$\epsilon \lll 1$.

Substituting equations (C-4.1), (C-3.1) into (C-2.1) and collecting terms of the same orders in ϵ yield the following three differential equations:

$$\frac{db_0(\theta_\infty)}{d\theta_\infty} + (1+\hat{K}_2)b_0(\theta_\infty) = K_1 f_{ss} \tag{C-5.1}$$

$$\frac{db_1(\theta_\infty)}{d\theta_\infty} + (1+\hat{K}_2)b_1(\theta_\infty) = \frac{\cos\Lambda\theta_\infty}{\Lambda}\left(\frac{db_0(\theta_\infty)}{d\theta_\infty} - K_1 f_{ss} + \hat{K}_2 b_0(\theta_\infty)\right) - \sin\Lambda\theta_\infty b_0(\theta_\infty) + K_1 P_1(\theta_\infty) \tag{C-5.2}$$

$$\frac{db_2(\theta_\infty)}{d\theta_\infty} + (1+\hat{K}_2)b_2(\theta_\infty) = \frac{\cos\Lambda\theta_\infty}{\Lambda}\left(\frac{db_1(\theta_\infty)}{d\theta_\infty} - K_1 P_1(\theta_\infty) + \hat{K}_2 b_1(\theta_\infty)\right) - \sin\Lambda\theta_\infty b_1(\theta_\infty) + K_1 P_2(\theta_\infty) \tag{C-5.3}$$

It is obvious that the integrating factor for equations (C-5.1), (C-5.2) and (C-5.3) are identical, i.e. $e^{(1+K_2)\theta_\infty}$: Notice that there is no need to specifiy the initial conditions for above three equations since at the limit cycle, the constants of integration vanish.

<u>Solution to b_o</u>

Equation (C-5.1) is readily integrated, at θ_∞, b_o yields the steady state solution, or

$$b_0 = b_{ss} = \frac{K_1 f_{ss}}{1+\hat{K}_2} \tag{C-6.1}$$

<u>Solution to $b_1(\theta_\infty)$</u>

Equation (C-5.2) can be equivalently written as

$$\frac{db_1}{d\theta_\infty} + (1+\hat{K}_2)b_1 = \frac{\cos\Lambda\theta_\infty}{\Lambda}(\hat{K}_2 b_{ss} - K_1 f_{ss}) - \sin\Lambda\theta_\infty \cdot b_{ss}$$

$$+ K_1\psi_3\left[(C_3-\Lambda^2)\cos\Lambda\theta_\infty + \Lambda(1+C_3)\sin\Lambda\theta_\infty\right] \tag{C-7.1}$$

the integration is straight forward and the solution is found to be

$$b_1(\theta_\infty)=\left[K_1\psi_3(C_3-\Lambda^2)-\frac{b_{ss}}{\Lambda}\right]\frac{(1+\hat{K}_2)\cos\Lambda\theta_\infty+\Lambda\sin\Lambda\theta_\infty}{(1+\hat{K}_2)^2+\Lambda^2}$$

$$+\left[K_1\psi_3\Lambda(C_3+1)-b_{ss}\right]\frac{(1+\hat{K}_2)\sin\Lambda\theta_\infty-\Lambda\cos\Lambda\theta_\infty}{(1+\hat{K}_2)^2+\Lambda^2} \qquad \text{(C-7.2)}$$

<u>Solution to $b_2(\theta_\infty)$</u>

A similar calculational process applies for the solution to equation (C-5.3). For convenience, we define the following variables

$$\gamma_{20}=\left[K_1\psi_3(C_3-\Lambda^2)-\frac{b_{ss}}{\Lambda}\right]\frac{\Lambda}{(1+\hat{K}_2)^2+\Lambda^2}+\left[K_1\psi_3\Lambda(1+C_3)-b_{ss}\right]\frac{1}{(1+\hat{K}_2)^2+\Lambda^2}$$

$$+\left[K_1\psi_3(C_3-\Lambda^2)-\frac{b_{ss}}{\Lambda}\right]\frac{\hat{K}_2(1+\hat{K}_2)}{\Lambda\left[(1+\hat{K}_2)^2+\Lambda^2\right]}-\frac{K_1\psi_3}{\Lambda}(C_3-\Lambda^2)$$

$$+\frac{K_1\gamma_{10}C_3}{C_3^2+4\Lambda^2}-\frac{K_1\psi_3(C_3-\Lambda^2)C_3}{\Lambda(C_3^2+4\Lambda^2)}+\frac{K_1(1-f_{ss})C_3}{\Lambda^2(C_3^2+4\Lambda^2)} \qquad \text{(C-8.1.1)}$$

$$\gamma_{21}=\left[K_1\psi_3(C_3-\Lambda^2)-\frac{b_{ss}}{\Lambda}\right]\frac{\Lambda}{(1+\hat{K}_2)^2+\Lambda^2}+\left[K_1\psi_3\Lambda(1+C_3)-b_{ss}\right]\frac{1+\hat{K}_2}{(1+\hat{K}_2)^2+\Lambda^2}$$

$$-\frac{K_1\gamma_5 C_3}{C_3^2+4\Lambda^2}+\frac{K_1\psi_3(1+C_3)C_3\Lambda}{C_3^2+4\Lambda^2} \qquad \text{(C-8.1.2)}$$

$$\gamma_{22}=\left[\frac{b_{ss}}{\Lambda}-K_1\psi_3(C_3-\Lambda^2)\right]\frac{2+\hat{K}_2}{(1+\hat{K}_2)^2+\Lambda^2}+\left[K_1\psi_3\Lambda(1+C_3)-b_{ss}\right]\frac{2\Lambda}{(1+\hat{K}_2)^2+\Lambda^2}-K_1\psi_3(1+C_3)$$

$$+\left[K_1\psi_3\Lambda(1+C_3)-b_{ss}\right]\frac{\hat{K}_2(1+\hat{K}_2)}{\Lambda[(1+\hat{K}_2)^2+\Lambda^2]}-\frac{2K_1\gamma_5\Lambda}{C_3^2+4\Lambda^2}+\frac{2K_1\gamma_{10}\Lambda}{C_3^2+4\Lambda^2}+\frac{2K_1\gamma_{15}C_3}{C_3^2+4\Lambda^2}-\frac{(1-f_{ss})K_1C_3}{\Lambda(C_3^2+4\Lambda^2)}$$

$$-\frac{K_1\psi_3(1+2C_3-\Lambda^2)C_3}{C_3^2+4\Lambda^2}-\frac{2K_1\psi_3(C_3-\Lambda^2)}{C_3^2+4\Lambda^2}+\frac{2K_1(1-f_{ss})}{\Lambda(C_3^2+4\Lambda^2)}+\frac{2K_1\psi_3(1+C_3)\Lambda^2}{C_3^2+4\Lambda^2}$$

(C-8.1.3)

$$\gamma_{23}=\frac{K_1\Lambda\psi_3(1+2C_3-\Lambda^2)-2\Lambda K_1\gamma_{15}-K_1(1-f_{ss})}{C_3^2+4\Lambda^2} \qquad \text{(C-8.1.4)}$$

$$\gamma_{24}=\frac{2K_1\Lambda^2}{C_3(C_3^2+4\Lambda^2)}\left[\gamma_5+\gamma_{10}-\frac{\psi_3(C_3-\Lambda^2)}{\Lambda}-\psi_3(1+C_3)\Lambda+\frac{1-f_{ss}}{\Lambda^2}\right] \qquad \text{(C-8.1.5)}$$

the solution to $b_2(\theta_\infty)$ is then expressed as:

$$\chi_2(\theta_\infty)=\frac{1}{(1+\hat{K}_2)^2+4\Lambda^2}\Bigg\{\gamma_{20}\left[(1+\hat{K}_2)\cos^2\Lambda\theta_\infty+\Lambda\sin 2\Lambda\theta_\infty+\frac{2\Lambda^2}{(1+\hat{K}_2)}\right]$$
$$-\gamma_{21}\left[(1+\hat{K}_2)\sin^2\Lambda\theta_\infty-\Lambda\sin 2\Lambda\theta_\infty+\frac{2\Lambda^2}{1+\hat{K}_2}\right]$$
$$+\gamma_{22}\left[(1+\hat{K}_2)\sin 2\Lambda\theta_\infty-2\Lambda\cos 2\Lambda\theta_\infty\right]$$
$$+\gamma_{23}\left[(1+\hat{K}_2)\cos 2\Lambda\theta_\infty+2\Lambda\sin 2\Lambda\theta_\infty\right]\Bigg\}+\frac{\gamma_{24}}{1+\hat{K}_2} \qquad \text{(C-8.2)}$$

By simply substituting equations (C-6.1), (C-7.2) and (C-8.2)into (C-4.1) will yield the solution to $x_2(\theta_\infty)$.

APPENDIX D

AVERAGE YIELD CALCULATION OF THE INTERMEDIATE PRODUCT

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AVERAGE YIELD CALCULATION OF THE INTERMEDIATE PRODUCT

The average yield of B at the limit cycle is obtained by carrying out the cyclic integration of $x_2(\theta_\infty)$. The cycle time is defined as

$$T = \frac{2\pi}{\Lambda} \tag{D-1.1}$$

hence,

$$\oint x_2(\theta_\infty) = \frac{1}{T}\oint_{\theta_\infty}^{\theta_\infty + T} x_2(\theta_\infty)\, d\theta_\infty \tag{D-1.2}$$

From equation (C-8.2) of Appendix C, the cyclic integration of sine and cosine functions vanish and also the terms that contain squares of sine and cosine will remain, hence

$$\oint x_2(\theta_\infty) = \frac{1}{(1+\hat{K}_2)^2 + 4\Lambda^2}\left[(\gamma_{20} - \gamma_{21})\left(\frac{1+\hat{K}_2}{2} + \frac{2\Lambda^2}{1+\hat{K}_2}\right)\right] + \frac{\gamma_{24}}{1+\hat{K}_2} \tag{D-2.1}$$

where γ_{20}, γ_{21}, γ_{24} are defined in Appendix C.

APPENDIX E

THE SECOND VARIATIONAL IN THE FREQUENCY DOMAIN

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THE SECOND VARIATIONAL IN THE FREQUENCY DOMAIN

Consider a system whose dynamics is given by

$$\dot{x} = \underline{f}(\underline{x},\underline{u}) \qquad \text{(E-1.1)}$$

$$\underline{x}(0) = \underline{x}_o \qquad \text{(E-1.2)}$$

where

$\underline{x}$ = state variable, $\underline{u}$ = a control vector.

Here, we wish to determine whether or not a control vector $\underline{u}$ in a periodic mode ($\underline{x}(\theta)=\underline{x}(\theta+T)$) would yield a local optimal of the objective function

$$J = \frac{1}{T}\oint g(\underline{x},\underline{u})d\theta \qquad \text{(E-2.1)}$$

In this work, $g(\underline{x},\underline{u})=x_2$ or the yield of B. Let J_s^o = objective function at the optimal steady state, hence for a small variation in u

$$\underline{u} = \underline{u}_s^o + \delta\underline{u} \qquad \text{(E-3.1)}$$

then $\delta\underline{u}$ will yield a local optimum if $\Delta J=J-J_s^o > 0$. Hence we wish to determine

$$\underset{\substack{\underline{x}\in\underline{X} \\ \underline{u}\in\underline{U}}}{\mathrm{Max}^m}\ \Delta J$$

subject to the limit cycle dynamics

$$\dot{\underline{x}} = \underline{f}(\underline{x},\underline{u}) \tag{E-4.1}$$

$$\underline{x}(\theta_\infty) = \underline{x}(\theta_\infty+T) \tag{E-5.1}$$

$$\frac{1}{T}\oint h(\underline{u})d\theta = \text{constant} \tag{E-6.1}$$

Now, by imposing $\delta\underline{u}$ a priori we can relax equation (E-6.1).

Now, define the Hamiltonian

$$H(\underline{x},\underline{u},\underline{\lambda}) = g(\underline{x},\underline{u}) + \underline{\lambda}^T(\theta)\underline{f}(\underline{x},\underline{u}). \tag{E-7.1}$$

H and f are twice differentiable and continuous in $\underline{x}\epsilon\underline{X}$, $\underline{u}\epsilon\underline{U}$.

The optimal staedy state is determined from

$$J_s^o = g(\underline{x}_s^o,\underline{u}_s^o) \Longleftarrow \begin{cases} H_{\underline{x}_s^o} = 0 & \text{(E-8.1)} \\ H_{\underline{u}_s^o} = 0 & \text{(E-8.2)} \\ \underline{f}_s^o = 0 & \text{(E-8.3)} \end{cases}$$

therefore,

$$J = \frac{1}{T}\oint g(\underline{x},\underline{u})d\theta \tag{E-9.1}$$

At the cycle, we assume that $\underline{\lambda}(\theta_\infty)$ becomes time independent.

$$J = \frac{1}{T}\oint\left[H(\underline{x},\underline{u},\underline{\lambda}_s^o)-(\underline{\lambda}_s^o)^T\underline{f}(\underline{x},\underline{u})\right] d\theta \tag{E-9.2}$$

$$J_s^o = \frac{1}{T}\oint H(\underline{x}_s^o,\underline{u}_s^o,\underline{\lambda}_s^o)d\theta \tag{E-10.1}$$

therefore,

$$J-J_s^o = \frac{1}{T}\oint\left[H(\underline{x},\underline{u},\underline{\lambda}_s^o)-H(\underline{x}_s^o,\underline{u}_s^o,\underline{\lambda}_s^o)\right] d\theta_\infty - (\underline{\lambda}_s^o)^T\frac{1}{T}\oint\underline{f}(\underline{x},\underline{u})d\theta_\infty \tag{E-11.1}$$

but,

$$\frac{d\underline{x}}{d\theta} = \underline{f}(\underline{x},\underline{u})$$

hence, the last term in equation (E-9.2) becomes

$$\oint \underline{f}(\underline{x},\underline{u})\,d\theta_\infty = \oint \frac{d\underline{x}}{d\theta_\infty}d\theta_\infty = \underline{x}(0)-\underline{x}(T)=0. \qquad \text{(E-12.1)}$$

Therefore,

$$\begin{aligned} J-J_s^o &= \frac{1}{T}\oint\left[H(\underline{x},\underline{u},\underline{\lambda}_s)-H(\underline{x}_s^o,\underline{u}_s^o,\underline{\lambda}_s^o)\right]\,d\theta_\infty \\ &= \frac{1}{T}\oint\left[H(\underline{x},\underline{u}_s^o+\delta\underline{u}\ \ ,\underline{\lambda}_s^o)-H(\underline{x}_s^o,\underline{u}_s^o,\underline{\lambda}_s^o)\right]\,d\theta_\infty \\ &= \frac{1}{T}\oint\left\{\sum_i \frac{\partial H}{\partial x_i}\bigg|_{s^o}\delta x_i+\sum_i \frac{\partial H}{\partial u_i}\bigg|_{s^o}\delta u_i+\frac{1}{2}\left[\sum_i\sum_j \frac{\partial^2 H}{\partial x_i\partial x_j}\bigg|_{s^o}\delta x_i\delta x_j+\sum_i\sum_j \frac{\partial^2 H}{\partial x_i\partial u_j}\bigg|_{s^o}\delta x_i\delta u_j\right.\right. \\ &\qquad\qquad \left.\left.+\sum_i\sum_j \frac{\partial^2 H}{\partial u_i\partial u_j}\bigg|_{s^o}\delta u_i\delta u_j\right]+\mathcal{O}^3\right\}d\theta_\infty \end{aligned}$$

$$\begin{aligned} \Delta J &= \frac{1}{T}\oint\left[\left(H_{\underline{x}}\Big|_{s^o}\delta\underline{x}+H_{\underline{u}_s^o}\delta\underline{u}\right)\right]\,d\theta_\infty+\frac{1}{T}\oint\underline{h}^T\underline{\underline{F}}\underline{h}\,d\theta_\infty \\ &= \delta^1 J+\delta^2 J \end{aligned} \qquad \text{(E-13.1)}$$

clearly $\delta^1 J=0$ and $\delta^2 J$ is a quadratic form.

Here:

$$\underline{h} = \left[\delta\underline{x}\quad \delta\underline{u}\right]$$

$$\underline{h}^T = \left[(\delta\underline{x})^T\quad (\delta\underline{u})^T\right]$$

$$\underline{\underline{F}} = \left[\begin{array}{c|c} \underline{\underline{P}}(nxn) & \underline{\underline{Q}}(mxn) \\ \hline \underline{\underline{Q}}^T(nxm) & \underline{\underline{R}}(mxm) \end{array}\right]$$

$\underline{\underline{P}} = \left[H_{xx}(\underline{x}_s^o, \underline{u}_s^o, \underline{\lambda}_s^o) \right]$

$\underline{\underline{Q}} = \underline{\underline{Q}}^T$(a symmetric matrix) $= \left[H_{xu}(\underline{x}_s^o, \underline{u}_s^o, \underline{\lambda}_s^o) \right]$

$\underline{\underline{R}} = \left[H_{uu}(\underline{x}_s^o, \underline{u}_s^o, \underline{\lambda}_s^o) \right]$

Now, the condition that gives rise to $\Delta J>0$ should depend on $\delta\underline{u}$ as well as $\underline{\underline{F}}$ and $\delta\underline{x}$. However, in order to derive a criterion for the sgn(ΔJ), the relationship between $\delta\underline{x}$ and $\delta\underline{u}$ should be known. Such can be determined from linear control theory. So, if we perform the first variation of the process dynamics,

$$\delta\frac{dx}{dt} = \frac{d}{dt}\delta\underline{x} = \delta\dot{\underline{x}} = \underline{f}(\underline{x},\underline{u}) - \underline{f}(\underline{x}_s^o,\underline{u}_s^o)$$

$$= \underline{f}(\underline{x},\underline{u}_s^o+\delta\underline{u}) - \underline{f}(\underline{x}_s^o,\underline{u}_s^o)$$

$$= \underline{f}(\underline{x}_s,\underline{u}_s^o+\delta\underline{u}) + \underline{\underline{A}}\delta\underline{x} + \underline{\underline{B}}\delta\underline{u} + \ldots\ldots$$

$$-\underline{f}(\underline{x}_s^o,\underline{u}_s^o) \qquad \text{(E-14.1)}$$

Hence,

$$\dot{\underline{x}} = \underline{\underline{A}}\delta\underline{x} + \underline{\underline{B}}\delta\underline{u} \qquad \text{(E-15.1)}$$

where

$$\underline{\underline{A}} = f_{\underline{x}}(\underline{x}_s^o,\underline{u}_s^o)$$

$$\underline{\underline{B}} = f_{\underline{u}}(\underline{x}_s^o,\underline{u}_s^o)$$

Now, from linear control theory; if

$$\delta\underline{u} = \sum_{k=-\infty}^{k=\infty} \underline{c}_k e^{jk\omega\theta_\infty} \qquad \text{(E-16.1)}$$

where $\underline{c}_k=0$ for $k=0$, $\underline{c}_k$ = a constant, $j=\sqrt{-1}$, ω = cycling frequency such that $\delta\underline{u}$ forms a Fourier trigonometric series, hence the solution to equation (E-16.1) should have a form expressed by

$$\delta\underline{x} = \sum_{k=-\infty}^{k=\infty} \underline{x}_k e^{jk\omega\theta_\infty} \tag{E-17.1}$$

and where $\underline{x}_k=0$ for $k=0$.

When equation (E-17.1) is substituted into equation (E-15.1), the value of $\underline{x}_k$ is determined. Hence

$$\delta\underline{x}(\theta_\infty) = \sum_{-\infty}^{\infty}{}_k \underline{\underline{G}}(jk\omega)\underline{c}_k e^{jk\omega t} \tag{E-18.1}$$

or,

$$\underline{x}_k = \underline{\underline{G}}(jk\omega)\underline{c}_k \tag{E-18.2}$$

with equations (E-18) the second variation $\delta^2 J$ is now evaluated, thus,

$$\delta^2 J = \frac{1}{T}\oint\left[(\delta\underline{x})^T\underline{\underline{P}}(\delta\underline{x})+(\delta\underline{u})^T\underline{\underline{Q}}^T(\delta\underline{x})+(\delta\underline{x})^T\underline{\underline{Q}}(\delta\underline{u})+(\delta\underline{u})^T\underline{\underline{R}}(\delta\underline{u})\right]d\theta_\infty$$

$$=2\sum_1^{\infty}{}_k\underline{x}_{-k}^T\underline{\underline{P}}\underline{x}_k+2\sum_1^{\infty}{}_k\underline{c}_{-k}^T\underline{\underline{Q}}^T\underline{x}_k+2\sum_1^{\infty}{}_k\underline{x}_{-k}^T\underline{\underline{Q}}\underline{c}_k+2\sum_1^{\infty}{}_k\underline{c}_{-k}^T\underline{\underline{R}}\underline{c}_k \tag{E-19.1}$$

replacing $\underline{x}_k$ by using equation (E-18.2)

$$\Delta J = \sum_1^{\infty}{}_k\underline{c}_{-k}^T\underline{\underline{\pi}}(k\omega)\underline{c}_k.$$

APPENDIX F

CALCULATION OF THE VELOCITY PROFILE IN THE PLUG FLOW TUBULAR REACTOR

APPENDIX F

CALCULATION OF THE VELOCITY PROFILE IN THE PLUG FLOW TUBULAR REACTOR

Here, the momentum conservation equation leads to

$$\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial z} = 0 \tag{F-1.1}$$

The disturbance in the inlet velocity, thus a disturbance in the inlet volumetric flow rate, is assumed to be in the form of a sine wave and is given as

$$v(t,0) = \langle v \rangle \left[1 + \epsilon \sin \omega t\right] \tag{F-1.2}$$

where ϵ is a small positive number indicating the degree of disturbance away from its steady state and ω is the frequency of the input disturbance.

Defining the residence time of the reactor as

$$\tau = \frac{L}{\langle v \rangle}$$

where L is the reactor length. Introducing the folowing dimensionless variables:

$$\theta = \frac{t}{\tau} \quad ; \qquad \bar{v} = \frac{v}{\langle v \rangle} \; ; \qquad \zeta = \frac{z}{L} \; ; \quad \Lambda = \omega\tau \tag{F-1.3}$$

when equation (F-1.3) is substituted into equation (F-1.1), we obtain the dimensionless equation of motion

$$\frac{\partial \bar{v}}{\partial \theta} + \bar{v}\frac{\partial \bar{v}}{\partial \xi} = 0. \qquad \text{(F-2.1)}$$

with the initial and boundary conditions

$$\bar{v}\,(\theta = 0, \xi) = 1 \qquad \text{(F-3.1)}$$

$$\bar{v}\,(\theta, \xi = 0) = 1 + \epsilon \sin \Lambda \theta \qquad \text{(F-3.2)}$$

It is obvious that an analytic solution to equation (F-2.1) is not possible. In order to obtain an approximate solution, we assume $\bar{v}$ to have a form composed of a steady state or a non-periodic term and a sum of periodic terms such that

$$\bar{v} = \bar{v}(\theta = 0, \xi) + \epsilon \bar{v}_1 + \epsilon^2 \bar{v}_2 \qquad \text{(F-4.1)}$$

where ϵ is very small so that terms with ϵ of order 3 or higher are neglected.

Substituting (F-4.1) into equations (F-2.1) and (F-3) and collecting terms of the same degree of ϵ yield

$$\frac{\partial \bar{v}_1}{\partial \theta} + \frac{\partial \bar{v}_1}{\partial \xi} = 0. \qquad \text{(F-5.1)}$$

with the following initial and boundary conditions

$$\bar{v}_1(\theta = 0, \xi) = 0 \qquad \text{(F-5.1.1)}$$

$$\bar{v}_1(\theta, \xi = 0) = \sin \Lambda \theta \qquad \text{(F-5.1.2)}$$

and

$$\frac{\partial \bar{v}_2}{\partial \theta} + \frac{\partial \bar{v}_2}{\partial \xi} + \bar{v}_1 \frac{\partial \bar{v}_1}{\partial \xi} = 0 \qquad \text{(F-5.2)}$$

with

initial condition $\bar{v}_2(\theta=0,\zeta)=0$ (F-5.2.1)

boundary condition $\bar{v}_2(\theta,\zeta=0)=0$ (F-5.2.2)

Notice that 0^{th} order term of ϵ in the equation yields the steady state velocity.

The method of characteristic is applied here to solve the partial differential equations (F-5), where the dependent variable is treated along its characteristic path. As a result, the partial differential equations for $\bar{v}_1$ and $\bar{v}_2$ in θ and ζ are transformed into ordinary differential equations in terms of the variables r and s. The transformation of the independent variables θ and ζ into the characteristic variables r and s is depicted in the figure below

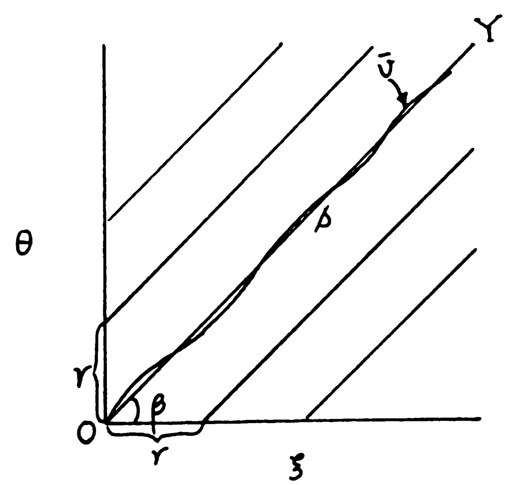

FIGURE F-1. Characteristic transformation for the independent variables

It is clear that for a fixed r, θ and ζ can be related to s.

Transforming equation (F-5.1) into the new independent variables yields

$$\left(\frac{\partial \bar{v}_1}{\partial s}\right)_r = \frac{\partial \bar{v}_1}{\partial s} = \frac{\partial \bar{v}_1}{\partial \xi}\left(\frac{\partial \xi}{\partial s}\right)_r + \frac{\partial \bar{v}_1}{\partial \theta}\left(\frac{\partial \theta}{\partial s}\right)_r = R \qquad \text{(F-6.1)}$$

where R is the right hand side of equation (F-5.1). Comparing equations (F-6.1) and (F-5.1) we have, at a fixed r,

$$\frac{\partial \xi}{\partial s} = 1 \qquad \text{(F-7.1)}$$

$$\frac{\partial \theta}{\partial s} = 1 \qquad \text{(F-7.2)}$$

hence $\frac{\partial \theta}{\partial \xi} = 1 = \tan\beta$ or $\beta = 45°$

Integration yields

$$\theta - \theta_o = \xi - \xi_o \qquad \text{(F-8.1)}$$

where θ_o and ξ_o are some arbitrary initial condition for θ and ξ, respectively.

Referring to figure F-1, two regions can be classified. The variable r, in the lower region, represents an arbitrary initial value for ξ, while in the region above OY, the parameter r represents an arbitrary initial value for θ. Mathematically, the following relations for each region can be written as

Region below OY:

$$\theta = s \cdot \sin\beta \qquad \text{(F-9.1)}$$

$$\xi = r + s\cos\beta \qquad \text{(F-9.2)}$$

Region above OY:

$$\theta = r + s \cdot \sin\beta \tag{F-10.1}$$

$$\zeta = s \cdot \cos\beta \tag{F-10.2}$$

As far as the limit cycle is concerned, only the upper region is used in the solution to $\bar{v}$. Furthermore, the initial transient (i.e., $\theta < \zeta$) is washed out at $\theta = \tau$ (or reaction residence time) and does not provide information for the solution at θ_∞. Hence, only the boundary condition ($\zeta = 0$) is significant at this region. It follows that $\zeta_o = 0$ and $\theta_o = r$ in equation (F-8.1).

As a conclusion, the foregoing calculations will be only for this upper region ($\theta > \zeta$), therefore the integration of equation (F-7.1) from $\zeta_o = 0$ to ζ and $s_o = 0$ to s yields

$$\zeta = s \tag{F-11.1}$$

while equation (F-8.1) gives

$$r = \theta - \zeta \tag{F-11.2}$$

It is clearly seen that equations (F-11) provide the transformation between independent variables. Here, the transformation of the partial differential equations (F-5) and their boundary conditions can be easily implemented. The solutions to the resulting ODE's are straight forward. After back transformation and using equations (F-11) yields the solution in terms of the original independent variables.

Thus,

$$\frac{\partial \bar{v}_1}{\partial s}=0$$

or, $\bar{v}_1(s,r)=f(r)$. Applying the boundary condition (in terms of r and s) yields

$$\bar{v}_1(r, s=0) = \sin\Lambda r$$

or $$\bar{v}_1(r, s) = \sin\Lambda r$$

Upon back transformation, the above equation is

$$\bar{v}_1(\theta, \xi) = \sin\Lambda(\theta-\xi) \tag{F-12.1}$$

Equation (F-5.1) is solved in a similar fashion. Substituting $\bar{v}_1(r,s)$ and $\left[\frac{\partial \bar{v}_1(\theta,\xi)}{\partial \xi}\right]_{r,s}$, an ODE similar to (F-6.1) is obtained except, here $R(s,r)=\sin\Lambda r\cos\Lambda r$. Integrating the equation and using the boundary condition at $\xi_0=0$ gives $\bar{v}_2(s,r)$. Back transformation yields

$$\bar{v}_2(\theta,\xi)=\frac{\xi}{2}\Lambda\sin 2\Lambda(\theta-\xi) \tag{F-12.2}$$

Substituting equations (F-12) into (F-4.1), we obtain the perturbation solution for $\bar{v}$

$$\bar{v}(\theta\xi)=1+\epsilon\sin\Lambda(\theta-\xi)+\epsilon^2\frac{\xi\Lambda}{2}\sin 2\Lambda(\theta-\xi). \tag{F-13.1}$$

APPENDIX G

GLOBAL SOLUTION TO x_1 AND x_2 IN A PLUG FLOW TUBULAR REACTOR (PERTURBATION SOLUTION)

APPENDIX G

GLOBAL SOLUTION TO x_1 AND x_2 IN A PLUG FLOW TUBULAR REACTOR (PERTURBATION SOLUTION)

For the proposed Van de Vusse kinetic scheme,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad , \quad A + A \xrightarrow{k_3} D$$

the material balance for A (species 1) and B (species 2) are, respectively:

$$\frac{\partial A}{\partial t} = -\frac{\partial}{\partial z}(v \cdot A) - k_1 A - k_3 A^2 \tag{G-1.1}$$

and

$$\frac{\partial B}{\partial t} = -\frac{\partial}{\partial z}(v \cdot B) + k_1 A - k_2 B \tag{G-1.2}$$

using the same τ as defined in Appendix F and introducing the following dimensionless variables:

$$x_1 = \frac{A}{A_{ref}} \; ; \; x_2 = \frac{B}{A_{ref}} \; ; \; K_1 = k_1\tau \; ; \; K_2 = k_2\tau ; \; K_3 = k_3 A_{ref}\tau \; ; \; K = \frac{K_3}{K_1} \tag{G-1.3}$$

where A_{ref} is the inlet concentration of reactant A. Substituting equations (G-1.3) and (F-1.3) of Appendix F into equations (G-1.1) and (G-1.2) yields the dimensionless material balance equations for A and B as

$$\frac{\partial x_1}{\partial \theta} + \frac{\partial}{\partial \xi}(\bar{v} x_1) = -K_1 x_1 - K_3 x_1^2 \tag{G-2.1}$$

and

$$\frac{\partial \chi_2}{\partial \theta} + \frac{\partial}{\partial \xi}(\bar{v}\chi_2) = K_1\chi_1 - K_2\chi_2 \qquad \text{(G-2.2)}$$

respectively, where the solution to $\bar{v}$ can be found in Appendix F.

It is clear the analytic solutionsto equations (G-2) are not possible, and in order to obtain an approximate solution, we assume the following asymptotic sequences:

$$\chi_1 = \chi_{1_s} + \epsilon P_1^1 + \epsilon^2 P_1^2 \qquad \text{(G-3.1)}$$

$$\chi_2 = \chi_{2_s} + \epsilon P_2^1 + \epsilon P_2^2 \qquad \text{(G-3.1)}$$

ϵ is restricted to small values in order to have the equations (G-3) meaningful. Furthermore, x_{1_s} and x_{2_s} satisfy

$$\frac{d\chi_{1_s}}{d\xi} = -K_1\chi_{1_s} - K_3\chi_{1_s}^2 \qquad \text{(G-4.1)}$$

and

$$\frac{d\chi_{2_s}}{d\xi} = K_1\chi_{1_s} - K_2\chi_{2_s} \qquad \text{(G-4.2)}$$

Solution to $x_1(\theta,\xi)$

Substituting equations (F-4.1) and (G-3.1) into equation (G-2.1), collecting terms of similar order in ϵ gives the following equations

$$\frac{\partial P_1^1}{\partial \theta} + \frac{\partial}{\partial \xi}(P_1^1 + \bar{v}_1\chi_{1_s}) = -K_1 P_1^1 - 2K_3 P_1^1 \chi_{1_s} \qquad \text{(G-5.1)}$$

$$\frac{\partial P_1^2}{\partial \theta}+\frac{\partial}{\partial \xi}(P_1^2+\bar{v}_1 P_1^1+\bar{v}_2 x_{1_s})=-K_1 P_1^2-K_3\left[2P_1^2 x_{1_s}+(P_1^1)^2\right] \quad \text{(G-5.2)}$$

the boundary conditions (from Appendix I) are:

$$x_{1_s}(\theta,\xi=0)=1 \quad \text{(G-6.1)}$$

$$P_1^1(\theta,\xi=0)=0 \quad \text{(G-6.2)}$$

$$P_1^2(\theta,\xi=0)=0 \quad \text{(G-6.3)}$$

The solution to equation (G-4.1) is very simple, thus,

$$x_{1_s}(\xi)=\frac{\alpha_0 e^{-K_1\xi}}{K(1-\alpha_0 e^{-K_1\xi})} \quad \text{(G-7.1)}$$

where $\alpha_0=\frac{K}{1+K}$, where $K=K_3/K_1$

The method of characteristics is applied again to solve for equations (G-5). Notice from the similarity of the mathematical structure between equations (G-5) and equations (F-5), we expect them to have the same ground characteristic path, thus the transformations between independent variables are

$$s=\xi \quad \text{(F-11.1)}$$

$$r=\theta-\xi \quad \text{(F-11.2)}$$

The transformation in (s;r) converts the hyperbolic equations (i.e.,(G-5)) into ordinary differential equations which have the independent variables given in terms of the ground characteristic path, s. The boundary conditions are also transformed into (s;r). The solution to the ordinary differential equations (in P_1^1 and P_1^2) are straight forward but heavy handed, unfortunately.

The transformed equation in terms of ground characteristic for equation (G-5.1) has the form

$$\frac{dP_1^1}{ds}+K_1\left[1+\frac{2\alpha_0 e^{-K_1 s}}{1-\alpha_0 e^{-K_1 s}}\right]P_1^1=\Lambda\cos\Lambda r\frac{\alpha_0 e^{-K_1 s}}{K(1-\alpha_0 e^{-K_1 s})}+\sin\Lambda r\frac{K_1\alpha_0 e^{-K_1 s}}{K(1-\alpha_0 e^{-K_1 s})^2} \qquad \text{(G-8.1)}$$

some clever manipulations are necessary on equation (G-8.1) to obtain the right integrating factor. Also using the binomial series expansion, the integrating factor, I, is

$$I=e^{K_1 s}(1-\alpha_0 e^{-K_1 s})^2 \qquad \text{(G-9.1)}$$

Completing the integration, and evaluating the constant of integration using (G-6.2) yields,

$$P_1^1(s,r)=\frac{e^{-K_1 s}}{(1-\alpha_0 e^{-K_1 s})^2}\left[\frac{\alpha_0\Lambda}{K}\cos\Lambda r\left(s+\frac{\alpha_0}{K_1}e^{-K_1 s}-\frac{\alpha_0}{K}\right)+\frac{K_1\alpha_0 s}{K}\sin\Lambda r\right]$$

back transformation yields

$$P_1^1(\xi,\theta)=\frac{e^{-K_1\xi}}{(1-\alpha_0 e^{-K_1\xi})^2}\left\{\frac{\alpha_0}{K}\left[\Lambda\cos\Lambda(\theta-\xi)+K_1\sin\Lambda(\theta-\xi)\right]\xi -\frac{\alpha_0^2}{K_3}\Lambda\cos\Lambda(\theta-\xi)+\frac{\alpha_0^2}{K_3}\Lambda\cos\Lambda(\theta-\xi)\cdot e^{-K_1\xi}\right\} \qquad \text{(G-10.1)}$$

A procedure similar to the above can be implemented, thus, in the transformed P_1^2 differential equation:

$$\frac{dP_1^2}{ds}+K_1(1+2K\chi_{1\xi})P_1^2=-\bar{v}_1(s,r)\left[\frac{\partial P_1^1(\theta,\xi)}{\partial\xi}\right]_{s,r}-P_1^1(s,r)\left[\frac{\partial\bar{v}_1(\theta,\xi)}{\partial\xi}\right]_{s,r}-\bar{v}_2(s,r)\left[\frac{d\chi_{1s}}{d\xi}\right]_{r,s}$$
$$-\chi_{1\xi}(r,s)\left[\frac{\partial\bar{v}_2(\theta,\xi)}{\partial\xi}\right]_{s,r}-K_3\left[P_1^1(s,r)\right]^2 \qquad \text{(G-11.1)}$$

comparing equations (G-11.1) and (G-8.1) yields an identical integrating factor for both equations. Therefore equation (G-11.1) can be readily integrated. Defining the following groups for convenience:

$$g_1 = \frac{\alpha_0}{K}\left[\Lambda\cos\Lambda(\theta-\xi)+K_1\sin\Lambda(\theta-\xi)\right] \qquad \text{(G-12.1)}$$

$$g_2 = -\frac{\alpha_0^2}{K_3}\Lambda\cos\Lambda(\theta-\xi) \qquad \text{(G-12.2)}$$

$$g_3 = \frac{\alpha_0^2}{K_3}\Lambda\cos\Lambda(\theta-\xi) \qquad \text{(G-12.3)}$$

with patience and care, the solution to P_1^2 was found. After back transformation, the solution to P_1^2 is expressed as

$$P_1^2(\theta,\xi) = \frac{e^{-K_1\xi}}{(1-\alpha_0 e^{-K_1\xi})^2}\Bigg\{-\sin\Lambda(\theta-\xi)\Big[\varphi_1(\theta,\xi)+\varphi_2(\theta,\xi)+\varphi_3(\theta,\xi)+\varphi_4(\theta,\xi)+\varphi_{5j}(\theta,\xi)+\varphi_{6j}(\theta,\xi)\Big]$$
$$+\Lambda\cos\Lambda(\theta-\xi)\varphi_7(\theta,\xi)+\varphi_8(\theta,\xi)+\varphi_9(\theta,\xi)$$
$$+K_3\Big[\varphi_{10j}(\theta,\xi)+\varphi_{11j}(\theta,\xi)+\varphi_{12j}(\theta,\xi)+\varphi_{13j}(\theta,\xi)+\varphi_{14j}(\theta,\xi)+\varphi_{15j}(\theta,\xi)\Big]\Bigg\} \qquad \text{(G-13.1)}$$

where

$$\varphi_1(\theta,\xi) = \Lambda^2\sin\Lambda(\theta-\xi)\left[\frac{\alpha_0\xi^2}{2K}-\frac{\alpha_0^2(e^{-K_1\xi}-1)}{K_1K_3}-\frac{\alpha_0^2\xi}{K_3}\right] \qquad \text{(G-13.1.1)}$$

$$\varphi_2(\theta,\xi) = \Lambda\cos\Lambda(\theta-\xi) \qquad \text{(G-13.1.2)}$$

$$\varphi_3(\theta,\xi) = \frac{\alpha_0 K_1}{K}\left[\xi\sin\Lambda(\theta-\xi)-\frac{\Lambda}{2}\cos\Lambda(\theta-\xi)\cdot\xi^2\right] \qquad \text{(G-13.1.3)}$$

$$\varphi_4(\theta,\xi) = -K_1\left[\frac{g_1}{2}\xi^2-\frac{g_3}{K_1}(e^{-K_1\xi}-1)+g_2\xi\right] \qquad \text{(G-13.1.4)}$$

$$\varphi_{5j}(\theta,\xi) = K_1\sum_{j=1}^{\infty}\alpha_0^{j}\left[\frac{g_1}{K_1 j}\left(\xi e^{-K_1 j\xi} + \frac{e^{-K_1 j\xi}-1}{K_1 j}\right) + \frac{g_3}{K_1(1+j)}\left(e^{-K_1(1+j)\xi}-1\right) + \frac{g_2}{K_1 j}\left(e^{-K_1 j\xi}-1\right)\right] \quad \text{(G-13.1.5)}$$

$$\varphi_{6j}(\theta,\xi) = K_1\sum_{j=0}^{\infty}\alpha_0^{1+j}\left[\frac{g_1}{K_1(1+j)}\left(\xi e^{-K_1(1+j)\xi} + \frac{e^{-K_1(1+j)\xi}-1}{K_1(1+j)}\right) + \frac{g_3}{K_1(2+j)}\left(e^{-K_1(2+j)\xi}-1\right) + \frac{g_2}{K_1(1+j)}\left(e^{-K_1(1+j)\xi}-1\right)\right] \quad \text{(G-13.1.6)}$$

$$\varphi_7(\theta,\xi) = -\frac{\varphi_4(\theta,\xi)}{K_1} \quad \text{(G-13.1.7)}$$

$$\varphi_8(\theta,\xi) = \frac{\alpha_0 K_1\Lambda}{4K}\xi^2\sin 2\Lambda(\theta-\xi) + \frac{\alpha_0^2\Lambda^2}{K_2}\cos 2\Lambda(\theta-\xi)\left[\xi e^{-K_1\xi} + \frac{e^{-K_1\xi}-1}{K_1}\right] \quad \text{(G-13.1.8)}$$

$$\varphi_9(\theta,\xi) = -\frac{\alpha_0\Lambda}{2}\sin 2\Lambda(\theta-\xi)\left[\frac{\xi}{K} + \frac{\alpha_0}{K_3}\left(e^{-K_1\xi}-1\right)\right] + \frac{\alpha_0\Lambda^2}{2K}\xi\cos 2\Lambda(\theta-\xi) \quad \text{(G-13.1.9)}$$

$$\varphi_{10j}(\theta,\xi) = g_1^2\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\left[\frac{e^{-K_1(1+j)\xi}}{K_1(1+j)}\left(\xi^2 + \frac{2\xi}{K_1(1+j)} + \frac{2}{K_1^2(1+j)^2}\right) - \frac{2}{K_1^3(1+j)^3}\right] \quad \text{(G-13.1.10)}$$

$$\varphi_{11j}(\theta,\xi) = 2g_1 g_2\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\left[\frac{e^{-K_1(1+j)\xi}}{K_1(1+j)}\left(\xi + \frac{1}{K_1(1+j)}\right) - \frac{1}{K_1^2(1+j)^2}\right] \quad \text{(G-13.1.11)}$$

$$\varphi_{12j}(\theta,\xi) = g_2^2\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\left[\frac{e^{-K_1(1+j)\xi}-1}{K_1(1+j)}\right] \quad \text{(G-13.1.12)}$$

$$\varphi_{13j}(\theta,\xi) = 2g_1 g_3\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\left[\frac{e^{-K_1(2+j)\xi}}{K_1(2+j)}\left(\xi + \frac{1}{K_1(2+j)}\right) - \frac{1}{K_1^2(2+j)^2}\right] \quad \text{(G-13.1.13)}$$

$$\varphi_{14j}(\theta,\xi) = 2g_2 g_3\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\left[\frac{e^{-K_1(2+j)\xi}-1}{K_1(2+j)}\right] \quad \text{(G-13.1.14)}$$

$$\varphi_{15j}(\theta,\xi) = g_3^2\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\left[\frac{e^{-K_1(3+j)\xi}-1}{K_1(3+j)}\right] \quad \text{(G-13.1.15)}$$

Substituting equations (G-7.1), (G-10.1) and (G-13) into equation (G-3.1) yields the complete global solution to $x_1(\theta,\xi)$

Solution to $x_2(\theta,\xi)$

The solution to x_2 is done in a similar fashion as for solution to x_1. Substituting the global solution to x_1 together with equations (F-13.1), and (G-3.2) into equation (G-2.2), collecting terms with similar orders in ϵ yields:

$$\frac{dx_{2s}}{d\xi} = K_1 x_{1s} - K_2 x_{2s} \tag{G-4.2}$$

$$\frac{dP_2^1}{d\xi} + \frac{dP_2^1}{d\theta} + \sin\Lambda(\theta-\xi)\frac{dx_{2s}}{d\xi} = -K_2 P_2^1 + \Lambda\cos\Lambda(\theta-\xi)\,x_{2s} + K_1 P_1^1 \tag{G-14.1}$$

$$\frac{dP_2^2}{d\xi} + \frac{dP_2^2}{d\theta} + \sin\Lambda(\theta-\xi)\frac{dP_2^1}{d\xi} + \frac{\Lambda}{2}\xi\sin 2\Lambda(\theta-\xi)\frac{dx_{2s}}{d\xi}$$
$$= -K_2 P_2^2 + \Lambda\cos\Lambda(\theta-\xi)P_2^1 - \left[\frac{\Lambda}{2}\sin\Lambda(\theta-\xi) - \xi^2\Lambda^2\cos 2\Lambda(\theta-\xi)\right]x_{2s} + K_1 P_1^2 \tag{G-14.2}$$

with the following boundary conditions:

$$x_{2_s}(\theta,\xi=0)=0 \tag{G-15.1}$$

$$P_2^1(\theta,\xi=0)=0 \tag{G-15.2}$$

$$P_2^2(\theta,\xi=0)=0 \tag{G-15.3}$$

For convenience, we can rewrite equation (G-7.1) equivalently by applying the binomial series as

$$x_{1s}(\xi) = \frac{1}{K}\sum_{j=0}^{\infty}\left(\alpha_0 e^{-K_1\xi}\right)^{1+j} \tag{G-16.1}$$

substituting equation (G-16.1) into equation (G-4.2), with the integrating factor of $e^{K_2\xi}$. The integration, with the condition given in equation (G-15.1) yields the solution to x_{2s}:

$$\chi_{2_\xi}(\xi)=\frac{K_1}{K}e^{-K_2\xi}\sum_{j=0}^{\infty}\alpha_0^{1+j}\begin{cases}\xi & \text{, if } K_2=K_1(1+j)\\ \dfrac{e^{[K_2-K_1(1+j)]\xi}-1}{K_2-K_1(1+j)} & \text{, otherwise}\end{cases} \qquad \text{(G-16.1)}$$

The solutions to partial differential equations (G-14) again apply the method of characteristics, since there is a similarity in form of differential equations (G-14) and (F-5), the ground characteristic transformation, i.e.,(s,r) can also be applied here, with the transformation, the following ordinary differential equations for P_2^1 and P_2^2 in r and s are obtained, respectively, as:

$$\frac{dP_2^1}{ds}+K_2P_2^1=\Lambda\cos\Lambda r\cdot\chi_{2_\xi}(r,s)-\sin\Lambda r\left[\frac{d\chi_{2\xi}}{d\xi}\right]_{r,s}+K_1P_1^1(s,r) \qquad \text{(G-17.1)}$$

$$\frac{dP_2^2}{ds}+K_2P_2^2=-\sin\Lambda r\left[\frac{\partial P_2^1(\theta,\xi)}{\partial\xi}\right]_{s,r}-\frac{\Lambda}{2}s\cdot\sin 2\Lambda r\left[\frac{d\chi_{2\xi}}{d\xi}\right]_{s,r}+\Lambda\cos\Lambda r\cdot P_2^1(s,r)$$
$$-\left[\frac{\Lambda}{2}\sin 2\Lambda r-s\cdot\Lambda^2\cos 2\Lambda r\right]\chi_{2_\xi}(s,r)+K_1P_1^2(s,r) \qquad \text{(G-17.2)}$$

The integrating factor for equations (G-17) is $e^{K_2 s}$.

Theoretically, the solutions to equations (G-17) are simple to solve. Upon applying the binomial series and other manipulations, the actual number of terms in each equation increases as integration is carried out.

Integrating equation (G-17.1) and imposing the condition that $P_2^1(s=0)=0$, and then, back transforming P_2^1 in terms of θ and ξ gives

$$P_2^1(\theta,\xi) = e^{-K_2\xi}(\phi_{1j} + \phi_{2j} + \phi_{3j}) \tag{G-18.1}$$

where,

$$\phi_{1j}(\theta,\xi) = \frac{K_1}{K}\sum_{j=0}^{\infty}\alpha_0^{1+j}\begin{cases} \frac{1}{R_1}\left[\left[\Lambda\cos\Lambda(\theta-\xi)+K_2\sin\Lambda(\theta-\xi)\right]\left(\frac{e^{R_1\xi}-1}{R_1}-\xi\right)-\sin\Lambda(\theta-\xi)(e^{R_1\xi}-1)\right] & \text{, if } R_1\neq 0 \\ \xi\left[\left[\Lambda\cos\Lambda(\theta-\xi)+K_2\sin\Lambda(\theta-\xi)\right]\frac{\xi}{2} - \sin\Lambda(\theta-\xi)\right] & \text{, otherwise} \end{cases} \tag{G-18.1.1}$$

$$\phi_{2j}(\theta,\xi) = K_1\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\begin{cases} g_1\frac{\xi^2}{2} + g_2\xi & \text{, if } R_1=0 \\ \frac{g_1}{R_1}\left[e^{R_1\xi}\left(\xi-\frac{1}{R_1}\right)+\frac{1}{R_1}\right] + \frac{g_2}{R_1}(e^{R_1\xi}-1) & \text{, otherwise} \end{cases} \tag{G-18.1.2}$$

$$\phi_{3j}(\theta,\xi) = K_1 g_3\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\begin{cases} -\frac{e^{-K_1\xi}-1}{K_1} & \text{, if } R_1=0 \\ \xi & \text{, if } R_2=0 \\ \frac{e^{R_2\xi}-1}{R_2} & \text{, otherwise} \end{cases} \tag{G-18.1.3}$$

with $R_1=K_2-K_1(1+j)$ and $R_2=K_2-K_1(2+j)$.

The first order term in the x_2 solution dose not contribute any information about the enhancement of x_2 at the limit cycle. This forces us to calculate the second order term, presumably some insights can be obtained.

The compexity of the P_2^2 solution is directly related to the number of terms in P_2^1 and P_1^2. It is found that the single summation terms in the P_1^2 solution generate double summation terms, i.e., expansion involving binomial series. In a more compact fashion, define the following terms:

$$g_1' = \frac{\alpha_0}{K}\left[\Lambda^2 \sin\Lambda(\theta-\xi) - K_1\Lambda\cos\Lambda(\theta-\xi)\right] \qquad \text{(G-19.1)}$$

$$g_2' = -\frac{\alpha_0^2\Lambda^2}{K_3}\sin\Lambda(\theta-\xi) \qquad \text{(G-19.2)}$$

$$g_3' = \frac{\alpha_0^2\Lambda^2}{K_3}\sin\Lambda(\theta-\xi) \qquad \text{(G-19.3)}$$

$$R_1 = K_2 - K_1(1+j) \qquad \text{(G-20.1)}$$

$$R_2 = K_2 - K_1(2+j) \qquad \text{(G-20.2)}$$

$$R_3 = K_2 - K_1(1+i+j) \qquad \text{(G-20.3)}$$

$$R_4 = K_2 - K_1(2+i+j) \qquad \text{(G-20.4)}$$

$$R_5 = K_2 - K_1(3+i+j) \qquad \text{(G-20.5)}$$

$$R_6 = K_2 - K_1(4+i+j) \qquad \text{(G-20.6)}$$

$$R_7 = K_1 i \qquad \text{(G-20.7)}$$

$$R_8 = K_1(i+1) \qquad \text{(G-20.8)}$$

$$R_9 = K_1(i+2) \qquad \text{(G-20.9)}$$

$$R_{10} = K_1(i+3) \qquad \text{(G-20.10)}$$

Integrating with great care, and after back transforming, the resulting equation for P_2^2 , in terms of the original independent variables, is

$$P_2^2(\theta,\xi) = e^{-K_2\xi}\Big\{-\sin\Lambda(\theta-\xi)\left[\alpha_{1j}(\theta,\xi)+\alpha_{2j}(\theta,\xi)+\alpha_{3j}(\theta,\xi)\right] - \frac{\Lambda}{2}\sin 2\Lambda(\theta-\xi)\cdot\alpha_{4j}(\theta,\xi)$$
$$+\Lambda\cos\Lambda(\theta-\xi)\left[\alpha_{5j}(\theta,\xi)+\alpha_{6j}(\theta,\xi)+\alpha_{7j}(\theta,\xi)\right]+\alpha_{8j}(\theta,\xi)+K_1\alpha_{9ij}(\theta,\xi)\Big\} \qquad \text{(G-21.1)}$$

where

$$\alpha_{1j}(\theta,\xi)=\frac{K_1}{K}\sum_{j=0}^{\infty}\alpha^{1+j}\begin{cases}\dfrac{\xi^3}{6}\left[(\Lambda^2-K_2^2)\sin\Lambda(\theta-\xi)-2K_2\Lambda\cos\Lambda(\theta-\xi)\right]+\xi^2\left[\Lambda\cos\Lambda(\theta-\xi)+K_2\sin\Lambda(\theta-\xi)\right] \\ \quad -\xi\sin\Lambda(\theta-\xi) & \text{, if } R_1=0 \\ \dfrac{1}{R_1}\left[\left(\dfrac{e^{R_1\xi}-1}{R_1^2}-\dfrac{\xi}{R_1}-\dfrac{\xi^2}{2}\right)\left[(\Lambda^2-K_2^2)\sin\Lambda(\theta-\xi)-2K_2\Lambda\cos\Lambda(\theta-\xi)\right]\right. \\ \quad \left.+2\left(\dfrac{e^{R_1\xi}-1}{R_1}-\xi\right)\left[\Lambda\cos\Lambda(\theta-\xi)+K_2\sin\Lambda(\theta-\xi)\right]-(e^{R_1\xi}-1)\sin\Lambda(\theta-\xi)\right] & \text{, otherwise}\end{cases}$$

(G-21.1.1)

$$\alpha_{2j}(\theta,\xi)=K_1\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\begin{cases}(g_1'-K_2g_1)\dfrac{\xi^3}{6}+(g_1+g_2'-K_2g_2)\dfrac{\xi^2}{2}+g_2\xi & \text{, if } R_1=0 \\ \dfrac{1}{R_1}\left[(g_1'-K_2g_1)\left[\dfrac{\xi}{R_1}(e^{R_1\xi}+1)-\dfrac{2(e^{R_1\xi}-1)}{R_1^2}\right]+g_1\left[e^{R_1\xi}\left(\xi-\dfrac{1}{R_1}\right)+\dfrac{1}{R_1}\right]\right. \\ \quad \left.+g_2(e^{R_1\xi}-1)+(g_2'-K_2g_2)\left[\dfrac{e^{R_1\xi}-1}{R_1}-\xi\right]\right] & \text{, otherwise}\end{cases}$$

(G-21.1.2)

$$\alpha_{3j}(\theta,\xi)=K_1\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\begin{cases}\dfrac{1}{K_1}\left[(g_3'-K_2g_3)\left(\dfrac{e^{K_1\xi}-1}{K_1}+\xi\right)-g_3(e^{-K_1\xi}-1)\right] & \text{, if } R_1=0. \\ \xi\left[g_3+(g_3'-K_2g_3)\dfrac{\xi}{2}\right] & \text{, if } R_2=0 \\ \dfrac{1}{R_2}\left[g_3(e^{R_2\xi}-1)+(g_3'-K_2g_3)\left[\dfrac{e^{R_2\xi}-1}{R_2}-\xi\right]\right] & \text{, otherwise}\end{cases}$$

(G-21.1.3)

$$\alpha_{4j}(\theta,\xi)=\frac{K_1}{K}\sum_{j=0}^{\infty}\alpha^{1+j}\begin{cases}\left(\frac{1}{2}-\frac{K_2\xi}{3}\right)\xi^2 & \text{, if } R_1=0\\[2ex] \frac{1}{R_1}\left[e^{R_1\xi}\left(\xi-\frac{1}{R_1}\right)+\frac{1}{R_1}-K_2\left[\frac{e^{R_1\xi}}{R_1}\left(\xi-\frac{1}{R_1}\right)+\frac{1}{R_1^2}-\frac{\xi^2}{2}\right]\right] & \text{, otherwise}\end{cases}$$

(G-21.1.4)

$$\alpha_{5j}(\theta,\xi)=\frac{K_1}{K}\sum_{j=0}^{\infty}\alpha^{1+j}\begin{cases}\frac{\xi^3}{6}-\frac{\xi^2}{2} & \text{, if } R_1=0\\[2ex] \frac{\Lambda\cos\Lambda(\theta-\xi)+K_2\sin\Lambda(\theta-\xi)}{R_1}\left(\frac{e^{R_1\xi}-1}{R_1^2}-\frac{\xi}{R_1}-\frac{\xi^2}{2}\right)-\sin\Lambda(\theta-\xi)\left(\frac{e^{R_1\xi}-1}{R_1^2}-\frac{\xi}{R_1}\right), & \text{otherwise}\end{cases}$$

(G-21.1.5)

$$\alpha_{6j}(\theta,\xi)=K_1\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\begin{cases}g_1\frac{\xi^3}{6}+g_2\frac{\xi^2}{2} & \text{, if } R_1=0\\[2ex] \frac{g_1}{R_1}\left[\frac{\xi}{R_1}\left(e^{R_1\xi}+1\right)-\frac{2\left(e^{R_1\xi}-1\right)}{R_1^2}\right]+\frac{g_2}{R_1}\left[\frac{e^{R_1\xi}-1}{R_1}-\xi\right] & \text{, otherwise}\end{cases}$$

(G-21.1.6)

$$\alpha_{7j}(\theta,\xi)=K_1\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}g_3\begin{cases}\frac{1}{K_1}\left(\frac{e^{-K_1\xi}-1}{K_1}+\xi\right) & \text{, if } R_1=0\\[2ex] \frac{\xi^2}{2} & \text{, if } R_2=0\\[2ex] \frac{1}{R_2}\left(\frac{e^{R_2\xi}-1}{R_2}-\xi\right) & \text{, otherwise}\end{cases} \quad \text{(G-21.1.7)}$$

$$\alpha_{8j}(\theta,\xi) = \frac{K_1}{K}\sum_{j=0}^{\infty}\alpha^{j+1}\begin{cases} \xi^2\Lambda\left[\frac{1}{4}\sin 2\Lambda(\theta-\xi) - \frac{\Lambda}{3}\xi\cos 2\Lambda(\theta-\xi)\right] & \text{, if } R_1=0 \\ \frac{1}{R_1}\left[\frac{\Lambda}{2}\sin 2\Lambda(\theta-\xi)\left[\frac{e^{R_1\xi}-1}{R_1}-\xi\right] - \Lambda^2\cos 2\Lambda(\theta-\xi)\left[\frac{e^{R_1\xi}}{R_1}\left(\xi-\frac{1}{R_1}\right)+\frac{1}{R_1^2}-\frac{\xi^2}{2}\right]\right] & \text{, otherwise} \end{cases}$$

(G-21.1.8)

$$\begin{aligned}\alpha_{9ij}(\theta,\xi) = {}& \alpha_{10j}(\theta,\xi) + \alpha_{11j}(\theta,\xi) + K_1\sin\Lambda(\theta-\xi)\left[\alpha_{12ij}(\theta,\xi) + \alpha_{13ij}(\theta,\xi) + \alpha_{14ij}(\theta,\xi)\right. \\ & \left. + \alpha_{15ij}(\theta,\xi) + \alpha_{16ij}(\theta,\xi) + \alpha_{17ij}(\theta,\xi)\right] \\ & + K_3\left[\alpha_{18ij}(\theta,\xi) + \alpha_{19ij}(\theta,\xi) + \alpha_{20ij}(\theta,\xi) + \alpha_{21ij}(\theta,\xi) + \alpha_{22ij}(\theta,\xi) + \alpha_{23ij}(\theta,\xi)\right]\end{aligned}$$

(G-21.1.9)

where

$$\alpha_{10j}(\theta,\xi) = \sum_{j=0}^{\infty}(1+j)\alpha_0^j\begin{cases} T_1(\theta,\xi) + T_2(\theta,\xi) + T_3(\theta,\xi) + T_4(\theta,\xi) & \text{, if } R_1=0 \\ T_{5j}(\theta,\xi) + T_{6j}(\theta,\xi) + T_{7j}(\theta,\xi) - T_{8j}(\theta,\xi) - T_{9j}(\theta,\xi) & \text{, otherwise} \end{cases}$$

(G-21.1.10)

with

$$\begin{aligned}T_1(\theta,\xi) = -\xi\alpha_0\sin\Lambda(\theta-\xi)\Big\{&\sin\Lambda(\theta-\xi)\left[\left(\frac{K_1}{K}-\frac{\Lambda^2\alpha_0}{K_3}\right)\frac{\xi}{2}+\frac{\xi^2}{6K}+\frac{\alpha_0}{K_1K_3}\right] \\ & +\Lambda\cos\Lambda(\theta-\xi)\left[\frac{\xi}{2K}-\frac{\alpha_0}{K_3}-\frac{K_1\xi^2}{6K}\right]\Big\}\end{aligned} \quad \text{(G-21.1.10a)}$$

$$T_2(\theta,\xi) = \xi\left[K_1\sin\Lambda(\theta-\xi) + \Lambda\cos\Lambda(\theta-\xi)\right]\left(g_1\frac{\xi^2}{6} + \frac{g_3}{K_1} + \frac{g_2}{2}\xi\right) \quad \text{(G-21.1.10b)}$$

$$T_3(\theta,\xi) = \alpha_0\Lambda\frac{\xi}{2}\sin 2\Lambda(\theta-\xi)\left(\frac{K_1\xi^2}{6K} - \frac{\xi}{2K} + \frac{\alpha_0}{K_3}\right) \quad \text{(G-21.1.10c)}$$

$$T_4(\theta,\xi) = \xi\alpha_0\Lambda^2\cos 2\Lambda(\theta-\xi)\left(\frac{\xi^2}{6K} - \frac{\alpha_0}{K_1K_3}\right) \quad \text{(G-21.1.10d)}$$

$$T_{5j}(\theta,\xi)=-\alpha_0\sin\Lambda(\theta-\xi)\Bigg\{\sin\Lambda(\theta-\xi)\Big[\frac{\Lambda^2 e^{R_1\xi}}{2KR_1}(\xi^2-\frac{2\xi}{R_1}+\frac{2}{R_1^2})-\frac{\Lambda^2}{KR_1^3}+\frac{\alpha_0\Lambda^2(e^{R_1\xi}-1)}{K_1K_3R_1}$$
$$\Big(\frac{1}{R_1^2}+\frac{e^{R_1\xi}}{R_1}(\xi-\frac{1}{R_1})\Big)\Big(\frac{K_1}{K}-\frac{\alpha_0\Lambda^2}{K_3}\Big)\Big]$$
$$+\Lambda\cos\Lambda(\theta-\xi)\Big[\Big(\frac{e^{R_1\xi}}{KR_1}(\xi-\frac{1}{R_1})+\frac{1}{KR_1^2}\Big)\Big(1-\frac{K_1}{R_1}\Big)-\frac{K_1e^{R_1\xi}\cdot\xi^2}{2KR_1}-\frac{\alpha_0(e^{R_1\xi}-1)}{K_3R_1}\Big]\Bigg\}$$

(G-21.1.10e)

$$T_{6j}(\theta,\xi)=\Big[K_1\sin\Lambda(\theta-\xi)+\Lambda\cos\Lambda(\theta-\xi)\Big]\Bigg\{\frac{g_1}{2}\Big[\frac{e^{R_1\xi}}{R_1}(\xi^2-\frac{2\xi}{R_1}+\frac{2}{R_1^2})-\frac{2}{R_1^3}\Big]+\frac{g_3}{K_1R_1}(e^{R_1\xi}-1)$$
$$+g_2\Big[\frac{e^{R_1\xi}}{R_1}(\xi-\frac{1}{R_1})+\frac{1}{R_1^2}\Big]\Bigg\}\qquad\text{(G-21.1.10f)}$$

$$T_{7j}(\theta,\xi)=\frac{\alpha_0\Lambda}{2K}\Big[\frac{K_1}{2}\sin2\Lambda(\theta-\xi)+\Lambda\cos2\Lambda(\theta-\xi)\Big]\Big[\frac{e^{R_1\xi}}{R_1}(\xi^2-\frac{2\xi}{R_1}+\frac{2}{R_1^2})-\frac{2}{R_1^3}\Big]$$

(G-21.1.10g)

$$T_{8j}(\theta,\xi)=\frac{\Lambda\alpha_0^2}{K_2}\Big[\frac{\Lambda}{K_1}\cos2\Lambda(\theta-\xi)-\frac{1}{2}\sin2\Lambda(\theta-\xi)\Big]\frac{e^{R_1\xi}-1}{R_1}\qquad\text{(G-21.1.10h)}$$

$$T_{9j}(\theta,\xi)=\frac{\alpha_0\Lambda\sin2\Lambda(\theta-\xi)}{2K}\Big[\frac{e^{R_1\xi}}{R_1}(\xi-\frac{1}{R_1})+\frac{1}{R_1^2}\Big]\qquad\text{(G-21.1.10i)}$$

$$\alpha_{11j}(\theta,\xi)=\sum_{j=0}^{\infty}(1+j)\alpha_0^j\begin{cases}-\dfrac{(e^{-K_1\xi}-1)T_{10}(\theta,\xi)}{K_1}-\dfrac{\alpha_0^2\Lambda^2}{K_1K_3}\cos2\Lambda(\theta-\xi)\Big[e^{-K_1\xi}(\xi+\frac{1}{K_1})-\frac{1}{K_1}\Big] & \text{, if } R_1=0\\[2ex] T_{10}(\theta,\xi)\cdot\xi+\dfrac{\alpha_0^2\Lambda^2}{2K_3}\cos2\Lambda(\theta-\xi)\cdot\xi^2 & \text{, if } R_2=0\\[2ex] T_{10}(\theta,\xi)\dfrac{e^{R_1\xi}-1}{R_1}+\dfrac{\alpha_0^2\Lambda^2}{K_3}\cos2\Lambda(\theta-\xi)\Big[\frac{e^{R_1\xi}}{R_1}(\xi-\frac{1}{R_1})+\frac{1}{R_1^2}\Big] & \text{, otherwise}\end{cases}$$

(G-21.1.11)

with

$$T_{10}(\theta,\xi)=\sin\Lambda(\theta-\xi)\left[\frac{\Lambda^2\alpha_0^2}{K_1K_3}\sin\Lambda(\theta-\xi)-\frac{\Lambda\alpha_0^2}{K_3}\cos\Lambda(\theta-\xi)-g_3\right]-\Lambda\cos\Lambda(\theta-\xi)\frac{g_3}{K_1}$$
$$+\frac{\alpha_0^2\Lambda^2}{K_1K_3}\cos 2\Lambda(\theta-\xi)-\frac{\alpha_0^2\Lambda}{2K_3}\sin 2\Lambda(\theta-\xi) \qquad \text{(G-21.1.11a)}$$

$$\alpha_{12ij}(\theta,\xi)=\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=1}^{\infty}\alpha_0^i\left[\frac{g_1}{R_7^2}+\frac{g_3}{R_8}+\frac{g_2}{R_7}\right]\begin{cases}\xi & \text{, if } R_1=0\\ \dfrac{e^{R_1\xi}-1}{R_1} & \text{, otherwise}\end{cases} \qquad \text{(G-21.1.12)}$$

$$\alpha_{13ij}(\theta,\xi)=\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}\alpha_0^{i+1}\left[\frac{g_1}{R_8^2}+\frac{g_3}{R_9}+\frac{g_2}{R_8}\right]\begin{cases}\xi & \text{, if } R_1=0\\ \dfrac{e^{R_1\xi}-1}{R_1} & \text{, otherwise}\end{cases} \qquad \text{(G-21.1.13)}$$

$$\alpha_{14ij}(\theta,\xi)=-\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=1}^{\infty}\frac{\alpha_0^i}{R_7}\begin{cases}g_1\left[-\dfrac{e^{-R_7\xi}}{R_7}\left(\xi+\dfrac{1}{R_7}\right)+\dfrac{1}{R_7^2}\right]-\dfrac{g_1}{R_7^2}\left(e^{-R_7\xi}-1\right)-\dfrac{g_2}{R_7}\left(e^{-R_7\xi}-1\right) & \text{if } R_1=0\\ \dfrac{g_1}{2}\xi^2+\left(\dfrac{g_1}{R_7}+g_2\right)\xi & \text{if } R_3=0\\ g_1\left[\dfrac{e^{R_3\xi}}{R_3}\left(\xi-\dfrac{1}{R_3}\right)+\dfrac{1}{R_3^2}\right]+\dfrac{g_1}{K_1 i}\dfrac{\left(e^{R_3\xi}-1\right)}{R_3}+\dfrac{g_2}{R_3}\left(e^{R_3\xi}-1\right), & \text{otherwise}\end{cases}$$

(G-21.1.14)

$$\alpha_{15ij}(\theta,\xi)=-\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=1}^{\infty}\frac{\alpha_0^i}{R_8}\begin{cases}-\dfrac{g_3}{R_8}\left(e^{-R_8\xi}-1\right) & \text{, if } R_1=0\\ g_3\xi & \text{, if } R_4=0\\ \dfrac{g_3}{R_4}\left(e^{R_4\xi}-1\right) & \text{, otherwise}\end{cases} \qquad \text{(G-21.1.15)}$$

$$\alpha_{16ij}(\theta,\xi)=-\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}\frac{\alpha_0^{i+1}}{R_8}\begin{cases}\frac{g_1}{R_8}\left[\frac{1}{R_8}-e^{-R_8\xi}\left(\xi+\frac{1}{R_8}\right)\right]-\frac{e^{-R_8\xi}-1}{R_8}\left(\frac{g_1}{R_8}+g_2\right), & \text{if } R_1=0\\ g_1\frac{\xi^2}{2}+\xi\left(\frac{g_1}{R_8}+g_2\right), & \text{if } R_4=0\\ g_1\left[\frac{e^{R_4\xi}}{R_4}\left(\xi-\frac{1}{R_4}\right)+\frac{1}{R_4^2}\right]+\left(\frac{g_1}{R_8}+g_2\right)\left(\frac{e^{R_4\xi}-1}{R_4}\right), & \text{otherwise}\end{cases}$$

(G-21.1.16)

$$\alpha_{17ij}(\theta,\xi)=-\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}\frac{\alpha_0^{i+1}}{R_9}\begin{cases}-\frac{g_3}{R_9}\left(e^{-R_9\xi}-1\right), & \text{if } R_1=0\\ g_3\xi, & \text{if } R_4=0\\ \frac{g_3}{R_5}\left(e^{R_5\xi}-1\right), & \text{otherwise}\end{cases}$$

(G-21.1.17)

$$\alpha_{18ij}(\theta,\xi)=\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}(1+i)\frac{\alpha_0^{i}}{R_8}\begin{cases}\frac{g_1^2}{R_8}\left[-e^{-R_8\xi}\left(\xi^2+\frac{2\xi}{R_8}+\frac{2}{R_8^2}\right)+\frac{2}{R_8^2}-\frac{2e^{-R_8\xi}}{R_8}\left(\xi+\frac{1}{R_8}\right)+\frac{2}{R_8^2}-\frac{2(e^{-R_8\xi}-1)}{R_8^2}\right]\\ \quad+\frac{2g_1g_2}{R_8}\left[-e^{-R_8\xi}\left(\xi+\frac{1}{R_8}\right)+\frac{1}{R_8}-\frac{e^{-R_8\xi}-1}{R_8}\right]-\frac{g_2^2}{R_8}\left(e^{-R_8\xi}-1\right), & \text{if } R_1=0\\ \xi g_1^2\left(\frac{\xi^2}{3}+\frac{\xi}{R_8}+\frac{2}{R_8^2}\right)+2g_1g_2\xi\left(\frac{\xi}{2}+\frac{1}{R_8}\right)+g_2^2\xi, & \text{if } R_4=0\\ g_1^2\left[\frac{e^{R_4\xi}}{R_4}\left(\xi^2-\frac{2\xi}{R_4}+\frac{2}{R_4^2}\right)-\frac{2}{R_4^3}+\frac{2e^{R_4\xi}}{R_4R_8}\left(\xi-\frac{1}{R_4}\right)+\frac{2}{R_4^2R_8}\right.\\ \quad\left.+\frac{2(e^{R_4\xi}-1)}{R_8^2R_4}\right]+2g_1g_2\left[\frac{e^{R_4\xi}}{R_4}\left(\xi-\frac{1}{R_4}\right)+\frac{1}{R_4^2}+\frac{e^{R_4\xi}-1}{R_8R_4}\right]+\frac{g_2^2(e^{R_4\xi}-1)}{R_4}, & \text{otherwise}\end{cases}$$

(G-21.1.18)

$$\alpha_{19ij}(\theta,\xi)=-\sum_{j=0}^{\infty}\alpha_0^j(1+j)\sum_{i=0}^{\infty}(1+i)\frac{\alpha_0^i}{R_8}\left(\frac{2g_1^2}{R_8^2}+\frac{2g_1g_2}{R_8}+g_2^2\right)\begin{cases}\xi & \text{, if } R_1=0\\ \frac{e^{R_1\xi}-1}{R_1} & \text{, otherwise}\end{cases} \quad \text{(G-21.1.19)}$$

$$\alpha_{20ij}(\theta,\xi)=\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}(1+i)\frac{\alpha_0^i}{R_9}\begin{cases}\frac{2g_1g_3}{R_9}\left[-e^{-R_9\xi}\left(\xi+\frac{1}{R_9}\right)+\frac{1}{R_9}-\frac{e^{-R_9\xi}-1}{R_9}\right]-\frac{2g_2g_3}{R_9}\left(e^{-R_9\xi}-1\right), & \text{if } R_1=0\\ 2g_1g_3\xi\left(\frac{\xi}{2}+\frac{1}{R_9}\right)+2g_2g_3\xi & \text{, if } R_5=0\\ 2g_1g_3\left[\frac{e^{R_5\xi}}{R_5}\left(\xi-\frac{1}{R_5}\right)+\frac{1}{R_5^2}+\frac{e^{R_5\xi}-1}{R_9R_5}\right]+\frac{2g_2g_3}{R_5}\left(e^{R_5\xi}-1\right), & \text{otherwise}\end{cases}$$

(G-21.1.20)

$$\alpha_{21ij}(\theta,\xi)=-\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}(1+i)\frac{\alpha_0^i}{R_9}\begin{cases}\left(\frac{2g_1g_3}{R_9}+2g_2g_3\right)\xi & \text{, if } R_1=0\\ \left(\frac{2g_1g_3}{R_9}+2g_2g_3\right)\frac{e^{R_1\xi}-1}{R_1}, & \text{otherwise}\end{cases} \quad \text{(G-21.1.21)}$$

$$\alpha_{22ij}(\theta,\xi)=\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}(1+i)\frac{\alpha_0^i}{R_{10}}g_3^2\begin{cases}-\frac{e^{-R_{10}\xi}-1}{R_{10}} & \text{, if } R_1=0\\ \xi & \text{, if } R_6=0\\ \frac{e^{R_6\xi}-1}{R_6} & \text{, otherwise}\end{cases} \quad \text{(G-21.1.22)}$$

$$\alpha_{23ij}(\theta,\xi)=-\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}(1+i)\frac{\alpha_0^i}{R_{10}}g_3^2\begin{cases}\xi & \text{, if } R_1=0\\ \frac{e^{R_1\xi}-1}{R_1} & \text{, otherwise}\end{cases} \quad \text{(G-21.1.23)}$$

Substituting equations (G-16.1), (G-18) and (G-21) into equation (G-3.2) yields the global solution for $x_2(\theta,\xi)$.

APPENDIX H

ASYMPTOTIC SOLUTION TO x_1 AND x_2 IN THE PLUG FLOW TUBULAR REACTOR AT θ_∞

APPENDIX H

ASYMPTOTIC SOLUTION TO x_1 AND x_2 IN THE PLUG FLOW TUBULAR REACTOR AT θ_∞

With the closed form solution to x_1 and x_2 available, long time behavior of the concentration of species A and B can be determined. This is done for comparison with respect to a steady state (i.e., optimal or non-optimal). Here it is assumed that at infinite time the process dynamics is a limit cycle. So the comparison should be the time-average at the limit cycle, i.e.,

$$J = \frac{1}{T^{\circ}} \oint g \, d\theta_\infty$$

(The notations are described in chapter 2)

Recalling equations (G-7.1), (G-10.1), (G-13) and equations (G-16.1), (G-18), (G-21) from Appendix G, the independent variable θ appears only in the trigonometric functions. Hence, these equations at θ_∞ yields the exact equations with θ replaced by θ_∞. The length of each time period is $\frac{2\pi}{\Lambda}$ for both x_1 and x_2 equations.

With the asymptotic form for equations (G-7.1), (G-10.1), (G-13), (G-16.1), (G-18) and (G-21), the first order terms (equations (G-10.1) and (G-18)) are all composed of only sines and cosines. Their integrals over a period vanish, and hence no information about enhancement can be provided.

The second order terms,as shown in equations (G-13) and (G-21) contain sines and cosines which drop out after time-averaging. However, those same second order terms in the perturbation solution also contain squares of sine and cosine which do not vanish upon time-averaging. In addition to this, there are other terms which are θ independent that are non-zero after time-averaging. Consequently, the contribution of these terms in ϵ^2 makes the final solution to the time-average x_1 and x_2 different from their respective steady state solution.

The solutions to time-average x_1 and x_2 yield, after simplification, (with ARG$=1-\alpha_0 e^{-K_1\xi}$ for convenience),

$$\bar{X}_1(\xi)=\frac{e^{-K_1\xi}}{ARG}\left[\frac{\alpha_0}{K}+\frac{\epsilon^2}{ARG}\left(\Omega_1-\Omega_{2i}-\Omega_{3i}+K_3\alpha_0^2\Lambda\Omega_{4i}\right)\right] \tag{H-1.1}$$

where

$$\Omega_1=\frac{K_1\alpha_0\Lambda}{2K}\xi\left(\frac{K_1\xi}{2}-1\right) \tag{H-1.1.1}$$

$$\Omega_{2i}=\frac{K_1^2\alpha_0\Lambda}{2K}\sum_{i=1}^{\infty}\frac{\alpha_0^i}{R_7}\left(e^{-R_7\xi}\cdot\xi+\frac{e^{-R_7\xi}-1}{R_7}\right) \tag{H-1.1.2}$$

$$\Omega_{3i}=\frac{K_1^2\alpha_0\Lambda}{2K}\sum_{i=0}^{\infty}\frac{\alpha_0^{R_8}}{R_8}\left(e^{-R_8\xi}\cdot\xi+\frac{e^{-R_8\xi}-1}{R_8}\right) \tag{H-1.1.3}$$

$$\Omega_{4i}=\sum_{i=0}^{\infty}(1+i)\alpha_0^i\left(\Omega_{5i}-\Omega_{6i}+\Omega_{7i}+\Omega_{8i}-\Omega_{9i}+\Omega_{10i}\right) \tag{H-1.1.4}$$

with

$$\Omega_{5i}=\frac{\Lambda^2+K_1^2}{2K_2^2}\left[\frac{e^{-R_8\xi}}{R_8}\left(\xi^2+\frac{2\xi}{R_8}+\frac{2}{R_8^2}\right)-\frac{2}{R_8^3}\right] \tag{H-1.1.5}$$

$$\Omega_{6i} = \frac{\alpha_0 \Lambda^2}{K_3 K}\left[\frac{e^{-R_8\xi}}{R_8}(\xi + \frac{1}{R_8}) - \frac{1}{R_8^2}\right] \tag{H-1.1.6}$$

$$\Omega_{7i} = \frac{\alpha_0^2 \Lambda^2}{2K_3^2}\left(\frac{e^{-R_8\xi}-1}{R_8}\right) \tag{H-1.1.7}$$

$$\Omega_{8i} = \frac{\alpha_0 \Lambda^2}{K_3 K}\left[\frac{e^{-R_9\xi}}{R_9}(\xi + \frac{1}{R_9}) - \frac{1}{R_9^2}\right] \tag{H-1.1.8}$$

$$\Omega_{9i} = \frac{\alpha_0^2 \Lambda^2}{K_3^2}\left(\frac{e^{-R_9\xi}-1}{R_9}\right) \tag{H-1.1.9}$$

$$\Omega_{10i} = \frac{\alpha_0^2 \Lambda^2}{2K_3^2}\frac{(e^{-R_9\xi}-1)}{R_9} \tag{H-1.1.10}$$

and

$$\bar{X}_2(\xi) = e^{-K_2\xi}\frac{K_1}{K}\sum_{j=0}^{\infty}\alpha_0^{1+j}\begin{cases}\xi & \text{, if } R_1=0\\ \dfrac{e^{R_1\xi}-1}{R_1} & \text{, otherwise}\end{cases}$$

$$+\epsilon^2 e^{-K_2\xi}\left[\beta_{1j} + \beta_{2j} + K_1\sum_{k=1}^{13}(\beta_{kij})\right] \tag{H-2.1}$$

where

$$\beta_{1j} = \frac{K_1}{K}\sum_{j=0}^{\infty}\alpha_0^{1+j}\begin{cases}\dfrac{\xi}{2}\left(\dfrac{K_2^2\xi^2}{6} - K_2\xi + 1\right) & \text{, if } R_1=0\\ \dfrac{1}{R_1}\left[\dfrac{K_2^2}{2}\left(\dfrac{e^{R_1\xi}-1}{R_1^2} - \dfrac{\xi}{R_1} - \dfrac{\xi^2}{2}\right) - K_2\left(\dfrac{e^{R_1\xi}-1}{R_1} - \xi\right) + \dfrac{e^{R_1\xi}-1}{2}\right] & \text{, otherwise}\end{cases} \tag{H-2.1.1}$$

$$\beta_{2j} = \frac{K_1^2\alpha_0}{2K}\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\begin{cases}\dfrac{\xi^2}{2}\left(\dfrac{K_2\xi}{3} - 1\right) & \text{, if } R_1=0\\ \dfrac{1}{R}\left[K_2\left[\dfrac{\xi}{R_1}(e^{R_1\xi}+1) - \dfrac{2(e^{R_1\xi}-1)}{R_1^2}\right] - \left[e^{R_1\xi}(\xi - \dfrac{1}{R_1}) + \dfrac{1}{R_1}\right]\right] & \text{, otherwise}\end{cases} \tag{H-2.1.2}$$

$$\beta_{3ij}=\frac{K_1\alpha_0}{2K}\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\begin{cases}\dfrac{\xi^2}{2}\left(\dfrac{K_1\xi}{3}-1\right) & \text{, if } R_1=0\\[2ex] \dfrac{1}{R_1}\left[\dfrac{K_1}{2}\left[e^{R_1\xi}\left(\xi^2-\dfrac{2\xi}{R_1}+\dfrac{2}{R_1^2}\right)-\dfrac{2}{R_1^2}\right]-\left[e^{R_1\xi}\left(\xi-\dfrac{1}{R_1}\right)+\dfrac{1}{R_1}\right]\right] & \text{, otherwise}\end{cases}$$

(H-2.1.3)

$$\beta_{4ij}=\frac{\alpha_0K_1^2}{2K}\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\sum_{i=1}^{\infty}\frac{\alpha_0^{i}}{R_7^2}\begin{cases}\xi & \text{, if } R_1=0\\[2ex] \dfrac{e^{R_1\xi}-1}{R_1} & \text{, otherwise}\end{cases}\qquad\text{(H-2.1.4)}$$

$$\beta_{5ij}=\frac{\alpha_0K_1^2}{2K}\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\sum_{i=0}^{\infty}\frac{\alpha_0^{i+1}}{R_8^2}\begin{cases}\xi & \text{, if } R_1=0\\[2ex] \dfrac{e^{R_1\xi}-1}{R_1} & \text{, otherwise}\end{cases}\qquad\text{(H-2.1.5)}$$

$$\beta_{6ij}=-\frac{\alpha_0K_1^2}{2K}\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\sum_{i=1}^{\infty}\frac{\alpha_0^{i}}{R_7}\begin{cases}-\dfrac{2(e^{-R_7\xi}-1)}{R_7^2}-\dfrac{\xi e^{-R_7\xi}}{R_7} & \text{, if } R_1=0\\[2ex] \xi\left(\dfrac{\xi}{2}+\dfrac{1}{R_7}\right) & \text{, if } R_3=0\\[2ex] \dfrac{e^{R_3\xi}}{R_3}\left(\xi-\dfrac{1}{R_3}\right)+\dfrac{1}{R_3^2}+\dfrac{e^{R_3\xi}-1}{R_7R_3} & \text{, otherwise}\end{cases}\qquad\text{(H-2.1.6)}$$

$$\beta_{7ij}=-\frac{K_1^2\alpha_0}{2K}\sum_{j=0}^{\infty}(1+j)\alpha_0^{j}\sum_{i=0}^{\infty}\frac{\alpha_0^{i+1}}{R_8}\begin{cases}-\dfrac{2(e^{-R_8\xi}-1)}{R_8^2}-\dfrac{\xi e^{-R_8\xi}}{R_8} & \text{, if } R_1=0\\[2ex] \xi\left(\dfrac{\xi}{2}+\dfrac{1}{R_8}\right) & \text{, if } R_4=0\\[2ex] \dfrac{e^{R_4\xi}}{R_4}\left(\xi-\dfrac{1}{R_4}\right)+\dfrac{1}{R_4^2}+\dfrac{e^{R_4\xi}-1}{R_8R_4} & \text{, otherwise}\end{cases}\qquad\text{(H-2.1.7)}$$

$$\beta_{8ij} = \frac{K_3\alpha_0^2(\Lambda^2+K_1^2)}{2K^2}\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}(1+i)\frac{\alpha_0^i}{R_8}\begin{cases} -\frac{4e^{-R_8\xi}}{R_8^2}\left(\xi+\frac{1}{R_8}\right)+\frac{4}{R_8^3}-\frac{\xi^2 e^{-R_8\xi}}{R_8}-\frac{2(e^{-R_8\xi}-1)}{R_8^3}-\frac{2\xi}{R_8^2}, & \text{if } R_1=0 \\ \frac{\xi^3}{3}+\frac{\xi^2}{R_8}+\frac{2\xi}{R_8^2}-\frac{2(e^{R_1\xi}-1)}{R_8^2R_1}, & \text{if } R_4=0 \\ \frac{e^{R_4\xi}}{R_4}\left(\xi^2-\frac{2\xi}{R_4}-\frac{2}{R_4^2}\right)+\frac{2e^{R_4\xi}}{R_8R_4}\left(\xi-\frac{1}{R_4}\right)-\frac{2}{R_4^3}+\frac{2}{R_8R_4^2} \\ \quad +\frac{2(e^{R_4\xi}-1)}{R_8^2R_4}-\frac{2(e^{R_1\xi}-1)}{R_8^2R_1}, & \text{otherwise} \end{cases} \tag{H-2.1.8}$$

$$\beta_{9ij} = \frac{\alpha_0^3\Lambda^2}{K}\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}\frac{\alpha_0^i}{R_8}\begin{cases} -\frac{2(e^{-R_8\xi}-1)}{R_8^2}-\frac{\xi}{R_8}(e^{-R_8\xi}+1), & \text{if } R_1=0 \\ \xi\left(\frac{\xi}{2}+\frac{1}{R_8}\right)-\frac{e^{R_1\xi}-1}{R_8R_1}, & \text{if } R_4=0 \\ \frac{e^{R_4\xi}}{R_4}\left(\xi-\frac{1}{R_4}\right)+\frac{1}{R_4^2}+\frac{e^{R_4\xi}-1}{R_8R_4}-\frac{e^{R_1\xi}-1}{R_8R_1}, & \text{otherwise} \end{cases} \tag{H-2.1.9}$$

$$\beta_{10ij} = \frac{\alpha_0^4\Lambda^2}{2K_3}\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{\infty}(1+i)\frac{\alpha_0^i}{R_8}\begin{cases} -\frac{(e^{-R_8\xi}-1)}{R_8}-\xi, & \text{if } R_1=0 \\ \xi-\frac{(e^{R_1\xi}-1)}{R_1}, & \text{if } R_4=0 \\ \frac{e^{R_4\xi}-1}{R_4}-\frac{e^{R_1\xi}-1}{R_1}, & \text{otherwise} \end{cases} \tag{H-2.1.10}$$

$$\beta_{11ij} = \frac{\alpha_0^3\Lambda^2}{K}\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{j}(1+i)\frac{\alpha_0^i}{R_9}\begin{cases} -\dfrac{2(e^{-R_9\xi}-1)}{R_9^2}-\dfrac{\xi}{R_9}(e^{-R_9\xi}+1), & \text{if } R_1=0 \\[2ex] \xi\left(\dfrac{\xi}{2}+\dfrac{1}{R_9}\right)-\dfrac{e^{R_1\xi}-1}{R_9R_1}, & \text{if } R_5=0 \\[2ex] \dfrac{e^{R_5\xi}}{R_5}\left(\xi-\dfrac{1}{R_5}\right)+\dfrac{1}{R_5^2}+\dfrac{e^{R_5\xi}}{R_9R_5}-\dfrac{e^{R_1\xi}-1}{R_9R_1}, & \text{otherwise} \end{cases} \qquad \text{(H-2.1.11)}$$

$$\beta_{12ij} = -\frac{\alpha_0^4\Lambda^2}{K_3}\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{j}(1+i)\frac{\alpha_0^i}{R_9}\begin{cases} -\dfrac{e^{-R_9\xi}-1}{R_9}-\xi, & \text{if } R_1=0 \\[2ex] \xi-\dfrac{e^{R_1\xi}-1}{R_1}, & \text{if } R_5=0 \\[2ex] \dfrac{e^{R_5\xi}-1}{R_5}-\dfrac{e^{R_1\xi}-1}{R_1}, & \text{otherwise} \end{cases} \qquad \text{(H-2.1.12)}$$

$$\beta_{13ij} = \frac{\alpha_0^4\Lambda^2}{2K_3}\sum_{j=0}^{\infty}(1+j)\alpha_0^j\sum_{i=0}^{j}(1+i)\frac{\alpha_0^i}{R_{10}}\begin{cases} -\dfrac{e^{-R_{10}\xi}-1}{R_{10}}-\xi, & \text{if } R_1=0 \\[2ex] \xi-\dfrac{e^{R_1\xi}-1}{R_1}, & \text{if } R_6=0 \\[2ex] \dfrac{e^{R_6\xi}-1}{R_6}-\dfrac{e^{R_1\xi}-1}{R_1}, & \text{otherwise} \end{cases} \qquad \text{(H-2.1.13)}$$

The equation for average conversion of A can be readily obtained by subtracting equation (H-1.1) from unity.

APPENDIX I

EVALUATION OF BOUNDARY CONDITIONS FOR P_1^1 AND P_1^2

APPENDIX I

EVALUATION OF BOUNDARY CONDITIONS FOR P_1^1 AND P_1^2

In the succeeding derivation of the boundary conditions for P_1^1 and P_1^2, all perturbation terms are evaluated at $\xi=0$.

From Appendix G,

$$\chi_1(\xi,\theta)=\chi_{1_S}(\xi)+\epsilon P_1^1(\xi,\theta)+\epsilon^2 P_1^2(\xi,\theta) \tag{G-3.1}$$

At the reactor entrance, only pure A is present,

$$\therefore \quad \chi_1(\xi=0,\theta)=1.0=\chi_{1_S}+\epsilon P_1^1(\xi=0,\theta)+\epsilon^2 P_1^2(\xi=0,\theta)$$

[when there is no perturbation, i.e., $\epsilon=0$, we recover $\chi_{1_S}(0)=1$]

$$\therefore \quad 0=\epsilon P_1^1(0,\theta)+\epsilon^2 P_1^2(0,\theta) \tag{I-1.1}$$

evaluate equations (G-5) at $\xi=0$:

$$\frac{\partial P_1^1}{\partial\theta}+\frac{\partial P_1^1}{\partial\xi}-(K_1+K_3)\sin\Lambda\theta-\Lambda\cos\Lambda\theta=-(K_1+2K_3)P_1^1 \tag{I-2.1}$$

$$\frac{\partial P_1^2}{\partial\theta}+\frac{\partial P_1^2}{\partial\xi}+\sin\Lambda\theta\,\frac{\partial P_1^1}{\partial\xi}-P_1^1\Lambda\cos\Lambda\theta+\frac{\Lambda}{2}\sin 2\Lambda\theta=-K_3P_1^2-K_3\left[2P_1^2+(P_1^1)^2\right] \tag{I-2.2}$$

evaluate equation (G-2.1) at $\xi=0$ yields:

$$(1+\epsilon\sin\Lambda\theta)\frac{d\chi_1}{d\xi}+\left(\frac{\Lambda\epsilon^2}{2}\sin 2\Lambda\theta-\epsilon\Lambda\cos\Lambda\theta\right)=-K_1-K_3 \tag{I-3.1}$$

Differentiate equation (G-3.1) with respect to ξ and then evaluate at ξ =0, thus,

$$\frac{\partial \chi_1}{\partial \xi} = \frac{\partial \chi_{1s}}{\partial \xi} + \epsilon \frac{\partial P_1^1}{\partial \xi} + \epsilon^2 \frac{\partial P_1^2}{\partial \xi} \qquad \text{(I-4.1)}$$

but

$$\frac{\partial \chi_{1s}}{\partial \xi} = -K_1 \chi_{1s} - K_3 \chi_{1s}^2$$

substitute this into equation (I-4.1) for $\frac{\partial \chi_{1s}}{\partial \xi}$ and multiplying the resulting equation by $(1+\epsilon \sin\Lambda\theta)$, thus

$$(1+\epsilon \sin\Lambda\theta)\frac{\partial \chi_1}{\partial \xi} = -(K_1+K_3)(1+\epsilon\sin\Lambda\theta) + \epsilon(1+\epsilon\sin\Lambda\theta)\frac{\partial P_1^1}{\partial \xi} + \epsilon^2(1+\epsilon\sin\Lambda\theta)\frac{\partial P_1^2}{\partial \xi} \qquad \text{(I-4.1.1)}$$

Rearranging equation (I-3.1) and equating to (I-4.1.1). Upon neglecting terms of 3rd or higher order in ϵ, thus

$$-(K_1+K_3) - \epsilon^2\frac{\Lambda}{2}\sin\Lambda\theta + \epsilon\Lambda\cos\Lambda\theta = -(K_1+K_3) - \epsilon\left[(K_1+K_3)\sin\Lambda\theta - \frac{\partial P_1^1}{\partial \xi}\right]$$
$$+ \epsilon^2\left(\sin\Lambda\theta\frac{\partial P_1^1}{\partial \xi} + \frac{\partial P_1^2}{\partial \xi}\right) \qquad \text{(I-4.1.2)}$$

Collecting terms of similar order in ϵ, we obtain

$$-\frac{\Lambda}{2}\sin 2\Lambda\theta = \sin\Lambda\theta\frac{\partial P_1^1}{\partial \xi} + \frac{\partial P_1^2}{\partial \xi} \qquad \text{(I-5.1)}$$

$$\Lambda\cos\Lambda\theta = -(K_1+K_3)\sin\Lambda\theta + \frac{\partial P_1^1}{\partial \xi} \qquad \text{(I-6.1)}$$

$$\Longrightarrow \quad \frac{\partial P_1}{\partial \xi} = \Lambda\cos\Lambda\theta + (K_1+K_3)\sin\Lambda\theta \qquad \text{(I-7.1)}$$

Substitute equation (I-7.1) into euqation (I-6.1), thus

$$\frac{\partial P_1^2}{\partial \xi} = -\frac{\Lambda}{2}\sin 2\Lambda\theta - (K_1+K_3)\sin^2\Lambda\theta - \Lambda\sin\Lambda\theta\cos\Lambda\theta$$

or,
$$\frac{\partial P_1^2}{\partial \xi} = -(K_1+K_3)\sin^2\Lambda\theta - \Lambda\sin 2\Lambda\theta \qquad \text{(I-8.1)}$$

Multiply equation (I-2.2) by ($-\epsilon$) and then add to equation (I-2.1), yields

$$\frac{\partial P_1^1}{\partial \xi} - (K_1+K_3)\sin\Lambda\theta - \Lambda\cos\Lambda\theta - \epsilon\sin\Lambda\theta\,\frac{\partial P_1^1}{\partial \xi} - \epsilon\frac{\partial P_1^2}{\partial \xi} + \epsilon P_1^1\Lambda\cos\Lambda\theta - \epsilon\frac{\Lambda}{2}\sin 2\Lambda\theta$$
$$= -(K_1+2K_3)P_1^1 + \epsilon K_3 P_1^2 + \epsilon K_3[2P_1^2 + (P_1^1)^2] \qquad \text{(I-9.1)}$$

substitute equations (I-7.1) and (I-8.1) into equation (I-9.1),

$$\epsilon\Lambda\cos\Lambda\theta\, P_1^1 = -(K_1+2K_3)P_1^1 + \epsilon K_3 P_1^2 + \epsilon K_3[2P_1^2 + (P_1^1)^2]$$

but from equation (I-1.1),

$$P_1^1 = -\epsilon P_1^2$$

$$-\epsilon\Lambda\cos\Lambda\theta\cdot P_1^2 = (K_1+2K_3)P_1^2 + 3K_3P_1^2 + \epsilon^2 K_3 P_1^2$$

$$0 = P_1^2(\epsilon\Lambda\cos\Lambda\theta + K_1 + 5K_3 + \epsilon^2 K_3 P_1^2)$$

thus, $P_1^2(0,\theta)=0$ and $P_1^1(0,\theta)=0$

or,

$$P_1^2(\xi,\theta) = -\frac{\epsilon\Lambda\cos\Lambda\theta + K_1 + 5K_3}{\epsilon^2 K_3}$$

This root is disgarded because the periodic functions do not explicitly and implicitly contain ϵ dependency.

APPENDIX J

EVALUATION OF BOUNDARY CONDITIONS FOR P_2^1 AND P_2^2

APPENDIX J

EVALUATION OF BOUNDARY CONDITIONS FOR P_2^1 AND P_2^2

At the reactor entrance, $x_2(0,\theta)=0$, or

$$x_2(0,\theta)=x_{2_s}(0)+\epsilon P_2^1(0,\theta)+\epsilon^2 P_2^2(0,\theta)=0.$$

from Appendix I, $x_{1_s}(0)=0$,

$$\Rightarrow x_{2_s}(0)=0.$$

$$\Rightarrow \quad P_2^1(0,\theta)=-\epsilon P_2^2(0,\theta) \tag{J-1.1}$$

$$\frac{\partial P_2^1}{\partial\theta}(0,\theta)=-\epsilon\frac{\partial P_2^2}{\partial\theta}(0,\theta) \qquad \text{(J-2.1)[1]}$$

Evaluate equation (G-2.2) at $\xi=0$,

$$\frac{\partial x_2}{\partial\theta}+(1+\epsilon\sin\Lambda\theta)\frac{\partial x_2}{\partial\xi}=K_1 \tag{J-3.1}$$

evaluate equations for x_{2_s}, P_2^1 and P_2^2 at $\xi=0$, thus

$$\frac{dx_{2s}}{d\xi}=K_1 \tag{J-4.1}$$

$$\frac{\partial P_2^1}{\partial\theta}+\frac{\partial P_2^1}{\partial\xi}+\sin\Lambda\theta\frac{\partial x_{2s}}{\partial\theta}=-K_2P_2^1 \tag{J-5.1}$$

$$\frac{\partial P_2^2}{\partial\theta}+\frac{\partial P_2^2}{\partial\xi}+\sin\Lambda\theta\frac{\partial P_2^1}{\partial\xi}=-K_2P_2^2+\Lambda\cos\Lambda\theta P_2^1 \tag{J-6.1}$$

[1] see Appendix K

$$\frac{\partial X_2}{\partial \theta} = \epsilon \frac{\partial P_2^1}{\partial \theta} + \epsilon^2 \frac{\partial P_2^2}{\partial \theta} \qquad \text{(J-7.1)}$$

$$\frac{\partial X_2}{\partial \xi} = K_1 + \epsilon \frac{\partial P_2^1}{\partial \xi} + \epsilon^2 \frac{\partial P_2^2}{\partial \xi} \qquad \text{(J-8.1)}$$

But equation (J-2.1) implies that $\frac{\partial X_2}{\partial \theta}$ =0, thus,

$$(1+\epsilon \sin \Lambda\theta)\frac{\partial X_2}{\partial \xi} = K_1$$

substitute this into equation (J-8.1) yields

$$K_1 \epsilon \sin \Lambda\theta + \epsilon \frac{\partial P_2^1}{\partial \xi} + \epsilon^2 \sin \Lambda\theta \frac{\partial P_2^1}{\partial \xi} + \epsilon^2 \frac{\partial P_2^2}{\partial \xi} + \epsilon^3 \sin \Lambda\theta \frac{\partial P_2^2}{\partial \xi} = 0.$$

collecting terms in like orders of ϵ ,

$$\frac{\partial P_2^1}{\partial \xi} = - K_1 \sin \Lambda\theta \qquad \text{(J-9.1)}$$

$$\frac{\partial P_2^2}{\partial \xi} = K_1 \sin^2 \Lambda\theta \qquad \text{(J-10.1)}$$

Multiplying equation (J-6.1) by ϵ and then adding to equation (J-5.1),

$$\epsilon \frac{\partial P_2^2}{\partial \xi} + (1+\epsilon \sin \Lambda\theta)\frac{\partial P_2^1}{\partial \xi} + K_1 \sin \Lambda\theta = - K_2 P_2^1 - \epsilon K_2 P_2^2 + \epsilon \Lambda \cos \Lambda\theta \cdot P_2^1$$

substituting equations (J-9.1) and (J-10.1) into the above equation, yields:

$$\epsilon K_1 \sin^2 \Lambda\theta - (1+\epsilon \sin \Lambda\theta)(K_1 \sin \Lambda\theta) + K_1 \sin \Lambda\theta = -K_2 P_2^1 - \epsilon K_2 P_2^2 + \epsilon \Lambda \cos \Lambda\theta P_2^1$$

or,

$$0 = -K_2 P_2^1 - \epsilon K_2 P_2^2 + \epsilon \Lambda \cos \Lambda\theta \cdot P_2^1$$

but, $-P_2^1 = \epsilon P_2^2$, thus,

$$0=\epsilon\Lambda\cos\Lambda\theta\cdot P_2^1 \qquad \text{(J-11.1)}$$

This implies $P_2^1=0$ or $\Lambda\theta=\frac{n\pi}{2}$; n=0,1,2......

To sufficiently satisfy equation (J-11.1) for all θ, P_2^1 must be zero. Hence,

$$P_2^1(\theta, \zeta=0)=P_2^2(\theta, \zeta=0)=0$$

APPENDIX K

PROOF OF THE DERIVATIVE OF THE BOUNDARY CONDITIONS FOR P_2^1 AND P_2^2

APPENDIX K

PROOF OF THE DERIVATIVE OF THE BOUNDARY CONDITIONS FOR P_2^1 AND P_2^2

For a linear partial differential operator, $\mathcal{L}[\underline{P}^1]_2$,

$$P_2^1(\xi,\theta) = g_1(\xi) g_2(\theta) \tag{K-1.1}$$

thus, at $\xi = 0$,

$$P_2^1(0,\theta) = g_1(0) g_2(\theta) \tag{K-2.1}$$

and differentiating equation (K-2.1) with respect to θ

$$\frac{dP_2^1(0,\theta)}{d\theta} = g_1(0) \frac{dg_2(\theta)}{d\theta} \tag{K-3.1}$$

For equation (J-2.1) to be valid, we follow the proof given below.

$$\frac{dP_2^1(\xi,\theta)}{d\theta} = g_1(\xi) \frac{dg_2(\theta)}{d\theta}$$

$$\left.\frac{dP_2^1(\theta,\xi)}{d\theta}\right|_{\xi=0} = g_1(0) \frac{dg_2(\theta)}{d\theta} \tag{K-4.1}$$

But the right hand side of equation (K-4.1) is identically equal to that of equation (K-3.1), hence

$$\frac{\partial P_1^2(0,\theta)}{d\theta} = \left.\frac{\partial P_1^2}{\partial \theta}\right|_{\xi=0}$$

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