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THE EFFECT OF DISPERSION ON OPTIMUM RESIDENCE TIMES OF CHEMICAL REACTOR SYSTEMS USING PERTURBATION EXPANSION TECHNIQUES

by

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Abstract

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This work is a mathematical study of the effect of dispersion on the optimum residence times of several chemical reactor systems. The models considered are (1) the axial dispersed plug flow tubular reactor, (2) the ideal tubular reactor and the perfectly mixed tank reactor connected in parallel, and (3) the ideal tubular reactor with a small zone of perfect mixing.

Attention is confined to the range of very small and very large dispersion. This allows us to use the technique of perturbation expansions to obtain asymptotic solutions which are excellent approximations in these limiting cases. The results of this work show the suitability of the technique.

The consecutive reaction system \( A \rightarrow B \rightarrow C \), where \( B \) is the desired intermediate product, is used exclusively. The optimum residence time is then defined as that which maximizes the yield of \( B \) from each isothermal reactor model.

The axial dispersed plug flow reactor model proves to be well suited for modeling more complex reactor systems in the range of small dispersion. Finally, an interesting maximum effect in the optimum residence time for the axial dispersed tubular reactor is discussed and compared to the results of another study.
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# TABLE OF CONTENTS

**ACKNOWLEDGMENTS** ii  
**LIST OF FIGURES** v  
**LIST OF TABLES** vi  
**NOTATION** vii  
**INTRODUCTION** 1  

I. REACTOR MODELS WITH SMALL DISPERSION 10  
1. The Axial Dispersed Plug Flow Tubular Reactor 10  
2. An Ideal Tubular Reactor with a Continuous Flow Stirred Tank Reactor Bypass 30  
3. An Ideal Tubular Reactor with a Small Zone of Perfect Mixing 39  

II. REACTOR MODELS WITH LARGE DISPERSION 44  
4. The Axial Dispersed Plug Flow Tubular Reactor 44  
5. A Continuous Flow Stirred Tank Reactor with an Ideal Tubular Reactor Bypass 62  

III. USE OF THE AXIAL DISPERSED PLUG FLOW REACTOR TO PREDICT OPTIMUM RESIDENCE TIMES FOR OTHER REACTOR MODELS IN THE REGION OF SMALL DISPERSION 68  
6. Modeling the Total Bypass Reactor 68  
7. Modeling a Partial Bypass Reactor 79  
8. Modeling a Total Bypass Reactor and Axial Dispersed Plug Flow Reactor in Series 88  

**CONCLUSIONS** 97  
**REFERENCES** 99  

**APPENDICES**  
A: Formulation of the Equations for a Series-Parallel Reaction System A-1
B: The Exact Solution to the Axial Dispersed Plug Flow Reactor with the Consecutive First Order Reaction System  
C: Comparison of the Solution of Freeman and Houghton with the Results of a Correct Perturbation Expansion Technique
LIST OF FIGURES

FIGURE 1.1  Semi-log plot of $\tau_1$ and $\tau_1/\tau_o$ vs $\alpha$ for the axial dispersed tubular reactor with small dispersion

FIGURE 2.1  Semi-log plot of $\tau_1$ vs $\alpha$ for the bypass reactor systems with small dispersion effects

FIGURE 2.2  Semi-log plot of $\tau_1/\tau_o$ vs $\alpha$ for the bypass reactor systems with small dispersion effects

FIGURE 3.1  Semi-log plot of $\tau_{opt}$ vs $\delta$ for a tubular reactor with a small zone of perfect mixing

FIGURE 4.1  Semi-log plot of $\tau_1$ and $\tau_1/\tau_o$ vs $\alpha$ for the axial dispersed tubular reactor with large dispersion

FIGURE 4.2  Axial dispersed tubular reactor optimum residence time vs $\frac{\gamma}{1+\gamma}$ for $\alpha = .1$.

FIGURE 4.3  $\phi_B$ vs $\tau_{opt}$ for values of $\alpha$ and $\gamma$ for the axial dispersed plug flow tubular reactor

FIGURE 5.1  Semi-log plot of $\tau_1$ and $\tau_1/\tau_o$ vs $\alpha$ for the total bypass reactor with very large dispersion effects

FIGURE 6.1  Admissable $\varepsilon$ vs $\alpha$ for a valid modeling of the total bypass reactor by the axial dispersed plug flow reactor
LIST OF TABLES

Table 6.1  Optimum Residence Time and Yield of Desired Intermediate for the Total Bypass Reactor System Predicted by the Axial Dispersed Tubular Reactor  77

Table 7.1  Optimum Resident Time and Yield of Desired Intermediate for the Partial Bypass Reactor System Predicted by the Axial Dispersed Tubular Reactor  86

Table 8.1  Optimum Residence Time and Yield of Desired Intermediate for the Series Reactor System Predicted by the Axial Dispersed Tubular Reactor  95

Table C.1  Perturbation Expansion Solution Comparison  C-2
NOTATION

Note: Subscripts appearing with these quantities are defined where used.

CAPITAL LETTERS:
A Reaction component
B Reaction component
C Reaction Component
C_1 Constant of Integration
C_2 Constant of Integration
C_3 Constant of Integration
D Axial Dispersion Coefficient
L Length of tubular reactor
L_1 Length of reactor zone I
L_2 Length of entire reactor
S_i Material source term for component i
T Residence time (often with various subscripts)
V Average or plug flow velocity in the axial direction of a tubular reactor

SMALL LETTERS:
b_1 Constant of Integration
b_2 Constant of Integration
c_i Concentration of component i
c_{i_0} Concentration of i upstream and away from the axial dispersed tubular reactor or concentration of i at the entrance to an ideal reactor
d₁  Constant of integration

d₂  Constant of integration

k₁  Linear kinetic rate constant in r₁

k₂  Linear kinetic rate constant in r₂

rₐ  Rate of formation of component A

r₇  Rate of formation of component B

rᵢ  Rate of formation of component i

r₁  Reaction rate for A → B

r₂  Reaction rate for B → C

r₁  Dimensionless reaction rate for A → B (Section I-1b; II-4b)

r₂  Dimensionless reaction rate for B → C (Section I-1b; II-4b)

r₁' Rate of change of reaction rate with change in concentration of A

r₂' Rate of change of reaction rate with change in concentration of B

s  Laplace transform variable

T  Time variable

V  Volume of a continuous flow stirred tank reactor

x  Dimensionless axial coordinate for tubular reactor

z  Tubular reactor axial coordinate

Δz  Length of zone of perfect mixing

GREEK LETTERS:

α  Ratio of the reaction rate constants

β  Parameter of the defect boundary layer stretching transformation

γ  Parameter of the defect boundary layer perturbation term

δ  Dimensionless axial dispersion coefficient
δ(t) Impulse or delta function

δ Dimensionless length of the zone of perfect mixing

e Fraction of the volumetric flow rate put through the bypass reactor

η Ratio of the bypass residence time to the total residence time for the partial bypass reactor; Defect boundary layer coordinate; Ratio of the axial dispersed reactor residence time to the total residence time in the series model.

μ First moment about the origin, t = 0; the mean or centroid

σ Second moment about the mean; the variance

τ Dimensionless residence time

τ_{opt} Optimum dimensionless residence time

τ_0 Optimum dimensionless residence time, zeroth order solution

τ_1 Optimum dimensionless residence time, first order perturbation term

τ_2 Optimum dimensionless residence time, second order perturbation term

φ_A Dimensionless concentration of A

φ_B Dimensionless concentration of B

φ_{i_0} Dimensionless concentration of i, zeroth order solution

φ_{i_1} Dimensionless concentration of i, first order perturbation term

φ_{i_2} Dimensionless concentration of i, second order perturbation term

Φ_j Residence time distribution function of reactor j

Ψ_i Defect boundary layer solution or singular perturbation term for the dimensionless concentration of i

ω Volumetric flow rate

SPECIAL SYMBOLS:

[=] Notational equivalence

^ Referring to the axial dispersed tubular reactor used to model the series system

ln Natural logarithm
INTRODUCTION

The effects of dispersion on the optimum residence time for several chemical reactor models are investigated in this work. The reactor residence time is chosen to maximize the yield of the desired intermediate product $B$ in a simple consecutive reaction, $A \rightarrow B \rightarrow C$. The mathematical technique of perturbation expansions is used to obtain solutions to the limiting cases of small and large dispersion in the various systems.

In chemical reaction engineering or chemical reactor analysis perhaps the two most common mathematical models are the ideal tubular flow reactor and the continuous flow stirred tank reactor. In the former, the assumption of no fluid mixing and of a plug flow velocity profile is made; while in the latter perfect fluid mixing is assumed. Actual reactors never satisfy either of these extremes; but in many cases these assumptions are accurate enough for the analysis required. In some situations reactor flow can deviate considerably from the ideal patterns.

In a tubular reactor, for example, the flow may be laminar with an approximately parabolic velocity profile. The presence of radial diffusion coupled with an established profile leads to the phenomenon called Taylor diffusion. In a packed bed catalytic reactor non-uniform packing may cause channeling of the fluid with a corresponding decrease in reactor efficiency. Finally, a stirred tank reactor may have stagnant pockets of unmixed fluid or bypass flow where a portion of the fluid enters and leaves the vessel without becoming mixed with the contents of the reactor. These are just a few examples of flow situations in real systems that violate the ideal flow assumptions made for the two
simple reactor models.

Many types of models can be used to represent the effects of non-ideal flow in tubular reactors, packed bed reactors, and stirred tank reactors. In this work, attention will be confined to models of tubular and packed bed reactors only. Each of these models characterizes non-ideal flow with a single dispersion parameter indicating the extent of fluid mixing taking place. The models to be considered are (1) the axial dispersed plug flow tubular reactor, (2) various series and parallel combinations of the ideal tubular reactor and the continuous flow stirred tank reactor, and (3) a combination of the ideal tube, stirred tank and axial dispersed reactors.

The consecutive reaction system, \( A \to B \to C \), is used exclusively where \( B \) is the desired product and \( C \) is a waste product. The reacting fluid is assumed to be a single phase with the reactions taking place homogeneously in the isothermal reactor. Thus the models are applicable to packed bed catalytic reactors with negligible mass transfer resistance between phases. The main item of interest is the effect of the dispersion parameter on the optimum residence time for the maximum yield of the desired reaction product.

To solve the various systems of differential and algebraic equations perturbation expansion solution techniques were used. Attention was confined to very small dispersion and very large dispersion parameter values. This was so that an approximate solution to the equations of the axial dispersion model for small dispersion could be considered as a small perturbation of the solution to the equations that describe the ideal tubular reactor which has no dispersion effects. Similarly, the case of very large dispersion was considered as a small perturbation
to the equations for the perfectly mixed tank reactor with infinite dispersion.

Much theoretical work has been done on dispersion in chemical reactors, but there is very little previous literature that relates directly to the objectives or the methods of this thesis. Bischoff and Levenspiel [2] give a good summary and comparison of dispersion models from the most general component mass balance to the relatively simple axial dispersed plug flow model. The effect of dispersion on the conversion in reactors has been investigated by many authors. Freeman and Houghton [6] have applied the perturbation expansion techniques of Erdelyi [5] and Carrier to the singular perturbation, concentration profile problem. However, in the formal solution procedure, they deliberately violated order relationships in the boundary conditions in order to bring their results into closer agreement with numerical solutions. Parish [11] has also applied perturbation expansions to the conversion problem with small dispersion for multiple reactions and general kinetics. He shows how dispersion can improve reactor yield of desired intermediate for a series-parallel reaction system.

Only a few articles have appeared dealing with dispersion and selectivity in chemical reactors [3,8,9,12,16]. Selectivity refers to the fraction of intermediate products formed under various operating conditions in a series of reactions. Kramers and Westerterp [9] have numerically evaluated the axial dispersed tube reactor for the consecutive reactions $A \rightarrow B \rightarrow C$. However, a discovery is presented in this report
that contradicts their graph of the effect of dispersion on the optimum residence time in the range of very large dispersion. For the same reaction system Tichacek [12] presents results on the decrease in intermediate yield due to dispersion in a tubular reactor. He considers several sets of reaction kinetics and uses a perturbation expansion solution in one case; but to simplify the equations, he makes the reactor length semi-infinite. Thus the results are slightly different than for the axial dispersion reactor with a finite reaction zone.

In review, one can say that only Parish handled perturbation expansion solutions to dispersion problems in finite chemical reactors in a rigorously correct manner. No one to date has presented work on optimum residence times for reactors with dispersion effects using perturbation expansion techniques.

At this point it is appropriate to present some general aspects of the mathematical technique and motivating idea behind perturbation expansion solutions of ordinary differential equations. Unfortunately, there is little published work on the theory of perturbation expansions. Mathematical justification of this topic is in its infancy.

The perturbation technique is an empirical method of obtaining approximate analytical solutions to otherwise insolvable problems that are only slightly different from problems that can be solved. Basically, we desire a solution to a differential equation containing one small parameter where all other terms are assumed to be of order one. If the equation can be solved exactly when the small parameter goes to zero,
then we are motivated to wonder if a good approximation to the exact solution of the entire differential equation can be obtained in the form of a perturbation expansion of the exact solution to the zeroth order equation. In other words, we expect a small change in the basic zeroth order solution due to the presence of a small additional term in the differential equation.

An assumed solution form, \( \varphi = \varphi_0 + \varepsilon \varphi_1 + \varepsilon^2 \varphi_2 + \ldots \), is inserted into the differential equation and boundary condition. The resulting sets of equations in orders of the small parameter \( \varepsilon \) are solved sequentially for \( \varphi_i \) starting with the zeroth order system. The various sets of equations must be satisfied identically in order for the complete solution to satisfy the differential equation and boundary conditions uniformly in the small parameter. If difficulties with order relations occur in the course of the formal solution process, a new solution form is assumed.

The result is assumed to be accurate to the order of the first truncated term, at which point the calculations are stopped. This is the basic Poincaré expansion procedure. Many individual variations to this basic technique have been developed, e.g., the two variable expansion method of Cole.

Perturbation or asymptotic expansions are highly dependent on order relationships. Mathematically, if a function \( f(x) \) is of order \( \varepsilon \), (written \( O(\varepsilon) \)) for \( \varepsilon \) small and positive, it means that as \( \varepsilon \) goes to zero, \( |f(x)| \leq A\varepsilon \) or \( \lim_{\varepsilon \to 0} \frac{|f(x)|}{\varepsilon} = A \) where \( A \) is a constant.
Order relations are distinct from physical order of magnitude statements because constants of proportionality are not retained. Thus $ke$ is of order $\varepsilon$ even if $k$ is 1000. In physical problems we hope that the concepts are related. If the error in a perturbation expansion is of order $\varepsilon$, we expect the actual numerical error to be of the same order of magnitude as $\varepsilon$ over the range of the independent variable. Of course, this is not a necessary condition for a valid perturbation expansion. In working with perturbation expansions, we must always be sure that order relations are not violated. In the course of solving the sets of equations in the various orders of the small parameter equating terms of mixed order would be a typical violation. Another might be that a term initially assumed to be of order one actually becomes of order greater than one in some region of the independent variable domain. This is the case in singular perturbation problems.

A better feel for order relations and expansion accuracy is obtained by looking at some of the basic properties of asymptotic expansions. Perturbation expansion solutions are a class of asymptotic representations of functions. Consider the following representation of a function $f(x)$ for $x$ near $x_o$:

$$f(x) = \sum_{i=1}^{N} a_i \tilde{\phi}_i(x) + O(\tilde{\phi}_{N+1}(x))$$

This is an asymptotic expansion for $f(x)$. $\tilde{\phi}_i(x)$ is the dominant term as $x$ approaches $x_o$ and $\lim_{x \to x_o} \frac{\tilde{\phi}_{i+1}(x)}{\tilde{\phi}_i(x)} = 0$.

There is a distinct difference between an asymptotic expansion and a convergent power series representation. A convergent power series
becomes a better approximation of the function as the number of terms in the series is increased. With \(|x-x_q|\) given, we use enough terms to satisfy a specified error limit. But in an asymptotic expansion we fix the number of terms to be used, then restrict \(|x-x_0|\) for a valid representation. A valid representation means that the error is of the order of the first truncated term. The approximation does not necessarily improve with the addition of more terms. In fact, after a certain number of terms the series may actually diverge; but this does not matter since only the first few terms are used in most cases. Thus the two advantages of an asymptotic expansion over a power series expansion are (1) the error in the approximation is of the order of the first neglected term, and (2) for \(x\) near enough to \(x_0\), only the first two or three terms are necessary for a good approximation.

Finally, it should be stated there is no formal justification of the validity of differentiation of an asymptotic expansion with respect to any of its variables. In other words, the derivative of an asymptotic expansion may no longer by an asymptotic expansion. The only recourse is to proceed formally, and to be alert for possible violations in order relations. In perturbation expansion solutions as obtained in this work, the problem of differentiability is not serious because only the general form of the expansion is assumed and the functions in the expansion are derived. The problem of differentiability is greater in methods where the actual functions in the asymptotic expansion are assumed.
In a perturbation problem, one form of difficulty that may occur is that the highest order derivative disappears as the small parameter goes to zero. This gives a singular perturbation problem. There is difficulty in making the solution satisfy all the boundary conditions because no single asymptotic expansion is uniformly valid throughout the solution domain. An expansion is uniformly valid if the error in the representation is uniformly small in all variables.

Suppose we have a boundary value problem in ordinary differential equations. Two approaches can be taken here. Both involve the addition of a boundary layer to enable both boundary conditions to be satisfied. One is to generate a perturbation expansion solution for the outer region that satisfies the outer boundary condition and an inner perturbation expansion solution, i.e. inside a boundary layer, that satisfies both the differential equation and the boundary condition of the inner region. Then "blend" the two solutions together where the boundary layer merges with the outer solution region to form a composite solution that is valid over the entire region. This technique is given by Erdelyi [5]. The other method is computationally easier and is often used in fluid mechanics problems involving partial differential equations [15]. A boundary layer coordinate stretching transformation is used to form a "defect boundary layer". In this layer a correction term added to the solution becomes sufficient in magnitude to enable the boundary condition to be satisfied. Away from the boundary layer the defect boundary layer term vanishes. Whitham [17]
discusses boundary layer solutions in his paper on wave propagation. The "defect boundary layer" technique for ordinary differential equations as given by Goldwyn [7] will be used in this work.

All of the above points should become clearer when they are illustrated by the systems solved in this work. Further discussion will appear with the examples of perturbation expansion solutions.
I. REACTOR MODELS WITH SMALL DISPERSION

I-1. The Axial Dispersed Plug Flow Tubular Reactor

This model characterizes non-ideal flow patterns in a tubular reactor by drawing an analogy between mixing and diffusion. In the differential component material balance, the molecular diffusivity is replaced by a dispersion coefficient that takes into account mixing effects due to velocity fluctuations from plug flow, radial and axial diffusion, and turbulent mixing. This axial dispersion model is one dimensional, and is obtained from the general component material balance [1]

\[ \frac{\partial c_i}{\partial t} + V \cdot \nabla c_i = \nabla \cdot (D \nabla c_i) + r_i + S_i \]

where \( D \) is diffusivity matrix, \( S \) is source term, \( V \) is fluid velocity, through the following assumptions: (For an excellent discussion see Bischoff [2]).

There are no sources of material within the system.
The reacting mixture is treated as a single phase.
The mixture is of constant density.
There is bulk flow in the axial direction only, and radial symmetry.
The dispersion coefficients are constant.
The time average velocity of the fluid is constant over the tubular cross-section and independent of axial position (plug flow).
There is no variation in properties in the radial direction.
The system is at steady state.

The differential equation for the \( i \)th component mass balance is then:

\[ -D \frac{d^2 c_i}{dz^2} + V \frac{dc_i}{dz} - r_i c_i = 0 \]  \hspace{1cm} (1.1)

where \( D \) is dispersion coefficient

\( r_i c_i \) is rate of formation of \( i \)th component/unit volume.
Looking at the terms of the differential equation (1.1), we see that the axial dispersion model describes dispersion and mixing by a diffusional mechanism, (i.e., driven by concentration gradients), superimposed on the plug flow velocity profile of the ideal tubular reactor model. The single parameter \( D \) characterizes the net effect of all dispersion phenomena which may be taking place.

To formulate the proper boundary conditions it is helpful to visualize the physical system as a tubular reactor which may or may not have packing. The tube itself is doubly infinite, but it has a finite reaction zone of length \( L \) as shown in the diagram below. Dispersion and mixing in the three regions are characterized by three dispersion coefficients which are not necessarily equal.

Let \( C_j \) be the concentration vector of components, \( j = I, II, III \) indicating the respective zones.

Writing Equation (1.1) for regions I and III to get the boundary conditions for region II gives:
Region I

\[-D_I \frac{d^2 c_I}{dz^2} + V \frac{dc_I}{dz} = 0\]  
\[(1.2a)\]

B.C. at \( z = -\infty \) \( c_I = c_o \)

at \( z = 0 \) \( D_I \frac{dc_I}{dz} \big|_0 = D_I \frac{dc_{II}}{dz} \big|_0 \)

Region II

\[-D_{II} \frac{d^2 c_{II}}{dz^2} + V \frac{dc_{II}}{dz} - r c_{II} = 0\]  
\[(1.2b)\]

at \( z = 0 \) \( c_I(0) = c_{II}(0) \)

at \( z = L \) \( c_{II}(L) = c_{III}(L) \)

Region III

\[-D_{III} \frac{d^2 c_{III}}{dz^2} + V \frac{dc_{III}}{dz} = 0\]  
\[(1.2c)\]

B.C. at \( z = \infty \) \( c_{III} \) is bounded

at \( z = L \) \( D_{II} \frac{dc_{II}}{dz} \big|_L = D_{III} \frac{dc_{III}}{dz} \big|_L \)

The boundary conditions arise from the following physical considerations:

\( c_I \) is at an initial concentration \( c_o \) some distance "away" from the reaction zone.

The concentration is bounded throughout the entire tube since there are no mass sources in the system.

At the ends of the reaction zone, \( z = 0 \) and \( z = L \), conservation of mass requires continuity of mass flux across these boundaries.

Solving the equations in Regions I and III and applying the boundary conditions, the following boundary conditions for each end of the reaction zone are obtained:
at \( z = 0 \) \( \xi_{II}(0) - D_{II} \frac{dc_{II}}{dz} \bigg|_0 = c_o \) (1.3a)

at \( z = L \) \( D_{II} \frac{dc_{II}}{dz} \bigg|_L = 0 \) (1.3b)

Note that these boundary conditions are independent of the values of the dispersion coefficients in Regions I and III, provided they are non-zero. These are the well known Danckwerts [4] boundary conditions for tubular reactors with dispersion. The reaction to be considered is the simple consecutive reaction \( A \rightarrow B \rightarrow C \) where \( B \) is the desired intermediate product. The reactor is assumed to be isothermal so no energy balance is required. Only component \( A \) enters the reactor. Furthermore, the dispersion coefficient is assumed to be the same for both substances \( A \) and \( B \) and independent of composition.

a. **Linear Reaction Kinetics**

Let the two consecutive reactions be irreversible and have first order kinetic rate expressions.

\[
A \rightarrow B \quad r_1 = k_1 c_A \quad \text{so} \quad r_A = -k_1 c_A \\
B \rightarrow C \quad r_2 = k_2 c_B \quad r_B = k_1 c_A - k_2 c_B
\]

Then the differential equations and boundary conditions for the system are

\[
-D \frac{d^2 c_A}{dz^2} + V \frac{dc_A}{dz} + k_1 c_A = 0 \quad (1.4a)
\]

B.C. at \( z = 0 \) \( Vc_A - D \frac{dc_A}{dz} \bigg|_0 = V c_A \)

at \( z = L \) \( D \frac{dc_A}{dz} \bigg|_L = 0 \)
\[-D \frac{d^2 c_B}{dz^2} + V \frac{dc_B}{dz} + k_2 c_B - k_1 c_A = 0 \quad (1.4b)\]

B.C. at \( z = 0 \) \( Vc_B - D \frac{dc_B}{dz} \bigg|_0 = 0 \)

at \( z = L \) \( D \frac{dc_B}{dz} \bigg|_L = 0 \)

At this point we introduce dimensionless variables.

\[ \varphi_A = \frac{c_A}{c_{A_0}}, \quad \varphi_B = \frac{c_B}{c_{B_0}}, \quad x = \frac{zk_1}{V}, \quad \gamma = \frac{Dk_1}{V^2}, \quad \frac{Lk_1}{V} = \tau \quad \text{(dimensionless residence time)} \]

\[ \alpha = \frac{k_2}{k_1} \]

Note: The usual dimensionless dispersion coefficient is the Peclet number defined as \( VL/D \). In this work a different dimensionless dispersion parameter that does not contain the reactor length is used since the length of the reactor is to be optimized.

Then in dimensionless form

\[-\gamma \frac{d\varphi_A}{dx} + \frac{d\varphi_A}{dx} + \varphi_A = 0 \quad (1.5a)\]

B.C. at \( x = 0 \) \( \varphi_A - \gamma \frac{d\varphi_A}{dx} \bigg|_0 = 1 \)

at \( x = \tau \) \( \gamma \frac{d\varphi_A}{dx} \bigg|_\tau = 0 \)

\[-\gamma \frac{d^2\varphi_B}{dx^2} + \frac{d\varphi_B}{dx} + \alpha \varphi_B = \varphi_A \quad (1.5b)\]

B.C. at \( x = 0 \) \( \varphi_B - \gamma \frac{d\varphi_B}{dx} \bigg|_0 = 0 \)

at \( x = \tau \) \( \gamma \frac{d\varphi_B}{dx} \bigg|_\tau = 0 \)

The above linear system can be solved analytically. This would not be true if the reaction rates were nonlinear. It will become clear that per-
turbation expansion solutions are simpler and easier to obtain than exact analytical solutions in those cases where both are possible.

Now suppose that the dispersion coefficient $\gamma$ is of order much less than one and that all other terms including the derivatives in the differential equations and boundary conditions are of order one. We can then assume a perturbation expansion solution of the form

$$\phi = \phi_0 + \gamma \phi_1 + \gamma^2 \phi_2 + \ldots$$

where $\phi_0, \phi_1, \phi_2$, etc. are of order one. $\phi$ is the concentration vector (dimensionless).

The above set of equations forms a singular perturbation problem since as $\gamma \to 0$ the highest order derivatives are lost and the equations become first order. This means that it will be impossible to satisfy the boundary conditions in all orders of $\gamma$ with a single ordinary perturbation expansion.

Fortunately we can solve the two differential equations sequentially rather than simultaneously due to the irreversibility of the reactions. Starting with the equation for $\phi_A$, assume an expansion of the form

$$\phi_A = \phi_{A0} + \gamma \phi_{A1} + \gamma^2 \phi_{A2} + \ldots$$

and insert it into Equations (1.5a).

$$-\gamma \phi''_{A0} - \gamma^2 \phi''_{A1} + \ldots + \phi'_{A0} + \gamma \phi'_{A1} + \ldots + \phi_{A0} + \gamma \phi_{A1} + \ldots = 0$$

where $\phi' = \frac{d\phi}{dx}$

B.C. at $x = 0$ \begin{align*}
\phi_{A0} + \gamma \phi_{A1} + \ldots - \gamma \phi'_{A0} - \gamma^2 \phi'_{A1} + \ldots &= 1 \\
\text{at } x &= \tau \quad \gamma \phi'_{A0} + \gamma^2 \phi'_{A1} + \ldots = 0
\end{align*}

For this to be uniformly satisfied in $\gamma$, i.e. for the equation to hold for all $\gamma$ as $\gamma \to 0$, we must require that the equations of order $\gamma^0, \gamma^1, \gamma^2$, etc. be individually satisfied to each order in the small
parameter $\gamma$. Thus the problem of finding a solution to (1.5a) has been broken down into finding the solution of a set of simpler differential equations which can be solved sequentially. The number of terms to be used in this and future asymptotic expansions is two -- the basic zeroth order solution and the first perturbation term.

**Terms of Order**

- **$\gamma^0$:**
  \[
  \frac{d\varphi_{A_0}}{dx} + \varphi_{A_0} = 0
  \]
  B.C. at $x = 0$ \hspace{1em} $\varphi_{A_0} = 1$
  B.C. at $x = \tau$ \hspace{1em} none of order $\gamma^0$

  Thus $\varphi_{A_0} = e^{-x}$ \hspace{1em} NOTE: This is the solution for an ideal tubular reactor.

- **$\gamma'$:**
  \[
  d^2\varphi_{A_0} - \frac{d\varphi_{A_1}}{dx} + \varphi_{A_1} = 0
  \]

  or
  \[
  \frac{d\varphi_{A_1}}{dx} + \varphi_{A_1} = e^{-x}
  \]

  B.C. at $x = 0$ \hspace{1em} $\varphi_{A_1} - \frac{d\varphi_{A_0}}{dx} \bigg|_0 = 0$
  B.C. at $x = \tau$ \hspace{1em} $\frac{d\varphi_{A_1}}{dx} \bigg|_\tau = 0$

  Thus $\varphi_{A_1} = xe^{-x} - e^{-x}$ using B.C. at $x = 0$ only.

We now have a solution to order $\gamma'$ but the second boundary condition (1.6) of order $\gamma'$ cannot be satisfied. Our solution as it now stands has a "defect" in it. This is a consequence of the singularity of the differential equation (1.5a) for $\gamma$ equal to zero. Therefore, we
suspect that the term \( \frac{d^2 \varphi_A}{dx^2} \) is not actually of order one when \( x \) is near \( \tau \). To correct this an additional term is introduced into the solution which is important near \( x = \tau \) but vanishes "far away" from that boundary. To express it another way, a boundary layer is inserted at the end of the reactor in which a correction term to the basic expansion solution appears. It is called a defect boundary layer and enables the solution, which is valid to order \( \gamma' \), to satisfy all boundary conditions to order \( \gamma' \) at both ends of the reactor.

Actually this boundary layer does not have a sharp border between it and the primary solution domain. It represents the region where the singular perturbation term is significant, and where the term \( \frac{d^2 \varphi_A}{dx^2} \) is of order greater than one. The edge of the boundary layer might be arbitrarily designated as the point where the singular perturbation or defect boundary layer term becomes greater than some small value.

Assume a revised solution of the form \( \varphi_A = \varphi_{A_0} + \gamma \varphi_{A_1} + \gamma^\beta \psi_A(\eta) + \ldots \) \((\beta \geq 0 \ \text{since} \ \varphi_A \ \text{is bounded as} \ \gamma^{-0})\) where \( \varphi_{A_0}, \varphi_{A_1}, \) etc. are the functions previously found. We want \( \psi_A(\eta) \to 0 \) as \( \eta \to \infty \). \( \eta \) is the boundary layer coordinate. So let \( \eta = (\tau - x) \gamma^{\tilde{\alpha}} \) (this is a coordinate stretching transformation) As \( x \to \tau \); \( \eta \to 0 \) as \( x \to -\infty \); \( \eta \to \infty \).

Thus \( \eta \) measures the distance away from the exit of the reactor.

Then
\[
\frac{d}{dx} = \frac{d}{d\eta} \frac{d\eta}{dx} \\
\frac{d^2}{dx^2} = \frac{d}{d\eta} \frac{d^2\eta}{dx^2} + \left( \frac{d\eta}{dx} \right)^2 \frac{d^2}{d\eta^2} \\
\frac{d}{dx} = -\gamma \frac{d}{d\eta} \\
\frac{d^2}{dx^2} = \gamma^2 \frac{d^2}{d\eta^2}
\]
Insert the above into the Equation (1.5a) to obtain:

\[-\gamma e^{-x} - \gamma^2 (-3e^{-x} + xe^{-x}) - \ldots - \gamma^{2\hat{\gamma} + \beta + 1} \frac{d^2 \psi_A}{d\eta^2} 0(\gamma^{\beta - 1})\]

\[+ (-e^{-x}) + \gamma(2e^{-x} - xe^{-x}) + \ldots - \gamma^{\hat{\gamma} + \beta} \frac{d\psi_A}{d\eta} 0(\gamma^{\beta - 1})\]

\[+ e^{-x} + \gamma(xe^{-x} - e^{-x}) + \ldots + \gamma^\beta \psi_A(\eta) = 0\]

0(\gamma^\beta) \quad (1.7)

(The orders of the \( \psi \) terms are given below them for \( \hat{\gamma} = -1 \).)

Note that \( \varphi_A + \gamma \varphi_A \) satisfies the differential equation identically as expected.

We ran into trouble with our previous solution because there were no terms in \( \frac{d^2 \varphi_A}{dx^2} \) to "balance" the terms in \( \frac{d\varphi_A}{dx} \) and \( \varphi_A \) so the boundary condition at \( x = \tau \) could be satisfied to order \( \gamma' \). Therefore, we would like the defect boundary layer term \( \psi_A(\eta) \) involving the second derivative to be of the same order in \( \gamma \) as the lower derivative term. Then the second derivative \( \frac{d^2 \varphi_A}{dx^2} \) will not disappear as \( \gamma \) goes to zero, especially near the reactor exit. For this reason pick \( \hat{\gamma} \) so that the highest derivative terms are retained and are of the same order as lower terms, i.e. set

\[2\hat{\gamma} + \beta + 1 = \hat{\gamma} + \beta \quad \text{so} \quad \hat{\gamma} = -1, \quad \text{then} \quad \eta = \frac{T - x}{\gamma} .\]

The differential equation (1.7) now looks like this:

\[\gamma^{\beta - 1} \frac{d^2 \psi_A}{d\eta^2} + \gamma^{\beta - 1} \frac{d\psi_A}{d\eta} - \gamma^\beta \psi_A = 0 \quad \text{with} \quad \beta \geq 0\]
or, multiplying by $\gamma^{1-\beta}$: 

$$\frac{d^2\psi_A}{d\eta^2} + \frac{d\psi_A}{d\eta} = \gamma \psi_A.$$ 

As $\gamma \to 0$ the dominant terms give 

$$\frac{d^2\psi_A}{d\eta^2} + \frac{d\psi_A}{d\eta} = 0$$ 

and this becomes the differential equation for $\psi_A$.

B.C. $\psi_A(\eta) \to 0$ as $\eta \to \infty$

$$\frac{d\varphi_A}{d\xi} = 0 \text{ at } x = \tau \quad \eta = 0$$

Then

$$\frac{d\psi_A}{d\eta} + \psi_A = C_1$$

$$\psi_A = C_1 + C_2 e^{-\eta}$$

First B.C. $= C_1 = 0$

$$\therefore \psi_A = C_2 e^{-\eta}$$

The exit boundary condition at $x = \tau$ that we wish to satisfy is

$$\gamma \frac{d\varphi_A}{d\xi} \bigg|_{x=\tau} = \gamma (-e^{-\tau}) + \gamma^2 (2e^{-\tau} - \tau e^{-\tau}) + \gamma^{\beta+1} (-\gamma^{-1})(-C_2)e^{0} + 0(\gamma^3) = 0$$

This is already satisfied to order $\gamma^0$. In order to satisfy it to order $\gamma'$, $\beta$ must be chosen equal to one so the defect boundary layer term will cancel the zeroth order derivative term. Thus $\beta = 1$.

Then to order $\gamma'$:

$$-e^{-\tau} + C_2 = 0 \quad \Rightarrow \quad C_2 = e^{-\tau}$$

Giving the defect boundary layer solution:

$$\psi_A(\eta) = e^{-\tau} e^{-\eta} = e^{-\tau} e^{-\frac{(\tau-x)}{\gamma}}$$

(1.8)
Then the total perturbation expansion solution to order $\gamma'$ is:

$$
\varphi_A(x) = e^{-x} + \gamma [xe^{-x} - e^{-x}] + \gamma e^{-T} e^{-\frac{(T-x)}{Y}} + O(\gamma^2)
$$

for $0 \leq x \leq T$.

(1.9)

Notice that the boundary layer solution is a term of order $\gamma'$ whose first derivative is of order $\gamma^0$. Also, as $x \to -\infty$; $\psi_A \to 0$ and as $\gamma \to 0$; $\psi_A \to 0$ which implies that the boundary layer gets thinner as $\gamma \to 0$.

Looking back at Equation (1.7) we see that the defect boundary layer solution or singular perturbation term does not satisfy the differential equation to order $\gamma'$. Nothing can be done to remedy this since an expansion of the singular term is not valid. However, the singular term vanishes outside of the boundary layer; thus only inside the boundary layer region is the differential equation not satisfied to order $\gamma'$. Considering the fact that as $\gamma$ gets smaller, the boundary layer gets thinner, it seems there will be few cases where the total solution is not uniformly valid through order $\gamma'$ for $\gamma$ sufficiently small.

Note that the defect boundary layer solution or singular perturbation term (1.8) can be derived entirely on physical grounds by looking at zeroth and first order reaction rate problems which can be solved exactly. This was done by Parish [11].

Now exactly the same procedure can be followed with Equation (1.5b) to get a perturbation expansion solution for $\varphi_B$. This is a singular
perturbation problem again, this time with an inhomogeneous differential equation. Proceeding as before, let \( \varphi_B = \varphi_{B_0} + \gamma \varphi_{B_1} + \gamma^2 \varphi_{B_2} + \ldots \)
then
\[
-\gamma \varphi''_{B_0} - \gamma \varphi''_{B_1} + \ldots + \varphi'_{B_0} + \gamma \varphi'_{B_1} + \ldots + \alpha \varphi_{B_0} + \alpha \varphi_{B_1} + \ldots = \varphi_{A_0} + \gamma \varphi_{A_1} + \ldots \text{ where } \varphi' = \frac{d\varphi}{dx}
\]

B.C. at \( x = 0 \) \( \varphi_{B_0} + \gamma \varphi_{B_1} + \ldots - \gamma \varphi'_{B_0} - \gamma^2 \varphi'_{B_1} + \ldots = 0 \)

at \( x = \tau \) \( \gamma \varphi'_{B_0} + \gamma^2 \varphi'_{B_1} + \ldots = 0 \)

Equate terms of like order in \( \gamma \) to obtain a solution that is uniform in \( \gamma \).

**Terms of Order**

\( \gamma^0 \):
\[
\frac{d\varphi_{B_0}}{dx} + \alpha \varphi_{B_0} = \varphi_{A_0}
\]

\[
\frac{d\varphi_{B_0}}{dx} + \alpha \varphi_{B_0} = e^{-x}
\]

B.C. at \( x = 0 \) \( \varphi_{B_0} = 0 \)

at \( x = \tau \) none of order \( \gamma^0 \)

Thus
\[
\varphi_{B_0} = \frac{1}{\alpha - 1} (e^{-x} - e^{-\alpha x})
\]

This is the solution for an ideal tubular reactor.
\[
\gamma' : -\frac{d^2 \phi_B}{dx^2} + \frac{d \phi_B}{dx} + \alpha \phi_{B_1} = \phi_{A_1}
\]

\[
\frac{d \phi_{B_1}}{dx} + \alpha \phi_{B_1} = xe^{-x} - e^{-x} + (e^{-x} - e^{\alpha x}) \frac{1}{\alpha - 1}
\]

B. C. at \( x = 0 \) \( \phi_{B_1} - \frac{d \phi_B}{dx} \bigg|_0 = 0 \)

at \( x = \tau \) \( \frac{d \phi_B}{dx} \bigg|_\tau = 0 \)  \( (1.10) \)

Solution using boundary condition at \( x = 0 \)

\[
\phi_{B_1} = \frac{1}{\alpha - 1} [x-1] e^{-x} - \frac{\alpha}{\alpha - 1} [\alpha x-1] e^{-\alpha x}
\]

As in the first system, at \( x = \tau \) a defect boundary layer solution is needed to satisfy the boundary condition \( (1.10) \) to order \( \gamma' \).

In the same manner as above, assume a solution of the form

\[
\phi_B = \phi_{B_0} + \gamma \phi_{B_1} + \ldots + \gamma^\beta \psi_B(\eta) + \ldots \text{ where } \phi_{B_0}, \phi_{B_1} \text{ are the known solutions. We want } \psi_B(\eta) \text{ to approach 0 as } \eta \to \infty. \eta \text{ is again the boundary layer coordinate. As before let } \eta = (\tau - x) \dot{\eta}
\]

as \( x \to \tau; \eta \to 0 \). As \( x \to -\infty; \eta \to -\infty \),

\[
\frac{d}{dx} = -\gamma \frac{d}{d\eta} \quad \frac{d^2}{dx^2} = \gamma^2 \frac{d^2}{d\eta^2}
\]

Insert the \( \phi_B \) expansion into Equation (1.5b):

\[
-\gamma \frac{1}{\alpha - 1} (e^{-x} - \alpha^2 e^{-\alpha x}) - \gamma^2 [\phi_{B_1}'] - \ldots - \gamma^{2\beta+1} \frac{d^2 \psi_B}{d\eta^2} + \frac{1}{\alpha - 1} (-e^{-x} + e^{-\alpha x})
\]

\[
+ \gamma \left[ \frac{1}{\alpha - 1} e^{-x} - \frac{1}{\alpha - 1} (x-1)e^{-x} - \frac{\alpha^2}{\alpha - 1} e^{-\alpha x} + \frac{\alpha^2}{\alpha - 1} (\alpha x-1)e^{-\alpha x} \right] + \ldots
\]

\[
-\gamma^{\beta+1} \frac{d\psi_B}{d\eta} + \alpha \frac{1}{\alpha - 1} (e^{-x} - e^{-\alpha x}) + \alpha \gamma (\frac{1}{\alpha - 1} (x-1)e^{-x} - \frac{\alpha}{\alpha - 1} (\alpha x-1)e^{-\alpha x})
\]
\[ + \ldots + \alpha_B^0 \gamma^\beta = e^{-x} \gamma(x-1)e^{-x} + \gamma e^{-\tau} e^{-(\frac{T-x}{\gamma})} \]  

(1.11)

Note that \((\alpha_B^0 + \gamma \alpha_B^1)\) satisfies the differential equation identically as expected. This leaves

\[ \gamma^2 \delta + \beta + 1 \frac{d^2 \psi_B}{d\eta^2} - \gamma \alpha + \beta \frac{d\psi_B}{d\eta} + \alpha \gamma^2 \psi_B + 0(\gamma^2) = \gamma e^{-\tau} e^{-(\frac{T-x}{\gamma})} + 0(\gamma^2) \]  

(1.12)

By the same arguments as before set \(2\delta + \beta + 1 = \delta + \beta \)

\[ = \delta = -1 \]

and choose \(\beta = 1\). Then \(\eta = \frac{T-x}{\gamma}\).

Then Equation (1.12) becomes

\[ - \frac{d^2 \psi_B}{d\eta^2} - \frac{d\psi_B}{d\eta} + \alpha \gamma \psi_B = \gamma e^{-\tau} e^{-(\frac{T-x}{\gamma})} \]

As \(\gamma \to 0\), the dominant terms are

\[ \frac{d^2 \psi_B}{d\eta^2} + \frac{d\psi_B}{d\eta} = 0 \]

B. C. as \(\eta \to \infty\); \(\psi_B(\eta) \to 0\), \(\gamma \frac{d\psi_B}{dx}\bigg|_\tau = 0\) at \(x = \tau\)

\[ \eta = 0 \]

Thus \(\psi_B = C_3 e^{-\eta}\), \(\frac{d\psi_B}{d\eta} = -C_3 e^{-\eta}\)

The boundary condition at the exit of the reactor is now:

\[ \gamma \frac{d\psi_B}{dx} \bigg|_{x=\tau} = \gamma \frac{1}{\alpha^{-1}} (-e^{-\tau} + \alpha e^{-\alpha \tau}) + \gamma^2 \frac{d\psi_B}{dx} \bigg|_\tau \]

\[ + \gamma^2 (-\gamma^{-1})(-C_3)e^{-\eta} + 0(\gamma^3) = 0 \]

This is already satisfied to order \(\gamma^0\).
To order $\gamma'$:

\[
\frac{1}{\alpha-1} (-e^{-\gamma} + \alpha e^{-\alpha\gamma}) + C_3 = 0 \quad \Rightarrow \quad C_3 = \frac{1}{\alpha-1} (e^{-\gamma} - \alpha e^{-\alpha\gamma})
\]

\[
\therefore \quad \psi_B(\eta) = \frac{1}{\alpha-1} (e^{-\gamma} - \alpha e^{-\alpha\gamma}) e^{-\eta} = \frac{1}{\alpha-1} (e^{-\gamma} - \alpha e^{-\alpha\gamma}) e^{-(\frac{\gamma-1}{\gamma})}
\]

Then the total perturbation expansion solution to order $\gamma'$ is

\[
\varphi_B(x) = \frac{1}{\alpha-1} (e^{-x} - e^{-\alpha x}) + \gamma\left[\frac{(x-1)}{\alpha-1} e^{-x} - \frac{\alpha}{\alpha-1} (\alpha x - 1) e^{-\alpha x}\right] \\
+ \gamma\left[\frac{1}{\alpha-1}(e^{-\gamma} - \alpha e^{-\alpha\gamma}) e^{-(\frac{\gamma-1}{\gamma})}\right] + 0(\gamma^2)
\]

(1.14)

Again note that the differential equation is no longer satisfied to order $\gamma'$ by the singular perturbation term in the boundary layer region. The boundary conditions are satisfied to order $\gamma'$.

At the exit of the reactor:

\[
\varphi_B(\tau) = \frac{1}{\alpha-1} (e^{-\tau} - e^{-\alpha\tau}) + \gamma\left[\frac{1}{\alpha-1} (\tau - 1) e^{-\tau} - \frac{\alpha}{\alpha-1} (\alpha \tau - 1) e^{-\alpha\tau}\right] \\
+ \gamma\left[\frac{1}{\alpha-1}(e^{-\gamma} - \alpha e^{-\alpha\gamma}) (1)\right] + 0(\gamma^2)
\]

(1.15)

Now to obtain a solution for optimum length or residence time to maximize the production of $B$, perturbation expansion techniques can be used to solve the nonlinear equation. Take the derivative of $\varphi_B(\tau)$ (1.15) with respect to $\tau$ and set it equal to zero. This locates the $\tau$ for maximizing $\varphi_B(\tau)$ since $\varphi_B(\tau)$ is a unimodal function.
\[
\frac{d\phi_B}{d\tau} = \frac{1}{\alpha-1}(-e^{-\tau} + \alpha e^{-\alpha\tau}) + \gamma \left[ \frac{1}{\alpha-1} e^{-\tau} + \frac{(-1)^\tau}{\alpha-1} e^{-\tau} - \frac{\alpha^2}{\alpha-1} e^{-\alpha\tau} + \frac{\alpha^2}{\alpha-1} e^{-\alpha\tau} \right] = 0
\]  
(1.16)

To get a perturbation expansion approximation let \( \tau = \tau_0 + \gamma \tau_1 + \ldots \), insert into the above Equation (1.16) and equate the terms in like orders of \( \gamma \). Physically, we expect the small dispersion \( \gamma \) to cause a small perturbation in the optimum residence time, \( \gamma \tau_1 + O(\gamma^2) \).

\( \gamma^0: \quad -e^{-\tau_0} + \alpha e^{-\alpha\tau_0} = 0 \)

\[ \tau_0 = \frac{\ln \alpha}{\alpha-1} \]

This is the solution for the optimum residence time of an ideal tubular reactor.

\( \gamma^1: \quad e^{-\tau_0} \tau_1 - \alpha^2 e^{-\alpha\tau_0} \tau_1 + e^{-\tau_0} (1-\tau_0) + \alpha^2 e^{-\alpha\tau_0} (\alpha\tau_0 - 1) = 0 \)

\[ \tau_1 = \frac{\ln \alpha}{\alpha-1} (\alpha+1) - 1 \]

It can be shown that \( \tau_1 \geq 0 \) for all \( 0 \leq \alpha \). Thus the asymptotic solution expansion for the optimum residence time is

\[ \tau_{opt} = \frac{\ln \alpha}{\alpha-1} + \gamma \left( \frac{\ln \alpha}{\alpha-1} (\alpha+1) - 1 \right) + O(\gamma^2) \]  
(1.17)

Thus, in a very straightforward and relatively simple manner we have obtained a relation for the effect of small dispersion on the optimum residence time for the maximum yield of the desired component in the consecutive reaction system: \( A \to B \to C \). Figure 1.1 is a graph of the first order perturbation term \( \tau_1 \), and the ratio of the
FIG. 1.1 - SEMI-LOG PLOT OF $\tau_1$ AND $\tau_1/\tau_0$ VS. $\alpha$ FOR THE AXIAL DISPERSED TUBULAR REACTOR WITH SMALL DISPERSION
perturbation term to the zeroth order solution \( \frac{\tau_1}{\tau_0} \), vs the ratio of the reaction rate constants, \( \alpha \). For this reactor model, dispersion has a minimum effect on optimum length when \( \alpha \) is one, i.e. \( \tau_1 \) is minimum.

There is not much that can be said quantitatively about the range of parameters over which an asymptotic expansion is uniformly valid such that the error is of the order of the first truncated term. A given expansion must be compared with numerical results, if available, to obtain a quantitative estimate of its range of validity. If this is not possible, the best we can do is make sure that the orders of the various terms in the expansion are as initially assumed. For an expansion of the form \( \varphi = \varphi_0 + \varepsilon \varphi_1 + O(\varepsilon^2) \), where \( \varphi_0, \varphi_1 \) are assumed to be of order one and \( \varepsilon \) is much less than one, we suspect the validity of the expansion if \( \varepsilon \varphi_1 \) becomes of order one.

A quantitative criterion for the validity of a perturbation expansion solution might be that \( \varphi_0 \) and \( \varphi_1 \) are of the same order of magnitude and that \( \varepsilon \) is, at most, one order of magnitude less than the order of \( \varphi_0 \) and \( \varphi_1 \). A slightly more general criterion might be that \( \frac{\varepsilon \varphi_1}{\varphi_0} \) is not greater than \( O(\varepsilon) \). This criterion will be applied to expansion solutions where numerical results are available. It will be referred to as the ratio test. Tying the order relations to physical orders of magnitude is helpful for making judgments about the region of validity of the perturbation expansion solutions obtained in this work. We shall see that the ratio test appears to be
a conservative criterion when comparisons with numerical results are made.

The plot of $\frac{\tau_1}{\tau_0}$ in Fig. 1.1 shows that for $\alpha$ less than 3, and $\gamma$ up to about .2, the expansion for $\tau_{\text{optimum}}$ should be valid. As $\alpha$ gets larger, the upper limit on $\gamma$ will have to decrease to satisfy the ratio test. For $\alpha$ greater than 10 the results are probably not accurate to order $\gamma^2$.

The one numerical check obtained was for $\alpha = .1$ (see Fig. 4.2). The order of the error in $\tau_{\text{optimum}}$ is of the order of the first truncated term for $\gamma \leq 1$. The actual error is less than 10% for $\gamma$ less than .5, and less than 3% for $\gamma$ less than .2. Thus the ratio test for a valid representation leads to correct conclusions for the result of this model in the range of $\alpha = .1$.

b. General Reaction Kinetics

Perhaps the most valuable application of perturbation expansion techniques is in those cases in which the reaction kinetics are nonlinear.

Reaction: $\text{A} \rightarrow \text{B} + \text{C}$

General reaction rate expressions:

$$r_1 = r_1(\phi_A) \quad r_2 = r_2(\phi_B) \quad \text{(dimensionless)}$$

The reactions are irreversible. The system of equations to be solved is
Parish [11] presents the concentration profile results for the reaction \( A \rightarrow P \) with a general rate expression, \( r(\varphi_A) \). From the previous section we know that for the \( B \rightarrow C \) reaction a differential equation of the form \( \frac{d\varphi_B}{dx} = \alpha_2(\varphi_B) - r_1(\varphi_A) \) must be solved. Therefore, to obtain the expansion solution for the concentration profile in the reactor, the restriction that the reaction \( B \rightarrow C \) must be of first order is necessary.

Yet, to obtain an expression for the optimum residence time, we only need to consider the output concentrations at the end of the reactor. There is a possibility that a general formulation of the effect of dispersion on the optimum residence time can be made through an integral equation approach without solving the concentration profile problem. In that case there would be no restriction on the general rate expressions given above. However, this is beyond the scope of this work.
I-2. An Ideal Tubular Reactor with a Continuous Flow Stirred Tank Reactor (CFSTR) Bypass

Suppose the dispersion effect in a tubular reactor could be modeled by bypassing a small portion of the reacting fluid (representing a small dispersion) through a tube which has perfect mixing and the same residence time as the main reactor, followed by mixing the outputs of the reactor and the bypass reactor to get the yield of the system. This total bypass system is called a mixed model of non-ideal flow effects. To avoid confusion over the term "mixed" it will be called the bypass model.

In the above sketch of the system Reactor one is an ideal tubular reactor of length L based on the following assumptions:

- There are no sources of material within the system.
- The reacting mixture is treated as a single phase.
- The mixture is of constant density.
- The time average fluid velocity is constant across a cross-section and independent of axial position (plug flow).
- There is no variation of properties in the radial direction and there is radial symmetry.

1 - ideal tubular reactor
2 - continuous flow stirred tank reactor
\( \omega \) - volumetric flow rate
The system is at steady state. No dispersion or mixing takes place in the reactor.

Then the differential equation for the ith component mass balance is

\[
V \frac{dc_i}{dz} - r_{c_i} = 0 \quad (2.1)
\]

where \( r_{c_i} \) is the rate of formation of component \( i \) per unit volume.

B.C. at \( z = 0 \)

\[ c_i = c_{i_o} \]

The boundary conditions are simpler for this finite length reactor model because there is no dispersion.

Reactor two is the CFSTR model based on the following assumptions:

There are no sources of material within the system.
The reacting fluid is perfectly mixed and homogeneous.
The mixture is of constant density.
The system is at steady state.

Then the ith component mass balance is

\[
c_i = c_{i_o} + T \ c_i \quad (2.2)
\]

where \( T \) is the mean residence time.

A small fraction \( \varepsilon \) of the feed flow rate \( w \) is bypassed through the tank reactor whose mean residence time \( T \) is the same as the ideal tube residence time. The reason for total bypass is to make this a one parameter model of dispersion effects. The consecutive reaction \( A \rightarrow B \rightarrow C \) takes place with only component \( A \) in the feed stream. The system is isothermal.
a. **Linear Reaction Kinetics**

Reaction: \(A \rightarrow B \rightarrow C\)  
Let \(r_1 = k_1 c_A\)  
so \(r_A = -k_1 c_A\)  
\(r_2 = k_2 c_A\)  
\(r_B = k_1 c_A - k_2 c_B\).

The material balances for each component in the reactors:

**Reactor 1:**

\[ \frac{d c_A}{d z} + k_1 c_A = 0 \quad \text{B. C. at } z = 0 \quad c_A = c_{A_0} \]

\[ V \frac{d c_B}{d z} - k_1 c_A + k_2 c_B = 0 \quad \text{B. C. at } z = 0 \quad c_B = 0 \]

**Reactor 2:**

\[ c_A = c_{A_0} - T k_1 c_A \]

\[ c_B = T k_1 c_A - T k_2 c_B \]

The same dimensionless variables are used as in section 1.

\[ \varphi_A = \frac{c_A}{c_{A_0}} \quad \varphi_B = \frac{c_B}{c_{A_0}} \quad x = \frac{z k_1}{V} \quad \frac{L}{V} k_1 = T k_1 = \tau \quad \alpha = \frac{k_2}{k_1} \]

So for Reactor 1:

\[ \frac{d \varphi_A}{d x} + \varphi_A = 0 \quad (2.3a) \]

B. C. at \(x = 0\) \(\varphi_A = 1\)

\[ \frac{d \varphi_B}{d x} + \alpha \varphi_B = \varphi_A \quad (2.3b) \]

B. C. at \(x = 0\) \(\varphi_B = 0\)

for Reactor 2:

\[ \varphi_A = 1 - \tau \varphi_A \quad (2.3c) \]

\[ \varphi_B = 0 + \tau \varphi_A - \tau \varphi_B \quad (2.3d) \]
Then at $x = \tau$: (subscript refers to reactor number)

$$\varphi_{A_1} = e^{-\tau} \quad \quad \quad \quad \quad \varphi_{A_2} = \frac{1}{1 + \tau}$$

$$\varphi_{B_1} = \frac{1}{\alpha-1} [e^{-\tau} - e^{-\alpha\tau}] \quad \quad \quad \quad \quad \varphi_{B_2} = \frac{\tau}{(1+\tau)(1+\alpha\tau)}$$

We combine the streams from the two reactors to obtain the expression for the output concentration of B.

$$\varphi_B(\tau) = (1-\epsilon) \frac{1}{\alpha-1} (e^{-\tau} - e^{-\alpha\tau}) + \epsilon \frac{\tau}{(1+\tau)(1+\alpha\tau)} \quad (2.4)$$

This is an exact solution.

To find the optimum residence time for maximization of $B$ we take the derivative of Equation (2.4) with respect to $\tau$ and set it equal to zero. Note that $\epsilon$, $\omega$ are kept constant.

$$\frac{d\varphi_B}{d\tau} = (1-\epsilon) \frac{1}{\alpha-1} (-e^{-\tau} + \alpha e^{-\alpha\tau}) + \epsilon \frac{(1 - \alpha\tau^2)}{((1+\tau)(1+\alpha\tau))^2} = 0 \quad (2.5)$$

To get a perturbation expansion approximation for $\tau_{\text{opt}}$ let

$\tau = \tau_0 + \epsilon \tau_1 + \epsilon^2 \tau_2 + \ldots \ (\epsilon \ll 1)$, insert the expansion into (2.5) and solve the equations in like order in $\epsilon$ as before. The following approximations are used for small $\epsilon$:

$$e^{-(\tau_0 + \epsilon \tau_1)} \approx e^{-\tau_0} (1 - \epsilon \tau_1)$$

$$e^{-\alpha(\tau_0 + \epsilon \tau_1)} \approx e^{-\tau_0} (1 - \alpha \epsilon \tau_1)$$

$$\epsilon^0: \quad -e^{-\tau_0} + \alpha e^{-\alpha\tau_0} = 0$$

$$\tau_0 = \frac{1}{\alpha-1}$$

This is the result for no bypass flow (no dispersion effects).
Thus for $\varepsilon \ll 1$ we have the following relation for the optimum residence time to maximize the yield of $B$ from this bypass model.

$$
\tau_{\text{opt}} = \frac{1}{\alpha-1} \ln \alpha + \varepsilon \frac{(1/\alpha-1)(1-\alpha(\ln \alpha)^2)}{(1+\alpha \frac{\ln \alpha}{\alpha-1})^2} + 0(\varepsilon^2)
$$

Equation (2.6) is valid to order $\varepsilon$ for the following mode of model operation. As $\varepsilon$ is varied the dimensions of the reactors are adjusted to keep the residence times equal for both. Then Equation (2.6) gives the optimum residence time for the tube reactor and the bypass. If the sizes of the reactors were allowed to remain constant, a variation of $\varepsilon$ would cause a lowering of $\tau$ in one reactor and a corresponding increase of $\tau$ in the other. Over some regions of $\alpha$ $\tau_{\text{opt}}$ would be positive and over others negative making the result for the predicted optimum residence time more difficult to interpret.

A plot of the first order perturbation term $\tau_{\text{opt}}$ vs the ratio of the reaction rate constants $\alpha$ appears in Figure 2.1. The ratio of
FIG. 2.1.-SEMI-LOG PLOT OF $\tau_1$ VS. $\alpha$ FOR THE BYPASS REACTOR SYSTEMS WITH SMALL DISPERSION EFFECTS
FIG. 2.2 - SEMI-LOG PLOT OF $\tau_1 / \tau_0$ VS. $\alpha$ FOR THE BYPASS REACTOR SYSTEMS WITH SMALL DISPERSION EFFECTS
the first and the zeroth order terms as a function of the rate constants appears in Figure 2.2. In both figures, the curves for $\eta = 1$ are those for this total bypass reactor. In Figure 2.1 we see that for $\alpha$ greater than one, small dispersion appears to have a negligible effect on optimum residence time; but, $\tau_o$ is also small in this region as the ratio curve in Figure 2.2 shows. This implies that the first order perturbation term is not as insignificant as it appears in Figure 2.1. The ratio of $\frac{\tau_1}{\tau_o}$ indicates that the optimum residence time solution, Equation (2.6), should be valid in the range of $\alpha$ from .001 to 1000 for $\epsilon$ less than about .2.

Extensive numerical evaluations of the optimum residence time were made in connection with section 6. They show that the actual numerical error between the true solution and the asymptotic approximation, Equation (2.6), is less than $10\%$ for $\alpha$ between .005 and 100 and $\epsilon$ less than .4. The error is less than $1.5\%$ in the optimum residence time and less than $.001\%$ in the maximum yield concentration of B, when $\epsilon = .1$ and the range of $\alpha$ is .005 to 100. Again the ratio test presented in section 1 gives correct conclusions. It is even conservative for this model.

b. General Reaction Kinetics

In extending the results for the bypass model to general reaction rate expressions, the restriction of linear kinetics for the $B \rightarrow C$ reaction applies if the concentration problem is to be solved. The
optimum residence time expansion has been obtained using perturbation techniques under the above restriction. However, the result is not very meaningful until the actual rate expression \( r_1 \) is specified. As in the previous model, an integral equation formulation may make it possible to obtain the optimum residence time expansion directly, thus eliminating the restriction on the rate expressions.
I-3. An Ideal Tubular Reactor with a Small Zone of Perfect Mixing

The final small dispersion model to be considered is an ideal tubular reactor with a small region of infinite dispersion, i.e. complete mixing. Outside the dispersion zone the assumptions for the ideal tubular reactor are made. The system is isothermal. Again the consecutive reactions $A \rightarrow B \rightarrow C$ are irreversible and have first order kinetics.

We are interested in the effect of this form of dispersion on the optimum length of the reactor.

\[ \frac{r_1}{r_2} \]

\[ r_1 = k_1 c_A \]
\[ r_2 = k_2 c_B \]

The reactor is divided into three regions. Regions I and III are ideal tubular reactors of length $L_1$ and $L_2 - (L_1 + \Delta z)$ respectively. Region II is the zone of infinite dispersion which may be regarded as a CFSTR with mean residence time $\frac{\Delta z}{V}$. Pure component $A$ enters the reactor.

Introducing the following dimensionless variables in addition to those previously defined: \[ \frac{k_1 \Delta z}{V} = \delta, \tau_1 = \frac{k_1 L_1}{V}, \tau = \frac{k_1 L_2}{V} \],
the component balance equations for $A$ and $B$ in each reactor zone are
**Substance A**

**Region I:**

\[ \frac{d\varphi_A}{dx} + \varphi_A = 0 \]

B.C. at \( x = 0 \) \( \varphi_A = 1 \)

**Solutions:**

\[ \varphi_A(T_1) = e^{-T_1} \] (3.1a)

**Region II:**

\[ \varphi_A = \varphi_A(T_1) - \delta\varphi_A \]

**Solutions:**

\[ \varphi_{A\,I\,I}(T_1+\delta) = \frac{\varphi_A(T_1)}{1 + \delta} \] (3.2a)

**Region III:**

\[ \frac{d\varphi_A}{dx} + \varphi_A = 0 \]

B.C. at \( x = \tau_1 + \delta \)

\[ \varphi_A = \varphi_{A\,I\,I}(T_1+\delta) \]

from (3.2a)

**Solutions:**

\[ \varphi_{A\,I\,I}(\tau) = \varphi_{A\,I\,I}(T_1+\delta)e^{+(T_1+\delta)-\tau} \] (3.3a)

**Substance B**

**Region I:**

\[ \frac{d\varphi_B}{dx} + \alpha\varphi_B - \varphi_A = 0 \]

B.C. at \( x = 0 \) \( \varphi_B = 0 \)

**Solutions:**

\[ \tau_B(T_1) = \frac{1}{\alpha-1}(e^{-T_1}-e^{-\alpha T_1}) \] (3.1b)

**Region II:**

\[ \varphi_B = \varphi_B(T_1) + \delta\varphi_A(T_1+\delta) - \alpha\delta\varphi_B(T_1 + \delta) \]

**Solutions:**

\[ \varphi_{B\,I\,I}(T_1+\delta) = \frac{\varphi_B(T_1)}{1 + \alpha\delta} \]

\[ \frac{\delta}{1 + \delta}(1 + \delta) \] (3.2b)

**Region III:**

\[ \frac{d\varphi_B}{dx} + \alpha\varphi_B - \varphi_A = 0 \]

B.C. at \( x = \tau_1 + \delta \)

\[ \varphi_B = \varphi_{B\,I\,I}(T_1 + \delta) \]

from (3.2b)

**Solutions:**

\[ \varphi_{B\,I\,I}(\tau) = \varphi_{B\,I\,I}(T_1+\delta)e^{\alpha(T_1+\delta-\tau)} \]

\[ \frac{1}{\alpha-1} \varphi_{B\,I\,I}(T_1+\delta)[e^{+\tau_1+\delta-T} - e^{-(\tau_1+\delta-\tau)}] \] (3.3b)
Then the total solution for the output of the reactor is

$$\varphi_A(\tau) = \frac{e^{-(\tau-6)}}{1 + \delta}$$  \hspace{1cm} (3.4)

$$\varphi_B(\tau) = \frac{1}{\alpha-1} \left[ \frac{e^{\tau-6}}{1 + \delta} - \frac{e^{-\alpha(\tau-6)}}{1 + \alpha\delta} \right]$$  \hspace{1cm} (3.5)

Due to linear kinetics, Equations (3.4) & (3.5) are independent of \( \tau_1 \) as expected. To find the optimum residence time, take the derivative of \( \varphi_B(3.5) \) with respect to \( \tau \) and set it equal to zero.

$$\frac{\partial \varphi_B}{\partial \tau} = \frac{1}{\alpha-1} \left[ \frac{-1}{1 + \delta} e^{-(\tau-6)} + \frac{\alpha e^{-\alpha(\tau-6)}}{1 + \alpha\delta} \right] = 0$$

so

$$\ln(\alpha(1+\delta)/(1+\alpha\delta))$$

$$\tau_{opt} = \frac{\ln(\alpha(1+\delta)/(1+\alpha\delta))}{\alpha-1} + \delta$$  \hspace{1cm} (3.6)

This solution is exact. No perturbation expansion has been made.

To get this in the form \( \tau = \tau_0 + \\delta \tau_1 \) we do a power series expansion of the logarithmic term. Using the approximations:

$$\frac{1}{1+\alpha\delta} \approx (1 - \alpha\delta) \quad \therefore \quad \frac{(1+\delta)}{(1+\alpha\delta)} \approx \alpha(1+\delta)(1-\alpha\delta) = \alpha(1+\delta - \alpha\delta + 0(\delta^2))$$

Also

$$\ln(1+\delta) \approx \delta + 0(\delta^2)$$ \hspace{0.5cm} for \( \delta < 1 \)

so

$$\tau = \frac{\ln \alpha}{\alpha-1} + \frac{\ln(1+(1-\alpha)\delta)}{\alpha-1} + \delta + 0(\delta^2)$$

$$\tau_{opt} = \frac{\ln \alpha}{\alpha-1} + \left[ \frac{-(\alpha-1)}{\alpha-1} \delta + \delta \right] + 0(\delta^2)$$

We see that a small zone of infinite dispersion does not change the optimum residence time to order \( \delta \). This result implies that we can
replace a small portion of the tube by a mixed reactor and keep the same optimum length. This seems reasonable since if we look at the Equation (3.5) for \( \varphi_B \) and use approximate expansions for small \( \delta \), we get

\[
\varphi_B = \frac{1}{\alpha - 1} \left[ e^{-\tau \frac{(1+6)}{(1+\delta)}} - e^{-\alpha \tau \frac{(1+\alpha \delta)}{(1+\alpha \delta)}} \right] = \frac{1}{\alpha - 1} \left[ e^{-\tau} - e^{-\alpha \tau} \right] + 0(\delta^2)
\]

for \( \delta \ll \tau \)

which again shows no effect of the dispersion to order \( \delta \) on the output concentration of \( B \). Figure 3.1 is a graph of the exact solution (3.6) and shows where \( \delta \) becomes large enough to give a significant effect on the optimum residence time for various values of \( \alpha \).

The results of this model make sense physically because in the limit as \( \delta \) goes to zero the model approaches that of an ideal tube with complete radial mixing and plug flow. Thus the dispersion section for small \( \delta \) has the same properties in mixing and flow characteristics as does an ideal tube reactor. The above result was obtained in a different manner by Tsai [13] in his study of reactor recycle systems.
FIG. 3.1 - SEMI-LOG PLOT OF $\tau_{\text{OPTIMUM}}$ VS. $\delta$ FOR A TUBULAR REACTOR WITH A SMALL ZONE OF PERFECT MIXING
II. REACTOR MODELS WITH LARGE DISPERSION

II-4. The Axial Dispersed Plug Flow Tubular Reactor

Consider the case where the axial dispersion coefficient in the axial dispersed plug flow reactor model is infinite. In this case the reactor behaves as a continuous flow perfectly stirred tank reactor (CFSTR). We want to look at the case where the dispersion coefficient is almost infinite and find the effect of a small reduction from perfect fluid mixing. Again, the consecutive reactions \( A \to B \to C \) take place irreversibly and isothermally.

a. Linear Reaction Kinetics

Let the reaction rate expressions be linear:

\[
\begin{align*}
    r_1 &= k_1 c_A \\
    r_2 &= k_2 c_B
\end{align*}
\]

The system equations and boundary conditions can be written in dimensionless form directly from Equations (1.5a) and (1.5b).

\[
\begin{align*}
    \frac{d^2 \phi_A}{dx^2} - \frac{1}{\gamma} \frac{d\phi_A}{dx} - \frac{1}{\gamma} \phi_A &= 0 \\
    \text{B.C. at } x = 0 & \quad \frac{\phi_A}{\gamma} - \frac{d\phi_A}{dx} \bigg|_0 = \frac{1}{\gamma} \\
    \text{at } x = \tau & \quad \frac{d\phi_A}{dx} \bigg|_\tau = 0
\end{align*}
\]

\[
\begin{align*}
    \frac{d^2 \phi_B}{dx^2} - \frac{1}{\gamma} \frac{d\phi_B}{dx} - \alpha \frac{1}{\gamma} \phi_B &= -\frac{1}{\gamma} \phi_A \\
    \text{B.C. at } x = 0 & \quad \frac{\phi_B}{\gamma} - \frac{d\phi_B}{dx} \bigg|_0 = 0
\end{align*}
\]
at \( x = \tau \) \[ \frac{d\varphi_B}{dx}\bigg|_\tau = 0 \]

Here \( \frac{1}{\gamma} \) is the small parameter for the perturbation expansion. Assume the following solution form \( \varphi_1 = \varphi_{10} + \frac{1}{\gamma} \varphi_{11} + \frac{1}{\gamma^2} \varphi_{12} + O\left(\frac{1}{\gamma^3}\right) \) where \( \varphi_{10}, \varphi_{11}, \text{etc.} \) are \( O(1) \). This system is an ordinary perturbation expansion problem since the highest derivative does not disappear as \( \gamma \to \infty \). No problems are anticipated in satisfying all boundary conditions through a given order of \( \frac{1}{\gamma} \). Therefore, we proceed formally just as in the case of small dispersion. Let us insert the expansion into Equations (4.1a) and (4.1b) and collect terms of like order in \( \frac{1}{\gamma} \). Again we are using only two terms in the asymptotic expansion. Solving the Equations (4.1a) for \( \varphi_A \):

Terms of Order:

\[
\left( \frac{1}{\gamma} \right)^0: \quad \frac{d^2 \varphi_{A0}}{dx^2} = 0
\]

B. C. at \( x = 0 \) \[ \frac{d\varphi_{A0}}{dx}\bigg|_0 = 0 \]

at \( x = \tau \) \[ \frac{d\varphi_{A0}}{dx}\bigg|_\tau = 0 \]

Thus \( \varphi_{A0} = b_1 \) where \( b_1 \) is independent of \( x \). \( b_1 \) is the constant concentration of a perfectly stirred tank reactor.

\[
\left( \frac{1}{\gamma} \right)^1: \quad \frac{d^2 \varphi_{A1}}{dx^2} - \frac{d\varphi_{A0}}{dx} - \varphi_{A0} = 0
\]
or \[ \frac{d^2 \varphi_{A_1}}{dx^2} = b_1 \]

B. C. at \( x = 0 \)
\[ \varphi_{A_0} - \frac{d\varphi_{A_1}}{dx} \bigg|_0 = 1 \]

at \( x = \tau \)
\[ \frac{d\varphi_{A_1}}{dx} \bigg|_\tau = 0 \]

Thus \[ \varphi_{A_0} = \frac{1}{1+\tau} \quad \varphi_{A_1} = b_2 - \frac{\tau x}{1+\tau} + \frac{1}{1+\tau} \frac{x^2}{2} \] (4.2)

where \( b_2 \) is a constant.

A partial solution to the equations of order \( \left( \frac{1}{\gamma^2} \right) \) is necessary to evaluate the constant \( b_2 \) in Equation (4.2).

\[ \left( \frac{1}{\gamma} \right)^2: \quad \frac{d^2 \varphi_{A_2}}{dx^2} - \frac{d\varphi_{A_1}}{dx} - \varphi_{A_1} = 0 \]

or \[ \frac{d^2 \varphi_{A_2}}{dx^2} = \frac{1}{1+\tau} \left[ x - \tau \right] + b_2 - \frac{\tau}{1+\tau} x + \frac{1}{1+\tau} \frac{x^2}{2} \]

B. C. at \( x = 0 \)
\[ \varphi_{A_1} - \frac{d\varphi_{A_2}}{dx} \bigg|_0 = 0 \]

at \( x = \tau \)
\[ \frac{d\varphi_{A_2}}{dx} \bigg|_\tau = 0 \]

so
\[ b_2 = \frac{1}{(1+\tau)^2} \left[ \frac{\tau^3}{3} + \frac{\tau^2}{2} \right]. \]

Then the expansion for \( \varphi_A \) is

\[ \varphi_A(x) = \frac{1}{1+\tau} + \frac{1}{\gamma} \left[ \frac{\tau^2}{(1+\tau)^2} \left[ \frac{\tau}{3} + \frac{1}{2} \right] - \frac{\tau}{1+\tau} x + \frac{1}{1+\tau} \frac{x^2}{2} \right] + O\left( \frac{1}{\gamma^2} \right) \] (4.3)

At the reactor outlet
\[ \varphi_A(\tau) = \frac{1}{1+\tau} - \frac{1}{\gamma} \left[ \frac{\tau^3}{6(1+\tau)^2} \right] + O\left( \frac{1}{\gamma^2} \right) \] (4.4)
Similarly we can solve the second set (4.1b) for $\varphi_B$.

Let $\varphi_B = \varphi_{B_0} + \frac{1}{\gamma} \varphi_{B_1} + \frac{1}{\gamma} \varphi_{B_2} + \ldots$

Inserting this expansion and collecting terms of like order in $\frac{1}{\gamma}$.

Terms of Order:

\[
\left(\frac{1}{\gamma}\right)^0: \quad \frac{d^2 \varphi_{B_0}}{dx^2} = 0
\]

B. C. at $x = 0$  \quad $\frac{d \varphi_{B_0}}{dx} \bigg|_0 = 0$

at $x = \tau$  \quad $\frac{d \varphi_{B_0}}{dx} \bigg|_\tau = 0$

Thus $\varphi_{B_0} = d_1$ where $d_1$ is a constant. $d_1$ is the constant concentration of $B$ in a CFSTR.

\[
\left(\frac{1}{\gamma}\right)^1: \quad \frac{d^2 \varphi_{B_1}}{dx^2} - \frac{d \varphi_{B_0}}{dx} - \alpha \varphi_{B_0} = -\varphi_A
\]

or \[
\frac{d^2 \varphi_{B_1}}{dx^2} = \alpha \frac{d_1}{1+\tau} - \frac{1}{1+\tau} \frac{1}{\gamma}
\]

B.C. at $x = 0$  \quad $d_1 - \frac{d \varphi_{B_1}}{dx} \bigg|_0 = 0$

at $x = \tau$  \quad $\frac{d \varphi_{B_1}}{dx} \bigg|_\tau = 0$

Thus \[
\varphi_{B_0} = \frac{\tau}{(1+\tau)(1+\alpha \tau)} \varphi_B
\]

\[
\varphi_{B_1} = d_2 + \left[ \alpha \frac{\tau}{(1+\tau)(1+\alpha \tau)} - \frac{1}{(1+\tau)} \right] \frac{x^2}{2} + \frac{\tau}{(1+\tau)(1+\alpha \tau)} \frac{x}{(1+\tau)} \varphi_B
\]  \hspace{1cm} (4.5)

where $d_2$ is a constant.
Again we need to partially solve the equations of order \((\frac{1}{\gamma})^2\) to evaluate \(d_2\) in Equation (4.5).

\[
\left(\frac{1}{\gamma}\right)^2: \quad \frac{d^2\varphi_{B2}}{dx^2} - \frac{d\varphi_{B1}}{dx} - \alpha \varphi_{B1} = -\varphi_{A1}
\]

or

\[
\frac{d^2\varphi_{B2}}{dx^2} = \left[\frac{\alpha x}{(1+\tau)(1+\alpha \tau)} - \frac{1}{(1+\tau)} \right] x + \frac{\tau}{(1+\tau)(1+\alpha \tau)} + \alpha d_2
\]

\[
+ \alpha \left[\frac{\alpha x}{(1+\tau)(1+\alpha \tau)} - \frac{1}{(1+\tau)} \right] \frac{x^2}{2} + \frac{\alpha x}{(1+\tau)(1+\alpha \tau)}
\]

\[
- \left[\frac{\tau^2}{(1+\tau)} \left[\frac{1}{3} + \frac{1}{2}\right] - \frac{\tau}{1+\tau} x + \frac{1}{1+\tau} \frac{x^2}{2}\right]
\]

B. C. at \(x = 0\)

\[
d_2 - \frac{d\varphi_{B2}}{dx} \bigg|_0 = 0
\]

at \(x = \tau\)

\[
\frac{d\varphi_{B2}}{dx} \bigg|_\tau = 0
\]

From this

\[
d_2 = \frac{-\tau^2}{6(1+\tau)(1+\alpha \tau)^3} \left[2\tau(\alpha+1) + \alpha^2 + 3\right]
\]

Then

\[
\varphi_{B1} = \frac{1}{(1+\tau)(1+\alpha \tau)} \left[\tau x - \frac{x^2}{2} - \frac{\tau^2}{2} \frac{\alpha^2 + 2\tau(\alpha+1) + 3}{(1+\tau)(1+\alpha \tau)}\right]
\]

and the perturbation expansion for \(\varphi_B\) is

\[
\varphi_B(x) = \frac{\tau}{(1+\tau)(1+\alpha \tau)} + \frac{1}{\gamma} \left[\frac{1}{(1+\tau)(1+\alpha \tau)} \left[\tau x - \frac{x^2}{2}\right]
\]

\[
- \frac{\tau^2}{2} \frac{\alpha^2 + 2\tau(\alpha+1) + 3}{(1+\tau)(1+\alpha \tau)}\right] + o\left(\frac{1}{\gamma}\right)
\]
At the end of the reactor this becomes

$$\varphi_B(\tau) = \frac{\tau}{(1+\tau)(1+\alpha\tau)} + \frac{1}{\gamma} \left[ \frac{\tau^3}{6((1+\tau)(1+\alpha\tau))^2} \right] + 0 \left( \frac{1}{\gamma^2} \right) $$  \hspace{1cm} (4.8)

Note that the zeroth order term is the solution for a CFSTR.

To obtain the optimum residence time, we take the derivative of Equation (4.8) with respect to \( \tau \), and set it equal to zero.

$$\frac{d\varphi_B(\tau)}{d\tau} = \frac{1 - \tau^2}{((1+\tau)(1+\alpha\tau))^2} + \frac{1}{\gamma} \left[ \frac{\tau(1-\alpha^2\tau^2)}{(1+\tau)(1+\alpha\tau)^2} \right] \left[ \frac{\tau}{1+\tau} + \frac{\alpha\tau}{1+\alpha\tau} \right]$$

$$+ \frac{\tau}{(1+\tau)(1+\alpha\tau)} \left[ \frac{\tau}{1+\tau} + \frac{\alpha\tau}{1+\alpha\tau} \right] + \frac{\tau^2}{(1+\tau)(1+\alpha\tau)} \left[ \frac{\tau^2}{1+\tau} \right]$$

$$+ \frac{\alpha}{(1+\alpha\tau)^2} ] = 0 \hspace{1cm} (4.9)$$

Since we expect the reduction from infinite dispersion to have a slight effect on the optimum residence time for the maximum yield of B, we assume the following expansion for \( \tau_{opt} \).

$$\tau_{opt} = \tau_o + \frac{1}{\gamma} \tau_1 + \frac{1}{\gamma^2} \tau_2 + 0 \left( \frac{1}{\gamma^3} \right) \hspace{1cm} (4.10)$$

Let us insert this expansion into Equation (4.9). For the solution to be uniform in \( \frac{1}{\gamma} \), the equations involving terms in the various orders of \( \frac{1}{\gamma} \) must be identically satisfied.

**Terms of Order:**

$$\left( \frac{1}{\gamma} \right)^0: \quad \frac{1 - \alpha^2 \tau_o^2}{((1+\tau_o)(1+\alpha\tau_o))^2} = 0$$

$$\tau_o = \sqrt{\frac{1}{\alpha}} \hspace{1cm} (4.11)$$
Using Equation (4.11) for \( \tau_o \) gives

\[
\tau_1 = \frac{1}{12} \left[ \frac{\alpha^2 + 6\alpha \sqrt{\alpha} + 10\alpha + 6 \sqrt{\alpha} + 1}{2\alpha^2 + \alpha^2 \sqrt{\alpha} + \alpha \sqrt{\alpha}} \right]
\](4.12)

Note that Equation (4.12) is always positive since \( \alpha \) is always positive. The perturbation expansion solution for the optimum residence time is

\[
\tau_{\text{opt}} = \sqrt{\frac{1}{\alpha} + \frac{1}{12} \left[ \frac{\alpha^2 + 6\alpha \sqrt{\alpha} + 10\alpha + 6 \sqrt{\alpha} + 1}{2\alpha^2 + \alpha^2 \sqrt{\alpha} + \alpha \sqrt{\alpha}} \right]} + O\left(\frac{1}{\sqrt{\gamma}}\right)
\](4.13)

This is a curious result because it means that as the amount of dispersion is reduced from infinity, \( \frac{1}{\gamma} \) becomes larger and the optimum residence time increases since \( \tau_1 \) is always positive. Since the maximum obtainable output concentration of component B, decreases monotonically as the dispersion increases from zero to infinity, and since the optimum residence time necessary to achieve this maximum concentration is less for the reactor with no dispersion than for the perfectly mixed reactor, one would initially expect the optimum residence time to increase monotonically as the dispersion coefficient goes from zero to infinity. Yet, Equation (4.13) implies that the optimum residence time as a function of the dispersion coefficient must pass through a maximum value for some finite dispersion.

Furthermore, this result is not expected from consideration of the
physical nature of mixing, non-ideal flow patterns, and homogeneous chemical reactions. Our physical feeling for mixing effects leads us to expect a monotonic increase in maximum yield of $B$ and a monotonic decrease in the required optimum residence time with a decrease in dispersion for this consecutive reaction system.

To verify this result, the equations of the axial dispersed plug flow model (1.5 a and b) were solved analytically and the optimum residence time was evaluated numerically. Figure 4.2 is a curve of the optimum residence time vs. a function of the dispersion coefficient for $\alpha = .1$. This function $\frac{\gamma}{1+\gamma}$ compresses the range zero to infinity into the range zero to one. From this curve it is clear that the effect indicated by the perturbation expansion solutions actually does exist. The tangents at $\gamma = 0$ and $\gamma = \infty$ are the perturbation expansion solutions, Equations (1.17) and (4.13).

Kramers and Westerterp [9] have studied the same consecutive reaction system and presented a graph of the maximum yield of desired intermediate vs. optimum residence time for various values of the reaction rate constant ratio. The curves were obtained by numerical evaluation of the axial dispersion model. They are compared with the results of this work in Figure 4.3. It is clear that they did not get the maximum effect for the optimum residence time. Perhaps it is due to the fact that throughout the present work, $\gamma$ is kept constant and only the reactor length is varied to change the residence time.
Although it is not made clear in their publication it seems likely that Kramers and Westerterp kept the dimensionless coefficient \( \frac{2p}{VL} \) constant by allowing the average velocity to vary as the reactor length was varied. This might account for the difference in the curves of constant \( \alpha \) in Figure 4.3.

It should be kept in mind that these are predictions of the axial dispersed plug flow reactor model. Its applicability in the region of perfect mixing is open to question, even though its behavior approaches the correct limit as \( \gamma \) goes to infinity.

In the bypass model of large dispersion, this unusual effect is not present.

Figure 4.1 is a plot of \( T_1 \) and \( \frac{T_1}{T_0} \) vs. \( \alpha \). Using the ratio test that \( \frac{1}{\gamma} \frac{T_1}{T_0} \) should be \( O(1) \), we see that for \( \alpha \) greater than 0.1 the limit on the admissible values of \( \gamma \) decreases from \( \gamma \approx 10 \). This corresponds to a decreasing allowable dispersion coefficient. For \( \alpha \) less than 0.1 the lower limit on allowable \( \gamma \) increases, e.g. for \( \alpha = 0.01 \), \( \gamma \) must be greater than about 50 for a valid solution expansion.

Numerical results have been obtained for \( \alpha = 0.1 \) (see Fig. 4.2). It should be noted that the error in the optimum residence time expansion is always of order greater than \( \frac{1}{2} \). However, the percent error between the numerical solution and the asymptotic expansion is less than 5% for \( \gamma \) greater than 10. This is in agreement with the region of validity predicted by the ratio test.
FIG. 4.1 - LOG-LOG PLOT OF $\tau_i$ AND $\tau_i/\tau_0$ VS. $\alpha$ FOR THE AXIAL DISPERSED TUBULAR REACTOR WITH LARGE DISPERSION
FIG. 4.2 - AXIAL DISPERSED TUBULAR REACTOR OPTIMUM RESIDENCE TIME VS. \( \frac{\delta^*}{\delta^*+1} \) FOR \( \alpha = 0.1 \) WITH THE ASYMPTOTIC EXPANSIONS FOR SMALL AND LARGE DISPERSION. MAXIMUM AT \( \gamma = 4.5 \)
FIG. 4.3 - \( \varphi_b \) VS. \( \tau_{\text{optimum}} \) FOR VALUES OF \( \gamma \) AND \( \alpha \) FOR THE AXIAL DISPERSED PLUG FLOW TUBULAR REACTOR
b. General Reaction Kinetics

The axial dispersed tubular reactor can be solved for both the concentration profiles and the optimum residence time using perturbation expansion methods with general reaction rate expressions. For the same reaction, \( A \rightarrow B \rightarrow C \), the dimensionless rate expressions are given as

\[
\frac{d^2 \varphi_A}{dx^2} - \frac{1}{\gamma} \frac{d\varphi_A}{dx} - \frac{1}{\gamma} r_1(\varphi_A) = 0
\]

(4.14a)

Boundary Conditions (B.C.):

- at \( x = 0 \) \( \frac{1}{\gamma} \varphi_A(0) - \frac{d\varphi_A}{dx} \bigg|_0 = \frac{1}{\gamma} \)
- at \( x = \tau \) \( \frac{d\varphi_A}{dx} \bigg|_\tau = 0 \)

\[
\frac{d^2 \varphi_B}{dx^2} - \frac{1}{\gamma} \frac{d\varphi_B}{dx} - \frac{1}{\gamma} r_2(\varphi_B) + \frac{1}{\gamma} \cdot r_1(\varphi_A) = 0
\]

(4.14b)

B.C.:

- at \( x = 0 \) \( \frac{\varphi_B}{\gamma} - \frac{d\varphi_B}{dx} \bigg|_0 = 0 \)
- at \( x = \tau \) \( \frac{d\varphi_B}{dx} \bigg|_\tau = 0 \)

In this case, \( \frac{1}{\gamma} \) is the small parameter, so an expansion of the form

\[
\varphi = \varphi_0 + \frac{1}{\gamma} \varphi_1 + \frac{1}{\gamma^2} \varphi_2 + 0 \left( \frac{1}{\gamma^3} \right)
\]

is inserted into the Equations (4.14a) and (4.14b). We also expand \( r_1(\varphi_A) \) and \( r_2(\varphi_B) \) in Taylor series expansions about the point of infinite dispersion.

\[
r_1(\varphi_A) = r_1(\varphi_A^0) + \frac{\partial r_1}{\partial \varphi} \bigg|_{\varphi_A^0} \frac{1}{\gamma} \varphi_A^1 + 0 \left( \frac{1}{\gamma^2} \right)
\]

(4.15a)

\[
r_2(\varphi_B) = r_2(\varphi_B^0) + \frac{\partial r_2}{\partial \varphi} \bigg|_{\varphi_B^0} \frac{1}{\gamma} \varphi_B^1 + 0 \left( \frac{1}{\gamma^2} \right)
\]

(4.15b)
In the usual manner, the equations in the various orders of $\frac{1}{\gamma}$ are solved. First, system (4.14a) is solved for $\varphi_A(x)$.

Terms of order:

$$\left(\frac{1}{\gamma}\right)^0: \quad \frac{d^2\varphi_A}{dx^2} = 0$$

B.C.: at $x = 0$: $\frac{d\varphi_A}{dx}\bigg|_0 = 0$

at $x = \tau$: $\frac{d\varphi_A}{dx}\bigg|_{\tau} = 0$

Thus $\varphi_A = b_1$ where $b_1$ is independent of $x$. $b_1$ is the constant concentration of A in a perfectly stirred tank reactor.

$$\left(\frac{1}{\gamma}\right)^1: \quad \frac{d^2\varphi_A}{dx^2} - \frac{d\varphi_A}{dx} - r_1(\varphi_A) = 0$$

B.C.: at $x = 0$: $\varphi_A - \frac{d\varphi_A}{dx}\bigg|_0 = 1$

at $x = \tau$: $\frac{d\varphi_A}{dx}\bigg|_{\tau} = 0$

The solution is $\varphi_A = r_1(b_1)\frac{x^2}{2} + (b_1 - 1)x + b_2$ \hspace{1cm} (4.16)

From the boundary conditions, $b_1$ satisfies $r_1(b_1)\tau = 1 - b_1$ \hspace{1cm} (4.17)

To evaluate $b_2$ in Equation (4.16), the system of order $\frac{1}{\gamma}$ must be partially solved.

$$\left(\frac{1}{\gamma}\right)^2: \quad \frac{d^2\varphi_A}{dx^2} - \frac{d\varphi_A}{dx} - \frac{d\varphi_A}{dx} - \frac{\partial r_1}{\partial \varphi_A} \varphi_A \varphi_A = 0$$

B.C.: at $x = 0$: $\varphi_A - \frac{d\varphi_A}{dx} = 0$

at $x = \tau$: $\frac{d\varphi_A}{dx}\bigg|_{\tau} = 0$
The solution for \( \varphi_{A2} \) and the boundary conditions give

\[
b_2 = \frac{r_1(b_1)\tau^2}{6} \left[ \frac{2r_1'\tau + 3}{2r_1'\tau + 1} \right] \quad \text{where} \quad r_1' = \left[ \frac{\partial r_1}{\partial \varphi_A} \right]_{A_0}
\]

The perturbation expansion solution for \( \varphi_A \) is

\[
\varphi_A(x) = b_1 + \frac{1}{\gamma} \left[ r_1(b_1)\left(\frac{x^2}{2} - \tau x\right) + \frac{r_1(b_1)\tau^2}{6} \left( \frac{2r_1'(b_1)\tau + 3}{r_1'(b_1)\tau + 1} \right) \right] + \left( \frac{1}{\gamma^2} \right)
\]

(4.18)

At the reactor exit

\[
\varphi_A(\tau) = b_1 + \frac{1}{\gamma} \left[ -\tau^3 \frac{r_1(b_1)b_1}{6r_1'(b_1)\tau + 1} \right] + \left( \frac{1}{\gamma^2} \right) \quad (4.19)
\]

where \( b_1 \) satisfies Equation (4.17).

Now Equations (4.14b) can be solved in exactly the same fashion using a perturbation expansion and the expansion for \( r_2 \) (4.15b).

**Terms of Order:**

\[
\left( \frac{1}{\gamma} \right)^0: \quad \frac{d^2 \varphi_B}{dx^2} = 0
\]

**B.C.:** at \( x = 0 \) \( \frac{d\varphi_B}{dx} \bigg|_0 = 0 \)

at \( x = \tau \) \( \frac{d\varphi_B}{dx} \bigg|_\tau = 0 \)

Then \( \varphi_B = d_1 \) where \( d_1 \) is independent of \( x \). \( d_1 \) is the constant concentration of \( B \) in a CFSTR.

\[
\left( \frac{1}{\gamma} \right)^1: \quad \frac{d^2 \varphi_B}{dx^2} - \frac{d\varphi_B}{dx} - \alpha r_2(\varphi_B) + r_1(\varphi_A) = 0
\]

**B.C.:** at \( x = 0 \) \( \varphi_B \bigg|_0 = 0 \)
\[
\begin{align*}
\text{at } x = \tau & \quad \frac{dq_{B_1}}{dx} \bigg|_{\tau} = 0 \\
\int dcp & = \frac{x^2}{2} + d_1 x + d_2 \\
\text{The solution is } q_{B_1} &= (\alpha r_2(d_1) - r_1(b_1)) \frac{x^2}{2} + d_1 x + d_2 \quad (4.20)
\end{align*}
\]
The reactor output concentration expansion is

\[ \varphi_B(\tau) = d_1 + \frac{1}{\gamma} \left[ \frac{3\tau^3}{6(\alpha r_{12}^3(\gamma+1))} \left( (r_1(b_1') - \alpha r_2(b_1)) \alpha r_2^1(d_1) + \frac{r_1^i(b_1')r_1(b_1)}{r_1^i(b_1')^2 + r_1(b_1')} \right) \right] + o \left( \frac{1}{\gamma} \right) \]

(4.23)

where \( d_1 \) satisfies Equation (4.21) and \( b_1 \) satisfies Equation (4.17)

To determine the optimum residence time for the maximum yield of B, \( \varphi_B(\tau) \) must be stationary with respect to \( \tau \).

(All \( r_i = r_i(\varphi_i) \) below)

\[ \frac{d\varphi_B(\tau)}{d\tau} = \frac{d}{d\tau} \left( d_1 + \frac{1}{\gamma} \left[ \frac{3\tau^3}{6(\alpha r_{12}^3(\gamma+1))} \left( (r_1(b_1') - \alpha r_2(b_1)) \alpha r_2^1(d_1) + \frac{r_1^i(b_1')r_1(b_1)}{r_1^i(b_1')^2 + r_1(b_1')} \right) \right] + o \left( \frac{1}{\gamma} \right) \right) \]

\[ = \frac{d}{d\tau} \left( d_1 \right) + \frac{1}{\gamma} \left[ \frac{3\tau^3}{6(\alpha r_{12}^3(\gamma+1))} \left( \frac{dr_1^i}{d\tau} - \alpha \frac{dr_2^i}{d\tau} \alpha r_2^1 + \frac{r_1^i r_1}{r_1^i + 1} \right) \right] + o \left( \frac{1}{\gamma} \right) \]

\[ + \frac{1}{r_1^i + 1} \left( \frac{dr_1^i}{d\tau} r_1 + \frac{dr_1}{d\tau} r_1' \right) - \frac{dr_1^i}{d\tau} \left( \frac{r_1^i r_1}{r_1^i + 1} \right) \]

(4.24)

To evaluate \( \frac{d}{d\tau} d_1 \) and \( \frac{d}{d\tau} b_1 \) we implicitly differentiate Equations (4.17) and (4.21). Note that:

\[ \frac{dr_1}{d\tau} = \frac{dr_1}{d\varphi} \varphi_A^o \frac{d\varphi}{d\tau} = r_1' \frac{d}{d\tau} \]

\[ \frac{dr_2}{d\tau} = \frac{r_2' \frac{d}{d\tau}}{d\tau} \]

\[ \frac{dr_1'}{d\tau} = \frac{r_1'' \frac{d}{d\tau}}{d\tau} \]

\[ \frac{dr_2'}{d\tau} = \frac{r_2'' \frac{d}{d\tau}}{d\tau} \]
\[
\frac{db_1}{d\tau} = \frac{-r_1(b_1)}{1 + r_1'(b_1)\tau} \tag{4.25a}
\]

\[
\frac{dd_1}{d\tau} = \frac{r_1(b_1) - \alpha r_2(d_1)}{(1 + \alpha r_2'(d_1)\tau)} - \frac{r_1(b_1) r_1'(b_1)\tau}{(1 + \alpha r_2'(d_1)\tau)(1 + r_1'(b_1)\tau)} \tag{4.25b}
\]

We expect a small change in optimum residence time due to the small reduction in dispersion. Letting \( \tau = \tau_o + \frac{1}{V} \tau_1 + O\left(\frac{1}{V^2}\right) \), inserting into Equation (4.24), and using Equations (4.25a) and (4.25b), we collect terms of like order in \( \frac{1}{V} \).

**Terms of Order:**

\[
\left(\frac{1}{V}\right)^0: \quad \frac{r_1 - \alpha r_2}{1 + \alpha r_2'\tau_o} - \frac{r_1 r_1'^\tau_o}{(1 + r_1'^\tau_o)(1 + \alpha r_2'\tau_o)} = 0 \quad \text{i.e.} \quad \left. \frac{d d_1}{d\tau} \right|_{\tau_o} = 0 \tag{4.26}
\]

\[
\tau_o = \frac{r_1(b_1) - \alpha r_2(d_1)}{\alpha r_2'(d_1) r_1'(b_1)} \tag{4.27}
\]

This is an implicit equation for \( \tau_o \).

The first order perturbation term has been obtained for general reaction kinetics. However, until actual kinetic rate expressions are specified, it does not give any criterion as to whether the optimum length increases or decreases as the dispersion parameter is reduced from infinity. Evaluation of the general result for a nonlinear reaction system involves extensive computer work which is beyond the scope of this research.
II-5. A Continuous Flow Stirred Tank Reactor with an Ideal Tubular Reactor Bypass

In this model imperfect fluid mixing is represented by withdrawing a small fraction of the feed stream to a perfectly mixed tank reactor and passing it through an ideal tubular reactor with no mixing or dispersion effects. The outputs of the perfectly mixed tank reactor and the ideal tube bypass are then joined to form the output stream of the system. The residence times of both reactors are kept equal. This is just the inverse of the small dispersion model of section 2.

Again the consecutive reaction, \( A \rightarrow B \rightarrow C \), takes place irreversibly and isothermally. Only pure \( A \) is in the feed stream. We are interested in optimizing the residence time for the maximum yield of \( B \).

\[ r_1 = k_1 c_A \]
\[ r_2 = k_2 c_B \]

From the Equations (2.3a,b,c,d) for the previous bypass model the equations for Reactor 1 and Reactor 2 can be written directly in dimensionless form.
Reactor 1:

\[ \varphi_A = 1 - \tau \varphi_A \]  
\[ \varphi_B = 0 + \tau \varphi_A - \tau \varphi_B \]  

Then at \( x = \tau \) (subscript refers to reactor number)

\[ \varphi_{A_1} = \frac{1}{1+\tau} \]  
\[ \varphi_{B_1} = \frac{\tau}{(1+\tau)(1+\alpha\tau)} \]

Reactor 2:

\[ \frac{d\varphi_A}{dx} + \varphi_A = 0 \]  
(5.1c)

B.C.: at \( x = 0 \) \( \varphi_A = 1 \)

\[ \frac{d\varphi_B}{dx} + \alpha \varphi_B = \varphi_A \]  
(5.1d)

B.C.: at \( x = 0 \) \( \varphi_B = 0 \)

Then at \( x = \tau \)

\[ \varphi_{A_2} = e^{-\tau} \]  
\[ \varphi_{B_2} = \frac{1}{\alpha-1} (e^{-\tau} - e^{-\alpha\tau}) \]

Combining the two reactor output streams, we obtain the output concentration of \( B \).

\[ \varphi_B(\tau) = (1-\varepsilon) \frac{\tau}{(1+\tau)(1+\alpha\tau)} + \frac{\varepsilon}{\alpha-1} (e^{-\tau} - e^{-\alpha\tau}) \]
(5.2)

This is an exact solution.
For the optimum residence time expansion, the derivative of Equation (5.2) with respect to \( \tau \) is set equal to zero. \( e \) and \( \omega \) are kept constant.

\[
\frac{d\alpha_B}{d\tau} = (1-e)\left(\frac{1 - \alpha\tau^2}{(1+\tau)(1+\alpha\tau^2)}\right)^2 + \frac{e}{\alpha-1} (-e^{-\tau} + \alpha e^{-\alpha\tau}) = 0 \quad (5.3)
\]

As before, let \( \tau = \tau_0 + e\tau_1 + e^2\tau_2 + \ldots \) (\( e \ll 1 \)) and insert the expansion into Equation (5.3) and solve the equations of like order in \( e \).

**Terms of Order:**

\( e^0 \):  
\[
\frac{1 - \alpha\tau_0^2}{((1+\tau_0)(1+\alpha\tau_0))^2} = 0
\]

\( \tau_0 = \sqrt[\alpha]{\frac{1}{\alpha}} \)  
This is the result for a CFSTR.

\( e^1 \):  
\[
-1(1 - \alpha\tau_0^2) - 2\alpha \tau_0 \tau_1 + \frac{(1+\tau_0)^2(1+\alpha\tau_0)^2}{\alpha-1} (\alpha e^{-\alpha\tau_0} - e^{-\tau_0}) = 0
\]

\[
\tau_1 = -\frac{1}{2\sqrt[\alpha]{\alpha-1}} \left(e^{-1/\sqrt[\alpha]{\alpha}} - \alpha e^{-\sqrt[\alpha]{\alpha}}\right)(6 + 4\frac{1}{\sqrt[\alpha]{\alpha}} + \sqrt[\alpha]{\alpha}) + \frac{1}{\alpha} + \alpha)
\]

Thus the asymptotic expansion for the optimum residence time is

\[
\tau_{opt} = \frac{1}{\sqrt[\alpha]{\alpha}} + e \left(\frac{\alpha e^{-\sqrt[\alpha]{\alpha}} - e^{-1/\sqrt[\alpha]{\alpha}}}{2\sqrt[\alpha]{\alpha} (\alpha-1)}\right)(6 + 4\left(\frac{1}{\sqrt[\alpha]{\alpha}} + \sqrt[\alpha]{\alpha}\right) + \frac{1}{\alpha} + \alpha) + 0(e^2)
\]  

Equation (5.4) gives the optimum residence time for the maximum yield of \( B \) from this bypass model of large dispersion effects. As \( e \) is varied, the dimensions of the two reactors are adjusted to keep the residence times equal. In Figure 5.1 is a plot of the first order perturbation term \( \tau_1 \) vs the reaction rate constant ratio \( \alpha \). It is
FIG. 5.1 - SEMI-LOG PLOT OF $\tau_1$ AND $\tau_1/\tau_0$ VS. $\alpha$ FOR THE TOTAL BYPASS REACTOR WITH VERY LARGE DISPERSION EFFECTS
approximately the negative of the small dispersion bypass model in section 2. For $\alpha$ greater than one the effect of a reduction in mixing is small. For $\alpha$ much less than one the effect of an increased bypass through the ideal tube reactor is very great.

Since the first order perturbation term is always negative, the optimum residence time for the bypass type of model decreases monotonically as the fluid flow pattern is changed continuously from perfect mixing to plug flow with no mixing. This is in agreement with our physical feeling for the mixing process and our expectation of a monotonic transition of the component concentrations and optimum residence time.

It should be noted that fluid mixing takes place in this model on a macro scale whereas mixing in the axial dispersed model is micro-mixing. Thus the fact that the optimum residence time changes in the opposite direction to that of the axial dispersion model as the dispersion parameter is reduced from infinity is not a direct contradiction of the axial dispersion model results.

b. General Reaction Kinetics

In order to be able to solve the concentration problem for the ideal tube reactor, the familiar restriction of linear kinetics for the $B \rightarrow C$ reaction applies to this reactor system. The bypass model of large dispersion with general rate expressions has been solved under this restriction for the optimum residence time perturbation expansion solution. However, the result does not give any meaningful information until the
actual reaction rate expression $r_1$ is specified. Therefore, the conclusions with regard to general rate expressions for the small dispersion bypass model apply directly to the inverse model.
III. USE OF THE AXIAL DISPERSED PLUG FLOW REACTOR TO PREDICT OPTIMUM RESIDENCE TIMES FOR OTHER REACTOR MODELS IN THE SMALL DISPERSION REGION.

We would like to know if the axial dispersed reactor can be used to predict the optimum residence time for other reactor models and hopefully actual reactors. A possible application would be the use of this simple model in some type of adaptive reactor control system. We shall restrict our attention to the range of small dispersion so the asymptotic expansions obtained in part I can be used. Only the consecutive reaction system $A \rightarrow B \rightarrow C$ with linear kinetic rate expressions will be considered.

III-6. **Modeling the Total Bypass Reactor**

Suppose the small dispersion effects in a tubular reactor were due to a fluid channeling and mixing phenomenon that could be represented by the total bypass reactor of section 2. We can characterize these dispersion effects by a constant dispersion coefficient in the axial dispersed tubular reactor model. The next step is to determine how well the expression for the optimum residence time for the axial dispersion model predicts the correct optimum residence time for the bypass reactor.

One of the ways to measure dispersion effects in a reactor is to send a pulse of inert tracer material through the reactor and measure the residence time distribution. The residence time distribution $\xi(t)$ is defined as the amount of tracer per unit time leaving the system at time $t$, after an impulse of a unit amount of tracer is injected at time $t = 0$. 
In other words, $\Phi(t)\,dt$ is the amount of tracer that left the system between the time $t$ and the time $t + dt$ after the injection. One way to obtain $\Phi(t)$ is to measure the output concentration of tracer after a delta function unit input of tracer. For a complete discussion of residence time distributions and non-ideal flow, see Levinspiel [10].

The emerging concentration distribution can be characterized by its moments about the origin, $t = 0$, and about the centroid of the distribution. An infinite number of moments completely defines the distribution.

The objective here is to model the bypass reactor system with the dispersed plug flow reactor. We will do this by making the residence time distribution functions for the two systems as nearly alike as possible. If we could make all moments equal for the two reactors this would mean an exact matching of both residence times and dispersion effects. However, the dispersed plug flow reactor with no reactions is a two parameter model -- the two parameters being residence time $T$ and dispersion coefficient $D$. Thus only two moments can be equal. The ones selected are the first moment about the origin, i.e. the mean or centroid, which gives the average residence time $T$, and the second moment about the centroid often called the variance, which measures the relative width of the spread in the pulse of inert tracer material.

The defining expressions are

First Moment:

$$
\mu = \frac{\int_0^\infty t f(t) \, dt}{\int_0^\infty f(t) \, dt} \quad (6.1)
$$

Second Moment:

$$
\sigma^2 = \frac{\int_0^\infty (t-\mu)^2 f(t) \, dt}{\int_0^\infty f(t) \, dt} \quad (6.2)
$$
To obtain the residence time distribution for the tube with tank bypass, we need to solve the unsteady state material balance on the tracer. Since the model is linear, the two parts can be solved separately, then combined for the residence time distribution function.

The input is a delta function.

The residence time distribution is related to concentration by

$\dot{\phi} = wc(t)|_{\text{system exit}} \quad \dot{\phi} \text{ has units of } \frac{1}{\text{time}}$

In Tube 1:

$\frac{\partial c}{\partial t} + V \frac{\partial c}{\partial x} = 0 \quad T = \frac{L}{V}$

B.C.:

at $t = 0 \quad c(0,x) = 0$

at $x = 0 \quad c(t,0) = \delta(t)/w$

then $c(x,t) = \delta(t - x/V)/w$

$c(L,t) = \delta(t-T)/w$

$\dot{\phi}_1 = \delta(t-T)$

where $\delta$ is the impulse or delta function.

Therefore, for the bypass reactor:

$\dot{\phi}_b(t) = (1-\epsilon)\delta(t-T) + \epsilon \frac{1}{T} e^{-t/T}$ \hspace{1cm} (6.3)

Using the definitions (6.1) and (6.2) for the moments, we get:

$\mu_b = \frac{\int_0^\infty t \dot{\phi}_b(t) \, dt}{\int_0^\infty \dot{\phi}_b(t) \, dt} = T \quad (6.4)$

and

$\sigma_b^2 = \frac{\int_0^\infty (t-T)^2 \dot{\phi}_b(t) \, dt}{\int_0^\infty \dot{\phi}_b(t) \, dt} = \epsilon T^2 \quad (6.5)$

The subscripts indicate: $b$- bypass reactor $t$- axial dispersed reactor
A sketch of $\dot{\xi}_b(t)$ appears below.

To get the desired moments for the dispersed plug flow tubular reactor we do not have to solve the concentration problem. This is due to a property of the Laplace transform by which differentiation with respect to time in function space corresponds to multiplication by $s$, the transform variable, in transform space, and vice versa.

Define the Laplace transform of $c(x,t)$ by

$$c(x,s) = \int_0^\infty e^{-st} c(x,t) \, dt \quad (6.6)$$

From Equations (6.6), (6.1), (6.2) the following relation can be derived:

$$- \frac{\omega d c(x,s)}{ds} \bigg|_{x=L} = \int_0^\infty w e^{-st} c(x,t) \, dt$$

then in the limit as $s \to 0$

we get:

$$\int_0^\infty t \omega c(L,t) \, dt = \int_0^\infty t \dot{\psi}(t) \, dt$$

$$\frac{\omega c(L,t)}{L} = \mu \quad (6.7)$$

Similarly for $\sigma^2$ consider the following expressions:

$$\frac{\omega d^2 c}{ds^2} \bigg|_L - \left( \frac{dwc}{ds} \right)^2$$

then in the limit as $s \to 0$

we get:
Thus all we need to do is obtain the transform of the tracer concentration, take various derivatives with respect to \( s \), and evaluate them at the end of the reactor as \( s \to 0 \).

The unsteady state equations for the dispersed tubular model subjected to a delta function input of inert tracer are:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - V \frac{\partial c}{\partial z} \quad \text{where} \quad L - \text{length of tube} \tag{6.9}
\]

B.C. at \( z = 0 \) \( Vc - D \frac{\partial c}{\partial z} \bigg|_0 = V\delta(t) \) \( V - \text{Velocity (average or plug flow)} \)

at \( z = L \) \( \frac{\partial c}{\partial z} \bigg|_L = 0 \) \( D - \text{Dispersion coefficient} \)

at \( t = 0 \) \( c(0,z) = 0 \)

We take a Laplace transform in time of Equation (6.9).

Let \( \mathcal{L}\{c(z,t)\} = \overline{c}(z,s) = \int_0^\infty e^{-st} c(z,t) \, dt \)

Then \( \mathcal{L}\{\overline{c} \} - 0 = D \frac{\partial^2 \overline{c}}{\partial z^2} - V \frac{\partial \overline{c}}{\partial z} \) or \( \mathcal{L}\{\overline{c} \} - 0 = D \frac{\partial^2 \overline{c}}{\partial z^2} - V \frac{\partial \overline{c}}{\partial z} - \overline{c} = 0 \) \tag{6.10}

B. C. at \( z = 0 \) \( V\overline{c} - D \frac{\partial \overline{c}}{\partial z} \bigg|_0 = V \)

at \( z = L \) \( \frac{\partial \overline{c}}{\partial z} \bigg|_L = 0 \)

These equations,(6.10), look like the dimensional form of the Equations (1.4a) for the reaction of A in the tube. We have already obtained a perturbation expansion solution for small D. Letting \( k_1 \) become \( s \) and
The solution is (from Equation (1.9))

\[
\bar{c}(z,s) = e^{-sz/V} + \frac{sd}{v^2} \left( \frac{sz}{v} - e^{-sz/V} \right) + \frac{sd}{v^2} e^{-sL/V}
\]

\[
+ O\left(\frac{(sd)^2}{v^2}\right)
\]

then

\[
\bar{c}(L,s) = e^{-sL/V} + \frac{sd}{v^2} \left( \frac{sl}{v} - 1 \right)e^{-sL/V} + \frac{sd}{v^2} e^{-sL/V} - 0\left(\frac{(sd)^2}{v^2}\right)
\]

As \(s\) goes to 0, \(\bar{c}(L,s)\) approaches 1.

\[
\frac{\partial c}{\partial s}\bigg|_L = -\frac{L}{V} e^{-sL/V} + \frac{D}{v^2} \left( \frac{sl}{v} - 1 \right)e^{-sL/V} + \frac{sd}{v^2} e^{-sL/V} - \frac{sd}{v^2} \left( \frac{sl}{v} - 1 \right)e^{-sL/V} + 0(\gamma^2)
\]

As \(s\) goes to 0; \(\frac{\partial c}{\partial s}\bigg|_L = -\frac{L}{V} + \frac{D}{v^2} \cdot 0 = -T
\]

From Equation (6.7)

\[
\mu_t = T_t + 0(\gamma^2)
\]

(6.11)

Now

\[
\frac{\partial^2 c}{\partial s^2}\bigg|_L = \frac{L^2}{v^2} e^{-sL/V} + \frac{D}{v^2} \left( \frac{L}{v} \right)e^{-sL/V} - \frac{D}{v^2} \left( \frac{sl}{v} - 1 \right)e^{-sL/V} - \frac{L}{V}
\]

\[
+ \frac{D}{v^2} \frac{L}{v} e^{-sL/V} + \frac{sd}{v^2} e^{-sL/V} - \frac{sd}{v^2} \left( \frac{L}{v} \right)e^{-sL/V} - \frac{sd}{v^2} \left( \frac{sl}{v} - 1 \right)e^{-sL/V}
\]

\[
- \frac{sd}{v^2} \left( \frac{L}{v} \right)e^{-sL/V} - \frac{sd}{v^2} \left( \frac{sl}{v} - 1 \right)e^{-sL/V} - \frac{D}{v^2} \left( \frac{2L}{v} \right) e^{-sL/V}
\]

\[
+ \frac{sd}{v^2} \left( \frac{L}{v} \right)^2 e^{-sL/V} + 0(\gamma^2)
\]
As \( s \) goes to 0; \( \frac{\partial^2 c}{\partial s^2} \) \( \rightarrow \frac{L^2}{V^2} + \frac{2DL}{V^3} \).

From Equation (6.8)

\[
\sigma_t^2 = T^2 + \frac{2D}{V^2} - \frac{T}{V} = \frac{2D}{VL} T^2 + O(\gamma^2)
\]  

(6.12)

A summary of results:

<table>
<thead>
<tr>
<th>Bypass Reactor System</th>
<th>Axial Dispersed Tubular Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu = T_b )</td>
<td>( \mu = T_t )</td>
</tr>
<tr>
<td>( \sigma_b^2 = c T_b^2 )</td>
<td>( \sigma^2 = \frac{2D}{VL} T_t^2 )</td>
</tr>
</tbody>
</table>

\( T_t \) - residence time, axial dispersed tube

\( T_b \) - residence time, bypass system

Therefore, to model the bypass reactor with an axial dispersed tube, we require that \( \mu_b = \mu_t \) and \( \sigma_b^2 = \sigma_t^2 \). This implies \( T_t = T_b \) (equal residence times) and \( \epsilon = \frac{2D}{VL} \). To put this into dimensionless form, let: \( \frac{L}{V} = T \), \( k_1T = \tau \) a dimensionless residence time, and \( \gamma = \frac{Dk_1}{V^2} \) as before.

From \( \epsilon = \frac{2D}{\gamma \frac{L}{V}} \) we have \( \tau \epsilon = 2\gamma \)  

(6.13)

The equation for optimum residence time for the dispersed plug flow reactor is

\[
\tau_{opt} = \frac{1}{\alpha-1} + \gamma \left( \frac{1}{\alpha-1} \right) + O(\gamma^2) = \tau_o + \gamma \tau_1 + O(\gamma^2)
\]  

(1.17)

Solving Equations (6.13) and (1.17) simultaneously gives the predicted optimum residence time.
\[ \tau_{\text{opt}} = \frac{\tau_0}{1 - e^{r_1}} \]

\[ = \frac{\ln \alpha}{\alpha - 1} \left( 1 - \frac{e^{r_1}}{2(\alpha - 1)(\alpha + 1) - 1} \right) \tag{6.14} \]

For a given \( \alpha \) it is easy to determine the range of \( e \) for which Equation (6.14) has a solution. From the graph of the two equations we see that if the slope of Equation (6.13) is less than or equal to the slope of (1.17) there will be no solution \( \tau_{\text{opt}} \) which is physically reasonable, i.e. positive or zero.

For a valid solution \( \frac{2}{\tau_1} > 1 \) where \( \tau_1 = \frac{\ln \alpha}{\alpha - 1(\alpha + 1) - 1} \tag{6.15} \)

A plot of Equation (6.15) showing the admissible range of \( e \) appears in Fig. 6.1. Note that \( e \leq 1 \) since \( e \) is the fraction of flow that goes through the bypass reactor. It is clear that over a wide range of the reaction rate constant ratio, all the reasonable values of \( e \) for small dispersion effects are included in the admissible region.

Sample numerical results of this modeling of a total bypass reactor with an axial dispersed plug flow reactor and prediction of the optimum residence time are given in Table 6.1. Only \( e = .1 \) is used. We expect the results for smaller \( e \) to be at least as accurate.
FIG. 6.1 - ADMISSIBLE $\varepsilon$ VS. $\alpha$ FOR A VALID MODELING OF THE TOTAL BYPASS REACTOR BY THE AXIAL DISPERSED PLUG FLOW REACTOR
<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\tau_{\text{optimum}}$ (numerical search)</th>
<th>$\tau_{\text{Predicted optimum}}$</th>
<th>Percent error</th>
<th>$\phi_B$ Maximum</th>
<th>$\phi_B$ Using Predicted optimum</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$100$</td>
<td>$.04913$</td>
<td>$.05707$</td>
<td>$16$</td>
<td>$.00938$</td>
<td>$.00936$</td>
<td>$.20$</td>
</tr>
<tr>
<td>$10$</td>
<td>$.2582$</td>
<td>$.2813$</td>
<td>$8.9$</td>
<td>$.0754$</td>
<td>$.0752$</td>
<td>$.23$</td>
</tr>
<tr>
<td>$5$</td>
<td>$.4040$</td>
<td>$.4329$</td>
<td>$7.2$</td>
<td>$.1300$</td>
<td>$.1300$</td>
<td>$0$</td>
</tr>
<tr>
<td>$1$</td>
<td>$1.000$</td>
<td>$1.052$</td>
<td>$5.3$</td>
<td>$.3574$</td>
<td>$.3574$</td>
<td>$0$</td>
</tr>
<tr>
<td>$.1$</td>
<td>$2.582$</td>
<td>$2.813$</td>
<td>$8.9$</td>
<td>$.7541$</td>
<td>$.7523$</td>
<td>$.23$</td>
</tr>
<tr>
<td>$.05$</td>
<td>$3.207$</td>
<td>$3.565$</td>
<td>$11$</td>
<td>$.8344$</td>
<td>$.8322$</td>
<td>$.26$</td>
</tr>
<tr>
<td>$.01$</td>
<td>$4.913$</td>
<td>$5.707$</td>
<td>$16$</td>
<td>$.9380$</td>
<td>$.9361$</td>
<td>$.20$</td>
</tr>
<tr>
<td>$.005$</td>
<td>$5.813$</td>
<td>$6.805$</td>
<td>$17$</td>
<td>$.9588$</td>
<td>$.9576$</td>
<td>$.13$</td>
</tr>
</tbody>
</table>
From Table 6.1 several observations can be made:

(1) The error between the numerical and the predicted optimum residence time is a minimum, 5%, at \( \alpha = 1 \) and is symmetric about this value of \( \alpha \). This is reasonable from the symmetry of \( \tau_1 \) vs \( \alpha \) in Figure 1.1.

(2) The maximum error in the range of \( \alpha \) from .005 to 100 is 17%.

(3) The error between the yield concentrations of desired intermediate B using the numerical optimum residence time and the predicted optimum residence time is less than .3% over the range of \( \alpha \) considered. This is due to the relatively flat concentration vs residence time curve in the neighborhood of the optimum.

From the above observations we conclude that for small dispersion the axial dispersed plug flow tubular reactor can successfully model the total bypass reactor system and predict the optimum residence time for maximization of desired intermediate B with sufficient accuracy over the entire practical range of the reaction rate constant ratio.
III-7. Modeling a Partial Bypass Reactor

A more general system than the total bypass reactor for small
dispersion effects is an ideal tubular reactor with a partial bypass
through a stirred tank reactor. Consider the following reactor system.
An ideal tubular reactor with no mixing effects is divided into three
sections as in the diagram below. A small fraction \( e \) of the flow
is diverted from Section II and bypassed through a tube with infinite
dispersion, i.e. perfectly stirred tank reactor. The residence time
in the bypass equals the residence time in the section bypassed. At
the entrance to Section III the bypass stream is returned to the ideal
tubular reactor. The reaction \( A \rightarrow B \rightarrow C \) takes place isothermally and
with linear kinetics. The feed stream consists of pure \( A \). The
asymptotic expansion for the optimum residence time for maximum
production of \( B \) is obtained in the same manner as for the total bypass
reactor.

Using the results of Section 2, the output concentration functions
for \( A \) and \( B \) for the reactor sections can be written directly in
dimensionless form. Additional dimensionless variables are defined as

\[ c_A, c_B, c_C \]
\[ T_i \]
\[ \omega \]
follows:

\[ k_{\text{I}} T_{\text{I}} = \tau_{\text{I}} \quad k_{\text{II}} T_{\text{II}} = \tau_{\text{II}} \quad k_{\text{III}} T_{\text{III}} = \tau_{\text{III}} \]

In the tubular reactor:

Section I:

\[ \varphi_{A_{\text{I}}} = e^{\tau_{\text{I}}} \]  
\[ \varphi_{B_{\text{I}}} = \frac{1}{\alpha-1} (e^{-\tau_{\text{I}}} - e^{-\alpha \tau_{\text{I}}}) \]  

(7.1a)
(7.1b)

Section II:

\[ \varphi_{A_{\text{II}}} = \varphi_{A_{\text{I}}} e^{-\tau_{\text{II}}} \]  
\[ \varphi_{B_{\text{II}}} = \varphi_{B_{\text{I}}} e^{-\alpha \tau_{\text{II}}} + \frac{1}{\alpha-1} \varphi_{A_{\text{I}}} (e^{-\tau_{\text{II}}} - e^{-\alpha \tau_{\text{II}}}) \]  

(7.1c)
(7.1d)

Section III:

\[ \varphi_{A_{\text{III}}} = [\varphi_{A_{\text{II}}} (1-e) + \varepsilon \varphi_{A_{\text{II}}} e^{-\tau_{\text{III}}} \]  
\[ \varphi_{B_{\text{III}}} = \frac{[\varphi_{A_{\text{II}}} (1-e) + \varepsilon \varphi_{A_{\text{II}}}]}{\alpha-1} (e^{-\tau_{\text{III}}} - e^{-\alpha \tau_{\text{III}}}) \]  

\[ + [\varphi_{B_{\text{II}}} (1-e) + \varepsilon \varphi_{B_{\text{II}}} e^{-\tau_{\text{III}}} \]  

(7.1e)
(7.1f)

In the stirred tank reactor:

\[ \varphi_{A_{\text{II}}} = \frac{1}{1 + \tau_{\text{II}}} \]  
\[ \varphi_{B_{\text{II}}} = \frac{\varphi_{B_{\text{II}}} + \tau_{\text{II}} \varphi_{A_{\text{I}}}}{1 + \alpha \tau_{\text{II}} + (1+\tau_{\text{II}})(1+\alpha \tau_{\text{II}})} \]

(7.1g)
(7.1h)
Let \( \tau = \tau_I + \tau_{II} + \tau_{III} \). Combining Equations (7.1a, b, c, d, e, f, g, and h) gives the exact output concentration of B. No approximations have been made.

\[
\varphi_B = \frac{1}{\alpha-1} [e^{-\tau} - e^{-\alpha\tau}] + \frac{\varepsilon}{\alpha-1} [e^{-\alpha\tau} - e^{-\tau}] + \frac{1}{1+\tau_{II}} e^{-(\tau_I + \tau_{III})} \]
\[
- \frac{1}{1+\alpha\tau_{II}} e^{-\alpha(\tau_I + \tau_{III})} \]  
\quad (7.2)

Note that Equation (7.2) is a function of \( \tau_I + \tau_{III} \) which says that the bypass section can be anywhere. Only its fraction of the total residence time is important. This is expected because the system is linear.

To optimize the residence time \( \tau \) consider a proportional bypass model, i.e. let \( \tau_{II} = \eta\tau \) where \( \eta \) is constant. Taking the derivative of Equation (7.2) with respect to \( \tau \) gives

\[
\frac{d\varphi_B(\tau)}{d\tau} = \frac{1}{\alpha-1} [-e^{-\tau} + \alpha e^{-\alpha\tau}] + \frac{\varepsilon}{\alpha-1} [-\alpha e^{-\alpha\tau} + e^{-\tau} - \frac{\eta}{(1+\eta)^2} e^{-(1-\eta)\tau} \]
\[
- \frac{(1-\eta)}{(1+\eta\tau)} e^{-(1-\eta)\tau} + \frac{\alpha\eta}{(1+\alpha\eta\tau)^2} e^{-\alpha(1-\eta)\tau} \]
\[
+ \frac{\alpha(1-\eta)}{(1+\alpha\eta\tau)} e^{-\alpha(1-\eta)\tau} = 0 \]  
\quad (7.3)

We expect the effect of a small bypass flow \( \varepsilon \) to be a small change in the optimum residence time. Let \( \tau_{opt} = \tau_0 + \varepsilon\tau_1 + O(\varepsilon^2) \). Insert into Equation (7.3). Solve the equations in the orders of \( \varepsilon \).
Terms of order:

ε^0: \[-e^{-\tau_o} + \alpha e^{-\alpha \tau_o} = 0\]  

(7.4a)

so \(\tau_o = \frac{1}{\alpha - 1}\) the familiar result for ideal tubular reactors

ε^1: \[-e^{-\tau_o} \tau_1 - 2e^{-\alpha \tau_o} \tau_1 + e^{-\tau_o} - \alpha e^{-\alpha \tau_o} - \frac{\eta}{(1+\eta \tau_o)^2} e^{-(1-\eta)\tau_o}\]

\[-\frac{(1-\eta)}{1+\eta \tau_o} e^{-(1-\eta)\tau_o} + \frac{\alpha \eta}{(1+\alpha \eta \tau_o)^2} e^{-(1-\eta)\tau_o} + \frac{\alpha(1-\eta)}{1+\alpha \eta \tau_o} e^{-(1-\eta)\tau_o} = 0\]

So \(\tau_1 = \frac{\alpha (\eta/\alpha - 1)}{[(1+\eta \tau_o)^2(1+\alpha \eta \tau_o)(1-\eta)]^{\alpha/\eta} - ((1+\alpha \eta \tau_o)^2(1+\eta \tau_o)(1-\eta))} \]

\[1 + \alpha \eta \tau_o)^2(1+\eta \tau_o)^2(\alpha - 1)\]

(7.4b)

where \(0 \leq \eta \leq 1\).

As \(\alpha\) goes to one Equation (7.4b) reduces to

\(\tau_1 = \frac{\eta^3(1-\eta) e^\eta}{(1 + \eta)^3}\)

(7.4c)

From this it is clear that when \(\eta = 1\) dispersion has no effect on the optimum residence time; but for \(\eta < 1\) there is a small effect given by Equation (7.4c), (see Fig. 2.1).

Thus the optimum residence time expansion is

\(\tau_{opt} = \tau_o + \varepsilon \tau_1 + 0(\varepsilon^2)\)

(7.5)

where \(\tau_o\) is given by Equation (7.4a) and \(\tau_1\) is given by Equation (7.4b). Note the similarity to the total bypass model result. As \(\eta\) goes to one, Equation (7.5) approaches Equation (2.6).

The curves for the first order perturbation term \(\tau_1\) vs the rate constant ratio \(\alpha\) are plotted in Figure 2.1 for several values of
the proportional bypass $\eta$. As $\eta$ goes from 0 to 1 this model makes a continuous transition from an ideal tubular reactor to a total bypass reactor.

We would like to model this simple two parameter dispersion reactor by the axial dispersed plug flow reactor and predict the optimum residence time as in the previous section. The dispersion coefficient and the residence time for the axial dispersion reactor are obtained by matching moments of the residence time distributions of the two reactor models.

The residence time distribution of the partial bypass model can be obtained by combining the residence time distributions for the total bypass model and the ideal tubular reactor model. The residence time distribution is given by the following convolution integral:

$$\hat{\phi}(t) = \int_0^t \hat{\phi}_2(t - t') \, \hat{\phi}_1(t') \, dt'$$  \hspace{1cm} (7.6)

where 1 refers to the total bypass reactor and 2 refers to the ideal tube reactor.

From Equation (6.3):

$$\hat{\phi}_1 = (1-\epsilon) \delta(t - \eta T_b) + \frac{\epsilon}{\eta T_b} e^{-t/\eta T_b}$$

$$\hat{\phi}_2 = \delta(t - (1-\eta)T_b)$$

where

$T_b$ is the total residence time of the partial bypass reactor.

$\delta$ is the impulse or delta function.
Then
\[ \hat{\xi}(t) = \int_0^t \delta((t'-(1-\eta)T_b) - t') \left[ (1-\epsilon) \delta(t'-\eta T_b) + \frac{\epsilon}{\eta T_b} e^{-\frac{t'-\eta T_b}{\eta T_b}} \right] dt' \]

\[ \hat{\xi}(t) = 0 \quad \text{for} \quad t < (1-\eta)T_b \]
\[ \hat{\xi}(t) = (1-\epsilon) \delta(t-T_b) + \frac{\epsilon}{\eta T_b} e^{-\frac{(t-(1-\eta)T_b)}{\eta T_b}} \]
\[ \text{for} \quad t > (1-\eta)T_b \]

The two moments are obtained from Equations (6.1) and (6.2):

<table>
<thead>
<tr>
<th>Partial Bypass Reactor</th>
<th>Axial Dispersed Tubular Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu = T_b )</td>
<td>( \mu = T_t )</td>
</tr>
<tr>
<td>( \sigma^2 = \epsilon T_b \eta^2 )</td>
<td>( \sigma^2 = 2 \frac{D}{VL} T_t \eta^2 )</td>
</tr>
</tbody>
</table>

To model the partial bypass model with the axial dispersed tube model we make the mean residence times equal and the second moments equal.

Thus equating (7.7) with (6.11) and (7.8) with (6.12)
\[ T_b = T_t \]
\[ \tau \epsilon \eta^2 = 2\gamma \]
or \[ \gamma = \frac{\epsilon \tau \eta^2}{2} \] (7.9)

This is similar to the previous results with the \( \eta^2 \) factor accounting for the partial bypass. Recall that the perturbation expansion results for the optimum length of the tube were of the form
\[ \tau_{opt} = \tau_o + \gamma \tau_1 \]

Inserting the equivalent dispersion coefficient (7.9)
\[ \tau_{opt} = \tau_o + \frac{\tau_{opt} \epsilon \eta^2}{2} \tau_1 \]
Thus the predicted optimum residence time for the partial bypass reactor is

\[ \tau_{\text{opt}} = \frac{\tau_0}{1 - \frac{e\eta^2 \tau_1}{2}} \]

\[ = \frac{\ln \eta}{\alpha - 1} \left( 1 - \frac{e\eta^2 \ln \eta}{2(\alpha + 1) - 1} \right) \]

(7.10)

We see that the criterion for the existence of a physically reasonable solution to Equation (7.10) is

\[ \frac{2}{\eta} > e\eta^2. \]

(7.11)

This is simply the criterion for the total bypass reactor attenuated by the factor \( \eta^2 \). For a given \( \alpha \), as \( \eta \) decreases from 1, the range of admissible \( e \) increases.

Some numerical results of modeling a partial bypass reactor with an axial dispersed tubular reactor and the prediction of the optimum residence time are given in Table 7.1. The values \( e = .1 \) and \( \eta = .5 \) were used. In general we expect the effect of \( \eta \) less than one for a given \( e \) to be the same as a reduction in \( e \). The numerical evaluations substantiate this.

Observations:

1. The error between the numerical and the predicted optimum residence time is less than 3\% over the range of \( \alpha \) from .005 to 100 with \( e = .1 \) and \( \eta = .5 \).

2. The error in the yield of \( B \) is .01\% or less under these conditions.
TABLE 7.1

OPTIMUM RESIDENCE TIME AND YIELD OF DESIRED INTERMEDIATE FOR THE
PARTIAL BYPASS REACTOR SYSTEM PREDICTED BY THE AXIAL DISPERSED
TUBULAR REACTOR

<table>
<thead>
<tr>
<th>$\varepsilon = .1$</th>
<th>$\eta = .5$</th>
<th>Predicted $\tau_{\text{optimum}}$</th>
<th>Percent Error</th>
<th>Maximum $\varphi_B$ Using Predicted $\tau_{\text{optimum}}$</th>
<th>Percent Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>.04755</td>
<td>.04877</td>
<td>2.6</td>
<td>.009526</td>
<td>.009525</td>
</tr>
<tr>
<td>10</td>
<td>.2579</td>
<td>.2617</td>
<td>1.5</td>
<td>.07699</td>
<td>.07699</td>
</tr>
<tr>
<td>5</td>
<td>.4046</td>
<td>.4096</td>
<td>1.2</td>
<td>.1328</td>
<td>.1328</td>
</tr>
<tr>
<td>1</td>
<td>1.001</td>
<td>1.012</td>
<td>1.2</td>
<td>.3654</td>
<td>.3654</td>
</tr>
<tr>
<td>.1</td>
<td>2.579</td>
<td>2.617</td>
<td>1.5</td>
<td>.7699</td>
<td>.7699</td>
</tr>
<tr>
<td>.05</td>
<td>3.189</td>
<td>3.247</td>
<td>1.8</td>
<td>.8505</td>
<td>.8504</td>
</tr>
<tr>
<td>.01</td>
<td>4.755</td>
<td>4.877</td>
<td>2.6</td>
<td>.9526</td>
<td>.9525</td>
</tr>
<tr>
<td>.005</td>
<td>5.476</td>
<td>5.631</td>
<td>2.8</td>
<td>.9724</td>
<td>.9723</td>
</tr>
</tbody>
</table>
(3) Reducing the bypass from a total bypass to a half-bypass decreased the error in the predicted optimum residence time by a factor of five. The error in the yield using the predicted residence time was reduced by a factor of twenty.

Therefore, modeling a partial bypass reactor by the axial dispersion model and predicting the optimum residence time is even more successful than modeling the total bypass system. The errors in the predicted optimum residence time and in the yield of intermediate decrease faster than the ratio of the bypass residence time to the total residence time.
III-8. Modeling a Total Bypass Reactor and Axial Dispersed Plug Flow Reactor in Series

The next stage of complexity is modeling a reactor system that has three dispersion parameters ($\gamma, \varepsilon, \eta$) by the one dispersion parameter axial dispersed tubular reactor. The model to be considered is a total bypass reactor in series with an axial dispersion plug flow tubular reactor. In this model dispersion effects arise from both the macro or large scale mixing of the bypass reactor and the diffusion type mixing superimposed on the plug flow of the axial dispersion reactor. Again we want to use the simple asymptotic results of the axial dispersion model to predict the optimum residence time for the series system. The usual consecutive reactions, $A \rightarrow B \rightarrow C$, take place in the system. The dispersion parameter and the bypass fraction are assumed small so the asymptotic expansions can be used. The series configuration is as shown below. The reactors could be in reverse order because the reaction kinetics are linear.

1 - axial dispersed plug flow tubular reactor
2 - total bypass reactor system
The solution for the output concentrations of Reactor 1 can be written directly from section 1.

\[ \varphi_{A_1}(\tau_1) = e^{-\tau_1} + \gamma \tau_1 e^{-\tau_1} + O(\gamma^2) \]  
\[ \text{(8.1a)} \]

\[ \varphi_{B_1}(\tau_1) = \frac{1}{\alpha-1} \left( e^{-\tau_1} - e^{-\alpha \tau_1} \right) + \gamma \left[ \frac{\tau_1}{\alpha-1} e^{-\tau_1} - \frac{2}{\alpha-1} e^{-\alpha \tau_1} \right] + 0(\gamma^2) \]  
\[ \text{(8.1b)} \]

where \( \tau_1 \) is the residence time in Reactor 1.

However, for Reactor 2 we need to generalize the bypass model to allow for a non-zero input concentration of component B. From Equations (7.1 c,g,d,h)

\[ \varphi_{A_2}(\tau_2) = \varphi_{A_1}(\tau_1) e^{-\tau_2} + \varepsilon \frac{\varphi_{A_1}(\tau_1)}{1 + \tau_2} \]  
\[ \text{(8.2a)} \]

\[ \varphi_{B_2}(\tau_2) = (1-\varepsilon) \left[ \varphi_{B_1}(\tau_1) e^{-\alpha \tau_2} + \frac{\varphi_{A_1}(\tau_1)}{\alpha-1} (e^{-\tau_2} - e^{-\alpha \tau_2}) \right] 
+ \varepsilon \left[ \frac{\varphi_{B_1}(\tau_1)}{1+\alpha \tau_2} + \frac{\varphi_{A_1}(\tau_1) \tau_2}{(1+\tau_2)(1+\alpha \tau_2)} \right] \]  
\[ \text{(8.2b)} \]

where \( \tau_2 \) is the residence time in Reactor 2.

It is assumed that both \( \gamma \) and \( \varepsilon \) are of order less than one. Let \( \tau \) be the total residence time and \( \tau_1 = \eta \tau \) where \( \eta \) is a constant.

Combining Equations (8.1) and (8.2) gives

\[ \varphi_B(\tau) = \frac{1}{\alpha-1} (e^{-\tau} - e^{-\alpha \tau}) + \gamma \left[ \frac{(1-\gamma)\tau}{\alpha-1} (e^{-\tau} - \alpha^2 e^{-\alpha \tau}) \right] 
+ \gamma \left( \frac{\varepsilon}{\gamma} \right) \left[ \frac{1}{\alpha-1} (e^{-(1-\eta)\tau} - e^{-\alpha(1-\eta)\tau}) \cdot \frac{1}{1 + \alpha^2 \eta} \right] \]

\[ + \frac{\eta \tau_1}{(1+\tau)(1+\alpha \tau_1)} - \frac{1}{\alpha-1} (e^{-\tau} - e^{-\alpha \tau}) + 0(\gamma^2) + 0(\varepsilon^2) + 0(\varepsilon \gamma) \]  
\[ \text{(8.3)} \]
It is assumed that $\frac{\xi}{\gamma}$ is $O(1)$.

For $\tau$ to be optimum $\phi_B(\tau)$ must be stationary with respect to $\tau$ with $\gamma$, $\epsilon$, $\eta$, $\alpha$ held constant.

$$\frac{d\phi_B(\tau)}{d\tau} = \frac{1}{\alpha-1} (-e^{-\tau} + \alpha e^{-\alpha \tau}) + \gamma \frac{1-\eta}{\alpha-1}(e^{-\tau} - \alpha^2 e^{-\alpha \tau}) + \frac{(1-\eta)\tau}{\alpha-1} (-e^{-\tau} + \alpha^3 e^{-\alpha \tau})$$

$$+ \frac{\epsilon}{\gamma} (\frac{1}{\alpha-1}(-(1-\eta)e^{-(1-\eta)\tau} + \alpha(1-\eta)e^{-(1-\eta)\alpha \tau}) \frac{1}{1 + \alpha \eta})$$

$$- \frac{1}{\alpha-1} (e^{-(1-\eta)\tau} - e^{-(1-\eta)\alpha \tau}) \frac{\alpha \eta}{(1+\alpha \eta \tau)^2} + \frac{\eta(1-\alpha \eta \tau)^2 e^{-(1-\eta)\tau}}{(1+\alpha \eta \tau)(1+\alpha \eta \tau)^2}$$

$$+ \frac{1}{\alpha-1} (-e^{-\tau} + \alpha e^{-\alpha \tau}) = 0 \quad (8.4)$$

Assume $\tau = \tau_o + \gamma \tau_1 + O(\gamma^2)$. Insert into Equation (8.4).

Terms of Order:

$\gamma^0$: $-\tau_o + \alpha e^{-\alpha \tau_o} = 0$

$$\tau_o = \frac{\ln \alpha}{\alpha - 1} \quad (8.5a)$$

$\gamma'$: $\tau_1(e^{-\tau_o} - \alpha^2 e^{-\alpha \tau_o}) + (1-\eta)(e^{-\tau_o} - \alpha^2 e^{-\alpha \tau_o} - \tau o e^{-\tau_o} + \alpha \tau o e^{-\alpha \tau_o})$

$$+ \frac{(\epsilon \gamma)}{(1-\eta)(\alpha e)} - \frac{-(1-\eta)\alpha \tau_0}{e^{-(1-\eta)\tau_0}} - \frac{1}{1+\alpha \eta \tau_0}$$

$$- \frac{\alpha \eta}{(1+\alpha \eta \tau_0)^2} (e^{-(1-\eta)\tau_0} - e^{-(1-\eta)\alpha \tau_0})]$$

$$+ \frac{\epsilon}{\gamma} (\frac{(1-\alpha \eta \tau_0)^2 \eta e^{-(1-\eta)\tau_0}(\alpha - 1)}{(1+\alpha \eta \tau_0)^2} + (e^{-\tau_o} - \alpha e^{-\alpha \tau_o}) = 0$$
\[ \tau_1 = (1-\eta)\left[\tau_o(\alpha+1)-1\right] + \left(\frac{\alpha}{\gamma}\right)\left[\frac{\eta/\alpha-1}{(1+\alpha\eta\tau_o)^2}\right] \left(\frac{1-\alpha}{1-\alpha}\right)(1 + \alpha\eta\tau_o(1-\eta)) \]

\[ - \eta + \frac{(1-\alpha\eta^2\tau_o^2)^2}{(1+\alpha\eta\tau_o)^2(1+\eta\tau_o)^2} \right] \]  

(8.5b)

As \( \eta \) goes to one; \( \tau_1 \) approaches Equation (2.6), the total bypass system.

As \( \eta \) goes to zero; \( \tau_1 \) approaches Equation (1.17), the axial dispersed tubular reactor.

Thus \( \tau_{opt} = \tau_o + \gamma \tau_1 + O(\gamma^2) \)  

(8.6)

where \( \tau_o \) is given by Equation (8.5a) and \( \tau_1 \) is given by Equation (8.5b).

It is important to note that if the series reactor system were in reverse order we would have to solve the axial dispersion model for none-zero input concentrations of B. Furthermore, the form of the concentration inputs to the reactor would have to be \( \varphi_i = \varphi_{i0} + \gamma \varphi_{i1} + O(\gamma^2) \) in order to maintain correct order relations. The solution to the reactor equations for input concentrations of order one is not valid for input concentrations in expansion form. Therefore, the entire perturbation expansion problem would have to be reworked. Obviously much effort is saved by considering the series system in the order that we did.

We now model this series system using an axial dispersed tubular reactor by matching the moments of the residence time distributions to determine values of the residence time and the dispersion coefficient.
Equation (6.10a) is the Laplace transform of the residence time distribution of the dispersed tubular reactor. Equation (6.3) is the residence time distribution of the total bypass reactor. In dimensional form

\[
\bar{\phi}_1 = e^{-sT_1} + \frac{sD}{V^2} T_1 e^{-sT_1} + O\left(\frac{sD}{V^2} \right)^2 \tag{6.10a}
\]

\[
\bar{\phi}_2 = (1-\varepsilon) \delta(t-T_2) + \frac{\varepsilon}{T_2} e^{-t/T_2} \tag{6.3}
\]

The residence time distribution of the series model is the convolution integral of \( \bar{\phi}_1 \) and \( \bar{\phi}_2 \). Computation is easier if we use the fact that the Laplace transform of the convolution integral is simply the product of the Laplace transforms of the two functions.

\[
\bar{\phi}(t) = \int_0^t \bar{\phi}_1(t-t') \bar{\phi}_2(t') \, dt' \quad \text{(convolution integral)}
\]

\[
\overline{\bar{\phi}}(s) = \overline{\bar{\phi}_1}(s) \cdot \overline{\bar{\phi}_2}(s) \quad \text{(transform product)}
\]

Now

\[
\overline{\bar{\phi}_2}(s) = (1-\varepsilon)e^{-sT_2} + \frac{\varepsilon}{1+sT_2}
\]

So

\[
\overline{\bar{\phi}}(s) = (1-\varepsilon) e^{-s(T_1+T_2)} + (1-\varepsilon) \frac{sD}{V^2} T_1 e^{-s(T_1+T_2)}
\]

\[
+ \frac{\varepsilon}{1+sT_2} e^{-sT_1} + \frac{\varepsilon}{1+sT_2} e^{-sT_1} \frac{sD}{V^2} T_1
\]

\[
+ O\left(\frac{sD}{V^2} \right)^2 + O(\varepsilon^2) + O\left(\frac{sD}{V^2} \varepsilon\right) \tag{8.7}
\]
The moments are obtained from the transform of the residence time distribution, Equation (8.7), through Equations (6.7) and (6.8). The necessary expressions to obtain the moments are:

\[
\lim_{s \to 0} \mathcal{F}(s) = 1 \\
\lim_{s \to 0} \frac{\partial^2 \mathcal{F}(s)}{\partial s^2} = \frac{2D}{V^2} T_1 + \varepsilon T_2^2 \\
\lim_{s \to 0} \frac{\partial \mathcal{F}(s)}{\partial s} = -(T_1 + T_2)
\]

So for the series model:

\[
\mu = T_1 + T_2 = T \quad (8.8) \\
\sigma^2 = \varepsilon \eta^2 T^2 + \frac{2D}{V^2} T(1-\eta) \quad (8.9)
\]

For the axial dispersion model:

\[
\mu = \hat{T} \quad (6.11) \\
\sigma^2 = \frac{2D}{V^2} \hat{T} \quad (6.12)
\]

Matching moments for a dispersed plug flow reactor with parameters \( \hat{D}, \hat{T}, \hat{V}, \hat{L} \), let \( \hat{T} = T \) and

\[
\frac{2\frac{\hat{D}}{\hat{V}\hat{L}}} = \varepsilon \eta^2 \quad + \frac{2D}{VL} (1-\eta)^2
\]

In dimensionless form

\[
\hat{T} = T \\
\hat{\gamma} = \frac{\tau \varepsilon \eta^2}{2} + \gamma(1-\eta) \\
\text{where } \hat{\gamma} = \frac{K_D}{\hat{V}^2} \text{ and } \gamma = \frac{K_D}{v^2}
\]

Then the predicted optimum residence time for the maximization of \( B \) from this modeling is

\[
T_{opt} = \frac{\ln \gamma + \gamma(1-\eta)(\frac{\ln \gamma}{\alpha-1} + 1)}{1 - \frac{\varepsilon \eta^2}{2} (\frac{\ln \gamma}{\alpha-1} + 1)} \quad \text{for } 0 \leq \eta \leq 1 \quad (8.10)
\]
The restriction on the admissible values of $\epsilon$ for a physically reasonable result is the same as for a partial bypass reactor system.

$$\frac{2}{\tau_1} \geq \epsilon \eta^2$$

This means a larger value of $\epsilon$ can be used if $\eta$ is made smaller.

Some typical numerical results are presented in Table 8.1. The values $\epsilon = .1$, $\gamma = .05$, and $\eta = .5$ were used.

The numerical optimum residence time was evaluated using the concentration equation (8.3) which is exact for the bypass reactor and accurate to within $.25\%$ when $\gamma = .05$ for the axial dispersion reactor. The equation for the exact output of the series reactor is much more complex.

**Observations:**

(1) The error between the numerical optimum residence time and that predicted by the axial dispersion model was less than $6\%$ over the range of $\alpha$ from .005 to 100, $\epsilon = .1$, $\gamma = .05$ and $\eta = .5$.

(2) The output concentration of B using the predicted optimum residence time is larger than that for the numerical optimum residence time when $\alpha$ is less than one. This is because the asymptotic approximation for the output of B was used in the determination of the numerical optimum residence time. Note that for $\alpha$ less than one, the concentration difference is less than $.25\%$ which is the order of the truncation error in the asymptotic expansion, Equation (8.3), for the parameters used.
TABLE 8.1

PREDICTION OF THE OPTIMUM RESIDENCE TIME AND YIELD OF DESIRED INTERMEDIATE OF THE SERIES REACTOR SYSTEM BY THE AXIAL DISPERSED TUBULAR REACTOR

$\varepsilon = .1 \quad \gamma = .05 \quad \eta = .5$

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$T_{\text{optimum}}$</th>
<th>$\tilde{T}_{\text{optimum}}$</th>
<th>Percent error</th>
<th>$\tilde{\phi}_B$</th>
<th>$\tilde{\phi}<em>B$ Using $T</em>{\text{optimum}}$</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>.1403</td>
<td>.1457</td>
<td>3.8</td>
<td>.00881</td>
<td>.00876</td>
<td>.5</td>
</tr>
<tr>
<td>10</td>
<td>.3060</td>
<td>.3081</td>
<td>.7</td>
<td>.0729</td>
<td>.0729</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>.4450</td>
<td>.4450</td>
<td>.13</td>
<td>.1266</td>
<td>.1266</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1.046</td>
<td>1.037</td>
<td>.8</td>
<td>.3559</td>
<td>.3554</td>
<td>.13</td>
</tr>
<tr>
<td>.1</td>
<td>2.714</td>
<td>2.664</td>
<td>1.8</td>
<td>.7649</td>
<td>.7651</td>
<td>.03</td>
</tr>
<tr>
<td>.05</td>
<td>3.383</td>
<td>3.306</td>
<td>2.3</td>
<td>.8469</td>
<td>.8472</td>
<td>.03</td>
</tr>
<tr>
<td>.01</td>
<td>5.196</td>
<td>4.974</td>
<td>4.3</td>
<td>.9511</td>
<td>.9515</td>
<td>.04</td>
</tr>
<tr>
<td>.005</td>
<td>6.081</td>
<td>5.746</td>
<td>5.5</td>
<td>.9713</td>
<td>.9717</td>
<td>.05</td>
</tr>
</tbody>
</table>
(3) The error in the yield concentration of B was less than 0.5% for \( \alpha \) between 0.005 and 100.

Thus the axial dispersion reactor model can model a complex reactor system with three dispersion parameters very well in the region of small dispersion.

From the limited numerical work presented above it is clear that the axial dispersed plug flow reactor can successfully model and predict the optimum residence time for simple reactor systems in the region of small dispersion. Models with three dispersion parameters can also be represented by the axial dispersed plug flow reactor. Therefore, it is reasonable to conclude that the axial dispersion model could be used to predict optimum residence times for real reactors with small dispersion effects.
CONCLUSIONS

The method of perturbation expansion solutions is a simple, straightforward method for obtaining approximate analytical solutions to differential and algebraic equations in regions of limiting behavior of one parameter. Its greatest potential lies in its application to nonlinear differential equations where an analytical solution is not otherwise possible. Even for linear systems, an asymptotic expansion often gives an accurate solution with much less work than a full and exact solution. The value of perturbation expansion solutions in reactor dispersion studies is clear from this paper.

The axial dispersed plug flow reactor appears to successfully model and predict optimum residence times for other reactor models in the region of small dispersion effects. It could probably be used to model a real reactor if the asymptotic solution for the reaction system taking place could be obtained. However, care must be taken to make sure that this simple model is not used to characterize effects for which it is unsuited, e.g. dead volume in a reactor.

The maximum in the optimum residence time of the axial dispersed plug flow reactor with the consecutive first order reaction system is an unusual phenomenon. It could be just an indication of the unsuitability of this model in the range of large dispersion. It is probably due to the choice of dimensionless parameters and the fact that the length of the reactor is optimized with the dispersion, flow velocity, and kinetic rate constants held fixed. Thus this maximum
phenomenon has significance for reactor design calculations. Although the bypass reactor model of large dispersion does not exhibit this effect, this can be explained by the fact that mixing occurs on a macro scale in this model rather than on a micro scale as in the dispersed plug flow reactor model.

There are two topics covered in this work that need further study. The first is the development of an optimum residence time formulation for general reaction rate expressions, and the second is a complete investigation of optimum residence time maximum phenomena.
REFERENCES


APPENDICES
APPENDIX A: Formulation of the Equations for a Series-Parallel Reaction System

It is easy to extend the results of this work to a series-parallel reaction system of the form:

\[ \begin{align*}
  A & \xrightarrow{r_1} B \xrightarrow{r_2} C \\
  A & \xrightarrow{r_3} D
\end{align*} \]

where B is the desired reaction product and C and D are waste products. The reaction rate expressions are linear as follows:

\[ r_1 = k_1 c_A \quad r_2 = k_2 c_B \quad r_3 = k_3 c_A \]

Then

\[ r_A = -(k_1 + k_3) c_A \quad (A.1a) \]

\[ r_B = k_1 c_A - k_2 c_B \quad (A.1b) \]

where \( r_i \) is the rate of formation of component \( i \) per unit volume.

Inserting Equations (A.1a) and (A.1b) into the reactor component balance Equations (1.4a) and (1.4b) we have in dimensionless form,

**Component A:**

\[ -\gamma \frac{d^2 \varphi_A}{dx^2} + \frac{d \varphi_A}{dx} + \alpha_2 \varphi_A = 0 \quad (A.2) \]

B.C. at \( x = 0 \)

\[ \varphi_A - \gamma \frac{d \varphi_A}{dx} \bigg|_0 = 1 \]

at \( x = \tau \)

\[ \gamma \frac{d \varphi_A}{dx} \bigg|_\tau = 0 \]

where \( \alpha_2 = \frac{k_1 + k_3}{k_1} \)

**Component B:**

\[ -\gamma \frac{d^2 \varphi_B}{dx^2} + \frac{d \varphi_B}{dx} + \alpha_1 \varphi_B - \varphi_A = 0 \quad (A.3) \]
The boundary conditions are the same as Equation (1.4a and b) provided only pure A enters in the feed stream. Thus the results already obtained can easily be modified to give the optimum residence time for the maximum production of B for this series-parallel reaction system.
APPENDIX B: The Exact Solution to the Axial Dispersed Plug Flow Reactor with the Consecutive First Order Reaction System

The numerical evaluation of the optimum residence time for the axial dispersed tubular reactor was relatively easy to obtain because the concentration profile problem for the linear kinetics case can be solved analytically. The exact solutions to Equations (1.5a) and (1.5b), evaluated at the exit of the reactor, are

\[ \varphi_A(\tau) = \frac{(\lambda_1^2 - \lambda_2^2) e^{(\lambda_1^2 + \lambda_2^2)\tau}}{(1-\gamma\lambda_2)\lambda_1^2 - (1-\gamma\lambda_1)\lambda_2^2 e^{(\lambda_1^2 + \lambda_2^2)\tau}} \]  

where

\[ \lambda_1 = \frac{1 + \sqrt{1 + 4\gamma}}{2\gamma}, \quad \lambda_2 = \frac{1 - \sqrt{1 + 4\gamma}}{2\gamma} \]

\[ \varphi_B(\tau) = \frac{1}{\alpha-1} \left[ \frac{(\lambda_4^2 - \lambda_3^2) e^{(\lambda_4^2 + \lambda_3^2)\tau}}{\lambda_3^2(1-\gamma\lambda_4)e^{(\lambda_3^2 + \lambda_4^2)\tau}} - \frac{(\lambda_4^2 + \lambda_3^2)\tau}{\lambda_3(1-\gamma\lambda_4)e^{(\lambda_3^2 + \lambda_4^2)\tau}} \right] \]

\[ + \frac{1}{\alpha-1} \left[ \frac{(\lambda_1^2 - \lambda_2^2) e^{(\lambda_1^2 + \lambda_2^2)\tau}}{\lambda_1^2(1-\gamma\lambda_2)e^{(\lambda_1^2 + \lambda_2^2)\tau}} - \frac{(\lambda_1^2 + \lambda_2^2)\tau}{\lambda_2(1-\gamma\lambda_1)e^{(\lambda_1^2 + \lambda_2^2)\tau}} \right] \]  

where

\[ \lambda_3 = \frac{1 + \sqrt{1 + 4\alpha\gamma}}{2\gamma}, \quad \lambda_4 = \frac{1 - \sqrt{1 + 4\alpha\gamma}}{2\gamma} \]

The derivative of Equation (B.2) was calculated and a simple false position numerical search procedure was used to locate the optimum residence time. Examination of the solution for \( \varphi_B(\tau) \) shows that for \( \gamma \) very large as well as \( \gamma \) very small, numerical truncation error will be a problem. Thus even in the cases where an analytical solution is possible, the perturbation expansion solution is valuable due to ease of numerical computation.
APPENDIX C: Comparison of the Solution of Freeman and Houghton with the Results of a Correct Perturbation Expansion Technique

As mentioned in the introduction, Freeman and Houghton [6] have applied perturbation expansion techniques to the concentration profile problem in the axial dispersed tubular reactor with small dispersion. The reaction \( A + A \rightarrow P \) with the rate expression \( r_1 = k_1 c_A^2 \) was considered. The boundary conditions they used were the following:

Terms of Order:

(C.1a) \[ \gamma^0: \text{at } x = 0 \quad \varphi_A - \gamma \frac{d\varphi_A}{dx} \bigg|_0 = 1 \]

(C.1b) \[ \gamma': \text{at } x = 0 \quad \varphi_A - \gamma \frac{d\varphi_A}{dx} \bigg|_0 = 0 \]

The correct boundary conditions to order zero and order one are

(C.2a) \[ \gamma^0: \text{at } x = 0 \quad \varphi_A = 1 \]

(C.2b) \[ \gamma': \text{at } x = 0 \quad \varphi_A - \frac{d\varphi_A}{dx} \bigg|_0 = 0 \]

The Freeman and Houghton composite solution is

\[
\varphi_A(x) = \frac{1}{c_1 + \alpha x} + \frac{2\gamma \alpha}{(c_1 + \alpha x)^2} \left[ \ln \left( 1 + \frac{\alpha x}{c_1} \right) + \frac{\gamma \alpha}{c_1 + 2\gamma \alpha} \right]
\]

\[+ \frac{\gamma \alpha}{(c_1 + \alpha x)^2} \left( \frac{1-x}{\alpha x} \right) e^\frac{-\gamma}{\alpha x} + O(\gamma^2) \]

(C.3)

where \( c_1 = \frac{1}{2}(1 + \sqrt{1 + 4\gamma \alpha}) \), \( \alpha = k_1 \frac{L}{V} c_A \).
The correct solution is

\[ \varphi_A(x) = \frac{1}{1+\alpha x} + \frac{2\gamma\alpha}{(1+\alpha x)^2} \left[ \ln(1+\alpha x) - \frac{\alpha}{2} \right] + \gamma \frac{\alpha}{(1+\alpha x)^2} e^{-\frac{(1-x)}{\gamma}} \]

+ \mathcal{O}(\gamma^2) \quad \text{(C.4)}

A numerical comparison of the two solutions is given below along with the results of a numerical integration of the differential equation.

**TABLE C.1**

PERTURBATION EXPANSION SOLUTION COMPARISON

\[
\begin{array}{cccc}
\gamma = .1 & \alpha = .5 \\
 x & \varphi_A \text{exact} & \varphi_A \text{numerical} & \varphi_A \text{Freeman & Houghton} & \varphi_A \text{Eq. (C.4)} \\
0 & .959 & .958 & .950 & \cdot \\
.05 & .940 & .938 & .930 & \cdot \\
.10 & .920 & .918 & .911 & \cdot \\
.15 & .900 & .900 & .893 & \cdot \\
.20 & .882 & .882 & .876 & \cdot \\
.30 & .847 & .847 & .842 & \cdot \\
.40 & .815 & .816 & .811 & \cdot \\
.50 & .786 & .786 & .782 & \cdot \\
.60 & .758 & .758 & .756 & \cdot \\
.70 & .730 & .733 & .731 & \cdot \\
.80 & .709 & .711 & .709 & \cdot \\
.85 & .699 & .702 & .700 & \cdot \\
.90 & .690 & .694 & .692 & \cdot \\
.95 & .683 & .688 & .686 & \cdot \\
1.00 & .680 & .685 & .685 & \cdot \\
\end{array}
\]
The maximum error in the correct asymptotic solution is .01 which is $O(\gamma^2)$ as expected from the asymptotic expansion theory. The Freeman and Houghton solution has a maximum error of .005 which is an improvement by a factor of two for this particular problem.

Thus Freeman and Houghton have shown that the perturbation expansion solution can be improved by violating order relations in the boundary conditions. In other words they have made the zeroth order solution "anticipate" some of the correction necessary when dispersion is present. While a technique of this type might bring an expansion into closer agreement with numerical results, it could easily have the opposite effect. It certainly could not be trusted for cases where the numerical solution is not obtained. Therefore, the value of their procedure is very marginal.