A STUDY OF THE OPTIMAL RATE

OF CATALYST ADDITION TO AND THE OPTIMAL TEMPERATURE

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by

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SCOPE AND CONTENTS:

The optimal temperature and catalyst addition policies, which
maximise the profit from reactions within a tubular catalytic reactor
over a fixed time, are sought. The catalyst activity is subject to decay.

Theoretical developments, involving a 1st order variational
analysis, determine certain features of the optimal policies. Numerical
computations then illustrate these and yield solutions for the cases
of irreversible and simple reversible reactions.

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INTRODUCTION

In the past decade extensive research has been made into optimal control policies for catalysed processes where the catalyst activity decays.

This decay may result from poisoning or sintering. The latter, the sequel of high temperature operation, creates a reduction in the surface area and number of active sites within the catalyst. Poisoning may be of an irreversible or reversible chemical form or it may be caused by a physical coating of the catalyst's internal or external surfaces. Frequently a decay model is assumed in which the rate of decline in the activity is dependent only upon the temperature and activity and not upon the ambient component concentrations. This assumption has been justified by the research of Szepe (I).

With such a model the determination of an optimal policy is complex as the activity of the catalyst at a point depends upon the previous history of that catalyst. The policy must therefore be set with regard both to present and future profit.

Previous work has been concerned with reactors of a fixed bed length:

Jackson (2, 3, 4) examined the optimal temperature profile in a tubular reactor with a reversible exothermic reaction but obtained only a numerical solution.

Crowe and others (5, 6, 7, 8, 9) have investigated reactions in single and multi-bed isothermal reactors employing Pontryagin's Maximum Principle.

Ogunye and Ray (10), applying first order variational analysis, derived a weak maximum principle for the distributed parameter (non-isothermal) case. Therien (11) has applied the strong maximum principle of Degtyarev and Sirazetdinov (13) to that same situation.

The problem to be examined here has a different emphasis. Its essence may be simply stated: if a reactor is filled with a catalyst, whose activity decays, then the catalyst towards the reactor exit may initially effect little conversion whilst sustaining a significant loss in its activity. It may thus be advantageous to delay the addition of this catalyst. It would seem reasonable to suggest that this further control, upon the timing of catalyst addition, would improve the overall reactor performance.

In the following pages various features of, and necessary conditions for, an optimal policy will be theoretically derived utilizing 1st order variational analysis. These features will then be illustrated and complete solutions given by numerical computation.

CHAPTER 2

STATEMENT OF THE PROBLEM

It is required to maximise the performance index, or objective function, over a fixed total reaction time τ, by choice of the temperature, at every point in time (t) - distance (z) space , and the rate of catalyst addition, at every instant.

The system is established with the following assumptions:

1.   The reactant flow rate at entry remains constant.

2.   There is a maximum bed length. Consequently, if there is no significant volume change with reaction these first two assumptions are equivalent to stating there is a maximum pressure drop.

3.   The reactor is in plug flow and may be represented by a continuum, there being a large number of catalyst particles per unit volume. Any rate limitation originates in the chemical reacions rather than in diffusion processes.

4.   A quasi-steady state is assumed as the space time is much shorter than the time scale for catalyst decay.

5.   The catalyst activity ψ is defined (12) as the ratio of the rate of reaction with the catalyst in question to the rate with fresh catalyst. All fresh catalyst is assumed to be identical.

6.   The rate of decay of the activity depends upon the temperature and activity alone

$$\frac{\partial \psi}{\partial t} = -k(T) \, g(\psi) \qquad (2.1)$$

$$\left. \begin{array}{l} 0 \le \psi \le 1 \\ 0 \le g \le 1 \end{array} \right\} \qquad (2.2)$$

The rate of decay increases with increasing temperature - the rate

constant k(T) behaves according to an Arrhenius expression.

7.   The same catalyst is assumed to be effective in all reactions
with the same activity, as defined above, pertaining to each.

8.   The m elementary reactions occurring involve ℓ species and may
be described by the material balances

$$\frac{\partial x_i}{\partial z} = \psi \sum_{j=1}^{m} \nu_{ji} \; K_j \; F_j \qquad i = 1, \ell \qquad (2.3)$$

where

ν_{ji} - is the stoichiometric mole number for the ith species
in the jth reaction.

K_j - is the rate constant of the jth reaction

and

$$F_j = F_J (x_1, \; .... \; x_\ell) \qquad (2.4)$$

9.   Any volume change with composition may be imbedded within F_j.

10.   The initial concentrations are specified

$$x_i (0, t) = x_{i0}(t) \qquad (2.5)$$

11.   The temperature has both upper and lower limits above zero.

12.   The rate constants K_j obey Arrhenius expressions. If E_{R_j} is the
activation energy for the jth reaction and E_C that for catalyst decay
then defining

$$P_j = E_{R_j} /E_C, \quad p_j > 0 \qquad (2.6)$$

and

$$K_j = b_j \; k^{p_j} \qquad (2.7)$$

it follows that

$$\frac{dK_j}{dk} = K_j \; p_j /k \qquad (2.8)$$

13.   No catalyst, once added, may be removed from the bed.

14.   There is an upper limit upon the rate of addition of catalyst to the bed.

The objective function will be the sum of the production of each species over the period of reaction weighted according to its desirability. This is the simplest form of performance index ignoring pumping, temperature control and catalyst regeneration costs.

DERIVATIONS

3.1   Policy for a General Reaction Scheme

3.1.1   Where the Reactor is Finally Filled

In this section a possible profile, giving the length of the catalyst bed at time t, is first established and the defining equations and objective function are set out. The catalyst decay rate constant, which increases monotonically with temperature, and the rate of addition of catalyst are introduced as controls. A 1st order variational analysis is performed to determine necessary conditions for extremal policies. A Hamiltonian is defined and it is asserted that with optimal temperature control this Hamiltonian should be a maximum. It is demonstrated that only in exceptional circumstances may an unconstrained temperature at the end of the reactor co-exist in an optimal policy with an unconstrained rate of catalyst addition.

First let us delineate the area in time (t) - distance (z) space with which we are concerned.

$r(t)$ is the length of the catalyst bed at time t such that

$$0 \le r(t) \le L$$

L being the maximum bed length.

t_1 is the time at which the reactor is filled.

i.e. $r(t \ge t_1) = L$ (3.1)

A typical profile for r(t) is sketched in Figure I.

<center>FIGURE I</center>
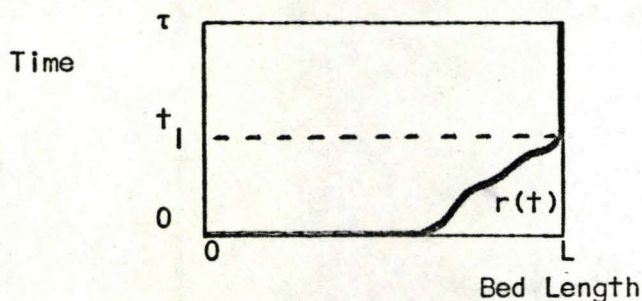
From Chapter 2 it will be recalled that within the reactor, m elementary reactions occur, involving ℓ components. For the ith component, the reactor being in a quasi-steady state:

$$\frac{\partial x_i}{\partial z} = \begin{cases} \psi_j \sum_{j=1}^{m} \nu_{ji} K_j F_j & , \quad 0 \leq z \leq r(t) \\ 0 & , \quad r(t) < z \leq L \end{cases} \tag{3.2}$$

Outside the bed, reaction ceases. It will be observed that the catalyst activity is the same in all reactions. (Assumption 7, Chapter 2).

The catalyst decays according to the equation

$$\frac{\partial \psi}{\partial t} = \begin{cases} -k(T).g(\psi) & , \quad 0 < z < r(t) \\ 0 & , \quad r(t) < z \leq L \end{cases} \tag{3.3}$$

Catalyst on entering the bed has unit activity.

Introduce the control u(t), the rate of addition of catalyst. It is bounded

$$0 \leq u \leq u^* \tag{3.4}$$

and is defined by

$$u(t) = \frac{\partial r(t)}{\partial t} \tag{3.5}$$

Instead of employing the temperature T as a control let us use k, the catalyst decay rate constant, defined in (3.3), which increases in a strictly monotonic fashion with T. k is bounded both above and below

$$0 < k_* \leq k \leq k^*$$ (3.6)

We wish to maximize the objective function

$$P = \int_o^\tau \sum_{i=1}^\ell (\alpha_i \int_o^{r(t)} \psi \sum_{j=1}^m \nu_{ji} K_j F_j \, dz) dt$$ (3.7)

where α_i is the weighting factor indicating the desirability of the ith component.

The function P is the sum of the weighted production of each species within the reaction period.

Let us introduce variations $\delta u(t)$ and $\delta k(z,t)$ into the controls and then perform a 1st order variational analysis to give the resulting variation in P, δP, in terms of δu and δk.

Assumption 13 of Chapter 2 stated that there may be no removal of catalyst from the bed. Hence, once the bed is filled (r(t) = L), the control u is no longer active, i.e. for

$$t_1 + \delta t_1 < t \leq \tau$$

$$u = 0 \text{ and } \delta u = 0$$ (3.8)

Recognising this, it may be shown (Appendix 1) that the variation in the objective function, resulting from variations in the two controls, is

$$\delta P = \int_o^\tau \int_o^{r(t)} (\sum_{i=1}^\ell \lambda_{1i} \psi \sum_{j=1}^m \nu_{ji} K_j p_j F_j / k - \lambda_2 g) \delta k . dz . dt + \int_o^{t_1} \lambda_3 \delta u \, dt$$ (3.9)

(ℓ+2) adjoint variables have been introduced:

they are

$$\lambda_{1i}, \ (i=1,\ell) \quad \text{adjoint to } x_i$$

$$\lambda_2 \qquad \text{adjoint to } \psi$$

$$\lambda_3 \qquad \text{adjoint to } r(t)$$

and they are defined by the following differential equations and boundary

conditions

$$\frac{\partial \lambda_{1i}}{\partial z} = -\sum_{q=1}^{\ell} \lambda_{1q} \, \psi \sum_{j=1}^{m} (\nu_{jq} K_j \frac{\partial F_j}{\partial x_i}) \tag{3.10}$$

$$\lambda_{1i} \, (r(t)) = \alpha_i \tag{3.11}$$

$$\frac{\partial \lambda_2}{\partial t} = \lambda_2 \, k \, \frac{\partial g}{\partial \psi} - \sum_{i=1}^{\ell} (\lambda_{1i} \sum_{j=1}^{m} \nu_{ji} K_j F_j) \tag{3.12}$$

$$\lambda_2 \, (z, \tau) = 0 \tag{3.13}$$

$$\frac{\partial \lambda_3}{\partial t} = (\lambda_2 kg - \sum_{i=1}^{\ell} (\alpha_i \psi \sum_{j=1}^{m} \nu_{ji} K_j F_j)) \Big|_{r(t)} \tag{3.14}$$

$$\left. \begin{array}{l} \lambda_3 \, (0) = 0 \\ \\ \lambda_3 \, (t_1) = 0 \quad \text{where } 0 < u(t_1) < u^* \end{array} \right\} \tag{3.15}$$

For an optimal policy no variation in the controls should be such

as to increase the value of the objective function. Hence, to revert to

(3.9), for any variation from an optimal policy

$$\delta P \le 0 \tag{3.16}$$

Let J be the term multiplying δk within the double integral in (3.9)

$$J = \sum_{i=1}^{\ell} \lambda_{1i} \, \psi \sum_{j=1}^{m} (\nu_{ji} \, K_j \, p_j \, F_j/k) - \lambda_2 g \qquad (3.17)$$

Now k and u are independent control variables. Where k is unconstrained, as the variation δk is arbitrary, to satisfy (3.16) and give extremal control

$$J = 0 \qquad (3.18)$$

If $k = k^*$, as any variation δk must then be negative, (for k must be such that $k_* \leq k \leq k^*$)

$$\text{Similarly if } k = k_*, \quad \left. \begin{array}{l} J \geq 0 \\ J \leq 0 \end{array} \right\} \qquad (3.19)$$

$$\text{The reverse is also true} - \quad \left. \begin{array}{l} \text{if } J < 0 \text{ for all } k \text{ then } k = k_* \\ \text{and if } J > 0 \text{ for all } k \text{ then } k = k^* \end{array} \right\} \qquad (3.20)$$

Let a Hamiltonian H be defined

$$H = \sum_{i=1}^{\ell} (\lambda_{1i} \, \psi \sum_{j=1}^{m} \nu_{ji} \, K_j \, F_j) - \lambda_2 \, kg \qquad (3.21)$$

It will now be asserted that for an optimal temperature this Hamiltonian should be a maximum.

It has been proven (13), that with an invariant r(t), for an optimal policy, H should be maximized subject to initial and boundary conditions. It is a further condition that H should be twice differentiable. Accordingly, when $t > t_1$, the reactor being filled, H should be made a maximum with respect to k.

When $0 \leq t \leq t_1$, for any predefined profile of the bed length, constraints upon the temperature may exist only at the bed exit. Such

constraints cannot affect the conversion. Any specified profile may thus be considered as an example of the general case of Degtyarev and Sirazetdinov (13) and again the optimal temperature is that which maximizes the Hamiltonian. This function yields no information about the profile $r(t)$.

Let us now examine the nature of extremal temperature control.

Differentiating the Hamilton with respect to k

$$\frac{\partial H}{\partial k} = J$$

and

$$\frac{\partial^2 H}{\partial k^2} = \sum_{i=1}^{\ell} \lambda_{li} \psi \sum_{j=1}^{m} \nu_{ji} K_j F_j (p_j - 1) p_j / k^2 \qquad (3.22)$$

With $J = 0$, where the second derivative is positive, the Hamiltonian has a local minimum and the extremal value of k at that point is non-optimal. Consequently, there, only the boundary values of k that maximize H will be optimal. This may be clearly seen by recollecting that for any deviation from an optimal policy

$$\delta P \leq 0 \qquad (3.16)$$

Here $J = 0$ yields non-optimal values of k. If $J \neq 0$ and k were not bounded then, as δk could take any sign, δP would not necessarily be non-positive. Only if k were bounded would δk be restricted to either positive or negative values, thus satisfying eq. 3.16 when the appropriate bound is chosen according to eq. 3.20. An example where extremal k is non-optimal is where all

$$\lambda_{li} \nu_{ji} p_j (p_j - 1) > 0$$

Where the second derivative is negative the extremal policy gives a local maximum. This policy may then form part of an optimal policy.

Now let us examine the conditions necessary for extremal un-constrained u where $t \leq t_1$. From (3.9) where u is unconstrained, as then δu is arbitrary, for extremal values of u

$$\lambda_3 = 0 \qquad (3.23)$$

If u is unconstrained over a period of time then over that same time interval

$$\lambda_3 = 0 \text{ and } \frac{\partial \lambda_3}{\partial t} = 0$$

or, from (3.14)

$$\left(\sum_{i=1}^{\ell} \alpha_i \psi \sum_{j=1}^{m} \nu_{ji} K_j F_j - \lambda_2 kg \right)\Bigg|_{r(t)} = 0 \qquad (3.24)$$

It will be recalled that for $t > t_1$, $u = 0$

Unconstrained u is compatible with unconstrained optimal $k(r(t))$ only in exceptional circumstances as will now be shown:

Comparing (3.24) with (3.17) where $J = 0$ we see unconstrained u precludes an optimal unconstrained value of $k(r(t))$, and vice versa, except where

$$\sum_{i=1}^{\ell} \alpha_i \sum_{j=1}^{m} (\nu_{ji} K_j F_j (p_j - 1))\Bigg|_{r(t)} = 0 \qquad (3.25)$$

This may be satisfied by a singular policy, where $p_j = 1$ for all j, and in other exceptional circumstances where a series of equations must hold. This result is obtained in Appendix 2.

The final temperature may be determined:

Recalling from (3.13) that

$$\lambda_2 (z, \tau) = 0$$

then if at $t = \tau$

$$\sum_{i=1}^{\ell} \lambda_{1i} \psi_{1i} \sum_{j=1}^{m} (\nu_{ji} K_j P_j F_j / k) > 0$$

from (3.20), as J, defined in (3.17), is positive

$$k(z, \tau) = k^* \qquad\qquad (3.26)$$

there being no gain in further conserving activity.

The temperature will lie upon its lower bound at time τ if

$$\sum_{i=1}^{\ell} \lambda_{1i} \psi_{1i} \sum_{j=1}^{m} (\nu_{ji} K_j p_j F_j / k) < 0$$

this being effectively an attempt to stop further reaction.

Previously we have considered the behaviour of u when $\lambda_3 = 0$.

Let us now investigate u when $\lambda_3 \neq 0$:

From (3.9), if $\lambda_3 > 0$

then

$$\delta u < 0$$

if

$$\delta P \leq 0 \ (3.16),$$ this last being the condition for an

optimal solution.

If $\delta u < 0$, u must lie upon its upper bound

i.e. $\qquad \lambda_3 > 0 \ , \qquad u = u^*$

$$\left. \begin{matrix} \\ \\ \end{matrix} \right\} \qquad\qquad (3.27)$$

Similarly if $\quad \lambda_3 < 0, \qquad u = 0$

the lower bound to u being 0 (3.4)

To complete this section the significance of the values of p will be noted:

If $p < 1$, then increasing the temperature will increase the rate of catalyst decay more rapidly than the rate of reaction. If the products

of the reaction, for which $p < 1$, were desired, then whilst the activity is high, the temperature is likely to be low. As the activity declines then an increasing temperature is to be expected to counter the effects of a low activity. The reverse is true where $p > 1$. This general statement must be qualified by mentioning that the temperature policy is determined also by the relative values of p of all the reactions.

3.1.2   Where Finally the Reactor is only Partially Filled

In this section it is demonstrated that the analysis differs only slightly from the previous section 3.1.1. It is shown that if u takes a bounding value this should be zero. Feasible cases in which the reactor may be finally partially filled are mentioned.

Here $t_1 \neq \tau$.

A typical profile for r(t) is sketched in Figure 2.

FIGURE 2
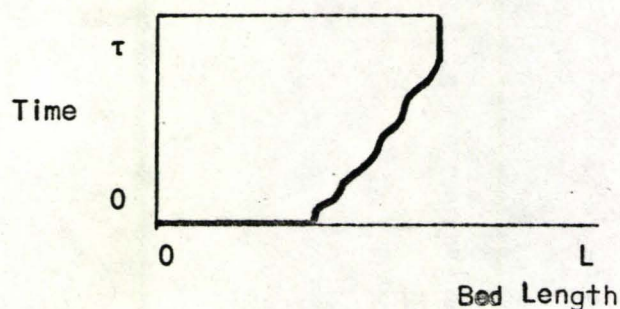
In Appendix 3 it is demonstrated that in this instance the analysis does not differ from that previously performed save that all time integrals are made between 0 and τ. Here both control variables, u and k, enter into the problem at all times. This is in contrast to the situation where $t_1 < \tau$, for when r(t) = L the addition rate control is removed. If at t = τ, u is to be unconstrained, from (3.24)

$$\left. \left(\sum_{i=1}^{\ell} \alpha_i \, \psi_i \sum_{j=1}^{m} \nu_{ji} \, K_j \, F_j \right) \right|_{r(t)} = 0$$

remembering that $\lambda_2(\tau) = 0$ (3.13).

Otherwise u will take a bounding value. As u^* is arbitrary, one would not expect $u(\tau) = u^*$ as this would suggest the solution is seeking to have $r(t) = L$. Therefore, $u(\tau) = 0$.

The situations, for which $t_1 \nleq \tau$ seems feasible, are series reactions where an intermediate product is desired and for other complex reaction schemes.

3.1.3 Extensions of the General Analysis

Here it is shown that with a little adaptation the analysis of the two previous sections is applicable elsewhere though a maximum principle is not necessarily available.

1.   Where the reactor is isothermal, the temperature being invariant in time, the control k is eliminated and the expression for δP becomes

$$\delta P = \int_o^{t_1} \lambda_3 \, \delta u.dt \qquad\qquad (3.28)$$

An extremal policy with unconstrained u requires that $\lambda_3=0$ for $0 \le t \le t_1$

i.e. $\lambda_3(0) = 0$

$$(3.29)$$

and $\dfrac{\partial \lambda_3}{\partial t} = 0 \qquad 0 \le t \le t_1$

2.   Where the reactor is isothermal, but the temperature varies with time subject to $k_* \le k \le k^*$, then

$$\delta P = \int_o^\tau \delta k \int_o^{r(t)} (\psi \sum_{i=1}^{\ell} \lambda_{1i} \sum_{j=1}^{m} p_j \nu_{ji} K_j F_j/k - \lambda_2 g) dz.dt + \int_o^{t_1} \lambda_3 \, \delta u.dt \qquad (3.30)$$

Extremal unconstrained k is possible when, from (3.9)

$$\int_o^{r(t)} (\psi \sum_{i=1}^{\ell} \lambda_{1i} \sum_{j=1}^{m} p_j \nu_{ji} K_j F_j/k - \lambda_2 g) \, dz = 0$$

As temperature here is a boundary control no maximum principle may be asserted.

3.2   The Irreversible Reaction

3.2.1   The Variational Analysis for an Irreversible Reaction

The irreversible reaction

$$A \quad \rightarrow \quad products$$

is considered in this section. With the simplification made by con-
sidering the conversion of A as a state variable rather than the con-
centrations, the analysis of 3.1 is followed. The adjoint variables
are investigated and it is shown that the variable, adjoint to the con-
centration, may be eliminated and that the one adjoint to the activity
is always positive. It is demonstrated that unconstrained u is incom-
patible with unconstrained $k(r(t))$. From the introduction of a
Hamiltonian and assertion of a maximum principle, unconstrained k is
found to be optimal only where $p < 1$.

A slight simplification of the previous analysis may be made if
χ is considered to be the conversion of A. Only 3 state variables χ, r
and ψ need then be introduced.

The mass balance becomes

$$\frac{\partial \chi}{\partial z} = \psi \, K \, F \, (\chi) \qquad 0 \leq z \leq r(t)$$
$$= 0 \qquad\qquad r(t) < z \leq L \qquad \Big\} \qquad (3.31)$$

and the objective function is the simplest

$$P = \int_o^\tau \int_o^{r(t)} \psi \, K \, F.dz.dt \qquad (3.32)$$

as we wish to obtain only the products.

Following (3.10) – (3.15), if the adjoint variables λ_1, λ_2 and λ_3 are defined so:

$$\frac{\partial \lambda_1}{\partial z} = -\lambda_1 \psi K \frac{\partial F}{\partial X} \tag{3.33}$$

$$\lambda_1(r(t)) = 1 \tag{3.34}$$

$$\frac{\partial \lambda_2}{\partial t} = \lambda_2 k \frac{\partial g}{\partial \psi} - \lambda_1 KF \tag{3.35}$$

$$\lambda_2(z, \tau) = 0 \tag{3.36}$$

$$\frac{\partial \lambda_3}{\partial t} = (\lambda_2 kg - \psi KF)\Big|_{r(t)} \tag{3.37}$$

$$\left.\begin{array}{l} \lambda_3(0) = 0 \\ \lambda_3(t_1) = 0 \quad \text{if } 0 < u(t_1) < u^* \end{array}\right\} \tag{3.38}$$

then from (3.9)

$$\delta P = \int_o^\tau \int_o^{r(t)} (\lambda_1 F\psi Kp/k - \lambda_2 g)\, \delta k.dz.dt + \int_o^{t_1} \lambda_3\, \delta u.dt \tag{3.39}$$

Here

$$K = bk^P \tag{3.40}$$

It will now be shown that λ_1 may be ignored and that λ_2 is always positive.

Investigating the adjoint variables it is proved in Appendix 4 that

$$\frac{\partial(\lambda_1 F)}{\partial z} = 0 \quad \text{or} \quad \lambda_1 F = F\Big|_{r(t)} \tag{3.41}$$

Since λ_1 is always found in the analysis in conjunction with F as the term $\lambda_1 F$ then from (3.41) this term may be replaced by $F\big|_{r(t)}$

In Appendix 4 it is also shown that

$$\lambda_2 > 0 , \quad 0 \leq t < \tau \tag{3.42}$$

Unconstrained u is incompatible with unconstrained $k(r(t))$ as will now

be demonstrated:

The condition for unconstrained u is, from (3.39),

$$\lambda_3 = 0$$

Over the period where $\lambda_3 = 0$, then

$$\frac{\partial \lambda_3}{\partial t} = 0$$

or from (3.37)

$$(\lambda_2 \ kg - \psi \ KF) \Big|_{r(t)} = 0 \tag{3.43}$$

From (3.39) we see too that for unconstrained k, as then δk is arbitrary,

that

$$J = \lambda_1 F \psi \ Kp/k - \lambda_2 g = 0 \tag{3.44}$$

Comparison of (3.43) and (3.44) shows that they may co-exist only in the

special case where $p = 1$. There a singular policy operates. This will

be further discussed in (3.2.4).

Let us now introduce a Hamiltonian H and investigate the nature

of extremal policies and determine the optimal control upon k, the decay

rate constant.

Define

$$H = \psi \ K F \Big|_{r(t)} - \lambda_2 \ kg \tag{3.45}$$

$$\frac{\partial H}{\partial k} = J = 0 \quad \text{for an extremal policy}$$

$$\frac{\partial^2 H}{\partial k^2} = \psi \ F \Big|_{r(t)} Kp(p - 1)/k^2 \tag{3.46}$$

As F, ψ, K and k are all positive this is negative only if p < 1. If p > 1, it is positive. Following 3.1.1 and asserting a maximum principle it may thus be stated that if p > 1, extremal unconstrained k is non-optimal whereas if p < 1 an extremal unconstrained k creates a local maximum in H. This may then form part of an optimal policy.

Hence if p < 1, the optimal value of k is such that J = 0. i.e. from (3.44)

$$k = (\lambda_2 g/\psi \ p \ b \ F\Big|_{r(t)} \ )^{\frac{1}{p-1}} \tag{3.47}$$

If k calculated from (3.47) exceeds k^* or is lower than k_* it takes the value of the bound traversed.

If p > 1, optimal k must be a bounding value of k with the property that, with that value of k, H is a maximum. A transition from $k = k^*$ to $k = k_*$ could occur when

$$H^* = H_* \tag{3.48}$$

or

$$\psi \ (F\Big|_{r(t)} \ K)^* - \lambda_2 g \ k^* = \psi(F\Big|_{r(t)} \ K)_* - \lambda_2 g \ k_*$$

as continuity exists in ψ, g and λ_2. If the transition were made for a single value of z alone at any given time, continuity would also exist in $F\Big|_{r(t)}$.

Finally, the reactor should be operated at its maximum temperature, there being no profit in the conservation of activity at this time:

At $t = \tau$ from (3.44) and (3.36)

$$J = F\Big|_{r(t)} \ K \ \psi \ p/k \ > \ 0$$

From (3.20) then

$$k = k^* \tag{3.49}$$

3.2.2   Optimal Policies where p < 1

It was earlier shown in 3.1.1 that unconstrained u precludes unconstrained k(r(t)) in optimal policies. It would, thus, seem logical to consider first those policies where k(r(t)) is the primary control and then those for which u is the primary control. It will be recalled that where p < 1, extremal unconstrained k can be optimal.

Where k(r(t)) is the Primary Control:

From a development in Appendix 5 it may be seen that where the entry conversion remains constant:

a) The temperature increases with time,

b) Whilst k is unconstrained for all $z \leq r(t)$, the exit conversion is constant

c) Either all the catalyst is initially present or it is all added at the highest possible rate at a later stage.

Where u is the Primary Control:

It will first be demonstrated that for $t \leq t_1$, $k(r(t)) = k_*$
Where u is unconstrained, (3.43) holds

i.e.
$$(\lambda_2 \, kg - \psi \, K \, F)\Big|_{r(t)} = 0$$

Hence examination of (3.44) shows that at r(t)

$$J < 0 \quad \text{where } p < 1$$

i.e. from (3.20) $k(r(t)) = k_*$ (3.50)

In Appendix 6 it is proved that for $z < r(t) < L$ where $k(z,t)$ is unconstrained, than any extremal policy with unconstrained $u(t)$ is non-optimal. The best policy in such circumstances is to operate with a full bed.

An optimal unconstrained u is possible where $k(z,t) = k_*$ for $z \leq r(t) < L$.

When $r(t) = L$, the bed is filled and the situation is that described for $k(r(t))$ as primary control.

3.2.3 Optimal Policies where p > 1

Where p > 1, unconstrained k is non-optimal. If the primary control takes a bounding value then the other variable takes the optimum value subject to the conditions imposed by the first lying upon a constraint.

Again it would appear natural to consider first the situation with k(r(t)) as primary control and then that with u as primary control.

Where k(r(t)) is the Primary Control:

Here $u = u^*$ or $u = 0$

If initially $k(r(0)) = k_*$, the problem becomes that of Therien (11) dealing with a full bed. This may easily be demonstrated as follows:

If $k(r(0)) = k_*$ from (3.37), (3.43) and (3.44)

$$\frac{\partial \lambda_3}{\partial t} > 0$$

As initially $\lambda_3 = 0$, (3.38) then for $t > 0$, $\lambda_3 > 0$.

Hence $u = u^*$ initially – the bed is filled as u^* may be arbitrarily large.

Where u is the Primary Control:

It will be shown that where u, the rate of addition of catalyst, is unconstrained $k(r(t)) = k^*$. If the conversion declines whilst u is unconstrained the temperature in the region $r_o \leq z \leq r(t)$ lies upon the upper limit.

Where u is unconstrained, we know $\frac{\partial \lambda_3}{\partial t} = 0$

Examination of (3.43) and (3.44) then shows that

$$k(r(t)) = k^*$$

Apart from the above observations the optimal policy must be determined for each particular case.

3.2.4   The Case where p = 1

The Hamiltonian function is shown here to be linear in the control k. Hence there exists the possibility that an optimal policy contains a singular segment. Whilst it does the exit conversion remains constant and an unconstrained extremal temperature is compatible with an unconstrained extremal rate of catalyst addition.

Where $p = 1$, $K = b\,k$ (3.40)

i.e. the Hamiltonian is linear in the control: $H = (\psi b F\big|_{r(t)} - \lambda_2 g)k$

When $\psi\, b\, F\big|_{r(t)} - \lambda_2 g = 0$ (i.e. $\frac{\partial H}{\partial K} = 0$)

the control policy is singular. If this policy is to be evident then it must persist for a certain period in time and distance

i.e. $\frac{\partial}{\partial t}\left(F\big|_{r(t)}\, \psi\, b - \lambda_2 g\right) = 0$

Differentiating and substituting (3.35) for the term

$$\frac{\partial \lambda_2}{\partial t}$$ and (3.3) for the term $\frac{\partial \psi}{\partial t}$

$$\frac{\partial F}{\partial t}\Big|_{r(t)}\, \psi\, b = 0$$

or the exit conversion remains constant.

Whilst the control policy is singular at $r(t)$ comparing (3.43) and (3.44) we see these equations are identical and thus, of course, may simultaneously hold. Unconstrained $k(r(t))$ is thus consistent with unconstrained u in an extremal control policy.

3.3.   The Reversible Reaction

3.3.1   The Variational Analysis for a Reversible Reaction

In this section a simple reversible reaction of the form

$$A \; \underset{\leftarrow}{\rightarrow} \; \nu B$$
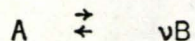
is considered. Such a form of reaction allows for considerable
simplification within the analysis as the concentration of A is simply
related to that of B. Again the variational analysis of the general re-
action scheme is followed. It is demonstrated that an unconstrained rate
of catalyst addition, u, is incompatible with an unconstrained temperature
at the end of the bed, $k(r(t))$, within an optimal solution. A Hamiltonian
is introduced, a maximum principle asserted, and the nature of extremal
and optimal temperature profiles investigated.

Consider the reversible reaction:

$$A \; \underset{\leftarrow}{\rightarrow} \; \nu B$$
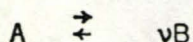
This is a single reaction with two stoichiometric coefficients. A con-
siderable simplification of the analysis for general kinetics may thus be
made, as the concentration of A is simply related to that of B

$$x_B = \nu(x_{A0} - x_A) + x_{B0}$$

Where

   x_{A0} is the entry concentration of A

   x_{B0} is the entry concentration of B

Hence only one concentration χ, that of B, need be introduced.

Let us reintroduce, from Chapter 2, assumption 8, the stoichiometric mole numbers, ν_{ij}. Basing them upon the reaction and formation of a mole of A, then

ν_{12} is the number of moles of B formed from I mole of A

$(-\nu_{22})$ is the number of moles of B removed to form I mole of A

A further simplification is thus to say

$$\nu = \nu_{12} = -\nu_{22}$$

It may be necessary to redefine the rate constants in the reaction rate equations so that they are consistent with the stoichiometric mole numbers chosen.

For this simple reaction the material balance (3.2) may be expressed as

$$\frac{\partial x}{\partial z} = \psi \, \nu (K_1 F_1(x) - K_2 F_2(x)) \tag{3.52}$$

Again we have only 3 state variables, x, r and ψ.

If we desire B alone, the objective function formulated in (3.7), simplifies to:

$$P = \int_0^\tau \int_0^{r(t)} \nu \, \psi (K_1 F_1 - K_2 F_2) \, dz.dt \tag{3.53}$$

a zero weighting being given to A.

Following (3.10) to (3.15) if adjoint variables λ_1, λ_2 and λ_3 are defined so:

$$\lambda_1(r(t)) = 1 \tag{3.54}$$

$$\frac{\partial \lambda_1}{\partial z} = -\lambda_1 \, \psi \, \nu (K_1 \frac{\partial F_1}{\partial x} - K_2 \frac{\partial F_2}{\partial x}) \tag{3.55}$$

$$\lambda_2(z,\tau) = 0 \tag{3.56}$$

$$\frac{\partial \lambda_2}{\partial t} = \lambda_2 \, k \, \frac{\partial g}{\partial \psi} - \lambda_1 \, \nu(K_1 F_1 - K_2 F_2) \qquad (3.57)$$

$$\lambda_3(0) = 0$$

$$\lambda_3(t_1) = 0 \quad \text{if} \quad 0 < u(t_1) < u^* \qquad \left.\right\} \qquad (3.58)$$

$$\frac{\partial \lambda_3}{\partial t} = (\lambda_2 kg - \psi \nu \, (K_1 F_1 - K_2 F_2)) \Big|_{r(t)} \qquad (3.59)$$

then from (3.9) the variation introduced into the objective function P by a variation in the controls u and k is

$$\delta P = \int_0^\tau \int_0^{r(t)} \lambda_1 \psi \, \nu(K_1 F_1 p_1 - K_2 F_2 p_2)/k - \lambda_2 g)\delta k.dz.dt + \int_0^{t_1} \lambda_3 \delta u.dt \qquad (3.60)$$

where

$$K_1 = b_1 \, k^{p_1}, \qquad K_2 = b_2 \, k^{p_2}$$

The variable λ_1 adjoint to χ, is always positive:

examining (3.55) it will be seen that if λ_1 should ever be zero at a

certain time, it is always zero at that time. But (3.54) states that

$$\lambda_1 \, (r(t)) = 1$$

and so

$$\lambda_1 > 0$$

If we deviate from an optimal unconstrained policy

$$\delta P \leq 0 \qquad (3.16)$$

and as δk, the variation in our temperature control is arbitrary, then from (3.60) J = 0 for extremal k

where

$$J = \lambda_1 \, \psi \, \nu(K_1 F_1 p_1 - K_2 F_2 p_2)/k - \lambda_2 g \qquad (3.61)$$

The introduction of a Hamiltonian and assertion of a maximum principle leads, as will be shown, to the conclusion that when the parameters p_1 and p_2 take certain values, then extremal unconstrained k is non-optimal.

Defining a Hamiltonian

$$H = \lambda_1 \, \psi \, \nu (K_1 F_1 - K_2 F_2 - \lambda_2 kg) \qquad (3.62)$$

its second derivative is

$$\frac{\partial^2 H}{\partial k^2} = \lambda_1 \, \psi \, \nu (K_1 F_1 p_1 \, (p_1 - 1) - K_2 F_2 p_2 (\varphi_2 - 1)) / k^2$$

Since we wish to maximize the Hamiltonian, the second derivative must not be positive if unconstrained extremal k is to be optimal. Where the second derivative is positive, as stated in section 3.1.1, the optimal temperature takes the bounding value that maximizes the Hamiltonain. If the unconstrained decay rate constant, k, may be optimal, then k, subject to

$$k_* \leq k \leq k^*$$

is determined from (3.61) knowing J = 0.

Examining (3.60) we observe that if δu is the variation from an extremal unconstrained value of u, the rate of catalyst addition, then for

$$\delta P \leq 0$$

as δu is arbitrary

$$\lambda_3 = 0$$

Following 3.1, if u is to be unconstrained over a period of time, then

$$\frac{\partial \lambda_3}{\partial t} = 0$$

or from (3.59)

$$(\psi \, \nu(K_1F_1 - K_2F_2) - \lambda_2 kg)\bigg|_{r(t)} = 0$$

A comparison of this with (3.61), where J = 0, shows unconstrained u to be incompatible with unconstrained k(r(t)) within an optimal solution as both equations cannot, in general, hold simultaneously. An exception to this in in the singular policy where

$$P_1 = 1 \quad \text{and} \quad P_2 = 1$$

The temperature profile at the final time may be determined. The temperatures will, in general, be bounding values as will now be demonstrated:

At $t = \tau$, recalling (3.56)

$$\lambda_2(z,\tau) = 0$$

we have from (3.61)

$$J = \lambda_1 \, \psi \, \nu(K_1F_1 \, _1 - K_2F_2 \, _2)/k \qquad (3.63)$$

If the reaction is to be effective in converting A to B then the overall direction of the reaction should be forward. A temperature switch, from the upper to the lower bound, that reversed the direction of the reaction would not be desirable,

i.e.
$$\nu(K_1F_1 - K_2F_2) > 0 \qquad (3.64)$$

      or

$$\frac{\partial x}{\partial z} > 0$$

Thus for $p_1 > p_2$, comparing (3.63) with (3.64) then

$$J > 0$$

and from (3.20)

$$k(z,\tau) = k^*$$

If $p_1 < p_2$, then perhaps $k(z, \tau) = k_*$

3.3-2   Optimal Policies

As in section 3.2 a distinction is made between the cases where $k(r(t))$, the decay rate constant at the end of the bed, is the primary control and where u, the rate of catalyst addition, takes that role. Where u is unconstrained, $k(r(t))$ may often be determined by the values of p_1 and p_2, the ratios of the activation energies of the forward and reverse reactions respectively, to that of the catalyst decay. A summary is made of information that may be obtained from a knowledge of p_1 and p_2 alone. The extreme cases, where $p_1 < 1$, $p_2 \geq 1$ and $p_1 > 1$, $p_2 \leq 1$ are examined in greater detail, employing semi-qualitative arguments.

Where the reaction is exothermic ($p_1 < p_2$) a falling temperature profile along the catalyst bed might be expected. The reverse would be anticipated when it is endothermic ($p_1 > p_2$).

Based on Appendix 7 information that may be obtained from knowledge of p_1 and p_2 may be summarized.

	$p_1 < 1$			$p_1 > 1$		
	$p_2 \geq 1$	$p_1 \leq p_2 < 1$	$p_2 < p_1$	$p_2 > p_1$	$p_1 \geq p_2 > 1$	$p_2 \leq 1$
Unconstrained k	Optimal	?	?	?	?	non-optimal
$k(r(t))$ at unconstrained u	k_*	k_*	?	?	k^*	k^*
$\dfrac{\partial \lambda_3}{\partial t}$ at unconstrained $k(r(t))$	neg.	neg.	?	?	pos.	—
$\dfrac{\partial \lambda_3}{\partial t}$ at $k(r(t)) = k^*$	neg.	neg.	?	?	?	?
$\dfrac{\partial \lambda_3}{\partial t}$ at $k(r(t)) = k_*$	?	?	?	?	pos.	pos.
$k(r(t))$ when $\dfrac{\partial \lambda_3}{\partial t} > 0$	k_*	k_*	?	?	?	?
$k(r(t))$ when $\dfrac{\partial \lambda_3}{\partial t} < 0$	?	?	?	?	k^*	k^*

The question mark indicates that information beyond p is required.

Where $p_1 < 1$, $p_2 \geq 1$

As observed in the summary this is an exothermic reaction where unconstrained extremal k are optimal. If u is the primary control, then $k(r(t)) = k_*$.

The temperature takes its lower bounding value towards the end of a temporary halt in catalyst addition.

If, initially, the rate constant at the end of the bed, $k(r(0))$, is unconstrained and optimal the situation reduces to a case of constant bed depth. The proof of this lies in Appendix 7.

Where $p_1 > 1$, $p_2 \leq 1$

This is an endothermic reaction where an optimal temperature policy requires that the temperature takes bounding values. If u is the primary control

$$k(r(t)) = k^*$$

if $k(r(0)) = k_*$

then initially the bed is filled completely. Again the proof of this is in Appendix 7.

NUMERICAL SOLUTIONS

4.1   The Calculation Methods

Both natural convergence techniques and numerical searches were employed. For the former an iterative procedure was utilized and pursued until the objective function improved between iterations by an amount smaller than a prespecified value.

The distance-time space was divided into a grid, the variables being ascertained only at each grid point.

Calculations to determine $r(t)$ were made in two ways:

1)   Using the derivations of Chapter 3 the value of λ_3, the adjoint of $r(t)$, is determined. Where u is unconstrained, λ_3 should be zero. Knowing $\lambda_3(0)$ to take that value, for an initial profile, λ_3 after the first time interval is calculated. If it lies within narrow limits about zero, λ_3 is set to 0 and $r(t)$ to one distance interval greater than $r(0)$, the initial bed length. If, however, λ_3 exceeds the upper limit then the reactor is filled completely; if it is less than the lower limit about 0, r is left equal to $r(0)$, its value one time interval earlier. Continuing in such a manner, for each $r(0)$ a profile is determined.

2)   It was assumed that any profile in $r(t)$ could be approximated by a straight line cutting across a corner of the $L \times \tau$ rectangle which

marks the area of concern in distance-time space. The approximated

profile is shown in Figure I, section 3.1. With the positions of the

intersections of this line with t = 0 and z = L as arguments a Davidon-

Fletcher-Powell search procedure was employed to determine the argument

values that maximized the objective function.

For the exothermic reaction (p < I in the irreversible case,

p_1 < I, p_2 > I in the reversible one) the decay rate constant, or

temperature, at all points within the bed was calculated from the

appropriate previously derived equation. For the endothermic reaction

no satisfactory algorithm utilizing natural convergence could be derived.

The results were very sensitive to the precise formulation of the

temperature switch control.

Again then it was assumed that the area in distance-time space

could be divided by a straight line. To catalyst upstream of this line

was assigned the lower bounding temperature, to that downstream the upper.

This temperature pattern is realistic in the reversible endothermic re-

action. In the irreversible reaction conversion is dependent only upon

the integral
$$\int_{o}^{r(t)} \psi \, K.dz$$
and not upon the temperature at specific positions.

Computer listings for these techniques follow the Appendices.

The values adopted for the calculations were:

$\tau = 10^5$ secs.

$L = 1$

$E_C = 15000\ deg^{-1}$

$k^* = 8.10^{-5}\ sec^{-1}$ $(T^* = 900K)$

$k_* = 2.5.10^{-6}\ sec^{-1}$ $(T_* = 745K)$

or $k_* = 5.10^{-5}\ sec^{-1}$ $(T_* = 875K)$

$K^* = 1$

$K_* = .00552$ when $p=1.5$ and $k_* = 2.5.10^{-6}\ sec^{-1}$

     $= .1767$ when $p=0.5$ and $k_* = 2.5.10^{-6}\ sec^{-1}$

     $= .79$ when $p=0.5$ and $k_* = 5.10^{-5}\ sec^{-1}$

$b = 1397584$ when $p=1.5$

     $= 111.8$ when $p=0.5$

Following Szepe (1) $g = \psi^n$ and here

$n = 2$

The reactions were first order.

The inlet conversion of the desired product was constant at zero.

u^* was taken to be a very large value.

A 20 x 20 interval grid is used.

4.2   The Numerical Results

4.2.1   The Irreversible Reaction

This was defined by:

$$\frac{\partial x}{\partial z} = K \psi(1 - \chi)$$

a.   Where $p = .5$ and $k_* \leq k \leq k^*$

1) $k_* = 2.5.10^{-6} sec^{-1}$

At no point within the bed was $k = k_*$. The best solution found required the reactor to be initially completely filled. The temperature rose monotonically to the upper limit, the profile in time being the same for all z even with sloping initial temperature profiles. Whilst k was unconstrained at all points within the bed, the conversion remained constant. These results are in complete accord with theory (section 3.2.2).

Figure 3 shows the activity, decay rate constant and concentration term F at the reactor exit as time progresses.

2) $k_* = 5.10^{-5} sec^{-1}$

If k_* was assigned a higher value then, whilst again the temperature increased monotonically, it lay upon the lower bound for a substantial initial period. Both numerical search and natural convergence techniques showed that the most profitable solution was to reduce the time of operation to 95000 seconds. This increased the value of the performance index P to $2.59.10^4$ from the value $2.47.10^4$ yielded with

the same full bed over 100000 seconds. This is reasonable as here insufficiently low temperatures are attainable to sufficiently conserve the activity. As before the conversion remains constant whilst k is unconstrained for $z \leq r(t)$.

Again no optimal solution with unconstrained u was found. Features of the best solution found are shown in Figure 4.

The results with $p = .5$ may be briefly summarized:

	$k_* = 2.5.10^{-6}$	$k_* = 5.10^{-5}$
P max.	$2.77.10^4$	$2.59.10^4$

It should be noted here that, as observed in Appendix 5, the constant decline in catalyst activity whilst k is unconstrained is a feature specific to the chosen values of p and n.

b. Where $p = 1.5$ and $k = k^*$ or k_*

The results obtained here represented only a slight improvement over the temperature invariant case.

The best solution computed for unconstrained u (obeying the condition that for $t \leq t_1$, $k(r(t)) = k^*$)was less profitable than the best where $k(r(t))$ exerted primary control. In both cases the bed exit conversion and activity exhibited decaying profiles.

A plot of $r(t)$ and the best temperature policy is to be found in Figures 5 and 6a.

Primary Control	$k(r(t))$	u
P max. with $p = 1.5$	$2.458.10^4$	$2.424.10^4$

c.   Where the temperature was invariant $(k = k^*)$

The sole control here was u. The most profitable solution required that the catalyst be added over several time increments. This is illustrated in Figure 6b.

$$P \text{ max.} = 2.37.10^4$$

In the absence of the control u, where the bed is of constant depth,

$$P \text{ max.} = 2.27.10^4$$

The employment of a control u consequently yields a 5% improvement in the objective function.

4.2.2. The Reversible Reaction

This was defined by:

$$\frac{\partial x}{\partial z} = \psi(K_1(1 - x) - K_2 x)$$

a. Where $p_1 = .5$, $p_2 = 1.5$ and $k_* \leq k \leq k^*$

Both where primary control was exercised by $k(r(t))$ and by u it proved advantageous to add catalyst over a period of time (Figures 7 & 8). The former result contradicts the theoretical prediction that all the bed should be present. Perhaps the natural convergence algorithm failed.

The temperature profile was a monotonically increasing one in time, the conversion monotonically decreasing though at one stage the rate of decline was very small. The activity displayed a uniform decay rate, whilst k was unconstrained throughout the bed. As observed earlier, this is not a general feature of an exothermic reaction.

As might be expected in such a reversible reaction the temperature profile with distance at any time was a monotonically decreasing one.

These features are plotted in Figures 9, 10 and 11.

Primary Control	$k(r(t))$	u
P max.	$2.56.10^4$	$2.57.10^4$

These values represent an improvement of 3.10^2 and 4.10^2 over the case where the bed is initially completely filled.

b. Where $p_1 = 1.5$, $p_2 = .5$ and $k = k^*$ or k_*

In this reversible endothermic reaction, as in the irreversible reaction previously discussed, the improvement over the case where the temperature remained invariant was only slight. As in the irreversible reaction where $k(r(t))$ was the primary control, there being then no restriction upon $k(r(t))$, a larger objective function resulted than when u was unconstrained.

Plots of temperature and $r(t)$ are given in Figures 12 and 13.

Primary Control	$k(r(t))$	u
Pmax.	$2.085 \cdot 10^4$	$2.063 \cdot 10^4$

4.2.3   The Temperature Invariant Reversible Reaction

Control here was exerted by u, the rate of catalyst addition.   The best solution had catalyst addition over several time intervals, u being unconstrained in this period (Figure 14)

$$Pmax = 2.03.10^4$$

This compares with a value of $1.94.10^4$ where the reactor is completely filled initially.

It must be stressed that, with the exception of the irreversible reaction where $p = .5$, these solutions do not necessarily represent the optimal solutions.   Resulting as they do from numerical search procedures they are but the best solutions obtained.
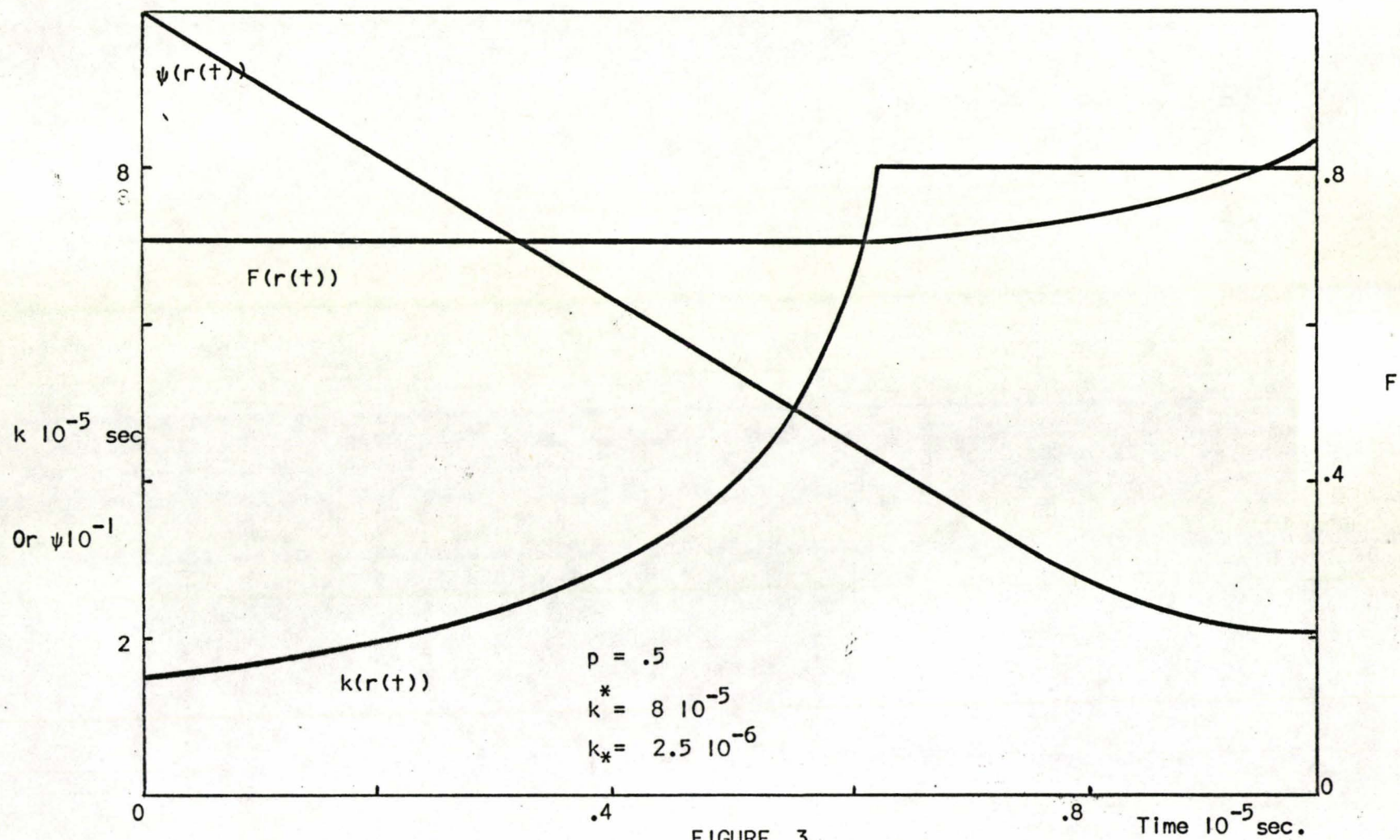
FIGURE 3

Plot of the optimal $k(r(t))$, $\psi(r(t))$ & $F(r(t))$ for 1st order irreversible reaction, $p < 1$, $k > k_*$.

The figure contains the following labels and annotations:

$\psi(r(t))$

$F(r(t))$

$k\ 10^{-5}\ sec$

Or $\psi 10^{-1}$

$k(r(t))$

$p = .5$

$k^* = 8\ 10^{-5}$

$k_* = 2.5\ 10^{-6}$

F

Time 10^{-5} sec.

43.
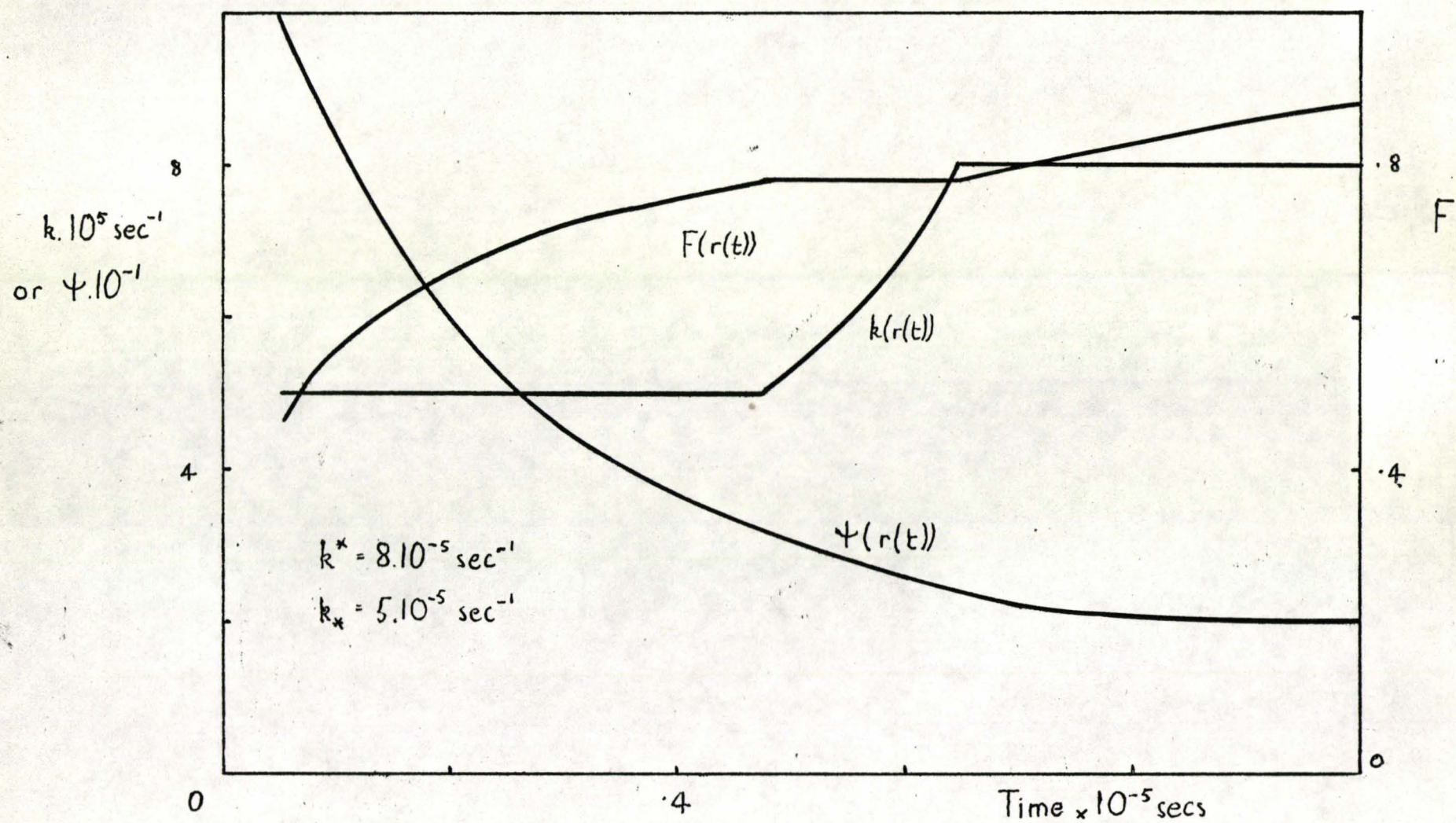
Figure 4 : Plot of the optimal $k(r(t))$, $\psi(r(t))$ & $F(r(t))$ for 1st order irreversible reaction, $p < 1$, $k \geq k_*$

44.
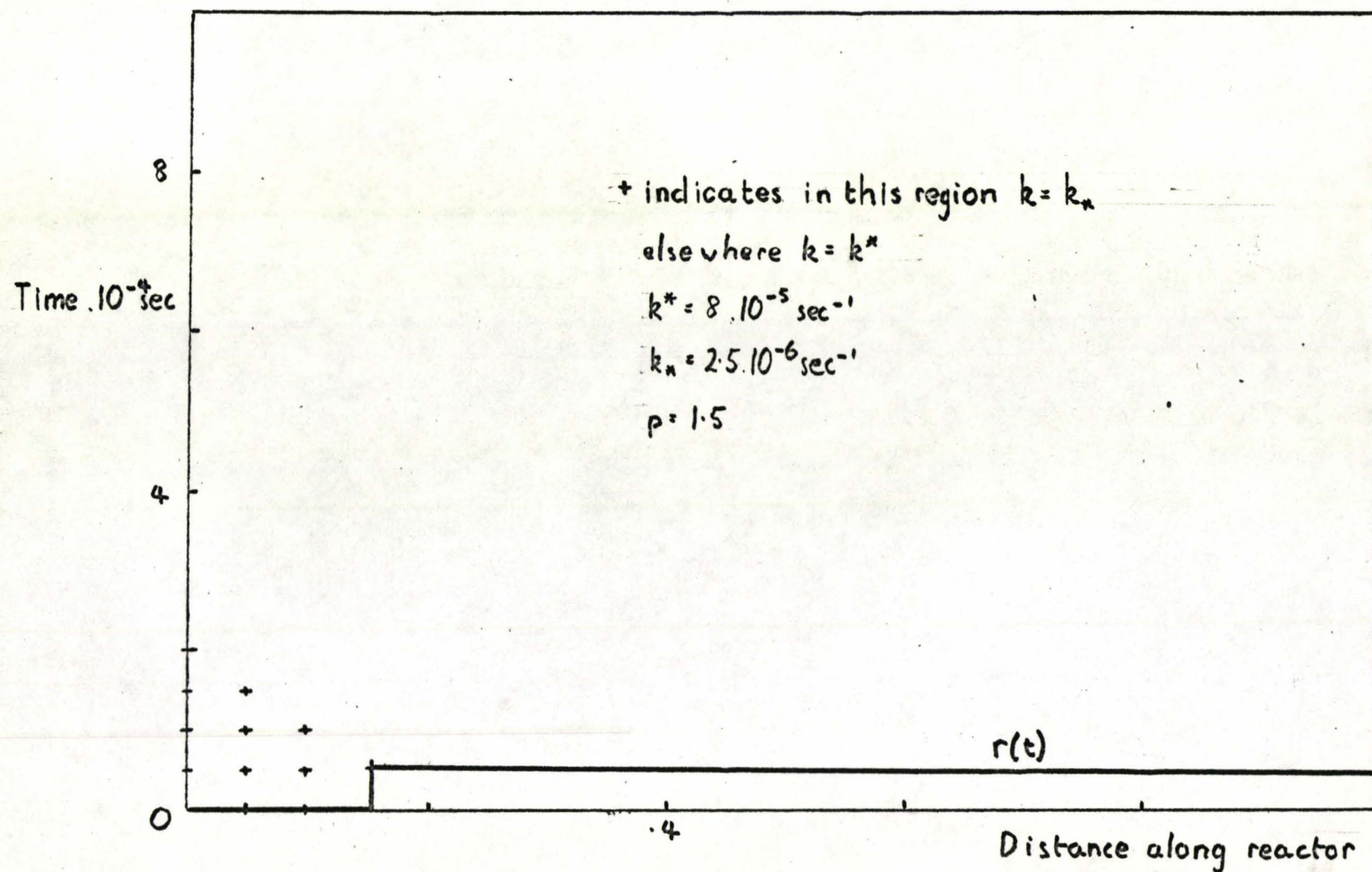
Figure 5: Profiles of k and r(t) in the irreversible reaction, k(r(t)) primary control p>1

Time $.10^{-4}$ sec (vertical axis, marked at 4 and 8)

Distance along reactor (horizontal axis, marked at .4)

+ indicates in this region $k = k_n$

elsewhere $k = k^*$

$k^* = 8 .10^{-5}$ sec^{-1}

$k_n = 2.5 .10^{-6}$ sec^{-1}

$p = 1.5$

r(t)

45.
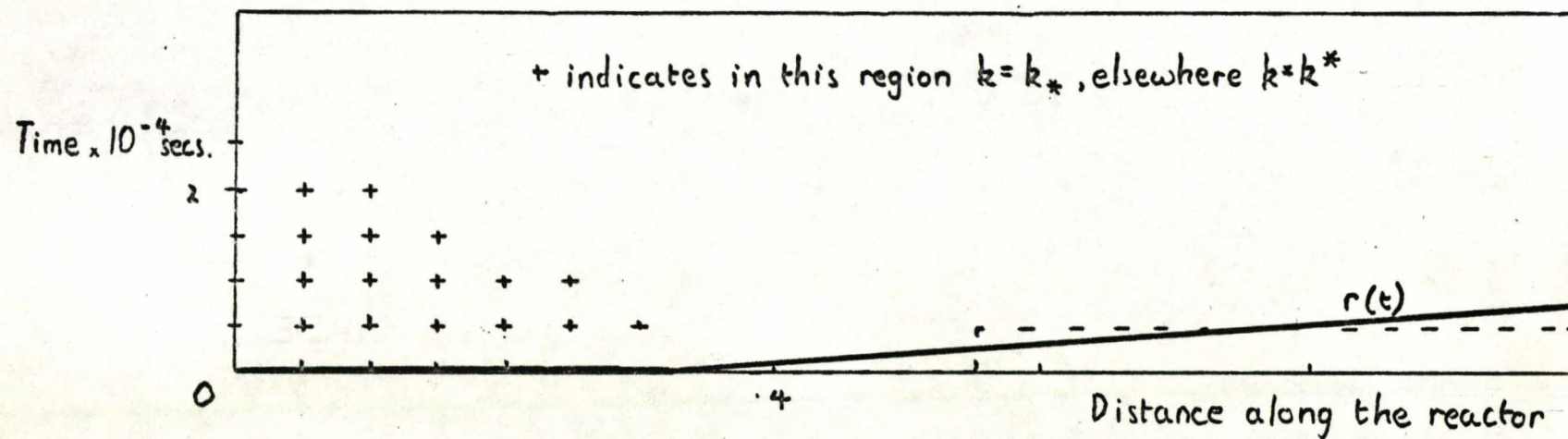
Figure 6a: Profiles of k and r(t) in the irrersible reaction, u primary control. p > 1
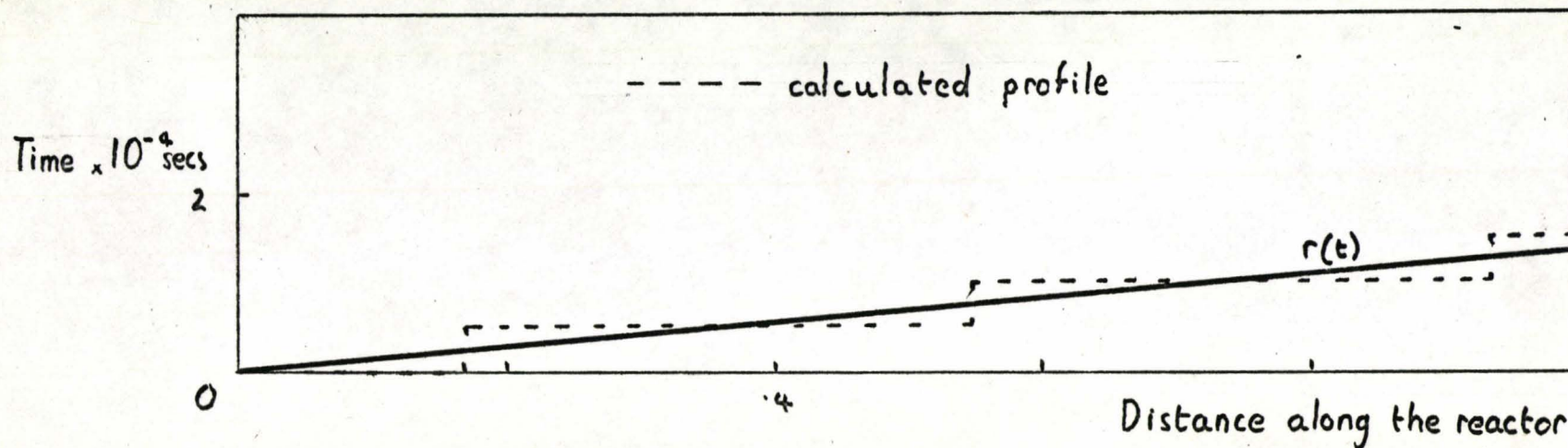
Figure 6b: Profile of r(t), irreversible reaction, invariant temperature.

Figure 7: Profile r(t), reversible exothermic reaction, k(r(t)) primary control

Text within the figure:

$k = k^*$

Time $\times 10^{-4}$ sec

k unconstrained.

$P_1 = .5$, $P_2 = 1.5$

$k^* = 8.10^{-5}$ sec^{-1}

$k_* = 2.5.10^{-6}$ sec^{-1}

r(t)

8

4

0

.4

Distance along the reactor

47.

Time.10^4sec,

k = k*

k unconstrained

p_1 = .5

p_2 = 1.5

k^* = 8.10^{-5} sec^{-1}

k_* = 2.5.10^{-6} sec^{-1}

0   2   4   6   8

Distance along the reactor
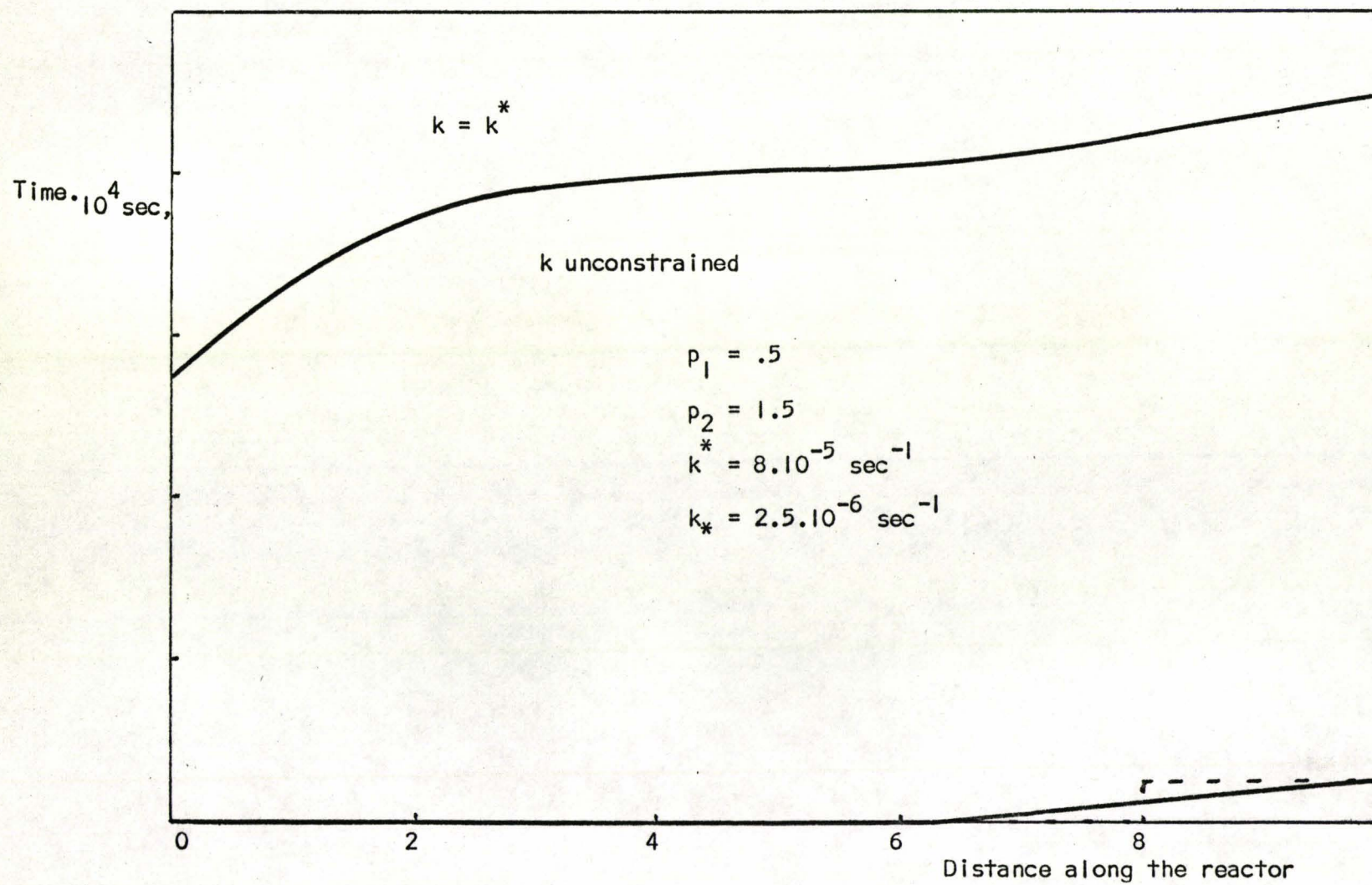
F I G U R E 8

PROFILE OF k AND r(t) IN THE REVERSIBLE EXOTHERMIC REACTION

WHERE u IS THE PRIMARY CONTROL
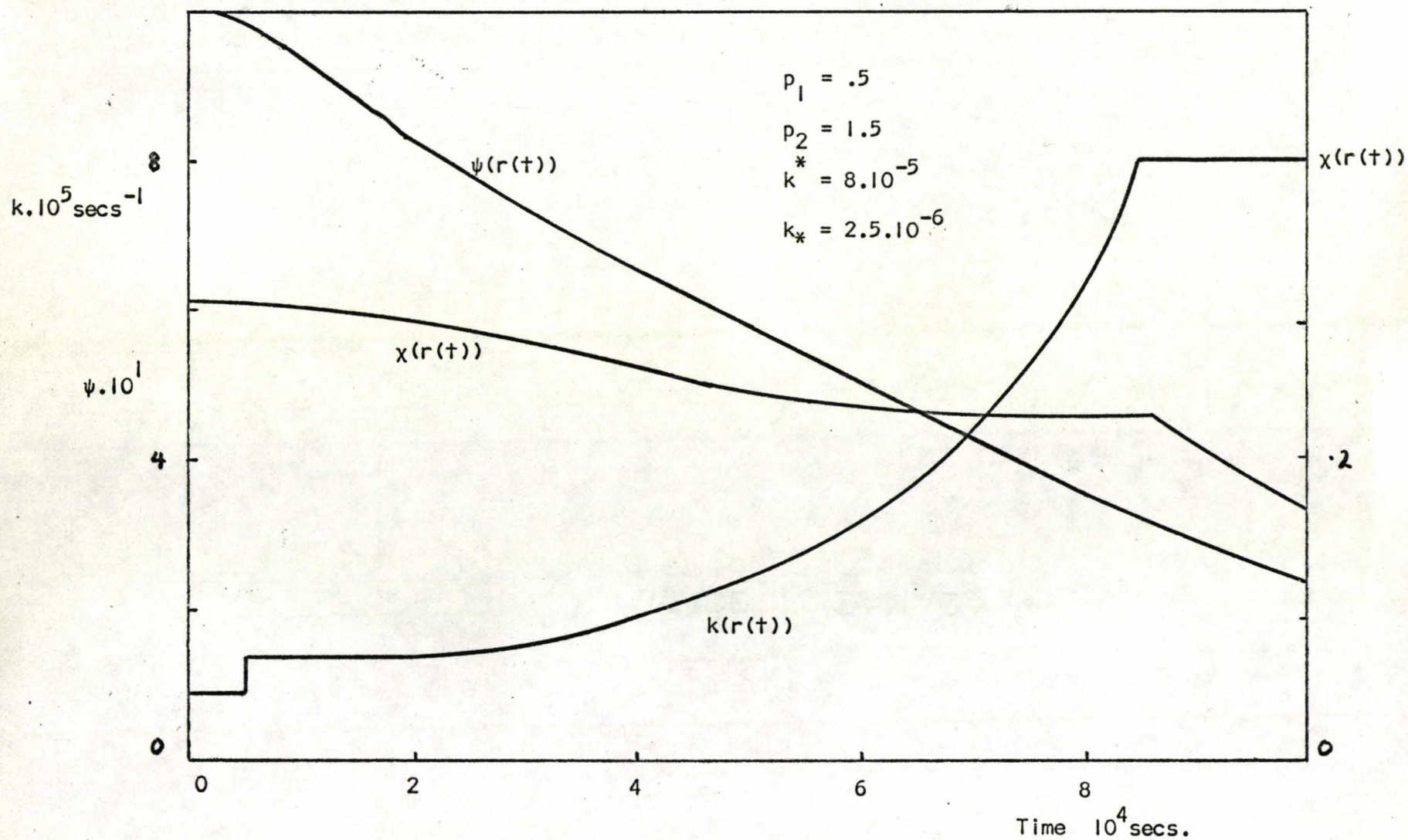
x, ψ and k at the bed exit in the reversible exothermic reaction $k(r(t))$ as primary control.

Figure 9
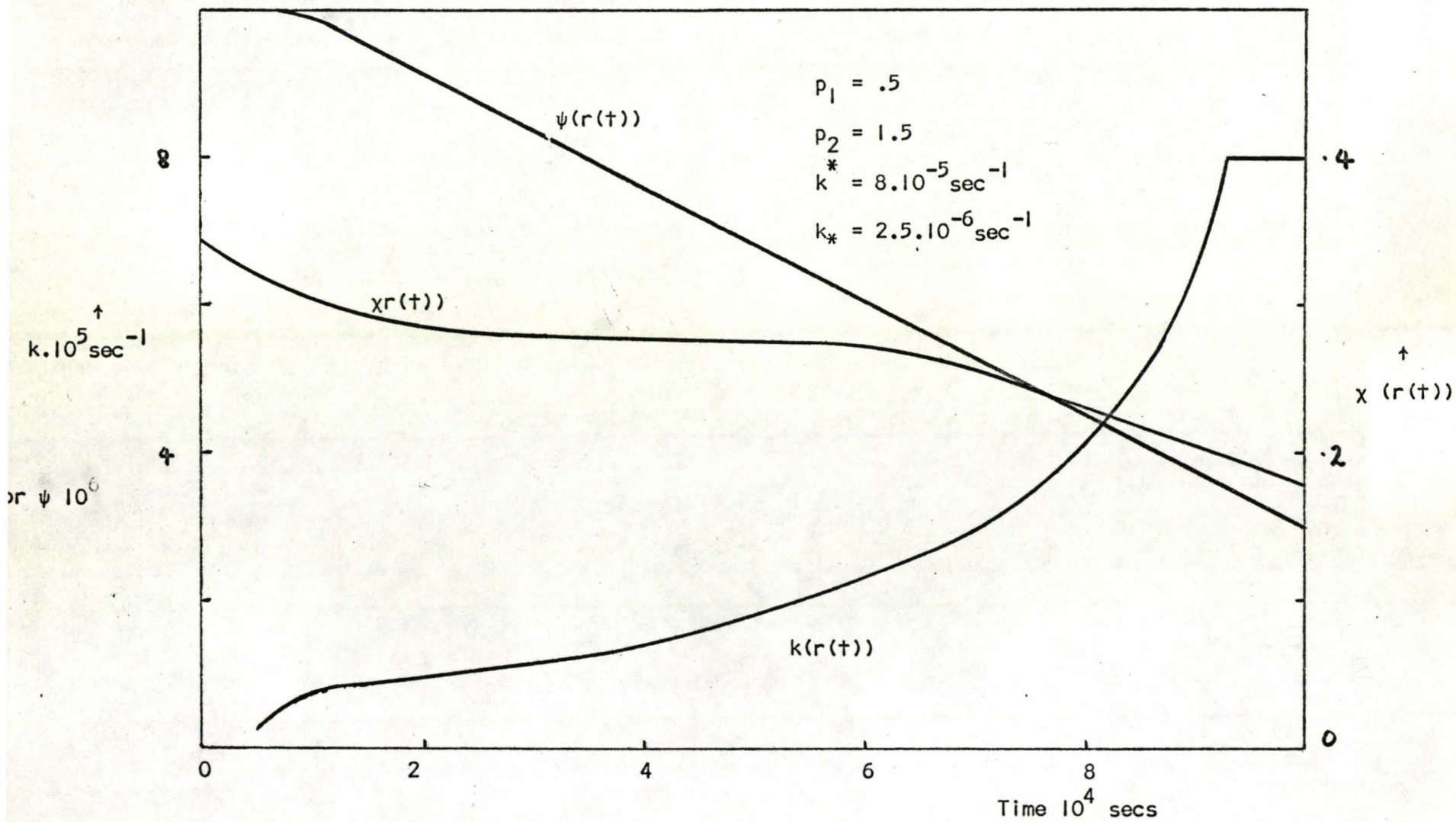
Figure 10: x, ψ and k at the reactor exit in the reversible exothermic reaction u as the primary control.
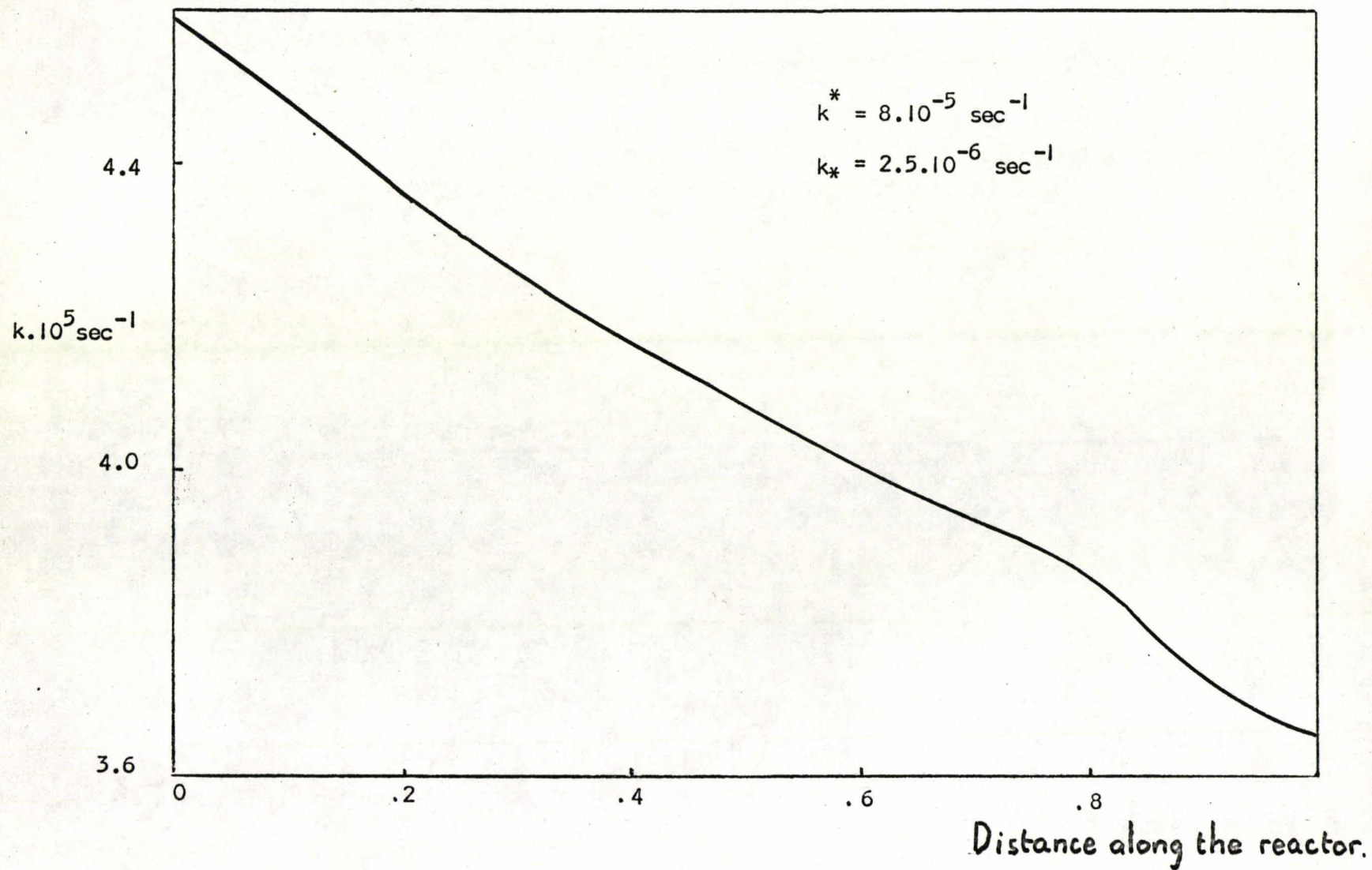
Figure 11: The rate constant profile along the reactor at $t = 45000$ secs, reversible exothermic reaction, $k(r(t))$ primary control.

The chart is labeled with:

$k^* = 8.10^{-5}$ sec^{-1}

$k_* = 2.5.10^{-6}$ sec^{-1}

Y-axis: $k.10^5$ sec^{-1}, with values 3.6, 4.0, 4.4

X-axis: Distance along the reactor, with values 0, .2, .4, .6, .8

Time 10^{-4} sec

+ indicates in this region k = k_* elsewhere k = k^*

$k^* = 2.10^{-5}$ sec^{-1}

$k_* = 2.5.10^{-6}$ sec^{-1}

$p_1 = 1.5$

$p_2 = 1.5$

r(t)

Distance along the reactor
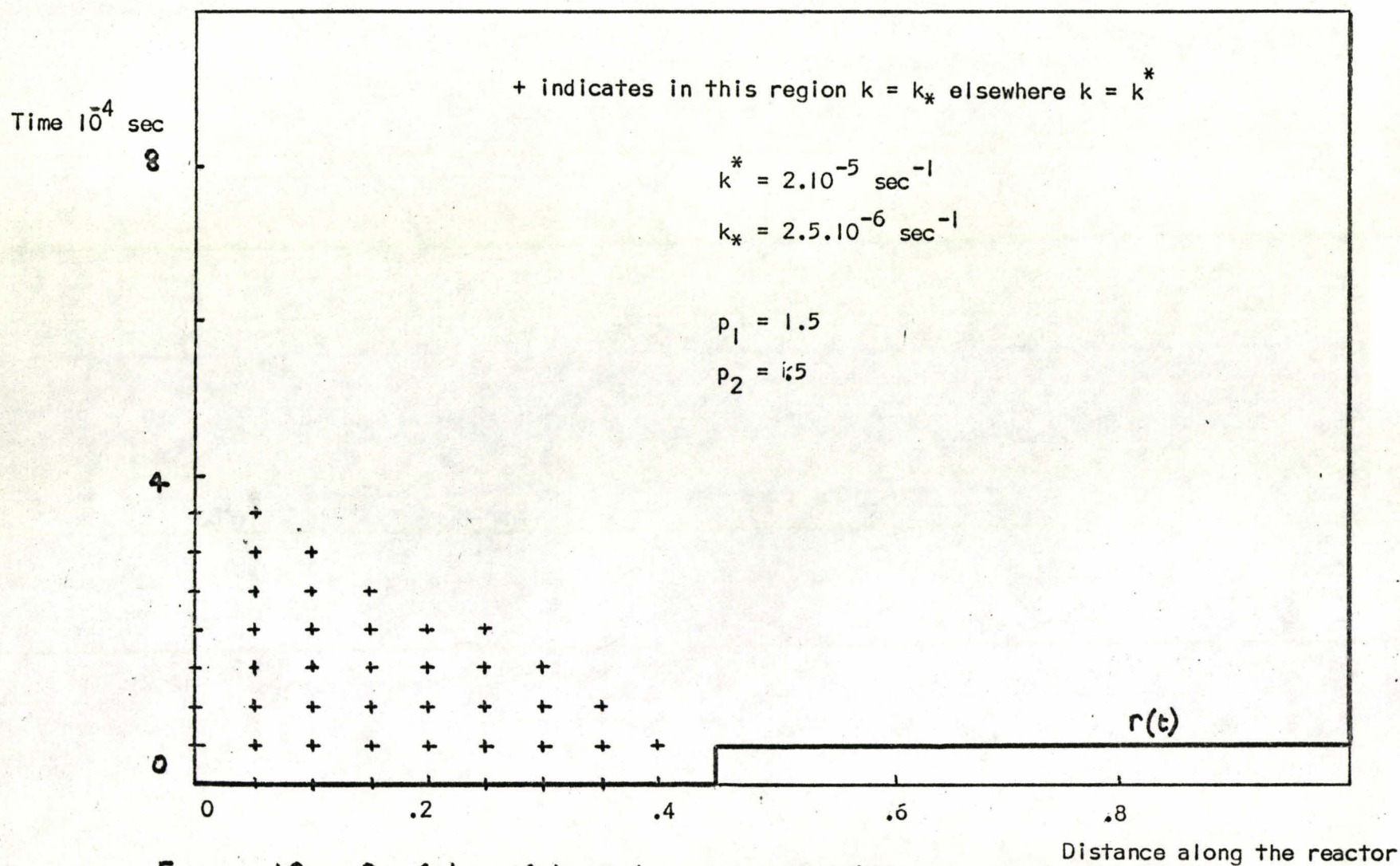
Figure 12: Profiles of k and r(t), reversible endothermic reaction, k(r(t)) primary control

52.
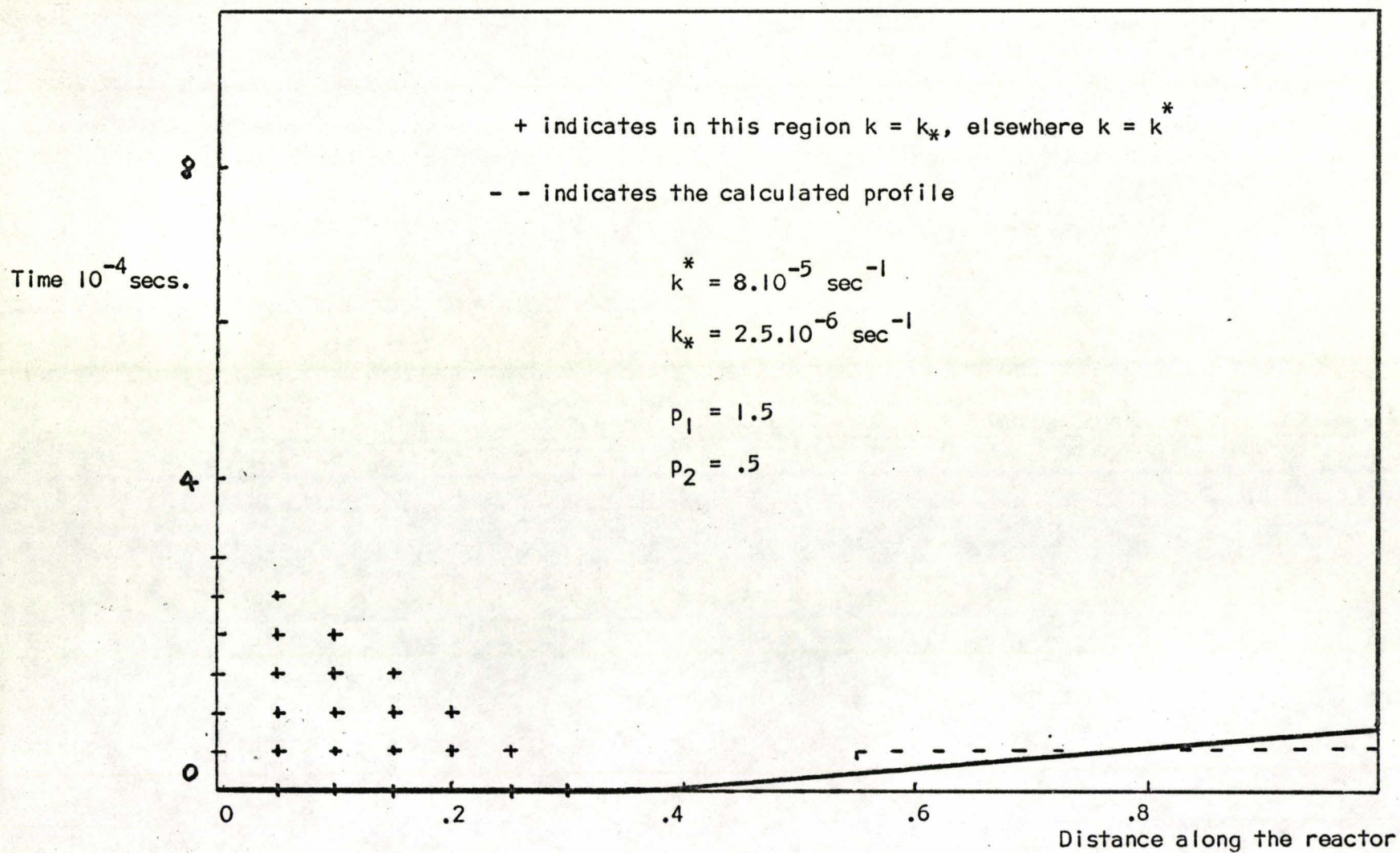
FIGURE 13

PROFILES OF k AND r(t) IN THE REVERSIBLE ENDOTHERMIC REACTION WHERE u IS
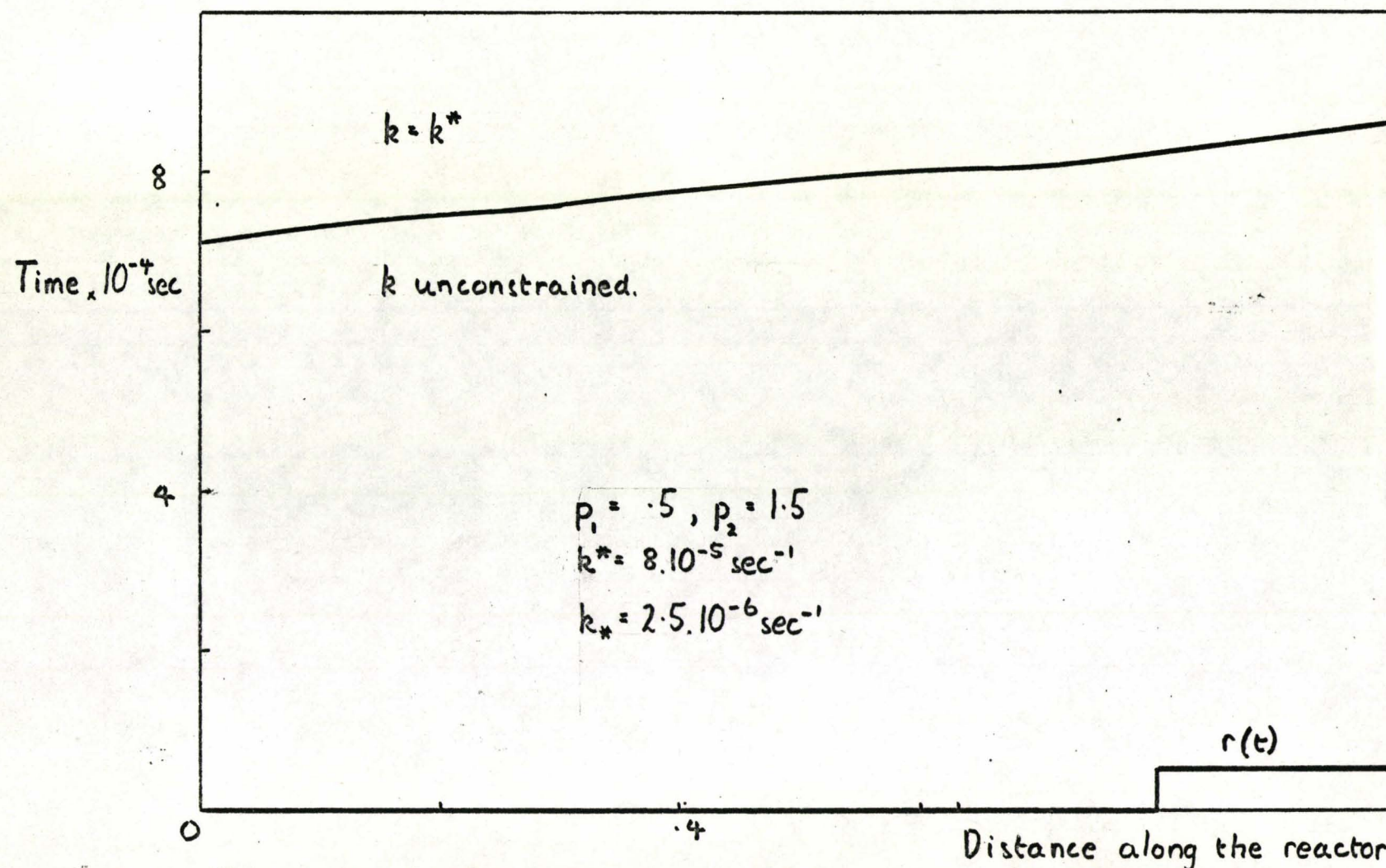
THE PRIMARY CONTROL

$$k = 8.10^{-5} \text{ sec}^{-1}$$

The dotted line indicates the calculated profile.
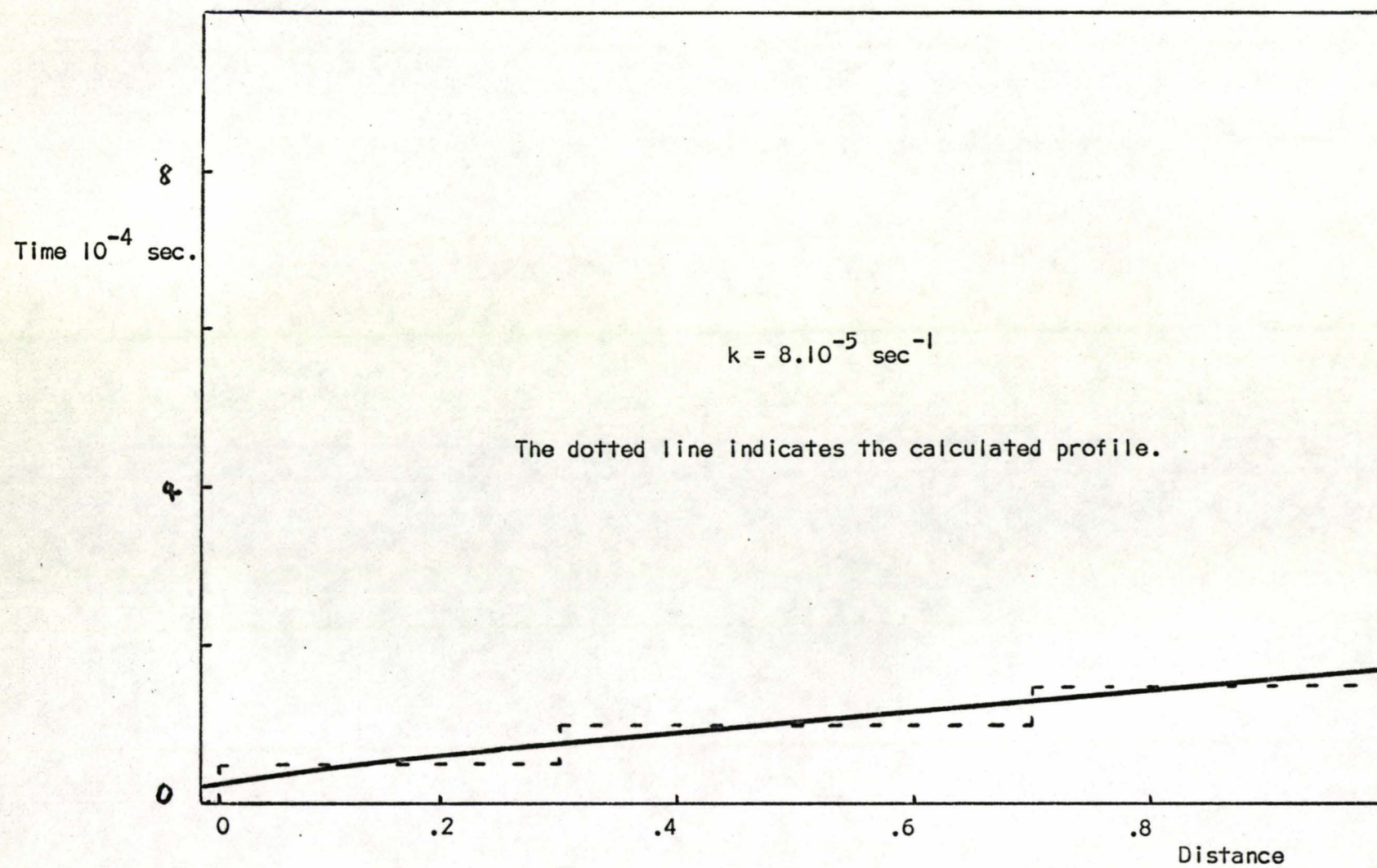
F I G U R E 14

PROFILE OF r(t) IN THE TEMPERATURE INVARIANT REVERSIBLE REACTION

CONCLUSIONS AND SUMMARY

Features of the optimal catalyst addition and temperature control policies have been deduced for general and specific catalyzed reaction schemes where the catalyst undergoes decay. The principal results are summarized below:

1.   Except under special circumstances an unconstrained rate of catalyst addition precludes an unconstrained bed-exit temperature, and vice-versa, within an optimal solution.

2.   Unconstrained extremal temperatures may be non-optimal. Where this is so, within any optimal solution a control policy in which the temperature switches between the limits is required.

3.   For an irreversible reaction, where the activation energy for the reaction is less than that for catalyst decay, the complete bed needs to be present or there should be no catalyst present at all. The temperature monotonically increases with time, here unconstrained temperatures may form part of an optimal policy.

4. i   Where the temperature switches between its bounds, within an optimal policy, for the irreversible and reversible reactions it is advantageous to delay the addition of some of the catalyst.

5.   If control over the temperature is absent the optimal delay in catalyst addition towards the reactor exit is larger than if temperature control may be exerted. In conserving catalytic activity a low temperature plays the same role as the postponed addition of catalyst.

CHAPTER 6

FUTURE WORK

Further aspects of this problem that could well be investigated
are:

1.   Where the pressure drop over the reactor rather than the space
time is held constant. Another possibility would be to have complete
control over the flow rate.

2.   Where the entry temperature is specified but where thereafter
it is determined by wall cooling and the evolution of heat from the
reactions.

3.   Where the reaction time is not fixed but allowed to vary so as to
maximize the overall conversion, over a period of reaction and regeneration.

4.   Where each reaction has its own specific catalyst, the catalyst
mix being one of the controls.

Within this study a stronger justification needs to be provided
for the assertion that for optimal temperature control, where this is not
subject to other constraints, the Hamiltonian should be maximized. The
nature of the bang-bang control could be examined and a new algorithm for
exercising this devised. The semi-qualitiative arguments that were
employed to show optimal policies should be investigated and strengthened.

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NOMENCLATURE

A, B   –   The components involved

b_j –   Constant of proportionality between K_j and k^{P_j}

E_C –   Arrhenius activation energy for catalyst decay

E_{R_j} –   Arrhenius activation energy for the jth reaction

F_j –   Conversion (or concentration) term in the rate expression for the jth reaction.

g   –   Activity dependent factor in the catalyst decay rate

H   –   Hamiltonian

J   –   Hamiltonian's 1st derivative

K_j –   Rate constant of the jth reaction

k   –   Catalyst decay rate constant

L   –   Maximum catalyst bed length

n   –   Exponent of ψ in g

P   –   Objective function

p_j –   Ratio of activation energies: $p_j = E_{R_j}/E_C$

r   –   Catalyst bed length

T   –   Temperature

t   –   Time

t_1 –   Time at which the bed is first filled

u   –   Rate of catalyst addition

x_i –   The concentration or conversion of the ith component

z   –   Distance

Greek Symbols

α —   Weighting factor within the objective function

λ_1 —   Adjoint variable to χ

λ_2 —   Adjoint variable to ψ

λ_3 —   Adjoint variable to r

ν —   Stoichiometric mole number

τ —   Total reaction time

ψ —   The catalyst activity

Subscripts

i,q   —   Components

j   —   Reaction

0   —   Inlet

*   —   Minimum

Superscripts

*   —   Maximum

<div align="center">APPENDIX I</div>

A First Order Variational Analysis

Consider the system defined by (3.1) - (3.8).

Introduce small variations into the controls, this creates small perturbations in all the other quantities such that:

$$\frac{\partial(\delta\chi_i)}{\partial z} = \delta(\psi \sum_{j=1}^{m} \nu_{ji} K_j F_j), \quad 0 \leq z \leq r(t) + \delta r(t)$$

$$= 0 \qquad\qquad , \quad r(t) + \delta r(t) < z \leq L$$

(A.1.1)

$$\frac{\partial(\delta\psi)}{\partial t} = -k \frac{\partial g}{\partial \psi} \delta\psi - g\delta k, \quad 0 \leq z \leq r(t) + \delta r(t)$$

$$= 0 \qquad\qquad , \quad r(t) + \delta r(t) < z \leq L$$

(A.1.2)

$$\frac{\partial(\delta r)}{\partial t} = \delta u ; \quad \delta u = 0 , \quad t > t_1 + \delta t_1$$

(A.1.3)

$$\delta P = \int_o^\tau (\sum_{i=1}^{\ell} \alpha_i \int_o^{r(t) + \delta r(t)} \psi \sum_{j=1}^{m} (\nu_{ji} K_j F_j) + \delta(\psi \sum_{j=1}^{m} \nu_{ji} K_j F_j).dz$$

$$- \sum_{i=1}^{\ell} \alpha_i \int_o^{r(t)} \psi \sum_{j=1}^{m} \nu_{ji} K_j F_j \, dz)dt$$

Applying the mean value theorem and ignoring second and higher order small terms

$$\delta P = \int_o^\tau (\sum_{i=1}^{\ell} \alpha_i \int_o^{r(t)} \delta(\psi \sum_{j=1}^{m} \nu_{ji} K_j F_j)dz)dt$$

$$+ \int_o^{t_1} \delta r(t)(\sum_{i=1}^{\ell} \alpha_i \psi \sum_{j=1}^{m} \nu_{ji} K_j F_j) \Big|_{r(t)} .dt \qquad (A.1.4)$$

Let us introduce the co-state variables λ_{1i}, $(i = 1,\ell)$, λ_2 and λ_3 and add to (A.1.4) the double integrals of (A.1.1) and (A.1.2) multiplied by $(\lambda_{1i} - \alpha_i)$ and λ_2 respectively, and the time integral of (A.1.3) multiplied by λ_3,

Then,

$$\delta P = \int_o^\tau \int_o^{r(t)} \left(\sum_{i=1}^\ell (\lambda_{1i} \delta(\psi \sum_{j=1}^m \nu_{ji} K_j F_j) - (\lambda_{1i} - \alpha_i) \frac{\partial(\delta \chi_i)}{\partial z}) \right.$$

$$\left. - \lambda_2 g \delta k - \lambda_2 k \frac{\partial g}{\partial \psi} \delta \psi - \lambda_2 \frac{\partial(\delta \psi)}{\partial t} \right) dz.dt$$

$$+ \int_o^{t_1} (\delta r(t) \sum_{i=1}^\ell (\alpha_i (\psi \sum_{j=1}^m \nu_{ji} K_j F_j \Big|_{r(t)}) + \lambda_3 \delta u - \lambda_3 \frac{\partial(\delta r)}{\partial t}) dt \qquad (A.1.5)$$

The order of integration within a double integral may be reversed when the limits of integration are finite and constant and when the integrand has at most a finite number of finite discontinuities of fixed position and size. The satisfaction of these conditions we may here ensure.

Thus integrating by parts

$$\int_o^\tau \int_o^{r(t)} (\lambda_{1i} - \alpha_i) \frac{\partial(\delta \chi_i)}{\partial z} dz.dt = \int_o^\tau ([(\lambda_{1i} - \alpha_i) \delta \chi_i]_o^{r(t)} - \int_o^{r(t)} \frac{\partial \lambda_{1i}}{\partial z} \delta \chi_i dz) dt$$

Defining

$$\lambda_{1i} (r(t),t) = \alpha_i \qquad (A.1.6)$$

and pre-specifying

$$\chi_{i0}(t)$$

$$\int_o^\tau \int_o^{r(t)} (\lambda_{1i} - \alpha_i) \frac{\partial(\delta \chi_i)}{\partial z} dz.dt = - \int_o^\tau \int_o^{r(t)} \frac{\partial \lambda_{1i}}{\partial z} \delta \chi_i dz.dt \qquad (A.1.7)$$

Now

$$\int_o^\tau \int_o^L \lambda_2 \frac{\partial(\delta\psi)}{\partial t} dz.dt = \int_o^L \left([\lambda_2 \delta\psi]_o^\tau - \int_o^\tau \frac{\partial\lambda_2}{\partial t} \delta\psi.dt \right) dz$$

If we define

$$\lambda_2 (z, \tau) = 0$$

and observe that there may be no change in the initial activity i.e. that

$$\delta\psi(z,0) = 0$$

then

$$\int_o^\tau \int_o^L \lambda_2 \frac{\partial(\delta\psi)}{\partial t} dz.dt = -\int_o^\tau \int_o^L \frac{\partial\lambda_2}{\partial t}.\delta\psi.dz.dt \qquad (A.1.8)$$

Now

$$\int_o^\tau \int_o^L \lambda_2 \frac{\partial(\delta\psi)}{\partial t} dz.dt = \int_o^{t_1+\delta t_1} \int_o^{r(t)+\delta r(t)} \lambda_2 \frac{\partial(\psi+\delta\psi)}{\partial t} dz.dt$$

$$+ \int_{t_1+\delta t_1}^\tau \int_o^L \lambda_2 \frac{\partial(\psi+\delta\psi)}{\partial t} dz.dt$$

$$- \int_o^{t_1} \int_o^{r(t)} \lambda_2 \frac{\partial\psi}{\partial t} dz.dt$$

$$- \int_{t_1}^\tau \int_o^L \lambda_2 \frac{\partial\psi}{\partial t} dz.dt$$

Applying the mean value theorem and noting $r(t_1) = L$

$$\int_o^\tau \int_o^{r(t)} \lambda_2 \frac{\partial(\delta\psi)}{\partial t} dz.dt = \int_o^\tau \int_o^L \lambda_2 \frac{\partial(\delta\psi)}{\partial t} dz.dt - \int_o^{t_1} \delta r \left(\lambda_2 \frac{\partial\psi}{\partial t} \right)\bigg|_{r(t)} .dt \qquad (A.1.9)$$

and so we have by-passed the difficulty caused by being unable to reverse the order of integration when one of the limits of integration is a variable.

Substituting (A.1.8) into the above and recognizing that for

$$r(t) < z \le L, \quad \delta\psi = 0 \quad (3.2)$$

$$\int_0^\tau \int_0^{r(t)} \lambda_2 \frac{\partial(\delta\psi)}{\partial t} dz.dt = -\int_0^\tau \int_0^{r(t)} \frac{\partial \lambda_2}{\partial t} \delta\psi.dz.dt - \int_0^{t_1} \delta r \left(\lambda_2 \frac{\partial\psi}{\partial t}\right)\bigg|_{r(t)} dt \qquad (A.1.10)$$

$$\int_0^{t_1} \lambda_3 \frac{\partial(\delta r)}{\partial t}.dt = [\lambda_3 \delta r]_0^{t_1} - \int_0^{t_1} \delta r \frac{\partial \lambda_3}{\partial t}.dt$$

Having no wish to fix $r(0)$ and $r(t_1)$, defining

$$\lambda_3(0) = 0 = \lambda_3(t_1)$$

then

$$\int_0^{t_1} \lambda_3 \frac{\partial(\delta r)}{\partial t}.dt = -\int_0^{t_1} \delta r \frac{\partial \lambda_3}{\partial t}.dt \qquad (A.1.11)$$

Substituting (A.1.7), (A.1.10) and (A.1.11) into (A.1.5)

$$\delta P = \int_0^\tau \int_0^{r(t)} \left(\sum_{i=1}^{\ell} (\lambda_{1i} \psi \sum_{j=1}^{m} (\nu_{ji} K_j \sum_{q=1}^{\ell} \frac{\partial F_j}{\partial x_q} \delta x_q) + \frac{\partial \lambda_{1i}}{\partial z} \delta x_i) \right.$$

$$+ (\sum_{i=1}^{\ell} (\lambda_{1i} \sum_{j=1}^{m} \nu_{ji} K_j F_j) + \frac{\partial \lambda_2}{\partial t} - \lambda_2 k \frac{\partial g}{\partial \psi}) \delta\psi$$

$$+ (\sum_{i=1}^{\ell} \lambda_{1i} \psi \sum_{j=1}^{m} \nu_{ji} K_j p_j F_j /k) - \lambda_2 g) \delta k) dz.dt$$

$$+ \int_0^{t_1} (((\sum_{i=1}^{\ell} (\alpha_i \psi \sum_{j=1}^{m} \nu_{ji} K_j F_j) - \lambda_2 kg)\bigg|_{r(t)} + \frac{\partial \lambda_3}{\partial t}) \delta r + \lambda_3 \delta u) dt \qquad (A.1.12)$$

Defining

$$\frac{\partial \lambda_{1q}}{\partial z} = - \sum_{i=1}^{\ell} \lambda_{1i} \, \psi \sum_{j=1}^{m} \left(\nu_{ji} K_j \frac{\partial F_j}{\partial x_q} \right) \qquad \text{(A.1.13)}$$

$$\frac{\partial \lambda_2}{\partial t} = \lambda_2 k \frac{\partial g}{\partial \psi} - \sum_{i=1}^{\ell} \left(\lambda_{1i} \sum_{j=1}^{m} \nu_{ji} K_j F_j \right) \qquad \text{(A.1.14)}$$

$$\frac{\partial \lambda_3}{\partial t} = -\left(\sum_{i=1}^{\ell} \left(\alpha_i \, \psi \sum_{j=1}^{m} \nu_{ji} K_j F_j \right) - \lambda_2 kg \right) \Bigg|_{r(t)} \qquad \text{(A.1.15)}$$

Substituting (A.1.13) – (A.1.16) in (A.1.12)

$$\delta P = \int_{o}^{\tau} \int_{o}^{r(t)} \left(\sum_{i=1}^{\ell} \lambda_{1i} \, \psi \sum_{j=1}^{m} \nu_{ji} K_j F_j p_j / k - \lambda_2 g \right) \delta k \cdot dz \cdot dt$$

$$+ \int_{o}^{t_1} \lambda_3 \, \delta u \cdot dt$$

APPENDIX 2

The Circumstances where Unconstrained k(r(t)) is Compatible with Unconstrained u within an Optimal Solution

Assume (3.25) holds

i.e.
$$L = \sum_{i=1}^{\ell} \alpha_i \sum_{j=1}^{m} (\nu_{ji} K_j F_j (p_j - 1)) \Big|_{r(t)} = 0 \qquad (A.2.1)$$

then if this is true for more than an instant

$$\frac{dL}{dt} = 0$$

or

$$\sum_{i=1}^{\ell} \sum_{j=1}^{m} \alpha_i \nu_{ji} (K_j F_j (p_j - 1) p_j / k \frac{dk}{dt} \Big|_{r(t)} + \sum_{i=1}^{\ell} \sum_{j=1}^{m} \alpha_i \nu_{ji} (K_j (p_j - 1) \frac{dF_j}{dt} \Big|_{r(t)} = 0 \quad (A.2.2)$$

A further requirement is that

$$\frac{\partial^2 H}{\partial k^2} \Big|_{r(t)} \leq 0 \qquad (A.2.3)$$

this term being given by (3.22).

Simultaneous satisfaction of (A.2.1), (A.2.2) and (A.2.3) will be rare. For example, where the exit conversion is constant, unconstrained k(r(t)) may co-exist with unconstrained u only when

$$\frac{\partial^2 H}{\partial k^2} = 0$$

and where the first non-zero even-ordered derivative of H is negative.

APPENDIX 3

Where $t_1 \neq \tau$

The derivation in Appendix I holds here until equation (A.I.9) with a slight alteration in that all time integrals should be made between O and τ.

Then, proceeding from (A.I.9)

$$\int_o^\tau \int_o^L \lambda_2 \frac{\partial(\delta\psi)}{\partial t} dz.dt = \int_o^\tau \int_o^{r(t)+\delta r(t)} \lambda_2 \frac{\partial(\psi+\delta\psi)}{\partial t} dz.dt$$

$$- \int_o^\tau \int_o^L \lambda_2 \frac{\partial\psi}{\partial t} dz.dt$$

$$= \int_o^\tau \int_o^{r(t)} \lambda_2 \frac{\partial(\delta\psi)}{\partial t} dz.dt$$

$$+ \int_o^\tau \delta r(\lambda_2 \frac{\partial\psi}{\partial t})\Big|_{r(t)} dt \qquad (A.3.1)$$

applying the mean value theorem, ignoring second and higher order small terms. Again we may proceed as previously with the above mentioned alteration.

APPENDIX 4

The Properties of the Adjoint Variables

1.   Examining (3.33), if at any time λ_1 should ever be zero then λ_1 always takes that value at that time.

As

$$\lambda_1(r(t),t) = 1$$

then

$$\lambda_1 > 0, \qquad 0 \leq z \leq r(t)$$

2.

$$\frac{\partial(\lambda_1 F)}{\partial z} = \frac{\partial \lambda_1}{\partial z} F + \lambda_1 \frac{\partial F}{\partial x} \frac{\partial x}{\partial z}$$

substituting (3.31) & (3.33) $= -\lambda_1 \psi K \frac{\partial F}{\partial x} F + \lambda_1 \frac{\partial F}{\partial x} \psi KF$

$$= 0$$

Thus

$$\lambda_1 F = F_{r(t)}$$

3.   From (3.36), as

$$\lambda_1 K F > 0$$

when $\lambda_2 = 0$,

$$\frac{\partial \lambda_2}{\partial t} < 0$$

but

$$\lambda_2(\tau) = 0 \quad (3.37)$$

and hence

$$\lambda_2 > 0, \qquad 0 \leq t < \tau$$

APPENDIX 5

The Optimal Policy when k(r(t)) is the Primary Control and p < 1

If initially $k(r(0)) > k_*$,

$$J \geq 0$$

and from (3.37), (3.43) and (3.44)

$$\frac{\partial \lambda_3}{\partial t} < 0$$

Thus as,

$$\lambda_3 < 0, \qquad t > 0$$

from (3.27)

$$u = 0$$

If however $k(r(0)) = k_*$, perhaps $u = u^*$. But u^*, being arbitrary may be set to a large value and hence at $t > 0$, the reactor will be filled.

Thus regardless of $k(r(0))$, initially $u = 0$ though perhaps later $u = u^*$.

Now let us digress to obtain some useful results:

We know

$$\frac{\partial \chi}{\partial z} = \psi K F \qquad (3.31)$$

integrating

$$\int_{\chi_0}^{\chi(r(t))} \frac{d\chi}{F(\chi)} = \int_0^{r(t)} \psi K \, dz$$

Differentiating with respect to time

$$\left(\frac{\partial \chi}{\partial t} \cdot \frac{1}{F}\right)\Big|_{r(t)} = u(\psi K)\Big|_{r(t)} + \int_0^{r(t)} \frac{\partial}{\partial t}(\psi K).dz \qquad (A.5.1.)$$

assuming the inlet conversion to remain constant.

From (3.44),

$$\frac{\partial J}{\partial t} = gKF\Big|_{r(t)} (1-p) + \psi Kp(p-1)\frac{\partial k}{\partial t} F\Big|_{r(t)} / k^2 + \frac{\psi Kp}{k} \frac{\partial F(r(t))}{\partial t} \qquad (A.5.2)$$

and whilst k is unconstrained and optimal

$$J = 0 \quad \text{and} \quad \frac{\partial J}{\partial t} = 0 \qquad (A.5.3)$$

Using (A.5.2) and (A.5.3), substituting the resulting expression for $\frac{\partial k}{\partial t}$ into (A.5.1) we have, where k is unconstrained and optimal

$$\frac{\partial x(r(t))}{\partial t} = u(\psi KF)\Big|_{r(t)} + \int_0^{r(t)} \frac{\psi Kp}{(1-p)} \frac{\partial F(r(t))}{\partial t} dz \qquad (A.5.4)$$

The expression for $\frac{\partial k}{\partial t}$ is

$$\frac{\partial k}{\partial t} = \frac{k}{(1-p) F\Big|_{r(t)}} \frac{\partial F(r(t))}{\partial t} + \frac{gk^2}{\psi p} \qquad (A.5.5)$$

Reverting to the question in hand, consider a bed of constant depth (u=0) where k is unconstrained and optimal

From (A.5.4)

$$\frac{\partial x(r(t))}{\partial t} = \int_0^{r(t)} \frac{\psi Kp}{(1-p)} \frac{\partial F(r(t))}{\partial t} dz \qquad (A.5.6)$$

As $\frac{\partial F}{\partial x} < 0$ this can only be reconciled with (A.5.1) if

$$\frac{\partial x(r(t))}{\partial t} = 0 = \frac{\partial F(r(t))}{\partial t}$$

Hence where u = 0 and k is unconstrained at all points within the bed the exit conversion is constant, and from (A.5.5) the temperature rises.

When at all points $k = k^*$ or $k = k_*$

$$\frac{\partial \chi(r(t))}{\partial t} < 0 \quad \text{and} \quad \frac{\partial F(r(t))}{\partial t} > 0$$

Thus, from examination of (A.5.3) we observe that as $p < 1$ and k is constant,

$$\frac{\partial J}{\partial t} > 0$$

Where at some t, for some z, k lies upon a bound and for other z it is un-constrained, from (A.5.1) where $u = 0$ and $Y = \frac{\partial}{\partial t} (\psi K)$

$$\left(\frac{\partial \chi}{\partial t} \frac{1}{F}\right)\Big|_{r(t)}^{r(t)} = \int_{0}^{r(t)} Y dz$$

$$Y = -Kkg \quad \text{where} \quad J \neq 0$$

$$Y = \frac{\psi Kp}{(1-p)} \frac{\partial \ln(F(r(t)))}{\partial t} \qquad \text{where} \quad J = 0$$

If

$$\frac{\partial F(r(t))}{\partial t} \leq 0, \qquad \frac{\partial \chi(r(t))}{\partial t} < 0$$

which is impossible as it contradicts the demand that

$$\frac{\partial F}{\partial \chi} < 0$$

Thus in the intermediate region

$$\frac{\partial F(r(t))}{\partial t} > 0$$

and where k is upon a constraint

$$\frac{\partial J}{\partial t} > 0$$

otherwise

$$J = 0$$

Thus we see that J will increase monotonically with time and hence, once $u = 0$, as

$$\frac{\partial \lambda_3}{\partial t} \leq 0$$

u will always take that value.

This, in conjunction with the knowledge that initially u = 0, rules out the partial initial filling of the reactor.

Furthermore, in general, the temperature will increase with increasing time except where J = 0 in a transition zone from unconstrained to constrained k. Finally though $k(z,\tau) = k^*$.

The above analysis is general for any activity profile at $\bar{t}$ = 0. However, if the bed has a uniform initial activity profile, then examination of the equations in this Appendix shows that the optimal temperature profile should be the same for all z. Then there will be no times at which a partial transition has been made along the bed from unconstrained to constrained k.

It is convenient at this point to observe that in the special case where p = 1/n, n being the exponent in the definition

$$g = \psi^n$$

it may easily be shown from (A.5.5) that where k is unconstrained for $z \leq r(t)$, the catalyst activity decays uniformly in time.

APPENDIX 6

The Optimal Policy for Unconstrained u as the Primary Control and p < 1

$$J = p \psi K F \Big|_{r(t)} /k - \lambda_2 g \quad (3.44)$$

Let us consider the value of J at any point. $F\Big|_{r(t)}$, K, k, ψ, λ_2 and g are here continuous functions with a finite rate of change with time. Hence also J will have a finite time derivative.

At a time t such that z = r(t)

$$k(r(t)) = k_*$$

and as

$$\frac{\partial \lambda_3}{\partial t} = 0$$

or

$$(\psi K F - \lambda_2 \, kg) \Big|_{r(t)} = 0 \quad (3.43)$$

Here

$$J < 0$$

For an unconstrained optimal temperature

$$J = 0$$

Now as $\frac{\partial J}{\partial t}$ is finite

then whilst u is unconstrained, in an optimal solution, the temperature at a point must take the lower bounding value for a time interval that is non-zero, though perhaps short, after catalyst addition is made.

APPENDIX 7

Properties of Optimal Solutions of the Reversible Reaction

Where u is the primary control, the value of $k(r(t))$ may often be determined.

If u is unconstrained, at $r(t)$, from the subtraction of (3.62) from (3.61)

$$Jk = \left. \left((p_1 - 1)\psi\nu \, K_1 F_1 - (p_2 - 1)\psi\nu \, K_2 F_2 \right) \right|_{r(t)} \qquad (A.7.1)$$

We recall (3.62), a condition for unconstrained u

$$\psi\nu(K_1 F_1 - K_2 F_2) - \lambda_2 kg = 0 \qquad (A.7.2)$$

Utilizing (3.20), as $k > 0$

if

$$Jk > 0, \quad k(r(t)) = k^*$$

and if

$$Jk < 0, \quad k(r(t)) = k_*$$

Recalling that $\mathring{\nu}_{12} > 0$, $\nu_{22} < 0$ (3.53) examining (A.7.1) and (A.7.2)

if

$$p_1 < 1 \quad \text{and} \quad p_2 < p_1 \quad \text{then} \quad k_* \le k(r(t)) \le k^*$$
$$p_2 \ge p_1 \quad \text{then} \quad k(r(t)) = k_*$$
$$p_1 = 1 \quad \text{and} \quad p_2 < 1 \quad \text{then} \quad k(r(t)) = k^*$$
$$p_2 = 1 \quad \text{then} \quad k_* \le k(r(t)) \le k^*$$
$$p_2 > 1 \quad \text{then} \quad k(r(t)) = k_*$$
$$p_1 > 1 \quad \text{and} \quad p_2 \le p_1 \quad \text{then} \quad k(r(t)) = k^*$$
$$p_2 > p_1 \quad \text{then} \quad k_* \le k(r(t)) \le k^*$$

The case where $p_1 = p_2 = 1$ involves a singular policy and is of little practical interest.

A temporary halt in catalyst addition may require that within an optimal solution $k(r(t))$ takes certain values:

During the temporary halt ($u = 0$ and $r(t) < L$), from (3.27)

$$\lambda_3 \leq 0$$

As before and after the halt $\lambda_3 = 0$

$$\frac{\partial \lambda_3}{\partial t} \leq 0$$

initially and

$$\frac{\partial \lambda_3}{\partial t} \geq 0$$

at a later stage.

Comparison of (3.61) and (3.62) shows that when

$$\frac{\partial \lambda_3}{\partial t} < 0 \quad \text{and} \quad p_1 \leq p_2, \ p_1 < 1, \ k(r(t)) = k_*$$

$$\frac{\partial \lambda_3}{\partial t} > 0 \quad \text{and} \quad p_1 \geq p_2, \ p_1 > 1, \ k(r(t)) = k^*$$

Similarly when $u = u^*$,

$$\frac{\partial \lambda_3}{\partial t} \geq 0$$

initially and then if

$$p_1 \geq p_2, \qquad k(r(t)) = k^*$$

If $k(r(t))$ is the primary control, information about λ_3 and hence u may be obtained:

If $k(r(t))$ is unconstrained and optimal

$$J = 0$$

and thus, adding (3.62) to (3.59)

$$\frac{\partial \lambda_3}{\partial t} = (\nu\psi((p_1-1)K_1F_1 - (p_2-1)K_2F_2))\Big|_{r(t)}$$

If initially $\frac{\partial \lambda_3}{\partial t} < 0$, no catalyst addition will be made to the original bed. If and when λ_3 becomes positive, the bed will be filled, if it is not already.

However where $p_1 < 1$ and $p_2 > 1$, $\frac{\partial \lambda_3}{\partial t} < 0$ at all times.

Thus we then deal with a bed of constant length – presumably with the filled reactor.

If $\frac{\partial \lambda_3}{\partial t} > 0$, following previous arguments the bed is filled.

If $k(r(t)) = k_*$, then where $p_1 \geq p_2$, from a comparison of (3.62) with (3.59), recognizing that $J < 0$,

$$\frac{\partial \lambda_3}{\partial t} > 0$$

Thus if $k(r(0)) = k_*$, the reactor is filled.

A similar result may be obtained where $k(r(t)) = k^*$

THIS 1ST LISTING IS THE PROGRAMME FOR A BANG-BANG TEMPERATURE CONTROL
POLICY, THE BOUNDARY BETWEEN THE UPPER AND LOWER TEMPERATURE REGIONS
BEING APPROXIMATED BY A STRAIGHT LINE ACROSS TIME -DISTANCE SPACE
THE SAME APPROXIMATION IS MADE FOR R(T).

```
PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
```

IT IS ASSUMED THAT THE PROFILE R(T) MAY BE APPROXIMATED BY A STRAIGHT
LINE JOINING R(O),O AND L,T1 IN DISTANCE-TIME SPACE.USING R(O) AND T1
AS ARGUMENTS A DAVIDON-FLETCHER-POWELL SEARCH PROCEDURE HERE DETERMINES
THE ARGUMENTS THAT MAXIMISE THE OBJECTIVE FUNCTION.THE TEMPERATURE
PROFILE IS CALCULATED BY A SIMPLEX METHOD.

FMFP IS THE D-F-P LIBRARY SUBROUTINE
FUNCT1 IS THE SUBROUTINE TRANSFERRING THE GRADIENTS GRAD AND THE
OBJECTIVE FUNCTION P TO FMFP
ARG(1)-ARGUMENT R(O)
ARG(2)-ARGUMENT T1
P-OBJECTIVE FUNCTION
GRAD(I)-GRADIENT OF P WITH RESPECT TO ARG(I)
EST-ESTIMATE OF THE MAXIMUM VALUE OF P
EPS-EXPECTED ABSOLUTE ERROR
LIMIT-MAX. NO. OF ITERATIONS WITHIN SEARCH
MN-NO. OF DIMENSIONS IN SEARCH-HERE 2
IER-ERROR PARAMETER

```
      DIMENSION ARG(2),GRAD(2),H(9)
      EXTERNAL FUNCT1
```

READ INITIAL ESTIMATES OF THE ARGUMENTS AND THE OTHER PARAMETERS

```
      READ(5,1)(ARG(I),I=1,2)
      READ(5,1)EST,EPS
      READ(5,2)LIMIT,MN
      WRITE(6,900)(ARG(I),I=1,2)
```

CALL THE NUMERICAL SEARCH PROCEDURE.

```
      CALL FMFP(FUNCT1,MN,ARG,P,GRAD,EST,EPS,LIMIT,IER,H)
```

WRITE OUT INFORMATION REGARDING THE STATE AND RESULTS OF THE SEARCH AT
ITS CONCLUSION.

```
      WRITE(6,900)(ARG(I),I=1,2)
      WRITE(6,900)P
      WRITE(6,901)IER
    1 FORMAT(2F10.4)
    2 FORMAT(2I5)
  900 FORMAT(2(5X,E13.6))
  901 FORMAT(2I5)
      STOP
      END
```

```
      SUBROUTINE FUNCT1(M,ARG,P1,GRAD)
```

A SUBROUTINE TO CALCULATE THE GRADIENTS OF P WITH RESPECT TO THE ARGUMENTS

```
C      BY A FINITE DIFFERENCE METHOD. WHERE THE ABSOLUTE VALUES OF THE ARGUMENTS
C      INCREASE SO ALSO DOES THE INCREMENT USED TO DETERMINE THE GREADIENTS.
C
C      SUB IS THE SUBROUTINE TO CALCULATE P FOR ASSIGNED ARGUMENTS
C
       DIMENSION ARG(2),GRAD(2)
C
C      CALCULATE P
C
       CALL SUB(ARG,Y)
       EPS1=.05
       P1=Y
       A=1.
       AM=-1.
       B=10.
       BM=-10.
C
C      EVALUATE THE GRADIENTS INDIVIDUALLY
C
       IF(ARG(1).LT.AM) EPS1=.5
       IF(ARG(1).LT.BM) EPS1=5.
       ARG(1)=ARG(1)-EPS1
       CALL SUB(ARG,Y)
       GRAD(1)=(P1-Y)/EPS1
       ARG(1)=ARG(1)+EPS1
       EPS1=.05
       IF(ARG(2).GT.A) EPS1=.5
       IF(ARG(2).GT.B) EPS1=5.
       ARG(2)=ARG(2)+EPS1
       CALL SUB(ARG,Y)
       GRAD(2)=(Y-P1)/EPS1
       ARG(2)=ARG(2)-EPS1
       RETURN
       END




       SUBROUTINE SUB(ARG,Y)
C
C      A SUBROUTINE TO CALCULATE P FOR THE ASSIGNED ARGUMENTS .FROM THESE IT
C      DERIVES THE PROFILE AND CALLS SUBROUTINES TO FIND THE TEMPERATURES AND
C      CONVERSIONS WITHIN THE BED.
C
C      I-GRID POINT-ALONG THE TIME AXIS.TIME
C      J-GRID POINT-ALONG THE DISTANCE AXIS. DISTANCE
C      ACT(I,J)-ACTIVITY
C      CK(I,J)-THE CATALYST DECAY RATE CONSTANT.
C      RK1(I,J)-THE FORWARD REACTION RATE CONSTANT.
C      RK2(I,J)-THE REVERSE REACTION RATE CONSTANT.
C      XF(I)-THE EXIT CONVERSION AT TIME I.
C      NR(J)-THE TIME (I) AT WHICH CATALYST AT A POSITION J ENTERS THE REACTOR.
C      NRI(I)-THE POSITION OF THE DOWNSTREAM END OF THE BED AT A TIME I.
C      AF1(I,J)-F1.HERE THIS IS (1.-X)
C      AF2(I,J)-F2.HERE THIS IS X.
C      NUC(I)-AN INDICATOR SHOWING IF THE CATALYST AT R(T) IS RECENTLY ADDED
C      NRIA(I)-THE POSITION OF THE BOUNDARY BETWEEN THE LOW AND HIGH TEMPERATURE
```

```
C      REGIONS AT TIME I.
C      WHERE U IS UNCONSTRAINED.IF IT IS ,NUC(I) IS 1,OTHERWISE IT IS 0.
C
       DIMENSION ARG(2),ACT(21,21),CK(21,21),XF(21),NR(21),NRI(21),
      *AF1(21,21),AF2(21,21),NUC(21),RK1(21,21),RK2(21,21),NRIA(21),P(3)
C
C      THE PARAMETER VALUES MUST HERE BE ASSIGNED.
C      CK1-THE MAXIMUM VALUE OF CK
C      RK11-     -------- DO ------- RK1
C      RK21-     -------- DO ------- RK2
C      CK2-THE MINIMUM VALUE OF CK
C      RK12-    --------- DO -------RK1
C      RK22-    --------- DO -------RK2
C      XO-THE ENTRY CONVERSION
C      NT-THE NUMBER OF GRID POINTS IN TIME.
C      NDIST- ----------- DO --------- DISTANCE.
C      NACT-THE POWER TO WHICH THE ACTIVITY IS RAISED IN ITS DECAY EQUATION.
C      MN,N,M AND D-SEE SIMPLEX.
C
       NT=21
       NDIST=21
       NACT=2
       MN=1
       N=2
       M=3
       CK1=.00008
       CK2=.0000025
       RK11=1.
       RK12=.00552
       RK21=0.
       RK22=0.
       XO=0.
       D=.1
       ZINC=.05
       TINC=5000.
       EPS=10.
       AE=0.
       AD=1.
C
C      THE TEMPERATURE IS PRESET.
C
       DO 98 I=1,NT
       DO 98 J=1,NDIST
       CK(I,J)=CK1
       RK1(I,J)=RK11
       RK2(I,J)=RK21
   98 CONTINUE
C
C      FROM THE VALUES OF THE ARGUMENTS THE PROFILE IS ESTABLISHED BY SETTING
C      NRI AND NR
C
       IF(ARG(1).GE.AD) GO TO 25
       IF(ARG(2).LT.AE) ARG(2)=AE
       A1=ARG(1)/ZINC
       A2=ARG(2)/ZINC
       AG1=NDIST-A1-1.
       NA1=A1+1.5
```

```
C
C      AN EXPANDING SIMPLEX METHOD NOW CALCULATES THE BEST TEMPERATURE AND VALUE
C      OF P.
C
   26 CALL SIMP(ZINC,NT,NDIST,CK,RK1,RK2,CK1,CK2,RK11,RK12,RK21,RK22,NRI
     *,NR,ACT,NACT,TINC,XO,P,NRIA,MN,N,M,D,IL,XF,AF1,AF2,NUC)
C
C      THE LARGEST P AT A VERTEX OF THE SIMPLEX IS SELECTED.
C
      Y=P(1)
      DO 109 LI=2,3
      IF(P(LI).GT.Y) Y=P(LI)
  109 CONTINUE
      RETURN
      END



      SUBROUTINE SIMP(ZINC,NT,NDIST,CK,RK1,RK2,CK1,CK2,RK11,RK12,RK21,
     *RK22,NRI,NR,ACT,NACT,TINC,XO,P,NRIA,MN,N,M,D,IL,XF,AF1,AF2,NUC)
C      SIMPLEX METHOD OF NELDER AND MEAD
C      X-VARIABLE PARAMETERS OF THE FUNCTION TO BE OPTIMIZED ,I-POSITION
C      J-COORDINATE
C      P-THE OBJECTIVE FUNCTION
C      MN-NO. OF REDUCTIONS
C      N-NO. OF DIMENSIONS
C      M-NO. OF MOVEMENTS FOR  WHICH A VERTEX IS ALLOWED TO BE STATIONARY
C      D-SIDE LENGTH OF THE INITIAL SIMPLEX.
C      ***************************************************************
      DIMENSION            CK(21,21),RK1(21,21),RK2(21,21),NRI(21),NR(21)
     *,ACT(21,21),NRIA(21),XF(21),AF1(21,21),AF2(21,21),X(3,2),P(3),
     *JT(3),SG(3),AZ(3),NUC(21)
C      ************* FORMATION OF STARTING SIMPLEX **************
      ALM=0.
      FY=0.
      K=N+1
      Y=FLOAT(N)
      Y1=Y+1
      DZ=D/(Y*SQRT(2.))
      EZ=SQRT(Y1)-1.
      PZ=DZ*(EZ+Y)
      QZ=DZ*EZ
      DO 50 I=1,K
      DO 50 J=1,N
      IF(I.EQ.1)GO TO 51
      NI=J+1
      IF (NI.EQ.I)GO TO 52
      X(I,J)=QZ+FY
      GO TO 50
   51 X(I,J)=FY
      GO TO 50
   52 X(I,J)=PZ+FY
   50 CONTINUE
      WRITE(6,798)
      WRITE(6,799)
      WRITE(6,800)((X(I,J),J=1,N),I=1,K)
  798 FORMAT(32H COORDINATES OF STARTING SIMPLEX)
```

```
      NA2=A2+1.5
      NA=NA1-1
      IF(NA.LT.1) GO TO 22
      DO 100 J=1,NA
      NR(J)=1
100   CONTINUE
      NAP=NA1
      GO TO 23
 22   NAP=1
 23   DO 101 J=NAP,NDIST
      NR(J)=1.5+A2*(J-NA1)/AG1
      IF(NR(J).GT.NT) NR(J)=NT
101   CONTINUE
      IF(NA2.GT.NT) NA2=NT
      DO 102 I=1,NA2
      DO 106 J=NAP,NDIST.
      IF(NR(J).EQ.I) GO TO 103
      GO TO 106
103   IF(J.EQ.NDIST) GO TO 24
      L=J+1
      IF(NR(L).EQ.NR(J)) GO TO 106
 24   NRI(I)=J
      GO TO 102
      IF(I.EQ.1) GO TO 27
106   CONTINUE
      LM=I-1
      NRI(I)=NRI(LM)
      GO TO 102
 27   NRI(I)=1
102   CONTINUE
      DO 104 I=NA2,NT
      NRI(I)=NDIST
104   CONTINUE
C
C
C     THE INDICATOR NUC(I) IS SET.
C
      DO 105 I=2,NT
      LM=I-1
      NUC(I)=1
      IF(NRI(I).EQ.NRI(LM)) GO TO 70
      GO TO 105
 70   NUC(I)=0
105   CONTINUE
      IF(NRI(1).NE.NDIST)  GO TO 71
      NUC(1)=0
      GO TO 26
 71   NUC(1)=1
      GO TO 26
 25   ARG(1)=AD
      ARG(2)=AE
      DO 107 J=1,NDIST
      NR(J)=1
107   CONTINUE
      DO 108 I=1,NT
      NUC(I)=0
      NRI(I)=NDIST
108   CONTINUE
```

```
152 IF(P(IL).GE.P(IS)) GO TO 120
122 DO 21 J=1,N
    X(IL,J)=2.*X(IL,J)-SG(J)
    IF(X(IL,J).LT.ALM)X(IL,J)=ALM
 21 CONTINUE
    CALL SUBOBJ(X,IL,ZINC,NT,NDIST,CK,RK1,RK2,CK1,CK2,RK11,RK12,RK21,
   *RK22,NRI,NR,ACT,NACT,TINC,XO,Z,NRIA,XF,AF1,AF2,NUC)
    P(IL)=Z
    IF(P(IL).GE.P(IS)) GO TO 121
    GO TO 122
121 DO 24 J=1,N
    X(IL,J)=(SG(J)+X(IL,J))/2.
    IF(X(IL,J).LT.ALM)X(IL,J)=ALM
 24 CONTINUE
    CALL SUBOBJ(X,IL,ZINC,NT,NDIST,CK,RK1,RK2,CK1,CK2,RK11,RK12,RK21,
   *RK22,NRI,NR,ACT,NACT,TINC,XO,Z,NRIA,XF,AF1,AF2,NUC)
    P(IL)=Z
    GO TO 120
153 IF(FG.LT.P(IL)) GO TO 154
    DO 22 J=1,N
    X(IL,J)=0.5*(X(IL,J)+SG(J))
 22 CONTINUE
    CALL SUBOBJ(X,IL,ZINC,NT,NDIST,CK,RK1,RK2,CK1,CK2,RK11,RK12,RK21,
   *RK22,NRI,NR,ACT,NACT,TINC,XO,Z,NRIA,XF,AF1,AF2,NUC)
    P(IL)=Z
    IF(P(IL).LT.FG) GO TO 120
    II=IS
    GO TO 131
154 DO 23 J=1,N
    X(IL,J)=0.5*(AZ(J)+SG(J))
    IF(X(IL,J).LT.ALM)X(IL,J)=ALM
 23 CONTINUE
    CALL SUBOBJ(X,IL,ZINC,NT,NDIST,CK,RK1,RK2,CK1,CK2,RK11,RK12,RK21,
   *RK22,NRI,NR,ACT,NACT,TINC,XO,Z,NRIA,XF,AF1,AF2,NUC)
    P(IL)=Z
C   ****SHORTENING OF SIMPLEX EDGE LENGTH IF A VERTEX STATIONARY  ****
120 DO 14 I=1,K
    IF(IL.NE.I)JT(I)=JT(I)+1
    IF(JT(I).EQ.M) GO TO 30
 14 CONTINUE
    GO TO 301
 30 II=I
131 DO 15 I=1,K
    DO 16 J=1,N
    X(I,J)=(X(I,J)+X(II,J))/2.
 16 CONTINUE
    JT(I)=0
 15 CONTINUE
    MNN=MNN+1
    WRITE(6,900)(((X(I,J),J=1,N),P(I)),I=1,K)
900 FORMAT(3(5X,E13.6))
    WRITE(6,901)
901 FORMAT(1H0)
C   *****END AFTER MN REDUCTIONS IN EDGE LENGTH  *********************
    IF(MNN.EQ.MN) GO TO 40
    GO TO 302
```

```
  799 FORMAT(54H                      ARG1                    ARG2                              )
  800 FORMAT(2(5X,E13.6))
      WRITE(6,801)
      WRITE(6,802)
  801 FORMAT(49H SIMPLEX COORDINATES AND OBJECTIVE FUNCTION VALUE)
  802 FORMAT(1H0,71H                      ARG1             ARG2
     *          OBJECTIVE FN )
C     ***********  ESTABLISH COUNTERS  **************************************C
      IL1=0
      MNN=0
      DO 10 I=1,K
      JT(I)=0
   10 CONTINUE
C     ********  DETERMINE OBJECTIVE FUNCTION  ***************************
C     ******* RESTART AFTER SIMPLEX EDGE REDUCTION ********************
  302 DO 17 I=1,K
      CALL SUBOBJ(X,I,ZINC,NT,NDIST,CK,RK1,RK2,CK1,CK2,RK11,RK12,RK21,
     *RK22,NRI,NR,ACT,NACT,TINC,XO,Z,NRIA,XF,AF1,AF2,NUC)
      P(I)=Z
   17 CONTINUE
C     **********  SELECTION OF LARGEST VALUE  **************************
C     **********  CONTINUING SEARCH ***********************************
  301 IM=2
      IL=1
      IS=1
      DO 11 I=2,K
      IF(P(I).LT.P(IL)) GO TO 150
      NIL=IL
      IL=I
      IM=NIL
      GO TO 11
  150 IF(P(I).LT.P(IM)) GO TO 151
      IM=I
  151 IF(P(I).GT.P(IS)) GO TO 11
      IS=I
   11 CONTINUE
C     *********  SELECTION OF NEW POSITION  ***************************
C     ******* MOST RECENTLY ACQUIRED VERTEX NOT REFLECTED ************
      IF(IL.EQ.IL1)IL=IM
      DO 12 J=1,N
      S=0.
      DO 13 I=1,K
      S=S+X(I,J)
   13 CONTINUE
      SG(J)=(S-X(IL,J))/Y
      AZ(J)=X(IL,J)
      X(IL,J)=2.*SG(J)-X(IL,J)
      IF(X(IL,J).LT.ALM)X(IL,J)=ALM
   12 CONTINUE
      IL1=IL
      FG=P(IL)
C     ******* EXPANSION OR CONTRACTION *******************************
      CALL SUBOBJ(X,IL,ZINC,NT,NDIST,CK,RK1,RK2,CK1,CK2,RK11,RK12,RK21,
     *RK22,NRI,NR,ACT,NACT,TINC,XO,Z,NRIA,XF,AF1,AF2,NUC)
      P(IL)=Z
      IF(P(IM).GE.P(IL)) GO TO 152
      GO TO 153
```

```
   40 RETURN
      END



      SUBROUTINE SUBOBJ(ARG,II,ZINC,NT,NDIST,CK,RK1,RK2,CK1,CK2,RK11,
     *RK12,RK21,RK22,NRI,NR,ACT,NACT,TINC,XO,P,NRIA,XF,AF1,AF2,NUC)
C
C     THIS SUBROUTINE CACULATES THE TEMPERATURE PROFILE BY ASSUMING THAT THE
C     BOUNDARY BETWEEN THE HIGH AND LOW TEMPERATURE REGIONS MAY BE APPROXIMATED
C     BY A STRAIGHT LINE IN TIME-DISTANCE SPACE.IT THEN DETERMINES THE OBJECTIVE
C     FUNCTION FOR THAT PROFILE.
C
      DIMENSION  ARG(3,2),CK(21,21),RK1(21,21),RK2(21,21),NRI(21),NR(21)
     *,ACT(21,21),NRIA(21),XF(21),AF1(21,21),AF2(21,21),NUC(21)
      AE=0.
C
C      IF AN ARGUMENT LIES OUTSIDE THE RECTANGLE OF TIME-DISTANCE SPACE THEN
C     THE TEMPERATURE IS AT ITS MAXIMUM AT ALL TIMES WITHIN THE REACTOR.
C
      IF(ARG(II,1).LE.AE.OR.ARG(II,2).LE.AE) GO TO 25
C
C     FROM THE VALUES OF THE ARGUMENTS ,THE POSITION OF THIS BOUNDARY AT ALL
C     TIMES IS DETERMINED.
C
      A1=ARG(II,1)/ZINC
      A2=ARG(II,2)/ZINC
      NA1=A1+1.5
      NA2=A2+1.5
      NAP=NA2
      IF(NA2.GT.NT) NAP=NT
      NAZ1=NA1-1
      NAZ2=NA2-1
      IF(NAZ1.EQ.0.OR.NAZ2.EQ.0) GO TO 25
      AZ1=FLOAT(NAZ1)
      AZ2=FLOAT(NAZ2)
      DO 100 I=1,NAP
      AZ3=FLOAT(NA2-I)
      NRIA(I)=AZ1*AZ3/AZ2+1.5
  100 CONTINUE
      DO 101 I=1,NAP
      NAI=NRIA(I)
      IF(NAI.GT.NRI(I)) NAI=NRI(I)
      DO 101 J=1,NAI
      CK(I,J)=CK2
      RK1(I,J)=RK12
      RK2(I,J)=RK22
  101 CONTINUE
      IF(NAP.EQ.NT) GO TO 28
      NAP1=NAP+1
      GO TO 26
   28 DO 102 I=1,NT
      NI=NRI(I)
      NAI1=NRIA(I)+1
      IF(NAI1.GT.NI) GO TO 102
      DO 103 J=NAI1,NI
```

```
      CK(I,J)=CK1
      RK2(I,J)=RK21
      RK1(I,J)=RK11
  103 CONTINUE
  102 CONTINUE
      GO TO 27
   25 NAP1=1
   26 DO 104 I=NAP1,NT
      NRIA(I)=0
  104 CONTINUE
      GO TO 28
C
C     IF U IS UNCONSTRAINED THEN IF THE CATALYST IS NEWLY ADDED K(R(T)) IS
C     GIVEN ITS PREDETERMINED VALUE.
C
   27 DO 105 I=1,NT
      NI=NRI(I)
      IF(NUC(I).EQ.1) GO TO 29
      GO TO 105
   29 CK(I,NI)=CK1
      RK1(I,NI)=RK11
      RK2(I,NI)=RK21
  105 CONTINUE
C
C     THE OBJECTIVE FUNCTION IS CALCULATED.
C
      CALL R1(NDIST,ACT,NT,NACT,TINC,CK,NR)
      CALL R2(XO,ACT,RK1,RK2,XF,AF1,AF2,NT,NRI,ZINC,NDIST)
      CALL SUBP(P,XF,NT,TINC)
C
C     THE TEMPERATURE PROFILE AND VALUE OF THE OBJECTIVE FUNCTION ARE WRITTEN.
C
      WRITE(6,909)P
      WRITE(6,905)(NRI(I),I=1,21)
      WRITE(6,905)(NRIA(I),I=1,21)
  909 FORMAT(6(5X,E13.6))
  905 FORMAT(21I5)
      RETURN
      END



      SUBROUTINE R1(NDIST,ACT,NT,N,TINC,CK,NR)
C
C     THIS SUBROUTINE IS A 4TH ORDER RUNGE-KUTTA METHOD FOR THE SOLUTION OF
C     THE DIFFERENTIAL EQUATION DEFINING THE ACTIVITY
C
C     ADX-AN AUXILARY VECTOR FOR USE IN THIS SUBROUTINE
C     THE CATALYST HAS UNIT ACTIVITY WHEN PLACED WITHIN THE REACTOR.
C     THEREAFTER IT DECAYS
C
      DIMENSION ACT(21,21),ADX(4),NR(21),CK(21,21)
      NTM=NT-1
      DO 100 J=1,NDIST
      NL=NR(J)
      DO 101 I=1,NL
```

```
      ACT(I,J)=1.
  101 CONTINUE
      IF(NL.EQ.NT) GO TO 100
      DO 100 I=NL,NTM
      L=I+1
      A=ACT(I,J)
      CALL FACT(A,DACT,N,CK,I,J)
      ADX(1)=DACT*TINC
      A=A+ADX(1)*.5
      CALL FACT(A,DACT,N,CK,I,J)
      ADX(2)=DACT*TINC
      A=A+.5*(ADX(2)-ADX(1))
      CALL FACT(A,DACT,N,CK,I,J)
      ADX(3)=DACT*TINC
      A=A+ADX(3)-.5*ADX(2)
      CALL FACT(A,DACT,N,CK,I,J)
      ADX(4)=DACT*TINC
      ACT(L,J)=ACT(I,J)+(ADX(1)+2.*(ADX(2)+ADX(3))+ADX(4))/6.
  100 CONTINUE
      RETURN
      END




      SUBROUTINE FACT(A,DACT,N,CK,I,J)
C
C     THIS SUBROUTINE GIVES THE RATE OF DECAY OF THE ACTIVITY WITH TIME.
C
      DIMENSION CK(21,21)
      DACT=-CK(I,J)*A**N
      RETURN
      END




      SUBROUTINE R2(XO,ACT,RK1,RK2,XF,AF1,AF2,NT,NRI,ZINC,NDIST)
C
C     THIS SUBROUTINE IS A 4TH ORDER RUNGE-KUTTA METHOD TO SOLVE THE REACTION
C     RATE EQUATIONS.INFORMATION YIELDED BY IT INCLUDES THE EXIT CONVERSIONS
C     AND THE FUNCTIONS OF THE CONVERSION IN THE RATE EQUATIONS
C
C     XF(I)-THE EXIT CONVERSION
C
      DIMENSION ADX(4),ACT(21,21),RK1(21,21),RK2(21,21),XF(21),
     *AF1(21,21),AF2(21,21),NRI(21)
      DO 100 I=1,NT
      X=XO
      NL=NRI(I)-1
      ND=NDIST-1
      AF1(I,1)=1.-XO
      AF2(I,1)=XO
      DO 100 J=1,ND
      CALL FX(X,ACT,I,J,AFX,RK1,RK2)
      ADX(1)=AFX*ZINC
      X=X+.5*ADX(1)
      CALL FX(X,ACT,I,J,AFX,RK1,RK2)
```

```
      ADX(2)=AFX*ZINC
      X=X+.5*(ADX(2)-ADX(1))
      CALL FX(X,ACT,I,J,AFX,RK1,RK2)
      ADX(3)=AFX*ZINC
      X=X+ADX(3)-.5*ADX(2)
      CALL FX(X,ACT,I,J,AFX,RK1,RK2)
      ADX(4)=AFX*ZINC
      X=X+(ADX(1)+2.*(ADX(2)+ADX(3))+ADX(4))/6.-ADX(3)
      L=J+1
      AF1(I,L)=1.-X
      AF2(I,L)=X
  100 CONTINUE
      DO 101 I=1,NT
      NI=NRI(I)
      XF(I)=AF2(I,NI)
  101 CONTINUE
      RETURN
      END




      SUBROUTINE FX(X,ACT,I,J,AFX,RK1,RK2)
C
C     THIS SUBROUTINE PROVIDES THE RATE OF REACTION .
C
      DIMENSION ACT(21,21),RK1(21,21),RK2(21,21)
      AFX=ACT(I,J)*(RK1(I,J)*(1.-X)-RK2(I,J)*X)
      RETURN
      END




      SUBROUTINE SUBP(P,XF,NT,TINC)
C
C     THIS SUBROUTINE EMPLOYS SIMPSON'S RULE TO CALCULATE THE OBJECTIVE FUNCTION
C     FROM THE EXIT CONVERSIONS.
C
      DIMENSION XF(21)
      P=0.
      NP=NT-2
      DO 100 I=1,NP,2
      P=P+TINC*(XF(I)+4.*XF(I+1)+XF(I+2))/3.
  100 CONTINUE
      P=-P
      RETURN
      END
```

```
C       IF ADJ3(I) IS GREATER THAN 0,U=U(MAXIMUM).
C       IF ADJ3(I) EQUALS 0,U IS UNCONSTRAINED.
C       IF ADJ3(I) IS LESS THAN,0 U=0.
C
        DIMENSION ADJ3(21),NRI(21),ACT(21,21),RK1(21,21),RK2(21,21),
       *AF1(21,21),AF2(21,21),ADJ1(21,21),ADJ2(21,21),CK(21,21),NR(21),
       *NUC(21)
        AE=0.
        AEP=AE-EPS1
        NTM=NT-1
C
C       ADJ3(1) IS SET TO 0.
C
        ADJ3(1)=AE
        DO 100 I=2,NTM
        LM=I-1
        LP=I+1
        NIM=NRI(LM)
        NIP=NRI(LP)
        NRP=NIM+1
C
C       THE GRADIENT OF THE ADJOINT VARIABLE IS DEFINED AND FROM THIS IS
C       DETERMINED THE VALUE OF THE ADJOINT VARIABLE AFTER THE NEXT TIME
C       INTERVAL BY THE EULER METHOD.
C
        GRAD=-ACT(LM,NIM)*(RK1(LM,NIM)*AF1(LM,NIM)-AF2(LM,NIM)*RK2(LM,NIM)
       *)+ADJ2(LM,NIM)*CK(LM,NIM)*ACT(LM,NIM)**N
        TG=TINC*GRAD
C
C       IF ADJ3(I) LIES WITHIN LIMITS ABOUT I IT IS SET EQUAL TO 0.
C       IF ADJ3(LM) IS LESS THAN THE LOWER BOUND ADJ3(I) MUST BE CALCULATED,U
C       REMAINING AT 0.
C       IF ADJ3(LM) EQUALS 0,IF THE INCREASE IN THIS TIME INCREMENT TAKES IT
C       OUTSIDE THE UPPER BOUND THE BED FILLS COMPLETELY.
C       IF ADJ3(I) IS LESS THAN THE LOWER BOUND ABOUT 0,U=0.
C       IF IT LIES WITHIN THE BOUNDS ADJ3(I)=0 AND THE LENGTH OF THE BED IS
C       INCREASED BY ONE DISTANCE INTERVAL ,ASSUMING THE BED IS NOT COMPLETELY
C       FILLED.
C
        IF(ADJ3(LM).LT.AEP) GO TO 25
        IF(TG.GT.EPS1) GO TO 20
        IF(TG.LT.AEP) GO TO 21
        ADJ3(I)=AE
        NRI(I)=NRP
        NP=NRI(I)
        IF(NP.EQ.NDIST) GO TO 20
        NR(NP)=I
   24   NRII=NP+1
        DO 101 LI=LP,NT
        IF(NRI(LI).GT.NP) GO TO 22
        GO TO 101
   22   NRIL=NRI(LI)
        DO 102 LJ=NRII,NRIL
        NR(LJ)=LI
  102   CONTINUE
        GO TO 23
```

```
      PO=0.
C
C     DETERMINE THE OPTIMAL TEMPERATURE PROFILE AND OBJECTIVE FUNCTION BY AN
C     ITERATIVE PROCESS.
C
   17 CALL R1(NDIST,ACT,NT,N,TINC,CK,NR)
      CALL R2(XO,ACT,RK1,RK2,XF,AF1,AF2,NT,NRI,ZINC,NDIST)
      CALL FADJ(NDIST,ADJ2,NR,NT,TINC,RK1,RK2,CK,N,AF1,AF2,ACT,ADJ1,
     *ZINC,NRI)
      CALL CONTRK(NT,NUC,NRI,CK1,CK2,RK11,RK12,RK21,RK22,CK,RK1,RK2,
     *AP1,AP2,B1,B2,N,AF1,AF2,NDIST,ACT,ADJ2,NR,CO,ZINC,ADJ1)
      CALL R1(NDIST,ACT,NT,N,TINC,CK,NR)
      CALL R2(XO,ACT,RK1,RK2,XF,AF1,AF2,NT,NRI,ZINC,NDIST)
      CALL SUBP(P,XF,NT,TINC)
      IF(P.GE.PO) GO TO 16
      GO TO 15
   16 PO=P+EPS
      GO TO 17
C
C     WHEN THE TEMPERATURE PROFILE APPEARS TO HAVE CONVERGED WRITE OUT THE
C     CURRENT VALUES OF THE VARIABLES.
C
   15 WRITE(6,909)P
      WRITE(6,905)(NRI(I),I=1,21)
      WRITE(6,905)(NR(J),J=1,21)
      WRITE(6,909)(AF1(I,21),I=1,21,4)
      WRITE(6,909)(AF2(I,21),I=1,21,4)
      WRITE(6,909)((CK(I,J),J=1,21,4),I=1,21)
      WRITE(6,909)(ACT(I,21),I=1,21)
      WRITE(6,909)(ADJ1(I,11),I=1,21)
      WRITE(6,909)(ADJ2(I,21),I=1,21)
      WRITE(6,909)(RK2(I,21),I=1,21,4)
C
C     REPEAT CALCULATIONS TO DETERMINE A NEW PROFILE FOR R(0) UNTIL THIS
C     CEASES TO INCREASE.
C
      IF(P.GE.P1) GO TO 19
      GO TO 21
   19 P1=P+EPS
      GO TO 12
   21 WRITE(6,910)
C
C     REPEAT THE PROCESS FOR A NEW R(0)
C
      IF(MN.LT.MM) GO TO 11
  905 FORMAT(21I5)
  909 FORMAT(6(5X,E13.6))
  910 FORMAT(5H CONV)
      STOP
      END



      SUBROUTINE SET(NRI,NDIST,ACT,RK1,RK2,AF1,AF2,ADJ1,ADJ2,CK,N,
     *EPS1,TINC,NR,NT,NUC)
C
C     THIS SUBROUTINE ATTEMPTS TO CALCULATE THE OPTIMAL PROFILE FOR R(T) FROM A
C     KNOWLEDGE OF THE VARIABLE ADJOINT TO R-ADJ3(I).
```

```
C      THIS LISTING IS FOR EITHER REACTION WITH UNCONSTRAINED U, WHERE
C      EXTREMAL K ARE OPTIMAL.IT RELIES UPON NATURAL CONVERGENCE-ITERATION UNTIL
C      THERE IS NO SIGNIFICANT IMPROVEMENT IN THE OBJECTIVE FUNCTION.
C      ADJ1(I,J)-THE VARIABLE ADJOINT TO THE CONVERSION.
C      ADJ2(I,J)- ------------- DO --------- ACTIVITY.
C      CONSTANTS IN THE EQUATIONS RELATING REACTION AND CATALYST DECAY RATE
C      CONSTANTS ARE
C         B1-VALUE B FOR THE FORWARD REACTION.
C         B2 --------------- REVERSE -------
C         AP1-VALUE P FOR THE FORWARD REACTION.
C         AP2 --------------- REVERSE -------
C      XO-THE ENTRY CONVERSION.
C      N-THE POWER TO WHICH THE ACTIVITY IS RAISED IN ITS TERM IN THE DECAY EQUN.
C      NRO-THE GRIDPOINT MARKING R(O)
C      MM-THE NUMBER OF VALUES OF R(0) FOR WHICH PROFILES ARE TO BE ESTABLISHED.
C
C      ALL OTHER VARIABLES ARE AS DEFINED IN THE PREVIOUS LISTING.
C
       PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
       DIMENSION NRI(21),NR(21),CK(21,21),ACT(21,21),XF(21),RK1(21,21),
      *RK2(21,21),AF1(21,21),AF2(21,21),ADJ2(21,21),ADJ1(21,21),NUC(21),
      *CO(21,21)
C
C      ASSEMBLE THE PARAMETER VALUES.
C
       READ(5,1)NT,NDIST,N,MM,NRO
       READ(5,2)EPS,EPS1,TINC,ZINC,XO
       READ(5,2)B1,B2,AP1,AP2,CK1,CK2,RK11,RK12,RK21,RK22
     1 FORMAT(5I5)
     2 FORMAT(7F10.4)
C
C      ESTABLISH COUNTERS.
C
       MN=0
    11 MN=MN+1
       NRO=NRO-1
       NMM=0
C
C      FOR EACH VALUE R(0) SET AN INITIAL PROFILE.
C
       CALL INIT(NR,NRI,CK,CK1,CK2,RK1,RK11,RK12,RK2,RK21,RK22,NRO,NT,
      *NDIST,CO)
C
C      CALCULATE THE ACTIVITIES AND CONVERSIONS.
C
       CALL R1(NDIST,ACT,NT,N,TINC,CK,NR)
       CALL R2(XO,ACT,RK1,RK2,XF,AF1,AF2,NT,NRI,ZINC,NDIST)
       P1=0.
C
C      CALCULATE THE THE ADJOINT VARIABLES.
C
    12 CALL FADJ(NDIST,ADJ2,NR,NT,TINC,RK1,RK2,CK,N,AF1,AF2,ACT,ADJ1,
      *ZINC,NRI)
C
C      DETERMINE THE PROFILE.
C
       CALL SET(NRI,NDIST,ACT,RK1,RK2,AF1,AF2,ADJ1,ADJ2,CK,N,EPS1,TINC,
      *NR,NT,NUC)
```

```
   101 CONTINUE
    23 GO TO 100
C
C       THE BED IS FILLED AND PROFILE IS NOW DETERMINED.
C
    20 DO 103 LI=I,NT
       NRI(LI)=NDIST
   103 CONTINUE
       DO 104 LJ=NRP,NDIST
       NR(LJ)=I
   104 CONTINUE
       GO TO 55
C
C       U=0
C
    21 ADJ3(I)=TG
       NRI(I)=NIM
       NP=NIM
       GO TO 24
C
C       U EQUALS 0,ADJ3(I) IS CALCULATED AND NR(J) IS UPDATED.
C
    25 ADJ3(I)=ADJ3(LM)+TG
       NRI(I)=NRI(LM)
       IF(NR(NRP).NE.I) GO TO 27
       NRII=NRI(I)+1
       DO 107 LI=I,NT
       IF(NRI(LI).GT.NRI(I)) GO TO 26
       GO TO 107
    26 NRIL=NRI(LI)
       DO 108 LJ=NRII,NRIL
       NR(LJ)=LI
   108 CONTINUE
       GO TO 27
   107 CONTINUE
C
C       CALCULATIONS ARE MADE FOR THE FINAL TIME.
C
C
    27 IF(ADJ3(I).LT.AEP) GO TO 100
       ADJ3(I)=AE
   100 CONTINUE
       K=NRI(NTM)
       KP=K+1
       IF(ADJ3(NTM).LT.AEP) GO TO 40
       GRAD=-ACT(NTM,K)*(RK1(NTM,K)*AF1(NTM,K)-AF2(NTM,K)*RK2(NTM,K))+
      *ADJ2(NTM,K)*CK(NTM,K)*ACT(NTM,K)**N
       TG=TINC*GRAD
       IF(TG.GT.EPS1) GO TO 41
       IF(TG.LT.AEP) GO TO 40
       NRI(NT)=KP
       GO TO 43
    41 NRI(NT)=NDIST
       GO TO 43
    40 NRI(I)=K
    43 DO 110 J=KP,NDIST
```

```
      NR(J)=NT
  110 CONTINUE
C
C     THE INDICATOR NUC(I) IS DETERMINED.WHILST U IS UNCONSTRAINED NUC(I)=1,
C     OTHERWISE IT EQUALS 0.
C
   55 DO 106 I=2,NT
      LM=I-1
      IF(NRI(I).GT.NRI(LM))NUC(I)=1
      IF(NRI(I).LE.NRI(LM))NUC(I)=0
  106 CONTINUE
      NUC(1)=1
      WRITE(6,904)(ADJ3(I),I=1,6)
  904 FORMAT(6(5X,E13.6))
      RETURN
      END



      SUBROUTINE INIT(NR,NRI,CK,CK1,CK2,RK1,RK11,RK12,RK2,RK21,RK22,NRO,
     *NT,NDIST,CO)
C
C     THIS SUBROUTINE SETS AN INITIAL PROFILE FOR R(T) AND FOR THE TEMPERATURE.
C
      DIMENSION NR(21),NRI(21),RK1(21,21),RK2(21,21),CK(21,21),CO(21,21)
      DO 101 I=1,4
      NRI(I)=NRO
  101 CONTINUE
      DO 102 I=5,NT
      NRI(I)=NDIST
  102 CONTINUE
      DO 105 J=1,NRO
      NR(J)=1
  105 CONTINUE
      NRP=NRO+1
      DO 106 J=NRP,NDIST
      NR(J)=5
  106 CONTINUE
      DO 103 I=1,NT
      DO 103 J=1,NDIST
      CK(I,J)=CK1
      CO(I,J)=CK1
      RK1(I,J)=RK11
      RK2(I,J)=RK21
  103 CONTINUE
      RETURN
      END



      SUBROUTINE CONTRK(NT,NUC,NRI,CK1,CK2,RK11,RK12,RK21,RK22,CK,RK1,
     *RK2,AP1,AP2,B1,B2,N,AF1,AF2,NDIST,ACT,ADJ2,NR,CO,ZINC,ADJ1)
C
C     THIS SUBROUTINE CALCULATES THE TEMPERATURE PROFILE BY SUBSTITUTION IN
C     IN EQUATIONS WHICH APPLY TO THE OPTIMAL CASE.
C     THIS PARTICULAR ROUTINE IS APPLICABLE TO THE IRREVERSIBLE REACTION.
```

```
C
      DIMENSION NUC(21),NRI(21),CK(21,21),RK1(21,21),RK2(21,21),
     *AF1(21,21),AF2(21,21),ACT(21,21),ADJ2(21,21),NR(21),CO(21,21),
     *ADJ1(21,21)
      APA=AP2*B2
      APB=AP1*B1
      APC=APA*APB
      BA=AP1*B1
      AE=0.
C
C     IF U IS UNCONSTRAINED K(R(T)) IS PREDETERMINED.
C
      DO 100 I=1,NT
      NI=NRI(I)
      IF(NUC(I).EQ.1) GO TO 10
      NL=NI
      GO TO 11
   10 CK(I,NI)=CK2
      RK1(I,NI)=RK12
      RK2(I,NI)=RK22
      IF(NI.EQ.1) GO TO 100
      NL=NI-1
C
C     THE TEMPERATURE IS CALCULATED.
C
   11 DO 100 J=1,NL
C
C     FINALLY THE TEMPERATURE IS UPON ITS UPPER BOUND.
C
      IF(ADJ2(I,J).EQ.AE) GO TO 13
      CK(I,J)=(ADJ1(I,J)*AF1(I,J)*BA/(ADJ2(I,J)*ACT(I,J)))**2
C
C     IF THE TEMPERATURE (OR K) EXCEEDS ITS UPPER LIMIT IT IS SET EQUAL TO THIS.
C     SIMILARLY FOR THE LOWER LIMIT.
C
      IF(CK(I,J).LT.CK2) GO TO 12
      IF(CK(I,J).GT.CK1) GO TO 13
C
C     OTHERWISE THE RATE CONSTANTS ARE CALCULATED.
C
      RK1(I,J)=B1*CK(I,J)**AP1
      RK2(I,J)=B2*CK(I,J)**AP2
      GO TO 100
   12 CK(I,J)=CK2
      RK1(I,J)=RK12
      RK2(I,J)=RK22
      GO TO 100
   13 CK(I,J)=CK1
      RK1(I,J)=RK11
      RK2(I,J)=RK21
  100 CONTINUE
      DO 103 I=1,NT
      DO 103 J=1,NDIST
      CO(I,J)=CK(I,J)
  103 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE FADJ(NDIST,ADJ2,NR,NT,TINC,RK1,RK2,CK,N,AF1,AF2,ACT,
     *ADJ1,ZINC,NRI)
C
C
C     THIS SUBROUTINE CALCULATES THE VARIABLES ADJOINT TO THE CONVERSION AND
C     ACTIVITY,THE FORMER EMPLOYING A 4TH ORDER RUNGE-KUTTA METHOD,THE LATTER
C     A MODIFIED EULER METHOD.BOTH INTEGRATIONS ARE IN A BACKWARDS DIRECTION.
C     AX-AN AUXILIARY VECTOR.
C
      DIMENSION ADJ2(21,21),NR(21),RK1(21,21),RK2(21,21),CK(21,21),
     *AF1(21,21),AF2(21,21),ACT(21,21),ADJ1(21,21),NRI(21),AX(4)
      DO 100 I=1,NT
      NI=NRI(I)
      NL=NI-1
C
C
C     THE FINAL VALUE IS ASSIGNED.
C
      ADJ1(I,NI)=1.
C
C
C     THE OTHERS ARE DETERMINED.
C
      DO 101 J=1,NL
      L=NI-J
      LP=L+1
      A=ADJ1(I,LP)
      CALL RA1(A,RK1,RK2,ACT,I,LP,AXF)
      AX(1)=AXF*ZINC
      A=A+.5*AX(1)
      CALL RA1(A,RK1,RK2,ACT,I,LP,AXF)
      AX(2)=AXF*ZINC
      A=A+.5*(AX(2)-AX(1))
      CALL RA1(A,RK1,RK2,ACT,I,LP,AXF)
      AX(3)=AXF*ZINC
      A=A+AX(3)-.5*AX(2)
      CALL RA1(A,RK1,RK2,ACT,I,LP,AXF)
      AX(4)=AXF*ZINC
      ADJ1(I,L)=A-AX(3)+(AX(1)+4.*(AX(2)+AX(3))+AX(4))/6.
  101 CONTINUE
      DO 100 J=NI,NDIST
      ADJ1(I,J)=1.
  100 CONTINUE
      DO 103 J=1,NDIST
C
C
C     THE FINAL VALUE IS ASSIGNED.
C
      ADJ2(NT,J)=0.
C
C
C     THE OTHERS ARE CALCULATED.
C
      NRL=NR(J)
      IF(NRL.EQ.NT) GO TO 20
      NR1=NRL+1
      DO 102 I=NR1,NT
      K=NT-I+NRL
      L=K+1
```

```
      NK=NRI(L)
      ADJ2(K,J)=ADJ2(L,J)+TINC*(ADJ1(L,J)*(RK1(L,J)*AF1(L,J)-RK2(L,J)*
     *AF2(L,J))-N*ADJ2(L,J)*CK(L,J)*ACT(L,J)**(N-1))
  102 CONTINUE
   20 DO 103 I=1,NRL
      ADJ2(I,J)=ADJ2(NRL,J)
  103 CONTINUE
      RETURN
      END



      SUBROUTINE RA1(A,RK1,RK2,ACT,I,LP,AXF)
C
C     THIS SUBROUTINE GIVES THE GRADIENT OF ADJ1.
C     AXF-THE GRADIENT.
C
      DIMENSION RK1(21,21),RK2(21,21),ACT(21,21)
      AXF=-A*ACT(I,LP)*(RK1(I,LP)+RK2(I,LP))
      RETURN
      END
```