

A THEORETICAL INVESTIGATION OF POISONING  
EFFECTS ON POLYFUNCTIONAL CATALYSTS

by 6408

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B. S., University of Nebraska, 1967

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A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY,  
Manhattan, Kansas

1971

Approved by:

  
Major Professor

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TABLE OF CONTENTS

	PAGE
1. Introduction . . . . .	1
2. Literature Survey . . . . .	5
3. Theoretical Development . . . . .	14
3-1. Mass Balances on Single Particles--Discrete Formulation . . .	16
3-2. Mass Balances on Stationary Bed Volume Element--Discrete Formulation . . . . .	25
3-3. Mass Balances on Single Particle--Composite Formulation . . .	35
3-4. Mass Balances on Stationary Bed Volume Element--Composite Formulation . . . . .	40
3-5. Mass Balances on a Fixed Bed Reactor Assuming no Diffusional Resistance . . . . .	47
3-6. Discussion of Fouling Models . . . . .	53
3-7. Tabulation of Transient Mass Balances after Incorporation of Fouling Model . . . . .	55
4. Numerical Solution of Particle and Bed Equations . . . . .	59
4-1. Qualitative Discussion . . . . .	59
4-2. Development of Finite Difference Schemes--Discrete Particle and Bed . . . . .	61
4-3. Development of Finite Difference Schemes--Negligible Diffusion Resistance Case . . . . .	72
4-4. Error Analysis of Finite Difference Formulations . . . . .	78
5. Results and Discussion . . . . .	88
6. Nomenclature . . . . .	102

	PAGE
7. Acknowledgments . . . . .	106
8. Bibliography . . . . .	107
9. Appendices . . . . .	109



## LIST OF TABLES

TABLE NO.	TITLE	PAGE
3-1	Optimum catalyst fractions and maximum product concentration for various choices of rate constants-- Discrete formulation . . . . .	34
3-2	Optimum catalyst fractions and maximum product concentration for various choices of rate constants-- Composite formulation . . . . .	46
4-1	Axial step size effect on reaction intermediate concentration at selected axial positions--Composite formulation . . . . .	79
4-2	Effect of time step size on reaction intermediate concentration at selected axial positions--Composite formulation . . . . .	81
4-3	Effect of axial step size on reaction intermediate concentration at selected axial distances--No diffusion resistance case . . . . .	84
4-4	Effect of time step size on reaction intermediate concentration at selected axial positions--No diffusion resistance case . . . . .	86
5-1	Chemical and physical properties and reactor dimensions for comparison of catalyst formulations . . . . .	91

## LIST OF FIGURES

FIG. NO.	TITLE	PAGE
1-1	Schematic representation of fixed bed reactors with different catalyst formulations . . . . .	3
3-1	Schematic representation of X catalyst particle . . . . .	17
3-2	Representation of stationary bed reactor with differential volume element . . . . .	26
3-3	Optimum catalyst fractions for various choices of rate constants--Discrete formulation . . . . .	33
3-4	Optimum catalyst fractions for various choices of rate constants--Composite formulation . . . . .	44
3-5	Comparison of maximum yields and optimal catalyst fractions for the two formulations . . . . .	45
3-6	Optimum catalyst fractions for various choices of rate constants--No diffusion resistance . . . . .	51
4-1	Representation of spatial lattice used in finite difference work . . . . .	62
4-2	Flow chart of computer calculations for discrete formulation . . . . .	69
4-3	Flow chart of computer calculations--No diffusion resistance case . . . . .	75
4-4	Effect of axial step size on accuracy--Composite case . . . . .	80
4-5	Effect of time increment on accuracy--Composite case . . . . .	82
4-6	Effect of axial step size on accuracy--No diffusion resistance case . . . . .	85

FIG. NO.	TITLE	PAGE
4-7	Effect of time increment size on accuracy--No diffusion resistance case . . . . .	87
5-1	Effect of varying radius ratios on product yield at reactor exit--Discrete formulation . . . . .	89
5-2	Exit product decay rates with time for both discrete and composite formulations . . . . .	92
5-3	Effect of product forming rate constant $k_3^0$ on decay rate difference of the two formulations . . . . .	93
5-4	Effect of equilibrium constant $K = k_1^0/k_2^0$ on exit product decay rate--Composite formulation . . . . .	96
5-5	Effect of equilibrium constant on exit product decay rate--Discrete formulation . . . . .	97
5-6	Comparison of intraparticle concentrations of poison precursor at various time levels. Axial distance $\bar{z} = 0.5$ . .	98
5-7	Comparison of intraparticle concentrations of poison precursor at various time levels. Axial distance $\bar{z} = 5.0$ . .	99
5-8	Comparison of intraparticle poison concentration profiles at various time levels. Axial distance $\bar{z} = 0.5$ . . . . .	100
5-9	Comparison of intraparticle poison concentration profiles at various time levels. Axial distance $\bar{z} = 5.0$ . . . . .	101

## CHAPTER 1

### INTRODUCTION

The production of a large percentage of commercial and industrial materials is accomplished by complex reactions in which catalysts play an indispensable role. In 1962, 18% of the total dollar value of manufactured goods was produced by catalytic technology and this percentage has been increasing steadily. Clearly, monetary as well as academic incentives provide the basis for growing research interest in the diversified field of catalysis.

Less than two decades ago the majority of investigators in catalysis were still of the opinion that even though a catalyst might consist of more than one component it was still monofunctional in nature. Consequently, if it were known that to produce a certain marketable chemical two separate catalytic steps were needed, a series of two reactors was designed; the first containing the pure catalyst for the initial reaction and the second containing the pure catalyst for the second reaction. The basic fact that two separate reactions zones were required was never questioned in the reactor design and the only characteristics of the catalysts which were considered were such things as pellet size, geometric shape, porosity, temperature and handling attrition resistances, etc.

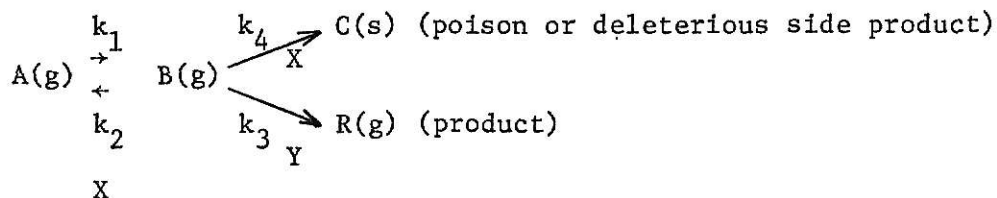
Then at the beginning of the 1950's, Haensel [1] and Ciapetta [2] obtained evidence that certain catalysts composed of more than one material were promoting more than one reaction simultaneously. This discovery opened up an entirely new field in catalytic research; the study of polyfunctional catalysts. A substantial volume of experiments followed which disclosed that a number of heterogeneous catalytic reactions, which proceed by several

distinct reactions steps, could be handled quite easily with these polyfunctional catalysts. Examples of these reactions, most of which are of commercial importance, are:

- (a) Dehydrogenation of cyclohexane to aromatics.
- (b) Isomerization of n-paraffins to branched paraffins.
- (c) Isomerization of alkyl-cyclopentane to cyclohexanes.
- (d) Dehydroisomerization of alkylcyclopentanes to aromatics.
- (e) Dehydrocyclization of paraffins to aromatics.
- (f) Hydrocracking to low molecular weight paraffins.

Before further discussion on polyfunctional catalysis a physical description of a polyfunctional catalyst particle is in order. For the sake of generality consider a particle of arbitrary geometric shape but porous in nature. Now consider the walls of the pores and the external particle surface to be made up of a uniform mixture of several distinct types of active sites, each of which perform separate catalytic functions, i.e. hydrogenation, dehydrogenation, isomerization, cracking, etc. Therefore each type of active site will catalyze a particular step of a polystep reaction.

Several of the polystep reaction examples given above may be represented schematically by



(X and Y are distinct and different catalyst types).

Three salient features of this type of reaction should be noted: First, it is indicative of the complex heterogeneous reactions which may be catalyzed

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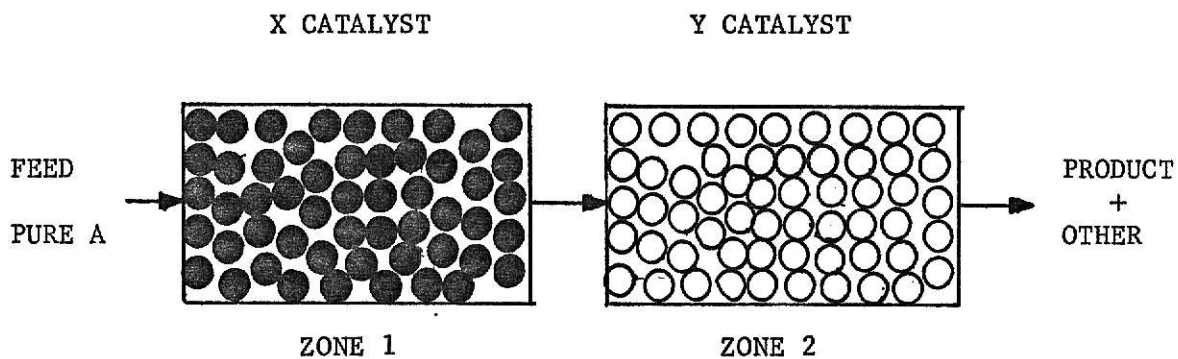


Fig. 1-1(a). Two zone system.

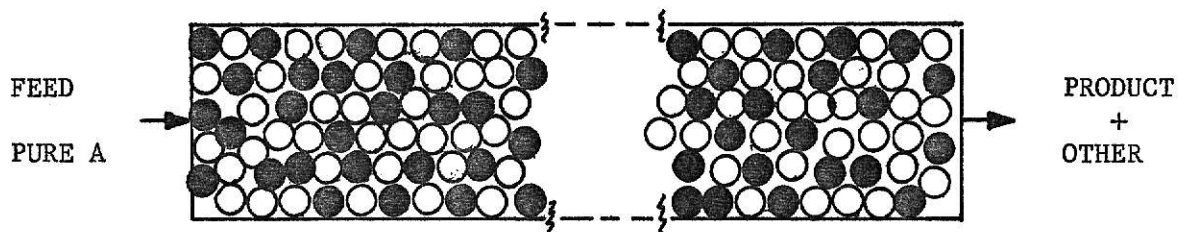


Fig. 1-1(b). Discrete well-mixed system.

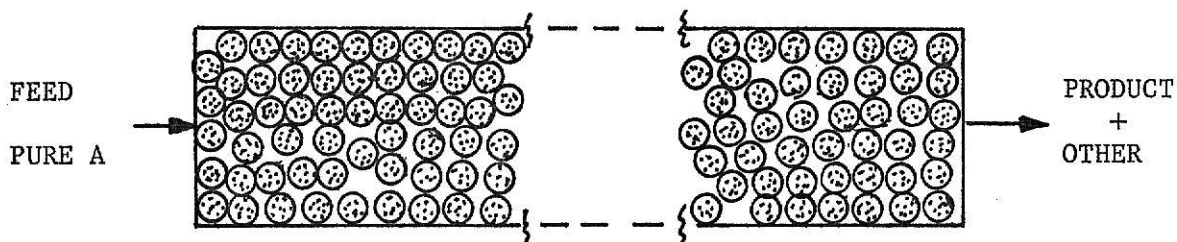


Fig. 1-1(c). Composite or impregnated system.

by polyfunctional catalysts. Second, prior to the previous decade, concerns wishing to produce R for market would have carried out the reaction in two separate fixed bed reaction zones; zone 1 being filled only with catalyst X and zone 2 filled only with catalyst Y (see Fig. 1-1 (a)). Even though this method is still widely used, it has been shown theoretically by a number of investigators that the formulations shown in Fig. 1-1 (b) and (c) are much superior to the former method on the basis of maximum product yield, reactor size or a combination of both. This is especially true when the initial step is reversible with a small equilibrium constant. Finally, it is the same complex reactions which, as a result of simultaneous parallel or consecutive side reactions, may produce a detrimental organic conglomerate called coke (C) or similar compound, which physically deposits on the active sites. This fouling process occurs continuously, reducing the activity of that particular catalyst type until it is economically infeasible to continue the operation without regeneration or replacement of the catalyst.

Therefore, it was deemed necessary, because of the ultimate importance of catalysis and especially this relatively new polyfunctional aspect, to make a theoretical study of the effects which poison buildup have on reactor performance for the various catalyst formulations previously discussed.



## CHAPTER 2

### LITERATURE SURVEY

At this time, to the author's knowledge, there exists no data or solutions with which this work can be compared. However, there are a number of papers which are pertinent. These may be divided into discussions of the performance of unfouled polyfunctional catalysts and discussions of fouling in monofunctional catalysts. Use of these works to provide insight for the present work, which combines ideas from both areas, seems logical.

#### STUDIES OF DUAL-FUNCTIONAL CATALYSTS

Haensel [3] and Ciapetta [4] were probably the two investigators most responsible for the discovery and successful application of polyfunctional catalysts to complex polystep reactions in the petroleum industry. For some time after industrial inception most results on the performance of polyfunctional catalysts were experimental. Theoretical work on the mass transfer and mechanistic properties of these catalysts was lacking. However, in the early 1960's Weisz [5], examined theoretically the mass transport properties of polyfunctional catalysts using his "nontrivial polystep reaction." He demonstrated that, when the initial steps are restricted by thermodynamic equilibrium, a single zone system with the distinct catalyst types in intimate contact, i.e. on the same particle, is much more advantageous than a multi-zone system with pure catalyst in each zone. He also demonstrated experimentally that for a two step reaction the yield of product, for a mechanical compaction of minute particles of both types, tended to increase with decreasing particle size until the component particles reached a size of

approximately 5 microns. The yields obtained with these compacted particles was comparable to that obtained with a porous carrier of one catalyst type impregnated with the other. This illustrates that intraparticle diffusion is negligible for the 5 micron particles making up the catalyst pellet.

Gunn and Thomas [6] published a theoretical work considering several different reaction schemes and two types of catalyst formulations. One type of formulation consisted of a homogeneous mixture of the pure catalyst particles in a single reaction zone (discrete formulation), while the other was the dual functional catalyst, i.e. both catalyst types uniformly dispersed in a single particle (composite formulation). Their analysis considered only diffusion inside the particle and surface reaction as rate controlling and comparisons were made between the two formulations for the different reaction schemes. In all cases the dual-functional catalysts provided better product yields with all other variables being equivalent. It was also illustrated that there is an optimum uniform catalyst fraction for both types and the existence of an axially dependent optimum catalyst fraction was discussed. In all cases the optimum catalyst fraction for the composite catalyst was considerably less than the fraction for the discrete formulation. In essence their analysis was a comparison of two modes of diffusional resistance and the physical "intimateness" of the two types of catalyst sites. In the discrete formulation the initial reactant diffused into the pure porous catalyst and formed an intermediate which consequently had to diffuse out of the particle, be carried by bulk flow to the proximity of a particle of the other catalyst type and diffuse into it and react to form product. The composite formulation, which allows both catalyst sites to be physically as close as possible, eliminates the bulk flow step as well as the diffusion of

intermediate out of a particle of one type and into a particle of the other type, and hence increases the efficiency with which the intermediate can be converted to product. Since this work was intended to be an elementary comparison between the formulations, fouling and nonisothermal effects were not considered.

### FOULING OF MONOFUNCTIONAL CATALYSTS

There are three main classifications of poisoning. The first is called reversible poisoning and is caused by the adsorption of an unwanted specie onto an active site. If the adsorptive forces are not sufficiently strong this specie may desorb and leave the active site completely unaltered. The second class is designated semi-reversible poisoning and is characterized by either a very strong adsorption or the physical deposition of a solid, such as coke or a tarlike substance on the active site. In order for the activity to be restored the catalyst must be regenerated in some way to remove these harmful deposits. Full activity can usually be restored in these cases. The third class is irreversible poisoning and is usually caused by thermal sintering where the catalyst is exposed to an extremely high temperature which alters the structure of the catalyst irreversibly and in consequence also the activity. The former and latter classes have received relatively little theoretical attention since through design modifications in reactors these may be somewhat alleviated. However, the second class, which is probably the most important in industrial significance, has received a substantial amount of both theoretical and experimental treatment.

Considering only gaseous reactions in a fixed bed reactor, there are three ways that poisoning may occur. The first is by the entrance of

impurities in the feed which may then be strongly adsorbed by an active site or sites and consequently lower the relative activity. Another way is by parallel or consecutive reactions of the reactants and intermediate species. An unsaturated conglomerate such as coke can be formed which physically deposits on the active site thereby reducing its activity. Reactor products can undergo unwanted side reactions which produce the same effects. All of these have been studied in some detail and the following discussion will attempt to elucidate the results and conclusions of each analysis.

Maxted et al. [7], performed experiments on the poisoning of platinum and nickel catalysts and found an initial linear decrease in the relative activity of the catalyst with poison concentration. This linear decay became nonlinear, after a certain amount of poison had been added, approaching asymptotically a limiting activity with increasing poison concentration. This type of behavior has been noted in a number of cases (Eley and Rideal [8], Maxted [9]), and an explanation of the inflection point based on random adsorption on a model lattice has been attempted by Herington and Rideal [10]. They assume that the poisoning atom or molecule is large enough to encompass more than one active site at a time, so that initially the poison finds ample open area available to situate. However, after sufficient amounts of poison have been deposited there remains only patches of active sites available and the poison will not be able to deposit quite as freely. Maxted proposed relating the rate constant decay to the poison concentration by an equation of the form

$$k = k_0(1 - \alpha c),$$

where  $k_0$  was the unpoisoned rate constant,  $c$  the poison concentration and  $\alpha$  the slope of the plot of  $k/k_0$  versus  $c$ . This expression is quite reasonable for the initial linear decay which is almost always observed in poisoning

reactions and could represent the entire poisoning curve if the correspondence of poison molecule to active site were one to one.

Wheeler [11] considered diffusion and surface reaction in single cylindrical pores and postulated several different models by which the relative activity decayed with surface area coverage by poison. In the case of nonselective poisoning and slow reaction (i.e. low Thiele modulus) the relative activity decayed linearly with surface coverage. For nonselective poisoning and rapid reaction (i.e. high Thiele modulus) the relative activity drops according to the relation,  $F = \sqrt{1 - \alpha}$ , where  $\alpha$  is the fraction of surface coverage. For a number of reduced metal catalysts he noted that the poison might be preferentially adsorbed at the pore mouth and continue progressively along the pore length. In these instances a small amount of surface coverage resulted in large decrease in activity. The relationship is hyperbolic,  $F = (1 + \alpha h_0)^{-1}$ , where  $h_0$  is the unpoisoned Thiele modulus. For a fast reaction (large  $h_0$ ), the activity could be reduced greatly for a very small surface coverage.

It suffices to say that even though Wheeler considered only poisoning of a single pore the relationships derived by him provide at least a valid starting point when looking at models of fouling in a particle.

Anderson and Whitehouse [12] have applied Wheeler's relationships to stationary reactor beds. Empirical models relating poison concentration to bed length were chosen and then these models were related, using other empirical models, to the decay of relative activity with poison concentration. Their results for their mode of poisoning, seem to be quite inclusive of what would happen industrially. However, it is evident from this author's readings that their assumption that most poisons enter with the feed is not

strictly true. Because of recent filter technology and feed pretreatment a majority of the poisons which used to appear in feedstocks have been eliminated. The main sources of poison now are more deleterious side reactions involving reactants, intermediates or products in the reactor.

Froment and Bischoff [13] were probably the first to make a theoretical study of the dynamics of poison formation by an unwanted side reaction in a fixed bed reactor. Their analysis considered the reaction rate coefficient, which they related directly to the poison content of the catalyst, as a measure of catalytic activity. Previously, the poison content of a catalyst, and hence activity, had been related to process time (Voorhies et al. [14]), and as one could imagine this was not in any way general and any conclusions arrived at were applicable only to the particular reacting system under investigation. In the study of Froment and Bischoff the rate constant was related to the poison concentration by both exponential and hyperbolic models. Both models were mainly empirical in nature but the hyperbolic model has some theoretical backing from Langmuir-Hinshelwood adsorption concepts. Their system dealt with poison formation by both parallel and consecutive reactions in an isothermal fixed bed reactor with negligible diffusion effects. The real importance of this paper was in the method of relating activity to poison concentration when the poison was actually being formed inside the reactor.

Smith et al. [15] studied the transient effects of fouling on catalyst pellets in which diffusion resistance was important. Their analysis considered surface reaction and intraparticle diffusion rates as being important and utilized a linear rate constant decay with poison concentration. Several mechanisms of fouling were studied: self-fouling; either by a parallel or

series reaction path and, reaction by an impurity in the feed, all of which produced a substance which deposited on and completely fouled the active site until regeneration. Slow fouling was assumed which allowed a pseudo-steady state solution to be obtained for the intraparticle diffusion equations. This is logical since the gaseous concentration profiles would develop much more rapidly in the particle than a significant change in catalyst activity (i.e. the time required for the development of gaseous concentration profiles into a pseudo-steady form would be much less than the time required for a change in the catalyst activity). The same type of argument was applied in neglecting the accumulation terms in the concentration balances on the bed. Therefore, since the boundary layer resistance around the particles was assumed negligible, pseudo-steady profiles of the surface concentrations of the gaseous species for very small times could be calculated. They were able to generate effectiveness factors, based on zero time and surface conditions, which varied mainly with process time and a Thiele modulus derived from the rate constant and diffusivity of the main reactant.

Considering first-order isothermal reactions, the following was concluded about the three types of fouling processes. For a series form of self fouling, a catalyst with the lowest intraparticle diffusion resistance gives the maximum activity for any process time. In contrast, for parallel self-fouling a catalyst with an intermediate diffusion resistance is less easily deactivated and can give a higher conversion to the desired product. Results for the independent fouling type showed that least deactivation will occur in a catalyst for which there is a minimum diffusion resistance for the main reactant and maximum diffusion resistance for the impurity into the particle. One minor discrepancy which came to this author's attention in the mathematical

development was the choice of a dimensionless B concentration. It appears that from the definition used by Smith this analysis would be useless when a pure feed is introduced to the reactor.

Murakami et al. [16], made both an experimental and theoretical analysis of intraparticle diffusion effects on catalyst fouling which was slanted primarily toward differential reactor studies. Several new points were introduced by these authors. First they considered fast fouling so that the transient terms on the gaseous species were included and also they considered boundary layer gas film resistance as being important. Parallel and consecutive poisoning schemes, which are known to occur industrially were analyzed theoretically. The disproportionation of toluene was a representative parallel scheme while dehydrogenation of primary alcohols was chosen to represent the series case. The bulk of their fouling studies were presented in the form of effectiveness factors which were defined as the ratio of the actual rate of reaction over the zero time reaction rate at bulk stream conditions. These are mainly functions of Biot number, process time and Thiele modulus.

Their results can be summarized as follows: for the parallel reaction scheme, poison laydown is fairly uniform for low values of Thiele modulus but becomes almost shell progressive in nature at high values of Thiele modulus. The series mechanism doesn't approximate the shell nature nearly as well for the same parameter values.

For the parallel scheme increasing diffusional resistance increases the rate of approach to complete fouling. This trend was also evident for the series reaction. The effect of selectivity, defined as poison rate constant divided by main reaction rate constant, for the series reaction scheme was to



decrease the effectiveness factor much more rapidly with increasing value of selectivity. Increasing the Biot number brought about consistent decreases in effectiveness factors with dimensionless time.

In their experimental work they found for the parallel case that for low diffusion resistance coke deposits nearly uniformly throughout the pellet while at high diffusion resistance the shell-progressive model was quite evident (a very easily discernible boundary between coked and uncoked parts). In the series case coke tended to deposit from the inner part of the particle for low Thiele modulus but for high Thiele modulus there was more deposition at the outer part of the particle. This, they say, may be a result of the fast fouling consideration since for slow fouling Smith has shown that the coke may still be deposited from inside out even with high Thiele modulus.

This work along with that of Ozawa and Bischoff [17] were the first to obtain experimental verification of their theoretical analysis.

This survey has outlined the analysis and conclusions of the main papers in all areas affecting the proposed research. Although work has not been forthcoming integrating the concepts of intraparticle fouling and polyfunctional catalysts it is reasonable to proceed by logical extension from the works done in simpler cases.

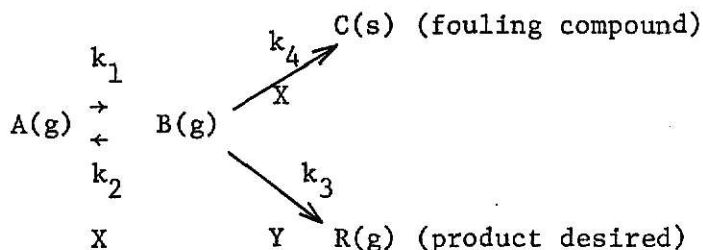
## CHAPTER 3

### THEORETICAL DEVELOPMENT

#### ORGANIZATION

The purpose of this thesis is to investigate the effects of catalyst poisoning on the discrete and compounded types of catalyst formulations. Therefore in each case transient mass balances have been written for the single particle and these balances incorporated into the mass balances for the stationary bed. The first and second sections consider the particle and bed balances for the discrete case. The third and fourth sections, respectively, treat the particle and bed balances for the compounded case. In the fifth section bed balances are formulated for the case where no intraparticle diffusion resistance is assumed. This final case should provide an upper limit on product yield and should aid in some valuable comparisons. The sixth section discusses the choice of a particular fouling model and section seven summarizes the pertinent equations for all cases considered.

Throughout this work a single polystep reaction scheme of the form



has been considered. The reasons for this type of scheme are manifold:

1) Weisz's criterion [5] for a non-trivial polystep reaction is satisfied if the ratio  $k_2/k_1$  is large enough, 2), the catalysts X and Y are physically distinct and catalyze separate reaction steps, and 3), the fouling compound C is actually formed as a product of the reaction taking place inside the

particle.

Inspection of the above reaction scheme shows that catalyst X is the only catalyst promoting the fouling compound formation. Of course there are several choices available here as to which catalyst or both (possibly) causes the fouling compound formation. Assuming that steric effects are not important, then Haensel [18] has shown that site-selective poisoning is indeed a reality.

The main reason for choosing only the X catalyst is that in a large number of petro-chemical reactions the first reaction step is usually an intermediate forming hydrogenation or dehydrogenation step which is catalyzed by metals such as Pt, Pd, Ni, etc. It is these partially or unsaturated intermediates which tend to become an agglomeration capable of doing the poisoning. The mathematics would have been no more tedious if Y had also been considered a catalytic agent for poison formation.

### 3-1. MASS BALANCES ON SINGLE PARTICLES--DISCRETE PARTICLE CASE

In a quantitative study of the effects of poisoning on mass transport in the two types of catalyst formulation, analysis must begin at the most basic level and several simplifying assumptions have been applied in the following analysis. These are:

- (1) Due to the types of catalyst being treated transport is accomplished mainly by Knudsen diffusion.
- (2) Isothermal pellets and overall system.
- (3) Each catalyst pellet has a homogeneous deposition of catalyst on the pore surfaces (i.e. no segregation of catalyst and no large dead spots on pore walls).
- (4) Catalyst particles are spherical.
- (5) Gas density remains constant.
- (6) Pore diffusion and surface reaction are controlling.
- (7) Each carrier is as consistently alike as possible in physical properties such as pore volume, pore size distribution, density, etc.
- (8) The rate of poison deposition is quite slow compared with other reaction rates.
- (9) Catalyst particles and bed are homogeneous mediums.

Recalling the basic reaction scheme, the following transient mass balances for the discrete formulation must be made.

- (i) Balance on A in X particle.
- (ii) Balance on B in X particle.
- (iii) Balance on B in Y particle.
- (iv) Balance on R in Y particle.

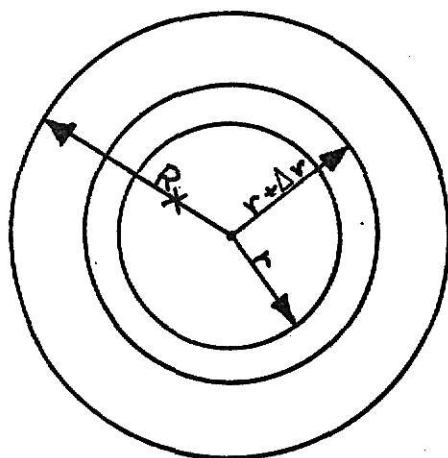


Fig. 3-1. Schematic representation of X catalyst particle.

(v) Balance on C in X particle.

Therefore, considering the spherical shell of thickness  $\Delta r$  in Fig. 3-1 we have

Specie A:

$$\left\{ \begin{array}{l} \text{molar flux} \\ \text{in @ } r = r \end{array} \right\} - \left\{ \begin{array}{l} \text{molar flux out} \\ \text{@ } r = r + \Delta r \end{array} \right\} + \left\{ \begin{array}{l} \text{rate of production} \\ \text{by chemical reaction} \end{array} \right\} = \left\{ \begin{array}{l} \text{rate of ac-} \\ \text{cumulation} \\ \text{in voidage} \end{array} \right\}$$

$$(4\pi r^2 N_{A_r}) \Big|_r - (4\pi r^2 N_{A_r}) \Big|_{r+\Delta r} + 4\pi r^2 \Delta r \rho_c R_A = \frac{\partial}{\partial t} (4\pi r^2 \Delta r e C_A) \quad (3-1.1)$$

$R_A$  is the rate of production of A per unit weight of catalyst X. Assuming first order kinetics  $R_A$  may be expressed as

$$R_A = k_2 C_{B(X)} - k_1 C_A \quad (3-1.2)$$

Incorporation of (3-1.1) into (3-1.2) and proceeding through limiting forms we obtain

$$e \frac{\partial C_A}{\partial t} = - \frac{1}{r^2} \nabla_r (r^2 N_{A_r}) + \rho_c (k_2 C_{B(X)} - k_1 C_A) \quad (3-1.3)$$

From Fick's first law of diffusion, the molar flux of a specie at any point  $r$  can be related to the concentration gradient of that specie at the same point by

$$N_{A_r} = - D_A \cdot \nabla_r C_A \quad (3-1.4)$$

where  $D_A$  is the effective diffusivity of specie A in particle X. Physically,  $N_A$  will be negative meaning that A is decreasing and hence diffusing from the outer surface to its center. Assuming  $D_A$  is constant Eq. (3-1.4) may be incorporated into Eq. (3-1.3) to yield

$$e \cdot \frac{\partial C_A}{\partial t} = D_A \nabla_r^2 C_A + \rho_c (k_2 C_{B(X)} - k_1 C_A) \quad (3-1.5)$$

Specie B in X particle:

$$\frac{\partial}{\partial t} (4\pi r^2 \Delta r e C_{B(X)}) = (4\pi r^2 N_{B_r}) \Big|_r - (4\pi r^2 N_{B_r}) \Big|_{r+\Delta r} + 4\pi r^2 \Delta r \rho_c R_{B(X)} \quad (3-1.6)$$

where

$$R_{B(X)} = k_1 C_A - k_2 C_{B(X)} - k_4 C_{B(X)} \quad (3-1.7)$$

By assuming that the poison formation rate is quite small compared with the other rates, the right hand side of Eq. (3-1.6) simplifies to

$$e \cdot \frac{\partial C_{B(X)}}{\partial t} = D_{B(X)} \nabla_r^2 C_{B(X)} + \rho_c (k_1 C_A - k_2 C_{B(X)}) \quad (3-1.8)$$

Specie C in X particle:

Since the poison C is a solid, there will only be two terms in the mass balance. Presupposing no solid-solid diffusion,

$$\left\{ \begin{array}{l} \text{rate of accumulation of} \\ \text{solid C on pore walls} \end{array} \right\} = \left\{ \begin{array}{l} \text{rate of production} \\ \text{by chemical reaction} \end{array} \right\}$$

$$\frac{\partial}{\partial t} [(4\pi r^2 \Delta r \rho_c) C_c] = \rho_c k_4 C_{B(X)} (4\pi r^2 \Delta r) \quad (3-1.9)$$

In this balance it has been supposed that once B strikes an X site and forms C, that site is irreversibly poisoned until bed regeneration procedures are initiated. Equation (3-1.9) may be simplified to give

$$\frac{\partial C_c}{\partial t} = k_4 C_{B(X)} \quad (3-1.10)$$

It may be noted that the units for specie C are gram-moles of C per gram of catalyst which is different from the gram-mole per cubic centimeter dimension of the other constituents. These units for the solid poison facilitate much easier analysis of catalyst poison content and provide a sharply defined boundary upon which to base regeneration procedures.

Mass balances for species in the Y particle will be made in the same way, but noting that  $R_Y$  may not necessarily equal  $R_X$ .

Specie B in Y particle:

$$\frac{\partial}{\partial t} (4\pi r^2 \Delta r c_{B(Y)}) = (4\pi r^2 N_{B_r}) \Big|_r - (4\pi r^2 N_{B_r}) \Big|_{r+\Delta r} + 4\pi r^2 \Delta r \rho_c R_{B(Y)} \quad (3-1.11)$$

where  $R_{B(Y)}$  may be expressed as

$$R_{B(Y)} = -k_3 C_{B(Y)} \quad (3-1.12)$$

Incorporation of (3-1.12) into (3-1.11) and simplification gives

$$e \cdot \frac{\partial C_{B(Y)}}{\partial t} = D_{B(Y)} \nabla_r^2 C_{B(Y)} - \rho_c k_3 C_{B(Y)} \quad (3-1.13)$$

Specie R in Y particle:

$$e \cdot \frac{\partial C_R}{\partial t} = D_R \nabla_r^2 C_R + \rho_c k_3 C_{B(Y)} \quad (3-1.14)$$

The accumulation terms for the gaseous species may be discarded by using Smith's [15] argument that the gaseous concentration profiles attain pseudo-steady form much faster than a change in catalyst activity. Therefore (3-1.5, 8, 13 and 14) become



$$D_A \nabla_r^2 C_A + \rho_c (k_2 C_{B(X)} - k_1 C_A) = 0 \quad (3-1.15)$$

$$D_{B(X)} \nabla_r^2 C_{B(X)} + \rho_c (k_1 C_A - k_2 C_{B(X)}) = 0 \quad (3-1.16)$$

$$D_{B(Y)} \nabla_r^2 C_{B(Y)} - \rho_c k_3 C_{B(Y)} = 0 \quad (3-1.17)$$

$$D_R \nabla_r^2 C_R + \rho_c k_3 C_{B(Y)} = 0 \quad (3-1.18)$$

In order to incorporate the effects of catalyst poisoning into the above mass balances, it will be assumed that the reaction rate constants decay according to some predefined function of poison concentration

$$k_i = k_i^0 \phi_i \quad (3-1.19)$$

The  $k_i^0$  are rate constants at zero poison deposition and  $\phi_i$  are dimensionless functions of poison concentration.

Substitution of (3-1.19) into (3-1.10, 15, 16, 17 and 18) yields

$$D_A \nabla_r^2 C_A + \rho_c (k_2^0 \phi_2 C_{B(X)} - k_1^0 \phi_1 C_A) = 0 \quad (3-1.20)$$

$$D_{B(X)} \nabla_r^2 C_{B(X)} + \rho_c (k_1^0 \phi_1 C_A - k_2^0 \phi_2 C_{B(X)}) = 0 \quad (3-1.21)$$

$$D_{B(Y)} \nabla_r^2 C_{B(Y)} - \rho_c k_3^0 \phi_3 C_{B(Y)} = 0 \quad (3-1.22)$$

$$D_R \nabla_r^2 C_R + \rho_c k_3^0 \phi_3 C_{B(Y)} = 0 \quad (3-1.23)$$

$$\frac{\partial C_c}{\partial t} = k_4^0 \phi_4 C_{B(X)} \quad (3-1.24)$$





The analytical, pseudo-steady solutions may be obtained quite easily using an operator method presented in Mickley, Sherwood and Reed [19]. These solutions are,<sup>†</sup>

$$y_A = y_{A_s} \cdot \left\{ \frac{\gamma_2}{\gamma_1 + \gamma_2} + \frac{\gamma_1}{\gamma_1 + \gamma_2} \cdot \frac{\sinh(\lambda_1 \xi)}{\sinh(\lambda_1)} \cdot \frac{1}{\xi} \right\} \\ - y_{B_s} \cdot \left\{ \frac{-\gamma_2}{\gamma_1 + \gamma_2} + \frac{\gamma_2}{\gamma_1 + \gamma_2} \cdot \frac{\sinh(\lambda_1 \xi)}{\sinh(\lambda_1)} \cdot \frac{1}{\xi} \right\} \quad (3-1.36)$$

$$y_{B(X)} = y_{B_s} \cdot \left\{ \frac{\gamma_1}{\gamma_1 + \gamma_2} + \frac{\gamma_2}{\gamma_1 + \gamma_2} \cdot \frac{\sinh(\lambda_1 \xi)}{\sinh(\lambda_1)} \cdot \frac{1}{\xi} \right\} \\ - y_{A_s} \cdot \left\{ \frac{-\gamma_1}{\gamma_1 + \gamma_2} + \frac{\gamma_2}{\gamma_1 + \gamma_2} \cdot \frac{\sinh(\lambda_1 \xi)}{\sinh(\lambda_1)} \cdot \frac{1}{\xi} \right\} \quad (3-1.37)$$

$$y_{B(Y)} = y_{B_s} \cdot \frac{\sinh(\lambda_2 \xi)}{m \cdot \sinh(\lambda_2/m)} \cdot \frac{1}{\xi} \quad (3-1.38)$$

$$y_R = y_{R_s} + y_{B_s} \cdot \left\{ 1 - \frac{\sinh(\lambda_2 \xi)}{m \sinh(\lambda_2/m)} \cdot \frac{1}{\xi} \right\} \quad (3-1.39)$$

These pseudo-steady solutions will provide boundary conditions for the numerical treatment of the mass balance equations when the  $\phi_i$ 's become designated functions of poison concentration.

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<sup>†</sup>The complete solutions are available in Appendix (A-1).

### 3.2 MASS BALANCES ON STATIONARY BED VOLUME ELEMENT--DISCRETE PARTICLE CASE.

Once balances have been obtained for the single particles it is logical to enlarge our study by considering balances over a differential element of the stationary bed. It is the solutions of these equations which will provide the basis for most of the comparisons of the two catalyst formulations. Several simplifying assumptions which will aid in conducting the analysis are:

- (1) Isothermal conditions.
- (2) Plug flow.
- (3) Regardless of axial position, there is a constant weight fraction of X over any cross section.

Utilizing Fig. 3-2, transient balances may be made on all gaseous species.

Balance on A in bed:

$$\left\{ \begin{array}{c} \text{rate of accumulation} \\ \text{in } \Delta V \end{array} \right\} = \left\{ \begin{array}{c} \text{rate in by} \\ \text{convection} \end{array} \right\} - \left\{ \begin{array}{c} \text{rate out by} \\ \text{convection} \end{array} \right\} + \left\{ \begin{array}{c} \text{rate of production} \\ \text{by chemical reaction} \end{array} \right\}$$

$$\frac{\partial}{\partial t} (\pi R^2 \Delta z \epsilon_B C_{A_s}) = U \pi R^2 C_{A_s} \Big|_z - U \pi R^2 C_{A_s} \Big|_{z+\Delta z} + \bar{R}_A \cdot \pi R^2 \Delta z \quad (3-2.1)$$

where  $\bar{R}_A$  is the rate of production of A per unit reactor volume.

Paralleling both Thomas' [6] and Smith's [15] work use will be made of the diffusion rate of the component in at the particle surface as a measure of the rate of reaction of that component. Therefore,

$$\begin{aligned} \text{rate of production} \\ \text{of A per particle} \end{aligned} = r_A = 4\pi R_X^2 N_A \Big|_{r=R_X} = -4\pi R_X^2 D \frac{\partial C_A}{\partial r} \Big|_{r=R_X} \quad (3-2.2)$$

Since we have two different types of catalyst particles in the bed we need to have an expression relating the number of X and Y catalyst particles per unit

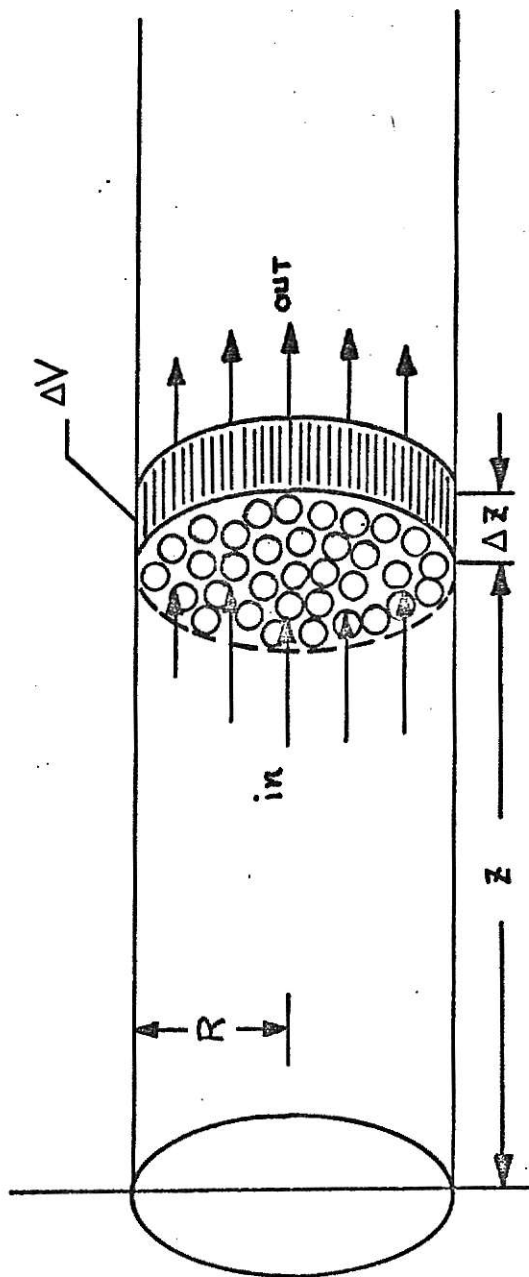


Fig. 3-2. Schematic representation of stationary packed bed with enlarged differential volume element.

reactor volume to physically measurable properties such as bed and catalyst density, particle size and weight fraction of catalyst per unit reactor volume. The general expression for the total number of particles per unit reactor volume is

$$N = N_X + N_Y = \frac{a\rho_B}{\frac{4}{3}\pi R_X^3 \rho_c} + \frac{(1-a)\rho_B}{\frac{4}{3}\pi \frac{R_X^3}{m^3} \cdot \rho_c} \quad (3-2.3)$$

or

$$N = \frac{3\rho_B}{4\pi R_X^3 \rho_c} [a + m^3(1-a)] \quad \text{where } m = R_X/R_Y. \quad (3-2.4)$$

It may be noted that for  $m = 1.0$  the result agrees with that obtained by Smith [15]. Equation (3-2.3) is important in that the numbers of the respective particles have been separated for use in the mass balances.

$$N_X = \frac{a\rho_B}{\frac{4}{3}\pi R_X^3 \rho_c} ; \quad N_Y = \frac{(1-a)m^3 \rho_B}{\frac{4}{3}\pi R_X^3 \rho_c} \quad (3-2.5(a), (b))$$

Combining the rate of production per particle with the number of particles per unit reactor volume, an expression for  $\tilde{R}_A$  may be obtained.

$$\begin{aligned} \tilde{R}_A &= N_X \cdot r_A = -4\pi R_X^2 D \cdot \frac{a\rho_B}{\frac{4}{3}\pi R_X^3 \rho_c} \cdot \left. \frac{\partial C_A}{\partial r} \right|_{r=R_X} \\ \tilde{R}_A &= -\frac{3a\rho_B D}{R_X \rho_c} \cdot \left. \frac{\partial C_A}{\partial r} \right|_{r=R_X} \end{aligned} \quad (3-2.6)$$

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<sup>†</sup>Complete derivation given in Appendix A-2.

Incorporation of Eq. (3-2.6) into Eq. (3-2.1) and simplification yields

$$\epsilon_B \frac{\partial C_{A_s}}{\partial t} + U \frac{\partial C_{A_s}}{\partial z} + \frac{3a\rho_B^D}{\rho_c R_X} \cdot \frac{\partial C_A}{\partial r} \bigg|_{r=R_X} = 0 \quad (3-2.7)$$

Balance on B in bed:

We know that specie B reacts in both types of particles so the only difference in the mass balances from that of specie A will be the expression for  $\tilde{R}_B$ . Whereas  $\tilde{R}_A$  contained only one term,  $\tilde{R}_B$  will contain two terms  $\tilde{R}_{B(X)}$  and  $\tilde{R}_{B(Y)}$ , defined by

$$\tilde{R}_{B(X)} = N_X \cdot r_{B(X)} = N_X \cdot 4\pi R_X^2 \cdot N_{B_X} \bigg|_{r=R_X} \quad (3-2.8)$$

and

$$\tilde{R}_{B(Y)} = N_Y \cdot r_{B(Y)} = N_Y \cdot 4\pi \frac{R_X^2}{m^2} N_{B_Y} \bigg|_{r=R_X/m} \quad (3-2.9)$$

Therefore, the total production of B per unit reactor volume is

$$\begin{aligned} \tilde{R}_B = \tilde{R}_{B(X)} + \tilde{R}_{B(Y)} &= \frac{-3\rho_B^D}{R_X \rho_c} \cdot \left\{ a \cdot \frac{\partial C_{B(X)}}{\partial r} \bigg|_{r=R_X} \right. \\ &\quad \left. + m(1-a) \frac{\partial C_{B(Y)}}{\partial r} \bigg|_{r=R_X/m} \right\} \end{aligned} \quad (3-2.10)$$

and the overall balance becomes



$$\epsilon_B \frac{\partial C_{B_s}}{\partial t} + U \frac{\partial C_{B_s}}{\partial z} + \frac{3\rho_B D}{R_X \rho_c} \cdot \left\{ a \frac{\partial C_{B(X)}}{\partial r} \right\} \bigg|_{r=R_X} + m(1-a) \frac{\partial C_{B(Y)}}{\partial r} \bigg|_{r=R_X/m} \} = 0 \quad (3-2.11)$$

Balance on Specie R:

Since R is produced only in the Y particle the only new term in the mass balance will be the expression for  $\dot{R}_R$ .

$$\dot{R}_R = N_Y \cdot 4\pi R_Y^2 \cdot N_R \bigg|_{r=R_Y} = N_Y \cdot 4\pi \frac{R_X^2}{m^2} \cdot N_R \bigg|_{r=R_X/m}$$

$$\dot{R}_R = \frac{-3(1-a)mD\rho_B}{R_X \rho_c} \cdot \frac{\partial C_R}{\partial r} \bigg|_{r=R_X/m} \quad (3-2.12)$$

The overall mass balance then becomes

$$\epsilon_B \frac{\partial C_{R_s}}{\partial t} + U \frac{\partial C_{R_s}}{\partial z} + \frac{3m(1-a)D\rho_B}{R_X \rho_c} \cdot \frac{\partial C_R}{\partial r} \bigg|_{r=R_X/m} = 0 \quad (3-2.13)$$

Utilizing the slow fouling assumption as was done previously for the single particle, one may argue that the accumulation terms be dropped in the above equations on the basis that the bed profiles will assume a pseudo-steady form much more rapidly than a measurable change in catalytic activity. Following this line of reasoning, Eqs. (3-2.7, 11 and 13) become

$$U \frac{\partial C_{A_s}}{\partial z} + \frac{3\rho_B aD}{R_X \rho_c} \cdot \frac{\partial C_A}{\partial r} \bigg|_{r=R_X} = 0 \quad (3-2.14)$$

$$U \frac{\partial C_{B_s}}{\partial z} + \frac{3\rho_B D}{R_X \rho_c} \cdot \left\{ a \frac{\partial C_{B(X)}}{\partial r} \right\}_{r=R_X} + m(1-a) \frac{\partial C_{B(Y)}}{\partial r} \Big|_{r=R_X/m} \} = 0 \quad (3-2.15)$$

$$U \frac{\partial C_{R_s}}{\partial z} + \frac{3m(1-a)D\rho_B}{R_X \rho_c} \cdot \frac{\partial C_R}{\partial r} \Big|_{r=R_X/m} = 0 \quad (3-2.16)$$

The boundary conditions on these equations may be stated quite simply:

Feed pure A to the reactor (i.e.,  $C_{A_s} = C_{A_0}$  @  $z = 0.0$  and  $C_{B_s} = C_{R_s} = 0$  @  $z = 0.0$ ).

The above equations may be solved for very small times by using the analytical expressions for the derivatives obtained from the single particle solutions. Before obtaining these solutions it is convenient to introduce dimensionless variables.

$$\bar{z} = \frac{z}{z_d}; \quad y_{A_s} = \frac{C_{A_s}}{C_{A_0}}; \quad y_{B_s} = \frac{C_{B_s}}{C_{A_0}}; \quad y_{R_s} = \frac{C_{R_s}}{C_{A_0}} \quad (3-2.17)$$

Substitution of these expressions into Eqs. (3-2.14, 15 and 16) and simplification yields,

$$\frac{\partial y_{A_s}}{\partial \bar{z}} + 3a \frac{\partial y_A}{\partial \xi} \Big|_{\xi=1} = 0; \quad y_{A_s} = 1.0 \text{ @ } \bar{z} = 0.0 \quad (3-2.18)$$

$$\frac{\partial y_{B_s}}{\partial \bar{z}} + 3\left\{ a \frac{\partial y_{B(X)}}{\partial \xi} \right\}_{\xi=1} + m(1-a) \frac{\partial y_{B(Y)}}{\partial \xi} \Big|_{\xi=\frac{1}{m}} \} = 0;$$

$$y_{B_s} = 0 \text{ @ } \bar{z} = 0.0 \quad (3-2.19)$$

$$\left. \frac{\partial y_{R_s}}{\partial \bar{z}} + 3m(1-a) \frac{\partial y_R}{\partial \xi} \right|_{\xi = \frac{1}{m}} = 0; y_{R_s} = 0 @ \bar{z} = 0.0 \quad (3-2.20)$$

Analytical solutions of these equations at small times may be obtained quite easily by substitution of the gradients obtained from Eqs. (3-1.36, 37, 38 and 39) and direct integration. These solutions are<sup>†</sup>

$$y_{A_s} = \frac{1}{(m_2 - m_1)} \{ (m_2 + w_1) \exp(m_1 \bar{z}) - (m_1 + w_1) \exp(m_2 \bar{z}) \} \quad (3-2.21)$$

$$y_{B_s} = \frac{w_1}{(m_2 - m_1)} \{ \exp(m_2 \bar{z}) - \exp(m_1 \bar{z}) \} \quad (3-2.22)$$

$$y_{R_s} = 1 - \frac{1}{(m_2 - m_1)} \{ m_2 \exp(m_1 \bar{z}) - m_1 \exp(m_2 \bar{z}) \} \quad (3-2.23)$$

Inspection of these pseudo-steady or no-fouling solutions shows that the product R is a complex function of a, the weight fraction of catalyst X per unit volume of reactor. Making judicious choices for the rate constants, effective diffusivity, and other physical properties, an optimal weight fraction, which maximizes the product concentration at the reactor exit can be obtained. This can either be done by classical calculus or by a one-dimensional search technique, of which there are many [20]. Table 3-1 and Fig. 3-3 show the optimal fractions for various choices of parameters.

These solutions will also provide additional necessary conditions needed for the numerical solution as fouling becomes important. This concludes the development for the discrete formulation with the exception of choosing a

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<sup>†</sup>Detailed solutions may be found in Appendix A-3.

fouling model,  $\phi$ , for the particle equations. This will be accomplished in a later section after the composite particle and negligible diffusion resistance developments are made.

## DISCRETE FORMULATION

- 1  $k_1^0 = 0.2$ ;  $k_2^0 = 2.0$ ;  $k_3^0 = 0.2$ ;  $a = 0.30$ ;  $y_{R_{MAX}} = 0.6266$
- 2  $k_1^0 = 0.1$ ;  $k_2^0 = 1.0$ ;  $k_3^0 = 0.2$ ;  $a = 0.34$ ;  $y_{R_{MAX}} = 0.5738$
- 3  $k_1^0 = 0.2$ ;  $k_2^0 = 4.0$ ;  $k_3^0 = 0.2$ ;  $a = 0.26$ ;  $y_{R_{MAX}} = 0.4343$

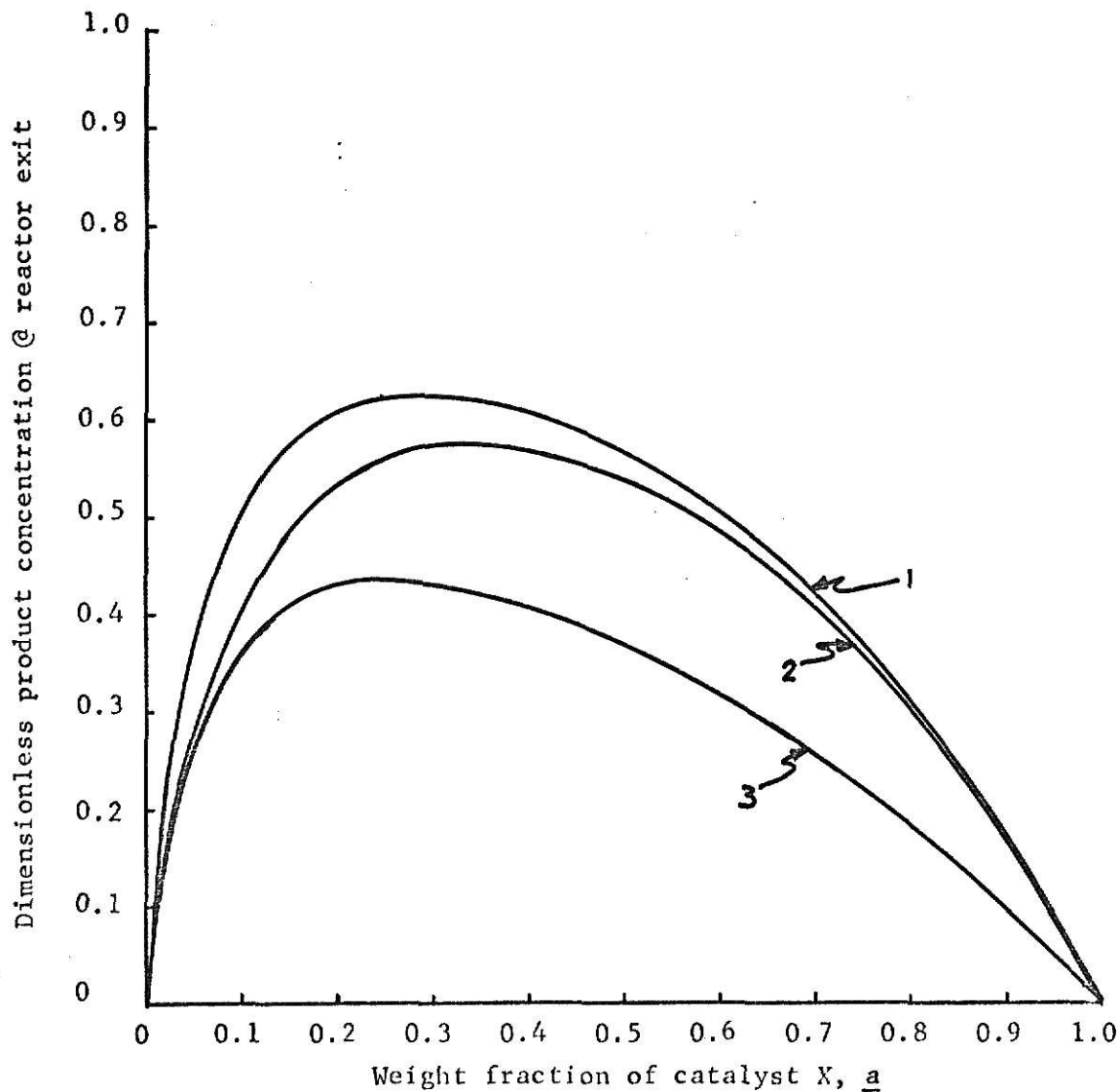


Fig. 3-3. Optimum catalyst fractions for various choices of rate constants.

TABLE 3-1. Optimum catalyst fractions and maximum product mole fraction for various choices of rate constants.

DISCRETE PARTICLES					
#	$k_1^0$ (cc/sec-gr.cat)	$k_2^0$ (cc/sec-gr.cat)	$k_3^0$ (cc/sec-gr.cat)	a	$y_{R_s}(\text{max.})$
1	0.2	4.0	0.2	0.26	0.4343
2	0.2	2.0	0.2	0.30	0.6266
3	0.1	1.0	0.1	0.28	0.4208
4	0.2	1.0	0.1	0.28	0.6441
5	0.1	2.0	0.2	0.30	0.3978
6	0.1	1.0	0.2	0.34	0.5738
7	0.2	4.0	0.1	0.20	0.2943
8	0.2	4.0	0.4	0.32	0.5804
9	0.5	4.0	0.1	0.20	0.5630
10	0.5	4.0	0.2	0.24	0.7431
11	1.0	4.0	0.1	0.18	0.7834

### 3-3. MASS BALANCES ON SINGLE PARTICLES--COMPOSITE PARTICLE CASE.

In generating the transient mass balances for the composite particles there is one distinct and most important difference between the composite and discrete formulations. The composite particle has sites of both the X catalyst and Y catalyst mechanically compacted or chemically impregnated into one particle. Therefore, in the following treatment it will be assumed that each particle has a constant weight fraction of catalyst X regardless of position in the bed. With this and the assumptions previously stated for the discrete case in mind, analysis of the composite particle may begin. Consider again the schematic particle of Fig. 3-1.

Specie A:

$$\begin{array}{l} \text{rate of} \\ \{ \text{accumulation} \} \\ \text{in spherical} \\ \text{shell} \end{array} = \begin{array}{l} \text{rate of} \\ \{ \text{diffusion} \} \\ \text{into shell} \end{array} - \begin{array}{l} \text{rate of} \\ \{ \text{diffusion} \} \\ \text{out of} \\ \text{shell} \end{array} + \begin{array}{l} \text{rate of} \\ \{ \text{production} \} \\ \text{by chemical} \\ \text{reaction} \end{array}$$

$$\frac{\partial}{\partial t} (4\pi r^2 \Delta r \rho C_A) = 4\pi r^2 N_A \Big|_r - 4\pi r^2 N_A \Big|_{r+\Delta r} + 4\pi r^2 \Delta r \rho_c \epsilon R_A \quad (3-3.1)$$

Where  $R_A$  is the molar rate of production of A per unit weight of catalyst, and  $\epsilon$  is the weight fraction of catalyst X per particle. Assuming first order kinetics  $R_A$  may be expressed as

$$R_A = k_2 C_B - k_1 C_A, \quad (3-3.2)$$

and using Fick's first law as before, Eq. (3-3.1) can be simplified to

$$\epsilon \frac{\partial C_A}{\partial t} = D_A \nabla^2 C_A + \rho_c \epsilon (k_2 C_B - k_1 C_A) \quad (3-3.3)$$

Specie B:

$$e \frac{\partial C_B}{\partial t} = D_B \nabla_r^2 C_B + \rho_c k_1 \epsilon C_A - (k_2 \epsilon + k_3 (1-\epsilon)) \rho_c C_B - \rho_c k_4 \epsilon C_B \quad (3-3.4)$$

Since poison formation is quite slow the last term in Eq. (3-3.4) may be neglected, being much smaller in magnitude than the other terms. Thus Eq.

(3-3.4) becomes

$$e \frac{\partial C_B}{\partial t} = D_B \nabla_r^2 C_B + \rho_c k_1 \epsilon C_A - (k_2 \epsilon + k_3 (1-\epsilon)) \rho_c C_B \quad (3-3.5)$$

Specie R:

$$e \frac{\partial C_R}{\partial t} = D_R \nabla_r^2 C_R + k_3 (1-\epsilon) \rho_c C_B \quad (3-3.6)$$

Specie C:

$$\left\{ \begin{array}{c} \text{rate of accumulation} \\ \text{on solid} \end{array} \right\} = \left\{ \begin{array}{c} \text{rate of production} \\ \text{by chemical reaction} \end{array} \right\}$$

$$\frac{\partial (4\pi r^2 \Delta r \rho_c C_c)}{\partial t} = k_4 \epsilon C_B (4\pi r^2 \Delta r) \rho_c$$

which reduces to

$$\frac{\partial C_c}{\partial t} = k_4 \epsilon C_B \quad (3-3.7)$$

As done previously for the discrete particles, the accumulation terms on gaseous species will be neglected and fouling models incorporated into the rate constants. Performing these steps, Eqs. (3-3.3, 5, 6 and 7) become

$$D_A \nabla_r^2 C_A + \rho_c \epsilon (k_2^0 \phi_2 C_B - k_1^0 \phi_1 C_A) = 0 \quad (3-3.8)$$



$$D_B \nabla_r^2 C_B + \rho_c k_1^0 \phi_1 \epsilon C_A - (k_2^0 \phi_2 \epsilon + k_3^0 \phi_3 (1-\epsilon)) \rho_c C_B = 0 \quad (3-3.9)$$

$$D_R \nabla_r^2 C_R + k_3^0 \phi_3 (1-\epsilon) \rho_c C_B = 0 \quad (3-3.10)$$

$$\frac{\partial C_c}{\partial t} = \epsilon k_4^0 \phi_4 C_B \quad (3-3.11)$$

The boundary and initial conditions are similar to those for the discrete case.

$$\begin{aligned} \text{B. C. 1} \quad C_A &= C_{A_s} \\ C_B &= C_{B_s} \quad \} \quad @ \ r = R_X, \ t \geq 0 \\ C_R &= C_{R_s} \end{aligned} \quad (3-3.12a)$$

$$\text{B. C. 2} \quad \left. \nabla_r C_A \right|_{r=0} = \left. \nabla_r C_B \right|_{r=0} = \left. \nabla_r C_R \right|_{r=0} = 0 \quad t \geq 0 \quad (3-3.12b)$$

$$\text{I. C.} \quad C_c = 0 \quad @ \ t = 0, \ 0 \leq r \leq R_X \quad (3-3.13)$$

Utilizing the same dimensionless variables as before and assuming that all diffusivities are equal the following dimensionless equations are obtained.

$$\nabla_\xi^2 y_A + \epsilon \gamma_2 \phi_2 y_B - \epsilon \gamma_1 \phi_1 y_A = 0 \quad (3-3.14)$$

$$\nabla_\xi^2 y_B + \epsilon \gamma_1 \phi_1 y_A - \epsilon \gamma_2 \phi_2 y_B - (1-\epsilon) \phi_3 \gamma_3 y_B = 0 \quad (3-3.15)$$

$$\nabla_\xi^2 y_R + (1-\epsilon) \gamma_3 \phi_3 y_B = 0 \quad (3-3.16)$$

$$\frac{\partial y_c}{\partial \theta} = \epsilon \phi_4 y_B \quad (3-3.17)$$

where

$$\gamma_i = \frac{\rho_c k_i^0 R_X^2}{D}, \quad i = 1, 2, 3, 4 \quad (3-3.18)$$

The dimensionless boundary and initial conditions are

$$\begin{aligned} \text{B. C. 1} \quad y_A &= y_{A_s} \\ y_B &= y_{B_s} \quad \} \quad \xi = 1, \theta \geq 0 \end{aligned} \quad (3-3.19a)$$

$$y_R = y_{R_s}$$

$$\text{B. C. 2} \quad \left. \nabla_{\xi} y_A \right|_{\xi=0} = \left. \nabla_{\xi} y_B \right|_{\xi=0} = \left. \nabla_{\xi} y_R \right|_{\xi=0} = 0, \quad \theta \geq 0 \quad (3-3.19b)$$

$$\text{I. C.} \quad y_c = 0 \quad @ \quad \theta = 0, \quad 0 \leq \xi \leq 1 \quad (3-3.20)$$

Now, with all equations and conditions in dimensionless form, analytical solutions may be obtained at small times by neglecting Eq. (3-3.17) and assuming that all  $\phi_i = 1$ . Both of these are physically logical due to the slow fouling assumption. The pseudo-steady solutions are<sup>†</sup>

$$\begin{aligned} y_A &= \frac{y_{A_s}}{(m_3^2 - m_1^2)} \left\{ (m_3^2 - \beta_1) \cdot \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} - (m_1^2 - \beta_1) \cdot \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi} \right\} \\ &+ \frac{y_{B_s}}{(m_3^2 - m_1^2)} \cdot \left\{ \beta_2 \cdot \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} - \beta_2 \cdot \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi} \right\} \end{aligned} \quad (3-3.21)$$

---

<sup>†</sup>These solutions may be found in detail in Appendix A-4.

$$\begin{aligned}
y_B = & \frac{y_{B_s}}{(m_3^2 - m_1^2)} \cdot \{(\beta_1 - m_1^2) \cdot \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} - (\beta_1 - m_3^2) \cdot \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi}\} \\
& + \frac{y_{A_s}}{(m_3^2 - m_1^2)} \cdot \left\{ \frac{(\beta_1 - m_1^2)(m_3^2 - \beta_1)}{\beta_2} \cdot \left[ \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} - \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi} \right] \right\}
\end{aligned}
\tag{3-3.22}$$

and

$$\begin{aligned}
y_R = y_{R_s} + & \frac{y_{B_s}}{(m_3^2 - m_1^2)} \cdot \left\{ \frac{\beta_3(\beta_1 - m_1^2)}{m_1^2} \cdot \left[ 1 - \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} \right] \right. \\
& - \frac{\beta_3(\beta_1 - m_3^2)}{m_3^2} \cdot \left[ 1 - \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi} \right] \Big\} \\
& + \frac{y_{A_s}}{(m_3^2 - m_1^2)} \cdot \left\{ \frac{\beta_3(\beta_1 - m_1^2)(m_3^2 - \beta_1)}{\beta_2} \cdot \left\{ \left[ \frac{1}{m_1^2} \left( 1 - \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} \right) \right] \right. \right. \\
& \left. \left. - \left[ \frac{1}{m_3^2} \left( 1 - \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi} \right) \right] \right\} \right\}
\end{aligned}
\tag{3-3.23}$$

These solutions will be of considerable use; first as initial conditions in the numerical solution of (3-3.14-17) once the  $\phi_i$ 's have a definite form, and second, in the solution of the bed equations for small values of time.

### 3-4. MASS BALANCES ON STATIONARY BED VOLUME ELEMENT--COMPOSITE PARTICLE CASE.

Proceeding from the analysis of the single particle to the bed analysis will be accomplished in the same way as for the discrete formulation. Use will be made of the schematic reactor in Fig. 3-2 to write the balances.

Specie A:

$$\left\{ \begin{array}{c} \text{rate of accumulation} \\ \text{in } \Delta V \end{array} \right\} = \left\{ \begin{array}{c} \text{convective} \\ \text{rate in} \end{array} \right\} - \left\{ \begin{array}{c} \text{convective} \\ \text{rate out} \end{array} \right\} + \left\{ \begin{array}{c} \text{rate of pro-} \\ \text{duction by} \\ \text{chemical reaction} \end{array} \right\}$$

$$\frac{\partial}{\partial t} (\pi R^2 \Delta z \epsilon_B C_{A_s}) = U \pi R^2 C_{A_s} \Big|_z - U \pi R^2 C_{A_s} \Big|_{z+\Delta z} + \tilde{R}_A \cdot \pi R^2 \Delta z \quad (3-4.1)$$

where  $\tilde{R}_A$  is the molar rate of production of A per unit reactor volume.  $\tilde{R}_A$  may be represented by the product of two terms; the rate of reaction per particle, which will be assumed equivalent to the rate of diffusion into the particle, and the number of composite particles per unit reactor volume. This latter term is just

$$N = \frac{\rho_B}{\frac{4}{3} \pi R_X^3}, \quad (3-4.2)$$

since the compounded particle sizes are identical. Therefore, the expression for  $\tilde{R}_A$  is

$$\tilde{R}_A = N \cdot r_A = \frac{-3\rho_B D}{R_X^3 c} \frac{\partial C_A}{\partial r} \Big|_{r=R_X} \quad (3-4.3)$$

So the balance for A becomes

$$\epsilon_B \frac{\partial C_{A_s}}{\partial t} + U \frac{\partial C_{A_s}}{\partial z} + \frac{3\rho_B D}{R_X^3 c} \cdot \frac{\partial C_A}{\partial r} \Big|_{r=R_X} = 0 \quad (3-4.4)$$

Specie B:

Since both catalytic species are now located in the same particle there is only one reaction term, which is analogous to that for specie A. The final form for the transient balance is

$$\epsilon_B \frac{\partial C_{Bs}}{\partial t} + U \frac{\partial C_{Bs}}{\partial z} + \frac{3\rho_B D}{R_X^0 c} \cdot \frac{\partial C_B}{\partial r} \bigg|_{r=R_X} = 0 \quad (3-4.5)$$

Specie R:

$$\epsilon_B \frac{\partial C_{Rs}}{\partial t} + U \frac{\partial C_{Rs}}{\partial z} + \frac{3\rho_B D}{R_X^0 c} \cdot \frac{\partial C_R}{\partial r} \bigg|_{r=R_X} = 0 \quad (3-4.6)$$

Following the same reasoning employed in the discrete case the accumulation terms may be dropped as being negligible compared to the other terms. The mass balances then become

$$U \frac{\partial C_{As}}{\partial z} + \frac{3\rho_B D}{R_X^0 c} \cdot \frac{\partial C_A}{\partial r} \bigg|_{r=R_X} = 0 \quad (3-4.7)$$

$$U \frac{\partial C_{Bs}}{\partial z} + \frac{3\rho_B D}{R_X^0 c} \cdot \frac{\partial C_B}{\partial r} \bigg|_{r=R_X} = 0 \quad (3-4.8)$$

$$U \frac{\partial C_{Rs}}{\partial z} + \frac{3\rho_B D}{R_X^0 c} \cdot \frac{\partial C_R}{\partial r} \bigg|_{r=R_X} = 0 \quad (3-4.9)$$

Designation of the feed as pure A provides the necessary boundary conditions for Eqs. (3-4.7, 8 and 9), i.e.

$$C_{A_s}(z=0) = C_{A_0}$$

$$C_{B_s}(z=0) = 0 \quad (3-4.10)$$

$$C_{R_s}(z=0) = 0$$

Equations (3-4.7-10) may be put into dimensionless form using those variables previously defined for the discrete case. In dimensionless form then, (3-4.7, 8, 9 and 10) become

$$\left. \frac{\partial y_{A_s}}{\partial \bar{z}} + 3 \frac{\partial y_A}{\partial \xi} \right|_{\xi=1} = 0 \quad y_{A_s}(\bar{z}=0) = 1 \quad (3-4.11)$$

$$\left. \frac{\partial y_{B_s}}{\partial \bar{z}} + 3 \frac{\partial y_B}{\partial \xi} \right|_{\xi=1} = 0 \quad y_{B_s}(\bar{z}=0) = 0 \quad (3-4.12)$$

$$\left. \frac{\partial y_{R_s}}{\partial \bar{z}} + 3 \frac{\partial y_R}{\partial \xi} \right|_{\xi=1} = 0 \quad y_{R_s}(\bar{z}=0) = 0 \quad (3-4.13)$$

Analytical solutions may be obtained for these equations for small values of time. Using analytic expressions for the gradients at the particle surface, obtained from the particle expressions, the solutions are found to be<sup>†</sup>

$$y_{A_s} = \frac{1}{(\ell_1 - \ell_2)} \{ (x_1 + \ell_1) \exp(\ell_2 \bar{z}) - (x_1 + \ell_2) \exp(\ell_1 \bar{z}) \} \quad (3-4.14)$$

$$y_{B_s} = \frac{(x_1 + \ell_2)(x_1 + \ell_1)}{x_2(\ell_1 - \ell_2)} \{ \exp(\ell_1 \bar{z}) - \exp(\ell_2 \bar{z}) \} \quad (3-4.15)$$

---

<sup>†</sup>Complete solutions may be found in Appendix A-5.

$$\begin{aligned}
y_{R_s} = & \frac{x_6}{l_1 l_2} \{ l_1 + l_2 + x_1 + \frac{1}{(l_1 - l_2)} \cdot [ l_2 (l_2 + x_1) \exp(l_1 \bar{z}) \\
& - l_1 (l_1 + x_1) \exp(l_2 \bar{z}) ] \} + \frac{x_5 (l_1 + x_1) (l_2 + x_1)}{l_1 l_2 x_2} \{ \frac{1}{(l_1 - l_2)} \cdot \\
& [ l_1 \exp(l_2 \bar{z}) - l_2 \exp(l_1 \bar{z}) ] - 1 \}
\end{aligned} \tag{3-4.16}$$

Careful examination of these solutions yield the fact that the product,  $y_{R_s}$ , is a function of the weight fraction  $\epsilon$ , and that an optimal fraction of catalyst X exists for a given set of physical properties and reaction parameters which will maximize the product at the reactor exit. This optimization may be carried out as previously mentioned in Section 3-2. Table 3-2 and Fig. 3-4 illustrate the optimum fractions for various values of parameters for the composite case. Figure 3-5 is merely a comparison of the two formulations which indicates that, holding all particle sizes identical and using the same rate constants and other physical properties, the composite case always produces a better yield of desired product, in addition to using a smaller weight fraction of catalyst X.

The above solutions will also be quite useful in the numerical solution of the unsteady state bed and particle equations as fouling becomes important.

- 1  $k_1^0 = 0.1$ ;  $k_2^0 = 1.0$ ;  $k_3^0 = 0.2$ ;  $\epsilon = 0.30$ ;  $y_{R_{MAX}} = 0.6706$   
 2  $k_1^0 = 0.1$ ;  $k_2^0 = 2.0$ ;  $k_3^0 = 0.2$ ;  $\epsilon = 0.24$ ;  $y_{R_{MAX}} = 0.4980$   
 3  $k_1^0 = 0.2$ ;  $k_2^0 = 4.0$ ;  $k_3^0 = 0.2$ ;  $\epsilon = 0.18$ ;  $y_{R_{MAX}} = 0.5490$

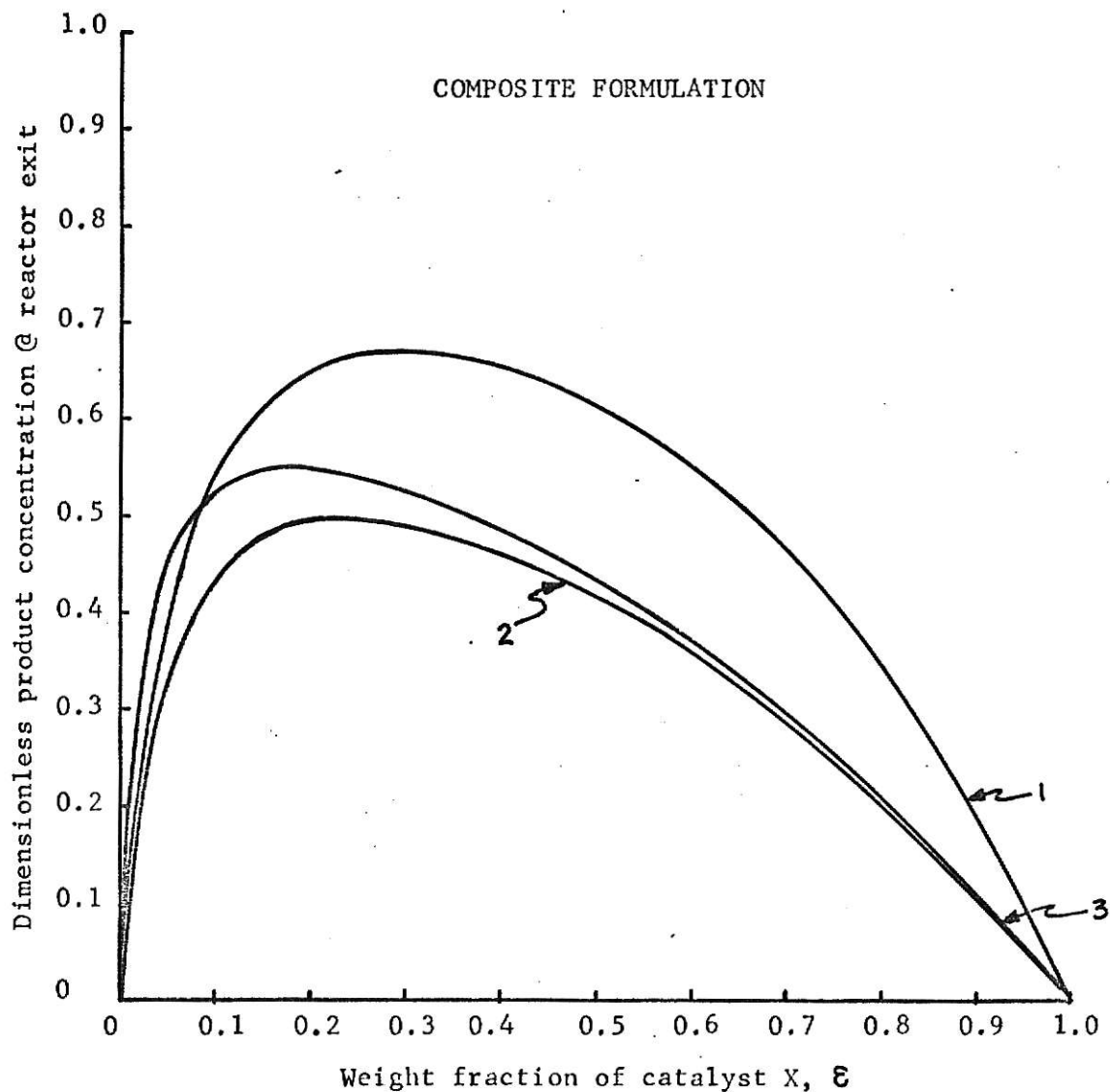


Fig. 3-4. Optimum catalyst fractions for various choices of rate constants.



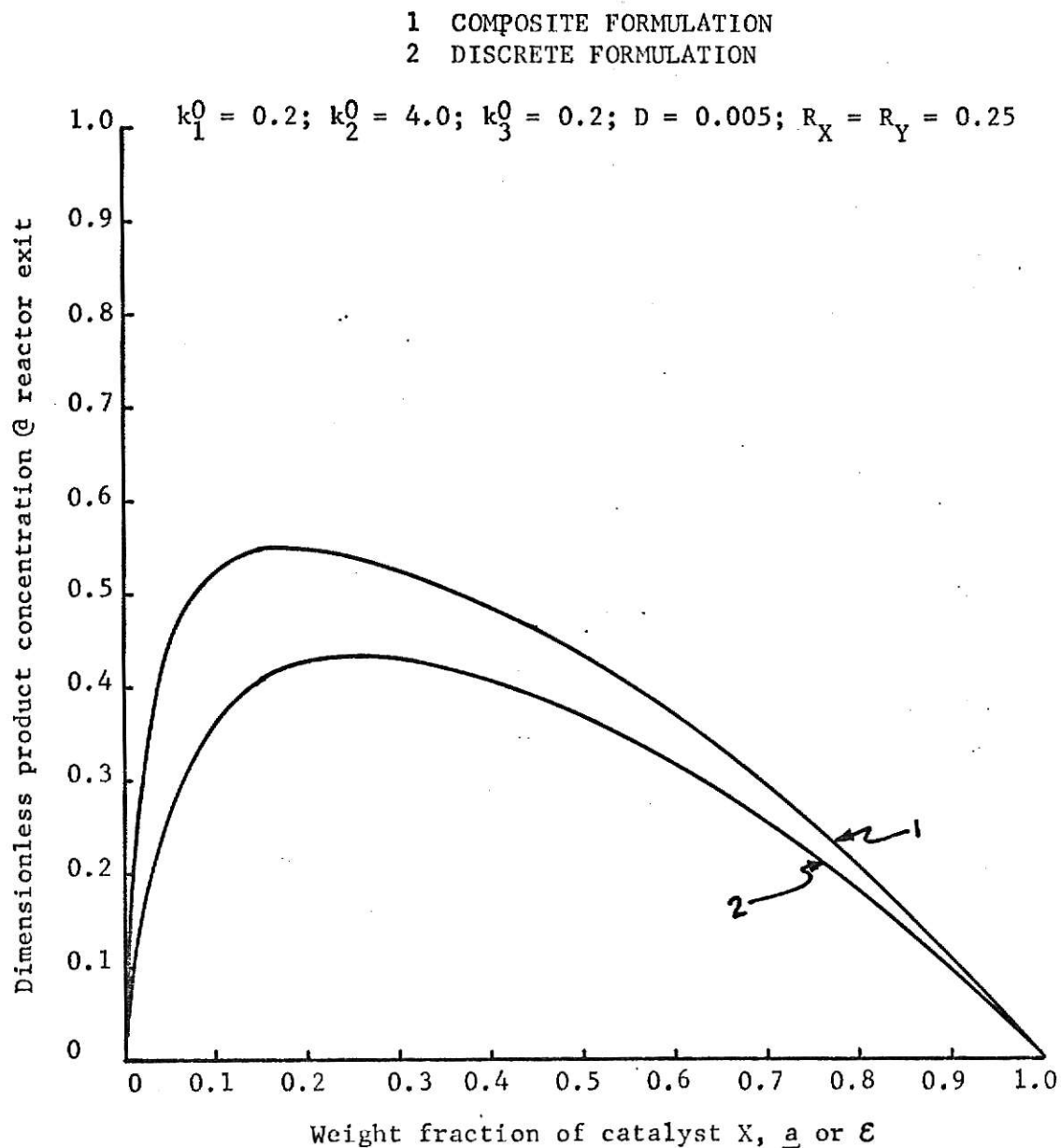


Fig. 3-5. Comparison of maximum yields and optimum catalyst fractions for the two formulations. All other properties are equivalent.

TABLE 3-2. Optimum catalyst fractions and maximum product mole fraction for various choices of rate constants.

COMPOSITE PARTICLES					
$R_X = 0.25 \text{ cm}$			$D = 0.005 \text{ cm}^2/\text{sec}$		
#	$k_1^0$	$k_2^0$	$k_3^0$	$\epsilon$	$y_{R_s(\text{max.})}$
	$\left(\frac{\text{cc}}{\text{sec-gr.cat}}\right)$	$\left(\frac{\text{cc}}{\text{sec-gr.cat}}\right)$	$\left(\frac{\text{cc}}{\text{sec-gr.cat}}\right)$		
1	0.1	1.0	0.2	0.30	0.6706
2	0.2	1.0	0.1	0.22	0.7137
3	0.1	2.0	0.2	0.24	0.4980
4	0.2	2.0	0.2	0.24	0.7367
5	0.1	1.0	0.1	0.24	0.4842
6	0.2	4.0	0.2	0.18	0.5490
7	0.2	4.0	0.1	0.14	0.3574
8	0.2	4.0	0.4	0.24	0.7485
9	0.5	4.0	0.1	0.13	0.6482
10	0.5	4.0	0.2	0.18	0.8480
11	1.0	4.0	0.1	0.12	0.8526

### 3.5. MASS BALANCES ON A FIXED BED REACTOR ASSUMING NO DIFFUSIONAL RESISTANCE.

Limiting cases, whether in experimental or theoretical work, are always beneficial for comparison's sake. The following treatment considers a packed bed in which diffusion resistance, both inter- and intraparticle is negligible, i.e., all surface area of the catalyst is immediately available for reaction. Since the only effective means of differentiating between the two types of formulation is with regard to diffusional considerations, there should be no distinction between the discrete or composite formulations in this case. All assumptions pertaining to the bed mentioned heretofore will be applicable and use will again be made of the packed bed schematic of Fig. 3-2.

Specie A:

$$\left\{ \begin{array}{c} \text{rate of accumulation} \\ \text{in } \Delta V \end{array} \right\} = \left\{ \begin{array}{c} \text{convective} \\ \text{rate in} \end{array} \right\} - \left\{ \begin{array}{c} \text{convective} \\ \text{rate out} \end{array} \right\} + \left\{ \begin{array}{c} \text{rate of pro-} \\ \text{duction by} \\ \text{chemical reaction} \end{array} \right\}$$

$$\frac{\partial}{\partial t} (\pi R^2 \Delta z \epsilon_B C_{A_s}) = U \pi R^2 C_{A_s} \Big|_z - U \pi R^2 C_{A_s} \Big|_{z+\Delta z} + R_A \cdot \pi R^2 \Delta z \cdot \rho_B \quad (3-5.1)$$

where  $R_A$  = rate of production of A per unit weight of catalyst.

$$R_A = k_2 \zeta C_{B_s} - k_1 \zeta C_{A_s} \quad (3-5.2)$$

and  $\zeta$  = weight fraction of catalyst X per particle.

Substitution of (3-5.2) into (3-5.1) and simplification results in

$$\epsilon_B \frac{\partial C_{A_s}}{\partial t} + U \frac{\partial C_{A_s}}{\partial z} + \rho_B k_1 \zeta C_{A_s} - \rho_B k_2 \zeta C_{B_s} = 0 \quad (3-5.3)$$

Specie B:

The rate of production term is

$$R_B = k_1 \zeta C_{A_s} - k_2 \zeta C_{B_s} - k_3 (1-\zeta) C_{B_s} - k_4 \zeta C_{B_s} \quad (3-5.4)$$

and the fourth term of the right hand side may be neglected due to the slow fouling assumption. The final balance for B is

$$\epsilon_B \frac{\partial C_{B_s}}{\partial t} + U \frac{\partial C_{B_s}}{\partial z} + (k_2 \zeta + k_3 (1-\zeta)) \rho_B C_{B_s} - \rho_B k_1 \zeta C_{A_s} = 0 \quad (3-5.5)$$

Specie R:

$$\epsilon_B \frac{\partial C_{R_s}}{\partial t} + U \frac{\partial C_{R_s}}{\partial z} - \rho_B k_3 (1-\zeta) C_{B_s} = 0 \quad (3-5.6)$$

Specie C:

$$\left\{ \begin{array}{c} \text{rate of accumulation} \\ \text{in } \Delta V \end{array} \right\} = \left\{ \begin{array}{c} \text{rate of production} \\ \text{by reaction} \end{array} \right\}$$

$$\frac{\partial}{\partial t} (\pi R^2 \Delta z \rho_B C_c) = R_c \cdot \pi R^2 \Delta z \cdot \rho_B \quad (3-5.7)$$

and

$$R_c = k_4 \zeta C_{B_s} = \begin{array}{l} \text{the rate of production of poison in gram-moles} \\ \text{per gram catalyst} \end{array} \quad (3-5.8)$$

Equation (3-5.7) reduces to

$$\frac{\partial C_c}{\partial t} = k_4 \zeta C_{B_s} \quad (3-5.9)$$

As was done in the two previous sections on the bed, the accumulation terms will be neglected in accord with the pseudo-steady gaseous profile

attainment and the slow fouling assumption. Therefore, the mass balance equations reduce to

$$U \frac{\partial C_{A_s}}{\partial z} + \rho_B k_1 \zeta C_{A_s} - \rho_B k_2 \zeta C_{B_s} = 0 \quad (3-5.10)$$

$$U \frac{\partial C_{B_s}}{\partial z} + (k_2 \zeta + k_3 (1-\zeta)) \rho_B C_{B_s} - \rho_B k_1 \zeta C_{A_s} = 0 \quad (3-5.11)$$

$$U \frac{\partial C_{R_s}}{\partial z} - k_3 (1-\zeta) \rho_B C_{B_s} = 0 \quad (3-5.12)$$

$$\frac{\partial C_c}{\partial t} = k_4 \zeta C_{B_s} \quad (3-5.13)$$

The boundary conditions for these bed balances will be identical to the conditions imposed previously, i.e.

$$\begin{aligned} C_{A_s} &= C_{A_0} \\ C_{B_s} &= 0 \end{aligned} \quad \} \quad @ \ z = 0 \quad t \geq 0 \quad (3-5.14)$$

$$\begin{aligned} C_{R_s} &= 0 \\ C_c &= 0 \end{aligned} \quad @ \ t = 0 \quad z \geq 0 \quad (3-5.15)$$

Reduction of the above equations to dimensionless form is quite easily accomplished using previously defined dimensionless variables. Here, however, since there is no diffusional resistance  $z'$ , the dimensionless axial distance will be of a different form. The equations obtained are

$$\frac{\partial y_{A_s}}{\partial z'} + \frac{\rho_B k_1 z_d}{U} \cdot \zeta y_{A_s} - \frac{\rho_B k_2 z_d}{U} \cdot \zeta y_{B_s} = 0 \quad (3-5.16)$$

$$\frac{\partial y_{B_s}}{\partial z'} + \frac{\rho_B k_2 z_d}{U} \cdot \zeta y_{B_s} + \frac{\rho_B k_3 (1-\zeta) z_d}{U} \cdot y_{B_s} - \frac{\rho_B k_1 z_d}{U} \cdot \zeta y_{A_s} = 0 \quad (3-5.17)$$

$$\frac{\partial y_{R_s}}{\partial z'} - \frac{\rho_B k_3 z_d}{U} \cdot (1-\zeta) y_{B_s} = 0 \quad (3-5.18)$$

and

$$\frac{\partial y_c}{\partial \theta} = \frac{k_4 \zeta C_{A_0} t_d}{C_{c_f}} \cdot y_{B_s} \quad (3-5.19)$$

Incorporation of the fouling model,  $\phi_1$ , into the rate constant as was previously done, and judicious choices of  $z_d$  and  $t_d$  result in the following equations,

$$\frac{\partial y_{A_s}}{\partial z'} - K^* \zeta \phi_2 y_{B_s} + \zeta \phi_1 y_{A_s} = 0; \quad y_{A_s} = 1.0 @ z' = 0.0 \quad (3-5.20)$$

$$\frac{\partial y_{B_s}}{\partial z'} + (K^* \zeta \phi_2 + K_1^* (1-\zeta) \phi_3) y_{B_s} - \zeta \phi_1 y_{A_s} = 0; \quad y_{B_s} = 0.0 @ z' = 0.0 \quad (3-5.21)$$

$$\frac{\partial y_{R_s}}{\partial z'} - K_1^* (1-\zeta) \phi_3 y_{B_s} = 0; \quad y_{R_s} = 0.0 @ z' = 0.0 \quad (3-5.22)$$

$$\frac{\partial y_c}{\partial \theta} = \zeta \phi_4 y_{B_s}; \quad y_c = 0.0 @ \theta = 0.0, z' \geq 0 \quad (3-5.23)$$

where  $z' = \frac{\rho_B k_1^0}{U} \cdot z$ ,  $\theta = \frac{k_4^0 C_{A_0}}{C_{c_f}} \cdot t$  and dimensionless parameters are

$$K^* = \frac{k_2^0}{k_1^0} \quad \text{and} \quad K_1^* = \frac{k_3^0}{k_1^0} \quad (3-5.24)$$

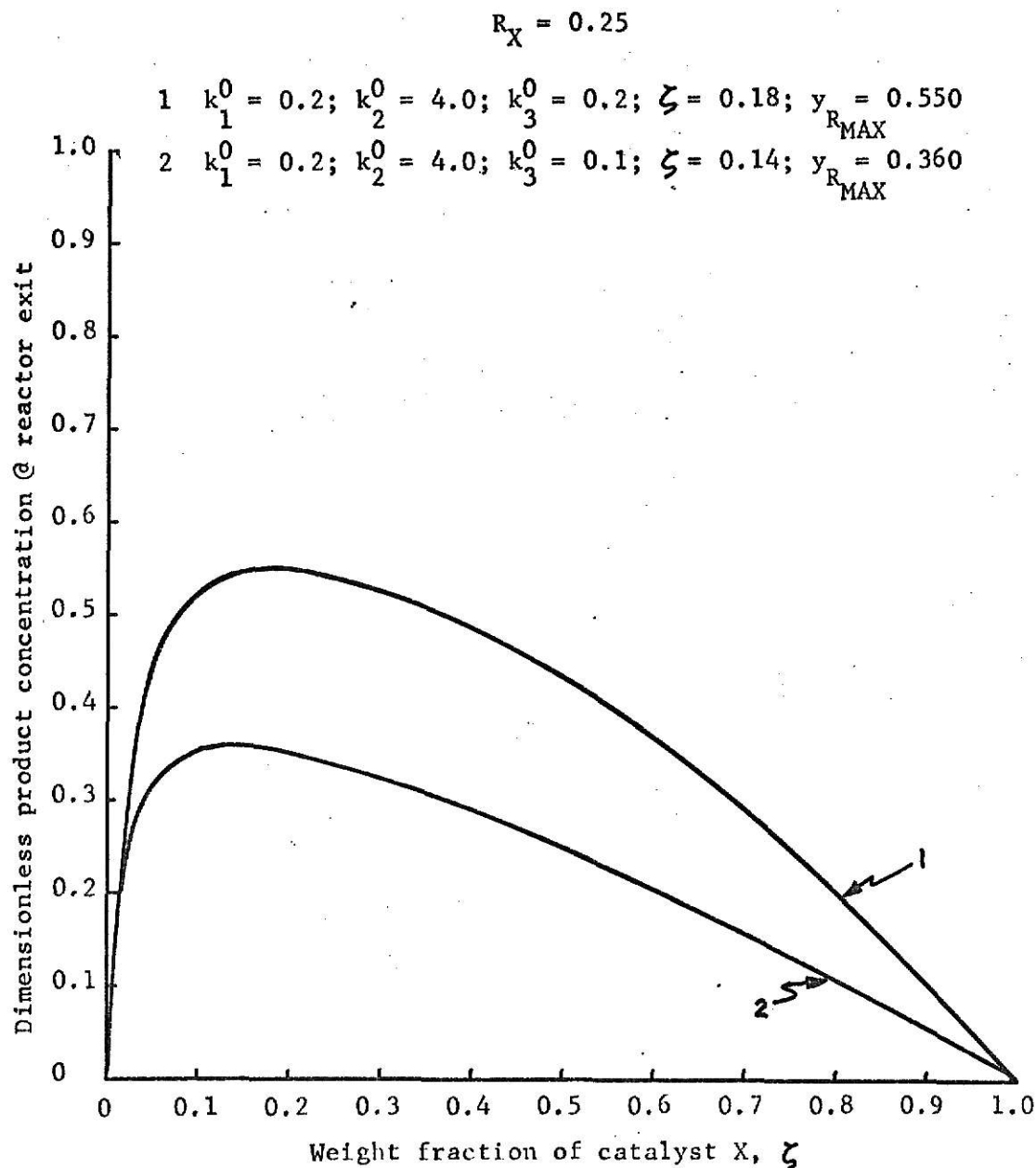


Fig. 3-6. Optimum catalyst fractions for various choices of rate constants. No diffusion resistance case,

It can easily be shown that  $\bar{z}$  and  $z'$  are related by

$$\bar{z} = \frac{D}{\frac{R_{Xc}^2}{k_1}} \cdot z' = \frac{z'}{\gamma_1} \quad (3-5.25)$$

and once representative physical properties, diffusivities, etc. are chosen for study, the difference will be just a numerical factor which may be accounted for in the actual bed length  $z$ .

Pseudo-steady solutions may be obtained, as in previous sections, which provide not only unfouled bed profiles for the case, but also a starting point in the numerical analysis of the nonlinear equations once fouling becomes important. These solutions are,<sup>†</sup>

$$y_{A_s} = \frac{1}{(\lambda_1 - \lambda_2)} \{ (\lambda_1 + W_1) \exp(\lambda_2 z') - (\lambda_2 + W_1) \exp(\lambda_1 z') \} \quad (3-5.26)$$

$$y_{B_s} = \frac{(\lambda_2 + W_1)(\lambda_1 + W_1)}{W_2(\lambda_1 - \lambda_2)} \cdot \{ \exp(\lambda_2 z') - \exp(\lambda_1 z') \} \quad (3-5.27)$$

$$y_{R_s} = \frac{W_3(\lambda_2 + W_1)(W_1 + \lambda_1)}{W_2(\lambda_1 - \lambda_2)} \cdot \left\{ \frac{1}{\lambda_2} \exp(\lambda_2 z') - \frac{1}{\lambda_1} \exp(\lambda_1 z') \right. \\ \left. - \frac{(\lambda_1 - \lambda_2)}{\lambda_1 \lambda_2} \right\} \quad (3-5.28)$$

As in previous cases,  $y_{R_s}$  is again a complex function of the weight fraction of catalyst  $X$ ,  $\zeta$ , and there does exist an optimum  $\zeta$  which maximizes  $y_{R_s}$  for a given choice of parameters. Figure 3-6 shows various optimal  $\zeta$  for choices of rate constants, particle radius, etc.

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<sup>†</sup> Complete solutions are available in Appendix A-6.



### 3-6. DISCUSSION OF FOULING MODELS.

Heretofore, almost no mention has been made of a fouling model which incorporates the effect of active site destruction into the mass balances, save for the defining symbol  $\phi$ . Deposition of solids on active sites can be described mainly as a composite of the following two regimes: uniform and non-uniform poison laydown. Uniform deposition occurs when the intraparticle diffusion resistance is low enough to allow the poison forming reaction to occur at any point within the catalyst and, assuming no steric or size effects the amount of poison deposited over any cross section is constant. Non-uniform deposition is characterized by either 1) a large intraparticle diffusion resistance or an extremely high poisoning reaction rate constant, which causes a buildup of poison in the outer shell, or 2) severe steric effects caused by the size of the poison molecule which may best be exemplified in pore-mouth blockage. What is probably the actual case lies somewhere between the two limits, i.e. slight steric effect plus some diffusional resistance. Maxted [21], Kwan [22] and Rideal [10], etc., have shown experimental evidence of the above conclusion. Plotting relative activity of the catalyst versus weight of poison present in the particle, Maxted [21] has shown an initial linear decay followed by a point of inflection and finally asymptotic behavior toward the poison axis. Uniform poisoning may be represented ideally by 1), a one to one relationship existing between the number of active sites occupied and the number of poison molecules and 2), the relative activity being solely a function of the number of active sites available. A plot of relative activity versus the amount of poison in the particle should be linear. Non-uniform poisoning may exhibit a linear relationship during the initial deposition period but neither of two conditions above is

satisfied over the entire deposition period.

Much work, both theoretical and experimental, has been done in an attempt to relate relative activity to poison concentration in such a way that poison laydown within a particle might be described by a concise formula. Thus far only empirical models attempting to fit experimental findings on poisoning have been utilized, due mainly to the fact that very little basic knowledge is available about actual catalytic action, let alone the poisoning of these catalysts. The three most important of the empirical models are: Linear, exponential and hyperbolic. Froment and Bischoff dealt rather extensively with the two latter models [13], but the linear model seems to have had the majority of exposure in the literature.

It was the author's decision to utilize the linear model in this work on the basis of several factors:

- (i) The linear model represents, at least partially, a large number of experimental findings,
- (ii) For the study being undertaken no new trends would be indicated by the more complex models, and
- (iii) Use of the linear model allows the definition of a complete deactivation concentration of poison which, in some cases has been measured experimentally.

Thus, in all reactions involving the X catalyst, the fouling model,  $\phi$ , will take the following form,

$$\phi = 1 - y_c \quad (3-6.1)$$

while there will be no fouling of the Y sites, or

$$\phi = 1.0 \quad (3-6.2)$$

### 3-7. TABULATION OF TRANSIENT MASS BALANCES AFTER INCORPORATION OF FOULING MODEL.

This section presents a concise statement of the systems of equations to be solved in the following chapter.

#### Particle Equations--Discrete Case

$$\nabla_{\xi}^2 y_A + \gamma_2(1 - y_c)y_{B(X)} - \gamma_1(1 - y_c)y_A = 0 \quad (3-7.1)$$

$$\nabla_{\xi}^2 y_{B(X)} + \gamma_1(1 - y_c)y_A - \gamma_2(1 - y_c)y_{B(X)} = 0 \quad (3-7.2)$$

$$\nabla_{\xi}^2 y_{B(Y)} - m^2 \gamma_3 y_{B(Y)} = 0 \quad (3-7.3)$$

$$\nabla_{\xi}^2 y_R + m^2 \gamma_3 y_{B(Y)} = 0 \quad (3-7.4)$$

$$\frac{\partial y_c}{\partial \theta} = (1 - y_c)y_{B(X)} \quad (3-7.5)$$

with boundary conditions

$$\begin{aligned} y_A = y_{A_s} & \quad y_{B(Y)} = y_{B_s} \\ & \} @ \xi = 1 \text{ and } \} @ \xi = 1/m; \theta \geq 0 \\ y_{B(X)} = y_{B_s} & \quad y_R = y_{R_s} \end{aligned} \quad (3-7.6)$$

and

$$\nabla_{\xi} y_A \Big|_{\xi=0} = \nabla_{\xi} y_{B(X)} \Big|_{\xi=0} = \nabla_{\xi} y_{B(Y)} \Big|_{\xi=0} = \nabla_{\xi} y_R \Big|_{\xi=0} = 0; \theta \geq 0 \quad (3-7.7)$$

and initial condition:

$$y_c = 0.0 @ \theta = 0 \quad 0 \leq \xi \leq 1 \quad (3-7.8)$$

### Bed Equations--Discrete Case

$$\frac{\partial y_{A_s}}{\partial \bar{z}} + 3a \left. \frac{\partial y_A}{\partial \xi} \right|_{\xi=1} = 0; \quad y_{A_s} = 1.0 @ \bar{z} = 0.0 \quad (3-7.9)$$

$$\frac{\partial y_{B_s}}{\partial \bar{z}} + 3 \left[ a \left. \frac{\partial y_{B(X)}}{\partial \xi} \right|_{\xi=1} + m(1-a) \left. \frac{\partial y_{B(Y)}}{\partial \xi} \right|_{\xi=1/m} \right] = 0;$$

$$y_{B_s} = 0.0 @ \bar{z} = 0.0 \quad (3-7.10)$$

$$\frac{\partial y_{R_s}}{\partial \bar{z}} + 3m(1-a) \left. \frac{\partial y_R}{\partial \xi} \right|_{\xi=1/m} = 0; \quad y_{R_s} = 0.0 @ \bar{z} = 0.0 \quad (3-7.11)$$

### Particle Equations--Composite Particle Case

$$\nabla_{\xi}^2 y_A + \epsilon \gamma_2 (1-y_c) y_B - \epsilon \gamma_1 (1-y_c) y_A = 0 \quad (3-7.12)$$

$$\nabla_{\xi}^2 y_B + \epsilon \gamma_1 (1-y_c) y_A - \epsilon \gamma_2 (1-y_c) y_B - (1-\epsilon) \gamma_3 y_B = 0 \quad (3-7.13)$$

$$\nabla_{\xi}^2 y_R + (1-\epsilon) \gamma_3 y_B = 0 \quad (3-7.14)$$

$$\frac{\partial y_c}{\partial \theta} = \epsilon (1-y_c) y_B \quad (3-7.15)$$

with boundary conditions

$$\begin{aligned} y_A &= y_{A_s} \\ y_B &= y_{B_s} \\ y_R &= y_{R_s} \end{aligned} \quad \} \quad @ \xi = 1; \theta \geq 0 \quad (3-7.16)$$

and

$$\nabla_{\xi} y_A \Big|_{\xi=0} = \nabla_{\xi} y_B \Big|_{\xi=0} = \nabla_{\xi} y_R \Big|_{\xi=0} = 0 \quad \theta \geq 0 \quad (3-7.17)$$

and the initial condition

$$y_c = 0.0 @ \theta = 0.0; \quad 0 \leq \xi \leq 1 \quad (3-7.18)$$

#### Bed Equations--Composite Particle Case

$$\frac{\partial y_{A_s}}{\partial \bar{z}} + 3 \frac{\partial y_A}{\partial \xi} \Big|_{\xi=1} = 0; \quad y_{A_s} = 1.0 @ \bar{z} = 0.0; \quad \theta \geq 0 \quad (3-7.19)$$

$$\frac{\partial y_{B_s}}{\partial \bar{z}} + 3 \frac{\partial y_B}{\partial \xi} \Big|_{\xi=1} = 0; \quad y_{B_s} = 0.0 @ \bar{z} = 0.0; \quad \theta \geq 0 \quad (3-7.20)$$

$$\frac{\partial y_{R_s}}{\partial \bar{z}} + 3 \frac{\partial y_R}{\partial \xi} \Big|_{\xi=1} = 0; \quad y_{R_s} = 0.0 @ \bar{z} = 0.0; \quad \theta \geq 0 \quad (3-7.21)$$

#### Bed Equations--Negligible Diffusion Resistance Case

$$\begin{aligned} \frac{\partial y_{A_s}}{\partial z'} - K^*_{\zeta}(1-y_c)y_{B_s} + \zeta(1-y_c)y_{A_s} &= 0; \\ y_{A_s} &= 1.0 @ z' = 0.0; \quad \theta \geq 0 \end{aligned} \quad (3-7.22)$$

$$\begin{aligned} \frac{\partial y_{B_s}}{\partial z'} + (K^*_{\zeta}(1-y_c) + K^*_{\zeta}(1-\zeta))y_{B_s} - \zeta(1-y_c)y_{A_s} &= 0; \\ y_{B_s} &= 0.0 @ z' = 0.0; \quad \theta \geq 0 \end{aligned} \quad (3-7.23)$$

$$\frac{\partial y_{R_s}}{\partial z'} - K_1^*(1-\zeta)y_{B_s} = 0; \quad y_{R_s} = 0.0 @ z' = 0.0; \quad \theta \geq 0 \quad (3-7.24)$$

$$\frac{\partial y_c}{\partial \theta} = \zeta(1-y_c)y_{B_s}; \quad y_c = 0 @ \theta = 0; \quad z' \geq 0 \quad (3-7.25)$$

## CHAPTER 4

## NUMERICAL SOLUTION OF PARTICLE AND BED EQUATIONS

4-1. QUALITATIVE DISCUSSION.

Inspection of the particle equations in Section 3-7 reveals the fact that all concentrations are functions of three independent variables; two spatial and a time variable. The radial dependence is quite evident; the axial dependence enters because of the surface boundary conditions and the implicit time dependence, for the gaseous species, enters by way of the assumed activity-poison concentration relationship. It may also be noted that the bulk or surface concentrations are also functions of these same three variables. Even though one variable is explicit in each case, use has been made of partial differentiation as a reminder of the implicit dependence on the remaining independent variables.

Solution schemes for the particle and bed equations will be generated following some comments on the general properties of the equations. All the systems of equations are nonlinear, nonhomogeneous, simultaneous, ordinary differential equations and the obstacle which prevents rapid, easy and accurate solution is the time dependence. The pseudo-steady solutions in all cases, as well as the boundary and initial conditions provide starting points but, once the finite difference nets are constructed there is no simple way of calculating the particle and bed concentrations for advanced time. Therefore, an iterative method was developed which proved to be quite acceptable both from the standpoint of accuracy and of computer time consumption.

Since the schemes for the composite and discrete formulations are similar, only the sequence for the discrete will be described completely. A different iterative scheme was used for the case of negligible diffusional

resistance and will be presented separately.

Accuracy studies were accomplished by empirical means, i.e., changing step sizes and comparison of results at identical net points. Further comments will be made after the development of the schemes.



#### 4.2. DEVELOPMENT OF FINITE DIFFERENCE SCHEMES--DISCRETE PARTICLE AND BED.

Equations (3-7.1) through (3-7.8) may be put into the following shorthand notation.

$$\nabla_{\xi}^2 y_A = f_1(y_A, y_{B(X)}, y_c) \quad (4-2.1)$$

$$\nabla_{\xi}^2 y_{B(X)} = f_2(y_A, y_{B(X)}, y_c) \quad (4-2.2)$$

$$\nabla_{\xi}^2 y_{B(Y)} = f_3(y_{B(Y)}) \quad (4-2.3)$$

$$\nabla_{\xi}^2 y_R = f_4(y_{B(Y)}) \quad (4-2.4)$$

$$\frac{\partial y_c}{\partial \theta} = f_5(y_{B(X)}, y_c) \quad (4-2.5)$$

$$\text{B.C.1.} \quad \left. \frac{\partial y_{\ell}}{\partial \xi} \right|_{\xi=0} = 0 \quad \ell = A, B_{(X)}, B_{(Y)}, R; \quad \theta \geq 0 \quad (4-2.6)$$

$$\text{B.C.2.} \quad y_{\ell} = y_{\ell s} \quad \left. \begin{array}{l} @ \xi = 1.0 \text{ for } \ell = A \text{ and } B_{(X)}; \\ @ \xi = 1/m \text{ for } \ell = B_{(Y)} \text{ and } R \end{array} \right\} \quad \theta \geq 0 \quad (4-2.7)$$

and

$$\text{I.C.1.} \quad y_c = 0 \quad @ \theta = 0 \quad 0 \leq \xi \leq 1 \quad (4-2.8)$$

Subscripts denoting radial position and axial position are:  $k = k\Delta\xi$ , and  $j = j\Delta\bar{z}$  or  $j\Delta z'$ . Time will be carried as a superscript;  $n = n\Delta\theta$ . Therefore, when a concentration term appears in the form,  $Y_{A(j,k)}^n$ , it means the A concentration  $n$  time steps advanced,  $j$  increments into the bed and  $k$  increments into the particle.

Forward difference formulas were used to approximate all derivatives.

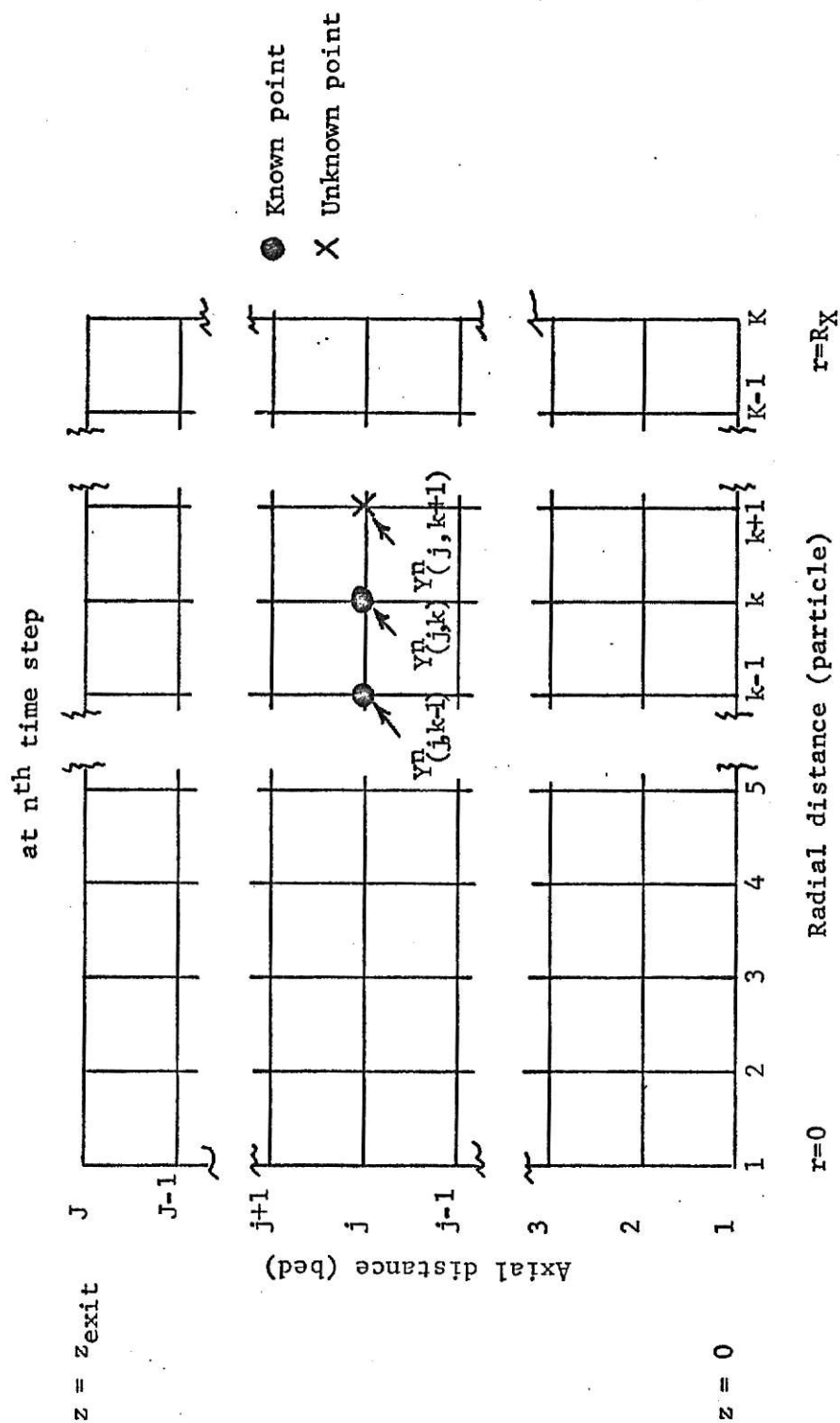


Fig. 4-1. Representation of spatial lattice used in finite difference work.

Consequently,

$$\begin{aligned} \nabla_{\xi}^2 y_{\ell} &= \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial y_{\ell}}{\partial \xi} \right) = \frac{\partial^2 y_{\ell}}{\partial \xi^2} + \frac{2}{\xi} \frac{\partial y_{\ell}}{\partial \xi} \\ &\doteq \frac{y_{\ell}^n(j, k+1) - 2y_{\ell}^n(j, k) + y_{\ell}^n(j, k-1)}{(\Delta \xi)^2} + \frac{2}{k \Delta \xi} \left\{ \frac{y_{\ell}^n(j, k+1) - y_{\ell}^n(j, k)}{\Delta \xi} \right\} \end{aligned} \quad (4-2.9)$$

and

$$\frac{\partial Y_c}{\partial \theta} \doteq \frac{y_{c(j,k)}^{n+1} - y_{c(j,k)}^n}{\Delta \theta} \quad (4-2.10)$$

Usually, because of the set formulas for finite difference approximation of derivatives no difficulty is encountered in their representation; accuracy and convenience being the factors most heavily weighed in making a choice. However, when functions of the variables appear, as in Eqs. (4-2.1-5), it is difficult to say exactly where these should be evaluated. This author felt that since forward difference approximations were being used, the functions should be averaged over the unknown value (whether axial, radial or time) and the previous calculated value. Figure 4-1 shows this procedure. If we wish to know  $Y_A$  at radial position  $k+1$ , with axial position  $j$  and time  $n$ , then the right hand side of Eq. (4-2.1) is evaluated at the average of the  $k^{\text{th}}$  and  $(k+1)^{\text{st}}$  net points. Since the  $(k+1)^{\text{st}}$  point is to be calculated, the above scheme seems to be as exact as any and it is not overly tedious to work with. It may easily be seen, however, that the averaging procedure introduces some unknowns initially in Eq. (4-2.5) which can only be estimated. Improvement is made by iteration. The finite difference representation of Eqs. (4-2.1-5) is as follows (beginning with Eq. (4-2.5)).

$$\begin{aligned}
\frac{Y_{c(j,k)}^{n+1} - Y_{c(j,k)}^n}{\Delta\theta} &= \frac{1}{2} \{f_{5(j,k)}^{n+1} + f_{5(j,k)}^n\} \\
&= \frac{1}{2} \{Y_{B(X)(j,k)}^{n+1} \cdot (1 - Y_{c(j,k)}^{n+1}) + Y_{B(X)(j,k)}^n \cdot (1 - Y_{c(j,k)}^n)\} \quad (4-2.11)
\end{aligned}$$

and rearrangement yields

$$Y_{c(j,k)}^{n+1} = \frac{\left\{ \left[ 1 - \frac{\Delta\theta}{2} Y_{B(X)(j,k)}^n \right] Y_{c(j,k)}^n + \frac{\Delta\theta}{2} \{ Y_{B(X)(j,k)}^{n+1} + Y_{B(X)(j,k)}^n \} \right\}}{\left\{ 1 + \frac{\Delta\theta}{2} Y_{B(X)(j,k)}^{n+1} \right\}} \quad (4-2.12)$$

Assuming that  $n = 1$  is our pseudo-steady starting point then  $Y_{B(X)(j,k)}^{n+1}$  is unknown for  $n \geq 1$  and  $j > 1$ . Therefore, a value such as  $Y_{B(X)(j,k)}^n$  is assumed initially and iteration is performed to improve accuracy. The boundary condition on the above equation is

$$\begin{aligned}
Y_{c(j,k)}^1 &= 0.0 & j &= 1, 2, \dots, J \\
& & k &= 1, 2, \dots, K
\end{aligned} \quad (4-2.13)$$

Once the above concentrations have been calculated utilizing the guess of  $Y_{B(X)(j,k)}^{n+1}$  then  $Y_A$ ,  $Y_{B(X)}$ ,  $Y_{B(Y)}$  and  $Y_R$  may be calculated by a somewhat more sophisticated scheme. The difference representation of Eq. (4-2.1) is

$$\begin{aligned}
\frac{Y_{A(j,k+1)}^{n+1} - 2Y_{A(j,k)}^{n+1} + Y_{A(j,k-1)}^{n+1}}{(\Delta\xi)^2} + \frac{2}{k\Delta\xi} \left\{ \frac{Y_{A(j,k+1)}^{n+1} - Y_{A(j,k)}^{n+1}}{\Delta\xi} \right\} \\
= \frac{1}{2} \{f_{1(j,k+1)}^{n+1} + f_{1(j,k)}^{n+1}\} \quad (4-2.14)
\end{aligned}$$

and rearrangement yields

$$\begin{aligned}
& - y_{A(j,k-1)}^{n+1} + \left\{ \frac{2k+2}{k} + \frac{(\Delta\xi)^2 \gamma_1}{2} (1 - y_{c(j,k)}^{n+1}) \right\} y_{A(j,k)}^{n+1} \\
& - \left\{ \frac{k+2}{2} - \frac{(\Delta\xi)^2 \gamma_1}{2} (1 - y_{c(j,k+1)}^{n+1}) \right\} y_{A(j,k+1)}^{n+1} \\
& = \frac{(\Delta\xi)^2}{2} \left\{ \gamma_2 (1 - y_{c(j,k+1)}^{n+1}) y_{B(X)(j,k+1)}^{n+1} + \gamma_2 (1 - y_{c(j,k)}^{n+1}) y_{B(X)(j,k)}^{n+1} \right\}
\end{aligned} \tag{4-2.15}$$

Several points may be noted about the above equation. First, it is written in implicit form (i.e. at an advanced time). Therefore, solution of a set of simultaneous algebraic equations must be accomplished, quickly and accurately. Secondly, since the time advanced  $B_{(X)}$  concentration is not known, iteration must be employed again. Boundary conditions for this equation

$$\begin{aligned}
y_{A(j,1)}^n &= y_{A(j,2)}^n & j &= 1, 2, \dots, J \\
&& n &= 1, 2, \dots
\end{aligned} \tag{4-2.16}$$

which is equivalent to  $\left. \frac{\partial y_A}{\partial \xi} \right|_{\xi=0} = 0$ ,

and

$$\begin{aligned}
y_{A(j,K)}^n &= y_{A_s(j)}^n & j &= 1, 2, \dots, J \\
&& n &= 1, 2, \dots
\end{aligned} \tag{4-2.17}$$

It is worth while to recall that

$$y_{A(1,K)}^n = 1.000 \quad n = 1, 2, \dots$$

$$y_{B(X)(1,K)}^n = y_{B(Y)(1,K)}^n = 0.0 \quad n = 1, 2, \dots$$

$$Y_{R(1,K)}^n = 0.0 \quad n = 1, 2, \dots \quad (4-2.18)$$

and that  $Y_{A(j,k)}^1$ ,  $Y_{B(X)(j,k)}^1$ ,  $Y_{B(Y)(j,k)}^1$  and  $Y_{R(j,k)}^1$  are known for all  $j$  and  $k$  from the analytic pseudo-steady solutions obtained in Section 3-1.

Equation (4-2.2) in difference form becomes

$$\begin{aligned} Y_{B(X)(j,k-1)}^{n+1} - \left(\frac{2k+2}{k}\right) Y_{B(X)(j,k)}^{n+1} + \left(\frac{k+2}{k}\right) Y_{B(X)(j,k+1)}^{n+1} \\ = \frac{(\Delta\xi)^2}{2} \{f_2^{n+1}(j,k+1) + f_2^{n+1}(j,k)\} \end{aligned} \quad (4-2.19)$$

and in final form becomes

$$\begin{aligned} - Y_{B(X)(j,k+1)}^{n+1} + \left\{ \frac{2k+2}{k} + \frac{(\Delta\xi)^2 \gamma_2}{2} (1 - Y_{c(j,k)}^{n+1}) \right\} Y_{B(X)(j,k)}^{n+1} \\ - \left\{ \frac{k+2}{k} - \frac{(\Delta\xi)^2 \gamma_2}{2} (1 - Y_{c(j,k+1)}^{n+1}) \right\} Y_{B(X)(j,k+1)}^{n+1} \\ = \frac{(\Delta\xi)^2}{2} \{ \gamma_1 (1 - Y_{c(j,k+1)}^{n+1}) Y_{A(j,k+1)}^{n+1} + \gamma_1 (1 - Y_{c(j,k)}^{n+1}) Y_{A(j,k)}^{n+1} \} \end{aligned} \quad (4-2.20)$$

The boundary conditions are

$$Y_{B(X)(j,1)}^n = Y_{B(X)(j,2)}^n \quad \begin{array}{l} n = 2, \dots \\ j = 1, 2, \dots, J \end{array} \quad (4-2.21)$$

and

$$Y_{B(X)(j,K)}^n = Y_{B_s(j)}^n \quad \begin{array}{l} n = 1, 2, \dots \\ j = 1, 2, \dots, J \end{array} \quad (4-2.22)$$

plus the pseudo-steady solutions and the bed entrance condition.

For specie B in the Y particle the difference equation is

$$\begin{aligned}
Y_{B(Y)(j,k-1)}^{n+1} - \left(\frac{2k+2}{k}\right) Y_{B(Y)(j,k)}^{n+1} &= \frac{(\Delta\xi)^2}{2} \{ \gamma_3 (Y_{B(Y)(j,k+1)}^{n+1} \\
&+ Y_{B(Y)(j,k)}^{n+1} ) \}
\end{aligned} \quad (4-2.23)$$

which rearranges to

$$\begin{aligned}
- Y_{B(Y)(j,k-1)}^{n+1} + \left\{ \frac{2k+2}{k} + \frac{\Delta\xi^2 \gamma_3}{2} \right\} Y_{B(Y)(j,k)}^{n+1} \\
- \left\{ \frac{k+2}{k} - \frac{\Delta\xi^2 \gamma_3}{2} \right\} Y_{B(Y)(j,k+1)}^{n+1} = 0
\end{aligned} \quad (4-2.24)$$

with

$$\begin{aligned}
Y_{B(Y)(j,1)}^n &= Y_{B(Y)(j,2)}^n & j &= 1, 2, \dots, J \\
n &= 2, 3, \dots
\end{aligned} \quad (4-2.25)$$

and

$$\begin{aligned}
Y_{B(Y)(j,K)}^n &= Y_{B_s(j)}^n & j &= 1, 2, \dots, J \\
n &= 1, 2, \dots
\end{aligned} \quad (4-2.26)$$

For specie R in the Y particle, the final form of the difference equation is

$$\begin{aligned}
- Y_{R(j,k-1)}^{n+1} + \left\{ \frac{2k+2}{k} \right\} Y_{R(j,k)}^{n+1} - \left( \frac{k+2}{k} \right) Y_{R(j,k+1)}^{n+1} \\
= \frac{(\Delta\xi)^2 \gamma_3}{2} \{ Y_{B(Y)(j,k+1)}^{n+1} + Y_{B(Y)(j,k)}^{n+1} \}
\end{aligned} \quad (4-2.27)$$

with

$$\begin{aligned}
Y_{R(j,1)}^n &= Y_{R(j,2)}^n & j &= 1, 2, \dots, J \\
n &= 2, 3, \dots
\end{aligned} \quad (4-2.28)$$

and

$$y_{R(j,K)}^n = y_{R_s(j)}^n \quad \begin{array}{l} j = 1, 2, \dots, J \\ n = 1, 2, \dots \end{array} \quad (4-2.29)$$

Since the surface concentrations at the front of the bed are known, the above equations may be solved for advanced time at  $j = 1$ , i.e. the particle concentration just inside the bed entrance. The Thomas method of solving large sets of tridiagonal simultaneous algebraic equations [23] was employed to get the time advanced concentrations of A, B and R. Iteration to improve accuracy was accomplished by substituting the calculated  $y_{B(X)(j,k)}^{n+1}$  for the assumed  $y_{B(X)(j,k)}^{n+1}$  and repeating all calculations. It will be shown later that two concentration checks were used to insure the convergence of the iterative scheme.

Once values were obtained for the particle concentrations at  $j = 1$  it was time to advance one step into the bed. This involved the numerical solution of the bed equations presented in Section 3-7. Forward difference approximations were used for the axial derivatives, i.e.

$$\frac{\partial y_{\ell s}}{\partial \bar{z}} = \frac{y_{\ell s(j+1)}^n - y_{\ell s(j)}^n}{\Delta \bar{z}} \quad \begin{array}{l} \ell = A, B, R \\ j = 1, 2, \dots \\ n = 2, 3, \dots \end{array} \quad (4-2.30)$$

The expressions for the particle concentration gradients at the surfaces were somewhat difficult to formulate. The gradient at the surface is not known for the  $(j+1)^{st}$  position, hence the gradient at the  $j^{th}$  position was used and the finite difference approximations to (3-7.9-11) become

$$y_{A_s(j+1)}^{n+1} = y_{A_s(j)}^{n+1} - 3a \frac{\Delta \bar{z}}{\Delta \xi} \{y_{A(j,K)}^{n+1} - y_{A(j,K-1)}^{n+1}\} \quad (4-2.31)$$



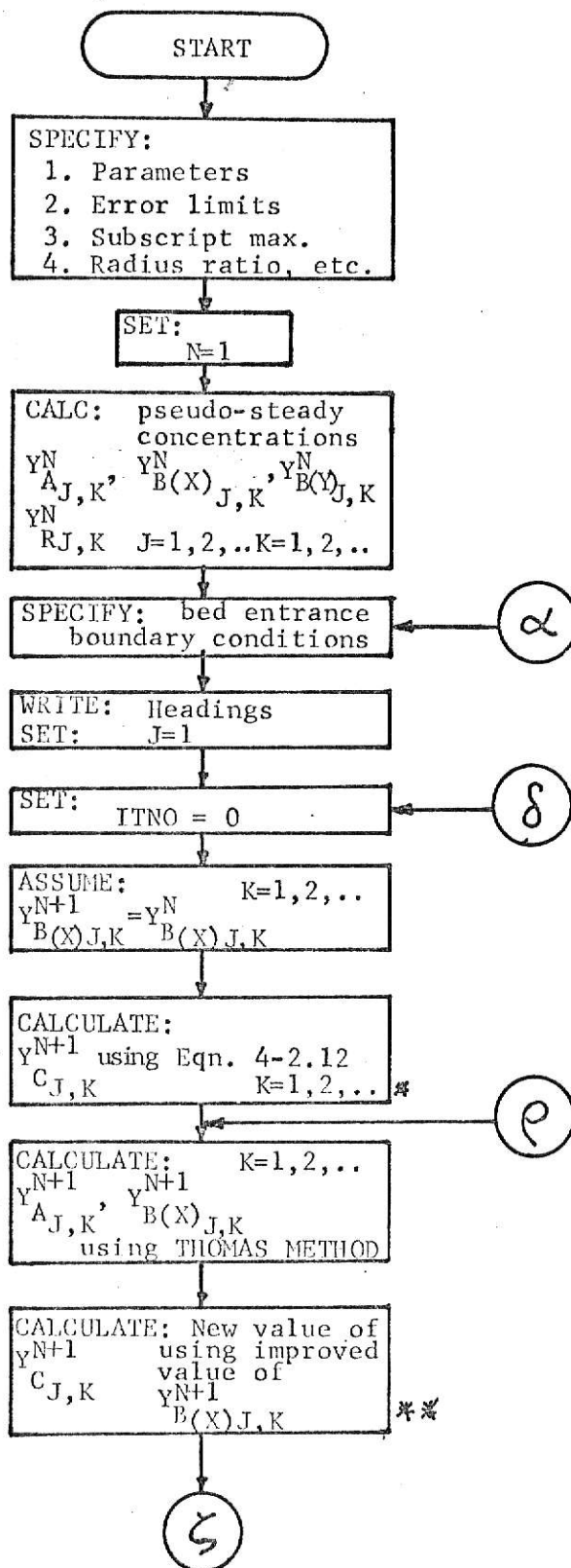


Fig. 4-2. Flow chart of calculations for discrete particle case.

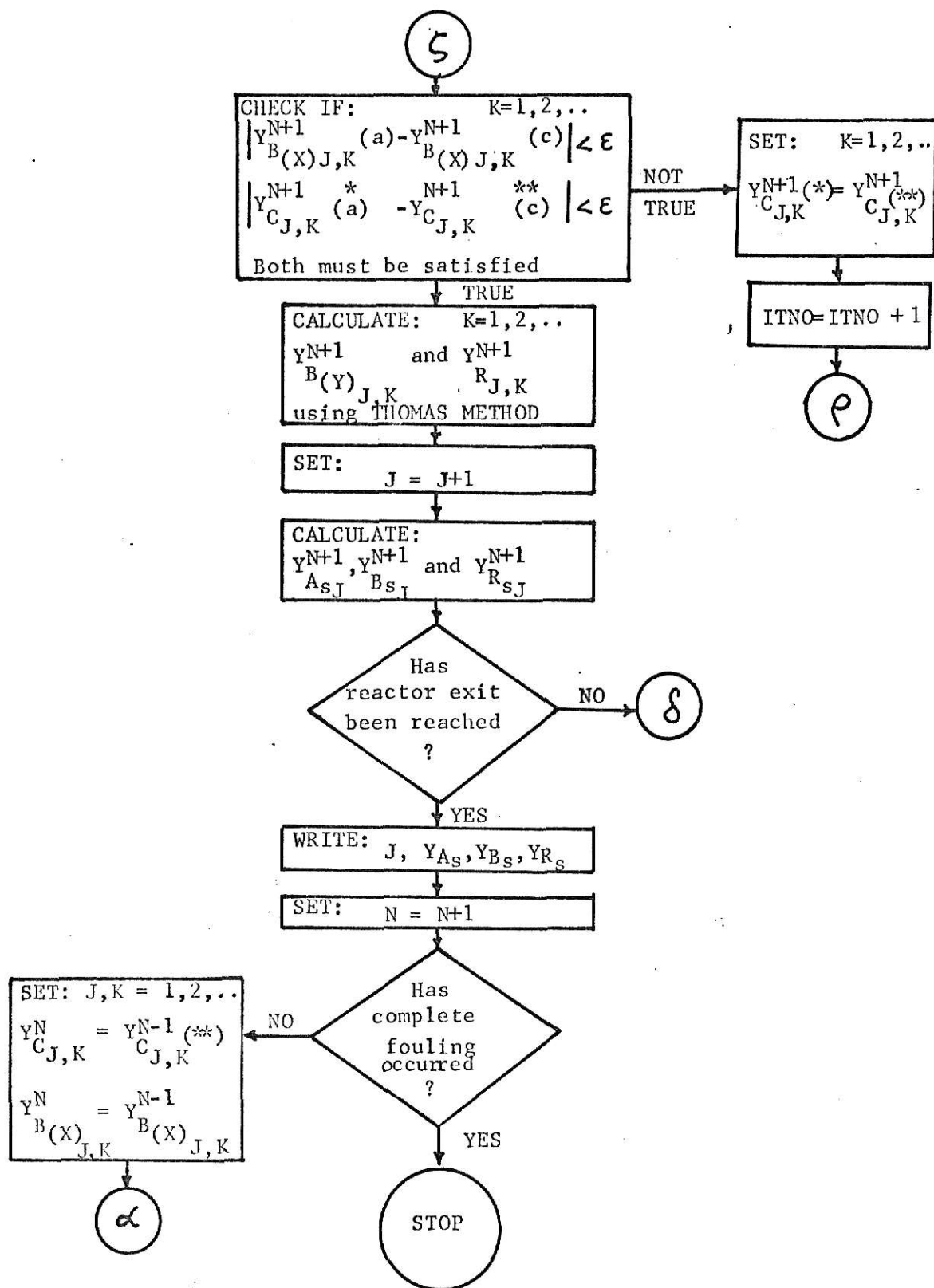


Fig. 4-2. (continued)

$$\begin{aligned}
Y_{B_s(j+1)}^{n+1} &= Y_{B_s(j)}^{n+1} - 3 \frac{\Delta \bar{z}}{\Delta \xi} \{ a(Y_{B(X)(j,K)}^{n+1} - Y_{B(X)(j,K-1)}^{n+1}) \\
&\quad + m^2(1-a)(Y_{B(Y)(j,K)}^{n+1} - Y_{B(Y)(j,K-1)}^{n+1}) \} \quad (4-2.32)
\end{aligned}$$

$$Y_{R_s(j+1)}^{n+1} = Y_{R_s(j)}^{n+1} - 3m^2 \frac{(1-a)\Delta \bar{z}}{\Delta \xi} \{ Y_{R(j,K)}^{n+1} - Y_{R(j,K-1)}^{n+1} \} \quad (4-2.33)$$

with

$$Y_{\ell s(1)}^n = \begin{cases} 1.0 & \text{for } = A \\ 0.0 & \text{for } = B, R \end{cases} \quad (4-2.34)$$

plus the pseudo-steady solutions, i.e.  $Y_{\ell s(j)}^1$ ;  $j = 1, 2, \dots, J$  are all known.

Once the surface concentrations were calculated for a step down the bed the particle concentrations could be calculated for the position. This kind of stepping procedure was utilized until the bed exit was reached. Then the time increment,  $n$ , was advanced and the entire procedure was begun again at the bed entrance. This entire cycle was repeated until the dimensionless poison concentration approached unity or the B concentration approached zero; indicative of complete fouling. Figure 4-2 presents the flow chart of calculations for both the discrete and composite cases.

#### 4-3. DEVELOPMENT OF FINITE DIFFERENCE SCHEMES--NEGLIGIBLE DIFFUSION RESISTANCE CASE.

The numerical solution of the equations describing this case was considerably simplified owing to the fact that no particle concentrations needed to be calculated. However, since the fouling model and hence the poison concentration, appears explicitly in the bed equations, it was concluded that an iterative scheme was necessary to achieve accuracy for the gaseous concentrations. Equations (3-7.22-25) may be represented in short form by

$$\frac{\partial y_{A_s}}{\partial z'} = f'_1(y_{A_s}, y_{B_s}, y_c); \quad y_{A_s} = 1.0 @ z' = 0.0 \quad (4-3.1)$$

$$\frac{\partial y_{B_s}}{\partial z'} = f'_2(y_{A_s}, y_{B_s}, y_c); \quad y_{B_s} = 0.0 @ z' = 0.0 \quad (4-3.2)$$

$$\frac{\partial y_{R_s}}{\partial z'} = f'_3(y_{B_s}); \quad y_{R_s} = 0.0 @ z' = 0.0 \quad (4-3.3)$$

$$\frac{\partial y_c}{\partial \theta} = f'_4(y_{B_s}, y_c); \quad y_c = 0.0 @ \theta = 0.0 \quad (4-3.4)$$

Forward difference equations were used to approximate the derivatives so

$$\frac{\partial y_{\ell_s}}{\partial z'} = \frac{y_{\ell_s}^n(j+1) - y_{\ell_s}^n(j)}{\Delta z'} \quad \ell = A, B, R \quad (4-3.5)$$

and

$$\frac{\partial y_c}{\partial \theta} = \frac{y_c^{n+1}(j) - y_c^n(j)}{\Delta \theta} \quad (4-3.6)$$

Here, as before,  $y_{\ell_s}^n$  will specify the concentration of the  $\ell^{\text{th}}$  specie  $y_{\ell_s}^n(j)$

at the  $j^{\text{th}}$  location down the bed and at the  $n^{\text{th}}$  time increment. The right hand sides of Eqs. (4-3.1-3) were averaged over the  $j^{\text{th}}$  and  $(j+1)^{\text{st}}$  axial steps while the right hand side of Eq. (4-3.4) was averaged over the  $n^{\text{th}}$  and  $(n+1)^{\text{st}}$  time steps. Equations (4-3.1-4) become

$$Y_{A_s(j+1)}^{n+1} = Y_{A_s(j)}^{n+1} + \frac{\Delta z'}{2} \{f_1^{n+1}(j+1) + f_1^{n+1}(j)\} \quad (4-3.7)$$

$$Y_{B_s(j+1)}^{n+1} = Y_{B_s(j)}^{n+1} + \frac{\Delta z'}{2} \{f_2^{n+1}(j+1) + f_2^{n+1}(j)\} \quad (4-3.8)$$

$$Y_{R_s(j+1)}^{n+1} = Y_{R_s(j)}^{n+1} + \frac{\Delta z'}{2} \{f_3^{n+1}(j+1) + f_3^{n+1}(j)\} \quad (4-3.9)$$

$$Y_{c(j)}^{n+1} = Y_{c(j)}^n + \frac{\Delta \theta}{2} \{f_4^{n+1}(j) + f_4^n(j)\} \quad (4-3.10)$$

with the boundary and initial conditions

$$Y_{\ell_s(1)}^n = \begin{cases} 1.0, & \ell = A \\ 0.0, & \ell = B, R \end{cases}; \quad n = 1, 2, \dots \quad (4-3.11)$$

$$Y_{c(j)}^1 = 0.0; \quad j = 1, 2, \dots, J \quad (4-3.12)$$

The pseudo-steady solutions obtained in Section 3-5 also provide a starting point. In final form Eqs. (4-3.7-10) are

$$\begin{aligned}
Y_{A_s(j+1)}^{n+1} &= \frac{[1 - \frac{\Delta z' W_1}{2} (1 - Y_{c(j)}^{n+1})]}{[1 + \frac{\Delta z' W_1}{2} (1 - Y_{c(j)}^{n+1})]} Y_{A_s(j)}^{n+1} \\
&+ \frac{\Delta z' W_2}{2} \cdot \frac{[(1 - Y_{c(j)}^{n+1}) Y_{B_s(j)}^{n+1} + (1 - Y_{c(j+1)}^{n+1}) Y_{B_s(j+1)}^{n+1}]}{[1 + \frac{\Delta z' W_1}{2} (1 - Y_{c(j+1)}^{n+1})]}
\end{aligned} \quad (4-3.13)$$

$$\begin{aligned}
Y_{B_s(j+1)}^{n+1} &= \frac{[1 - \frac{\Delta z'}{2} \{W_2(1 - Y_{c(j)}^{n+1}) + W_3\}]}{[1 + \frac{\Delta z'}{2} \{W_2(1 - Y_{c(j+1)}^{n+1}) + W_3\}]} \cdot Y_{B_s(j)}^{n+1} \\
&+ \frac{\Delta z' W_1}{2} \cdot \frac{[(1 - Y_{c(j)}^{n+1}) Y_{A_s(j)}^{n+1} + (1 - Y_{c(j+1)}^{n+1}) Y_{A_s(j+1)}^{n+1}]}{[1 + \frac{\Delta z'}{2} W_1 (1 - Y_{c(j+1)}^{n+1})]}
\end{aligned} \quad (4-3.14)$$

$$Y_{R_s(j+1)}^{n+1} = Y_{R_s(j)}^{n+1} + \frac{W_3 \Delta z'}{2} [Y_{B_s(j)}^{n+1} + Y_{B_s(j+1)}^{n+1}] \quad (4-3.15)$$

$$Y_{c(j)}^{n+1} = \frac{[Y_{c(j)}^n + \frac{\Delta \theta W_1}{2} [(1 - Y_{c(j)}^n) Y_{B_s(j)}^n + Y_{B_s(j)}^{n+1}]]}{[1 + \frac{\Delta \theta W_1}{2} Y_{B_s(j)}^{n+1}]} \quad (4-3.16)$$

where

$$W_1 = \zeta; \quad W_2 = K^* \zeta \quad \text{and} \quad W_3 = K_1^* (1 - \zeta) \quad (4-3.17)$$

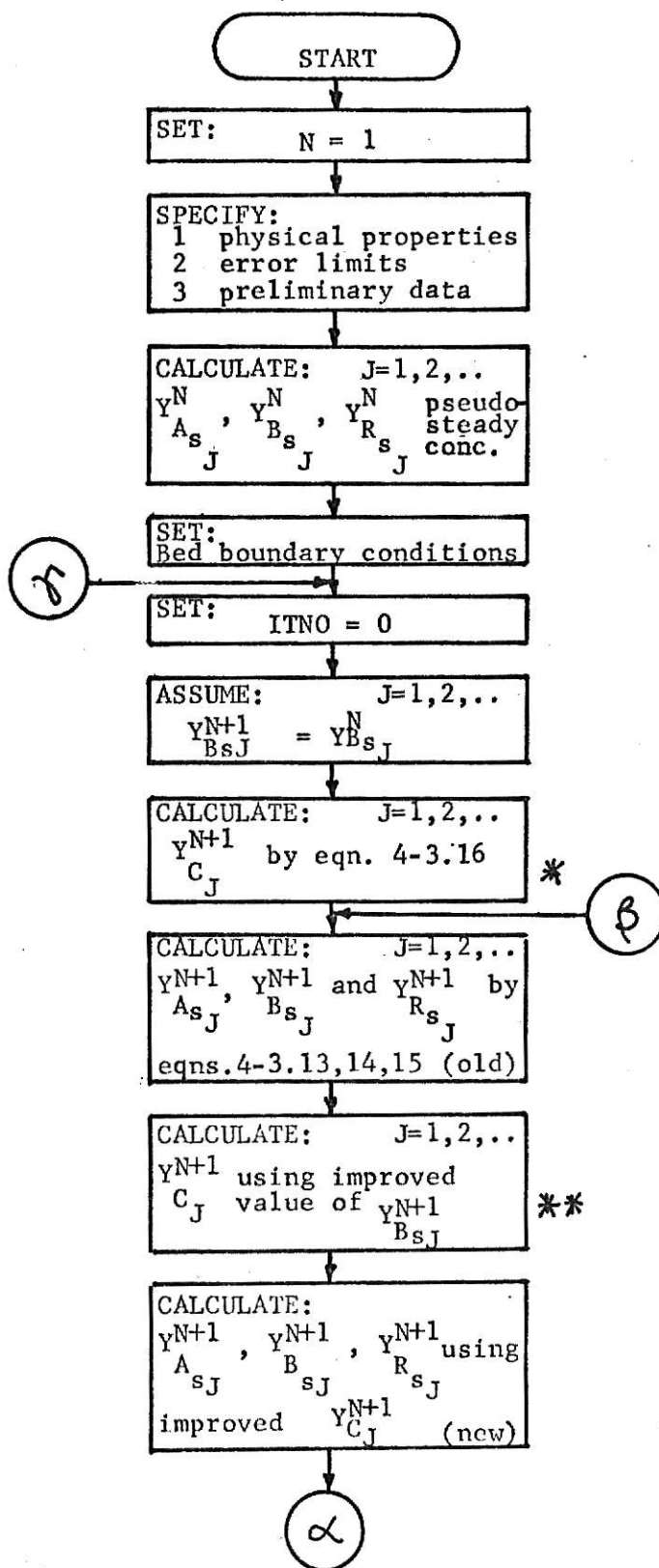


Fig. 4-3. Flow chart of calculations for no diffusion resistance.

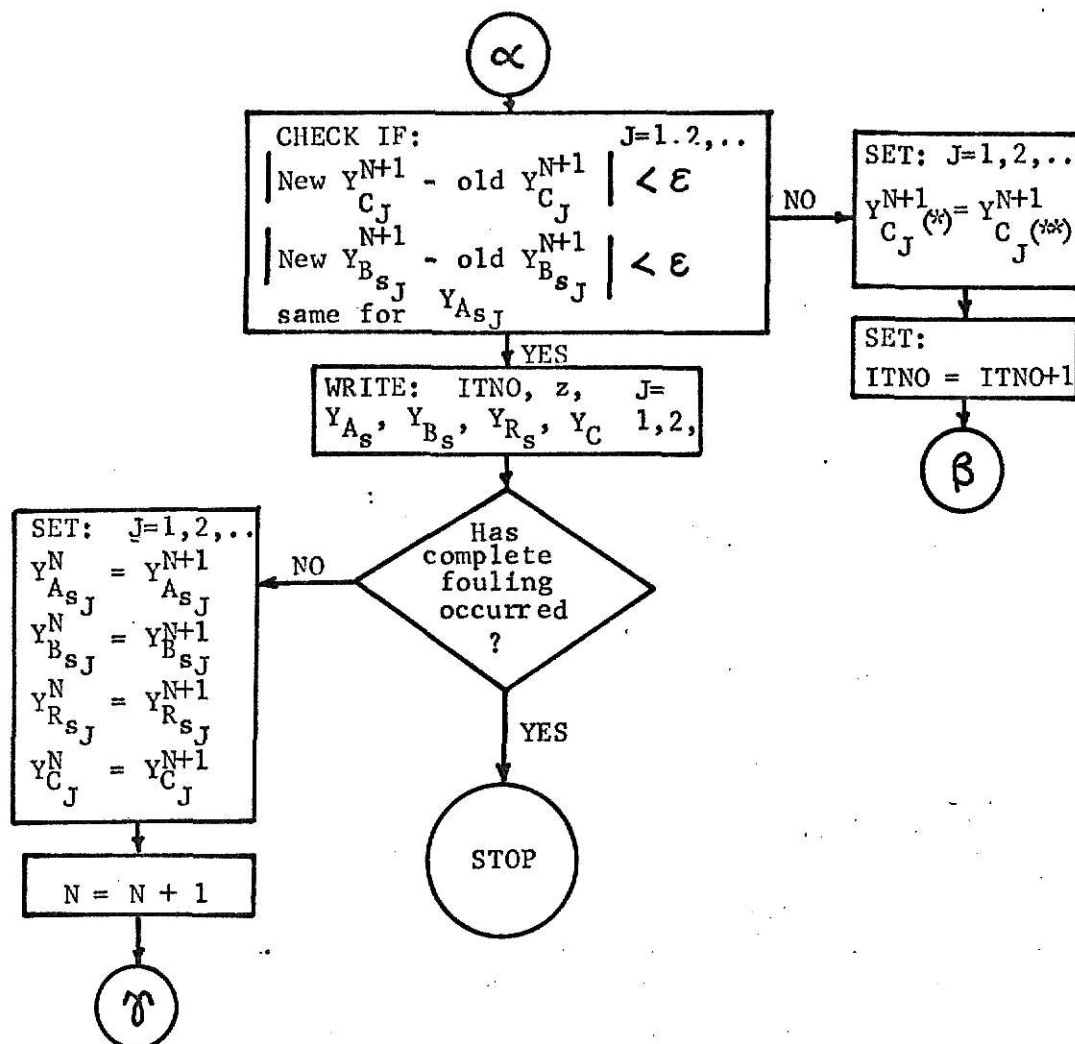


Fig. 4-3. (continued)



It may easily be seen both in Eqs. (4-3.13) and (4-3.16) that  $y_{B_s(j+1)}^{n+1}$  is not known and initially a value will have to be assumed. Iteration will improve the accuracy of  $y_{B_s(j+1)}^{n+1}$  and hence the other concentrations. Figure 4-3 shows the calculational sequence and illustrates the use of accuracy checks in the iteration procedure.

#### 4.4. ERROR ANALYSIS OF FINITE DIFFERENCE FORMULATIONS.

Accuracy studies have been made by considering step size variations and their effect on the values calculated for the concentrations at identical lattice points. For instance, if the effect of axial step size was to be studied, the radial and time increment sizes would be held constant and only the axial step size would be varied. The values obtained for each concentration could then be compared at identical axial positions. This same type of procedure is applicable in ascertaining the effects of the other step sizes on the accuracy of calculations.

It was felt that since the same calculational procedures were utilized in both the discrete and composite cases, and in order to avoid excessive use of computer time, only one of the cases would be studied for accuracy in detail. By chance it was decided to use the composite case although later developments indicated that the discrete case was much more sensitive. It was found that the size of the time increment and the radius ratio,  $\underline{m}$ , had marked effects on the convergence of the iterative scheme in the discrete case while very little effect was noted in the composite case. No particular cause could be found for the difference in effects, but it was found that small time increments ( $\Delta\theta \leq 20$ ) and low values of  $m$  (i.e.,  $m < 5$ ) were necessary to insure relatively rapid convergence.

The composite case was studied rather extensively for increment effects on accuracy. Tables 4-1 and 4-2 along with Figs. 4-4 and 4-5 show the effect of varying axial and time step sizes on the accuracy of the concentration of the intermediate B, which is the least prevalent specie and the one most subject to variance. It can be seen in Fig. 4-4 that increasing the axial increment made a large difference near the entrance of the reactor. This is

TABLE 4-1. Axial step size effect on reaction intermediate concentration at several axial positions.

(Radial step size is constant,  $\Delta r = 0.04$ )  
 (Overall dimensionless time is constant,  $\theta = 20$ )

$\frac{Y_{Bs}}{\Delta z}$	@ $\bar{z} = 0.4$	@ $\bar{z} = 0.8$	@ $\bar{z} = 1.6$	@ $\bar{z} = 4.0$	@ $\bar{z} = 10.0$
0.08	0.03669	0.03635	0.03421	0.02845	0.01783
0.10	0.03709	0.03636	0.03421	0.02844	0.01782
0.20	0.03310	0.03593	0.03418	0.02840	0.01775

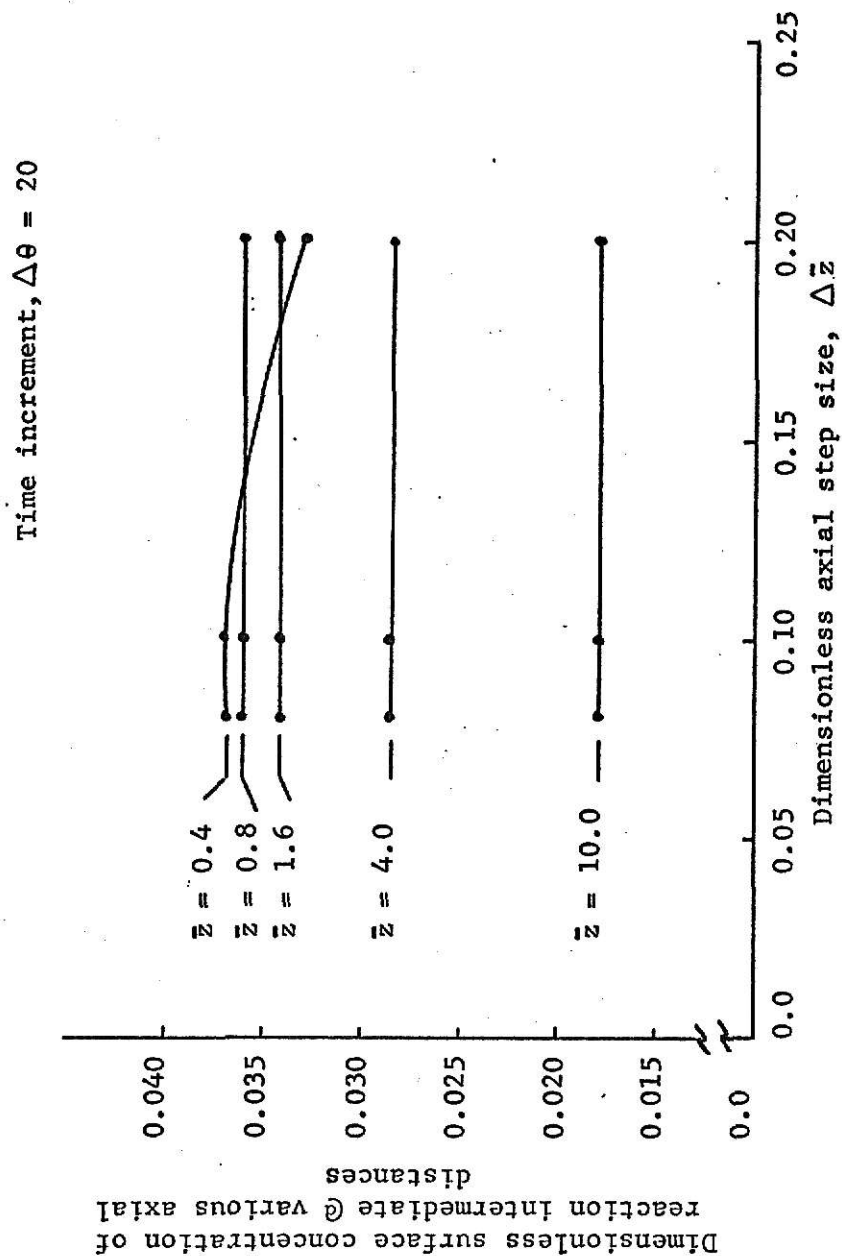


Fig. 4-4. Effect of axial step size on accuracy -- composite case.

TABLE 4-2. Effect of time step size on reaction intermediate concentration at selected values of axial distance.

(Axial step size is constant  $\Delta \bar{z} = 0.10$ )  
(Radial step size is constant  $\Delta \xi = 0.04$ )

$\theta$ (total)	$\begin{matrix} Y_{B_s} \\ \Delta \theta \end{matrix}$	@ $\bar{z} = 0.4$	@ $\bar{z} = 0.8$	@ $\bar{z} = 5.0$	@ $\bar{z} = 10.0$
20	10	0.03669	0.03635	---	---
	20	0.03709	0.03636	0.02632	0.01782
	20	0.03249	0.03245	0.02519	0.01800
100	50	0.03252	0.03240	0.02518	0.01801
	100	0.03250	0.03219	0.02516	0.01804
	20	0.02691	0.02707	0.02325	0.01810
200	50	0.02689	0.02697	0.02323	0.01812
	100	0.02669	0.02656	0.02317	0.01787

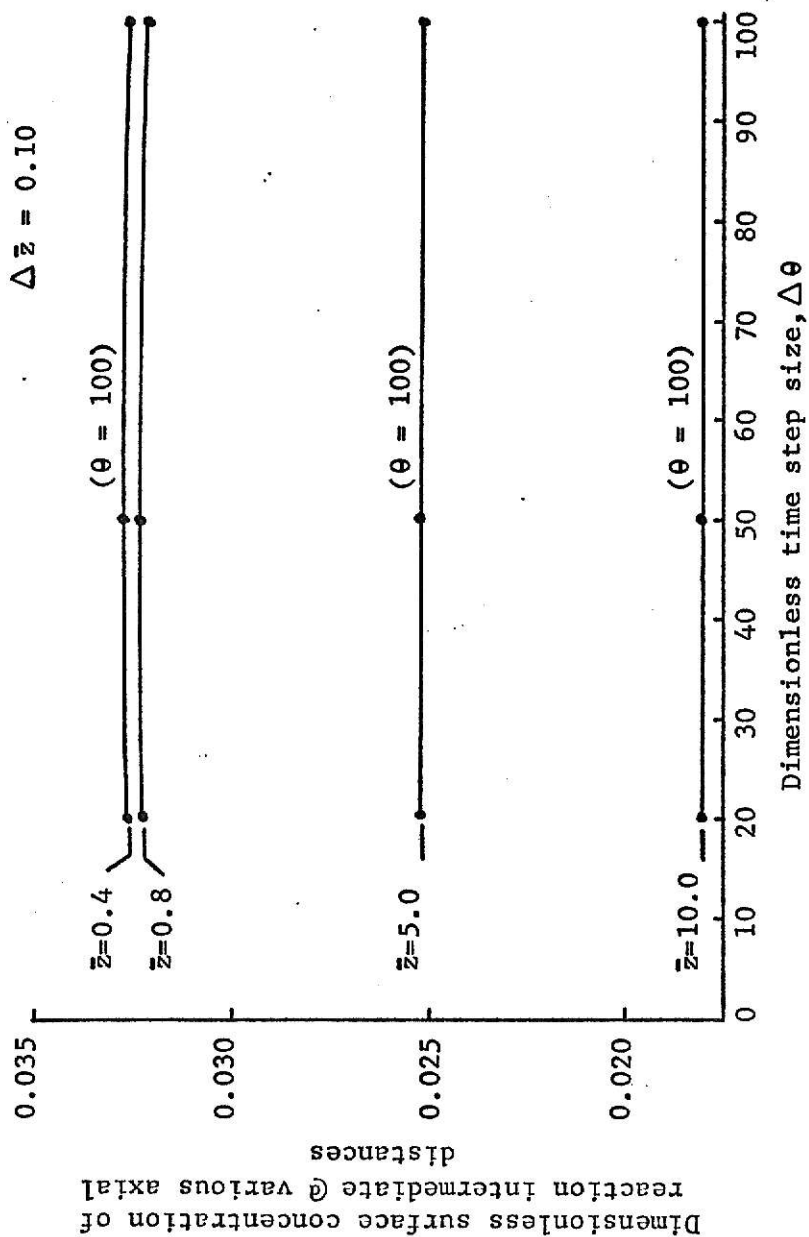


Fig. 4-5. Effect of time increment on accuracy -- composite case.

expected since  $Y_B$  rapidly attains a maximum somewhere in the range  $0 < \bar{z} < 1.5$ , and then slowly falls with increasing  $\bar{z}$ . Therefore smaller axial step sizes are required near the entrance to insure accuracy while larger increments give nearly the same accuracy beyond the maximum.

For identical axial and radial increment sizes there was very little effect on accuracy with increasing time step. The only noticeable variance came for small overall values of  $\theta$  and short distances into the bed; but is explainable on the basis of statements made in the previous paragraph. Increasing time increments also increased the average number of iterations required for predefined convergence limits to be satisfied.

Tables 4-3 and 4-4 as well as Figs. 4-6 and 4-7 illustrate the effects of varying axial and time step sizes on the reaction intermediate concentration at selected locations within the reactor for the case of no diffusional resistance. Equivalent conclusions can be drawn for this case as was done for the composite analysis. Large axial step sizes result in a fairly large inaccuracy near the front of the bed but all step sizes studied gave good results once the axial position corresponding to the maximum  $Y_{B_s}$  concentration had been passed. For the same axial increment there is little variation with changing time increments. The area of most concern lay between the reactor entrance and the point where  $Y_{B_s}$  exhibits its maximum value. Here there were minor discrepancies which increased with increasing time step. The average number of iterations increased with increasing  $\Delta\theta$  also.

In conclusion, judging from Figs. 4-4, 4-5, 4-6 and 4-7, the numerical analysis of these cases is quite accurate and is not inordinately time consuming on the digital computer.

TABLE 4-3. Effect of axial step size on reaction intermediate concentration at selected values of axial distance. No diffusion resistance.

(time step size is held constant,  $\Delta\theta = 20$ )

OVERALL  $\theta = 40$

$\begin{matrix} Y_{B_s} \\ \Delta z' \end{matrix}$	@ $z' = 0.5$	@ $z' = 1.0$	@ $z' = 5.0$	@ $z' = 25.0$
.10	0.03269	0.03590	0.03250	0.01780
.125	0.03280	0.03592	0.03250	0.01780
.250	0.03384	0.03612	0.03249	0.01779



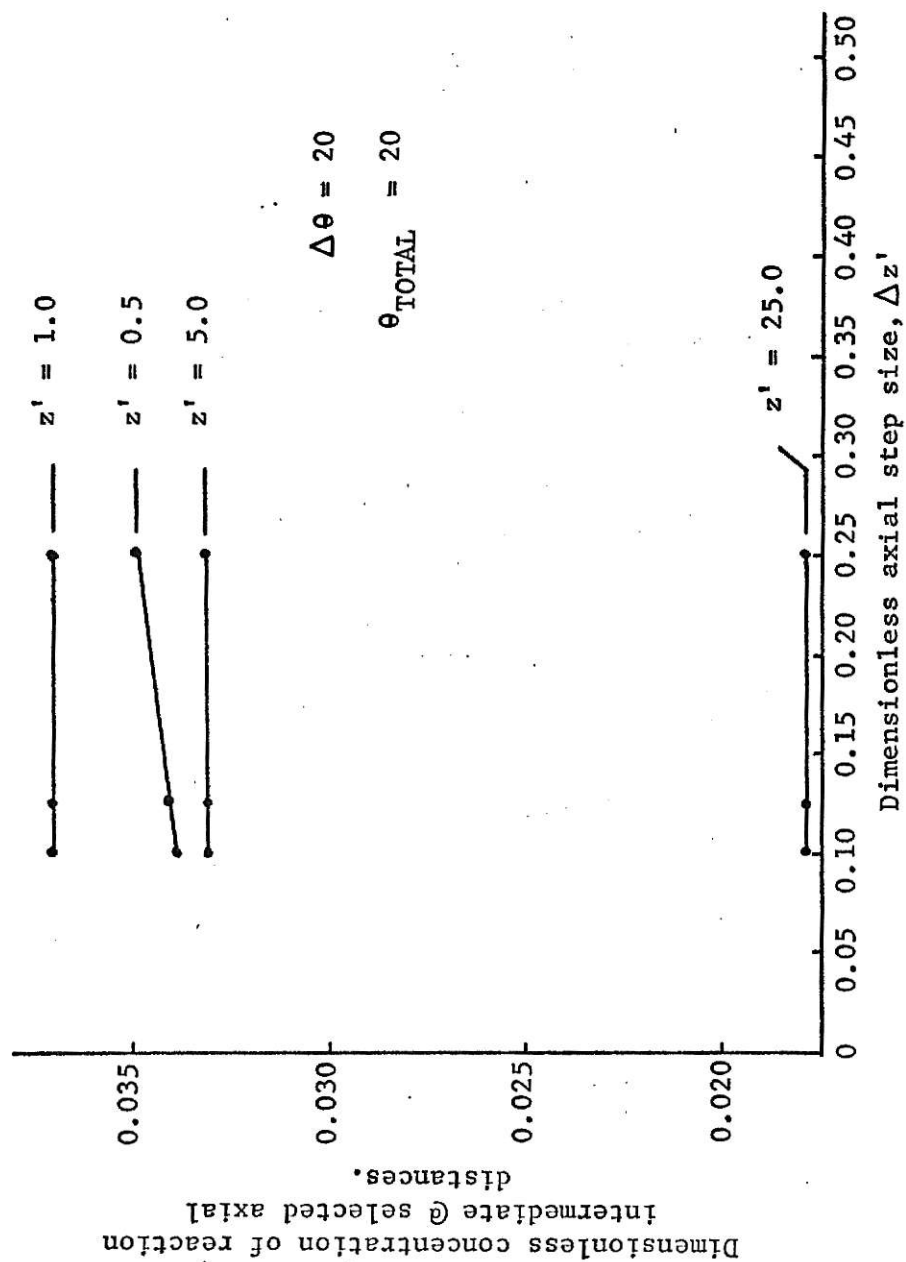


Fig. 4-6. Effect of axial step size on accuracy -- no diffusional resistance case.

TABLE 4-4. Effect of time step size on reaction intermediate concentration at selected values of axial distance. No diffusion resistance.

(Axial step size is held constant,  $\Delta z' = 0.25$ )

$\theta$ (total)	$\begin{matrix} Y_{Bs} \\ \Delta\theta \end{matrix}$	@ $z' = 0.5$	@ $z' = 1.0$	@ $z' = 5.0$	@ $z' = 25.0$
40	10	0.03382	0.03612	0.03239	0.01779
	20	0.03384	0.03612	0.03249	0.01779
50	10	0.03328	0.03556	0.03214	0.01787
	50	0.03332	0.03555	0.03212	0.01782
100	20	0.03073	0.03272	0.03027	0.01793
	50	0.03073	0.03267	0.03023	0.01793
200	20	0.02657	0.02733	0.02606	0.01802
	50	0.02655	0.02724	0.02598	0.01804

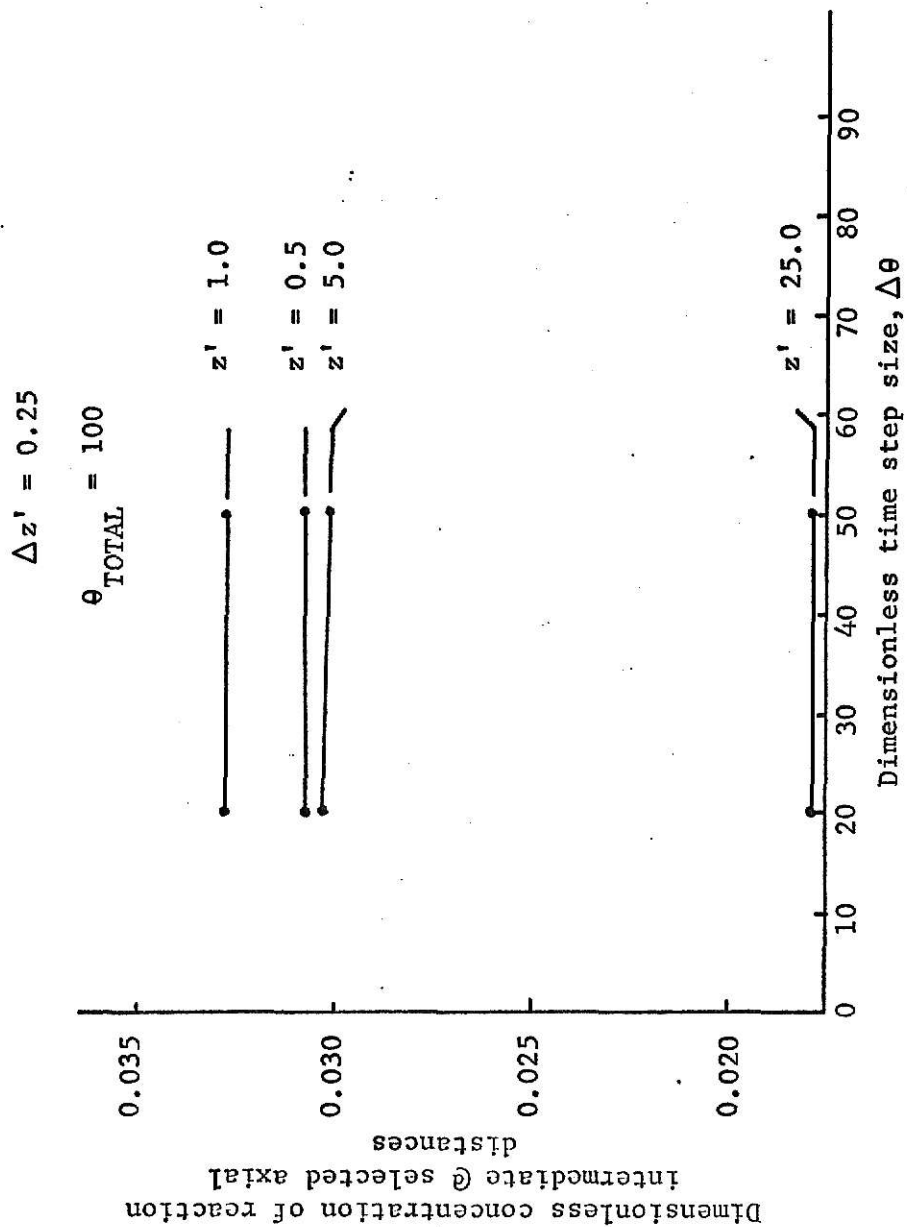


Fig. 4-7. Effect of time increment size on accuracy, no diffusional resistance case.

## CHAPTER 5

## RESULTS AND DISCUSSION

Prior to investigating poison buildup effects on intraparticle mass transfer in the two catalyst formulations the possibility of increasing yields by using unequal particle sizes in the discrete formulation was considered.

A parameter  $\underline{m}$  was employed to specify the radius ratio of the X particle to the Y particle. Various values of  $\underline{m}$  (holding  $R_X$  at 0.25cm.) were used indicative of the relative magnitudes of diffusion resistance associated with each particle. Figure 5-1 shows that using larger Y particles and hence larger diffusion resistance ( $\underline{m} < 1.0$ ) results in a lower maximum yield of product with an attendant drop in the optimal weight fraction of catalyst X. Increasing  $\underline{m}$  above unity, which is equivalent to reducing the Y particle size, reduces the diffusional resistance and enhances the maximum yield obtainable. It may be seen though, for  $\underline{m} > 5$ , that the importance of diffusional resistance becomes negligible in determining the maximum yield of R. The broken curve shows the maximum product concentration and optimal weight fraction of X for the composite case (using particles of radius  $R_X$ ). Two points are evident: 1), under equivalent circumstances the composite particles provide better yields than any value of  $\underline{m}$  for the discrete, and at a lower optimal weight fraction of X, and 2), better yields are obtainable in the discrete case for  $\underline{m}$  values greater than unity, but these larger particle ratios may be subject to mechanical limitations.

Employing the numerical integration procedures previously described, bed and particle concentration profiles for each formulation were computed and conclusions, based on the physical and chemical properties and reactor

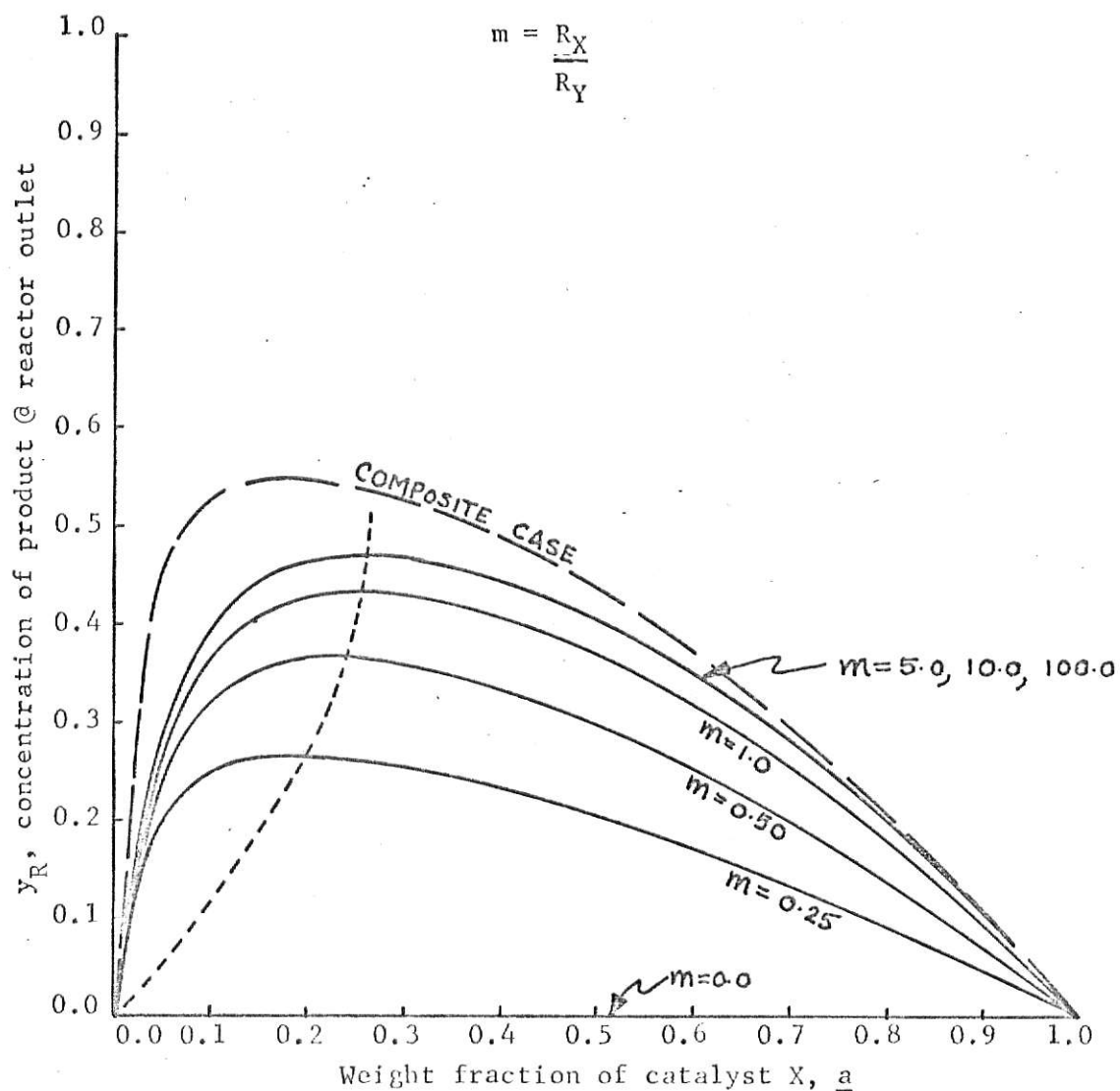


Fig. 5-1. Effect of varying radius ratio on product yield at reactor outlet. Discrete formulation.

dimensions given in Table 5-1 were drawn. Comparisons were also made with negligible diffusion resistance results. Once this phase was completed parameter studies were conducted on the following:

- (1) The effect of varying the equilibrium constant  $K = k_1^0/k_2^0$  on the fouling rates of the two formulations, and
- (2) Effect of varying the product forming rate constant  $k_3^0$  on the fouling rates of the two formulations.

Figure 5-2 clearly indicates the superiority of the composite formulation over the discrete formulation with a much higher initial exit product concentration and a slower decay rate with time. Curve 1 of this figure utilizes those values given in Table 5-1 for the comparison of the formulations. Curves 2 and 3 show the effect of varying the product forming rate constant. Increasing  $k_3^0$  gives an attendant increase in the initial exit concentration of R but also causes an increase in the decay rate for both formulations. The curves for the case of negligible diffusion resistance were nearly superimposeable on the composite case curves and hence were not plotted.

Figure 5-3 was utilized to illustrate the effect the product forming rate constant had on the rates of product concentration decay with time. The difference of the exit concentrations was plotted versus dimensionless time and as can be seen the effect of increasing  $k_3^0$  is to increase the difference in decay rates with time until a maximum difference is obtained. This is followed by a gradual decline in the decay rate difference. This latter trend is easily evidenced by the rapid levelling off of the discrete formulation curves with time in Fig. 5-2.

The magnitude of the equilibrium constant will have an important effect on the fouling rates of both formulations. Both Figs. 5-4, which illustrates

Table 5-1. Chemical and physical properties and reactor dimensions for catalyst formulation comparison.

	Discrete Formulation	Composite Formulation	No Diffusion Resistance
$\rho_c$ (gr./cc.)	1.0	1.0	1.0
$\rho_B$ (gr./cc.)	0.8	0.8	0.8
$R_X$ (cm.)	0.25	0.25	0.25
$R_Y$ (cm.)	0.25	0.25	0.25
$z$ (cm.)	156.25	156.25	156.25
$k_1^0$ (cc./sec.-gr.catalyst)	0.2	0.2	0.2
$k_2^0$ (cc./sec.-gr.catalyst)	4.0	4.0	4.0
$k_3^0$ (cc./sec.-gr.catalyst)	0.2	0.2	0.2
optimum catalyst weight fraction	$a = 0.26$	$\epsilon = 0.18$	$\zeta = 0.18$
$R$ (cm.)	3.5	3.5	3.5

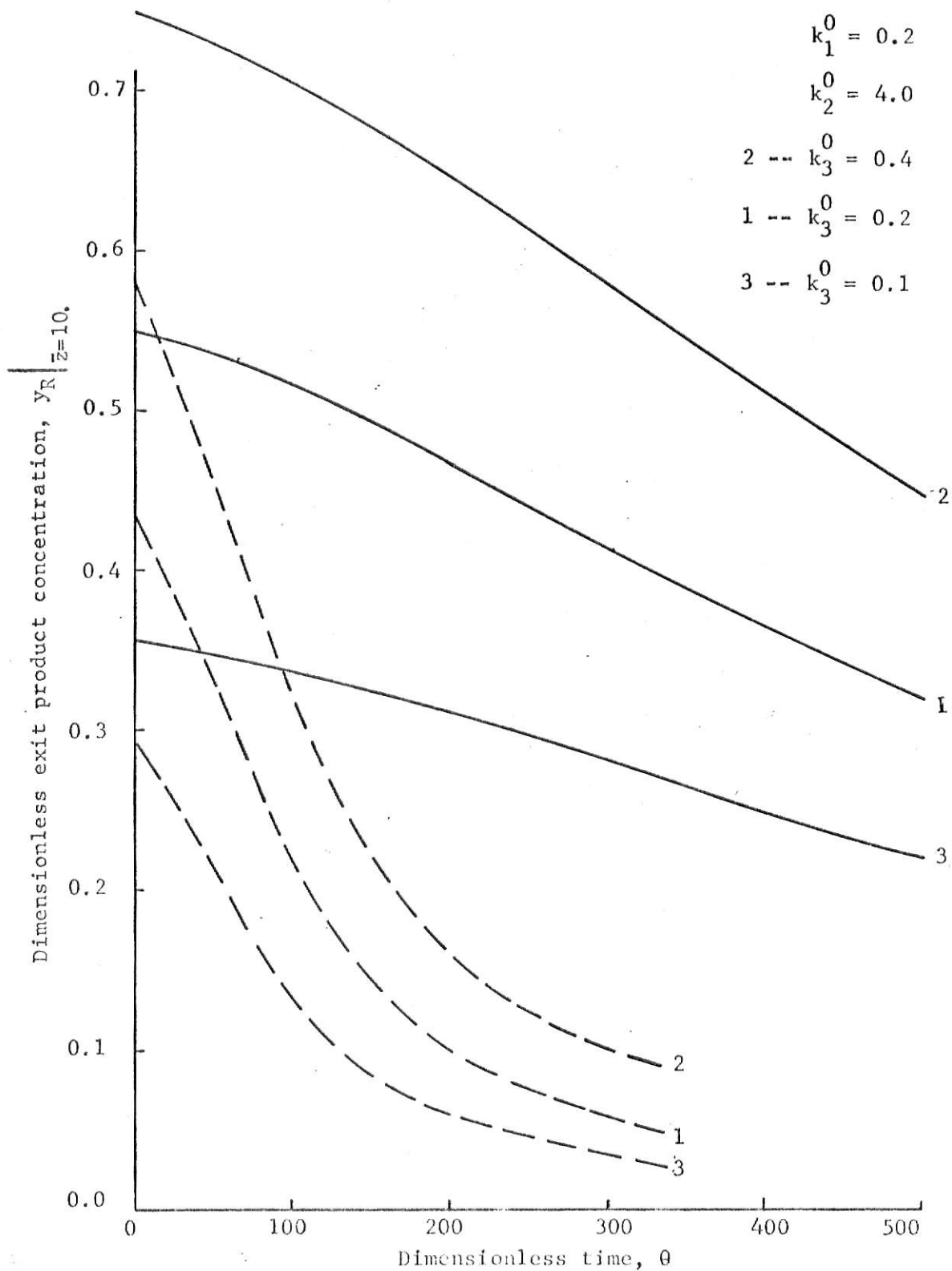


Fig. 5-2. Exit product decay rates with time. — Composite particle results. - - - Discrete particle results.



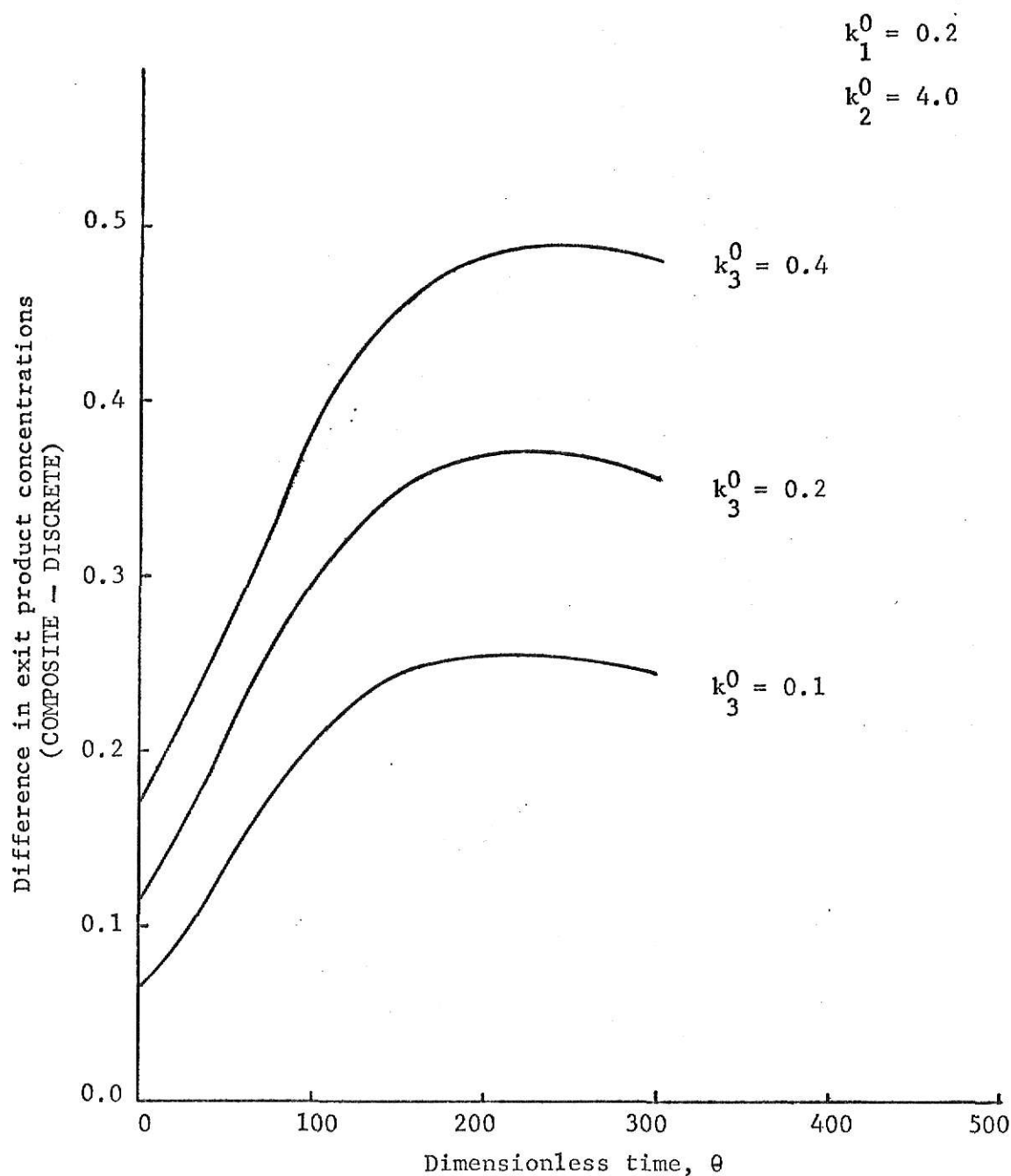


Fig. 5-3. Effect of product rate constant on decay rate difference of the two formulations.

the effect on the composite case, and 5-5, which is the equivalent plot for the discrete case, show increased initial values of exit  $y_R$  with increased  $K$  but also more rapid decay rates, especially for the discrete case, which would be expected.

Examination of poison precursor and poison profiles within individual particles yielded some important results. Figures 5-6 and 5-7, which are plots of the precursor concentration versus radial distance (with time and axial position as parameters), show a definite diffusional driving force for B out of the discrete particle while the B concentration in the composite particle is nearly that which would be expected for negligible diffusion resistance. This is explainable since Y sites are available on the same particle to catalyze the product forming reaction. Evident also in the much more rapid depletion of B in the discrete case, indicative of more severe poisoning. This can be rationalized as follows. Assuming Knudsen diffusion and no strong surface adsorption effects, for an equivalent number of wall collisions specie B has a finite probability of striking a Y site in the composite particle and converting to product which will not cause poisoning. However, in the discrete case, B, in its journey out of the X particle can strike only X sites and will poison some of them. The poisoned sites will then, by their elimination, reduce the concentration of B possible from the X particle. This is not to say there won't be poisoning in the composite particle but, that by the nature of Knudsen diffusion and the physical presence of Y sites some conversion of B to product instead of poison will occur. The poison buildup in the two formulations represented in Figs. 5-8 and 5-9 supports the above conclusion.

Thus the composite catalyst formulation is superior to the discrete not

only because it results in higher conversions but also because it is less susceptible to poisoning. There is then no doubt that when considering a new facility the composite formulation is desired unless factors such as cost of manufacture, which has not been considered in this work, offsets the obvious advantages. In existing facilities it is hoped that the techniques and results offered in this thesis will be helpful for either formulation.

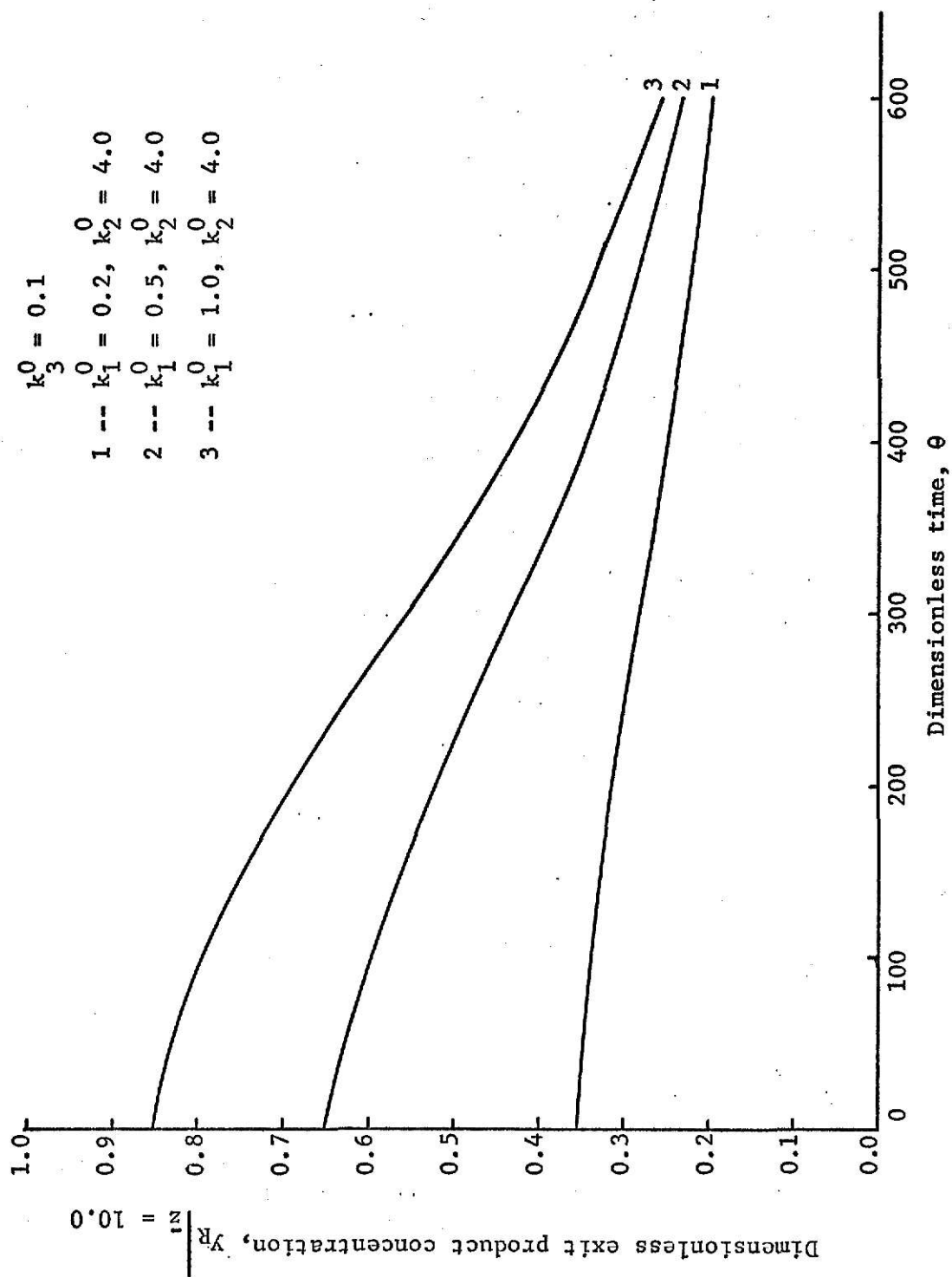


Fig. 5-4. Effect of equilibrium constant  $K = k_1^0/k_2^0$  on decay rate of exit product concentration with time. Composite formulation.

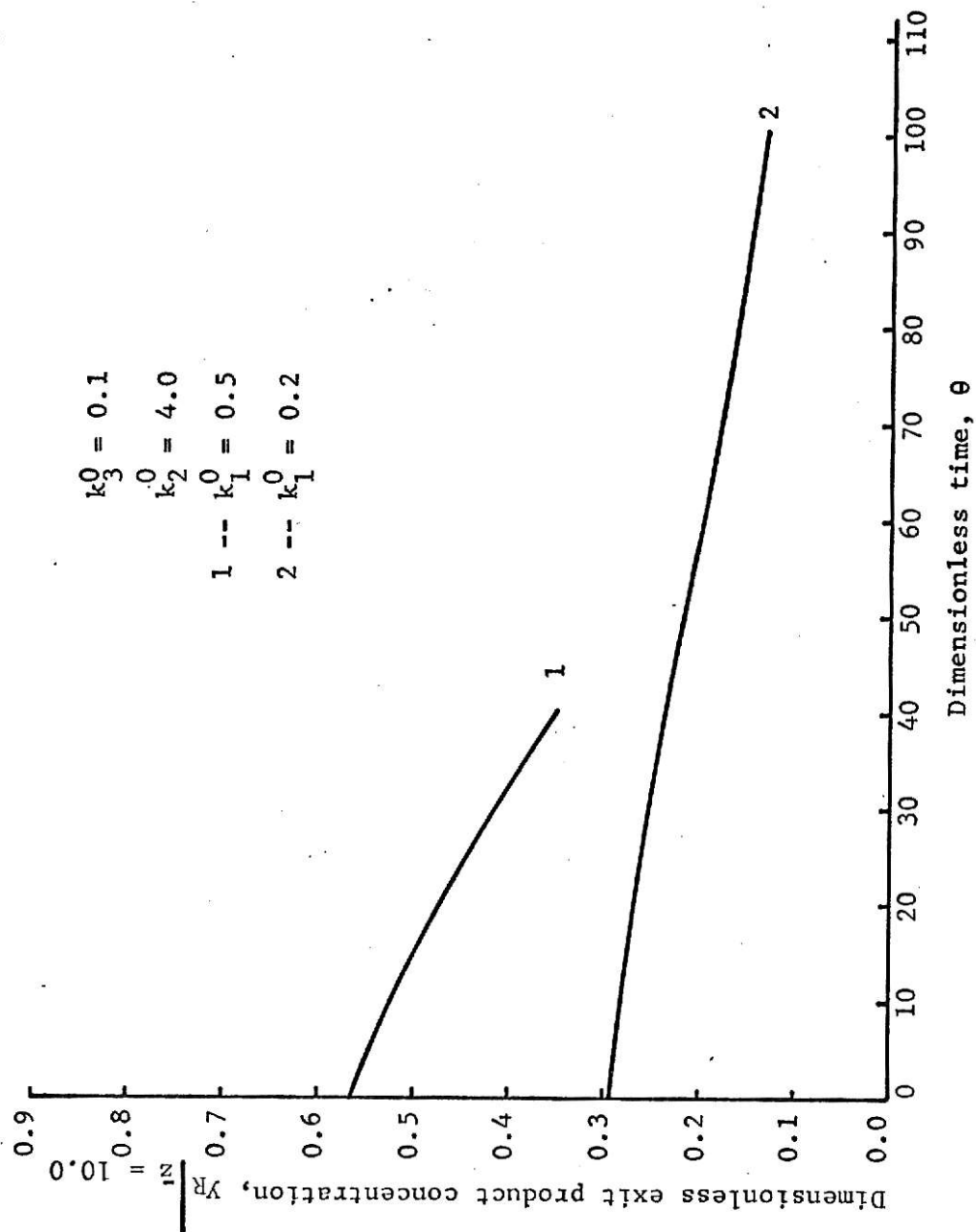


Fig. 5-5. Effect of equilibrium constant  $K = k_1^0/k_2^0$  on decay rate of exit product concentration. Discrete formulation.

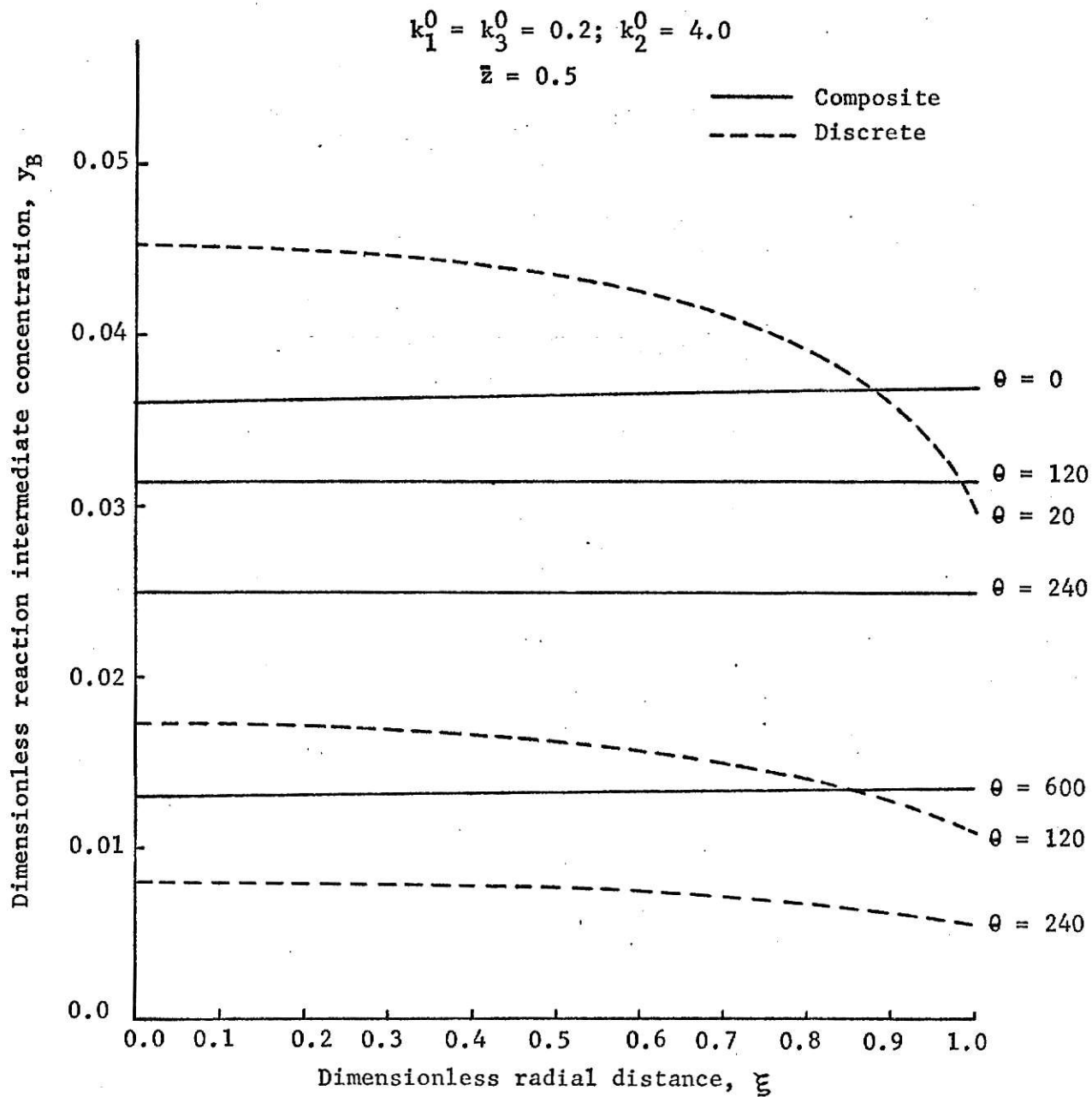


Fig. 5-6. Comparison of intraparticle concentrations of poison precursor at various time levels.

$$k_1^0 = k_3^0 = 0.2; \quad k_2^0 = 4.0$$

$$\bar{z} = 5.0$$

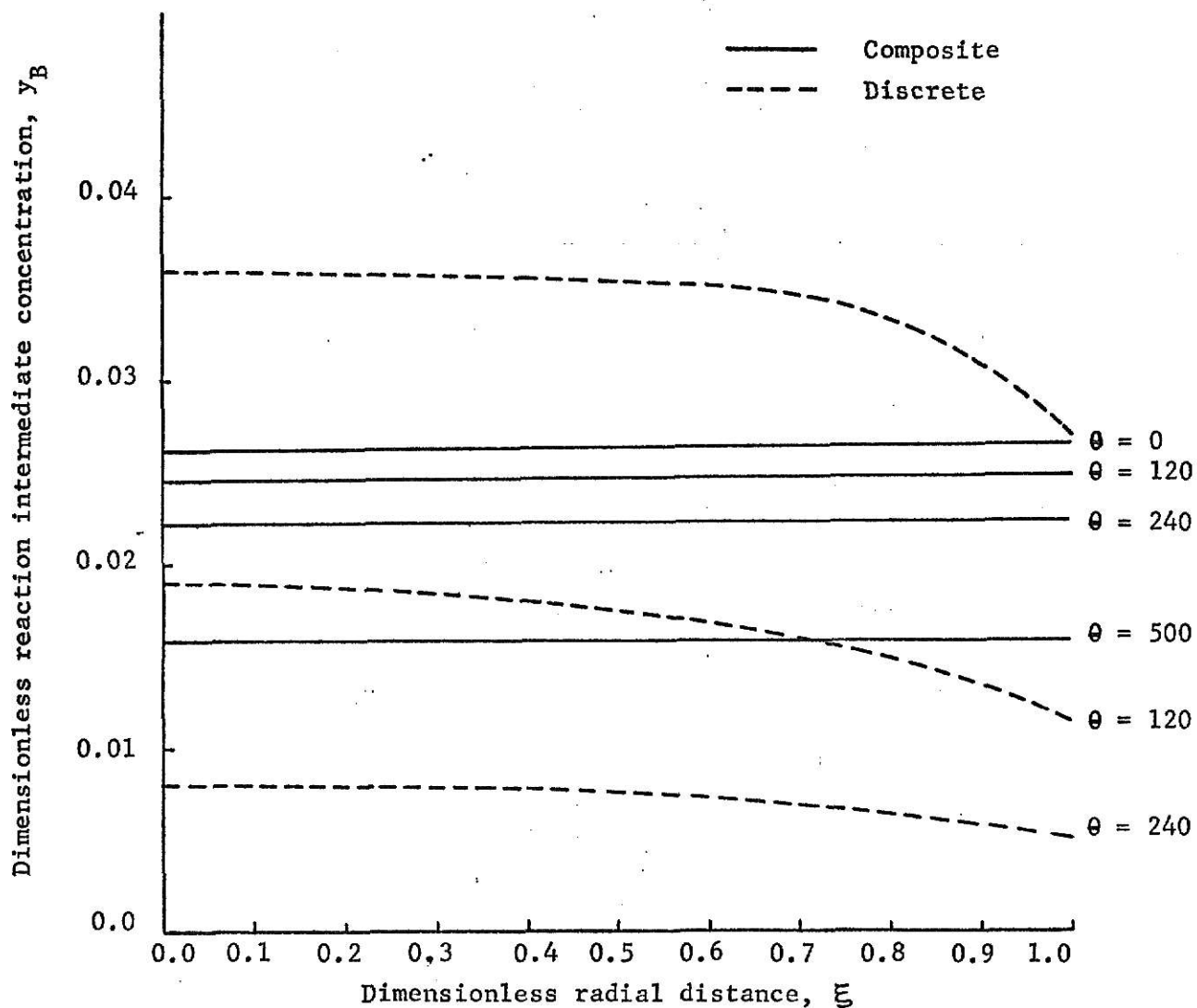


Fig. 5-7. Comparison of intraparticle concentrations of poison precursor at different time levels. Note axial distance.

$$k_1^0 = k_3^0 = 0.2; \quad k_2^0 = 4.0$$

$$\bar{z} = 0.5$$

— Composite  
- - - Discrete

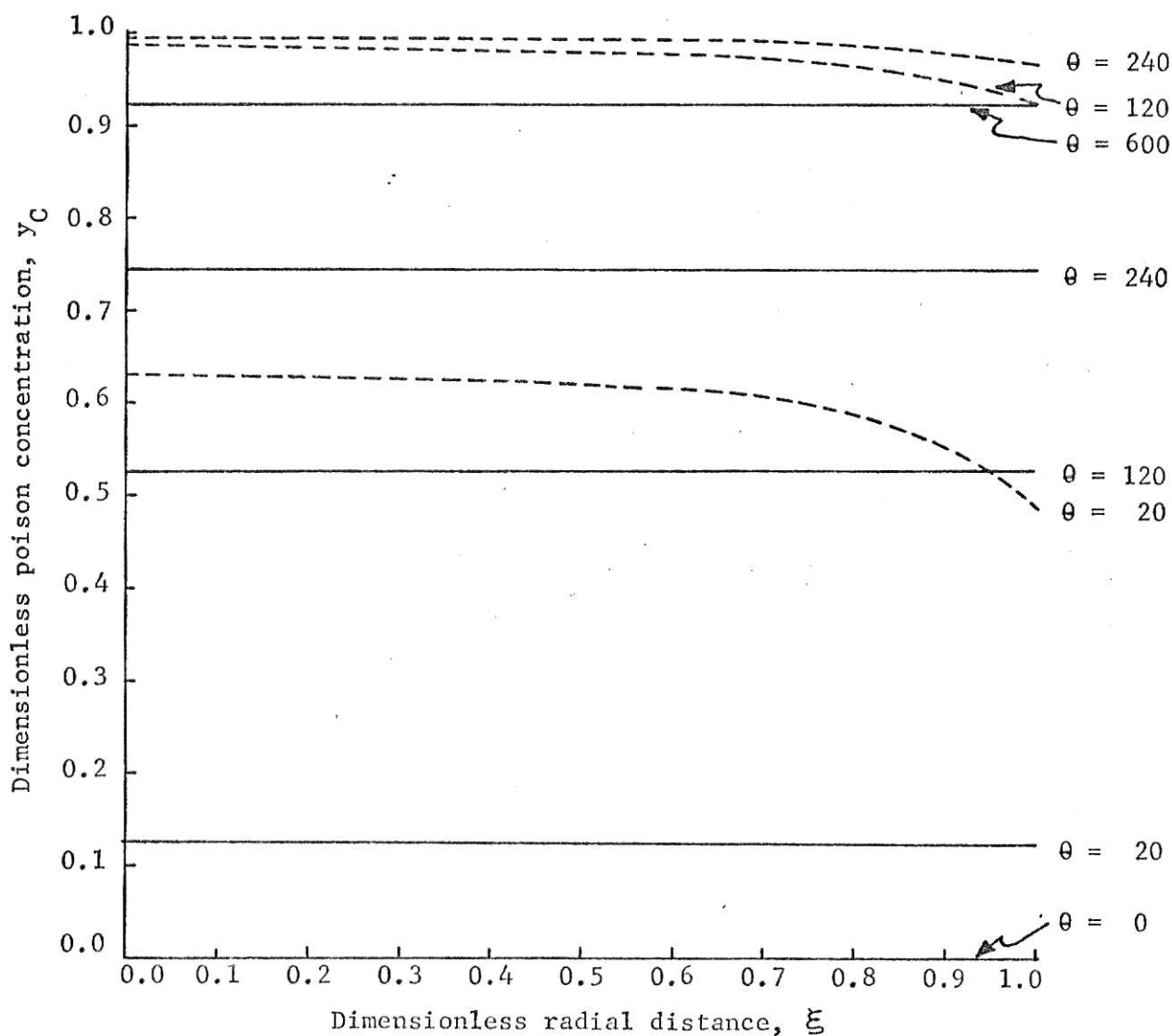


Fig. 5-8. Comparison of intraparticle poison concentration profiles at various time levels. Note axial distance.



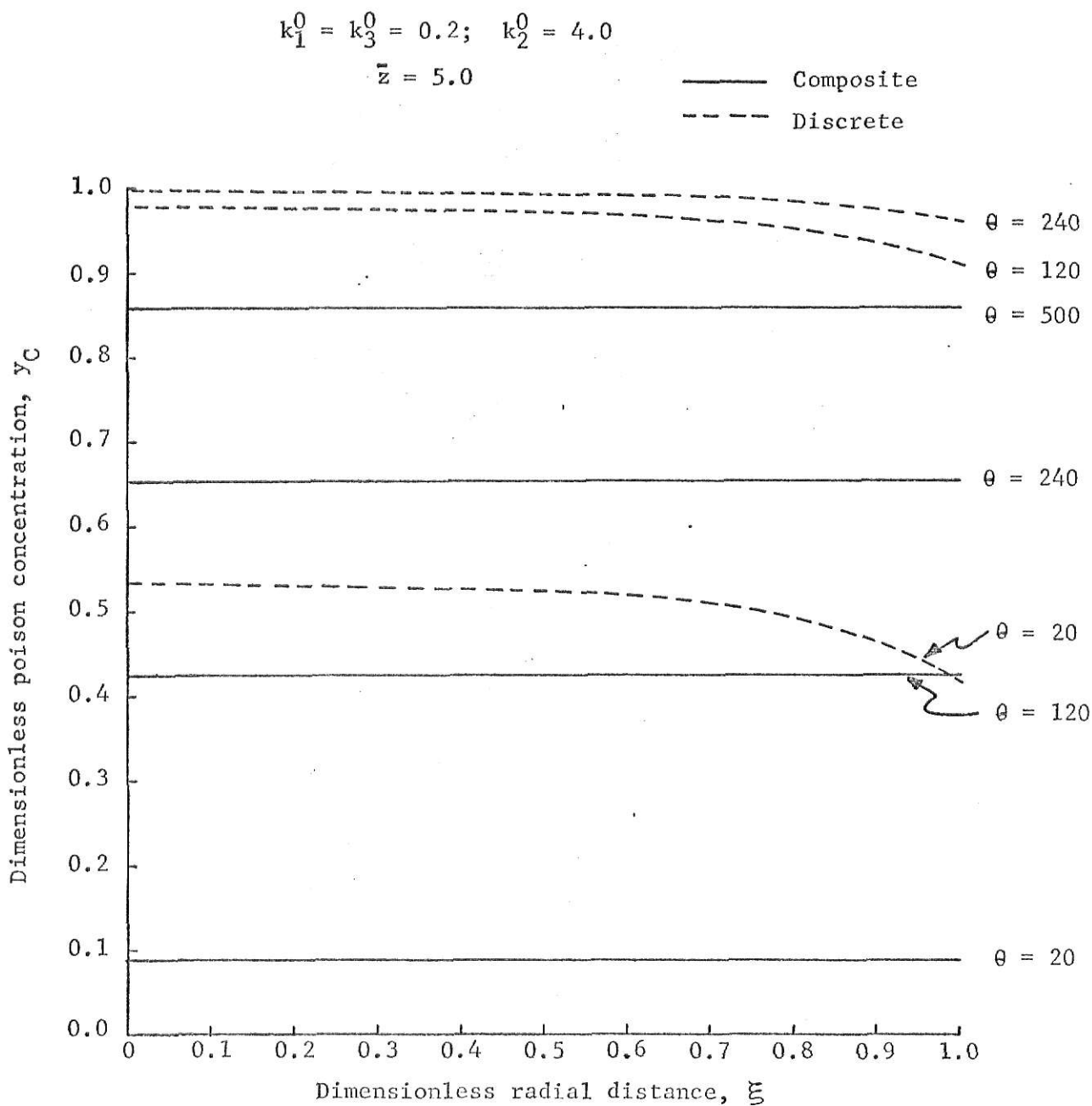


Fig. 5-9. Comparison of intraparticle poison concentration profiles at various time levels. Note axial distance.

## NOMENCLATURE

SYMBOLS

$a$	weight fraction of catalyst X in unit reactor volume, dimensionless.
A, B, R	gaseous species participating in chemical reaction.
C	solid fouling compound formed by chemical reaction.
$C_i$	particle concentration of component i, gr. mole/cc.
$C_c$	concentration of poison on catalyst particle, gr. mole/gr. cat.
$C_{i_s}$	particle surface concentration of specie i, gr. moles/cc.
$C_{cf}$	complete deactivation concentration of poison on catalyst, gr. moles/gr. cat.
$C_{i0}$	concentration of specie i entering reactor, gr. moles/cc.
$D_i$	effective diffusivity of specie i, $\text{cm}^2/\text{sec}$ .
$e$	void fraction of catalyst particle.
$k_i$	$i^{\text{th}}$ reaction velocity constant, $\text{cc./sec.-gr. cat.}$
$k_i^0$	$i^{\text{th}}$ reaction velocity constant at zero poison deposition, $\text{cc./sec.-gr. cat.}$
$K^*, K_1^*$	rate constant ratios, dimensionless.
$m$	radius ratio $R_X/R_Y$ , a parameter measuring diffusional resistance, dimensionless.
$N_i$	molar flux of specie i, $\text{gr. moles/sec.-cm}^2$ .
$N$	total number of catalyst particles per unit reactor volume, dimensionless.
$N_X, N_Y$	total number of X and Y catalyst particles per unit reactor volume, dimensionless.
$r$	radial distance as measured from center of catalyst particle, cm.
$R_X, R_Y$	radii of X and Y particles, respectively, cm.
$R$	radius of fixed bed reactor, cm.

$\tilde{R}_i$	molar rate of production of specie i per unit reactor volume, <u>gr. mole</u> sec.-cc.
$r_i$	molar rate of production of specie i per particle, $\frac{\text{gr. mole}}{\text{sec.-particle}}$
$R_i$	molar rate of production of specie i per unit weight of particular catalyst, gr. mole/sec.-gr. cat.
$t$	process time, sec.
$U$	superficial gas velocity based on cross sectional area available for flow in reactor, cm./sec.
$X, Y$	designations for distinct catalytic agents.
$y_i$	dimensionless conc. of specie i, $C_i/C_{A0}$
$y_{i_s}$	dimensionless surface conc. of specie i, $C_{i_s}/C_{A0}$ .
$y_i^n(j,k)$	finite difference approximation for $y_i$ at spatial points $j\Delta\bar{z}$ , $(j\Delta z')$ and $k\Delta\xi$ and time coordinate $n\Delta\theta$ .
$\bar{z}$	dimensionless axial coordinate, $\bar{z} = z'/\gamma_1 = \frac{D}{R_{Xc}^2 \rho k_1^0} \cdot z' = \frac{D\rho_B}{R_{Xc}^2 \rho U} \cdot z$ .
$z'$	dimensionless axial coordinate, $z' = z/z'_d$ for negligible diffusion resistance case $z' = \frac{\rho_B k_1^0}{U} \cdot z$ .
$z$	axial coordinate in reactor, cm.

GREEK AND MATHEMATICAL SYMBOLS

$\rho_c$	catalyst particle density, gr. cat./cc. cat.
$\rho_B$	catalyst bed density, gr. cat./cc. bed.
$\epsilon_B$	catalyst bed void volume, dimensionless.
$\epsilon$	weight fraction of catalyst X per particle, dimensionless.
$\theta$	dimensionless time, $\theta = t/t_d$ ; $t_d = C_{c_f}^0 / k_4 C_{A_0}$ .
$\xi$	dimensionless radial distance, $r/R_X$ .
$\gamma_i$	parameters somewhat similar to Thiele Modulus, dimensionless. $\frac{\rho_c k_i^0}{D}$ . either $R_X^2$ or $R_Y^2$ .
$\zeta$	weight fraction of catalyst X per particle for negligible diffusion resistance case, dimensionless.
$\phi_i$	activity-poison concentration relationship, dimensionless.
$\nabla_r^2$	$\frac{\partial^2 ( )}{\partial r^2} + \frac{2}{r} \frac{\partial ( )}{\partial r}$ .
$\nabla_\xi^2$	$\frac{\partial^2 ( )}{\partial \xi^2} + \frac{2}{\xi} \frac{\partial ( )}{\partial \xi}$ .
$\Delta$	small unit or increment of distance in a specified direction.

SUBSCRIPTS

- A, B, C, R    pertaining to those chemical species.
- $\xi$             in or pertaining to the  $\xi$ -direction.
- j,k           specifies axial and radial position in finite difference formulas.
- r            in or pertaining to the r-direction.
- X, Y          pertaining to that particular catalyst type.

SUPERSCRIPTS

- n            specifies position in time in finite difference work.

## ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. John C. Matthews for his advice and encouragement during all stages of this work. Financial support was provided by a three-year NASA Fellowship and is deeply appreciated. The author also gratefully acknowledges the Computing Center of Kansas State University for the use of the IBM 360 Model 50 Computer.

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## APPENDICES

A-1. STEADY-STATE SOLUTIONS TO PARTICLE MASS BALANCES. DISCRETE CASE.

Solve:

$$\nabla_{\xi}^2 y_A + \gamma_2 y_{B(X)} - \gamma_1 y_A = 0 \quad (\text{A-1.1})$$

$$\nabla_{\xi}^2 y_{B(X)} + \gamma_1 y_A - \gamma_2 y_{B(X)} = 0 \quad (\text{A-1.2})$$

$$\nabla_{\xi}^2 y_{B(Y)} - m^2 \gamma_3 y_{B(Y)} = 0 \quad (\text{A-1.3})$$

$$\nabla_{\xi}^2 y_R + m^2 \gamma_3 y_{B(Y)} = 0 \quad (\text{A-1.4})$$

subject to:

- |   |  |
|---|--|
| 1. $y_A = y_{A_s}$<br><div style="margin-left: 150px;"><math>y_{B(X)} = y_{B_s}</math></div> <div style="margin-left: 150px;"><math>y_{B(Y)} = y_{B_s}</math></div> <div style="margin-left: 150px;"><math>y_R = y_{R_s}</math></div> | 2. All concentrations are finite<br>@ $\xi = 0$ .<br><br><div style="margin-left: 100px;">} @ <math>\xi = 1</math></div> <div style="margin-left: 100px;">} @ <math>\xi = \frac{1}{m}</math></div> |
|---|--|

Solution:

Assume solutions of the form

$$y_A = \frac{f_1(\xi)}{\xi} ; y_{B(X)} = \frac{f_2(\xi)}{\xi} ; y_{B(Y)} = \frac{f_3(\xi)}{\xi} ; y_R = \frac{f_4(\xi)}{\xi}$$

then  $\nabla_{\xi}^2 y_i$  transforms to  $\frac{f_i''(\xi)}{\xi}$ .

Equations (A-1.1-4) become

$$f_1''(\xi) + \gamma_2 f_2 - \gamma_1 f_1 = 0 \quad (\text{A-1.5})$$

$$f_2''(\xi) + \gamma_1 f_1 - \gamma_2 f_2 = 0 \quad (\text{A-1.6})$$

$$f_3''(\xi) - m^2 \gamma_3 f_3 = 0 \quad (\text{A-1.7})$$

$$f_4''(\xi) + m^2 \gamma_3 f_3 = 0 \quad (\text{A-1.8})$$

Placing in D-form we have

$$(D^2 - \gamma_1) f_1 + \gamma_2 f_2 = 0 \quad (\text{A-1.9})$$

$$(D^2 - \gamma_2) f_2 + \gamma_1 f_1 = 0 \quad (\text{A-1.10})$$

Now, multiply (A-1.9) by  $\gamma_1$  and (A-1.10) by  $(D^2 - \gamma_1)$  and subtract to get

$$[D^4 - (\gamma_1 + \gamma_2)D^2] f_1 = [D^4 - (\gamma_1 + \gamma_2)D^2] f_2 = 0 \quad (\text{A-1.11})$$

(A-1.11) may be factored to give

$$\{D^2[D^2 - (\gamma_1 + \gamma_2)]\} f_1, f_2 = 0 \quad (\text{A-1.12})$$

and the solution of this equation is

$$f_1(\xi) = C_1 + C_2 \xi + C_3 \sinh(\lambda_1 \xi) + C_4 \cosh(\lambda_1 \xi) \quad (\text{A-1.13})$$

$$f_2(\xi) = C_5 + C_6 \xi + C_7 \sinh(\lambda_1 \xi) + C_8 \cosh(\lambda_1 \xi) \quad (\text{A-1.14})$$

where  $\lambda_1 = \sqrt{\gamma_1 + \gamma_2}$ .

By performing the indicated operations on (A-1.13-14) and substitution into (A-1.9 or 10) the following relations may be obtained.

$$C_5 = \frac{\gamma_1}{\gamma_2} C_1 ; C_6 = \frac{\gamma_1}{\gamma_2} C_2 ; C_7 = - \frac{(\lambda_1^2 - \gamma_1)}{\gamma_2} C_3 ; C_8 = - \frac{(\lambda_1^2 - \gamma_1)}{\gamma_2} C_4 \quad (\text{A-1.15})$$

Therefore

$$y_A = \frac{f_1(\xi)}{\xi} = \frac{C_1}{\xi} + C_2 + C_3 \frac{\sinh(\lambda_1 \xi)}{\xi} + C_4 \frac{\cosh(\lambda_1 \xi)}{\xi} \quad (\text{A-1.16})$$

$$y_{B(X)} = \frac{f_2(\xi)}{\xi} = \frac{\gamma_1}{\gamma_2} \cdot \frac{C_1}{\xi} + \frac{\gamma_1}{\gamma_2} C_2 - C_3 \frac{\sinh(\lambda_1 \xi)}{\xi} - C_4 \frac{\cosh(\lambda_1 \xi)}{\xi} \quad (\text{A-1.17})$$

Applying boundary condition 2 to (A-1.16 and 17) it is easily seen that for  $y_A$  and  $y_{B(X)}$  to remain finite  $C_1$  and  $C_4$  must be zero.

Therefore

$$y_A = C_2 + C_3 \frac{\sinh(\lambda_1 \xi)}{\xi} \quad (\text{A-1.18})$$

$$y_{B(X)} = \frac{1}{2} C_2 - C_3 \frac{\sinh(\lambda_1 \xi)}{\xi} \quad (\text{A-1.19})$$

Applying B. C. 1 we have

$$y_{A_s} = C_2 + C_3 \sinh(\lambda_1)$$

$$y_{B_s} = \frac{\gamma_1}{\gamma_2} C_2 - C_3 \sinh(\lambda_1)$$

solution of these two equations gives  $C_2$  and  $C_3$ .

$$C_2 = \frac{\gamma_2}{\gamma_1 + \gamma_2} \{y_{A_s} + y_{B_s}\} \quad (\text{A-1.20})$$

$$C_3 = \left\{ \frac{\gamma_1}{\gamma_1 + \gamma_2} \cdot y_{A_s} - \frac{\gamma_2}{\gamma_1 + \gamma_2} \cdot y_{B_s} \right\} \frac{1}{\sinh(\lambda_1)} \quad (\text{A-1.21})$$

Hence, our final solutions are

$$\begin{aligned} y_A = y_{A_s} \cdot \left\{ \frac{\gamma_2}{\gamma_1 + \gamma_2} + \frac{\gamma_1}{\gamma_1 + \gamma_2} \cdot \frac{\sinh(\lambda_1 \xi)}{\sinh(\lambda_1)} \cdot \frac{1}{\xi} \right\} \\ - y_{B_s} \cdot \left\{ - \frac{\gamma_2}{\gamma_1 + \gamma_2} + \frac{\gamma_2}{\gamma_1 + \gamma_2} \cdot \frac{\sinh(\lambda_1 \xi)}{\sinh(\lambda_1)} \cdot \frac{1}{\xi} \right\} \end{aligned} \quad (\text{A-1.22})$$

$$\begin{aligned}
y_{B(X)} = y_{B_s} \cdot \left\{ \frac{\gamma_1}{\gamma_1 + \gamma_2} + \frac{\gamma_2}{\gamma_1 + \gamma_2} \cdot \frac{\sinh(\lambda_1 \xi)}{\sinh(\lambda_1)} \cdot \frac{1}{\xi} \right\} \\
- y_{A_s} \cdot \left\{ -\frac{\gamma_1}{\gamma_1 + \gamma_2} + \frac{\gamma_1}{\gamma_1 + \gamma_2} \cdot \frac{\sinh(\lambda_1 \xi)}{\sinh(\lambda_1)} \cdot \frac{1}{\xi} \right\}
\end{aligned} \quad (A-1.23)$$

Equations (A-1.7 and 8) are not coupled so they may be solved separately.

$$\begin{aligned}
(D^2 - \gamma_3)f_3 &= 0 \\
f_3(\xi) &= A \sinh(\lambda_2 \xi) + B \cosh(\lambda_2 \xi)
\end{aligned} \quad (A-1.24)$$

where

$$\lambda_2 = \sqrt{\gamma_3}$$

Therefore

$$y_{B(Y)} = \frac{A \sinh(\lambda_2 \xi)}{\xi} + \frac{B \cosh(\lambda_2 \xi)}{\xi} \quad (A-1.25)$$

Application of boundary condition 2 gives

$$B = 0 \quad (A-1.26)$$

and boundary condition 1 gives

$$A = \frac{y_{B_s}}{m \cdot \sinh\left(\frac{\lambda_2}{m}\right)}$$

Therefore,

$$y_{B(Y)} = y_{B_s} \cdot \frac{\sinh(\lambda_2 \xi)}{m \sinh\left(\frac{\lambda_2}{m}\right)} \cdot \frac{1}{\xi} \quad (A-1.27)$$

Equation (A-1.8) may be solved similarly to give

$$y_R = y_{R_s} + y_{B_s} \cdot \left\{ 1 - \frac{1}{m} \cdot \frac{\sinh(\lambda_2 \xi)}{\sinh\left(\frac{\lambda_2}{m}\right)} \cdot \frac{1}{\xi} \right\} \quad (A-1.28)$$

A-2. DERIVATION OF GENERAL EXPRESSION FOR TOTAL NUMBER OF X AND Y CATALYST PARTICLES PER UNIT REACTOR VOLUME.

Consider the discrete particle case where the X particle has radius  $R_X$  and Y particle has radius  $R_Y$ .

$$\text{The weight of catalyst particle X} = \frac{4}{3}\pi R_X^3 \cdot \rho_c \quad (\text{A-2.1})$$

$$\text{The weight of catalyst particle Y} = \frac{4}{3}\pi R_Y^3 \cdot \rho_c \quad (\text{A-2.2})$$

Let  $m = \frac{R_X}{R_Y}$ , then the weight of catalyst particle Y becomes

$$\frac{4}{3} \frac{R_X^3}{m^3} \cdot \rho_c = \frac{1}{m^3} (\text{weight of X particle}) \quad (\text{A-2.3})$$

By definition, the total weight of catalyst in unit reactor volume is  $\rho_B$ ; therefore

$$\left[ \begin{array}{l} \text{the total number} \\ \text{of particles per} \\ \text{unit reactor} \\ \text{volume} \end{array} \right] = \frac{\text{weight of catalyst X}}{\text{per unit reactor volume}} + \frac{\text{weight of catalyst Y}}{\text{per unit reactor volume}} + \frac{\text{weight per particle of X}}{\text{weight per particle of Y}} \quad (\text{A-2.4})$$

Since  $a$  has been defined as the weight fraction of catalyst X per unit reactor volume, then (neglecting weight of gases in bed),

$$N = \frac{a\rho_B}{\frac{4}{3}\pi R_X^3 \rho_c} + \frac{(1-a)\rho_B}{\frac{4}{3} \frac{\pi R_X^3}{m^3} \cdot \rho_c} \quad (\text{A-2.5})$$

Equation (A-2.5) may be simplified to

$$N = \frac{3\rho_B}{4\pi R_X^3 \rho_c} (a + m^3(1-a)). \quad (\text{A-2.6})$$

This is the general expression for the discrete case.

When the particle radii are equivalent, as is true for the composite case,  $m = 1$  and

$$N = \frac{3\rho_B}{4\pi R_X^3 \rho_c} \quad (\text{A-2.7})$$

Note: Since the catalyst fractions are defined differently for the two cases it would be useful to see how they are related.

$$a = \frac{\text{weight fraction of X}}{\text{unit reactor volume}} \quad (\text{for DPC}) \quad (\text{A-2.8})$$

$$\epsilon = \frac{\text{weight fraction of X}}{\text{per particle}} \quad (\text{for CPC}) \quad (\text{A-2.9})$$

To get the weight fraction of X per unit reactor volume for the CPC we have from (A-2.7)

$$\epsilon' = \frac{\epsilon \cdot N}{\epsilon \cdot N + (1-\epsilon)N} = \frac{\frac{\text{weight of catalyst X}}{\text{unit reactor volume}}}{\frac{\text{total weight of catalyst}}{\text{unit reactor volume}}} \quad (\text{A-2.10})$$

which reduces to

$$\epsilon' = \epsilon, \quad (\text{A-2.11})$$

so  $\epsilon$  is also the weight fraction of catalyst X per unit reactor volume.

A-3. STEADY-STATE SOLUTIONS FOR BED MASS BALANCES--DISCRETE CASE.

Solve:

$$\frac{\partial y_{A_s}}{\partial \bar{z}} + 3a \left. \frac{\partial y_A}{\partial \xi} \right|_{\xi=1} = 0; \quad y_{A_s} = 1.0 \text{ @ } \bar{z} = 0 \quad (\text{A-3.1})$$

$$\frac{\partial y_{B_s}}{\partial \bar{z}} + 3 \left\{ a \left. \frac{\partial y_{B(X)}}{\partial \xi} \right|_{\xi=1} + m(1-a) \left. \frac{\partial y_{B(Y)}}{\partial \xi} \right|_{\xi=\frac{1}{m}} \right\} = 0; \quad y_{B_s} = 0.0 \text{ @ } \bar{z} = 0 \quad (\text{A-3.2})$$

$$\frac{\partial y_{R_s}}{\partial \bar{z}} + 3m(1-a) \left. \frac{\partial y_R}{\partial \xi} \right|_{\xi=\frac{1}{m}} = 0; \quad y_{R_s} = 0.0 \text{ @ } \bar{z} = 0 \quad (\text{A-3.3})$$

Solution:

$$\left. \frac{\partial y_A}{\partial \xi} \right|_{\xi=1} = \beta_1 y_{A_s} - \beta_2 y_{B_s} \quad (\text{A-3.4})$$

$$\text{where } \beta_1 = \frac{\gamma_1}{\gamma_1 + \gamma_2} \cdot (\lambda_1 \coth(\lambda_1) - 1)$$

$$\beta_2 = \frac{\gamma_2}{\gamma_1 + \gamma_2} \cdot (\lambda_1 \coth(\lambda_1) - 1)$$

$$\left. \frac{\partial y_{B(X)}}{\partial \xi} \right|_{\xi=1} = \beta_2 y_{B_s} - \beta_1 y_{A_s} \quad (\text{A-3.5})$$

$$\left. \frac{\partial y_{B(Y)}}{\partial \xi} \right|_{\xi=\frac{1}{m}} = \beta_3 y_{B_s} \quad (\text{A-3.6})$$



where

$$\beta_3 = m((\lambda_2/m) \coth(\lambda_2/m) - 1)$$

$$\left. \frac{\partial y_R}{\partial \xi} \right|_{\xi = \frac{1}{m}} = \beta_4 y_{B_s} \quad (\text{A-3.7})$$

$$\beta_4 = -\beta_3$$

Therefore (A-3.1, 2, 3) become

$$\frac{\partial y_{A_s}}{\partial \bar{z}} + 3a[\beta_1 y_{A_s} - \beta_2 y_{B_s}] = 0 \quad (\text{A-3.8})$$

$$\frac{\partial y_{B_s}}{\partial \bar{z}} + 3[a(\beta_2 y_{B_s} - \beta_1 y_{A_s}) + m(1-a)\beta_3 y_{B_s}] = 0 \quad (\text{A-3.9})$$

$$\frac{\partial y_{R_s}}{\partial \bar{z}} + 3m(1-a)\beta_4 y_{B_s} = 0 \quad (\text{A-3.10})$$

Now let

$$w_1 = 3a\beta_1$$

$$w_2 = 3a\beta_2 \quad (\text{A-3.11})$$

$$w_3 = 3m(1-a)\beta_3$$

then (A-3.8, 9, 10) simplify to

$$\frac{\partial y_{A_s}}{\partial \bar{z}} + w_1 y_{A_s} - w_2 y_{B_s} = 0 ; \quad y_{A_s} = 1.0 @ \bar{z} = 0.0 \quad (\text{A-3.12})$$

$$\frac{\partial y_{B_s}}{\partial \bar{z}} + (w_2 + w_3) y_{B_s} - w_1 y_{A_s} = 0 ; \quad y_{B_s} = 0.0 @ \bar{z} = 0.0 \quad (\text{A-3.13})$$

$$\frac{\partial y_{R_s}}{\partial \bar{z}} - w_3 y_{B_s} = 0 ; \quad y_{R_s} = 0.0 @ \bar{z} = 0.0 \quad (A-3.14)$$

Utilizing the operator D-form we may solve the simultaneous equations

$$(D + w_1)y_{A_s} - w_2 y_{B_s} = 0 \quad (A-3.15)$$

$$(D + (w_2 + w_3))y_{B_s} - w_1 y_{A_s} = 0 \quad (A-3.16)$$

Multiply (A-3.15) by  $w_1$  and (A-3.16) by  $(D + w_1)$  and add to get

$$[D^2 + (w_1 + w_2 + w_3)D + w_1 w_3] y_{A_s}, y_{B_s} = 0 \quad (A-3.17)$$

Solving the quadratic equation we have

$$m_1 = \frac{-(w_1 + w_2 + w_3) + \sqrt{(w_1 + w_2 + w_3)^2 - 4w_1 w_3}}{2} \quad (A-3.18)$$

$$m_2 = \frac{-(w_1 + w_2 + w_3) - \sqrt{(w_1 + w_2 + w_3)^2 - 4w_1 w_3}}{2} \quad (A-3.19)$$

Therefore

$$y_{A_s} = A \exp\{m_1 \bar{z}\} + B \exp\{m_2 \bar{z}\} \quad (A-3.20)$$

$$y_{B_s} = C \exp\{m_1 \bar{z}\} + D \exp\{m_2 \bar{z}\} \quad (A-3.21)$$

Performing the indicated operations on (A-3.20, 21) and substitution into (A-3.15 or 16) gives

$$C = \left( \frac{m_1 + w_1}{w_2} \right) A \quad (A-3.22)$$

$$D = \left( \frac{m_2 + w_1}{w_2} \right) B \quad (\text{A-3.23})$$

Applying the boundary conditions A and B may be found to equal

$$A = \frac{m_2 + w_1}{m_2 - m_1} ; \quad B = - \frac{(m_1 + w_1)}{m_2 - m_1} \quad (\text{A-3.24})$$

The solutions for  $y_{A_s}$  and  $y_{B_s}$  are then

$$y_{A_s} = \frac{1}{m_2 - m_1} \cdot \{ (m_2 + w_1) \exp\{m_1 \bar{z}\} - (m_1 + w_1) \exp\{m_2 \bar{z}\} \} \quad (\text{A-3.25})$$

$$y_{B_s} = \frac{w_1}{m_2 - m_1} \cdot \{ \exp\{m_2 \bar{z}\} - \exp\{m_1 \bar{z}\} \} \quad (\text{A-3.26})$$

Equation (A-3.14), after substitution of (A-3.26) can be integrated in a straightforward manner to give

$$y_{R_s} = 1 - \frac{1}{(m_2 - m_1)} \cdot \{ m_2 \exp\{m_1 \bar{z}\} - m_1 \exp\{m_2 \bar{z}\} \} \quad (\text{A-3.27})$$

A-4. STEADY-STATE SOLUTIONS TO PARTICLE MASS BALANCE. COMPOSITE CASE.

Solve:

$$\nabla_{\xi}^2 y_A + \epsilon \gamma_2 y_B - \epsilon \gamma_2 y_A = 0 \quad (\text{A-4.1})$$

$$\nabla_{\xi}^2 y_B + \epsilon \gamma_1 y_A - [\epsilon \gamma_2 + (1-\epsilon) \gamma_3] y_B = 0 \quad (\text{A-4.2})$$

$$\nabla_{\xi}^2 y_R + (1-\epsilon) \gamma_3 y_B = 0 \quad (\text{A-4.3})$$

Subject to:

1.  $y_A = y_{A_s}$   
 $y_B = y_{B_s} \quad \} \quad @ \xi = 1.0$   
 $y_R = y_{R_s}$
2.  $y_A, y_B, y_R$  finite @  $\xi = 0.0$

Solution:

$$\text{Assume } y_A = \frac{f_1(\xi)}{\xi}; \quad y_B = \frac{f_2(\xi)}{\xi} \text{ and } y_R = \frac{f_3(\xi)}{\xi},$$

then (A-4.1, 2, 3) become

$$f_1''(\xi) + \epsilon \gamma_2 f_2 - \epsilon \gamma_1 f_1 = 0 \quad (\text{A-4.4})$$

$$f_2''(\xi) + \epsilon \gamma_1 f_1 - (\epsilon \gamma_2 + (1-\epsilon) \gamma_3) f_2 = 0 \quad (\text{A-4.5})$$

$$f_3''(\xi) + (1-\epsilon) \gamma_3 f_2 = 0 \quad (\text{A-4.6})$$

Letting  $\epsilon \gamma_1 = \beta_1$ ;  $\epsilon \gamma_2 = \beta_2$  and  $(1-\epsilon) \gamma_3 = \beta_3$ , and putting Eqs. (A-4.4, 5, 6) into operator form, we have,

$$(D^2 - \beta_1)f_1 + \beta_2 f_2 = 0 \quad (\text{A-4.7})$$

$$(D^2 - (\beta_2 + \beta_3))f_2 + \beta_1 f_1 = 0 \quad (\text{A-4.8})$$

$$D^2 f_3 + \beta_3 f_2 = 0 \quad (\text{A-4.9})$$

Multiply (A-4.7) by  $\beta_1$  and (A-4.8) by  $(D^2 - \beta_1)$  and subtract

$$[D^4 - (\beta_1 + \beta_2 + \beta_3)D^2 + \beta_1\beta_3]f_1, f_2 = 0 \quad (\text{A-4.10})$$

$$D = \pm \sqrt{\frac{(\beta_1 + \beta_2 + \beta_3) \pm \sqrt{(\beta_1 + \beta_2 + \beta_3)^2 - 4\beta_1\beta_3}}{2}} \quad (\text{A-4.11})$$

Let

$$m_1 = + \sqrt{\frac{(\beta_1 + \beta_2 + \beta_3) + \sqrt{(\beta_1 + \beta_2 + \beta_3)^2 - 4\beta_1\beta_3}}{2}} \quad (\text{A-4.12})$$

$$m_2 = - m_1 \quad (\text{A-4.13})$$

$$m_3 = + \sqrt{\frac{(\beta_1 + \beta_2 + \beta_3) - \sqrt{(\beta_1 + \beta_2 + \beta_3)^2 - 4\beta_1\beta_3}}{2}} \quad (\text{A-4.14})$$

$$m_4 = - m_3 \quad (\text{A-4.15})$$

In general, the solutions  $f_1$  and  $f_2$  are

$$f_1(\xi) = A \cosh(m_1 \xi) + B \sinh(m_1 \xi) + C \cosh(m_3 \xi) + D \sinh(m_3 \xi) \quad (\text{A-4.16})$$

$$f_2(\xi) = E \cosh(m_1 \xi) + F \sinh(m_1 \xi) + G \cosh(m_3 \xi) + H \sinh(m_3 \xi) \quad (\text{A-4.17})$$

Performing the indicated operations on (A-4.16, 17) and substitution into either (A-4.7) or (A-4.8) gives,

$$E = - \left[ \frac{m_1^2 - \beta_1}{\beta_2} \right] A ; \quad F = - \left[ \frac{m_1^2 - \beta_1}{\beta_2} \right] B$$

$$G = - \left[ \frac{m_3^2 - \beta_1}{\beta_2} \right] C ; \quad H = - \left[ \frac{m_3^2 - \beta_1}{\beta_2} \right] D$$

Therefore,

$$y_A = \frac{f_1(\xi)}{\xi} = \frac{A \cosh(m_1 \xi)}{\xi} + \frac{B \sinh(m_1 \xi)}{\xi} + \frac{C \cosh(m_3 \xi)}{\xi} + \frac{D \sinh(m_3 \xi)}{\xi}$$

$$y_B = \frac{f_2(\xi)}{\xi} = - \left[ \frac{m_1^2 - \beta_1}{\beta_2} \right] \frac{A \cosh(m_1 \xi)}{\xi} - \left[ \frac{m_1^2 - \beta_1}{\beta_2} \right] \frac{B \sinh(m_1 \xi)}{\xi} \\ - \left[ \frac{m_3^2 - \beta_1}{\beta_2} \right] \frac{C \cosh(m_3 \xi)}{\xi} - \left[ \frac{m_3^2 - \beta_1}{\beta_2} \right] \frac{D \sinh(m_3 \xi)}{\xi}$$

Applying B. C. 2 we find that

$$A, C \equiv 0, \quad (A-4.18)$$

and B. C. 1 may be used to evaluate B and D

$$B = \frac{y_{A_s}}{\sinh(m_1)} - \frac{1}{(m_1^2 - m_3^2) \sinh(m_1)} (\beta_2 y_{B_s} + (m_1^2 - \beta_1) y_{A_s})$$

$$D = \frac{\beta_2 y_{B_s}}{(m_1^2 - m_3^2) \sinh(m_3)} + \frac{(m_1^2 - \beta_1)}{(m_1^2 - m_3^2)} \cdot \frac{1}{\sinh(m_3)} \cdot y_{A_s}$$

and the final solutions are

$$\begin{aligned}
y_A = & \frac{y_{A_s}}{(m_3^2 - m_1^2)} \left\{ (m_3^2 - \beta_1) \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} - (m_1^2 - \beta_1) \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi} \right\} \\
& + \frac{y_{B_s}}{(m_3^2 - m_1^2)} \left\{ \frac{\beta_2}{\xi} \left\{ \frac{\sinh(m_1 \xi)}{\sinh(m_1)} - \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \right\} \right\}
\end{aligned} \tag{A-4.19}$$

$$\begin{aligned}
y_B = & \frac{y_{B_s}}{(m_1^2 - m_3^2)} \left\{ (m_1^2 - \beta_1) \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} - (m_3^2 - \beta_1) \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi} \right\} \\
& + \frac{y_{A_s}}{(m_1^2 - m_3^2)} \left\{ \frac{(m_1^2 - \beta_1)(m_3^2 - \beta_1)}{\beta_2} \cdot \left\{ \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} - \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi} \right\} \right\}
\end{aligned} \tag{A-4.20}$$

The solution for  $y_R$  may be obtained by substitution of (A-4.20) into (A-4.6) and direct integration

$$\begin{aligned}
y_R = & y_{R_s} + y_{B_s} \cdot \left\{ \frac{\beta_3(m_3^2 - \beta_1)}{m_3^2(m_3^2 - m_1^2)} \left\{ 1 - \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi} \right\} \right. \\
& - \frac{\beta_3(m_1^2 - \beta_1)}{m_1^2(m_3^2 - m_1^2)} \left\{ 1 - \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} \right\} \left. + y_{A_s} \cdot \left\{ \frac{\beta_3(m_1^2 - \beta_1)(m_3^2 - \beta_1)}{\beta_2 m_3^2(m_3^2 - m_1^2)} \right. \right. \\
& \cdot \left\{ 1 - \frac{\sinh(m_3 \xi)}{\sinh(m_3)} \cdot \frac{1}{\xi} \right\} - \frac{\beta_3(m_1^2 - \beta_1)(m_3^2 - \beta_1)}{\beta_2 m_1^2(m_3^2 - m_1^2)} \cdot \left. \left\{ 1 - \frac{\sinh(m_1 \xi)}{\sinh(m_1)} \cdot \frac{1}{\xi} \right\} \right\}
\end{aligned} \tag{A-4.21}$$

A-5. STEADY-STATE SOLUTIONS TO BED MASS BALANCES. COMPOSITE CASE.

Solve:

$$\left. \frac{\partial y_{A_s}}{\partial \bar{z}} + \frac{3\partial y_A}{\partial \xi} \right|_{\xi=1} = 0 ; \quad y_{A_s} = 1.0 @ \bar{z} = 0 \quad (\text{A-5.1})$$

$$\left. \frac{\partial y_{B_s}}{\partial \bar{z}} + \frac{3\partial y_B}{\partial \xi} \right|_{\xi=1} = 0 ; \quad y_{B_s} = 0.0 @ \bar{z} = 0 \quad (\text{A-5.2})$$

$$\left. \frac{\partial y_{R_s}}{\partial \bar{z}} + \frac{3\partial y_R}{\partial \xi} \right|_{\xi=1} = 0 ; \quad y_{R_s} = 0.0 @ \bar{z} = 0 \quad (\text{A-5.3})$$

Solution:

$$\left. \frac{\partial y_A}{\partial \xi} \right|_{\xi=1} = \alpha_1 y_{A_s} + \alpha_2 y_{B_s} \quad (\text{A-5.4})$$

where

$$\alpha_1 = \frac{1}{(m_3^2 - m_1^2)} \cdot \{ (m_3^2 - \beta_1)(m_1 \coth(m_1) - 1) - (m_1^2 - \beta_1)(m_3 \coth(m_3) - 1) \}$$

$$\alpha_2 = \frac{1}{(m_3^2 - m_1^2)} \cdot \{ \beta_2(m_1 \coth(m_1) - m_3 \coth(m_3)) \}$$

$$\left. \frac{\partial y_B}{\partial \xi} \right|_{\xi=1} = \alpha_3 y_{B_s} + \alpha_4 y_{A_s} \quad (\text{A-5.5})$$

where

$$\alpha_3 = \frac{1}{(m_3^2 - m_1^2)} \cdot \{ (m_3^2 - \beta_1)(m_3 \coth(m_3) - 1) - (m_1^2 - \beta_1)(m_1 \coth(m_1) - 1) \}$$

$$\alpha_4 = \frac{1}{(m_3^2 - m_1^2)} \cdot \left\{ \frac{(m_1^2 - \beta_1)(m_3^2 - \beta_1)}{\beta_2} (m_3 \coth(m_3) - m_1 \coth(m_1)) \right\}$$



and

$$\left. \frac{\partial y_R}{\partial \xi} \right|_{\xi=1} = \alpha_5 y_{B_s} + \alpha_6 y_{A_s} \quad (\text{A-5.6})$$

where

$$\alpha_5 = \frac{1}{(m_3^2 - m_1^2)} \cdot \left\{ \frac{\beta_3(m_3^2 - \beta_1)}{m_3^2} \cdot (1 - m_3 \coth(m_3)) - \frac{\beta_3(m_1^2 - \beta_1)}{m_1^2} \cdot (1 - m_1 \coth(m_1)) \right\}$$

$$\alpha_6 = \frac{\beta_3(m_1^2 - \beta_1)(m_3^2 - \beta_1)}{\beta_2(m_3^2 - m_1^2)} \cdot \left\{ \frac{1}{m_3^2} (1 - m_3 \coth(m_3)) - \frac{1}{m_1^2} (1 - m_1 \coth(m_1)) \right\}$$

Therefore (A-5.1, 2, 3) becomes

$$\frac{\partial y_{A_s}}{\partial \bar{z}} + 3\alpha_1 y_{A_s} + 3\alpha_2 y_{B_s} = 0 \quad (\text{A-5.7})$$

$$\frac{\partial y_{B_s}}{\partial \bar{z}} + 3\alpha_3 y_{B_s} + 3\alpha_4 y_{A_s} = 0 \quad (\text{A-5.8})$$

$$\frac{\partial y_{R_s}}{\partial \bar{z}} + 3\alpha_5 y_{B_s} + 3\alpha_6 y_{A_s} = 0 \quad (\text{A-5.9})$$

Letting  $x_i = 3\alpha_i$ ;  $i = 1, \dots, 6$  and solving (A-5.7 and 8) by the operator method as done in A-3 we obtain

$$y_{A_s} = \frac{1}{(\ell_1 - \ell_2)} \{ (\ell_1 + x_1) \exp\{\ell_2 \bar{z}\} - (\ell_2 + x_1) \exp\{\ell_1 \bar{z}\} \} \quad (\text{A-5.10})$$

$$y_{B_s} = \frac{(\ell_1 + x_1)(\ell_2 + x_1)}{x_2(\ell_1 - \ell_2)} \cdot \{ \exp\{\ell_1 \bar{z}\} - \exp\{\ell_2 \bar{z}\} \} \quad (\text{A-5.11})$$

where

$$l_1 = \frac{-(x_1 + x_3) + \sqrt{(x_1 + x_3)^2 - 4(x_1x_3 - x_2x_4)}}{2}$$

and

$$l_2 = \frac{-(x_1 + x_3) - \sqrt{(x_1 + x_3)^2 - 4(x_1x_3 - x_2x_4)}}{2}$$

The solution for  $y_{R_s}$  can be obtained by direct integration of (A-5.9) after substitution of (A-5.10, 11).

$$\begin{aligned} y_{R_s} &= \frac{x_5(l_1 + x_1)(l_2 + x_1)}{x_2(l_1 - l_2)} \cdot \left\{ \frac{1}{l_2} \exp\{l_2 \bar{z}\} - \frac{1}{l_1} \exp\{l_1 \bar{z}\} \right\} \\ &+ \frac{x_6}{(l_1 - l_2)} \left\{ \frac{(l_2 + x_1)}{l_1} \cdot \exp\{l_1 \bar{z}\} - \frac{(l_1 + x_1)}{l_2} \cdot \exp\{l_2 \bar{z}\} \right\} \\ &+ \frac{x_6}{l_1 l_2} (l_1 + l_2 + x_1) - \frac{x_5(l_1 + x_1)(l_2 + x_1)}{x_2 l_1 l_2} \end{aligned} \quad (A-5.12)$$

A-6. STEADY-STATE SOLUTIONS TO BED MASS BALANCES. NEGLIGIBLE DIFFUSION RESISTANCE CASE.

Solve:

$$\frac{\partial y_{A_s}}{\partial z'} - K^* \zeta y_{B_s} + \zeta y_{A_s} = 0 ; \quad y_{A_s} = 1.0 @ z' = 0 \quad (\text{A-6.1})$$

$$\frac{\partial y_{B_s}}{\partial z'} + (K^* \zeta + K_1^* (1 - \zeta)) y_{B_s} - \zeta y_{A_s} = 0 ; \quad y_{B_s} = 0.0 @ z' = 0 \quad (\text{A-6.2})$$

$$\frac{\partial y_{R_s}}{\partial z'} - K_1^* (1 - \zeta) y_{B_s} = 0 ; \quad y_{R_s} = 0.0 @ z' = 0 \quad (\text{A-6.3})$$

Solution:

Let  $W_1 = \zeta$ ;  $W_2 = K^* \zeta$ ; and  $W_3 = K_1^* (1 - \zeta)$ .

Then (A-6.1, 2 and 3) may be written

$$\frac{\partial y_{A_s}}{\partial z'} - W_2 y_{B_s} + W_1 y_{A_s} = 0 \quad (\text{A-6.4})$$

$$\frac{\partial y_{B_s}}{\partial z'} + (W_2 + W_3) y_{B_s} - W_1 y_{A_s} = 0 \quad (\text{A-6.5})$$

$$\frac{\partial y_{R_s}}{\partial z'} - W_3 y_{B_s} = 0 \quad (\text{A-6.6})$$

Putting the equations in operator form and solving we obtain

$$y_{A_s} = A \exp\{\lambda_1 z'\} + B \exp\{\lambda_2 z'\} \quad (\text{A-6.7})$$

$$y_{B_s} = C \exp\{\lambda_1 z'\} + D \exp\{\lambda_2 z'\} \quad (\text{A-6.8})$$

where

$$\lambda_1 = \frac{-(W_1 + W_2 + W_3) + \sqrt{(W_1 + W_2 + W_3)^2 - 4W_1W_3}}{2} \quad (\text{A-6.9})$$

and

$$\lambda_2 = \frac{-(W_1 + W_2 + W_3) - \sqrt{(W_1 + W_2 + W_3)^2 - 4W_1W_3}}{2} \quad (\text{A-6.10})$$

Relations between C and A and D and B may be determined as in Section A-3.

These are

$$C = \frac{(\lambda_1 + W_1)A}{W_2} \quad (\text{A-6.11})$$

$$D = \frac{(\lambda_2 + W_1)B}{W_2} \quad (\text{A-6.12})$$

Therefore

$$y_{A_s} = A \exp\{\lambda_1 z'\} + B \exp\{\lambda_2 z'\} \quad (\text{A-6.13})$$

$$y_{B_s} = \frac{(\lambda_1 + W_1)}{W_2} A \exp\{\lambda_1 z'\} + \frac{(\lambda_2 + W_1)}{W_2} B \exp\{\lambda_2 z'\} \quad (\text{A-6.14})$$

Applying the boundary conditions

$$B = \frac{\lambda_1 + W_1}{\lambda_1 - \lambda_2} \quad (\text{A-6.15})$$

and

$$A = 1 - B = -\frac{(\lambda_2 + W_1)}{\lambda_1 - \lambda_2} \quad (\text{A-6.16})$$

The final solutions for  $y_{A_s}$  and  $y_{B_s}$  are

$$y_{A_s} = \frac{1}{(\lambda_1 - \lambda_2)} \{ (\lambda_1 + W_1) \exp\{\lambda_2 z'\} - (\lambda_2 + W_1) \exp\{\lambda_1 z'\} \} \quad (A-6.17)$$

$$y_{B_s} = \frac{(\lambda_2 + W_1)(\lambda_1 + W_1)}{W_2(\lambda_1 - \lambda_2)} \cdot \{ \exp\{\lambda_2 z'\} - \exp\{\lambda_1 z'\} \} \quad (A-6.18)$$

The solution for  $y_{R_s}$  may be found by substitution of (A-6.18) into (A-6.6) and direct integration.

$$y_{R_s} = \frac{W_3(\lambda_2 + W_1)(W_1 + \lambda_1)}{W_2(\lambda_1 - \lambda_2)} \left\{ \frac{1}{\lambda_2} \exp\{\lambda_2 z'\} - \frac{1}{\lambda_1} \exp\{\lambda_1 z'\} - \frac{(\lambda_1 - \lambda_2)}{\lambda_1 \lambda_2} \right\} \quad (A-6.19)$$

A-7. COMPUTER PROGRAMS USED IN THE THEORETICAL ANALYSIS OF THE THREE  
POLYFUNCTIONAL CATALYST FORMULATIONS.

A-7.1. CALCULATION OF INTRAPARTICLE AND BULK CONCENTRATIONS ONCE FOULING HAS  
BEGUN--DISCRETE CASE.

# **ILLEGIBLE DOCUMENT**

**THE FOLLOWING  
DOCUMENT(S) IS OF  
POOR LEGIBILITY IN  
THE ORIGINAL**

**THIS IS THE BEST  
COPY AVAILABLE**



```

      DIMENSION YAO(26,126),YBOX(26,126),YBOY(26,126),YRO(26,126),YCO(
126,126),YAN(26,126),YBXN(26,126),YBYN(26,126),YRN(26,126),YCN(26,
2126),YBSO(126),YASO(126),YRSO(126),YBSN(126),YRSN(126),YASN(126),
3A(60),B(60),C(60),D(60),W(60),Q(60),G(60),YCN1(26,126),YB1(26,126)
1 FORMAT(1H1,10X,53H)CALCULATION OF PARTICLE AND BED CONCENTRATIONS
  USING)
2 FORMAT(1H ,24X,40H4 LINEAR FOUling MODEL      D.P.C.//)
3 FORMAT(1H0,13X,3I20)
4 FORMAT(1H0,10X,7F12.8)
5 FORMAT(1H0,10X,4F16.8)
6 FORMAT(1H0,20X,4HJ= ,13,/)
7 FORMAT(1H0,10X,110,4F14.8)

```

C

C

```

      EPS = 0.00001
      IMAX = 100
      JMAX = 101
      KMAX = 26

```

C

C INITIALIZE STORAGE ARRAYS.

C

```

      DO 8 J=1,JMAX
      DO 8 K=1,KMAX
      YAO(K,J) = 0.0
      YRO(K,J) = 0.0
      YCO(K,J) = 0.0
      YAN(K,J) = 0.0
      YRN(K,J) = 0.0
      YBOX(K,J) = 0.0
      YBOY(K,J) = 0.0
      YBXN(K,J) = 0.0
      YBYN(K,J) = 0.0
      YCN1(K,J) = 0.0
      YB1(K,J) = 0.0
8 YCN(K,J) = 0.0
      DO 9 J=1,JMAX
      YBSO(J) = 0.0
      YRSO(J) = 0.0
      YASO(J) = 0.0
      YBSN(J) = 0.0
      YRSN(J) = 0.0
9 YASN(J) = 0.0

```

C

C START OF CALCULATIONS CALCULATION OF STEADY-STATE VALUES

C NEEDED TO INITIATE PROBLEM.

C

```

      F = 0.26
      EC = 1.0
      DB = 0.8
      RO = 0.25
      ED = 0.005
      DELZ = 10./FLOAT(JMAX-1)
      T10 = 0.2
      T20 = 4.0
      T30 = 0.2
      U = 1.0
      ZETA = 1.0
      DELET = 1.0/FLOAT(KMAX-1)

```

DEL1 = 10.

AM = 1.0

C  
C

G1 = DC\*T10\*RC\*RC/DD

G2 = DC\*T20\*RC\*RC/DD

G3 = DC\*T30\*RC\*RC/DD

GAM1 = G1

GAM2 = G2

GAM3 = G3

D1 = 3.

DEL1 = D1

ZB = 0.0

AA = 1.-F

H1 = (G1+G2)\*\*0.5

H2 = (G3)\*\*0.5

B4 = G1/(G1+G2)

B5 = G2/(G1+G2)

B6 = H1\*1.0/TANH(H1)-1.0

B1 = B4\*B6

B2 = B5\*B6

B3 = ((H2/AM)\*1./TANH(H2/AM)-1.)\*AM

W1 = F\*D1\*B1

W2 = F\*D1\*B2

W3 = AA\*D1\*B3\*AM

W4 = W1+W2+W3

W5 = (W4\*(4-4.\*W1\*W3)\*\*0.5

AM1 = -(W4-W5)/2.

AM2 = -(W4+W5)/2.

B7 = 1./(AM2-AM1)

B8 = AM2+W1

B9 = AM1 + W1

C

J = 1

C

K = KMAX

LL = KMAX-1

88 CC1 = AM1\*ZB

CC2 = AM2\*ZB

IF(CC2+40.0)61,61,63

61 YASO(J) = B7\*B8\*EXP(CC1)

YBSO(J) = -B7\*W1\*EXP(CC1)

YRSO(J) = 1.-B7\*AM2\*EXP(CC1)

GO TO 64

63 YASO(J) = B7\*(B8\*EXP(AM1\*ZB)-B9\*EXP(AM2\*ZB))

YBSO(J) = B7\*W1\*(EXP(AM2\*ZB)-EXP(AM1\*ZB))

YRSO(J) = 1.-B7\*(AM2\*EXP(AM1\*ZB)-AM1\*EXP(AM2\*ZB))

64 AL1 = H1

AL2 = H2

G4 = B4

G5 = B5

F1 = AL1/SINH(AL1)

F2 = AL2/SINH(AL2)

F3 = 1.-F2

C  
C

IF(ZETA)40,40,30

40 YAO(1,J) = YASO(J)\*(G5+G4\*F1)-YBSO(J)\*(-G5+G4\*F1)

```

YBOX(1,J) = YBSO(J)*(G4+G5*F1)-YASO(J)*(-G4+G4*F1)
YBOY(1,J) = YBSO(J)*F2
YRO(1,J) = YRSO(J)+YBSC(J)*F3
IF(J-JMAX)10,11,11
10 J = J+1
   ZB = ZB+DELZ
   ZETA = 1.0
   ZET = ZETA/AM
   K = KMAX
   GO TO 88
30 L = 0
33 G6 = SINH(AL1*ZETA)/SINH(AL1)
   G7 = SINH(AL2*ZET)/(AM*SINH(AL2/AM))
   G8 = 1.0-G7/ZET
   YAO(K-L,J) = YASO(J)*(G5+G4*G6/ZETA)-YBSO(J)*(-G5+G5*G6/ZETA)
   YBOX(K-L,J) = YBSO(J)*(G4+G5*G6/ZETA)-YASO(J)*(-G4+G4*G6/ZETA)
   YBOY(K-L,J) = YBSO(J)*G7/ZET
   YRO(K-L,J) = YRSO(J)+YBSO(J)*G8
   ZETA = ZETA-DELET
   ZET = ZET-DELET/AM
   L = L+1
   IF(L-LL)33,40,40
11 CONTINUE
   DO 22 J=1,JMAX,10
   WRITE(3,6)J
   DO 22 K=1,KMAX,5
22 WRITE(3,7)K,YAO(K,J),YBOX(K,J),YBOY(K,J),YRO(K,J)
C
C THE INITIAL CONCENTRATIONS NEEDED FOR
C PROGRAM HAVE BEEN CALCULATED.
   WRITE(3,1)
   WRITE(3,2)
   I = 1
83 J = 1
   YASO(J) = 1.0
   YBSO(J) = 0.0
   YRSO(J) = 0.0
   YASN(J) = YASO(J)
   YBSN(J) = YBSO(J)
   YPSN(J) = YRSO(J)
54 ITNO = 0
C *****
C
C CALCULATION OF CARBON CONCENTRATION FOR ADVANCED TIME.
C THE INITIAL GUESS OF THE NEW B CONCENTRATION WILL BE THE
C OLD B CONCENTRATION,
C *****
C
   DO 884 K=1,KMAX
   YB1(K,J) = YBOX(K,J)
884 YBXN(K,J) = YBOX(K,J)
   DO 12 K=1,KMAX
12 YCN(K,J) = ((1.-DELT*0.5*YBOX(K,J))*YCD(K,J)+DELT*0.5*(YBXN(K,J)
   +YBOX(K,J)))/(1.+DELT*0.5*YBXN(K,J))
C
C NOW SOLVE FOR PARTICLE CONCENTRATIONS USING THOMAS METHOD.
C
60 DO 80 N=1,KMAX

```

```

      A(N) = 0.0
      B(N) = 0.
      C(N) = -1.
80  D(N) = 0.
      N = 2
      A(N-1) = 2.+DELET*DELET*0.5*GAM1*(1.-YCN(N,J))
      C(N-1) = 0.
      E(N-1) = -(2.-DELET*DELET*0.5*GAM1*(1.-YCN(N+1,J)))
      D(N-1) = DELET*DELET*0.5*GAM2*((1.-YCN(N+1,J))*YBXN(N+1,J)+(1.-YCN
1(N,J))*YBXN(N,J))
      NMAX = KMAX
      NP = NMAX-2
      NM = NMAX-1
      DO 81 N=3,NP
      AN = N
      A(N-1) = (2.*AN+2.)/AN+DELET*DELET*0.5*GAM1*(1.-YCN(N,J))
      B(N-1) = -((AN+2.)/AN-DELET*DELET*0.5*GAM1*(1.-YCN(N+1,J)))
81  D(N-1) = DELET*DELET*0.5*GAM2*((1.-YCN(N+1,J))*YBXN(N+1,J)+(1.-YCN
1(N,J))*YBXN(N,J))
      N = NM
      AN = N
      A(N-1) = (2.*AN+2.)/AN+DELET*DELET*0.5*GAM1*(1.-YCN(N,J))
      B(N-1) = 0.
      YAN(KMAX,J) = YASN(J)
      D(N-1) = ((AN+2.)/AN-DELET*DELET*0.5*GAM1*(1.-YCN(N+1,J)))*YAN(N+1
1,J)+DELET*DELET*0.5*GAM2*((1.-YCN(N+1,J))*YBXN(N+1,J)+(1.-YCN(N,J)
2)*YBXN(N,J))
C*****
C
C  SHOULD HAVE ALL COEFFICIENTS AND QUANTITIES NEEDED
C  TO CALCULATE YAN'S. THOMAS METHOD.
C
C  *****
      W(1) = A(1)
      Q(1) = B(1)/W(1)
      G(1) = D(1)/W(1)
      NNM = NM-1
      DO 84 N=2,NNM
      W(N) = A(N)-C(N)*Q(N-1)
      G(N) = (D(N)-C(N)*G(N-1))/W(N)
84  Q(N) = B(N)/W(N)
      N = NMAX
      YAN(N-1,J) = G(N-2)
      DO 85 K=2,NNM
85  YAN(N-K,J) = G(N-(K+1))-C(N-(K+1))*YAN(N-K+1,J)
      YAN(1,J) = YAN(2,J)
C *****
C
C  THE YAN'S HAVE NOW BEEN CALCULATED.
C  CALC. THE YBXN.
C
C *****
      N = 2
      AN = N
      A(N-1) = 2.+DELET*DELET*0.5*GAM2*(1.-YCN(N,J))
      B(N-1) = -(2.-DELET*DELET*0.5*GAM2*(1.-YCN(N+1,J)))
      D(N-1) = DELET*DELET*0.5*GAM1*((1.-YCN(N+1,J))*YAN(N+1,J)+(1.-YCN(
1,N,J))*YAN(N,J))

```

```

DO 86 N=3, NP
  AN = N
  A(N-1) = (2.*AN+2.)/AN+DELET*DELET*0.5*GAM2*(1.-YCN(K,J))
  B(N-1) = -((AN+2.)/AN-DELET*DELET*0.5*GAM2*(1.-YCN(N+1,J)))
86 D(N-1) = DELET*DELET*0.5*GAM1*((1.-YCN(N+1,J))*YAN(N+1,J)+(1.-YCN(
  N,J))*YAN(N,J))
  N = NM
  AN = N
  A(N-1) = (2.*AN+2.)/AN+DELET*DELET*0.5*GAM2*(1.-YCN(N,J))
  B(N-1) = 0.
  YBXN(KMAX,J) = YBSN(J)
  D(N-1) = ((AN+2.)/AN-DELET*DELET*0.5*GAM2*(1.-YCN(N+1,J)))*YBXN(N+
  1,J)+DELET*DELET*0.5*GAM1*((1.-YCN(N+1,J))*YAN(N+1,J)+(1.-YCN(N,J)
  2)*YAN(N,J))
  W(1) = A(1)
  C(1) = B(1)/W(1)
  G(1) = D(1)/W(1)
DO 87 N=2, NKM
  W(N) = A(N)-C(N)*G(N-1)
  G(N) = (D(N)-C(N)*G(N-1))/W(N)
87 C(N) = B(N)/W(N)
  N = NMAX
  YBXN(N-1,J) = G(N-2)
DO 89 K=2, NKM
89 YBXN(N-K,J) = G(N-(K+1))-Q(N-(K+1))*YBXN(N-K+1,J)
  YBXN(1,J) = YBXN(2,J)
C *****
C
C THE YBXN'S HAVE NOW BEEN CALCULATED.
C NOW SINCE A TIME LAGGING BX CONC. WAS USED WE HAVE TO
C ITERATE TO IMPROVE ACCURACY.
C NO ITERATION IS REQUIRED ON THE YBYN'S.
C
DO 46 K=1, KMAX
46 YCN1(K,J) = ((1.-DELT*0.5*YBOX(K,J))*YCO(K,J)+DELT*0.5*(YBXN(K,J)+
  YBOX(K,J)))/(1.+DELT*0.5*YBAN(K,J))
DO 43 K = 1, KMAX
  IF(ABS(YCN1(K,J)-YCN(K,J))-EPS) 110, 110, 44
110 IF(ABS(YBXN(K,J)-YB1(K,J))-EPS) 43, 43, 44
43 CONTINUE
  GO TO 101
44 DO 222 K=1, KMAX
  YB1(K,J) = YBXN(K,J)
222 YCN(K,J) = YCN1(K,J)
  ITNO = ITNO + 1
  GO TO 60
101 CONTINUE
C *****
C
C NOW CALCULATE YBYN AND YRN USING T. M.
C
C *****
C
  N = 2
  AN = N
  A(N-1) = 2.+DELET*DELET*GAM3*0.5
  B(N-1) = -(2.-DELET*DELET*GAM3*0.5)
  C(N-1) = 0.
DO 70 N=3, NP

```

```

AN = N
A(N-1) = (2.*AN+2.)/AN+DELET*DELET*GAM3*0.5
B(N-1) = -((AN+2.)/AN-DELET*DELET*GAM3*0.5)
70 C(N-1) = 0.
N = NM
AN = N
A(N-1) = (2.*AN+2.)/AN+DELET*DELET*GAM3*0.5
B(N-1) = 0.
YBYN(KMAX,J) = YBSN(J)
C(N-1) = ((AN+2.)/AN-DELET*DELET*0.5*GAM3)*YBYN(N+1,J)
C *****
C
C START OF THE T. M. SOLUTION.
C
W(1) = A(1)
C(1) = B(1)/W(1)
G(1) = D(1)/W(1)
DO 71 N=2,NM
W(N) = A(N)-C(N)*Q(N-1)
G(N) = (D(N)-C(N)*G(N-1))/W(N)
71 C(N) = B(N)/W(N)
N = NMAX
YBYN(N-1,J) = G(N-2)
DO 72 K=2,NM
72 YBYN(N-K,J) = G(N-(K+1))-C(N-(K+1))*YBYN(N-K+1,J)
YBYN(1,J) = YBYN(2,J)
C *****
C
C NOW CALC. YRN'S BY THE SAME METHOD.
C
C *****
N = 2
AN = N
A(N-1) = 2.
B(N-1) = -2.
C(N-1) = DELET*DELET*0.5*GAM3*(YBYN(N+1,J)+YBYN(N,J))
DO 73 N=3,NP
AN = N
A(N-1) = (2.*AN+2.)/AN
B(N-1) = -(AN+2.)/AN
73 C(N-1) = DELET*DELET*0.5*GAM3*(YBYN(N+1,J)+YBYN(N,J))
N = NM
AN = N
A(N-1) = (2.*AN+2.)/AN
B(N-1) = 0.
YRN(KMAX,J) = YRSN(J)
C(N-1) = ((AN+2.)/AN)*YRN(N+1,J)+DELET*DELET*GAM3*0.5*(YBYN(N+1,J)
+YBYN(N,J))
C *****
C
C START OF THE T. M. SOLN.
C
W(1) = A(1)
C(1) = B(1)/W(1)
G(1) = D(1)/W(1)
DO 74 N=2,NM
W(N) = A(N)-C(N)*Q(N-1)
G(N) = (D(N)-C(N)*G(N-1))/W(N)

```

```

74 C(N) = B(N)/K(N)
   N = NMAX
   YRN(N-1,J) = G(N-2)
   DO 75 K=2,NMM
75 YRN(N-K,J) = G(N-(K+1))-Q(N-(K+1))*YRN(N-K+1,J)
   YRN(1,J) = YRN(2,J)
C *****
C
C NOW ALL PARTICLE CONCENTRATIONS HAVE BEEN CALCULATED
C FOR X AND Y PARTICLES.
C NOW CALC NEW BED CONCENTRATIONS ONE STEP DOWN THE BED.
   K = KMAX
   J = J+1
   YASN(J) = YASN(J-1)-DELZ*DEL1*(F*(YAN(K,J-1)-YAN(K-1,J-1))/DELET
   YBSN(J) = YBSN(J-1)-DELZ*DEL1*(F*(YBXN(K,J-1)-YBXN(K-1,J-1))
1+(1.-F)*AM*AM*(YBYN(K,J-1)-YBYN(K-1,J-1)))/DELET
   YRSN(J) = YRSN(J-1)-DELZ*DEL1*(1.-F)*AM*AM*(YRN(K,J-1)-YRN(K-1,J-1
1))/DELET
   MP = J-1
   WRITE(3,3)ITNO,I,MP
   ZETA = 0.0
   ZET = 0.
   DO 76 K=1,KMAX,5
   AK = K
   WRITE(3,4)ZETA,YCN1(K,MP),YAN(K,MP),YBXN(K,MP),ZET,YBYN(K,MP),YRN(
1K,MP)
   ZET = ZET+5.*DELET/AM
76 ZETA = ZETA+5.*DELET
   MMB = JMAX+1
   IF(J-MMB)50,51,51
50 GO TO 54
51 ZBAR = 0.0
   JJI = 20
   DO 55 J=1,JJI,1
   AJ = J
   WRITE(3,5)ZBAR,YASN(J),YBSN(J),YRSN(J)
55 ZBAR = ZBAR+1.*DELZ
   DO 993 J=21,JMAX,10
   WRITE(3,5) ZBAR,YASN(J),YBSN(J),YRSN(J)
993 ZBAR = ZBAR+10.*DELZ
C *****
C
C HAVE NOW CALCULATED ONCE THRU THE BED AND
C RECORDED THE RESULTS. NOW INCREMENT TIME
C AND GO THRU AGAIN.
C
   I = I+1
   IF(I-IMAX)99,99,98
99 WRITE(3,1)
   WRITE(3,2)
   TO 82 J=1,JMAX
   DO 82 K=1,KMAX
   YCN(K,J) = YCN(K,J)
82 YBXN(K,J) = YBXN(K,J)
   GO TO 83
98 CONTINUE
   STOP
   END

```

A-7.2. CALCULATION OF PARTICLE AND BULK CONCENTRATION ONCE FOULING HAS  
BEGUN--COMPOSITE PARTICLE CASE.



```

    DIMENSION YAO(26,126),YBO(26,126),YRO(26,126),YASO(126),YBSO(126),
    1YRSO(126),YASN(126),YBSN(126),YRSN(126),YAN(26,126),YBN(26,126),
    2YRN(26,126),YCN(26,126),YCO(26,126),A(60),B(60),C(60),D(60),W(60),
    3Q(60),G(60),YCI(26,126),YBI(26,126),YAI(26,126)

```

```

    1 FORMAT(1H1,10X,53H)CALCULATION OF PARTICLE AND BED CONCENTRATIONS
    1USING)

```

```

    2 FORMAT(1H ,24X,40HA LINEAR FOULING MODEL I. P. C.//)

```

```

    3 FORMAT(1H0,13X,3I20)

```

```

    4 FORMAT(1H ,10X,7F14.8)

```

```

    5 FORMAT(1H ,10X,4F16.8)

```

```

    6 FORMAT(1H-,20X,4HJ= ,13,/)

```

```

    7 FORMAT(1H0,10X,110,3F14.8)

```

```

    EPS = 0.000001

```

```

    IMAX = 10

```

```

    JMAX = 126

```

```

    KMAX = 26

```

```

    C INITIALIZE ARRAYS.

```

```

    DO 8 J=1,JMAX

```

```

    DO 8 K=1,KMAX

```

```

    YCO(K,J) = 0.0

```

```

    YBO(K,J) = 0.0

```

```

    YRO(K,J) = 0.0

```

```

    YAO(K,J) = 0.0

```

```

    YBN(K,J) = 0.0

```

```

    YBI(K,J) = 0.0

```

```

    YAN(K,J) = 0.0

```

```

    YRN(K,J) = 0.0

```

```

    YCI(K,J) = 0.0

```

```

    8 YCN(K,J) = 0.0

```

```

    DO 9 J=1,JMAX

```

```

    YBSO(J) = 0.0

```

```

    YRSO(J) = 0.0

```

```

    YASO(J) = 0.0

```

```

    YBSN(J) = 0.0

```

```

    YASN(J) = 0.0

```

```

    9 YRSN(J) = 0.0

```

```

    C START OF CALCULATIONS. CALCULATION OF STEADY STATE VALUES NEEDED
    C TO INITIATE PROBLEM.

```

```

    C *****

```

```

    E = 0.18

```

```

    DC = 1.0

```

```

    DB = 0.8

```

```

    RO = 0.25

```

```

    DD = 0.005

```

```

    DELZ = 10./FLOAT(JMAX-1)

```

```

    T10 = 0.2

```

```

    T20 = 4.0

```

```

    T30 = 0.2

```

```

    U = 1.0

```

```

    ZETA = 1.00

```

```

    DELE1 = 1.0/FLOAT(KMAX-1)

```

```

    DELT = 10.

```

C  
C

$G1 = DC * T10 * R0 * R0 / DD$   
 $G2 = DC * T20 * R0 * R0 / DD$   
 $G3 = DC * T30 * R0 * R0 / DD$   
 $GAM1 = G1$   
 $GAM2 = G2$   
 $GAM3 = G3$   
 $D1 = 3.$   
 $OEL1 = D1$   
 $ZB = 0.0$   
 $EE = 1.0 - E$   
 $B1 = E * G1$   
 $B2 = E * G2$   
 $B3 = EE * G3$

C  
C

$B4 = B1 + B2 + B3$   
 $B5 = (B4 * B4 - 4. * B1 * B3) ** 0.5$   
 $AM1 = ((B4 + B5) / 2.) ** 0.5$   
 $AM3 = ((B4 - B5) / 2.) ** 0.5$   
 $B6 = AM1 * 1.0 / \tanh(AM1) - 1.0$   
 $B7 = AM3 * 1.0 / \tanh(AM3) - 1.0$   
 $B8 = B6 - B7$   
 $B9 = -B8$   
 $C1 = AM3 * AM3 - B1$   
 $C2 = AM1 * AM1 - B1$   
 $C3 = 1.0 / (AM3 * AM3 - AM1 * AM1)$   
 $P1 = (C1 * B6 - C2 * B7) * C3$   
 $P2 = B2 * C3 * B8$   
 $P3 = C3 * (C1 * B7 - C2 * B6)$   
 $P4 = C1 * C2 * C3 * B9 / B2$   
 $P5 = ((AM3 * AM3 * B3 * C2 * B6 - AM1 * AM1 * B3 * C1 * B7) / (AM1 * AM1 * AM3 * AM3)) * C3$   
 $P6 = B3 * C3 * C2 * C1 * (B6 / (AM1 * AM1) - B7 / (AM3 * AM3)) / B2$   
 $X1 = D1 * P1$   
 $X2 = D1 * P2$   
 $X3 = D1 * P3$   
 $X4 = D1 * P4$   
 $X5 = D1 * P5$   
 $X6 = D1 * P6$   
 $X7 = X1 + X3$   
 $X8 = (X7 * X7 - 4. * (X3 * X1 - X2 * X4)) ** 0.5$   
 $AL1 = -(X7 - X8) / 2.$   
 $AL2 = -(X7 + X8) / 2.$   
 $A1 = 1.0 / (AL1 - AL2)$   
 $A2 = X1 + AL1$   
 $A3 = X1 + AL2$   
 $A4 = X6 * 1.0 / (AL1 * AL2)$   
 $A5 = X5 * A2 * A3 / (AL1 * AL2 * X2)$   
 $A6 = A3 * A2 * A1 / X2$   
 $R3 = AM3 * AM3 - B1$   
 $R4 = AM1 * AM1 - B1$   
 $R5 = 1. / (AM3 * AM3 - AM1 * AM1)$   
 $R6 = -R3$   
 $R7 = -R4$   
 $R8 = R7 * R3 / B2$   
 $F7 = B3 * R7 * R3 / B2$   
 $G4 = AM1 / \sinh(AM1)$

```

      G5 = AM3/SINH(AM3)
C
C
      K = KMAX
      LL = KMAX-1
      J = 1
88  CC1 = AL1*ZB
      CC2 = AL2*ZB
      IF(CC2+40.)61,61,63
61  YASO(J) = -A1*A3*EXP(CC1)
      YBSO(J) = A6*EXP(CC1)
      YRSO(J) = A4*(AL1+AL2+X1+A1*(AL2*A3*EXP(CC1)))-A5*(A1*AL2*EXP(CC1)
1+1.)
      GO TO 64
63  YASO(J) = A1*(A2*EXP(AL2*ZB)-A3*EXP(AL1*ZB))
      YBSO(J) = A6*(EXP(AL1*ZB)-EXP(AL2*ZB))
      YRSO(J) = A4*(AL1+AL2+X1+A1*(AL2*A3*EXP(AL1*ZB)-AL1*A2*EXP(AL2*ZB)
1))+ A5*(A1*(AL1*EXP(AL2*ZB)-AL2*EXP(AL1*ZB))-1.0)
C
C
64  IF(ZETA)40,40,30
40  YAO(1,J) = YASO(J)*R5*(R3*G4-R4*G5)+YBSO(J)*R5*(B2*G4-B2*G5)
      YBO(1,J) = YBSO(J)*R5*(R7*G4-R6*G5)+YASO(J)*R5*(R8*(G4-G5))
      YRO(1,J) = YRSO(J)+YBSO(J)*R5*(B3*R7*(1.-G4)/(AM1*AM1)-B3*R6*(1.-G
15)/(AM3*AM3))+YASO(J)*R5*(F7*((1.-G4)/(AM1*AM1)-(1.-G5)/(AM3*AM3))
2)
      IF(J-JMAX)10,11,11
10  J = J+1
      ZB = ZB+DELZ
      ZETA = 1.0
      K = KMAX
      GO TO 88
30  L = 0
33  R1 = SINH(AM1*ZETA)/SINH(AM1)
      R2 = SINH(AM3*ZETA)/SINH(AM3)
      F1 = R3*R1/ZETA-R4*R2/ZETA
      F2 = B2*R1/ZETA-B2*R2/ZETA
      F3 = R7*R1/ZETA-R6*R2/ZETA
      F4 = R7*R3*(R1-R2)/(B2*ZETA)
      F5 = B3*R7*(1.-R1/ZETA)/(AM1*AM1)
      F6 = B3*R6*(1.-R2/ZETA)/(AM3*AM3)
      F8 = (1.-R1/ZETA)/(AM1*AM1)
      F9 = (1.-R2/ZETA)/(AM3*AM3)
      YAO(K-L,J) = YASO(J)*F1*R5+YBSO(J)*F2*R5
      YBO(K-L,J) = YBSO(J)*F3*R5+YASO(J)*F4*R5
      YRO(K-L,J) = YRSO(J)+YBSO(J)*(F5-F6)*R5+YASO(J)*F7*(F8-F9)*R5
      ZETA = ZETA-DELET
      L = L+1
      IF(L-LL)33,40,40
11  CONTINUE
      DO 22 J=1,JMAX,10
      WRITE(3,5)J
      DO 22 K=1,KMAX,5
22  WRITE(3,7)K,YAO(K,J),YBO(K,J),YRO(K,J)
C
C *****
C
C THE INITIAL CONCENTRATIONS NEEDED FOR PROGRAM
C HAVE BEEN CALCULATED.

```

```
WRITE(3,1)
```

```
WRITE(3,2)
```

```
C
C SPECIFICATION OF BOUNDARY CONDITIONS ON PARTICLE AND
C BED.
```

```
C I = 1
```

```
83 J = 1
```

```
YASO(J) = 1.0
```

```
YBSO(J) = 0.0
```

```
YRSO(J) = 0.0
```

```
YASN(J) = YASO(J)
```

```
YBSN(J) = YBSO(J)
```

```
YRSN(J) = YRSO(J)
```

```
54 ITNO = 0
```

```
C
C CALCULATION OF CARBON CONCENTRATION FOR ADVANCED TIME.
C THE INITIAL GUESS OF NEW B CONCENTRATION WILL
C BE THE OLD B CONCENTRATION.
```

```
DO 100 K=1,KMAX
```

```
YB1(K,J) = YBO(K,J)
```

```
100 YBN(K,J) = YBO(K,J)
```

```
DO 12 K=1,KMAX
```

```
12 YCN(K,J) = ((1.-DELT*0.5*E*YBO(K,J))*YCO(K,J)+DELT*0.5*E*(YBN(K,J)
1+YBO(K,J)))/(1.+DELT*0.5*E*YBN(K,J))
```

```
C
C NOW WISH TO SOLVE FOR YAN, YBN, YRN BY THOMAS METHOD.
C YAN'S FIRST.
```

```
C *****
60 DO 92 N=1,KMAX
```

```
A(N) = 0.0
```

```
B(N) = 0.0
```

```
C(N) = -1.0
```

```
92 D(N) = 0.0
```

```
N = 2
```

```
A(N-1) = 2.+DELET*DELET*0.5*E*GAM1*(1.-YCN(N,J))
```

```
C(N-1) = 0.0
```

```
D(N-1) = (E*GAM2*(1.-YCN(N+1,J))*YBN(N+1,J)+E*GAM2*(1.-YCN(N,J))*
1YBN(N,J))*0.5*DELET*DELET
```

```
B(N-1) = -(2.-DELET*DELET*0.5*E*GAM1*(1.-YCN(N+1,J)))
```

```
NMAX = KMAX
```

```
NP = NMAX-2
```

```
NM = NMAX-1
```

```
DO 31 N=3,NP
```

```
AN = N
```

```
A(N-1) = (2.*AN+2.)/AN+DELET*DELET*0.5*E*GAM1*(1.-YCN(N,J))
```

```
B(N-1) = -((AN+2.)/AN-DELET*DELET*0.5*E*GAM1*(1.-YCN(N+1,J)))
```

```
31 D(N-1) = (E*GAM2*(1.-YCN(N+1,J))*YBN(N+1,J)+E*GAM2*(1.-YCN(N,J))*Y
1BN(N,J))*DELET*DELET*0.5
```

```
N = NM
```

```
AN = N
```

```
A(N-1) = (2.*AN+2.)/AN+DELET*DELET*0.5*E*GAM1*(1.-YCN(N,J))
```

```
B(N-1) = 0.0
```

```
YAN(KMAX,J) = YASN(J)
```

```

      D(N-1) = ((AN+2.)/AN-DELET*DELET*GAM1*0.5*E*(1.-YCN(N+1,J)))*YAN(N+
      11,J)+DELET*DELET*0.5*(E*GAM2*(1.-YCN(N+1,J))*YBN(N+1,J)+E*GAM2*(1.
      2-YCN(N,J))*YBN(N,J))

```

```

C
C SHOULD HAVE ALL COEFFICIENTS AND QUANTITIES NEEDED
C TO CALCULATE YAN'S BY THOMAS METHOD.

```

```

C START OF THE THOMAS METHOD SOLUTION.
C

```

```

      W(1) = A(1)
      Q(1) = B(1)/W(1)
      G(1) = D(1)/W(1)
      NMM = NM-1
      DO 84 N=2,NMM
        W(N) = A(N)-C(N)*Q(N-1)
        G(N) = (D(N)-C(N)*G(N-1))/W(N)
84    Q(N) = B(N)/W(N)
      N = NMAX
      YAN(N-1,J) = G(N-2)
      DO 85 K=2,NMM
85    YAN(N-K,J) = G(N-(K+1))-Q(N-(K+1))*YAN(N-K+1,J)
      YAN(1,J) = YAN(2,J)

```

```

C *****
C THE YAN'S HAVE BEEN CALCULATED.
C NOW SOLVE FOR THE YBN'S, YRN'S ETC. BY THE SAME METHOD.
C THE YBN'S FIRST.

```

```

C *****
      N = 2
      A(N-1) = 2.+DELET*DELET*0.5*(E*GAM2*(1.-YCN(N,J))+EE*GAM3)
      B(N-1) = -(2.-DELET*DELET*0.5*(E*GAM2*(1.-YCN(N+1,J))+EE*GAM3))
      D(N-1) = (E*GAM1*(1.-YCN(N+1,J))*YAN(N+1,J)+E*GAM1*(1.-YCN(N,J))*Y
      1AN(N,J))*DELET*DELET*0.5
      DO 45 N=3,NP
      AN = N
      A(N-1) = (2.*AN+2.)/AN+DELET*DELET*0.5*(E*GAM2*(1.-YCN(N,J))+EE*GA
      1M3)
      B(N-1) = -((AN+2.)/AN-DELET*DELET*0.5*(E*GAM2*(1.-YCN(N+1,J))+EE*G
      1AM3))
45    D(N-1) = (E*GAM1*(1.-YCN(N+1,J))*YAN(N+1,J)+E*GAM1*(1.-YCN(N,J))*Y
      1AN(N,J))*DELET*DELET*0.5
      N = NM
      AN = N
      A(N-1) = (2.*AN+2.)/AN+DELET*DELET*0.5*(E*GAM2*(1.-YCN(N,J))+EE*GA
      1M3)
      B(N-1) = 0.0
      YBN(KMAX,J) = YBSN(J)
      D(N-1) = ((AN+2.)/AN-DELET*DELET*0.5*(E*GAM2*(1.-YCN(N+1,J))+EE*GA
      1M3))*YBN(N+1,J)+DELET*DELET*0.5*(E*GAM1*(1.-YCN(N+1,J))*YAN(N+1,J)
      2+E*GAM1*(1.-YCN(N,J))*YAN(N,J))

```

```

C
C NOW CALCULATE THE YBN'S.
C

```

```

C START OF THOMAS METHOD TO CALCULATE THE YBN'S.
C

```

```

      W(1) = A(1)
      Q(1) = B(1)/W(1)

```

```

G(1) = D(1)/W(1)
DO 91 N=2,NMM
  W(N) = A(N)-C(N)*Q(N-1)
  G(N) = (D(N)-C(N)*G(N-1))/W(N)
91 Q(N) = B(N)/W(N)
  N = NMAX
  YBN(N-1,J) = G(N-2)
  DO 93 K=2,NMM
93 YBN(N-K,J) = G(N-(K+1))-Q(N-(K+1))*YBN(N-K+1,J)
  YBN(1,J) = YBN(2,J)
C *****
C
C THE NEW PARTICLE CONCENTRATIONS HAVE BEEN
C CALCULATED USING A TIME LAGGING B CONCENTRATION,
C NOW MUST ITERATE TO OBTAIN BETTER ACCURACY.
C
875 DO 46 K=1,KMAX
46 YC1(K,J) = ((1.-DELT*0.5*E*YB0(K,J))*YCO(K,J)+DELT*0.5*E*(YBN(K,J)
  1+YBO(K,J)))/(1.+DELT*0.5*E*YBN(K,J))
  DO 43 K=1,KMAX
  IF(ABS(YCN(K,J)-YC1(K,J))-EPS) 110,110,44
110 IF(ABS(YBN(K,J)-YB1(K,J))-EPS) 43,43,44
43 CONTINUE
  GO TO 101
44 DO 222 K=1,KMAX
  YCN(K,J) = YC1(K,J)
222 YB1(K,J) = YBN(K,J)
  ITND = ITND+1
  GO TO 60
101 CONTINUE
C
C THE YBN'S ARE SATISFACTORY, NOW CALCULATE
C THE YRN'S AND PROCEED ON.
C
C *****
C
  N = 2
  A(N-1) = 2.
  B(N-1) = -2.
  D(N-1) = DELET*DELET*0.5*(EE*GAM3*YBN(N+1,J)+EE*GAM3*YBN(N,J))
  DO 36 N=3,NP
  AN = N
  A(N-1) = (2.*AN+2.)/AN
  B(N-1) = -(AN+2.)/AN
36 D(N-1) = DELET*DELET*0.5*(EE*GAM3*YBN(N+1,J)+EE*GAM3*YBN(N,J))
  N = NM
  AN = N
  A(N-1) = (2.*AN+2.)/AN
  B(N-1) = 0.0
  YRN(KMAX,J) = YRSN(J)
  D(N-1) = ((AN+2.)/AN)*YRN(N+1,J)+DELET*DELET*0.5*(EE*GAM3*YBN(N+1,J)
  1+EE*GAM3*YBN(N,J))
C
C START OF THOMAS METHOD CALCULATION OF YRN'S.
C
  W(1) = A(1)
  C(1) = B(1)/W(1)
  G(1) = D(1)/W(1)
  DO 87 N=2,NMM

```

```

      W(N) = A(N)-C(N)*Q(N-1)
      G(N) = (D(N)-C(N)*G(N-1))/W(N)
87  Q(N) = B(N)/W(N)
      N = NMAX
      YRN(N-1,J) = G(N-2)
      DO 89 K=2,NMM
89  YRN(N-K,J) = G(N-(K+1))-Q(N-(K+1))*YRN(N-K+1,J)
      YRN(1,J)= YRN(2,J)
C *****
C
C THE YRN'S HAVE NOW BEEN CALCULATED.
C
C NOW CALCULATE THE NEW BED CONCENTRATIONS USING NEWLY CALCULATED
C AND PREVIOUS VALUES.
      K = KMAX
      J = J+1
      YASN(J) = YASN(J-1)-DELZ*DEL1*(YAN(K,J-1)-YAN(K-1,J-1))/DELET
      YBSN(J) = YBSN(J-1)-DELZ*DEL1*(YBN(K,J-1)-YBN(K-1,J-1))/DELET
      YRSN(J) = YRSN(J-1)-DELZ*DEL1*(YRN(K,J-1)-YRN(K-1,J-1))/DELET
      MP = J-1
      WRITE(3,3)ITNO,I,MP
      ZETA = 0.0
      DO 62 K=1,KMAX,5
      AK = K
      WRITE(3,4)ZETA,YC1(K,MP),YAN(K,MP),YBN(K,MP),YRN(K,MP)
62  ZETA = ZETA+5.*DELET
      MMB = JMAX+1
      IF(J-MMB)50,51,51
50  GO TO 54
51  ZBAR = 0.0
      JJI = 20
      DO 55 J=1,JJI,1
      AJ = J
      WRITE(3,5)ZBAR,YASN(J),YBSN(J),YRSN(J)
55  ZBAR = ZBAR+1.*DELT
      DO 993 J=21,JMAX,10
      WRITE(3,5) ZBAR,YASN(J),YBSN(J),YRSN(J)
993 ZBAR = ZBAR+10.*DELT
C
C NOW HAVE CALCULATED ONCE THRU THE BED AND HAVE RECORDED THEM.
C NOW INCREMENT TIME AND GO THRU THE BED AGAIN.
C
      I = I+1
      IF(I-IMAX)99,99,98
99  WRITE(3,1)
      WRITE(3,2)
      DO 82 J=1,JMAX
      DO 82 K=1,KMAX
      YC0(K,J) = YCN(K,J)
82  YB0(K,J) = YBN(K,J)
      GO TO 83
98  CONTINUE
      STOP
      END

```

A-7.3. CALCULATION OF CONCENTRATION PROFILES IN REACTOR BED WITH FOULING INCLUDED. NO DIFFUSION RESISTANCE CASE.



```

      DIMENSION YCO(300),YCN(300),YBS(300),YAS(300),YRS(300),
      1YPSN(300),YASN(300),YRSN(300),YCN2(300),YAS1(300),YBS1(300),YRS1(3
      200)

```

```

      1 FORMAT(1H1,20X,'THE STEADY STATE SOLUTIONS ARE'/)
      2 FORMAT(1H ,10X,'ZP',10X,'YAS',10X,'YBS',10X,'YRS')
      3 FORMAT(1H ,6X,F7.3,3F14.8)
      4 FORMAT(1H ,10X,'DIFFUSION RESISTANCE CONSIDERED NEGLIGIBLE'/)
      5 FORMAT(1H1,20X,'THE UNSTEADY SOLUTIONS ARE'/)
      6 FORMAT(1H ,10X,'N =',I6,20X,'ITND =',I6)
      7 FORMAT(1H ,10X,'ZP',10X,'YC',11X,'YAS',10X,'YBS',13X,'YRS')
      8 FORMAT(1H ,6X,F7.3,4F14.8)

```

C

C SPECIFICATION OF CONSTANTS AND PHYSICAL PROPERTIES.

C

C \*\*\*\*\*

```

      ET = 0.18
      JEND = 101
      NEND = 120
      CZ = 25./FLOAT(JEND-1)
      DB = 0.80
      T10 = 0.2
      T20 = 4.0
      T30 = 0.2
      U = 1.0
      DT = 50.
      EPS = 0.000001

```

C

C \*\*\*\*\*

```

      DO 9 J=1,JEND
      YCN(J) = 0.0
      YCN2(J) = 0.0
      YCO(J) = 0.0
      YBSO(J) = 0.0
      YASO(J) = 0.0
      YRSO(J) = 0.0
      YASN(J) = 0.0
      YBSN(J) = 0.0
      9 YRSN(J) = 0.0

```

C

C CALCULATION OF STEADY STATE CONCENTRATIONS SECTIONC.

C \*\*\*\*\*

```

      ZP = 0.0
      N = 1
      J = 1
      EET = 1.-ET
      W1 = ET
      W2 = ET*T20/T10
      W3 = EET*T30/T10
      W4 = W1+W2+W3
      W5 = W4*(4.-4.*W1*W3)
      AL1 = (-W4+(W5)**0.5)/2.
      AL2 = (-W4-(W5)**0.5)/2.
      A1 = 1./(AL1-AL2)
      A2 = AL1+W1
      A3 = AL2+W1
      A4 = (A2*A3*A1)/W2
      A5 = (A2*A3*W3*A1)/W2
      A6 = 1./AL2

```

```

      A7 = 1./AL1
      A8 = (AL1-AL2)/(AL1+AL2)
33  CC1 = AL1*ZP
      CC2 = AL2*ZP
      IF(CC2+40.)61,61,63
61  YASQ(J) = -A1*A3*EXP(CC1)
      YBSQ(J) = -A4*EXP(CC1)
      YRSQ(J) = -A5*(A7*EXP(CC1)+A8)
      GO TO 64
63  YASQ(J) = A1*(A2*EXP(CC2)-A3*EXP(CC1))
      YBSQ(J) = A4*(EXP(CC2)-EXP(CC1))
      YRSQ(J) = A5*(A6*EXP(CC2)-A7*EXP(CC1)-A8)
64  ZP = ZP+DZ
      J = J+1
      IF(ZP-25.)10,10,11
10  GO TO 33
11  CONTINUE
      WRITE(3,1)
      WRITE(3,4)
      WRITE(3,2)
      ZP = 0.
      JJI = 20
      DO 12 J=1,JJI
      WRITE(3,3)ZP,YASQ(J),YBSQ(J),YRSQ(J)
12  ZP = ZP+DZ
      DO 95 J=21,JEND,10
      WRITE(3,3)ZP,YASQ(J),YBSQ(J),YRSQ(J)
95  ZP = ZP+10.*DZ

```

```

C
C *****
C
C NOW START CALCULATION OF FOULING EFFECTS ON CONCENTRATIONS.
C
C *****

```

```

      WRITE(3,5)
      WRITE(3,4)
      N = 2
29  ITNO = 3
      ZP = 0.0

```

```

C
C BOUNDARY CONDITION SPECIFICATION
C

```

```

      J = 1
      YASN(J) = YASQ(J)
      YBSN(J) = YBSQ(J)
      YRSN(J) = YRSQ(J)
      YAS1(J) = YASQ(J)
      YBS1(J) = YBSQ(J)
      YRS1(J) = YRSQ(J)

```

```

C
C THE INITIAL GUESS OF NEW B CONCENTRATION WILL BE THE
C PSEUDO-STEADY B CONCENTRATION.
C

```

```

      DO 100 J=1,JEND
100 YBSN(J) = YBSQ(J)

```

```

C
C CALCULATION OF CARBON VS. BED LENGTH.
C

```

```

DO 14 J=1,JEND
14 YCN(J) = (YCN(J)+DT*0.5*ET*((1.-YCN(J))*YBSN(J)+YBSN(J)))/(1.+DT*
10.5*ET*YBSN(J))
JJ = JEND-1
56 DO 15 J=1,JJ
YASN(J+1) = ((1.-DZ*0.5*W1*(1.-YCN(J)))*YASN(J)+DZ*0.5*(W2*(1.-
1-YCN(J))*YBSN(J)+W2*(1.-YCN(J+1))*YBSN(J+1)))/(1.+DZ*0.5*W1*(1.-
2YCN(J+1)))
YBSN(J+1) = ((1.-DZ*0.5*(W2*(1.-YCN(J))+W3))*YBSN(J)+DZ*0.5*(W1*(
11.-YCN(J))*YASN(J)+W1*(1.-YCN(J+1))*YASN(J+1)))/(1.+DZ*0.5*(W2*(
21.-YCN(J+1))+W3))
15 YRSN(J+1) = YASN(J) + DZ*0.5*W3*(YBSN(J)+YBSN(J+1))
ZP = 0.
38 DO 16 J=1,JEND
16 YCN2(J) = (YCN(J)+DT*0.5*ET*((1.-YCN(J))*YBSN(J)+YBSN(J)))/(1.+DT*
10.5*ET*YBSN(J))
DO 58 J=1,JJ
YAS1(J+1) = ((1.-DZ*0.5*W1*(1.-YCN2(J)))*YAS1(J)+DZ*0.5*(W2*(1.-
1-YCN2(J))*YBS1(J)+W2*(1.-YCN2(J+1))*YBSN(J+1)))/(1.+DZ*0.5*W1*(1.-
2YCN2(J+1)))
YBS1(J+1) = ((1.-DZ*0.5*(W2*(1.-YCN2(J))+W3))*YBS1(J)+DZ*0.5*(W1*(
11.-YCN2(J))*YAS1(J)+W1*(1.-YCN2(J+1))*YAS1(J+1)))/(1.+DZ*0.5*(W2*(
21.-YCN2(J+1))+W3))
58 YRS1(J+1) = YAS1(J) + DZ*0.5*W3*(YBS1(J)+YBS1(J+1))
DO 17 J=1,JEND
IF(ABS(YCN(J)-YCN2(J))-EPS)42,42,18
42 IF(ABS(YBSN(J)-YBS1(J))-EPS)19,19,18
19 IF(ABS(YASN(J)-YRS1(J))-EPS)41,41,18
41 IF(ABS(YASN(J)-YAS1(J))-EPS)17,17,18
18 GO TO 20
17 CONTINUE
GO TO 23
20 DO 21 J=1,JEND
21 YCN(J) = YCN2(J)
ITNO = ITNO+1
GO TO 56
23 NN = NEND+1
WRITE(3,6)N,ITNO
WRITE(3,7)
ZP = 0.
JJI = 23
DO 65 J=1,JJI
WRITE(3,8)ZP,YCN(J),YASN(J),YBSN(J),YRSN(J)
65 ZP = ZP+DZ
DO 66 J= 21,JEND,10
WRITE(3,8)ZP,YCN(J),YASN(J),YBSN(J),YRSN(J)
66 ZP = ZP+10.*DZ
N = N+1
IF(N-NN)25,26,26
25 DO 27 J=1,JEND
YCN(J) = YCN(J)
YASN(J) = YASN(J)
YBSN(J) = YBSN(J)
27 YRSN(J) = YRSN(J)
GO TO 29
26 CONTINUE
STOP
END

```

A THEORETICAL INVESTIGATION OF POISONING  
EFFECTS ON POLYFUNCTIONAL CATALYSTS

by

ADRIAN CHARLES SNYDER

B. S., University of Nebraska, 1967

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

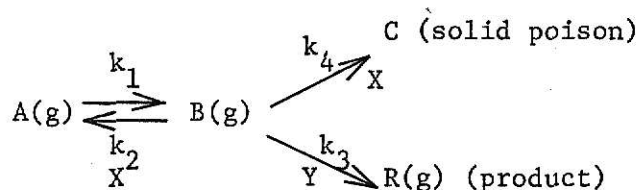
MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1971

In situ poisoning effects on two dual functional catalyst formulations, both capable of promoting polystep reactions of the type



in a single zone fixed bed system, have been investigated.

A relatively slow change in catalyst activity with poison deposition was accounted for by relating rate coefficients directly to the poison content of the catalyst. A linear relationship was employed in the particle mass balances and numerical solutions were obtained. The investigation considered both bed and particles at constant temperature.

The effects of several factors on product yield and catalyst fouling rate were considered. These were:

- (1) Unequal particle sizes in the discrete formulation,
- (2) The magnitude of the equilibrium restriction,  $k_1^0/k_2^0$ , and
- (3) Varying the product forming rate constant.

Comparisons made between the two formulations indicate that the composite formulation is more efficient; both with respect to product yield and catalyst fouling rate.