An Algorithmic Method For Reactor Network Synthesis

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ABSTRACT

Given a kinetic mechanism and expressions for the reaction rate, one is frequently concerned with appropriate choices for · mixing patterns and heat addition/removal for reactor design. This study presents a novel nonlinear programming (NLP) formulation for optimally generating this reactor network. Building on earlier ideas for adjoint networks, we also include networks with ideal and nonideal reactors as well as complex mixing patterns. In addition, by controlling heat addition/removal in the network, this work also extends to nonisothermal reactors.

Model and adjoint equations of this formulation form a two-point boundary value problem that interfaces with an efficient optimization strategy. Decisions representing network structure, reactor type and the amount of heat addition are made through continuous parameters in the model. The method · is therefore fairly general and can be applied to large kinetic mechanisms with almost any objective function. Literature examples are presented and solved in order to demonstrate the effectiveness of this approach.

INTRODUCTION

Over the past twenty years, process synthesis has developed into an active research area. An extensive review has been given by Nishida, et al (1981), where powerful methods for synthesizing heat exchanger networks and separation sequences are discussed. However, relatively few studies deal with the synthesis of reactor networks.

While this is a classical area of research for chemical reactor design, reactor network synthesis also represents a difficult problem because, unlike other synthesis problems, reactors are described by differential equation models, and heuristics and intuitive methods can only deal with limited cases.

Because of the nature of these problems, variational concepts have been successful in describing the sensitivity of reactor networks to decision variables. Horn and Tsai (1967) and Jackson (1968) developed adjoint networks for reactor systems. To account for local mixing Ravimohan (1971) extended Jackson's superstructure to include CSTR's. However, in his formulation, addition of a continuous stirred tank reactor (CSTR) to the network was a discrete decision and the CSTR volume could not be considered automatically by the optimization algorithm. As discussed later, we avoid this difficulty by representing CSTR's and plug flow reactors (PFR's) as limiting cases of continuous decision variables.

Waghmare and Lirh (1981) dealt with the optimal configuration of isothermal reactors by noting that optimal feeding strategies have spatial duals with PFR and CSTR combinations. Consequently, feeding strategies for batch and semibatch reactors have analogies with steady-state reactor networks.

While the above studies dealt with general objective functions based on final product rates, Chitra and Govind (1981, 1985) dealt exclusively with reactor networks that maximize yield. After classifying different reaction mechanisms from previous literature studies, and applying heuristic strategies for simpler cases, they apply a direct search procedure to optimize a serial network of recycle reactors. Finally Conti and Paterson (1985), point out that to improve overall "process" yield, reactor selectivity, not reactor yield. should be the criterion for deriving a reactor network. Using heuristics derived from experience, they derive an overall process that is more profitable than with reactors based on maximum yield.

In order to avoid discrete decisions on reactor type, as observed in Ravimohan(1971), Paynter and Haskins (1970) used a dispersion model, in which the dimensionless dispersion coefficient D was a continuous function of position in the reactor. They concluded that at the optimal solution the control variable u (derivative of D with respect to position along the reactor) was at a bound; however, this conclusion ignores constraints on D, a state variable. Also it can be shown that, at least for a zero order reaction, D need not be at a bound to satisfy the optimally conditions.

In the constant dispersion model (COM) discussed here, D is a piece-wise constant control variable; this strategy is based on the approach used by Sargent and Sullivan (1977). It is well known that in the limit as D approaches

infinity the differential equations of CDM reduce to the algebraic CSTR equations; the latter limit can be proved formally by a perturbation argument. The PFR limit, on the other hand, can be derived through a singular perturbation approach (Nayfeh, 1973 and O'Malley, 1974) . Thus there is a justification for using CDM.

This paper presents a nonlinear programming formulation for generating complex reactor networks. Following the concepts proposed by Jackson, an optimization problem is developed with split fractions, source points and sink points as continuous parameters in order to determine the mixing pattern (i. e. possible bypasses and recycles). With adiabatic and non-isothermal operation in mind, the inlet temperature and the temperature of the reactor jacket (assumed constant) are also included as continuous parameters. In the constant dispersion model, the reactor type is determined by its corresponding dispersion coefficient. A PFR (CSTR) corresponds to the lower (upper) bound on the dispersion coefficient. Any other value of this coefficient characterizes a reactor with an intermediate degree of mixing.

From this framework a system of adjoint equations is developed using optimal control theory to calculate gradients for a nonlinear programming algorithm. In the limit as the dispersion coefficient goes to zero (the PFR limit) the adjoint system of the isothermal version of the formulation coincides with Jackson's formulation. The resulting NLP problem thus has the ability to handle arbitrary, nonlinear reaction mechanisms and can generate optimal reactor networks based on a wide range of quantifiable objective functions such as yield and selectivity.

Optimal reactor networks are generated efficiently by coupling COLSYS, a code for solving two-point boundary value problems, with Successive Quadratic Programming (SQP) to solve the optimization problem. The interface for the combined algorithm allows for synthesis using multiple reaction paths that interact with each other via side streams. Interaction of the reactor network with the rest of the flowsheet is also possible. Moreover, the nonlinear programming framework is flexible enough to accommodate additional side conditions and constraints. The current formulation is presented for non-isothermal homogeneous reactions, which can also be specialized to treat isothermal and adiabatic systems.

1. PROBLEM DEFINITION

The reactor network synthesis problem can be stated as: "Given the reaction mechanism, the kinetic expressions and an objective function (e.g. reactor yield, process yield, selectivity, profit, etc.) what is the optimal reactor network that maximizes this objective?" In this study our objective functions include those that depend directly on concentrations of all species at the exit of the reactor network. It should be borne in mind that this form can be made sufficiently general by introducing new state variables and equations that account for heat duties, volumes, etc.

In Jackson's approach to solving this problem he postulates a network of reactors and deals specifically with plug flow reactor models (PFR). An objective function is then optimized with respect to ·the source or sink positions and the split fractions. In our approach we consider the general non-isothermal reaction in an axial dispersion reactor, instead of a PFR, allowing for interstage cooling or heating. We first describe the Jackson superstructure and the changes that we have made to it. We will point out the assumptions inherent in the mass and energy balances. The latter will then be coupled with this superstructure. This will be followed by a summary of the ODE's that determine the adjoint variables (Lagrange multipliers corresponding to differential equations, that change with position along the reactor). Next an optimization algorithm which uses these adjoint variables to select the optimal decision variables in the network will be presented. Finally, some test examples will be discussed.

2. GENERAL REACTOR NETWORK — THE JACKSON SUPERSTRUCTURE

• The reactor superstructure given in figure -1 is one in which are embedded a number of smaller structures. It is the goal of an optimization algorithm to select the best substructure that optimizes the objective function. Jackson's superstructure consists of a network of reactors as given below.
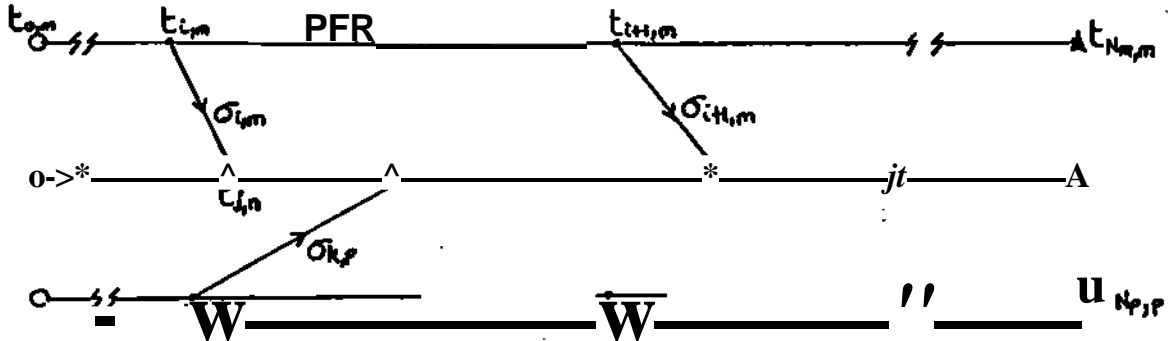

Figure 1: Network of PFR's

For example the section $(t_x$, $t_\_$) may represent the i-th reactor of the m-th reaction path. The point, t_{im} is a source point with separation matrix $<r_{im}$ which may be assumed diagonal from physical considerations. Thus an element $<r^k_{ljin}$ of $<r_{im}$ is the fraction of species k that is diverted from the exit of reactor (i-1,m) to the entrance of reactor (j,n). Als<? a simple splitting of a stream corresponds to $a * aI$, where a is less than one. Other values of $<r$ can be used to describe separation operations. Point t_{jn} is a sink point linked to the source point t_{jm} by a sidestream. In addition one can think of point $t_{fc+1,p}$ as a 'degenerate' source point with $<r = 0$; in this respect t_{Qm} (an origin) and $t_{,m}$ (a terminus) are examples of degenerate source points. Without loss of generality the origin is fixed at zero while the terminus is allowed to vary.

This network has one obvious shortcoming in that it does not influence or control mixing on the micro scale. Moreover, Jackson's approach is limited to reactors that are either isothermal, adiabatic or those for which the reaction temperature -ean be expressed solely as a function of concentrations.

To introduce micro mixing we replace the PFR model by an axial dispersion reactor (ADR), a tubular reactor with mixing in the axial direction. Mixing in an ADR is characterized by the dimensionless dispersion coefficient, D, whose lower (upper) bound corresponds to a PFR (CSTRK Note that throughout the rest of this paper D (the inverse of the Peclet number) will simply be called the "dispersion coefficient". With non-isothermal reactions in mind interstage cooling or heating will be used. Heat.exchange with a jacket or heat exchanger is modelled by specifying a position independent reactor jacket temperature and a dimensionless heat transfer coefficient. In addition to gaining extra degrees of 'freedom for optimization this approach allows for heat integration in the network.
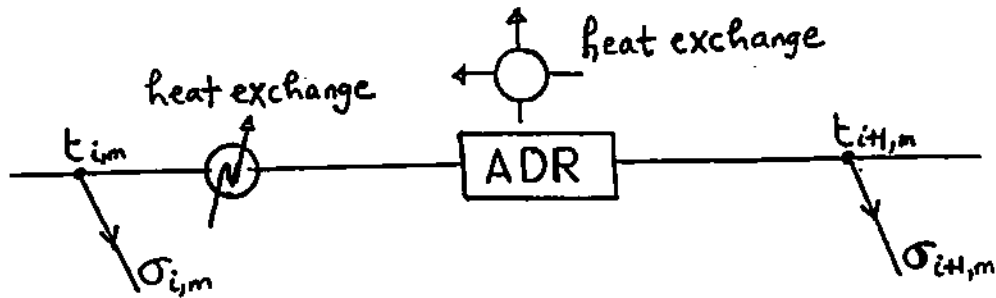
Figure 2: ADR and Heat Exchanger combination

3. MASS **AND** ENERGY BALANCES

The following quantities will be defined for the development in the following sections:

u = average axial velocity in the reactor

D – turbulent diffusion coefficient

K_y = thermal diffusivity in the axial direction

y « position along reactor

T = temperature

C = vector of concentrations of reacting species

R = vector of reaction rates

p – average density of reaction mixture

C_p ˢ heat capacity per mole of reaction mixture

q_E ˢ heat exchanged with surroundings

q_R = heat produced by reaction

h – overall heat transfer coefficient based on

bulk temperature, wall temperature difference

A_t * effective area for heat transfer through wall of reactor

$T_\S$ ^{e} coolant or heat source temperature (assumed constant)

T_o ^{s} reference temperature

r_p = rate of reference reactant of p-th independent reaction

AH_p = heat of reaction (based on one reactant) of p-th independent

   reaction

Q * volumetric flow rate in reactor

Q_o * volumetric flow rate entering reactor network

C_o * concentration of one reactant (used as a reference) in initial feed,

   (note that C is scalar)
                o
L = reference length.

Consider a non-isothermal axial dispersion reactor model (AOR) with constant temperature for the heating or cooling jacket We now restrict the system to homogeneous reactions only. Then **at steady state,** assuming radial concentration and temperature gradients are negligible **and** that the density of the reaction mixture takes on **a** constant **average value, the** species continuity equations and the energy balance are given by Carberry (1976)

$$U\frac{dC}{dy} - D\frac{d^*C}{dy^2} * R(C,T) \qquad y_1 \lessgtr, y \lessgtr y_2 \quad (1a)$$

$$u\frac{dT}{dy} - K_r\frac{\triangle}{dy^2} = (q_E + q_R)/(\rho C_p^\bullet) \qquad \text{Mb.}$$

with boundary conditions (due to Danckwerts, 1953):

$$uC(y;) \ll uC(y_1^*) - D\frac{dC}{dy}|_{y_1^*} \qquad (2a)$$

$$\frac{dC}{dy}|_{y'} = 0 \qquad (2b)$$

$$uT(\cdot) - T(\cdot^*) - K\frac{dT}{dy}| \cdot \qquad (2c)$$

$$\frac{dT}{dy}|_{y_2} = 0 \qquad (2d)$$

and the energy terms given by

$$q_{R} = \sum_{p=1}^{k} r_p (\Delta H_p) \tag{3a}$$

$$q_{E} = hA_s(T_s - T) . \tag{3b}$$

k is the number of stochiometrically independent reactions. For convenience we non-dimensionalize equations (1), (2) and (3) by introducing the following relations:

$$t = y/L \qquad \theta = T/T_o \qquad D_T = K_y /uL$$

$$D = D/uL \qquad X = QC/(Q_o C_o) \qquad W = T_s /T_o$$

$$\Gamma = LhA_s/(u\rho C_p) \qquad G(X,\theta) = (L/uT_o\rho C_p)q_R \tag{4}$$

$$F(X,\theta) = QLR(X,\theta)/(uQ_o C_o)$$

Assume also that $D_T \propto D$, i.e. let $D_T = \epsilon D$, where ϵ is a positive constant. To determine the adjoint system it is convenient to rewrite equations (1) as a system of first order differential equations. Thus

$$\frac{dX}{dt} = Z \qquad \qquad t_1^+ \leq t \leq t_2^- \tag{5a}$$

$$\frac{dZ}{dt} = [Z - F(X,\theta)]/D \tag{5b}$$

$$\frac{d\theta}{dt} = V \tag{5c}$$

$$\frac{dV}{dt} = [V - G(X,\theta) - \Gamma(W-\theta)]/(\epsilon D) \tag{5d}$$

with boundary conditions

$$x(tp \ll x(t;) + pzu;) \qquad , \qquad \text{(6a)}$$

$$Z(t_2^-) = 0 \qquad \text{(6b)}$$

$$\theta(t_1^+) = \theta(t_1^-) + \epsilon DV(t_1^+) \qquad \text{(6c)}$$

$$V(t_2^-) = 0 . \qquad \text{(6d)}$$

4. THE OPTIMIZATION PROBLEM

Consider M reaction paths such that the m-th path has N sources and/or sinks (excluding the origin). For reactor (i,m) the following boundary conditions can be written:
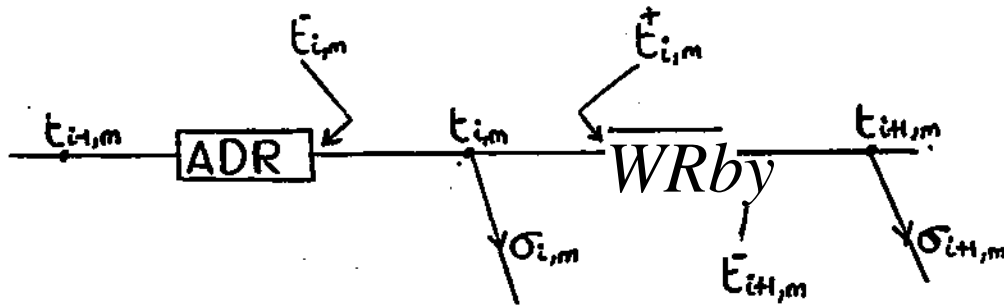

Figure 3: A segment of one reaction path in the CDM

$$X(t_{i,m}^+) = X(t_{i,m}^-) + D_{i,m} Z(t_{i,m}^+)$$

$$\theta(t_{i,m}^+) = \theta(t_{i,m}^-) + \epsilon D_{i,m} V(t_{i,m}^+)$$

where

$$X(t_J^{'X} K_m >^+ *u_i X(_*^{\wedge} L \} \qquad \text{if } *_{,\ll} \text{ is a sink}$$

$$X(t.) = (W.)x(t:) \qquad \text{if } t. \text{ is a source.}$$

Note that here $''V$ is the identity matrix. Also the tilde $''\sim''$ will be used to relate corresponding sink and source points, $t_{j,n}$ and t_{jm}, and will be used to differentiate between a sink and a source when the context does not

make it clear. For example $t_{i,m} = t^*_{j,n}$ and $t^*_{i,m} = t_{j,n}$ in figure 1, $\tilde{\sigma}_{i,m}$ is the separation matrix of the corresponding source.

Since the model must allow for preheating or precooling of the feed to reactor (i,m), we make the inlet temperature $\theta(t_{i,m})$ a decision variable by setting it equal to $\gamma_{i,m}$. In this study we follow Jackson and use an objective function that depends only on the sum of the flows p at the termini of the reaction paths. More explicitly we define the vector

$$p = \sum_{m=1}^{M} X(t^-_{Nm,m}) .$$

Then, given a superstructure, the optimization problem that needs to be solved is:

maximize (or minimize) $J = \Phi(p)$

subject to the state equations

$$\frac{dX}{dt} = Z \qquad\qquad \text{for } t^+_{i,m} \leq t \leq t^-_{i+1,m} \quad (7a)$$

$$\frac{dZ}{dt} = [Z - F(X,\theta)]/D \qquad\qquad i=0,....(N_m-1) \quad (7b)$$

$$\frac{d\theta}{dt} = V \qquad\qquad (7c)$$

$$\frac{dV}{dt} = [V - G(X,\theta) - \Gamma(W-\theta)]/(\epsilon D) \qquad\qquad (7d)$$

and boundary conditions

if $t_{i,m}$ is an origin : $X(t^+_{0,m}) = X(t^-_{0,m}) + D_{0,m}Z(t^+_{0,m})$ $\qquad\qquad$ (7e)

if $t_{i,m}$ is a sink : $X(t^+_{i,m}) = X(t^-_{i,m}) + \tilde{\sigma}_{i,m}X(\tilde{t}^-_{i,m}) + D_{i,m}Z(t^+_{i,m})$ $\qquad$ (7f)

if $t_{i,m}$ is a source : $X(t^+_{i,m}) = (1 - \sigma_{i,m})X(t^-_{i,m}) + D_{i,m} Z(t^+_{i,m})$ $\qquad$ (7g)

$Z(t^-_{i+1,m}) = 0$ $\qquad\qquad$ (7h)

$\theta(t^+_{i,m}) = \gamma_{i,m} + \epsilon D_{i,m}V(t^+_{i,m})$ $\qquad\qquad$ (7i)

$V(t^-_{i+1,m}) = 0$ $\qquad\qquad$ (7j)

ten $^{C\ 0}$ (7k)

where $X(t^\wedge)$ is fixed at a given value. Note that in fig. 3 $t_{|m}$ is a source. To convert it to a sink simply reverse the arrow. Note that the introduction of y makes it unnecessary to consider temperature relations at source and sink points.

The following bounds on the decision variables are appropriate from physical considerations:

$0 \pounds T_{,\ mm}$ (adiabatic)$\pounds T_{i,m} \pounds T_{max}$ (isothermal)$<oo$

(bounds on the heat transfer coefficient)

$0 \leq W_{min} \leq W_{i,m} \leq W_{max} < \infty$

(bounds on the temperature of cooling or heating jacket)

$0 < D_{min}$ (PFR) $\leq D_{s,r} < D_{max}$ (CSTR)$<oo$

(bounds on the dispersion coefficient)

$0 \pounds y_{min}, \pounds_{/i,m} \pounds y_{max} <00$

(bounds on inlet temperatures)

$0 \leq \sigma_{i,m} \leq 1$

$0 \leq t_{i,f} \leq t_{NfTif,J} < \infty$

Finally, note that source and sink points may cross, thus allowing recycle structures involving more than one reaction path.

5. **A SUMMARY OF THE ADJOINT SYSTEM**

To solve the above non-linear program (NLP) an algorithm will be proposed in which the decision variables, which represent the degrees of freedom in the system/ will be chosen iteratively using a gradient based approach. To apply this method we need to develop relations for adjoint variables (Lagrange multipliers associated with the differential equations) which measure the sensitivity of the objective function to changes in the decision variables $\{t_-.$, t , $\sphericalangle.$, v , W_t , $T.$ and $D, \}\}$. The derivation of this system of equations is carried out using the standard approach of adjoining the objective function J with the state equations and boundary conditions via position dependent multipliers X_A, X_B, X_c, X_Q, and constant multipliers v. A, // respectively. Employing variational techniques, for example as outlined in Bryson and Ho (1968), the following system of adjoint equations result (see appendix for the derivation):

$$\frac{dX_{.}}{dt} = \frac{1}{D}\left[(\nabla_x F)\lambda_B + (\nabla_x G/(\epsilon))\lambda_D\right] \qquad \text{for } t^+_{i,m} \leq t \leq t^-_{i+1,m} \quad (8a)$$

$$\frac{dx_B}{dt} - - (K \bullet V^D) \qquad (8b)$$

$$\frac{d\lambda_c}{dt} = \left[(\nabla_\theta F)^T \lambda_B + (\nabla_\theta G - \Gamma)\lambda_D/\epsilon\right] \qquad (8c)$$

$$\frac{d\lambda}{\text{if}} \bullet \bullet (^X e + {}^X D^{/UD}) \qquad (8d)$$

if $t_i{}^{\star}i_{JB}$ is a terminus: $X_A(t^{\wedge}_{mm}) = \dfrac{d\Phi}{dp}$ $\qquad (8e,$

if $\wedge \bullet i \wedge$ is a terminus: $X \wedge J = 0$ $\qquad (8f>$

if $t_{j+1}{}^{\wedge}$ is a sink: $X_A(t_{;+lm}) = X_A(t_{;im})$ $\qquad (8g,$

if $t^{\wedge}$ is a source: $X_A(f_{Mjm}) « (1 - {}^{\wedge}Jxjt^{\wedge}j \bullet {}^{\wedge}xjc^{\wedge}) \qquad <8h)$

$$\lambda_B(t^+_{i,m}) = - D_{i,m}\lambda_A(t^+_{i,m}) \qquad (8i)$$

$$\lambda_c(t^-_{i+1,m}) = 0 \qquad (8;)$$

$$\lambda_D(t^+_{i,m}) = - \epsilon D_{i,m}\lambda_c(t. > \qquad .(8k)$$

The gradient of the objective function. J, with respect to the decision

variables t_{Nmm}, t_{tm}, $_{,i,m'}$ $y^\wedge$. $W_{,m}$. $r_{,m}$ and D_{im} is related to the adjoint variables as follows:

$$dJ = \sum_{m=1}^{M} H(t_{Nm,m})dt_{Nm,m} + \sum_{m=1}^{M} \sum_{i=1}^{Nm-1} \left[H(t_{i,m}) - H(t_{i,m}^*) \right] dt_{i,m} +$$

$$\sum_{m=1}^{M} \sum_{i \in source}^{Nm-1} \left[\lambda_A^T(t_{i,m}^*) - \lambda_A^T(t_{i,m}^*) \right](d\sigma_{i,m})X(t_{i,m}) \bullet K^* 3T^{X}c<C^{)d}r_{,,m} +$$

$$\sum_{m=1}^{M} \sum_{i=0}^{Nm-1} \left\{ \left[\epsilon \lambda_c(t_{i,m}^*)V(t_{i,m}^*) + \lambda_A^T(t_{i,m}^*)Z(t_{i,m}^*) + \int_{t_{i,m}}^{t_{i+1,m}} (\nabla_D H)dt \right]dD_{i,m} +$$

$$\left[\int_{t_{i,n}}^{t_{i+1,m}} (\nabla_w H)dt \right]dW_{i,m} + \left[J_{t_{i,m}}^{t_{i+1,m}} ({}^{V}rH)^{dt} \right]^{dr} \ll 4 \tag{9}$$

where

$$H = X^\wedge Z * XJ[2 - F(X.<?)] /D \bullet X_C V \bullet X_D[V - G(X,^\wedge) - T(W - d)] /<^*D) ,$$

$$\nabla_W H = - (r/(_{<D})) X_D$$

$$\nabla_\Gamma H = \lambda_D (\theta - W) /(\ll D)$$

$$\nabla_D H \, s \, " \, X_B[{}^{Z} " F^{\wedge\wedge*}]^{/D*} - {}^{X}_O[{}^{V} " {}^{G}<^{X_I_\wedge>} + N^* - W)] \, /(\epsilon D^2)$$

6. PROPOSED ALGORITHM

Let Y be the vector of decision variables $[t\_ , t, , \ll r, , y, , W, , r .0]$. Then in terms of Y the NLP takes the simpler form

$$\text{MAX (or MIN)} \bullet = 4KY) \tag{a}$$

subject to:

$$Y_{rrstrs} \quad * \quad Y\pounds \quad Y_{max} \tag{b}$$

$$S_{min} \quad \pounds \quad AYS \quad S_{max} \tag{c}$$

where A is the coefficient matrix. The linear constraint set (c) may involve some or all the decision variables. For example we may require the source and sink points not to cross; for a reaction path source and sink points should be located before the terminus. Note also that we can replace (c) by a more general non-linear constraint

$$S_{min} \quad \pounds \quad S\{Y\}Z \quad S_{max} \tag{c\#}$$

at the expense of making the algorithm only slightly more complicated.

Based on the above derivation the following algorithm is proposed:

(i) Choose a superstructure of reactor networks as shown in figure 1.

(ii) Provide an initial guess for the decision variables $t_{i,m}$, $<r_{i,m}$, $y._{i,m}$, $W_{i,m}$, $r_{i,m}$ and $D._{i,m}$.

(iii) For reactor (i,m) solve the state equations (7), a set of non-linear two-point boundary value ODE's. Here we used COLSYS (Ascher et al , 1979), a TPBVP ODE solver that uses orthogonal collocation on finite elements. Store X, Z, 6. V and, the objective function J.

(iv) Using state variables from (iii) solve the linear Adjoint equations (8) with COLSYS.

(v) Use equation (9) to calculate the derivatives of the objective function with respect to the above decision variables.

(vi) Calculate a search direction for the decision variables by setting up and solving the following quadratic program at Y_{fc}.

$$\text{MAX (or MIN)} \quad Q = \nabla^T \Phi\{Y_k\} (d_k \quad * \quad 1/2 <j_k^T \quad B^\wedge d_{fc}$$
$$d_k$$

subject to:

$$Y_{min} \quad \bullet \quad Y_k \quad * \quad <_k \quad * \quad Y_{max} \quad - \quad Y_k$$

$$S_{min} \quad - \quad AY_k \quad * \quad Ad_k \quad \pounds \quad S_{max} \quad "AY_k$$

Here B^k is a positive definite hessian matrix constructed by a quasi-Newton updating formula; it serves as an approximation to $V^2 4KY_k)$. With the search direction d_{fc}, update Y by $Y_{k-M} = Y_k \bullet «_k d_{k\#}$ where $«_k$ is a stepsize selected so that a sufficient decrease in • is found at Y_{fc+1}. This Successive Quadratic

Programming (SQP) algorithm is given in Han (1977) and Powell (1977). A complete description of an updated algorithm is given in Biegler and Cuthrell (1985).

(vii) If the Kuhn-Tucker conditions for a stationary point of the NLP are satisfied to a specified tolerance, δ, STOP (see appendix). Else go to (iii).

It should be noted that depending on the general nature of the objective function J there could be multiple local optima for the NLP. To gain confidence that a global optimum is found it might therefore be useful to restart the algorithm from different initial points. However, unless the objective function exhibits special features (such as convexity in the decision variables) there is no guarantee that a global optimum can be found.

7. TEST EXAMPLES

In order to illustrate the properties and performance of the above algorithm we consider the following test problems. All of them are drawn from the literature and involve interesting and non-trivial kinetic mechanisms. It is our aim to show that the above algorithm finds optimal reactor networks efficiently and, in some cases, yields better solutions than those reported in the literature. Due to space limitations, presentation of the examples will be brief. The reaction models for these examples can be found in the corresponding references.

(a) The isothermal version of the Constant Dispersion Model has been tested on the Van de Vusse reaction (1964) (Chitra et al, 1981). We now consider three different cases for this mechanism in order to demonstrate the algorithm and properties of the superstructure. For this problem

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
$$A \xrightarrow{k_3} D$$
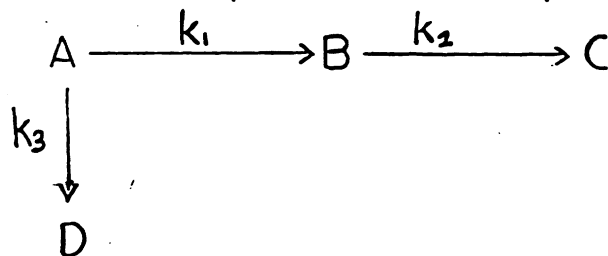
the objective function is the yield of B and the kinetic parameters are:

$k_1 = 10 \ s^{-1}$, first order

$k_2 = 1 \ s^{-1}$, first order

$k_3 = 1 \ L/gmol \ s$, second order

feed flow rate (pure A) = 100 L/s.

The reaction rate expressions and kinetic model are given in Chitra and Govind (1981). The following two cases were considered by Chitra and Govind. The third case considers a more complex superstructure .consisting of two reaction paths.

χ (i) feed concentration of A = 5.8 gmol/L

The initially guessed configuration consists of two PFR's in series. The final optimum structure is a CSTR followed by a PFR (' Chitra and Govind's results are shown in parentheses). See fig. 4a for a schematic of the initial and final configurations. The results are:

maximum B-yield = 3.6806 gmol/L   (3.6772 gmol/L)

V_{CSTR} = 9.562 L (11.21 L) $V^$ = 14.25 L (16.81 L)
                                              PFR
D_{CSTR} = 20   (note that an upper bound of 50 did not change the results to any significant extent).

D_{PFR} = 0.001   (lower bound)

$_v$\(ii) feed concentration of A = 0.58 gmol/L

The initially guessed configuration has two CSTR's in series. The final optimum structure is a single PFR (see fig. 4b) with the following characteristics:

maximum B-yield = 0.4368 gmol/L   (0.4362 gmol/L)

V_{ppR} = 29.65 L   (25.51 L)

D_{CSTR} = 50 D_{PFR} = 0.001

"$\!\!\nearrow$ (iii) feed concentration of A = 0.58 gmol/L

The initially guessed configuration has two reaction paths with two CSTR's each. In addition, the two paths have one side stream connecting them. The final optimum structure has two PFR's in series, with all of B removed from the reaction path at the exit of the first PFR (see fig. 4c) with the following characteristics:

maximum B-yield = 0.4969 gmol/L a = diag[0_f 1, 0]

$V_{PFR,1}$ = $V_{PFR,2}$ = 4.412 L

λ (b) The following isothermal reaction is due to Trambouze et al, (1959) (also see fig 4d):

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$
$$A \xrightarrow{k_3} D$$
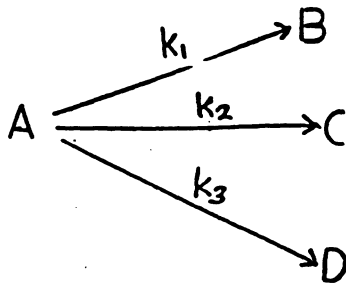
with kinetic constants and other parameters

k_1 = 0.025 gmol/L min, zero order

k_2 = 0.2 min^{-1}, first order

k_3 = 0.4 L/gmol min, second order

feed flow rate (pure A) = 100 L/min

A_0 = 1 gmol/L
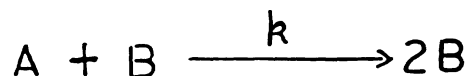
D_{PFR} = 0.001, D_{CSTR} = 20

The objective function considered is the selectivity of C to A defined by $X_C/(1 - X_A)$, where X (the dimensionless concentration) is defined in equation (4) of section 3. Paynter et al, (1970) solved this example using a dispersion model in which D varied continuously with the position along the reactor. They reported an optimal configuration of a CSTR in series with a PFR. For comparison their results are shown in parentheses.

The initially guessed reactor configuration is two PFR's in series. Two CSTR's in series are found to be optimum. The results are:

maximum selectivity = 0.4999 (0.495)

$\tau_{CSTR,1}$ = 7.721 min, $\tau_{CSTR,2}$ = 0.0975 min, (τ_{CSTR} = 9.1 min, τ_{PFR} = 0.9 min) where τ is the residence time. Note that we checked the accuracy of our results by solving the CSTR equations with our values of the residence times.

(c) Here we consider an isothermal autocatalytic reaction due to Levenspiel (1962). One peculiarity of this reaction is that the rate of the reaction increases with conversion up to a point. The following scheme characterizes this reaction (also see fig 4e):

$$A + B \xrightarrow{k} 2B$$

with kinetic constant and other parameters ;

k « 1.0 L/gmol min$_f$ second order

feed flow rate of ☞ 100 Umin

A_o = 0.45 gmol/L

B_6 * 0.55 gmol/L

$_{Dpni}$- 0.001. D_{CSTR}«20

The objective function considered is the yield of B. Paynter et al, (1970) reported an optimal D profile that is "close" to a single PFR. For comparison their results are shown in parentheses. The initially guessed reactor configuration is a PFR in series with a CSTFL A single PFR is found to be optimum. The results are:

maximum B yield ^{s} 0.769 (0.739)

r $_{,,}$ = 1.0 min (r$_{..o}$ ^{s} 1.0 min), where *r* is the residence time. Note that in
PFR   PFR
order to make a fair comparison with results from the literature we fixed the total residence time for the reaction path at 1.0 minute, the same residence time used by Paynter and Haskins.

$_v\Lambda$ (d) Adiabatic naphthalene oxidation (Chitra et al,1985h

This is a highly exothermic reaction,
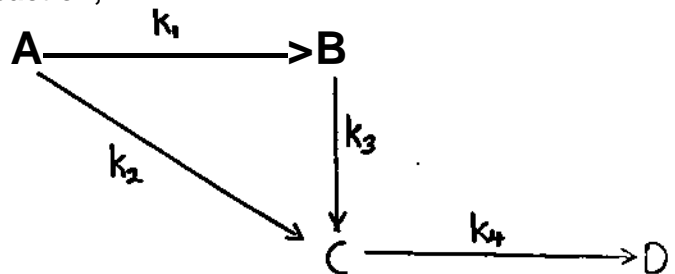
where   A = naphthalene,   B = naphthaquinone,   C = Phthalic Anhydride.   and D « co, • H;O.

The objective function is the yield of C with rate constants given as:

k, = k, = 2.0 X 10^{13}exp(-38000/RT) h^M

k_3 = 8.15 X 10^{17}exp(-50000/RT) h$^{'1}$

k_4 = 2.1 X 10^5exp(-20000/RT) h$^{'1}$

Ifi,./S$_2$./3$_y$/I$_4$I = [0.12. 0.43, 0.36 .0.74]   where
J3$_j$ « (- A H$_,$.)A$_0$/(/>C$_p$ T$_{f\#<d}$) « dimensionless heat of reaction.

R « 1.987 cal/gmol °K and T [=] °K. All reactions are first order with the following information:

feed flow rate (pure A) = 10*L/h

feed concentration of A (A_Q) = 1.0 gmol/L

T. . « 1018°K . Here T, _ was assumed to be fixed and no attempt was made to optimize it.

The initial reactor configuration has four PFR's in series. The final optimum structure has one PFR with an exit temperature of 1481 °K. The initial and final configurations are given in fig. 4f with:

maximum C-yield is 0.9999 gmol/L   (0.995 gmol/L)

$V_{PTM}S$ 9 _ 5 L $D_{CSTB}S50$ D_{PF*} = 0.001

Figure 4a: Initial and Optimum Structures for (i) of (a)
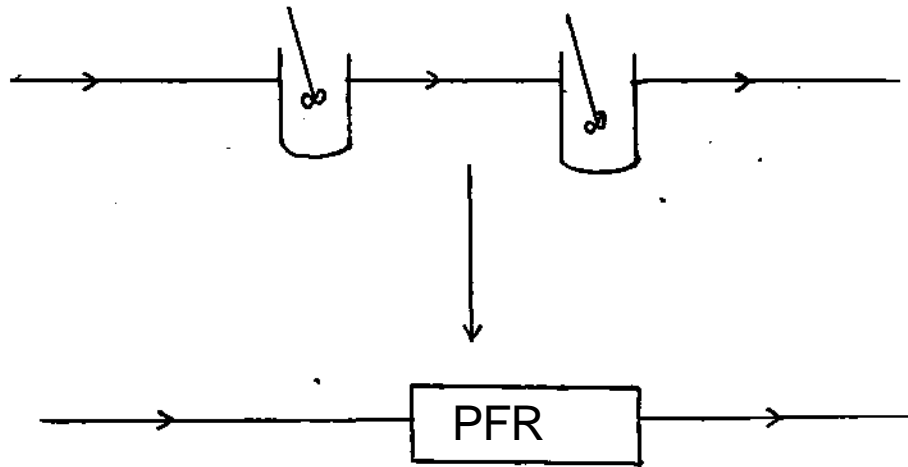
Figure 4b: Initial and Optimum Structures for (ii) of (a)

A →

ZERO
INPUT >

21

$0=0$

A → [PFR]

$\sigma_\beta = 1$

A
B
C
D

B

Figure 4c: Initial and Optimum Structures for (iii) of (a)

[PFR]   PFR

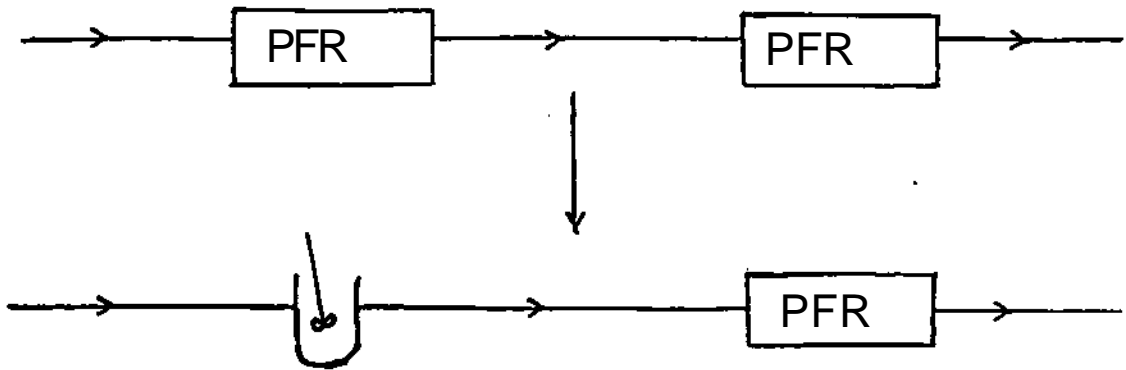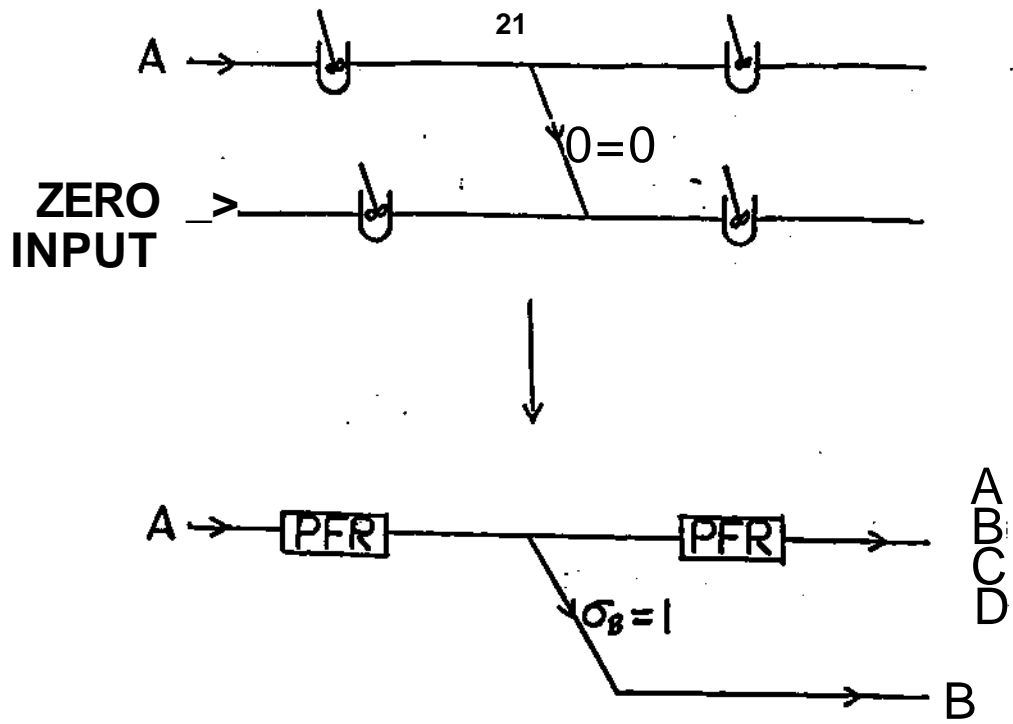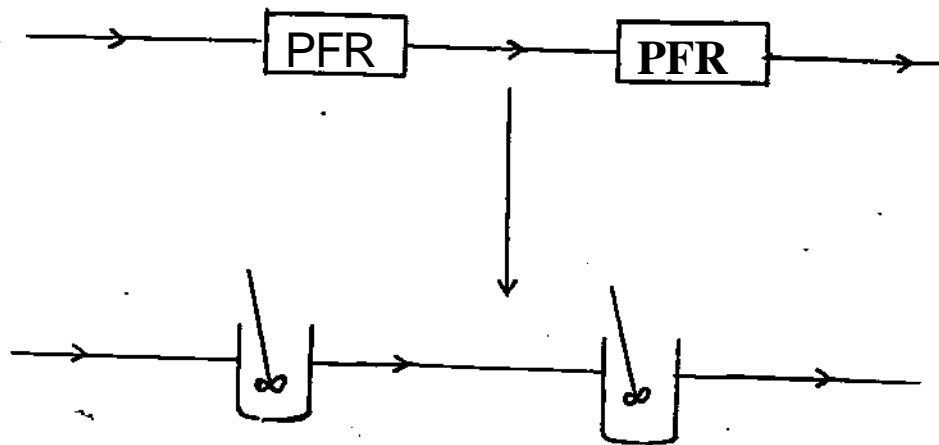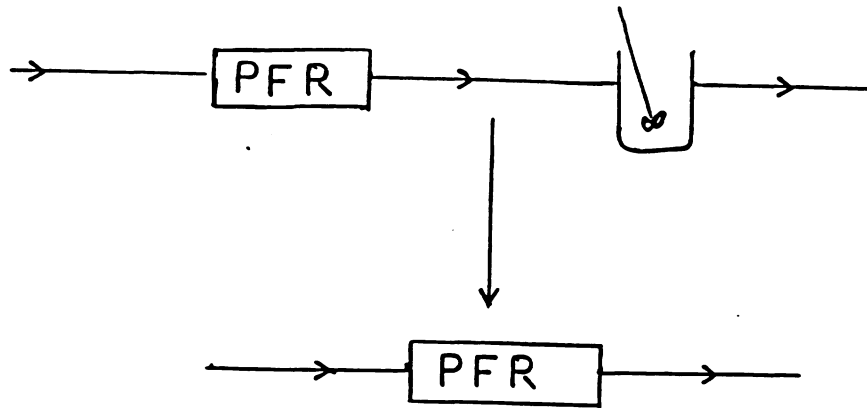**Figure 4ck Initial and Optimum Structures for (b)**

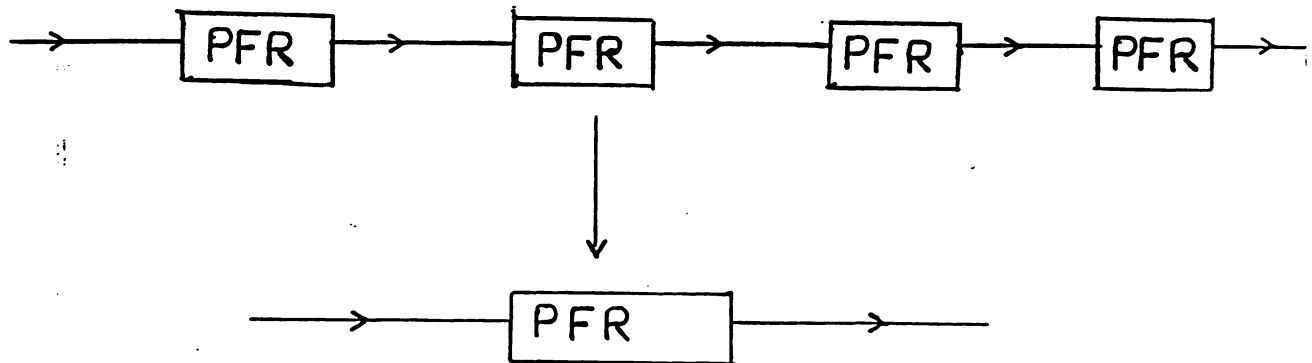**Figure 4e: Initial and Optimum Structures for (c)**

Figure 4f: Initial and Optimum Structures for (d)

8. DISCUSSION

In example (a) the results compare favorably with those of Chitra and Govind. In general we noted slight improvements in the objective function. Moreover, the fact that our results were obtained from starting points far from the optimum makes our approach even more viable. In case (iii) of example (a) the use of two reaction paths and one sidestream led to a smaller total volume of reactor (10.92 L compared to 29.65 L) and a larger B-yield (0.4969 gmol/L versus 0.4362 gmol/L). Note that a theoretical bound on the B-yield is 0.58 gmol/L The results in (iii) are not surprising because one way to increase B-yield is to prevent it from reacting to form C by removing B from the mixture as soon as it is formed. This seems to suggest that we include more sidestreams in the superstructure to make removal of B possible.

We reworked example (b) using an initially guessed configuration of two reaction paths, each with two PFR's in series. The two paths were connected by one sidestream (just like in part (iii) of example (a)). However, the optimal configuration and the objective did not change. Thus one reaction path is probably adequate for the chosen objective function, selectivity of C to A. This example also shows the viability of our approach.

The theoretical optimum yield of species B in the autocatalytic reaction (example c) is 0.768 (see Paynter et al, 1970) which is very close to our results (0.769). Here again our algorithm has been able to derive the optimum reactor type, a single PFR, from an initially guessed serial network of a PFR followed by a CSTR (each with half the total residence time of 1 minute).

In the naphthalene oxidation (example d) k_2 and k_3 are much larger than k_4. As a result the C to D reaction is negligible. Since all the other reactions lead to the production of C it is to be expected that there will be virtually a complete conversion of A to C.

All of -the examples require from four to ten iterations of the SQP optimization algorithm to converge. The most time consuming part of these computations lies in solving the two point boundary value problems with COLSYS (see step (iii) in the algorithm). COLSYS applies Newton's method to collocation equations over finite elements and for certain values of the decision variables it may be difficult for this method to converge.

One reason for this difficulty is that for small D (the PFR limit) the solution has a "boundary layer", a small region near the reactor exit in which the derivative of concentration with respect to position rapidly goes to zero m order to satisfy the right end boundary condition. For COLSYS to converge properly the mesh selection algorithm has to be able to recognize this

boundary layer and tailor the mesh to that segment. To deal with nonconvergence we tried a combination of the following:

(i) change the initial mesh sent to COLSYS,

(ii) change the minimum step size that is used in the Newton iteration step in COLSYS,

(iii) rescale the problem (presently done by inspection) by a judicious choice of reference length, temperature and so on.

Since most of the computation time was spent in solving the non-linear system differential equations we are looking at better ways to scale the ODE's and ways to accelerate convergence in COLSYS. Also we will look into the prospect of modifying the formulation of the algorithm and using other TPBVP methods.

9. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Of the advantages of the constant dispersion model, the ones that stand out are

- the adjoint variables that are needed to update the parameters in the optimization are relatively cheap to compute, since the adjoint system of ODE's is linear ,

- its ability to handle a wide range of objective functions and kinetic mechanisms,

- the heat exchanges that it allows and,

- the apparent ease with which it can be modified to handle non-linear side constraints and other process parameters such as the reactor volume.

The main drawbacks with the constant dispersion model are

- the authors do not yet know how to interpret reactor networks that include segments with intermediate dispersion coefficient and.

- the choices of D_{mm} (D_{max}), lower (upper) bound on the dispersion coefficient, are somewhat arbitrary (with good estimates being verified by trial and error, after solving the problem), and can have a big impact on the performance of COLSYS.

In the above examples however, we have checked our selected bounds on D with the actual CSTR and PFR profiles and found excellent agreement.

As a result of these drawbacks a second model has been developed which uses a recycle reactor, instead of a dispersion reactor, as the basic unit of the reactor network. The goal is to find some comparison between the two formulations. This will be reported in a companion paper.

The objective function is also being expanded to include the split fractions and the reactor volumes. Thus it will be possible to incorporate the cost of separation at source points and the cost of reactor volumes into the objective. Also since most of the computation time (about 85%) is spent on solving the non-linear ODE'S of the state variables it is of utmost importance to find ways of accelerating convergence in COLSYS.

The final question that has not been posed so far is how does one come up with a superstructure? The present strategy is to use a trial and error approach based on heuristics. A more systematic procedure will be addressed in the future. Finally the ultimate goal of this research is to incorporate the reactor synthesis problem into the total process flowsheet.

10. ACKNOWLEDGEMENTS

APPENDIX

COUPLING THE JACKSON SUPERSTRUCTURE WITH THE MASS AND ENERGY BALANCES: THE DERIVATION OF THE ADJOINT SYSTEM

(a) $\dfrac{dX}{dt} = Z$ $\qquad t_{i,m}^* \le t \le t_{i+1,m}^*$

(b) $\dfrac{dZ}{dt} = [Z - F(X,\theta)]/D$ $\qquad i=0,\dots (N_m-1)$

(c) $\dfrac{d\theta}{dt} = V$

d) $\dfrac{dV}{dt}$ = $_{CV}$ - $G(X,\theta)$ - $\Gamma(W-\theta)]/(\epsilon D)$

with boundary conditions

(e) origin : $*_{0\,m}$ - $X(t^\wedge)$ • $D^\wedge Zft^\wedge,)$ - $X(t^\wedge)$. 0

(f) if $t_{,m}$ is a sink : $V^{x(t_u->}$ * * u A > * VC > " ^{X}<C > = 0

(g) if t, is a source : ¥, * (1 - *a.*)X(t!) • D. Z{t*) - X(C) * 0

(h) $Z(t^\cdot_{i+1,m})$ = 0

(i) $\Omega_{i,m}$ = $\gamma_{i,m}$ + $\epsilon D_{i,m} V(t^+_{i,m})$ - $\theta(t^\cdot_{i,m})$ = 0

(j) $V(t^\cdot_{i+1,m})$ = 0

(k) Δ = $\displaystyle\sum_{m=1}^{M} X(t^\cdot_{Nm,m})$ - p = 0

(l) J = *(p) , **which is the objective function.**

To obtain adiabatic operation from this formulation merely set T $\rightarrow$ 0 in (d). For isothermal operation disregard (c), (d) and the corresponding boundary conditions and set F(X,0) » F(X) in (b).

Before proceeding the following reminder is in order

p, X, Z. F $\in$ IR^n and   4>, e, *V.* t, D$_\#$ G, W, *d.* V, $_r$ G IR^1. Also every vector is a column vector unless it has the transpose (T) superscript.

Adjoin (a) through (k) to the objective function (l) with position dependent multipliers X_A, X_B, $X_{C\#}$ X_Q, and constant multipliers v. A, //. Hence

J = Φ(p) + $\mu^T\Delta$ + $\sum_{m=1}^{M} \nu^T_{0,m}\Psi_{0,m}$ + $\sum_{m=1}^{M}\sum_{i\,\in\,sink}^{Nm-1} \nu^T_{i,m}\Psi_{i\,n}$ + $\sum_{m=1}^{M}\sum_{i\,\in\,source}^{Nm-1}$ i.m.m •

$\sum^M_{m=1}$ $_f$ ZJJT^{-1} A$_{i}$ $\Omega_{i,m}$ +
  i*0   i.m$^T_{i+1,m}$

$\sum^M_{m=1}\sum_{i=0}^{Nm-1}$ ($\int$ { λ^T_A(Z - $\dot X$) • $\underline{\,}$ f[Z - F(X$^\wedge$)]/D - $\dot Z$ I • X_r(V - $\dot 6$)

  i.m

• X_D F[V - G<X.0) - T(W - $^\wedge$)]/(«D) - $\dot V_i$)dt\ •   (1)

Define the hamiltonian, H as

H = X^Z + XJ[Z - F(X,0)]/D • X_cV • X_O[V - *Q{X.6)* - T(W - *O)V(tD)* .

Note that T = J since the differential equations and the boundary conditions **are satisfied. A small change in the augmented objective function 7 yields**

$$dJ = d(Wp) \ll \bullet \ i^T dA \bullet \ \sum_{m=1}^{Z''} \sum_{\theta_m}^{} v^T dV \bullet \ \sum_{m=1}^{Z''} Z_{i,f\,sink}^{\wedge\,1} \ v_{i,m}^T d\Psi_{ijn} + \sum_{m=1}^{M} \sum_{i=source}^{Nm-1} v_{i,m}^T d\Psi_{i,m}$$

$$+ \sum_{m=1}^{M} \sum_{i=0}^{Nm-1} \Lambda_{i,m} d\xi$$

$$\sum_{m=1}^{M} \sum_{i=0}^{Nm''} d(\int_{t_{i,m}^+}^{t_{i+1,m}} [H - x^\wedge \dot{x} - x;\dot{z} - x_c^\wedge - x_D \dot{v}] \, dt) \tag{2}$$

Focusing on the last term we have (Bryson and Ho, 1968)

$$d(\int_{t_{i,m}^+}^{t_{i+1,m}} [H \,''\, ^X I \,\dot{*}\,'' \, ^X\dot{B}^\wedge - M^\bullet - \,^X{}_o v] \, dt) =$$

$$\frac{\partial}{\partial t_{i+1,m}^-} (\int_{t_{i,m}}^{t_{i+1,m}} [\quad] \, dt) \, dt_{i+1,m} + \frac{\partial}{\partial t_{i,m}^+} (\int_{t_{i,m}}^{t_{i+1,m}} [\quad] \, dt) \, dt_{i,m} + \int_{t_{i,m}}^{t_{i+1,m}} (\delta[\quad]) \, dt \tag{3}$$

Then integrate by parts, use Leibnitz's rule and the relation $\pounds s(t) \ll ds(t) - \dot{s}(t) dL$ **Collecting terms together and noting that** $dt_j^\wedge = dt_\delta^\wedge$**, leads to the** following **expression from** (3)

$$d(\int_{t_{i,m}^+}^{t_{i+1,m}} [H - \,^X I \,*\, - \,^X\!\!\ggeq \dot{Z} - M^\bullet \,''\, ^X{}_o \dot{v}] \, dt) =$$

$$H(t_{i+1,m}^-) dt_{i+1,m} - H(t_{i,m}^+) dt_{i,m} - \lambda_A^T(t_{i+1,m}^-) dX(t_{i+1,m}^-) + \lambda_A^T(t_{i,m}^+) dX(t_{i,m}^+) - \lambda_B^T(t_{i+1,m}^-) dZ(t_{i+1,m}^-)$$

$$+ \lambda_B^T(t_{i,m}^+) dZ(t_{i,m}^+) - \lambda_c(t_{i+1,m}^-) d\theta(t_{i+1,m}^-) + \lambda_c(t_{i,m}^+) d\theta(t_{i,m}^+) - \lambda_D(t_{i+1,m}^-) dV(t_{i+1,m}^-) +$$

$$\lambda_D(t_{i,m}^+) dV(t_{i,m}^+) + \int_{t_{i,m}}^{t_{i+1,m}} [(\nabla_X^T H + \dot{\lambda}_A^T) \delta X + (\nabla_Z^T H + \dot{\lambda}_B^T) \delta Z +$$

$$(\nabla_\theta H + \dot{\lambda}_c) \delta\theta + (\nabla_V H \bullet \dot{x}_o) \delta v \bullet (\nabla_D H)^* D \bullet (\nabla_w H) \delta w + (\nabla_r H) \delta r] \, dt \tag{4}$$

Up until now the relations describing the adjoint variables (multipliers) have **been completely arbitrary. However, to remove the influence of** *δX, δZ, δθ* **and, *δV* on dJ one can set their coefficients to zero. Thus let**

$$\dot{\lambda}_A = - V_X K * (V_X F/D) X_B - (V_X G/\{\ll D\}) X_0 \tag{5a}$$

$$\dot{\lambda}_B = - V_2 H - (\lambda_A + X_B/D) \tag{5b}$$

$$\dot{K} = - V_* H \cdot (V_* F/D)^T V (V<?^G " ^r) V<<^D> \tag{5c}$$

$$\dot{X}_0 " ' V_V H " " (X_C * X_0' < \ll^D) \tag{5d}$$

where for example.

$$(\nabla_X F)_{ij} = \frac{\partial F_j}{\partial x_i} \cdot$$

From now on the goal is to determine the boundary conditions for the adjoint system. By summing over all reactors and bearing in mind the fact that $Z(t^* ,...)$ is fixed at zero, (4) becomes

$$\sum_{m=1}^M \sum_{i=1}^{Nm-1} d\left(\int_{t_{i,m}^+}^{t_{i+1,m}^-} [H "X_*""X" " X_* \bullet ' X \gg ' \gg \right) =$$

$$\sum_{m=1}^M \sum_{i=1}^{Nm-1} \left[H(t_{,m}^-) - H(t_{i,m}^+) \right] dt_{i,m} + \sum_{m=1}^M \left[H(t_{Nm,m}^-)dt_{Nm,m}^- - H(t_{0,m}^+)dt_{0,m}^+ \right]$$

$$\sum_{m=1}^M \sum_{i \in sink}^{Nm-1} \left[\lambda_X)dxu_{;m}) - xx)dx(t_{;m}) \right] \bullet$$

$$\sum_{m=1}^M \sum_{i \in source}^{Nm-1} \left[\lambda_A^T(t_{i,m}^+)dX(t_{i,m}^+) - \lambda_A^T(t_{i,m}^-)dX(t_{i,m}^-) \right] +$$

$$\sum_{m=1}^M \left[\lambda_A^T(t_{0,m}^+)dX(t_{0,m}^+) - \lambda_A^T(t_{Nm,m}^-)dX(t_{Nm,m}^-) \right] + \sum_{m=1}^M \sum_{i=0}^{Nm-1} \lambda_0(t_{i,m}^+)dV(t_{i,m}^+) +$$

$$\sum_{m=1}^M \sum_{i=0}^{Nm-1} \left[\lambda_B^T(t_{i,m}^+)dZ(t_{i,m}^+) + \lambda_c(t_{i,m}^+)d\theta(t_{i,m}^+) \right] - \sum_{m=1}^M 5: \lambda_c(t_{i,m}^-)d\theta(t_{i,m}^-) +$$

$$\sum_{m=1}^M \sum_{i=0}^{Nm-1} \left\{ \left[\int_{t_{i,m}^+}^{t_{i+1,m}^-} (\nabla_D H)dt \right]dD_{i,m} + \left[\int_{t_{i,m}^+}^{t_{i+1,m}^-} (\nabla_W H)dt \right]dW_{i,m} + \left[\int_t^{t_{i+1,m}^-} (\nabla_\Gamma)H] dt_{i,m}\Gamma \right\} \tag{6»}$$

Note that since D, W and T are independent of t, $\partial W = dW$, $\partial T = dT$. and $\partial D = dD$. Note also that $dt_0^{*\wedge} = 0$ since t_{Qm} is fixed at the origin.

The other terms in equation (2) are as follows:

$$d\yen_n = dX(r_{0,m}) \wedge Z(t_{O^\wedge n}^*)dD_{A_{0,m}} * D_n dZ(t_{0,m}^*) - dX<C_{0,m}) \tag{^3}$$

Since $X(t_{..}^{"})$ is the initial feed to reaction path m, $dX(t_{..}^{"}) = 0$.

$$d\Psi_{i,m} = dX(t^-_{i,m}) + \tilde{\sigma}_{i,m}dX(\tilde{t}^-_{i,m}) + (d\tilde{\sigma}_{i,m})X(\tilde{t}^-_{i,m}) + D_{i,m}dZ(t^+_{j,m})) \cdot Z^\wedge)dD_{,m} - dX(t^+_{i,m})$$

$$\text{if } t_{i,\ldots} \text{ is a sink} \qquad (7b)$$

$$d\Psi_{i,m} = (1 - \sigma_{i,m})dX(t^-_{i,m}) - (d\sigma_{i,m})X(t^-_{i,m}) + D_{i,m}dZ(t^+_{i,m}) + Z(t^+_{i,m})dD_{i,m} - dX(t^+_{i,m})$$

$$\text{if } t_{Jm} \text{ is a source} \qquad (7c)$$

$$d\Omega_{i,m} = d\gamma_{i,m} + \epsilon D_{i,m}dV(t^+_{i,m}) + \epsilon V(t^+_{i,m})dD_{j>m} - 6\,8^\wedge) \qquad (7d)$$

$$dA \; \underset{m=1}{\overset{M}{-2}} \ll \ll^\wedge .> \text{ "} {}^dP \text{ '} \qquad <7e)$$

Finally insert (6) and (7) into (2) and gather terms, then have

$$dJ \, \text{''} \left(\; f \bullet {}^{\text{''}T} \right)^{dp} + \wedge \; i\,l'^T - x_-(t^-_{Nm,m})\right] dX(t^-_{Nm,m}) +$$

$$\sum_{m=1}^{M} \sum_{i \in \text{sink}}^{Nm-1} \left(\left[\; \nu^T_{i,m} - \lambda^T_A(t^-_{i,m}) \right] dX(t^-_{i,m}) + \left[\; \lambda^T_A(t^+_{i,m}) - \nu^T_{i,m} \right] dX(t^+_{i,m}) \right) +$$

$$\sum_{m=1}^{M} \sum_{i \in \text{source}}^{Nm-1} \left(\left[\; \nu^T_{i,m}(1 - \sigma_{i,m}) - \lambda^T_A(t^-_{i,m}) + \overline{\nu}^T_{i,m}\sigma_{i,m} \right] dX(t^-_{i,m}) +$$

$$\left[\; \lambda^T_A(t^+_{i,m}) - \nu^T_{i,m} \right] dX(t^+_{i,m}) + \left[\overline{\nu}^T_{i,m} - \nu^T_{i,m} \right] (d\sigma_{i,m})X(t^-_{i,m}) \right) +$$

$$\sum_{m=1}^{M} \sum_{i=1}^{Nm-1} \left[\; H(t^-_{i,m}) - H(t^+_{i,m}) \right] dt_{i,m} +$$

$$\sum_{m=1}^{M} H(t^-_{Nm,m})dt^-_{Nm,m} + \sum_{m=1}^{M} \sum_{i=0}^{Nm-1} \left(\left[\; \lambda^T_B(t^+_{i,m}) + \nu^T_{i,m}D_{i,m} \right] dZ(t^+_{i,m}) + \Lambda_{i,m} \, d\gamma_{i,m} \right) +$$

$$\sum_{m=1}^{M} \sum_{i=0}^{Nm-1} \left(\left[\lambda_C(t^+_{i,m}) - \Lambda_{i,m} \right] d\theta(t^+_{i,m}) - \lambda_C(t^-_{i,m})d\theta(t^-_{i,m}) +$$

$$\left[\epsilon D_{i,m}\Lambda_{i,m} + \lambda_D(t^+_{i,m}) \right] dV(t^+_{i,m}) \right) +$$

$$t^-_{i+1,m}$$

$$\sum_{m=1}^{M} \sum_{i=0}^{Nm-1} \left\{ \left[\epsilon \Lambda_{i,m} \; V(t^* \quad) \bullet \; Y^* \; Z(t^+ \quad) \bullet \; \underline{\;} \; f \; (V_D H\backslash dt\text{''}|dD_{i,m} + \right. \right.$$

$$\left[\int_{t^+_{i,m}}^{t^-_{i+1,m}} \left(\nabla_W H \right) dt \right] dW_{i,m} + \left[\int_{t^+_{i,m}}^{t^-_{i+1,m}} \left(\nabla_\Gamma H \right) dt \right] d\Gamma_{i,m} \right\} \qquad (8)$$

An appropriate choice of boundary conditions for the adjoint system is obtained if the direct influence of dX, dZ, dθ, and dV on dJ are removed. This implies setting their coefficients to zero. This leads to a system of equations which can be solved to give the boundary conditions

$$\mu = \lambda_A(t^-_{Nm,m}) = \frac{d\Phi}{dp} \qquad (9a)$$

$$\nu_{i,m} = \lambda_A(t^-_{i,m}) = \lambda_A(t^+_{i,m}) \quad \text{if } t_{i,m} \text{ is a sink} \qquad (9b)$$

$$\nu_{i,m} = \lambda_A(t^+_{i,m}) \qquad\qquad\qquad i = 0,...Nm-1 \qquad (9c)$$

$$\lambda_A(t^-_{i,m}) = (1 - \sigma_{i,m})\lambda_A(t^+_{i,m}) + \sigma_{i,m}\lambda_A(\tilde{t}^+_{i,m}) \quad \text{if } t_{i,m} \text{ is a source} \qquad (9d)$$

$$\lambda_B(t^+_{i,m}) = -D_{i,m}\lambda_A(t^+_{i,m}) \qquad\qquad i = 0,...Nm-1 \qquad (9e)$$

$$\Lambda_{i,m} = \lambda_C(t^+_{i,m}) \qquad\qquad\qquad i = 0,...Nm-1 \qquad (9f)$$

$$\lambda_C(t^-_{i,m}) = 0 \qquad\qquad\qquad i = 1,...Nm \qquad (9g)$$

$$\lambda_D(t^+_{i,m}) = -\epsilon D_{i,m}\lambda_C(t^+_{i,m}) \qquad\qquad i = 0,...Nm-1 \qquad (9h)$$

Equations (9) reduce (8) to

$$dJ = \sum_{m=1}^{M} H(t^-_{Nm,m})dt^-_{Nm,m} + \sum_{m=1}^{M} \sum_{i=1}^{Nm-1} \left[H(t^-_{i,m}) - H(t^+_{i,m}) \right] dt_{i,m} +$$

$$\sum_{m=1}^{M} \sum_{i \in source}^{Nm-1} \left[\lambda_A^T(\tilde{t}^+_{i,m}) - \lambda_A^T(t^+_{i,m}) \right](d\sigma_{i,m})X(t^-_{i,m}) + \sum_{m=1}^{M} \sum_{i=0}^{Nm-1} \lambda_C(t^+_{i,m})d\gamma_{i,m} +$$

$$\sum_{m=1}^{M} \sum_{i=0}^{Nm-1} \left\{ \left[\epsilon\lambda_C(t^+_{i,m})V(t^+_{i,m}) + \lambda_A^T(t^+_{i,m})Z(t^+_{i,m}) + \int_{t^+_{i,m}}^{t^-_{i+1,m}} \left(\nabla_D H \right) dt \right] dD_{i,m} +$$

$$\left[\int_{t_{i,m}}^{t_{i+1,m}} (\nabla_W H)\, dt\right] dW_{i,m} + \left[\int_{t^+_{i,m}}^{t_{i+1,m}} (\nabla_\Gamma H)\, dt\right] d\Gamma_{i,m}\Bigg\} \qquad\qquad (10)$$

where

$H - XJZ + XJEZ - F(X.^\wedge)]/D + X_C V \cdot X_o tV - G(K6) - HW - \theta\}]/(\epsilon D)$

$V_W H - - \left(\Gamma/(\epsilon D)\right) \lambda_D$

$\nabla_\Gamma H = \lambda_D \left(\theta - W\right) /(\epsilon D)$

$^V D^{H\ e\ \shortmid\shortmid\ X}\tilde{B}\ [^{\ Z\ \shortmid\shortmid}\ F^{\wedge}-^{\wedge})]/^{02\ \shortmid\shortmid\ \ X}o[^{\ V\ \shortmid\shortmid}\ G^{\wedge\shortmid *}) ^+ Htf - W)] \ /(\epsilon D^2)$

From (10) it is seen that the derivative of the objective function with respect to V *'ijnt yum'* ^{W} i V ^{r} i $^\wedge$ ^{and} ^{D}.$^\wedge$n ^{are} **9**^{iven} ^{b}Y ^{tne} **coefficients** of these **parameters.**

APPENDIX B

Here in this appendix the optimality conditions for the NLP algorithm in chapter 2 are presented. To be able to make the case that the volumes and concentration profiles gotten from the ADR (or RR) model coincide with those of the CSTR and the PFR at the upper and lower limits of D (or R) respectively, there is the need to give a formal proof of the two limits. It should be pointed out that it is well known in the Chemical Engineering literature that the CSTR and the PFR are limiting cases of both the ADR and the RR. However, the proofs of the limiting cases have been based on specific reaction systems, usually those that exhibit simple kinetics and involve few reaction species. The usual strategy is to determine the limit of the analytic solution (for the ADR and RR equations) as D (or R) tends to a limit. Here in this appendix it is shown that it is possible to employ perturbation techniques to make these proofs without knowing the form of the analytic solution.

B.1. NECESSARY CONDITIONS FOR A STATIONARY POINT

Let $g_1 = Y_{min} - Y$, $g_2 = Y - Y_{max}$, $g_3 = S_{min} - AY$, $g_4 = AY - S_{max}$ (see section 2.6) and define the Lagrangian

$$L = \Phi + \sum_{i=1}^{4} U_i^T g_i$$

where U_i is the Lagrange multiplier associated with the i-th set of constraints in the QP (these multipliers are not to be confused with the adjoint variables discussed in previous sections). The Kuhn-Tucker conditions for stationary solutions Y and U_i (Gill et al, 1981) are given by

$$\nabla_Y L(Y) = \nabla_Y \Phi(Y) + \sum_{i=1}^{4} U_i^T \nabla_Y g_i(Y)$$

$$U_i^T g_i(Y) = 0, \quad i = 1,... 4$$

In the proposed algorithm the termination criterion is

$$\| \nabla_Y L(Y) \| \leq \delta \ll 1$$

where $\| \cdot \|$ is a norm (for example the square or distance norm). At a local constrained minimum (if minimizing objective function) the following holds for any Z:

$Z^T\{V_Y^2 < HY)\}Z \gtrsim 0$

for all Z in the null space defined by

$(V_Y g_i(Y))^T Z = 0$ where $I - \{ i \mid g_i(Y) - o\}$.

One can use perturbation to approximate $V_{Y_k}^{2*}$ thus

$$\nabla^2_{Y_k}\Phi \sim \frac{[V_{y_k}^* < Y_k \bullet AY_k) - V^\wedge Y_j]}{\pm I}$$

B.2. CSTR AS A LIMITING CASE OF ADR

In the CSTR limit the ODE's governing the axial dispersion model are (note that the temperature equation is of the same form as the mass continuity equations):

$$\frac{d^2 X}{dt^2} \quad \frac{dX}{dt} = <F(X) \qquad 0 < t \lesssim 1$$

with boundary' conditions

$«X(0) = at * \dfrac{dX(0)}{dt}$

$\dfrac{dX\{1\}}{dt} - u$

where $0 < \not= = \dfrac{1}{D} = Pe \ll 1$ and *a* is the feed.

If F is continuously differentiable (a property of most rate equations) assume a Taylor expansion of the form $X = 2^{\infty} \cdot <^m U (t)$.

Then $\displaystyle -\sum_{m=0}^{\infty} \epsilon^m U_m(t) + \sum_{m=0}^{\infty} \epsilon^{m+1}\dot{U}_m(t) = \epsilon F[\sum_{m=0}^{\infty} \epsilon^m U_m(t)]$

and $£ ,-iUjO) - a< * Co '^ $ $'$ $Co \epsilon^m \dot{U}_m(1) = 0$

aside:

$$F(X) = F[Z_{fn^*u}^{\infty}\; «^{m}U_{n\backslash}(t)] = F[U_{ft}(t) \bullet Z_{u}^{\infty}_{\bullet"\bullet I} \; <^{m}U_{in}(t)]$$

$$- F[U_{0}(t)] \bullet (V^{T}F[U_{B}(t)])Z^{\circ\circ}_{HI^*I}, \; «^{TM}U_{m}(t) \bullet \text{ higher order terms in } Z^{\circ\circ}_{tn^{m}t}, \; «^{m}U_{tn}(t).$$

Let us look at the first three terms of the ODE's.

(i) e° term:

$U_0(t) = 0$

$\overset{\bullet}{U_o}(0) = 0$

$\overset{\bullet}{U_o}(1) \; * \; 0$

Solving these equations we obtain $U_0 = C$, a constant.

(ii) «' term:

$U,(t) - \overset{\bullet}{U_0}(t) = - F(C)$

$U_0(0) = a \; * \; \overset{\bullet}{U},(0)$

$\overset{\bullet}{U},(1) = 0$

Integrating twice (note that $\overset{\bullet}{U_Q}(t)$ is zero) and applying the boundary conditions we ·obtain the algebraic CSTR equations

$C = a \bullet F(C)$ 　　　　　　　　　　　　　　　　　> I)

and $11,(0 = - \{'/it^2 - t)F(C) \bullet A_2$ 　　　　　　　　　‹2)

A_2 **is a constant yet to be determined.**

(Hi) t^2 term:

$$u_2(t) - \overset{\bullet}{u},(t) \; \bullet\!\!-\; \{V^{T}F[\; u_0(t)]\} \; u,(\dot{t})$$

$A_2 \; * \; U,(0) = \overset{\bullet}{U_2}(0) \qquad \overset{\bullet}{U_2}(1) = 0$

Using luiCwri functions, ^Q^, <3iiU u,\i/, HoHi duuvc we inleyiaie lwiue aiiu apply boundary conditions to obtain

$$A_2 = [V \ F(C) - I j T^L 0.51 - 0.3333 V^T F(C)] \ F(C).$$ (3)

If

$V \ F(C) - I j-$ does not exist one may try an expansion of the form $X = Z^{\infty}_{m=0} *^{n-m} U^m(t)$ where n is an appropriate positive integer.

In general for the e^k term we have

$$u_k(t) - 6_M(t) * - \{ V^T F [u_o(t)]\} u_M(t)$$

$$u_{k-1}(0) = \dot{U}_k(0) \qquad \dot{U}_k(1) = 0$$

Thus $U_{fc}(t)$ is a polynomial in t. Existence of a solution requires existence of $U_{k-1}(t)$. Thus we have $X = U_Q(t) \cdot cU^t) \cdot O(e^2)$. For uniform expansion we require

$$\frac{U_{k,i}(t)}{} < \infty \ or$$

Ufc n wW

less stringently $\frac{U^{+i}}{U_{Qi}(t)} < \infty \quad V$ k and i. $U_{k,i}$ is the i-th element of U_k.

Since $0 \pounds t \pounds 1$ and both U_{fc} and U_Q are polynomials in t, unless $U_{Q,i} = 0$

(i.e. non existence of a species in the "almost completely mixed" reactor) the above condition will be met. Thus in the limit as « tends to zero (D tends to infinity) CSTR operation is realized.

The expansion above motivates a reasonable choice for D OM. it <s r max

proposed that ϵ be chosen such that

«$V \pounds i$ where $0 < S \ll 1$

and $V \ll \max_M \left| \frac{u_u(t)}{\bar{u}^t)} \right|$ .Then $D_{m*K} = 1/f$ ^—.

An example:

$$k_. \qquad k_-$$

Consider the reaction A ^ B ^{z}-» D. where k_1 is second order and k_2 is first order. For $\{k_{1\#} k_2 J = \{2_\# 1\}_\#$ $a = [1, 0]^T$ and unit volume of reactor we have

$F(C) = [-2C_A^*, \quad C_A^* - C_B]^T$. Solving the CSTR equations $C = a + F(C)$ we obtain $C = [0.5, \quad 0.125]^T$. Therefore $U_Q(t) = [0.5. \quad 0.125]^T$ and $U_1(t) \approx (0.5t^2 - t)[0.5, -0.125]^T \cdot A_2$. Also

$$V^T F(C) = F - 4C_A \qquad \text{ol}$$

$$L\, 2C_A \quad -1J$$

Therefore $A_2 * [0.194. \quad 0.052]$. Now $\max[U_1/O/U^\wedge U)] * 0.388$ and $\max[U_1^\wedge(t)/U_{02}(t)] \approx 0.916$. Hence $V = 0.916$. Suppose $S \ll 0.01$ (i.e. first order correction is only 1% of the zero order, CSTR, **term)** then D_{max} should be at least 91.6. On the other hand if $\& * 0.05$ then D_{max} should be at least 18.3 .

B.3. PFR AS A LIMITING CASE OF ADR

The equations governing CDM are

$$- \epsilon\frac{d^2X}{dt^2} + \frac{dX}{dt} = F(X) \qquad\qquad 0 \leq t \leq 1 \quad (1a)$$

with boundary conditions

$$X(0) = a * i\frac{dX(0)}{dt} \qquad\qquad (1b)$$

$$\frac{dX(D}{dt} = 0 \qquad\qquad (1c)$$

where for a PFR $D = \epsilon \ll 1$

We see that as $*$ approaches zero the second order ODE's become first order ODE's with Boundary conditions at both ends of the interval. Thus it is impossible for the first order ODE's to satisfy the two BC's simultaneously and one of them will have to be dropped. The vanishing,, of the highest derivative as ϵ tends to zero gives rise to what is called a "singular perturbation problem". The usual strategy for solving such problems involves the two solution concept. The "outer" and the "boundary layer" solution each satisfies only one of the two boundary conditions. The two solutions are then combined, sometimes using Van Dykes Matching Principles (Nayfeh, 1973), to form one global solution. The location of the boundary layer: depends on the signs of the coefficients of the derivatives. The presence of a boundary layer, typically a small region in which the solution changes rather rapidly, poses numerical difficulties and as a result, for a PFR, one is forced to use an $<$ not too close to zero.

O'Malley (1974) has solved the singular perturbation problem for a general class of problems. It is the purpose of this section to specialise his treatment to the ODE's above. As a first order system the above ODE's become

$$\frac{dX}{ds} = - Y \qquad\qquad 0 \leq s \leq 1 \quad (2a)$$

$$\epsilon \frac{dY}{ds} = - Y + F(X) \qquad\qquad 0 < \epsilon \ll 1 \quad (2b)$$

$$X(1) - \epsilon Y(1) = \beta \qquad\qquad (2c)$$

$$Y(0) = 0 \qquad\qquad (2d)$$

and where s = 1 - t and β is the feed.

Using O'Malley's notation $f_1(X,s,\epsilon) = 0$, $f_2(X,s,\epsilon) = - 1$, $g_1(X,s,\epsilon) = F(X)$, $g_2(X,s,\epsilon) = - 1$, $a_1(\epsilon) = 0$, $a_2(\epsilon) = 1/\epsilon$, $\alpha(\epsilon) = 0$, $b_1(\epsilon) = 1$, $b_2(\epsilon) = - \epsilon$ and $\beta(\epsilon) = \beta$.

Let us seek an asymptotic solution of (2) of the form

$$X(s,\epsilon) = \chi(s,\epsilon) + \xi(\tau,\epsilon), \qquad Y(s,\epsilon) = \gamma(s,\epsilon) + \eta(\tau,\epsilon)/\epsilon \qquad\qquad (3)$$

where

$$\chi(s,\epsilon) = \sum_{j=0}^{\infty} \chi_j(s)\epsilon^j, \qquad \gamma(s,\epsilon) = \sum_{j=0}^{\infty} \gamma_j(s)\epsilon^j, \qquad \xi(s,\epsilon) = \sum_{j=0}^{\infty} \xi_j(s)\epsilon^j,$$

$\eta(s,\epsilon) = \sum_{j=0}^{\infty} \eta_j(s)\epsilon^j$, and $\tau = s/\epsilon$ as ϵ tends to zero. The boundary layer is located at s = 0 (t = 1) since the following conditions derived by O'Malley are satisfied:

$g_2(X,s,\epsilon) = - 1 \leq - K$ for some K > 0

and $b_1(0) - b_2(0)\nabla_x g[\chi_0(1), \gamma_0(1), 1, 0]/g_2(\chi_0(1), 1, 0) = 1 \neq 0$.

For uniform expansion, i.e. $O(\epsilon^k) \leq O(\epsilon^{k-1})$ correction, we require ξ_j and η_i to go to zero as τ tends to infinity.

Away from s = 0, (X,Y) will be asymptotically represented by the outer solution [$\chi(s,\epsilon)$, $\gamma(s,\epsilon)$]. The boundary layer correction [$\xi(\tau,\epsilon)$, $\eta(\tau,\epsilon)/\epsilon$] is needed to obtain the non-uniform convergence at s = 0. Therefore the outer solution and the boundary layer solution must satisfy the B.C. at s = 1 and at s = 0 respectively. Let "•" denote the derivative with respect to s. Then (2) becomes

$$\sum_{j=0}^{\infty} [\dot{A}/S) + \dot{\wedge}(r)].' = - I_{j=0}^{\infty} [_{7j}<8» \bullet \eta_j(\tau)/\epsilon] \epsilon^j$$

$$\sum_{j=0}^{\infty} [\epsilon \dot{\gamma}_j(s) + \dot{\eta}_j(\tau)] \epsilon^j = - \sum_{j=0}^{\infty} [y/s) + \eta_j(\tau)/\epsilon] \epsilon^j + F\left(\sum_{j=0}^{\infty} [X_j(s) + \xi_j(\tau)] \epsilon^j\right)$$

$$\sum_{j=0}^{00} [X_j(1) + \xi_j(1/\epsilon) - \epsilon \gamma_j(1) - \eta_j(1/\epsilon)] \epsilon^j = \beta$$

$$\sum_{j=0}^{\infty} Cy/0) \bullet _{9j}(0)/\epsilon] \epsilon^j = 0$$

Now let us look at the outer solution and the boundary layer solution **separately.**

(a) OUTER SOLUTION (r-»oo, therefore $\int$. **and** $\wedge$ Oh

The outer solution satisfies

$$\frac{dX}{ds} \bullet - Y \qquad\qquad OS\ s\pounds\ 1 \text{(4a)}$$

$$«\frac{dY}{ds} - - Y \bullet F(X) \qquad\qquad \text{(4b)}$$

(i) 0(1) term:

$$\frac{dX_0}{ds} \qquad \circ$$

$$^0 \ast \bullet" \ r_\ll \bullet FU_0J \qquad\qquad \text{(5b)}$$

$$\ast_0(^1) \ast \qquad\qquad fi \qquad\qquad \textbf{(5c)}$$

From this we obtain

$$\frac{d\wedge_0}{ds}\ ^s\ "\ \wedge_0\wedge \qquad^{anc\iota}\ \ast_0\wedge = fi^m$$ These are **the PFR** equations.

$$\lim_{\epsilon \to 0} F\left(\Sigma_{j=0}^{\infty} \ [X_j(s) + \xi_j(\tau)]\epsilon^j\right) = F[X_0(s)] + \left\{\nabla \ F[X_0(s)]\right\}^T \Sigma_{j=1}^{\infty} \ \epsilon^j X_j(s)$$

since $\lim_{\epsilon \to 0} \tau = \infty$ and $\lim_{\epsilon \to 0} \xi_j, \ \eta_j = 0.$

(ii) higher order terms:

$$\frac{dX_j}{ds} = -\gamma_j \qquad\qquad\qquad 0 \le s \le 1 \quad \text{(6a)}$$

$$0 = - \gamma_j + \nabla_x \ F(X_0)X_j + Q_{j-1}(s) \qquad\qquad \text{(6b)}$$

$$X_j(1) = Y_{j-1}(1) \qquad\qquad\qquad \text{(6c)}$$

The last term is determined from the $O(\epsilon^{j-1})$ solution. $Q_{j-1}(s)$ is a function of $[X_k \ ; \ k = 0, \ ... \ j-1]$. Thus one can solve for $O(\epsilon^j)$ using the $O(\epsilon^{j-1})$ solution.

BOUNDARY LAYER SOLUTION (s→0) in terms of τ:

Note that in the outer region, $\tau \to \infty$; also ξ and $\eta \to 0$. The boundary layer correction must satisfy the non linear system

$$\frac{d\xi}{d\tau} = - \eta \qquad\qquad\qquad 0 \le \tau \le 1/\epsilon$$

$$\frac{d\eta}{d\tau} = - \eta + \epsilon\left[F[X(\epsilon\tau,\epsilon) + \xi(\tau,\epsilon)] - F[X(\epsilon\tau,\epsilon)]\right]$$

$$\eta(0,\epsilon) = - \epsilon Y(\theta,\epsilon).$$

Note that $\dfrac{d\eta}{ds} = \dfrac{1}{\epsilon}\dfrac{d\eta}{d\tau}$

$$F[X(\epsilon\tau,\epsilon) + \xi(\tau,\epsilon)] - F[X(\epsilon\tau,\epsilon)] =$$

$$F\left[\Sigma_{j=0}^{\infty} \ [X_j(\epsilon\tau) + \xi_j(\tau)]\epsilon^j\right] - F\left[\Sigma_{j=0}^{\infty} \ X_j(\epsilon\tau)\epsilon^j\right]$$

$$= F[X_0(\epsilon\tau) + \xi_0(\tau)] + \left[\nabla_x F[X_0(\epsilon\tau) + \xi_0(\tau)]\right]^T \Sigma_{j=1}^{\infty} \ [X_j(\epsilon\tau) + \xi_j(\tau)]\epsilon^j -$$

$$F[X_0(\epsilon\tau)] - \left[\nabla_x F[X_0(\epsilon\tau)]\right]^T \Sigma_{j=1}^{\infty} \ X_j(\epsilon\tau)\epsilon^j$$

Let $Q_j(r) = [V \ FU_O(O)]]^{*}{,.,}\{^{*}-), \quad j-1. \ 2 \ .... $ then

$$\int_{\delta}^{r} e^{P} a_{j,}(p)dp = [V \ F[X_o(0)]]^{T} \int_{\delta}^{T} \theta^{P} e_{t} J p)dp$$

OU'h

$$\frac{-i}{dr} \ll - ,(r) \qquad\qquad 0 \leq \tau \leq 1/\epsilon$$

$$\mathbf{J}. - {}_{\eta}\mathbf{W} + \overline{q}_{j,}(r)$$

$^{\wedge}_j(0) \ll - y_{j}{}^{\wedge}O)$ (from the outer solution)

Thus $\theta_j(r) \ll - e^{\wedge}Fy_j/O) \cdot {}^{P}j._{t}1'$ where P_{j-y} is a finite degree polynomial in r. Hence $e^{\tau T}P_{j}{}^{\wedge}$ is bounded since $e^{"r}$ goes to zero faster than r goes to infinity (as ϵ goes to zero). Therefore if $y_j/O)$ is finite then $\theta_j(r)$ and $\pounds_j(r)$ are also finite.

Finally we have $X = X_Q(s) \cdot f_Q(s) \cdot Z_{jm1}^{\infty} [X.(s) + f.(s)]\epsilon^{j}$. Taking the limit as ϵ goes to zero gives us the PFR equations (5).

On the basis of what has been discussed we see that the PFR is a limiting case of ADR, i.e. the PFR term (the zero order term) is the dominant term in the expansion of the ADR equations when $* = D$ is small.

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