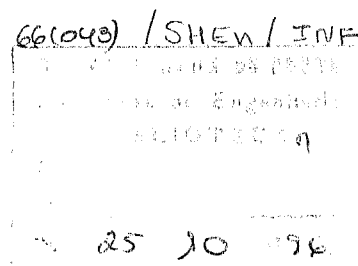


INFLUENCE OF FORCED CONVECTION ON MASS TRANSPORT AND REACTION IN POROUS CATALYST PELLETS AND REACTOR PERFORMANCE

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PREFACE

The subject of diffusion and reaction in porous heterogeneous catalysts has been a main research topic in chemical engineering for a long time. To model intraparticle mass transport it is necessary to develop mathematical expressions for fluxes of multicomponent mixtures valid throughout the entire range between the limits of Knudsen diffusion control and bulk diffusion control. In large-pore catalysts intraparticle mass transport is not only due to diffusion but also to forced convection inside pores which is generated by the pressure gradient across the particle. The fundamental quantity which forms the basis for calculations of diffusion and reaction in porous catalysts is the particle effective diffusivity. The enhancement of forced convection to the intraparticle mass transport can be expressed in terms of an *augmented* intraparticle effective diffusivity. Chromatography measurement techniques have been successfully applied for the determination of intraparticle effective diffusivity. With reaction kinetic equations and intraparticle effective diffusivity the behaviour of a fixed-bed reactor can be predicted.

This thesis focuses upon the intraparticle mass transport and reaction in large-pore catalysts in both aspects of theoretical analysis and experimental measurements. After the Introduction section (Chapter 1) the effect of forced convection on reaction with mole changes in porous catalysts based on the dusty gas model is studied in Chapter 2. In Chapter 3 the enhancement of intraparticle forced convection for finite cylinder particle and an analogy between the slab and the cylinder geometries are analysed. Chapter 4 deals with the measurements of effective diffusivity in large-pore permeable pellets with various geometries (hollow cylinder, solid finite cylinder and sphere) using the chromatographic method. In Chapter 5 the kinetics of ethylene oxide on a silver catalyst supported in α -alumina is measured and used in the simulation of ethylene oxidation in a fixed-bed reactor (Chapter 6).

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RESUMO

O efeito da convecção intraparticular em reacções irreversíveis, de 1ª ordem, isotérmicas com variação do número de moles foi analisado em catalisadores de poros-largos com geometria de placa plana. Um modelo, que tem em conta a convecção intraparticular e a variação do número de moles e que é válido em todos os regimes difusivos, foi formulado com base no “dusty gas model”. O modelo envolve 4 parâmetros: módulo de Thiele, ω ; razão entre a difusividade de Knudsen e a difusividade molecular efectiva, α ; razão entre momento viscoso e difusividade molecular, β ; e queda de pressão externa normalizada, Δf .

Estudou-se o problema de difusão, reacção de 1ª ordem e convecção forçada em catalisadores de poros largos com geometria de cilindro finito. O efeito da convecção no factor de eficiência foi analisado e obtida uma relação para a difusividade efectiva *aumentada*. Foi ainda obtida uma relação de equivalência entre as dimensões características da placa plana e do cilindro finito.

A difusividade intraparticular foi medida pelo método cromatográfico para catalisadores de poros largos com geometria de cilindro finito, cilindro oco e esfera. Foi obtida uma relação de equivalência entre o cilindro oco e a placa plana.

A cinética de oxidação do etileno a óxido de etileno num catalisador $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ foi medida num reactor de Berty e aplicada à simulação dum reactor de leito fixo.

ABSTRACT

The effect of intraparticle forced convection on a heterogeneous reaction within a catalyst pellet was studied. The extended dusty gas model was used to describe mass transport for a first-order, irreversible, isothermal reaction with mole changes within a slab geometry catalyst pellet. Four dimensionless parameters are introduced and studied: the Thiele modulus, ϕ ; the ratio between Knudsen and effective molecular diffusivities, α ; the ratio between viscous momentum and effective molecular diffusivity, β ; and the normalised external pressure drop, Δf . A general model which considers both intraparticle convection and mole changes for isothermal first-order reaction in porous catalyst, valid in all diffusion regimes, was derived.

Forced intraparticle convection in a finite cylinder porous catalyst particle was studied. An analytical solution for steady state, simultaneous diffusion, convection and reaction has been obtained and the effect of intraparticle convection on the catalyst performance, i.e., its effectiveness factor, was analysed. The relationship for the *augmented* intraparticle effective diffusivity and an equivalence ratio between the slab and the finite cylinder characteristic dimensions, valid in the whole range of Thiele modulus, have been obtained.

Mathematical models for solid cylinder and hollow cylinder pellets, where intraparticle convection was considered, have been established and solutions in the Laplace domain have been obtained. Consequently, the equivalence between the hollow cylinder and the slab characteristic dimensions was presented for the first-order-reaction/diffusion/convection problem. A modified chromatographic method has been developed to measure the intraparticle diffusivity in solid cylinder pellets. The axial dispersion of the column packed with the hollow cylinder pellets was determined and a correlation for the Peclet number versus Reynolds number has been obtained. Intraparticle convection was measured with large-pore sphere pellets which present a "foam structure" by using the conventional chromatographic method. Intraparticle Peclet numbers and the permeability of this pellet were determined.

The kinetics of ethylene oxidation over α -alumina supported commercial silver catalysts has been studied with a Berty reactor. Rate equations for the ethylene oxidation for gas mixtures containing excess oxygen was determined. These rate equations can be used under the experimental conditions of this work. The selectivity of the reaction has been studied.

The reaction of ethylene oxidation in a fixed-bed reactor packed with silver catalysts supported in α -alumina was studied experimentally. A mathematical model in which intraparticle diffusion is considered was proposed. The performance of the reactor was simulated. The effects of intraparticle convection on the results of the reaction were discussed.

RÉSUMÉ

L'effect de la convection intraparticulaire sur l'efficacité de catalyseurs macroporeux (plaque plane) pour une reaction irreversible, du 1^{er} ordre, isotherme avec changement du nombre de moles a été étudié. Le modèle, basé sur le "dusty gas model" contient 4 paramètres: module de Thiele, ω ; rapport diffusivité de Knudsen/diffusivité moléculaire effective, α ; rapport moment visqueux/diffusivité moléculaire effective, β ; et chute de pression normalisé, Δf .

Le problème de diffusion/reaction du 1^{er} ordre/convection dans les catalyseurs cylindre fini a été analysée. L'efficacité du catalyseur a été calculée et des relations de diffusivité effective *augmentée* et equivalence entre plaque plane et cylindre fini ont été obtenues.

La diffusivité intraparticulaire a été mesurée par la méthode chromatographique pour trois catalyseurs macroporeux (cylindre fini, cylindre creux et sphère). Une relation d'equivalence entre plaque plane et cylindre creux a été dérivée.

La cinétique d'oxidation d'éthylène sur catalyseur $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ a été mesurée dans un reactor Berty et appliquée à la simulation et étude d'un reacteur à lit fixe.

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1. Introduction

1.1 IMPORTANCE AND MOTIVATION

In heterogeneous catalytic systems, observed reaction rates can be significantly affected by the mass transfer rate of reactants between the surface of the pellet and the active sites deep within the porous structure. In general, mass transport inside a porous pellet occurs by diffusion in the pores (molecular diffusion, Knudsen diffusion), surface diffusion and viscous flow. There is a very extensive literature concerning the behaviour of this type of systems. However, the case in which all three mass transport processes occur simultaneously is not yet fully understood. This is mainly due to the complexity of the pore structures. To describe diffusion in the pores it is necessary to use mathematical expressions for multicomponent mixtures, valid throughout the entire range between the limits of Knudsen diffusion control in very small pores and bulk diffusion control in large pores. The starting point for any mathematical description of porous catalysts is a set of flux relationships expressing the flux vector for the various species in terms of pressure gradients, temperature and composition.

It was assumed for a long time that the external forced convection does not penetrate in the catalyst pores and has no effect on the intraparticle concentration distribution. Recent studies have shown that this mechanism can be important for large-pore catalysts and an increase of the catalyst effectiveness factor due to forced convection was observed. An analytical relationship between intraparticle convection and effective diffusivity within the catalyst pellet has been obtained. This relationship not only gives a successful explanation of the variation of effective diffusivities with flowrate in experimental measurements but also makes it possible to quantify intraparticle convection experimentally.

1.2 OBJECTIVES

The main purpose of this work is to study mass transport and reaction within catalytic pellets taking into account the effect of intraparticle forced convection, including both theoretical analysis and experimental work.

A description of the various chapters in which this thesis is divided is given next.

- In Chapter 2 the effect of forced convection on reaction with mole changes in porous catalysts is studied.

The literature contains numerous statements to the fact that reaction involving a change in the number of moles will generate pressure gradients when they are carried out in porous catalyst pellets. When the number of moles increases, the pressure within the pellet is expected to be higher than the pressure at the surface, while the reverse is true when there is

a decrease in the number of moles. Clearly, such pressure variations will affect the concentration of the various reacting species, and might, therefore, be expected to influence the value of the effectiveness factor for the pellet as a whole. The question of the existence, magnitude and practical importance of pressure gradients within porous catalyst pellets have, therefore, attracted some attention.

The dusty gas model (DGM) is one of the widely acceptable models for predicting mass transport of gas inside porous pellets. This model treats the porous medium as an assembly of stationary particles (dust) dispersed in the gas on a molecular scale. The dusty gas model is particularly attractive because in the transition regime, it correctly combines the simultaneous effects of ordinary molecular diffusion and Knudsen diffusion in any array of pores. To account for the flux resulting from a pressure gradient, a Darcy flow term can be simply added.

The objective of Chapter 2 is to establish a general model, based on the dusty gas model, that shows the combined effect of both mole changes (reaction stoichiometry) and of intraparticle forced convection (due to an imposed pressure drop) on the catalyst performance. The work includes two aspects: one is the variation of pressure within the pellet; and the other is the effectiveness factor. We confine our attention to an isothermal first-order reaction $A \rightarrow nB$ taking place in a catalyst pellet of slab geometry.

In Chapter 3 the problem of diffusion, convection and reaction in catalyst particles is addressed in order to develop an analogy between the slab and the cylinder geometries.

Previously, an explicit expression of the enhancement by convection of the mass transport within the particle has been obtained by introducing an *augmented* intraparticle effective diffusivity. This concept of augmented effective diffusivity allows the use of the classical model for mass transport derived for the case of diffusion only when simultaneous diffusion and convection occur, simply by replacing the effective diffusivity by its augmented value. In the case of no reaction, an analytical expression of the augmented diffusivity as a function of the intraparticle flow has been derived. For a system in which reaction takes place, the augmented diffusivity depends not only on the intraparticle Peclet number but also on the Thiele modulus. The enhancement of intraparticle forced convection for both slab and sphere particles in the case of simultaneous intraparticle diffusion, convection and reaction has been studied before. Relationships between the *augmented* intraparticle effective diffusivity and the intraparticle Peclet number were obtained for both geometries in the transient region and at steady state.

In the treatment of mass transport inside porous pellets, the equivalence between the various geometries is an interesting subject in chemical engineering. In theoretical analysis the slab and sphere geometries are widely used due to their symmetry characteristics. In the absence of intraparticle convection, equivalencies have been provided between the slab geometry

and the sphere and cylinder geometries, valid in the whole range of Thiele modulus. When intraparticle convection is considered, a simple explicit solution for the slab geometry can be obtained. Therefore, establishing the equivalence between slab and other geometries, which are common in industrial applications, allows for an easier mathematical treatment of complex processes. The equivalence ratio between the slab and the sphere characteristic dimensions has been studied for diffusion, convection and reaction in steady state and transient operation based on the equality of particle effectiveness factors.

In the engineering practice catalyst particles used in commercial processes are often finite cylinders due to their easy of manufacture by automatic pelleting machines. The objectives of Chapter 3 are: first, to obtain the augmented intraparticle effective diffusivities for a finite cylinder geometry catalyst pellet when diffusion, convection and reaction take place; second, to obtain the equivalence ratio between the characteristic dimensions of slab and finite cylinder geometries at steady state, valid in the whole range of Thiele modulus in the presence of intraparticle convection.

Chapter 4 deals with the measurement of effective diffusivity in large-pore permeable pellets with various geometries using the chromatographic method.

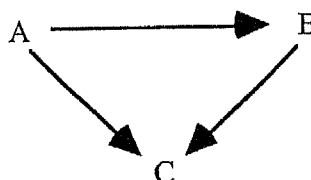
Effective diffusivity is an essential parameters for predicting the mass transport rate inside the catalyst pellets. Generally, accurate estimation of the effective diffusivity inside the porous pellets are not possible, since this is severely dependent on the details of the pore structure. Experimental methods always play an important role in the study of the effective diffusivity of gases in porous media.

Several techniques have been employed to measure the effective diffusivity. Among them, chromatographic measurements are receiving increasing attention as a procedure for measuring rate parameters in fixed bed reactors. The theory of gas chromatography permits the determination of mass transfer resistance such as axial diffusion, interphase diffusion, and intraparticle diffusion in beds packed with catalyst pellets. For the measurement of diffusivity a carrier gas, which is not adsorbed, is passed continuously through the column. A pulse of a diffusing non-adsorbable component is injected into the stream and some property of the effluent pulse, related with its concentration, is recorded. For linear processes, rapid and simple experiments can provide information about the contributions of each transport mechanism and surface process in gas-solid catalytic reactors. Depending on to the experimental conditions, a set of dynamic equations to describe the system behaviour can be developed, whose solution provides the theoretical responses. Mass transport parameters in the model equations can be determined by fitting the theoretical to the experimental response values. Another interesting problem which can be addressed by this technique is the measurement of intraparticle convection. An analytical relationship between intraparticle convection and effective diffusivity within the catalyst pellet has been obtained

by introducing the intraparticle Peclet number. This relationship makes it possible to quantify intraparticle convection by using the chromatographic method.

In Chapter 4 mathematical models are established for pellets with different geometries - solid cylinder, hollow cylinder and sphere. These pellet geometries are common in the industry and may have large-pore structures and thus intraparticle convection is considered in these mathematical models. Consequently, the equivalence between the hollow cylinder and the slab characteristic dimensions is presented for a first-order-reaction, diffusion and convection problem. A modified gas chromatographic technique is developed and applied to measure intraparticle diffusivities in such permeable catalysts with cylinder geometry. In the case of the hollow cylinder pellets axial dispersion is independently measured with the column packed with non-porous hollow cylinder pellets with similar dimensions and a correlation for the Peclet number versus Reynolds number is obtained. The traditional gas chromatographic technique is then applied to identify and measure intraparticle convection. Conditions for the determination of the intraparticle convection are discussed. Intraparticle convection is measured with large pore sphere pellets which present a "foam structure" by using the conventional chromatographic method. Intraparticle Peclet numbers and the permeability of this pellet are then determined.

Chapter 5 deals with the kinetics of ethylene oxidation on a silver catalyst. Ethylene oxidation is commonly used as a model reaction in chemical engineering for experimental and theoretical investigations due its triangular scheme. It is a typical complex reaction which includes both a serial and a parallel reaction.



Furthermore, in the petrochemical industry ethylene oxidation is an important reaction, and the oxidation of ethylene to ethylene oxide on a silver catalyst, with concurrent formation of carbon dioxide and water as by-products, has been extensively studied. It has been shown that parallel oxidation of ethylene to carbon dioxide is more significant than consecutive oxidation. Most kinetic studies agree on the major importance of direct oxidation of ethylene to carbon dioxide and water.

Several mechanisms of the oxidation of ethylene over silver catalyst have been proposed, and, accordingly, various kinetic rate equations have been obtained. In general, these rate equations and mechanisms can only be applied to a narrow range of experimental conditions owing to the fact that different conditions lead to different surface situations. The most common kinetic model is a Langmuir-Hinshelwood equations in which all reactants and products are supposed to compete for adsorption on the same catalytic sites and dissociative

adsorption is assumed. This model is adequate to fit the experimental data and is able to describe the maximum in the reaction rate as function of the ethylene and oxygen partial pressures.

In most of the previous works research has been focused on the reaction mechanism on silver catalysts with the objective of obtaining higher selectivity in the industrial process. The objective of the work described in Chapter 5 was to study the kinetics of ethylene oxidation over a supported silver catalyst in a Berty reactor and to propose a kinetic equation of reaction which can be used in further studies in a fixed-bed reactor under specified experimental conditions. With the kinetic equation, some of the characteristics of reaction of ethylene selective oxidation can be predicted. The selectivity of the reaction is discussed.

Usually a multitubular reactor is applied for the ethylene oxidation in industrial processes. Outside the reactor a liquid coolant or a boiling coolant is applied in the shell to remove the heat of reaction. It is not difficult to simulate these conditions in the laboratory and to use the results in industrial reactor design. Essentially, ethylene oxide is produced by the careful controlled oxidation of ethylene over a silver catalyst. The reaction conditions are critical. If they are too mild, little oxide is produced; if they are too severe, the reaction runs away and carbon dioxide and water are the only end products. The major problem in the product of ethylene oxide is thus to control the oxidation reaction so that while maintaining an adequate production rate, the wasteful production of carbon dioxide and water is limited. In this sense, the mathematical simulation of the system is an interesting subject.

Heat transfer in the fixed-bed have been intensively studied. However, in an heterogeneous catalytic reactor mass transfer is an important factor. For most cases encountered in practice diffusion inside the catalysts should be considered.

The objective of Chapter 6 is to simulate the reaction of ethylene oxidation in a fixed-bed reactor packed with silver catalysts. A mathematical model in which intraparticle diffusion is considered is proposed. The results are compared with experimental data. Finally, the effects of intraparticle convection on the reaction results are discussed.

2. Effect of Forced Convection on Reaction with Mole Changes in Porous Catalysts

2.1 INTRODUCTION

Gas-phase mass transport in porous catalysts is an important factor in predicting observed reaction rates for heterogeneous catalytic systems. Observed reaction rates and selectivity in porous catalyst pellets are strongly affected by rate limitations associated with diffusion of reactants between the surface of the pellet and the active sites deep within the porous structure, and there is now a very extensive literature concerning the behaviour of this type of systems. Unfortunately, the knowledge of mass transport in porous catalysts is not well developed for the situation in which molecular diffusion, Knudsen diffusion, and hydrodynamic flow all occur simultaneously, mainly due to the complexity of the pore structure.

In real catalyst pellets, multicomponent mixtures diffuse through a porous matrix composed of irregular channels of various sizes, ranging from micropores of dimensions much smaller than the mean molecular free path lengths in the reaction mixture, to macropores of dimensions substantially larger than the mean free path lengths. To model diffusion in such systems it is necessary to use mathematical expressions for multicomponent mixtures, valid throughout the entire range between the limits of Knudsen diffusion control in very small pores and bulk diffusion control in large pores. The starting point for any mathematical description of porous catalysts is a set of flux relations expressing the flux vector for the various species in terms of pressure gradients, temperature and composition. At the present time, there exists no flux relation with a completely sound theoretical basis, capable of describing transport in porous media over the whole range of pressure and/or pore sizes. All the existing relationships involve empiricism to some degree, or are based on a physically unrealistic representation of the structure of the porous medium. Existing models fall into two main classes. The first is the capillary model in which the porous media is modelled as a network of interconnected capillaries. The capillary model has provided a number of useful results and has played an important part in the development of the theory of mass transport in porous materials. Although this type of model is closely related to the physical structure of the medium, its development is hampered by the lack of solution to the problem of transport in a capillary whose diameter is comparable to mean free path lengths in the gas mixture. The second is the well known dusty gas model (DGM) that treats the porous medium as an assembly of stationary particles (dust) dispersed in the gas on a molecular scale. The history of this model is well described in the book by Mason and Malinauskas (1983). It was first invented by Maxwell in 1860 who developed a theory of transport phenomena in gases by momentum transfer and mean free path methods. The momentum-transfer method was independently applied to diffusion phenomena by Stefan in 1871-1872. The DGM was forgotten for almost a century, until it was re-invented by Deriaguin and Bakanov in 1957, who solved the Maxwell-Boltzmann equation in order to

obtain numerical expressions for the effective diffusivities in terms of the properties of the dusty molecules. Since the Maxwell-Boltzmann equation is valid only for dilute gases, one might expect that the dusty gas model, which is based on this equation, should fail for most type of media, which are usually very dense. This is not necessarily true, however, because the only dense component is the dust, which is constrained by boundary conditions to a zero net diffusion rate. The diffusing components behave as dilute gases both in their interactions with each other and in their interactions with the dust particles. The dusty gas model is particularly attractive because in the transition regime, it correctly combines the simultaneous effects of ordinary molecular diffusion and Knudsen diffusion in any array of pores (Weekman and Gorring, 1965). Furthermore, the model reduces to the correct limiting forms under restricted conditions. To account for the flux resulting from a pressure gradient, a Darcy flow term can be simply added (Gunn and King, 1969). It is now generally agreed that the most convenient approach to combine both bulk and Knudsen diffusion is through the dusty gas model (see Jackson, 1977; Cunningham and Williams, 1980; Wesselingh and Krishna, 1990; and Taylor and Krishna, 1993). In a recent paper, Krishna (1993) has shown that in the case of multicomponent diffusion Fick's formulation fails, even at the qualitative level, to describe the observed behaviour of multicomponent diffusion.

The literature contains numerous statements to the fact that reaction involving a change in a number of molecules will generate pressure gradients when they are carried out in porous catalyst pellets. When there is an increase in number of molecules in the reaction, the pressure within the pellet is expected to be higher than the pressure at the surface, while the reverse is true when there is a decrease in number of molecules. Clearly, such pressure variations will affect the concentrations of the various reacting species, and might, therefore, be expected to influence the value of effectiveness factor for the pellet as a whole. The question of the existence, magnitude and practical importance of pressure gradients within porous catalyst pellets have, therefore, attracted some attention (Hite and Jackson, 1977).

Otani *et al.* (1964) studied the case of Knudsen and bulk diffusion for an irreversible, first-order reaction, using a single-pore model of the catalyst pellet, concluding that when Knudsen diffusion dominates in systems with mole changes, the effectiveness factor becomes a function of the Thiele modulus only, even though a significant intraparticle pressure gradient can develop. Lin and Lih (1971) used Fick's formulation to describe mass transport and obtained analytical expressions for the reactant concentration distribution and for the effectiveness factor of a zero-order catalytic reaction in slab, infinite cylinder and sphere geometries. Numerical solutions for higher-order reactions on all three geometries had been previously provided by Weekman and Gorring (1965). Studies that take into account all three, Knudsen, transition and ordinary molecular diffusion regimes, include the works of Otani *et al.* (1965a,b), for a first-order reaction and using a random pore model for the porous matrix and the works of Abed and Rinker (1973), for zero-order reaction, and of Kehoe and Aris (1973) for zero, first and second-order reactions, both using the dusty-gas model. In the Knudsen regime, the

effectiveness factor has been shown to be dependent only on the Thiele modulus, but in the molecular diffusion regime, the effectiveness factor is also dependent on a volume-change parameter which contains both the stoichiometric factor describing the change in moles and the mole fraction of the reactant on the external surface of the pellet. In the transition regime, which often dominates under operating catalyst conditions used in many industrial processes, the catalyst effectiveness factor is a function not only of the Thiele modulus and of the volume-change parameter, but also of a flow parameter which measures the relative effect of both slip and Darcy flows inside the pellet due to the volume change. Hite and Jackson (1977) used the dusty gas model to derive simple upper bounds for the pressure variation in the two limiting situations of bulk diffusion control and Knudsen diffusion control, and studied the influence of pressure variations on the effectiveness factor.

In all the above mentioned studies it was always assumed that the external forced convection does not penetrate inside the catalyst pores and has no effect on the intraparticle concentration distribution. Nir and Pismen (1977) analysed the effect of intraparticle forced convection on the effectiveness factor for an isothermal, first-order reaction in three particle geometries (slab, sphere and cylinder) with uniform internal flow, having shown that this mechanism can be important for large-pore catalysts. An increase of the catalyst effectiveness factor due to forced convection, which depends not only on the Thiele modulus but also on the intraparticle Peclet number, was observed. An analogy between the slab and the sphere geometries for the problem of diffusion and convection in permeable isothermal particles was developed by Rodrigues *et al.* (1992) and an extension of this analogy to an isothermal reactive particle was done by Lu *et al.* (1993). However, in these studies the effect of mole changes was not considered.

The objective of this work is to establish a general model that shows the combined effect of both mole changes (reaction stoichiometry) and of intraparticle forced convection (due to an imposed pressure drop) on the catalyst performance and which includes two aspects: one is the variation of pressure within the pellet and the other is the effectiveness factor. We confine our attention to an isothermal first-order reaction $A \rightarrow nB$ taking place in a catalyst pellet of slab geometry. The dusty gas model, whose validity has been established for a wide range of pore sizes, is used to describe the mass transport inside the porous catalyst.

2.2 PROBLEM FORMULATION

2.2.1 Flux Relationships

Equations describing mass transport by diffusion, based on the dusty-gas model, and convective flow in porous media have been derived by Gunn and King (1969). Following this work, the molar fluxes of each species A and B in a one-dimensional porous catalyst, can be described as follows:

$$N_A = -\frac{D_{AB}^0 D_{KA} P}{(D_{AB}^0 + D_{Km} P) \mathfrak{R} T} \frac{dy_A}{dz} - \frac{D_{KA} (D_{AB}^0 + D_{KB} P) y_A}{(D_{AB}^0 + D_{Km} P) \mathfrak{R} T} \frac{dP}{dz} + v \frac{Py_A}{\mathfrak{R} T} \quad (2.1a)$$

$$N_B = -\frac{D_{AB}^0 D_{KB} P}{(D_{AB}^0 + D_{Km} P) \mathfrak{R} T} \frac{dy_B}{dz} - \frac{D_{KB} (D_{AB}^0 + D_{KA} P) y_B}{(D_{AB}^0 + D_{Km} P) \mathfrak{R} T} \frac{dP}{dz} + v \frac{Py_B}{\mathfrak{R} T} \quad (2.1b)$$

Here, z is the space coordinate, T is the temperature, $\mathfrak{R}$ is the ideal gas constant, P is the total pressure, and y_A and y_B are the molar fractions for species A and B , respectively, such that for a binary system

$$y_A + y_B = 1 \quad (2.2)$$

In Equations 2.1a and 2.1b, the first term represents the diffusive flux due to molar fraction gradients, the second represents the diffusive flux due to the pressure gradient, and the third represents the viscous flux, also called Darcy or convective flux. The applicability of the individual terms in these equations and of its complete form has been experimentally verified (Cunningham and Williams, 1980). Equations 2.1a and 2.1b remain valid when a pressure difference is imposed across the porous medium (Gunn and King, 1969). D_{KA} and D_{KB} are the Knudsen diffusivities for species A and B , respectively, and are given by

$$D_{KA} = \frac{2}{3} \bar{r} \sqrt{\frac{8 \mathfrak{R} T}{\pi M_A}} \quad (2.3a)$$

$$D_{KB} = \frac{2}{3} \bar{r} \sqrt{\frac{8 \mathfrak{R} T}{\pi M_B}} \quad (2.3b)$$

where M_A and M_B are the molecular weights for species A and B , respectively, and $\bar{r}$ is the mean pore radius. If the ratio of molecular weights is introduced

$$n = \frac{M_A}{M_B} \quad (2.4)$$

the following relationship is verified

$$D_{KB} = \sqrt{n} D_{KA} \quad (2.5)$$

and D_{Km} is defined as

$$D_{Km} = y_B D_{KA} + y_A D_{KB} \quad (2.6)$$

and may be expressed as

$$D_{km} = D_{KA} (1 - y_A m) \quad (2.7)$$

where $m = 1 - \sqrt{n}$

The quantity D_{AB}^0 is pressure independent and given by

$$D_{AB}^0 = \frac{\varepsilon}{\tau} D_{AB} P = D_e P = D_{eo} P_o \quad (2.8)$$

where ε is the particle porosity, τ is the tortuosity factor, D_{AB} is the free gas mutual diffusivity in a binary mixture of components A and B , D_e is the effective molecular diffusivity, and D_{eo} is the effective diffusivity at the bottom end of the pellet pressure, P_o .

2.2.2 Momentum Equation

The momentum equation for the flow inside the particle is given by Darcy's law

$$v = -\frac{B}{\mu} \frac{dP}{dz} \quad (2.9)$$

where v is the intraparticle velocity, B is the particle permeability and μ is the gas viscosity.

2.2.3 Mass Balance Equations

For a first order irreversible reaction $A \xrightarrow{k} nB$, the molecular weight ratio in the Equation 2.4 is equal to the reaction stoichiometry. The mass balances at steady-state for species A and B inside the catalyst pellet are, respectively:

$$\frac{d}{dz} \left[-\frac{D_{AB}^0 D_{KA} P}{(D_{AB}^0 + D_{Km} P) \Re T} \frac{dy_A}{dz} - \frac{D_{KA} (D_{AB}^0 + D_{KB} P) y_A}{(D_{AB}^0 + D_{Km} P) \Re T} \frac{dP}{dz} + v \frac{Py_A}{\Re T} \right] + k \frac{Py_A}{\Re T} = 0 \quad (2.10a)$$

$$\frac{d}{dz} \left[-\frac{D_{AB}^0 D_{KB} P}{(D_{AB}^0 + D_{Km} P) \Re T} \frac{dy_B}{dz} - \frac{D_{KB} (D_{AB}^0 + D_{KA} P) y_B}{(D_{AB}^0 + D_{Km} P) \Re T} \frac{dP}{dz} + v \frac{Py_B}{\Re T} \right] - nk \frac{Py_A}{\Re T} = 0 \quad (2.10b)$$

where k is the reaction rate constant.

If an external pressure drop, ΔP is imposed across the particle, the pressure, P , and the molar fraction of species A , y_A , are the two independent variables, and the boundary conditions are

$$z = 0 \quad y_A = y_{As} \quad P = P_o + \Delta P \quad (2.11a)$$

$$z = \ell \quad y_A = y_{As} \quad P = P_o \quad (2.11b)$$

where y_{As} is the surface mole fraction of species A . Although the mole fraction varies within the whole reactor and may even vary around a single pellet, if the yield of a single particle is much lower than the yield of the reactor, the mole fraction around a single particle can be assumed to be uniform.

2.2.4 Dimensionless Model Equations

Introducing the dimensionless variables

$$x = \frac{z}{\ell} \quad f = \frac{P}{P_o} \quad (2.12)$$

where ℓ is the thickness of the slab particle, and replacing Equations 2.2, 2.6 and 2.7, the dimensionless model equations are obtained

$$\frac{d}{dx} \left\{ g(y_A, f) \left[-f \frac{dy_A}{dx} - (1 + \sqrt{n}\alpha f) y_A \frac{df}{dx} \right] - \beta f y_A \frac{df}{dx} \right\} + \phi^2 f y_A = 0 \quad (2.13a)$$

$$\frac{d}{dx} \left\{ \sqrt{n} g(y_A, f) \left[f \frac{dy_A}{dx} - (1 + \alpha f)(1 - y_A) \frac{df}{dx} \right] - \beta f (1 - y_A) \frac{df}{dx} \right\} - n \phi^2 f y_A = 0 \quad (2.13b)$$

$$x = 0 \quad y_A = y_{As} \quad f = 1 + \Delta f \quad (2.13c)$$

$$x = 1 \quad y_A = y_{As} \quad f = 1 \quad (2.13d)$$

where

$$g(y_A, f) = \frac{D_{KA}}{D_{eo} + D_{Km}f} = \frac{\alpha}{1 + \alpha(1 - m y_A)f} \quad (2.14)$$

The relevant dimensionless model parameters are the following:

Thiele Modulus	$\phi = \sqrt{\frac{\ell^2 k}{D_{eo}}}$
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Knudsen and Molecular Diffusivities Ratio	$\alpha = \frac{D_{KA}}{D_{eo}}$
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Viscous Momentum and Molecular Diffusivity Ratio	$\beta = \frac{BP_o}{\mu D_{eo}}$
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Reaction Stoichiometric Coefficient	n
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Dimensionless External Pressure Drop	Δf
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where the Thiele modulus ϕ is defined in terms of the effective molecular diffusivity.

2.3 PRESSURE VARIATIONS WITHIN THE PELLET

An important issue to be analysed is the magnitude of the maximum pressure variation expected to occur within the catalyst pellet. Here the limiting cases of Knudsen and molecular diffusion regimes are analysed.

2.3.1 Knudsen Diffusion Regime

From Equations 2.1a and 2.1b and using the dimensionless variables in Equation 2.12, the following equations for the fluxes of species A and B are obtained

$$N_A = \frac{D_{eo}P_o}{\Re T \ell} \left[-g f \frac{dy_A}{dx} - g(1 + \sqrt{n} \alpha f) y_A \frac{df}{dx} - \beta f y_A \frac{df}{dx} \right] \quad (2.15a)$$

$$N_B = \frac{D_{eo}P_o}{\Re T \ell} \left[-\sqrt{n} g f \frac{dy_B}{dx} - \sqrt{n} g(1 + \alpha f) y_B \frac{df}{dx} - \beta f y_B \frac{df}{dx} \right] \quad (2.15b)$$

In the Knudsen diffusion regime, that is when the pores are small, $\alpha \rightarrow 0$, $\beta \rightarrow 0$ and $g(y_A, f) \rightarrow \alpha$, and Equations 2.15a and 2.15b reduce to

$$N_A = \frac{D_{eo}P_o}{\Re T \ell} \left[-\alpha f \frac{dy_A}{dx} - \alpha y_A \frac{df}{dx} \right] \quad (2.16a)$$

$$N_B = \frac{D_{eo}P_o}{\Re T \ell} \left[-\sqrt{n} \alpha f \frac{dy_B}{dx} - \sqrt{n} \alpha y_B \frac{df}{dx} \right] \quad (2.16b)$$

Noting that $f y_A = f_A$ and $f y_B = f_B$ represent the dimensionless partial pressures of species A and B, respectively, and that $\alpha D_{eo} = D_{KA}$, the following relationships are obtained

$$N_A = -\frac{D_{KA}}{\Re T \ell} \frac{d(f y_A)}{dx} = -\frac{D_{KA}}{\Re T \ell} \frac{df_A}{dx} \quad (2.17a)$$

$$N_B = -\sqrt{n} \frac{D_{KA}}{\Re T \ell} \frac{d(f y_B)}{dx} = -\sqrt{n} \frac{D_{KA}}{\Re T \ell} \frac{df_B}{dx} \quad (2.17b)$$

Since $N_B = -n N_A$ as a consequence of the stoichiometry of the reaction, it follows that

$$\frac{df_B}{df_A} = \frac{1}{\sqrt{n}} \frac{N_B}{N_A} = -\sqrt{n} \quad (2.18)$$

Integrating this equation, taking as initial conditions, $f_{A0} = 1 + \Delta f$ and $f_{B0} = 0$, that correspond to the surface of the pellet conditions (see Equation 2.13c).

$$\int_0^{f_B} df_B = -\sqrt{n} \int_{1+\Delta f}^{f_A} df_A \quad (2.19)$$

or

$$f_B = \sqrt{n}(1 + \Delta f - f_A) \quad (2.20)$$

The total pressure can be obtained by adding f_A to both sides of Equation 2.20

$$f = \sqrt{n}(1 + \Delta f) - (\sqrt{n} - 1)f_A \quad (2.21)$$

Strictly speaking, the external pressure drop should influence the pressure inside the pellets and the real pressure should be slightly smaller than that given in Equation 2.21. However, the rough estimation given by Equation 2.21 is useful, and, furthermore, considering the fact that in practice the pressure drop across the pellet is small, a good approximation can be expected.

From Equation 2.21, when $n > 1$, the pressure rises from the surface value towards a maximum value of $\sqrt{n}(1 + \Delta f)$, attained when $f_A \rightarrow 0$ within the pellet that is when the reactant is exhausted. When $n < 1$, it follows similarly that the pressure falls from the value at the surface towards a minimum value of $\sqrt{n}(1 + \Delta f)$. Thus, the dimensionless pressure within the pellet always lies between the bounds 1 and $\sqrt{n}(1 + \Delta f)$. The former value is attained at the bottom end of pellet but the latter bound is approached asymptotically near the top end of the pellet. In the absence of forced convection, $\Delta f = 0$, the pressure limits derived here agree with those predicted by Hite and Jackson (1977).

2.3.2 Molecular Diffusion Regime

At the opposite limit of molecular diffusion control and viscous flow, corresponding to pore sizes much larger than the mean free path lengths, or a pellet of very high permeability, $D_e/D_{KA} \ll 1$ and $BP/\mu \gg D_{KB}$, and Equations 2.1a and 2.1b reduce to

$$N_A = -\frac{1}{\Re T} \frac{D_{eo} P_o}{1 - y_A m} \frac{dy_A}{dz} - \frac{y_A}{\Re T} \frac{BP}{\mu} \frac{dP}{dz} \quad (2.22a)$$

$$N_B = -\frac{1}{\Re T} \frac{\sqrt{n} D_{eo} P_o}{1 - y_A m} \frac{dy_B}{dz} - \frac{y_B}{\Re T} \frac{BP}{\mu} \frac{dP}{dz} \quad (2.22b)$$

Since $N_B + nN_A = 0$, and introducing the dimensionless variables

$$\frac{\sqrt{n} m}{y_A m [1 + y_A (n - 1)] - 1} \frac{dy_A}{dx} = \beta f \frac{df}{dx} \quad (2.23)$$

or

$$\frac{\sqrt{n} m}{y_A m [1 + y_A (n - 1)] - 1} dy_A = \beta f df \quad (2.24)$$

Integrating, from the initial conditions $y_A = 1$ and $f = 1 + \Delta f$ at the surface of the pellet, gives

$$f^2 - (1 + \Delta f)^2 = \frac{2}{\beta} \ln \left[\sqrt{n} \frac{1 - y_A m}{1 + (n - 1)y_A} \right] \quad (2.25)$$

This result is a generalised form of the one obtained by Hite and Jackson (1977), where the effective molecular diffusivity was considered as a constant since the pressure variations were very small. When $y_A \rightarrow 0$, the maximum pressure can be expressed as

$$f^2 - (1 + \Delta f)^2 = \frac{2}{\beta} \ln \sqrt{n} \quad (2.26)$$

2.4 EFFECTIVENESS FACTOR

The effects of intraparticle transport on the kinetics of reaction in porous catalysts can be described in terms of the effectiveness factor. The effectiveness factor is defined in the usual manner

$$\eta = \frac{1}{V} \frac{\int_V P y_A dV}{\langle P_s \rangle y_{As}} \quad (2.27)$$

where $\langle P_s \rangle$ is the average pressure at the external surface of the particle. The integration in the above equation may lead to large numerical errors when the reactant profiles in the catalyst particle are very stiff, as in the case of large Thiele modulus values. This can be avoided by calculating the effectiveness factor through the net mass flux, which in dimensionless variables becomes

$$\eta = \frac{1}{\phi^2 \langle f y_A \rangle_s} \left\{ g(y_A, f) \left[-f \frac{dy_A}{dx} - (1 + \sqrt{n} \alpha f) y_A \frac{df}{dx} \right] - \beta f y_A \right\}_{x=0}^{x=1} \quad (2.28)$$

and

$$\langle f y_A \rangle_s = \left(1 + \frac{\Delta f}{2} \right) y_{As} \quad (2.29)$$

2.5 NUMERICAL SOLUTION

The combination and expansion of Equations 2.13a, 2.13b and 2.14 results in a system of two ordinary, second-order, non-linear differential equations in y_A and f .

$$g_{11} \frac{d^2 y_A}{dx^2} + g_{12} \frac{d^2 f}{dx^2} + g_{13} \frac{dy_A df}{dx dx} + g_{14} \left(\frac{df}{dx} \right)^2 + g_{15} \left(\frac{dy_A}{dx} \right)^2 + \phi^2 f y_A = 0 \quad (2.30a)$$

$$g_{21} \frac{d^2 y_A}{dx^2} + g_{22} \frac{d^2 f}{dx^2} + g_{23} \frac{dy_A df}{dx dx} + g_{24} \left(\frac{df}{dx} \right)^2 + g_{25} \left(\frac{dy_A}{dx} \right)^2 - n \phi^2 f y_A = 0 \quad (2.30b)$$

where

$$g_{11} = -gf \quad (2.31a)$$

$$g_{12} = -[\beta f + g(1 + \sqrt{n}\alpha f)]y_A \quad (2.31b)$$

$$g_{13} = [g^2(1 - my_A) - mg^2(1 + \sqrt{n}\alpha f)y_A - \beta]f - g(2 + \sqrt{n}\alpha f) \quad (2.31c)$$

$$g_{14} = [g^2(1 - my_A)(1 + \sqrt{n}\alpha f) - \beta - g\sqrt{n}\alpha]y_A \quad (2.31d)$$

$$g_{15} = -mg^2f^2 \quad (2.31e)$$

$$g_{21} = \sqrt{n}gf \quad (2.31f)$$

$$g_{22} = -[\beta f + \sqrt{n}g(1 + \alpha f)](1 - y_A) \quad (2.31g)$$

$$g_{23} = [-m\sqrt{n}g^2(1 + \alpha f)(1 - y_A) - \sqrt{n}g^2(1 - my_A) + \beta]f + \sqrt{n}g(2 + \alpha f) \quad (2.31h)$$

$$g_{24} = [\sqrt{n}g^2(1 - my_A)(1 + \alpha f) - \beta - \sqrt{n}g\alpha](1 - y_A) \quad (2.31i)$$

$$g_{25} = m\sqrt{n}g^2f^2 \quad (2.31j)$$

The numerical integration of this system, associated with the boundary conditions (2.13c) and (2.13d), was accomplished by using the PDECOL package (Madsen and Sincovec, 1977) which implements finite element collocation methods based on piecewise polynomials for the spatial discretization techniques for the solution of coupled systems of nonlinear partial differential equations in time and one space dimension. Although PDECOL has been written for PDE's, it is well suited for the solution of boundary value problems as the one proposed. The piecewise polynomial space used in the computations was specified, giving the order of the polynomial (KORD=4), the number of continuity conditions to be imposed on the polynomial pieces across all of the interior points (NCC=2) and the number of intervals into which the spatial domain is to be divided (NINT=40 or larger). These values for the parameters were chosen in order to obtain smooth pressure profiles and reactant molar fraction profiles. In the cases of large Thiele modulus, these profiles become very steep near the pellet surface and larger values of NINT (up to 200) were required to obtain more precise pressure gradients and allow for the calculation of accurate values of the effectiveness factor. The PDECOL package, being a general purpose software, requires that the boundary conditions must be consistent with the initial conditions. In this problem, the initial conditions represent an initial guess of the final approximate solution for both the pressure and molar fraction profiles. A second order polynomial in y_A , $y_A = 1 - ax + ax^2$, where a is an arbitrary constant whose value depends on the value of the Thiele modulus (a increases with ϕ) and a first order approximation in f , $f = 1 + \Delta f - x\Delta f$, were chosen as the initial conditions (guesses).

2.6 RESULTS AND DISCUSSION

The five model parameters were varied in the ranges of values listed in Table 2.6.1.

Table 2.6.1. Range of values of parameters used in the numerical simulations.

Δf	ϕ	α	β	n
0-0.5	0-100	0.01-10	0.01-100	0.25-4

The dimensionless pressure drop, Δf , is usually small taking values of up to 0.1, but in cases of reactors operating at very low pressures or in membrane reactors, values as large as $\Delta f = 0.5$ can be achieved. The values of α were chosen to be 0.1, 1 and 10, to characterise the Knudsen, transition and molecular regimes, respectively. Smaller values, $\alpha = 0.01$, were used to investigate the maximum pressure variation within the pellet. The parameter β can take a wide range of values. The range of values studied in this work corresponds to mean pore diameters between $100 \text{ \AA}$ and $10000 \text{ \AA}$, atmospheric pressure conditions, and estimating the permeability by the relationship $B = \bar{r}^2 / 8$. The values of $n = 0.25$ and $n = 4$ have been chosen as representative of the cases of decrease and increase in number of moles. The surface mole fraction of species A, y_{As} , is held constant at unity through out this study.

2.6.1 Intraparticle Profiles

The following figures show the effect of the different model parameters on the shape of the dimensionless pressure and reactant molar fraction profiles. In these figures the Thiele modulus is held constant at a value in which the reaction inside the catalyst is appreciable, $\phi = 3$.

Figure 2.1 shows the intraparticle pressure profiles for different values of the dimensionless external pressure drop in the Knudsen diffusion regime. The small values of α and β were chosen in order to check the values of the maximum expected dimensionless pressure given by Equation 2.21 (represented by black dots). Good agreement between these values and the maximum values obtained with the numerical solution is observed, although, as expected, the approximated solution of Equation 2.21 tends to slightly overestimate the actual value. In these plots the dominant convective effect is that resulting from the change in moles, and the imposed external pressure drop has a smaller effect.

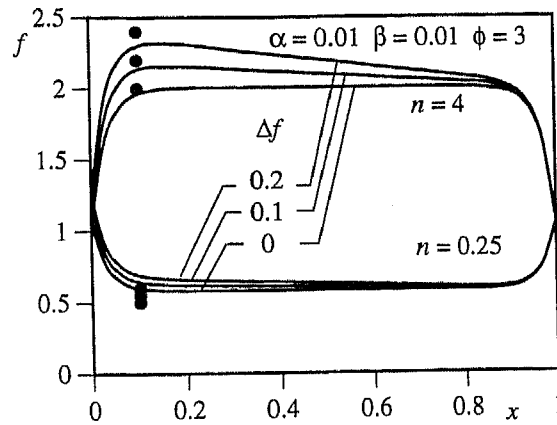


Figure 2.1 Dimensionless pressure profiles in the Knudsen regime, with $\alpha = 0.01$, $\beta = 0.01$ and $\phi = 3$, for different values of the dimensionless pressure drop, $\Delta f = 0, 0.1$ and 0.2 , and for $n = 4$ and $n = 0.25$. The points represent the estimated maximum pressure drop in each case obtained by Equation 21.

The intraparticle dimensionless pressure profiles for different values of the dimensionless external pressure drop in the Knudsen regime with higher β values are shown in Figure 2.2. As β increases (higher permeabilities), the imposed external pressure drop plays a more important role, and as $\beta \rightarrow \infty$ the intraparticle pressure profiles approach the imposed external pressure profiles. Figure 2.3 shows the corresponding intraparticle reactant molar fraction profiles. For low β values, forced convection has little or no effect on the profiles, but for large β values, there is a marked improvement on the catalyst performance. The intraparticle reactant concentration increases, and the molar fraction profiles are no longer symmetric, showing a clear shift in the direction of the imposed external pressure drop. This effect is more pronounced for $n < 1$ since in this case the pressure drop due to the change in moles and the external pressure drop take the same direction when $x \rightarrow 0$.

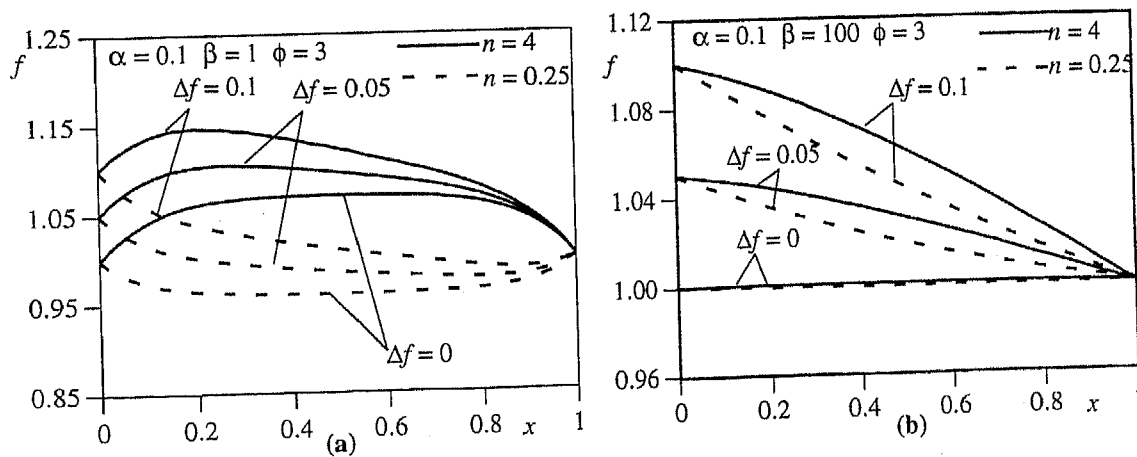


Figure 2.2 Dimensionless pressure profiles in the Knudsen regime, with $\alpha = 0.1$ and $\phi = 3$, for different values of the dimensionless pressure drop, $\Delta f = 0, 0.05$ and 0.1 , and for $n = 4$ and $n = 0.25$, showing the effect of β : a) $\beta = 1$; b) $\beta = 100$.

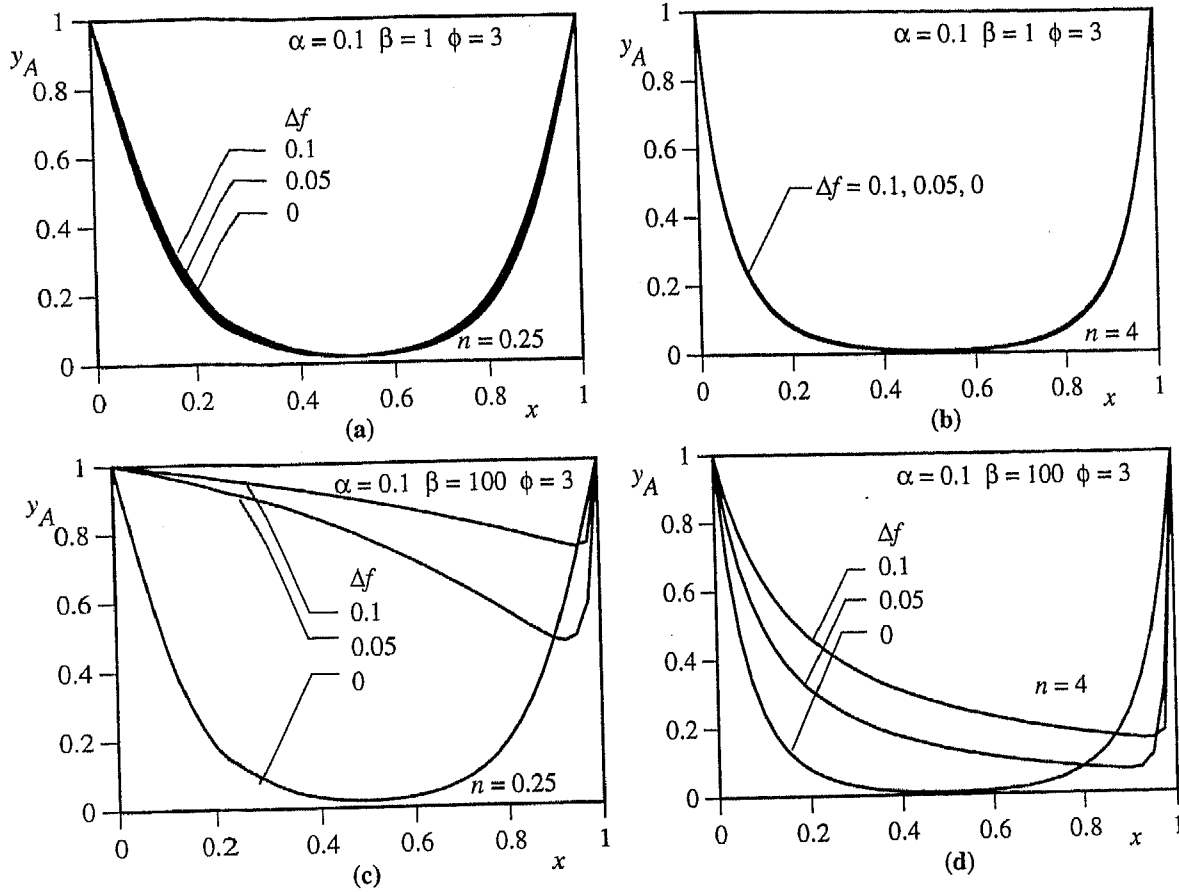


Figure 2.3 Reactant molar fraction profiles in the Knudsen regime, with $\alpha = 1$ and $\phi = 3$, for different values of the dimensionless pressure drop, $\Delta f = 0, 0.05$ and 0.1 , showing the effect of β : a) $\beta = 1$, $n = 0.25$; b) $\beta = 1$, $n = 4$; c) $\beta = 100$, $n = 0.25$; d) $\beta = 100$, $n = 4$.

Profiles in the transition regime are shown in Figures 2.4 (dimensionless pressure profiles) and 2.5 (reactant molar fraction profiles). The same general behaviour as in the Knudsen regime is observed. Again, the effect of forced convection is more important for large values of β .

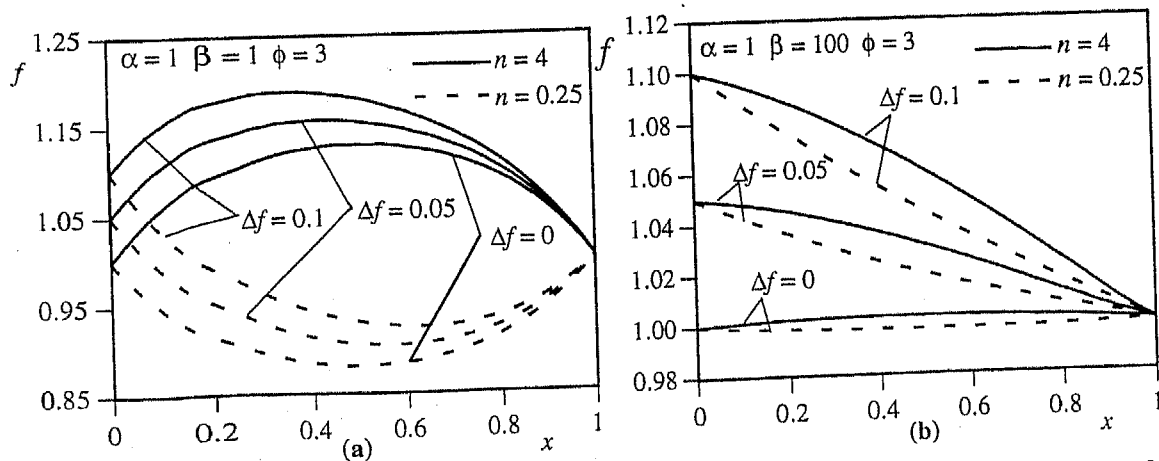


Figure 2.4 Dimensionless pressure profiles in the transition regime, with $\alpha = 1$ and $\phi = 3$, for different values of the dimensionless pressure drop, $\Delta f = 0, 0.05$ and 0.1 , and for $n = 4$ and $n = 0.25$, showing the effect of β : a) $\beta = 1$; b) $\beta = 100$.

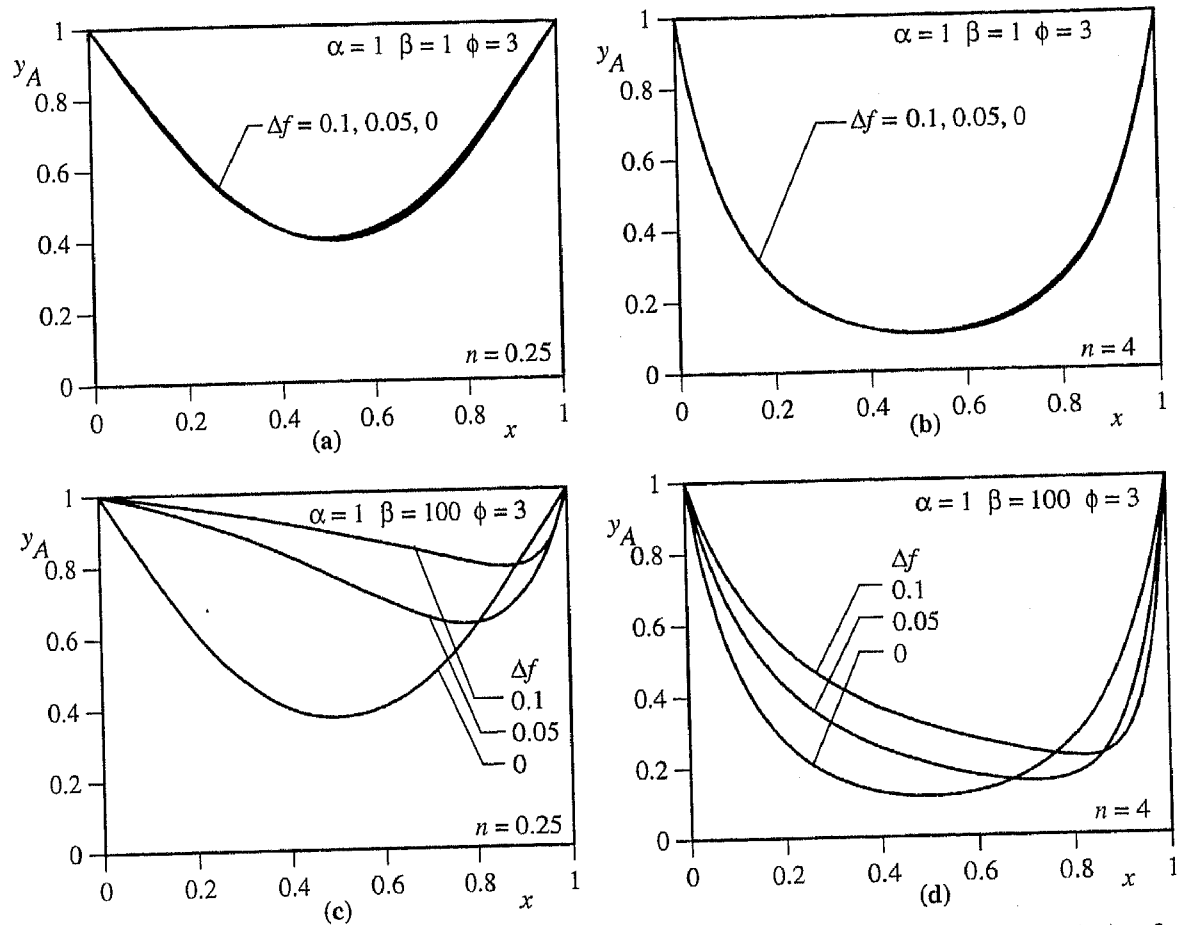


Figure 2.5 Reactant molar fraction profiles in the transition regime, with $\alpha = 1$ and $\phi = 3$, for different values of the dimensionless pressure drop, $\Delta f = 0, 0.05$ and 0.1 , showing the effect of β : a) $\beta = 1, n = 0.25$; b) $\beta = 1, n = 4$; c) $\beta = 100, n = 0.25$; d) $\beta = 100, n = 4$.

Figures 2.6 and 2.7 show, respectively, the dimensionless pressure profiles and the reactant molar fraction profiles in the molecular diffusion regime. The effect of the change in moles is now even smaller, even for low values of β . The performance of the catalyst is now better than in the Knudsen and transition regimes, and forced convection plays an important role in the case of high permeability pellets (large β).

Figure 2.8a shows the dimensionless pressure profiles in the three diffusion regimes, for $\Delta f = 0$, (no forced convection) and for $\Delta f = 0.1$. The surprising effect here is that the maximum pressure variation is higher in the transition regime than in the Knudsen diffusion regime, looking as if the effect of the mole changes is more important in the transition regime. This result is a consequence of changing the parameters α and β independently. In fact, for a particular pellet with a given mean pore radius, $\bar{r}$, these two parameters are related, and it can be easily shown that $\beta \propto \alpha^2$, where the proportionality constant is only dependent on the operating conditions (pressure and temperature). Figure 2.8b shows the dimensionless pressure profiles in the three diffusion regimes in the case of $\beta \propto \alpha^2$. It is clear now that the maximum pressure variation occurs in the Knudsen regime.

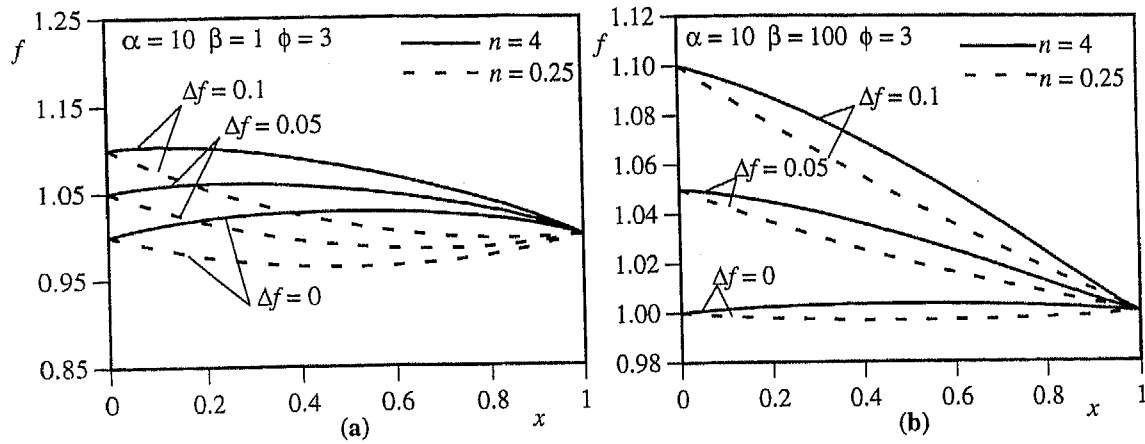


Figure 2.6 Dimensionless pressure profiles in the molecular diffusion regime, with $\alpha = 10$ and $\phi = 3$, for different values of the dimensionless pressure drop, $\Delta f = 0, 0.05$ and 0.1 , and for $n = 4$ and $n = 0.25$, showing the effect of β : a) $\beta = 1$; b) $\beta = 100$.

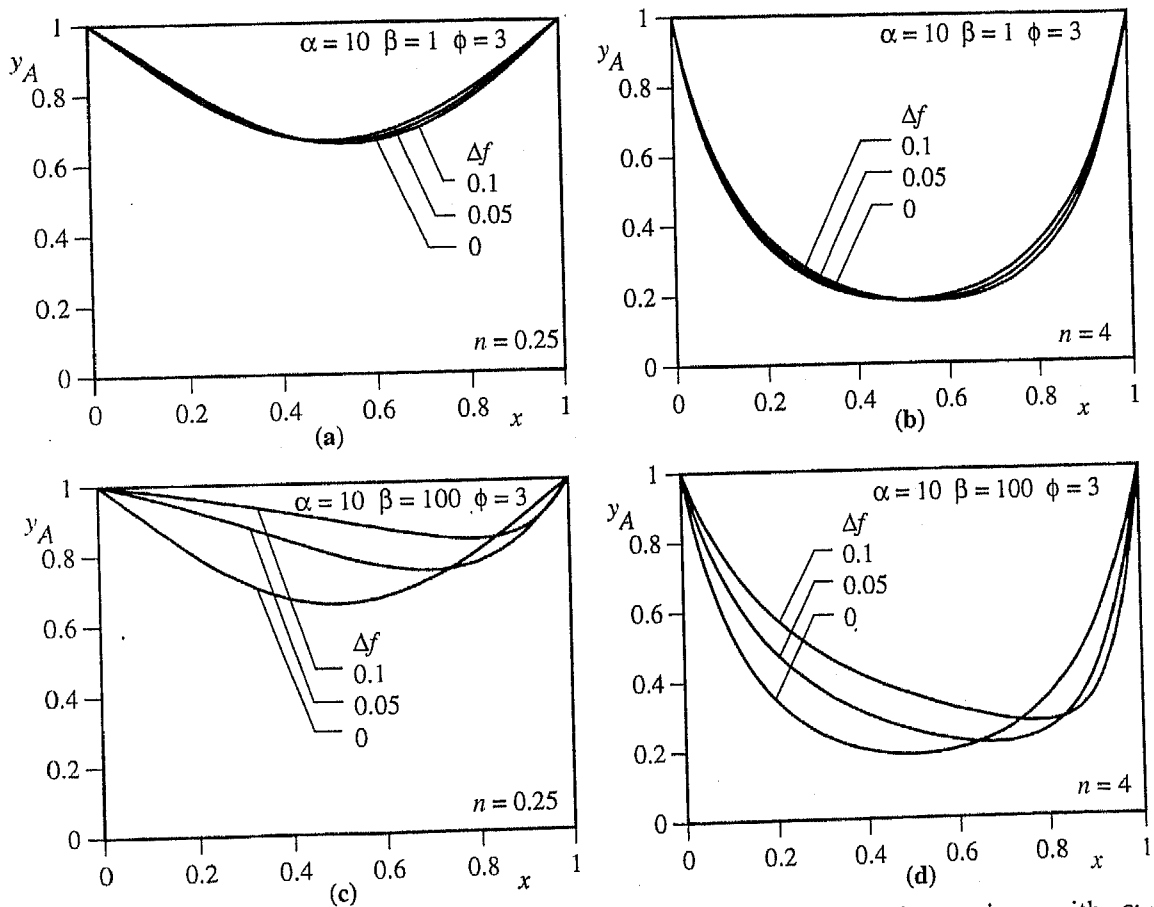


Figure 2.7 Reactant molar fraction profiles in the molecular diffusion regime, with $\alpha = 10$ and $\phi = 3$, for different values of the dimensionless pressure drop, $\Delta f = 0, 0.05$ and 0.1 showing the effect of β : a) $\beta = 1$, $n = 0.25$; b) $\beta = 1$, $n = 4$; c) $\beta = 100$, $n = 0.25$; d) $\beta = 100$, $n = 4$.

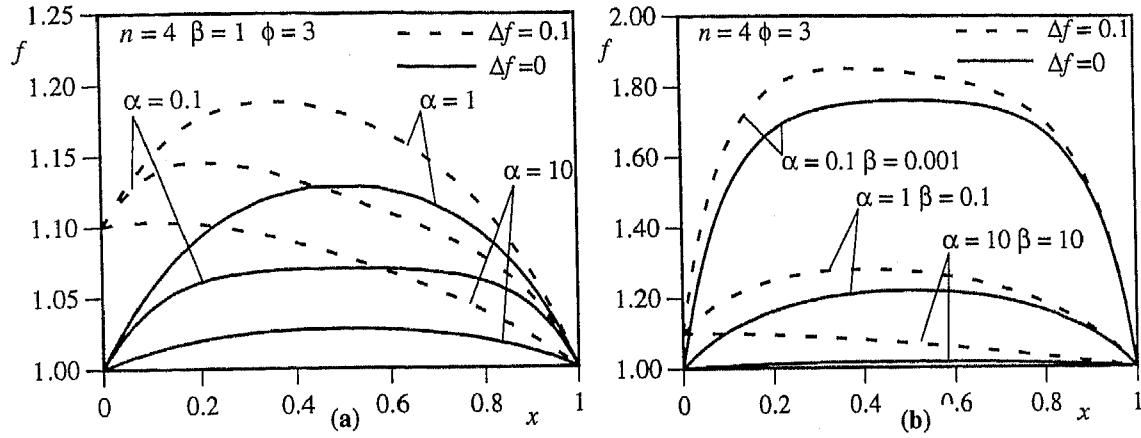


Figure 2.8 a) Dimensionless pressure profiles, with $n=4$, $\beta=1$ and $\phi=3$, for different values of the dimensionless pressure drop, $\Delta f=0$ and 0.1 , and for different diffusion regimes, $\alpha=0.1, 1$ and 10 b) Dimensionless pressure profiles, with $n=4$ and $\phi=3$, for different values of the dimensionless pressure drop, $\Delta f=0$ and 0.1 , keeping the proportionality $\beta \propto \alpha^2$ representative of a given pellet at different operating conditions.

2.6.2 Effectiveness Factor

In this section the effect of the different model parameters on the particle effectiveness factor is presented. Figures 2.9, 2.10 and 2.11 show the plots of the effectiveness factor, η , as a function of the Thiele modulus, ϕ .

Starting in the Knudsen regime, $\alpha=0.1$, Figures 2.9a and 2.9b show that for small values of β , forced convection has little or no effect on the effectiveness factor. As β increases, the effect of the imposed external pressure drop becomes important, as it is seen in Figures 2.9c and 2.9d. This result appears to be contradictory with the concept that only in the molecular diffusion regime, does forced convection become important. The reason for this result is that, for large-pore pellets, as the average pressure within the pellet decreases (that is β decreases) the molecular diffusivity, which is inversely proportional to the pressure, increases. Although this is uncommon in practice, it is worth being pointed out from the theoretical point of view. These figures also show that in the Knudsen regime, if the forced convection does not exist, the effectiveness factor is independent of β . This result has been explained elsewhere (Cunningham and Williams, 1980), and is due to the fact that as β increases the viscous flux increases in the same proportion as the pressure diffusion flux decreases. Another result that can be extract from the plots is that the effect of forced convection is more significant for $n < 1$.

The effectiveness factor plots in the transition and the molecular diffusion regimes are shown in Figures 2.10 and 2.11, respectively. The same type of behaviour as that in Knudsen regime is observed.

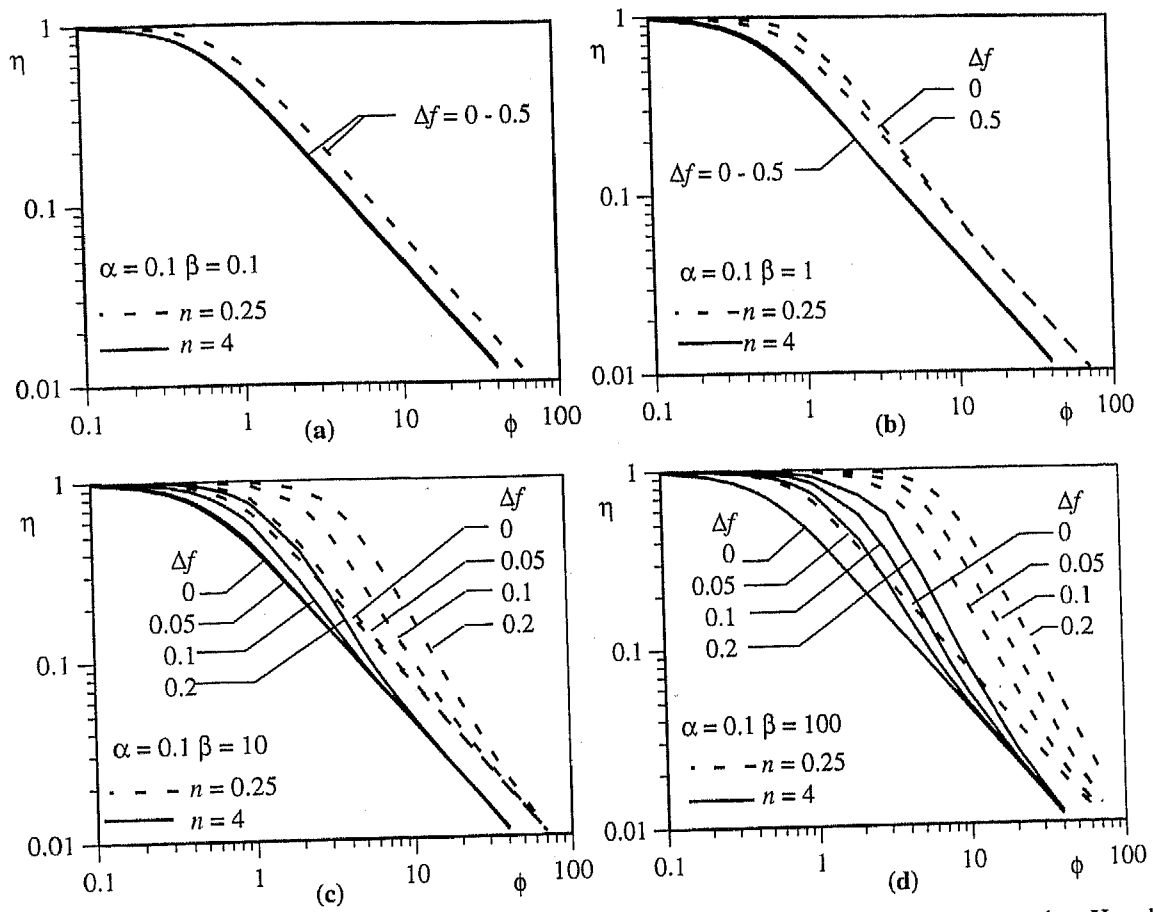


Figure 2.9 Effectiveness factor, η , versus the Thiele modulus, ϕ , plots in the Knudsen regime, $\alpha = 0.1$, for $n = 0.25$ and $n = 4$, and for various values of the dimensionless pressure drop, Δf , showing the effect of β : a) $\beta = 0.1$; b) $\beta = 1$; c) $\beta = 10$; d) $\beta = 100$.

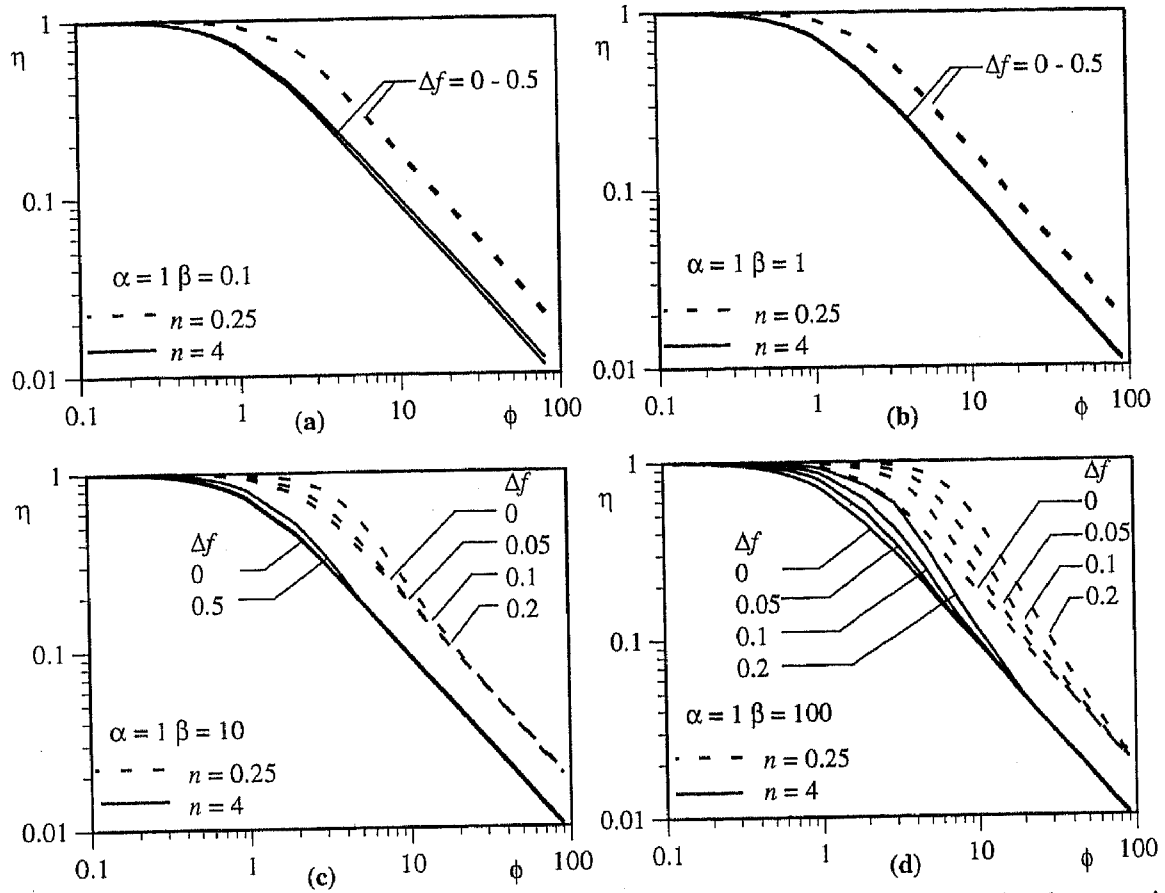


Figure 2.10 Effectiveness factor, η , versus the Thiele modulus, ϕ , plots in the transition regime, $\alpha = 1$, for $n = 0.25$ and $n = 4$, and for various values of the dimensionless pressure drop, Δf , showing the effect of β : a) $\beta = 0.1$; b) $\beta = 1$; c) $\beta = 10$; d) $\beta = 100$.

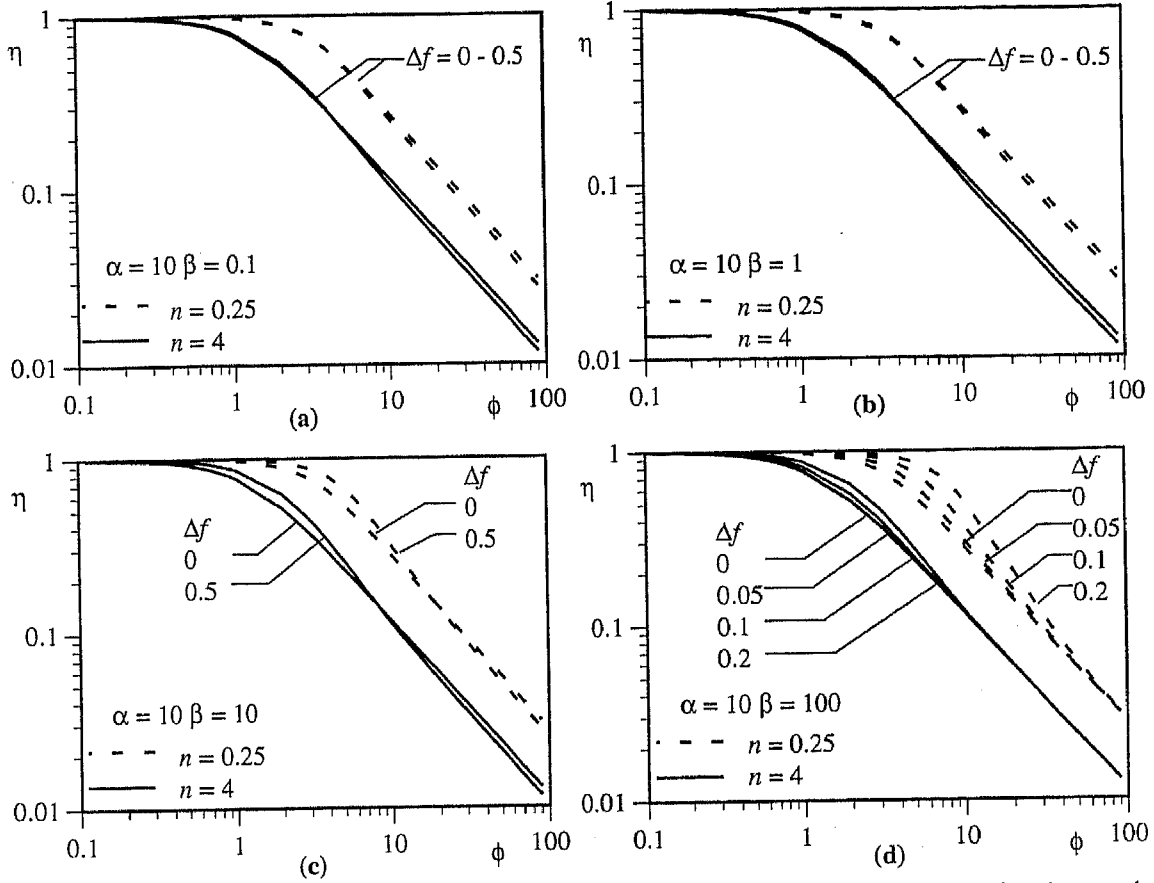


Figure 2.11 Effectiveness factor, η , versus the Thiele modulus, ϕ , plots in the molecular diffusion regime, $\alpha = 10$, for $n = 0.25$ and $n = 4$, and for various values of the dimensionless pressure drop, Δf , showing the effect of β : a) $\beta = 0.1$; b) $\beta = 1$; c) $\beta = 10$; d) $\beta = 100$.

Figure 2.12 shows the relative increase in the effectiveness factor due to forced convection. Here the magnitude of the forced convection is characterised by the intraparticle Peclet number, $\lambda = \beta \Delta f = v_o \ell / D_{eo}$, and η_o is the effectiveness factor for $\Delta f = 0$. These plots show that the relative performance of the catalyst particle depends not only on the intraparticle Peclet number, but also on the magnitude of β . For large values of β , this increase is higher in the Knudsen diffusion regime, but in the molecular diffusion regime this increase is noticeable even for small values of β .

From the previous figures it is clear that the effect of forced convection is strongly associated with the magnitude of β . Figure 2.13 shows plots of the effectiveness factor versus β for a fixed value of the Thiele modulus in the Knudsen and the molecular diffusion regimes. In the Knudsen regime, $\alpha = 0.1$, when β is small, forced convection has a very small effect on the effectiveness factor. In this range of small β , for $n = 4$ (> 1), increasing β decreases η , by reducing the viscous flux due to the imposed external pressure drop, which is running against the concentration gradient. For $n = 0.25$ (< 1), the pressure and the concentration gradients are in the same direction and increasing β increases η . As β increases a point is reached where the effect forced convection becomes important, and the value of β at which this occurs is dependent of Δf .

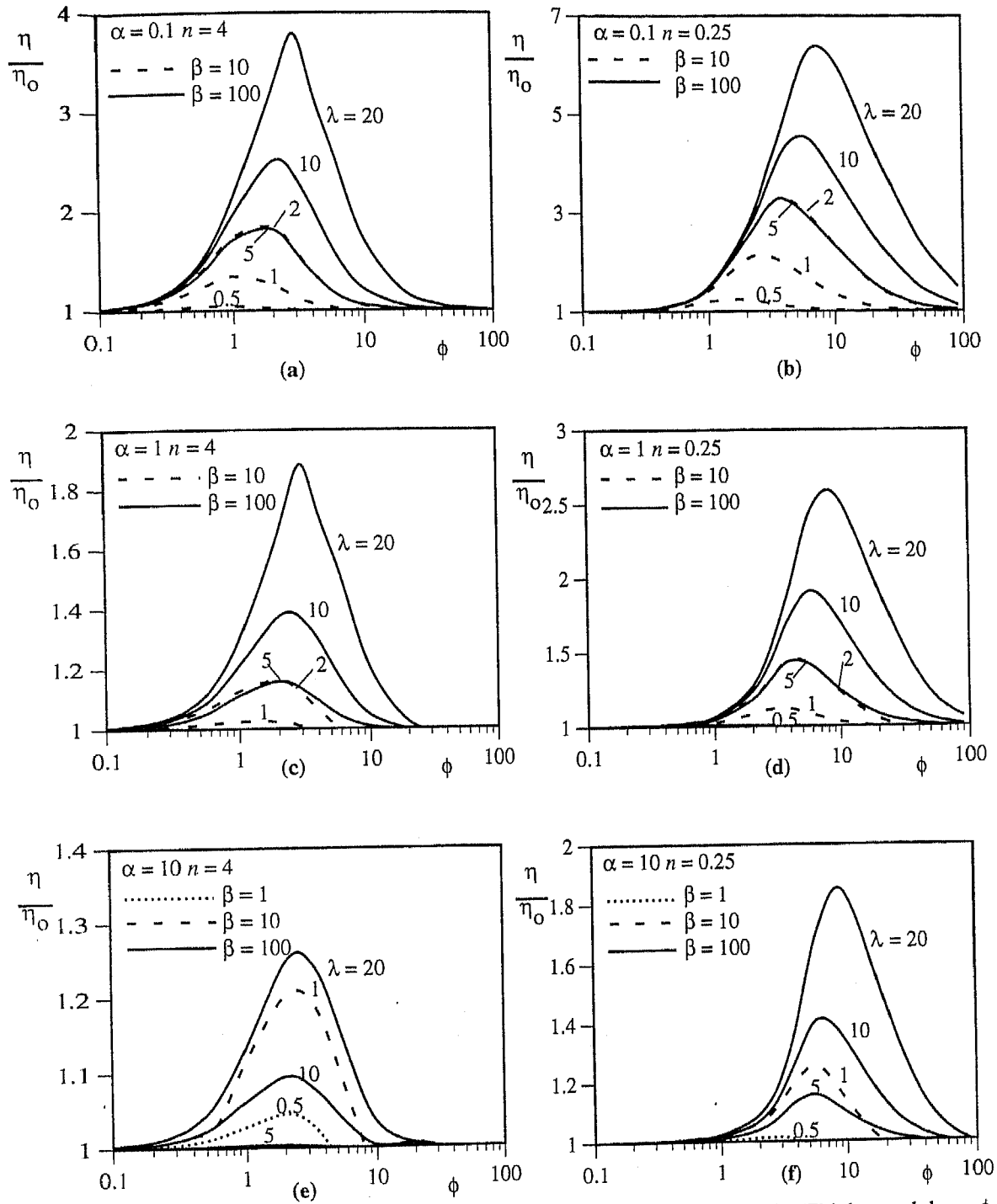


Figure 2.12 Relative increase in the effectiveness factor, η/η_0 , versus the Thiele modulus, ϕ , for: a) $\alpha = 0.1, n = 4$; b) $\alpha = 0.1, n = 0.25$; c) $\alpha = 1, n = 4$; d) $\alpha = 1, n = 0.25$; e) $\alpha = 10, n = 4$; f) $\alpha = 10, n = 0.25$.

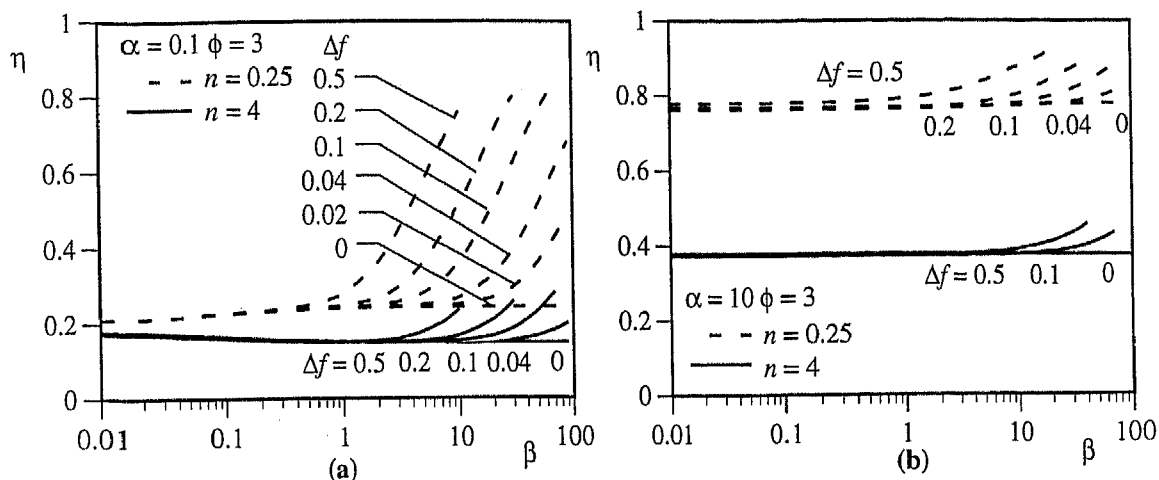


Figure 2.13 Effectiveness factor, η , versus β for different stoichiometric ratios, $n = 0.25$ and $n = 4$, for various values of the dimensionless pressure drop, Δf , and different diffusion regimes: a) $\alpha = 0.1, \phi = 3$; b) $\alpha = 10, \phi = 3$.

Noting that in Figure 2.13 the rate of increase of η is practically the same for all values of Δf , the curves in Figure 2.14 were constructed by taking the tangent to each curve in this constant slope regime, extending these lines to the curve of $\Delta f = 0$ and reading the corresponding value of β . These curves represent the pair of values $(\Delta f, \beta)$ below which forced convection is not important. The value of the intraparticle Peclet number, determined by $\lambda = \beta \Delta f$, is constant for each of these curves.

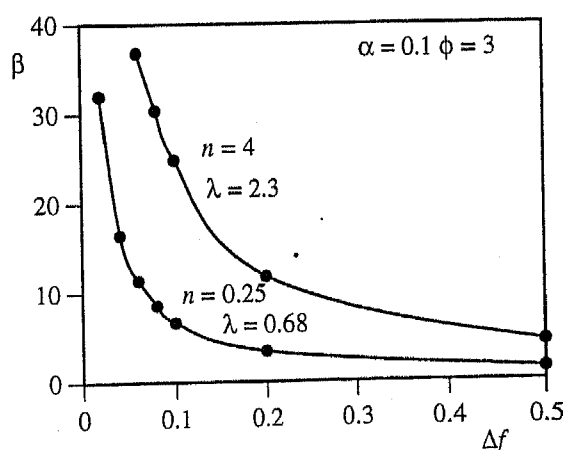


Figure 2.14 Plot of the value of β where forced convection is important versus Δf for different stoichiometric ratios, $n = 0.25$ and $n = 4$, and $\alpha = 0.1, \phi = 3$.

These results can be condensed by representing the increase in the effectiveness factor relative to $\Delta f = 0$ as a function of the intraparticle Peclet number, as is shown in Figure 2.15.

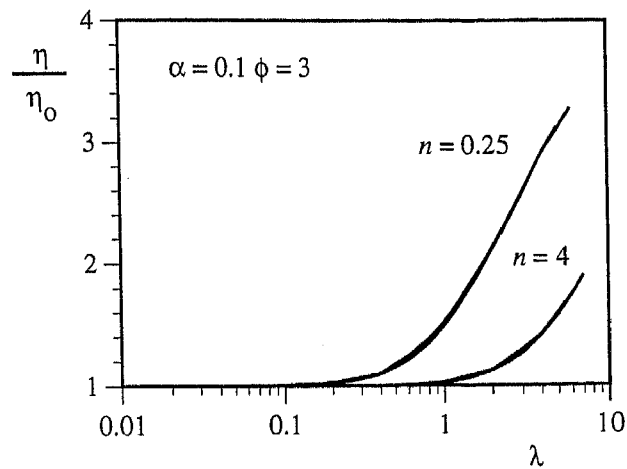


Figure 2.15 Relative increase in the effectiveness factor, η/η_0 , versus the intraparticle Peclet number, λ , for different stoichiometric ratios, $n = 0.25$ and $n = 4$, and $\alpha = 0.1$, $\phi = 3$.

Figure 2.16 shows the effect of the stoichiometric ratio, n , on the effectiveness factor for various values of α and β .

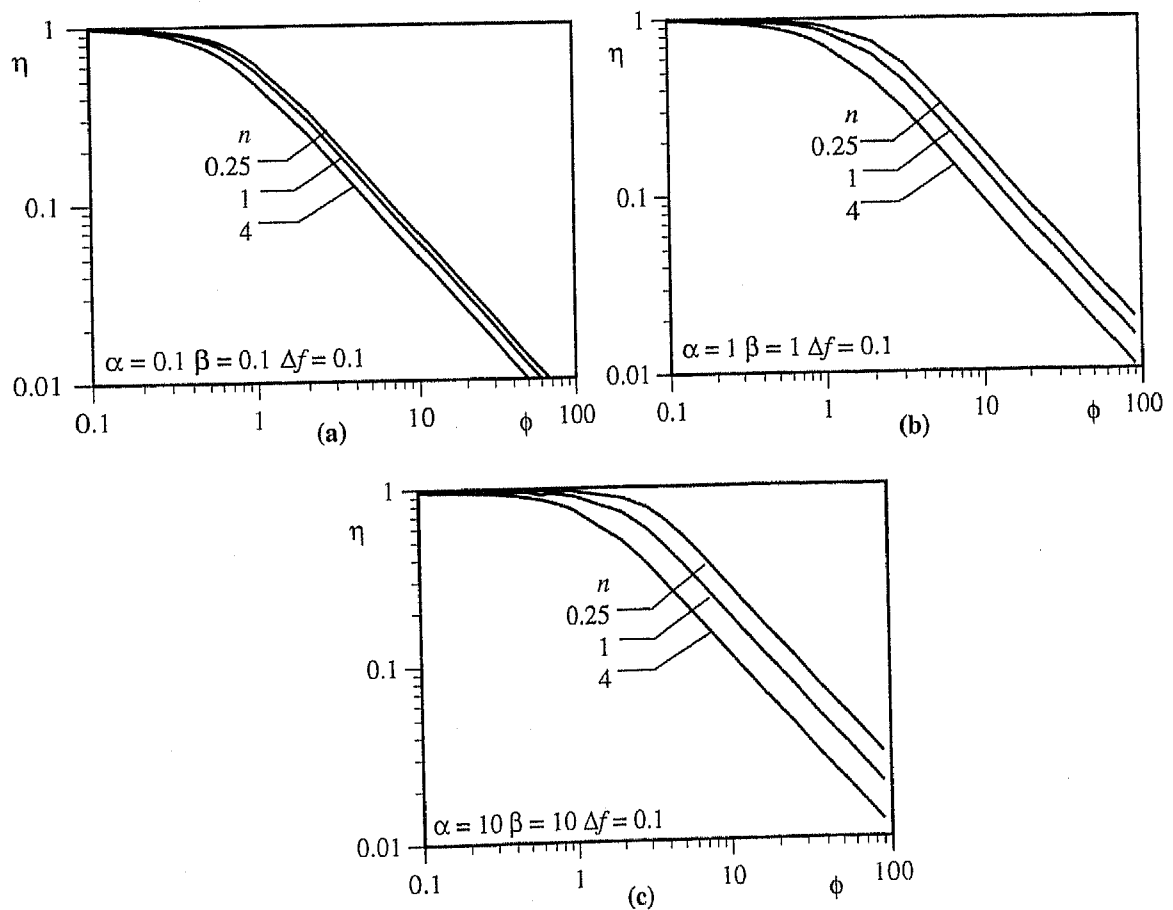


Figure 2.16 Effectiveness factor, η versus the Thiele modulus, ϕ , for different stoichiometric ratios, $n = 0.25$, 1 and 4 ; a) $\alpha = 0.1$, $\beta = 0.1$; b) $\alpha = 1$, $\beta = 1$; c) $\alpha = 10$, $\beta = 10$.

2.7 CONCLUSIONS

A general model which considers both intraparticle convection and mole changes for isothermal first-order reaction in porous catalyst, valid in all diffusion regimes was derived. Results show that pressure gradients can exist within the pellet due to the reaction stoichiometry and the external pressure gradient. The maximum pressure variation is obtained in the Knudsen diffusion regime and its value can be estimated asymptotically. The effectiveness factor is not only dependent on the Thiele modulus and on the change in moles, but it is also dependent on and enhanced by the intraparticle forced convection. The intraparticle Peclet number can be used as a criteria for establishing the regime where forced convection is important.

2.8 NOTATION

B	pellet permeability, m^2
D_{AB}	free gas mutual diffusivity in a binary mixture of components A and B , m^2/s
D_{AB}^0	$= D_e P$, N/s
D_e	effective molecular diffusivity, m^2/s
D_{eo}	effective molecular diffusivity at pressure P_o , m^2/s
D_{Ki}	Knudsen diffusivity for species i , m^2/s
D_{Km}	$= y_B D_{KA} + y_A D_{KB}$, m^2/s
f	dimensionless pressure
f_i	dimensionless partial pressure of species i
$g(y_A, f)$	auxiliary function defined by Equation 2.14
g_{ii}	auxiliary parameters defined by Equations 2.31f through 2.31j
k	reaction rate constant, s^{-1}
ℓ	slab thickness, m
M_i	molecular weight of species i Kg/Kgmole
m	$= 1 - \sqrt{n}$
N_i	intraparticle molar flux of species i , $\text{Kgmole}/\text{m}^2/\text{s}$
n	reaction stoichiometry coefficient
P	pressure, N/m^2
P_o	pressure at bottom end of the pellet, N/m^2
$\bar{r}$	mean pore radius, m
$\mathfrak{R}$	ideal gas constant, J/Kgmole/K
T	temperature, K
V	particle volume, m^3
v	intraparticle velocity, m/s
v_o	$= (B / \mu)(\Delta P / \ell)$, superficial intraparticle velocity, m/s
x	dimensionless space coordinate
y_i	mole fraction of species i
y_{As}	surface mole fraction of species A
z	space coordinate, m

Greek Symbols

α	Knudsen and effective diffusivities ratio
β	momentum and molecular diffusivity ratio
Δf	dimensionless external pressure drop
ΔP	external pressure drop, N/m^2
ε	particle porosity
ϕ	Thiele modulus
η	effectiveness factor
λ	intraparticle Peclet number

μ gas viscosity, Pa.s
 τ particle tortuosity factor

2.9 LITERATURE CITED

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3. Diffusion, Convection and Reaction in Catalyst Particles: Analogy between Slab and Cylinder Geometries

3.1 INTRODUCTION

The effect of intraparticle forced convection on the observed rate of a heterogeneous reaction within a porous catalyst particle has been increasingly studied. An enhancement of the catalyst performance, i.e., its effectiveness factor, has been reported, especially in the region where the kinetics just becomes diffusion controlled. Quantitative analysis has been made by introducing the intraparticle Peclet number, λ , defined as the ratio between the intraparticle convective flux and the diffusive flux (Komiyama and Inoue, 1974; Nir and Pismen, 1977). Furthermore, an explicit expression of the enhancement of the mass transport inside the particle by convection was obtained by introducing an *augmented* intraparticle effective diffusivity (Rodrigues *et al.*, 1982). The concept of augmented effective diffusivity allows the use of the classical model for mass transport derived for the case of diffusion only when simultaneous diffusion and convection occur, simply by replacing the effective diffusivity by its augmented value. In the case of no reaction, an analytical expression of the augmented diffusivity as a function of the intraparticle flow has been derived by Rodrigues *et al.* (1982). For a system in which reaction takes place, the augmented diffusivity depends not only on the intraparticle Peclet number but also on the Thiele modulus. Lu *et al.* (1993) studied the enhancement of intraparticle forced convection for both slab and sphere particles in the case of simultaneous intraparticle diffusion, convection and reaction. Relationships between the *augmented* intraparticle effective diffusivity and the intraparticle Peclet number were obtained for both geometries in the transient region and at steady state. Direct experimental evidence of the effect of intraparticle convection has been referenced by several authors: Cresswell (1985) reported values of the intraparticle Peclet number between 0.5 and 10 for a permeable bimodal α -alumina catalyst support with an estimated permeability of $1.9 \times 10^{-12} \text{ m}^2$; Rodrigues *et al.* (1982) studied the partial oxidation of butene to maleic anhydride in a highly porous catalyst and reported experimental values of λ from 1 to 15; Rodrigues and Quinta Ferreira (1990) considered the oxidation of o-xylene to phthalic anhydride catalysed by vanadium pentoxide in a tubular reactor at atmospheric pressure and estimated a value of 10 for the intraparticle Peclet number.

The equivalence between the various geometries is an interesting subject in chemical engineering (Aris, 1957; Kucera, 1965; Greco, *et al.*, 1975). In theoretical analysis the slab and sphere geometries are widely used due to their symmetry characteristics. In the absence of intraparticle convection, Miller and Lee (1983) provided equivalences between the slab geometry and the sphere and cylinder geometries, valid in the whole range of Thiele modulus. This work was based on the idea that the equivalent half-thickness of the slab is given by the

ratio between particle volume and external particle area in the diffusion-controlled region plus an additional thickness for the diffusion-free regime. The equivalence ratio between the slab and the sphere characteristic dimensions has been studied by Lu *et al.* (1993) for diffusion, convection and reaction in steady state and transient operation; this equivalence was based on the equality of particle effectiveness factors. When intraparticle convection is considered, a simple explicit solution for the slab geometry can be obtained; therefore, establishing the equivalence between slab and other geometries, which are common in industrial applications, allows for an easier mathematical treatment of complex processes.

Engineering practice shows that catalyst particles used in commercial processes are often finite cylinders due to their easy of manufacture by automatic pelleting machines. Therefore, the objectives of the present work are:

1. To obtain the augmented intraparticle effective diffusivities for a cylindrical geometry catalyst pellet when diffusion, convection and reaction take place;
2. To obtain the equivalence ratio between the characteristic dimensions of slab and finite cylinder geometries at steady state, valid the whole range of Thiele modulus in the presence of intraparticle convection.

3.2 MATHEMATICAL MODEL FOR THE CYLINDER PARTICLE

3.2.1 Model Development

The model can be described as follows:

1. A cylindrical catalyst of length L and radius R is placed parallel with the bulk flow, as shown in Figure 3.1;
2. Uniform intraparticle convective flow and constant external concentration are assumed;
3. A first-order irreversible reaction takes place within the catalyst particle;
4. Isothermal operation is assumed.

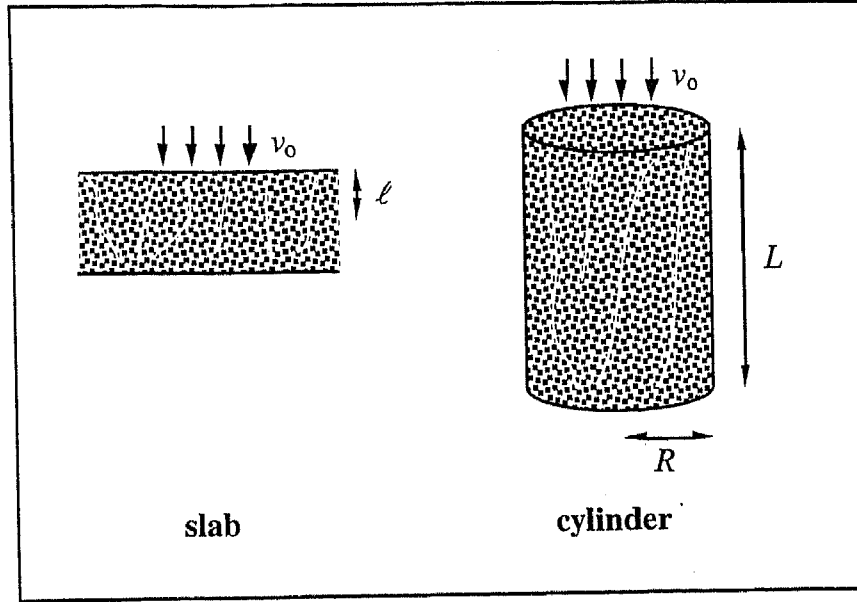


Figure 3.1 Schematic representation of permeable particle geometries

The species mass balance in a volume element of the particle at steady state leads to the following partial differential equation:

$$D_e \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) + \frac{\partial^2 C}{\partial z^2} \right) - v_o \frac{\partial C}{\partial z} - kC = 0 \quad (3.1)$$

where D_e is the effective diffusivity; C is the gas concentration inside the particle; r and z are the radial and longitudinal coordinates, respectively; k is the reaction rate constant; and v_o is the superficial intraparticle flow velocity.

The boundary conditions are

$$r = R, \forall z \quad C = C_s \quad (3.1a)$$

$$\forall r, z = 0 \text{ and } z = L \quad C = C_s \quad (3.1b)$$

$$r = 0 \quad C = \text{finite} \quad (3.1c)$$

where C_s is the concentration at the particle surface.

Introducing the following dimensionless variables

$$x = \frac{z}{L} \quad \rho = \frac{r}{R} \quad c = \frac{C}{C_s} \quad (3.2)$$

the dimensionless model equation becomes

$$\omega^2 \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial c}{\partial \rho} \right) \right] + \frac{\partial^2 c}{\partial x^2} - 2\lambda_c \frac{\partial c}{\partial x} - 4\phi_c^2 c = 0 \quad (3.3)$$

with the associated boundary conditions

$$\forall x, \rho = 0 \quad c = 1 \quad (3.3a)$$

$$\forall \rho, x = 0 \text{ and } x = 1 \quad c = 1 \quad (3.3b)$$

$$\rho = 0 \quad c = \text{finite} \quad (3.3c)$$

The model parameters are

- Intraparticle Peclet Number (ratio between convective and diffusive fluxes) $\lambda_c = \frac{v_o L}{2D_e}$

- Aspect Ratio (ratio between cylinder length and radius) $\omega = \frac{L}{R}$

- Thiele Modulus $\phi_c = \frac{L}{2} \sqrt{\frac{k}{D_e}}$

3.2.2 Intraparticle Concentration Profiles

Equation 3.3 is a partial differential equation with heterogeneous boundary conditions given by Equations 3.3a-c. The solution of this problem can be obtained by the method of integral transforms. In order to obtain homogeneous boundary conditions, the variable $f = 1 - c$ is introduced in Equation 3.3

$$\omega^2 \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial f}{\partial \rho} \right) \right] + \frac{\partial^2 f}{\partial x^2} - 2\lambda_c \frac{\partial f}{\partial x} - 4\phi_c^2 (f - 1) = 0 \quad (3.4)$$

and in the boundary conditions

$$\forall x, \rho = 0 \quad f = 0 \quad (3.4a)$$

$$\forall \rho, x = 0 \text{ and } x = 1 \quad f = 0 \quad (3.4b)$$

$$\rho = 0 \quad f = \text{finite} \quad (3.4c)$$

Now, introducing the finite Hankel transform (see, for example, Collins, 1968)

$$f_n = \int_0^1 f \rho J_0(\alpha_n \rho) d\rho \quad (3.5)$$

with the inverse

$$f = 2 \sum_{n=1}^{\infty} f_n \frac{J_0(\alpha_n \rho)}{J_1^2(\alpha_n)} \quad (3.6)$$

where J_0 and J_1 are the zeroth and first order Bessel functions of the first kind, respectively, and α_n are the roots of

$$J_0(\alpha_n) = 0 \quad (3.7)$$

and were chosen according to the homogeneous boundary conditions.

Applying this transformation to Equation 3.4 and its boundary conditions, gives

$$\frac{d^2 f_n}{dx^2} - 2\lambda_c \frac{df_n}{dx} - (\omega^2 \alpha_n^2 + 4\phi_c^2) f_n + \frac{4\phi_c^2}{\alpha_n^2} J_1(\alpha_n) = 0 \quad (3.8)$$

$$x = 0 \quad f_n = 0 \quad (3.8a)$$

$$x = 1 \quad f_n = 0 \quad (3.8b)$$

which a linear boundary value problem in x .

Introducing the variable

$$F_n = f_n - \frac{4\phi_c^2}{\alpha_n^2(\omega^2 \alpha_n^2 + 4\phi_c^2)} J_1(\alpha_n) \quad (3.9)$$

in Equation 3.8 and its boundary conditions results in

$$\frac{d^2 F_n}{dx^2} - 2\lambda_c \frac{dF_n}{dx} - (\omega^2 \alpha_n^2 + 4\phi_c^2) F_n = 0 \quad (3.10)$$

$$x = 0 \quad F_n = -\frac{4\phi_c^2}{\alpha_n^2(\omega^2 \alpha_n^2 + 4\phi_c^2)} J_1(\alpha_n) \quad (3.10a)$$

$$x = 1 \quad F_n = -\frac{4\phi_c^2}{\alpha_n^2(\omega^2 \alpha_n^2 + 4\phi_c^2)} J_1(\alpha_n) \quad (3.10b)$$

The general solution of this homogeneous ordinary differential equation is given by

$$F_n = A_1 e^{r_1 x} + A_2 e^{r_2 x} \quad (3.11)$$

where

$$r_{1,2} = \lambda_c \pm \sqrt{\lambda_c^2 + \omega^2 \alpha_n^2 + 4\phi_c^2} \quad (3.12)$$

The integration constants are determined using the boundary conditions and the solution becomes

$$F_n = \frac{4\phi_c^2 J_1(\alpha_n)}{\alpha_n^2(\omega^2 \alpha_n^2 + 4\phi_c^2)} \left(\frac{e^{r_2} - 1}{e^{r_1} - e^{r_2}} e^{r_1 x} + \frac{e^{r_1} - 1}{e^{r_2} - e^{r_1}} e^{r_2 x} \right) \quad (3.13)$$

Back substituting of F_n in Equation 3.9 results in

$$f_n = \frac{4\phi_c^2 J_1(\alpha_n)}{\alpha_n^2 (\omega^2 \alpha_n^2 + 4\phi_c^2)} \left(\frac{e^{r_2} - 1}{e^{r_1} - e^{r_2}} e^{r_1 x} + \frac{e^{r_1} - 1}{e^{r_2} - e^{r_1}} e^{r_2 x} + 1 \right) \quad (3.14)$$

Finally, from Equation 3.6, the dimensionless concentration, $c = c(\rho, x)$, inside the particle is obtained

$$c(\rho, x) = 1 - 2 \sum_{n=1}^{\infty} \frac{4\phi_c^2 J_0(\alpha_n \rho)}{\alpha_n^2 (\omega^2 \alpha_n^2 + 4\phi_c^2) J_1(\alpha_n)} \left(\frac{e^{r_2} - 1}{e^{r_1} - e^{r_2}} e^{r_1 x} + \frac{e^{r_1} - 1}{e^{r_2} - e^{r_1}} e^{r_2 x} + 1 \right) \quad (3.15)$$

Contour plots of the dimensionless concentration inside a cylinder particle for various values of the intraparticle Peclet number, λ_c , and the aspect ratio, ω , are shown in Figures 3.2 through 3.6. For visualisation purposes in these plots the ratio between the actual lengths of the coordinate axes, ρ and x , is proportional to the respective aspect ratio, ω .

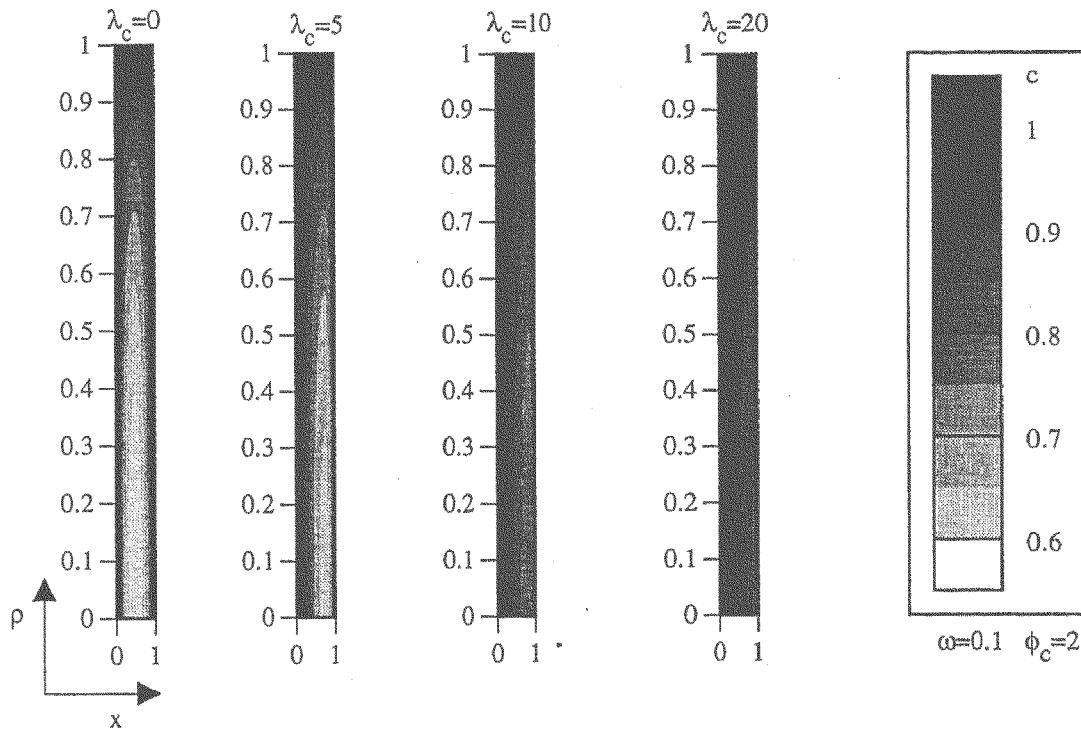


Figure 3.2 Dimensionless concentration contours within the pellet for Thiele modulus, $\phi_c = 2$, aspect ratio, $\omega = 0.1$, and various values of the intraparticle Peclet number: $\lambda_c = 0$; $\lambda_c = 5$; $\lambda_c = 10$ and $\lambda_c = 20$.

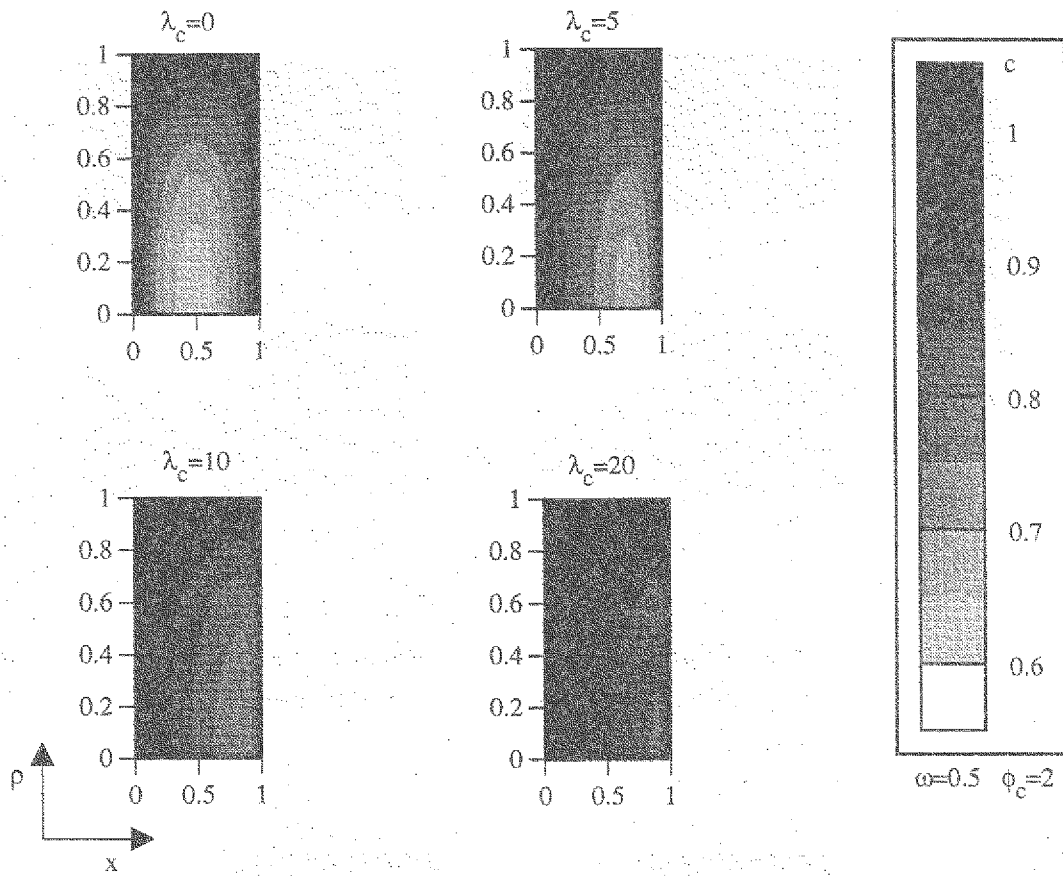


Figure 3.3 Dimensionless concentration contours within the pellet for Thiele modulus, $\phi_c = 2$, aspect ratio, $\omega = 0.5$, and various values of the intraparticle Peclet number.

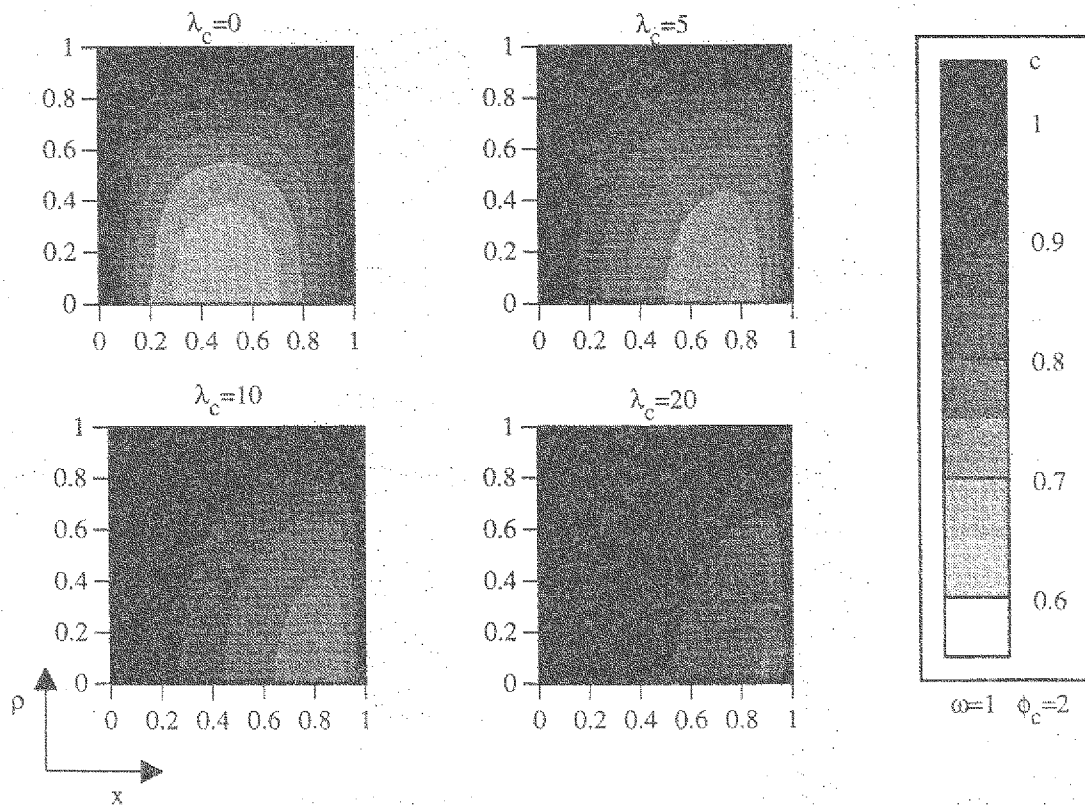


Figure 3.4 Dimensionless concentration contours within the pellet for Thiele modulus, $\phi_c = 2$, aspect ratio, $\omega = 1$, and various values of the intraparticle Peclet number.

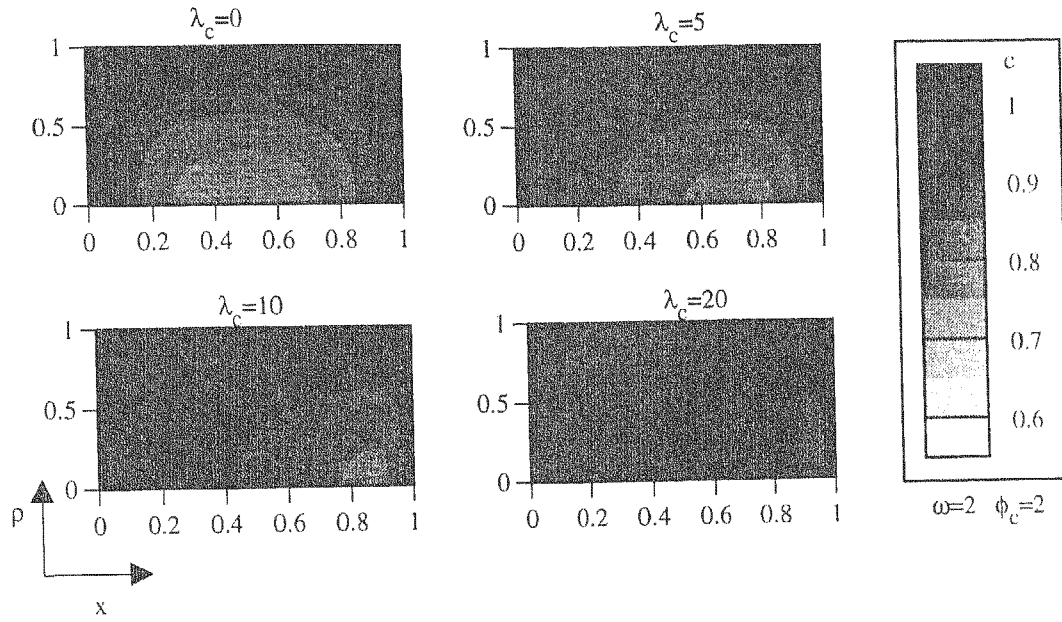


Figure 3.5 Dimensionless concentration contours within the pellet for Thiele modulus, $\phi_c = 2$, aspect ratio, $\omega = 2$, and various values of the intraparticle Peclet number.

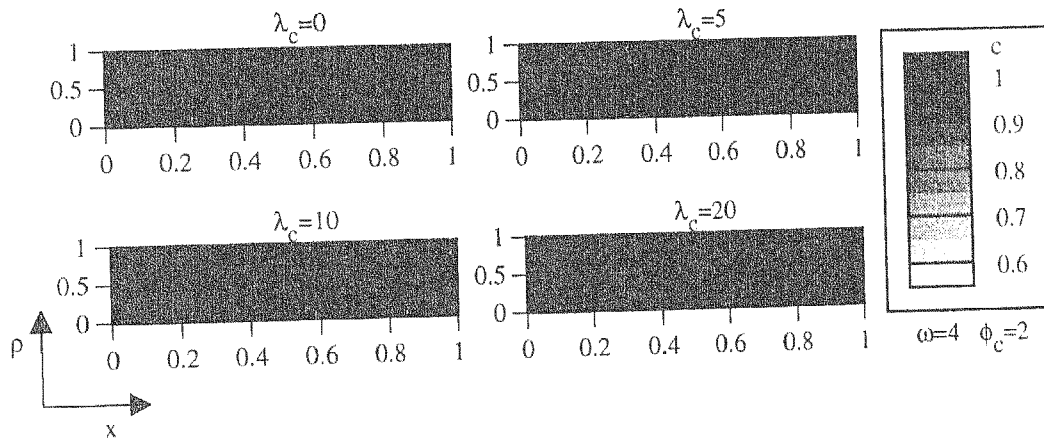


Figure 3.6 Dimensionless concentration contours within the pellet for Thiele modulus, $\phi_c = 2$, aspect ratio, $\omega = 4$, and various values of the intraparticle Peclet number.

3.2.3 Effectiveness Factor

The effectiveness factor for the cylinder particle can be calculated by

$$\eta_c = \frac{\int_0^1 \int_0^1 2\pi k c \rho d\rho dx}{k \int_0^1 \int_0^1 2\pi \rho d\rho dx} \quad (3.16)$$

Substituting Equation 3.15 into Equation 3.16 yields

$$\eta_c = 1 - \sum_{n=1}^{\infty} \frac{16\phi_c^2}{\alpha_n^2 (\omega^2 \alpha_n^2 + 4\phi_c^2)} \left[1 + \frac{(e^{r_1} - 1)(e^{r_2} - 1)}{e^{r_1} - e^{r_2}} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \right] \quad (3.17)$$

Taking the limit $\omega \rightarrow 0$, and noting that $\sum_{n=1}^{\infty} 1/\alpha_n^2 = 1/4$, the effectiveness factor becomes

$$\lim_{\omega \rightarrow 0} \eta_c = \frac{(e^{r_1} - 1)(e^{r_2} - 1)}{e^{r_1} - e^{r_2}} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (3.17a)$$

which is identical to the result obtained by Nir and Pismen (1977) for the slab geometry.

For the case without intraparticle convection, $\lambda = 0$, following expression can be obtained

$$\lim_{\lambda \rightarrow 0} \eta_c = 1 - \sum_{n=1}^{\infty} \frac{16\phi_c^2}{\alpha_n^2 (\omega^2 \alpha_n^2 + 4\phi_c^2)} \left[1 - \frac{2}{r} \tanh \frac{r}{2} \right] \quad (3.17b)$$

where

$$r = \sqrt{\omega^2 \alpha_n^2 + 4\phi_c^2} \quad (3.17c)$$

On the other hand, when $\omega \rightarrow \infty$ (infinite cylinder) and in the absence of intraparticle convection ($\lambda_c = 0$), Equation 3.17 reduces to the known solution for diffusion and reaction in an infinite cylinder

$$\lim_{\omega \rightarrow \infty} \eta_c = 4 \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2 + \phi^2} = \frac{2I_1(\phi)}{\phi I_0(\phi)} \quad (3.18)$$

where $\phi^2 = 4\phi_c^2 / \omega^2 = R^2 k / D_e$ and the last equality was obtained using some relationships given by Aris (1975).

Figure 3.7 shows the effect of the aspect ratio, ω , on the effectiveness factor, η_c , as a function of the Thiele modulus, ϕ_c , for different values of intraparticle Peclet number, λ_c . For a given value of the Thiele modulus, the effectiveness factor increases with the aspect ratio. The effect of the intraparticle Peclet number, λ_c , on the effectiveness factor, for various values of the aspect ratio, ω , is shown in Figure 3.8. Intraparticle convection enhances the effectiveness factor considerably for values of the Thiele modulus between $\phi_c = 1$ and $\phi_c = 10$, i.e., in the region where the kinetics becomes diffusion controlled. This enhancement is more important at low values of ω , that is, when the geometry approaches that of a slab.

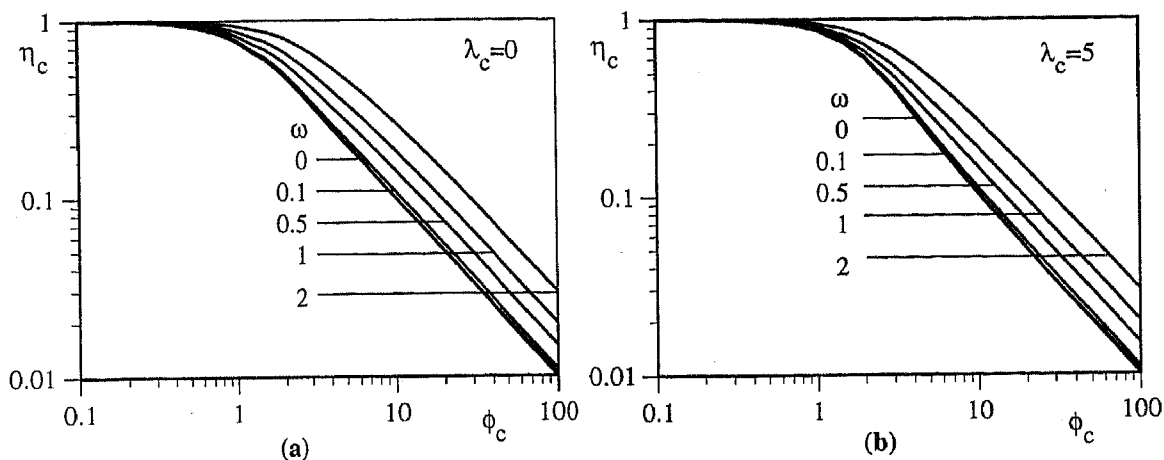


Figure 3.7 Effect of the aspect ratio, ω , on the effectiveness factor, η_c , as a function of the Thiele modulus, ϕ_c , for different values of the intraparticle Peclet number: a) $\lambda_c = 0$; b) $\lambda_c = 5$.

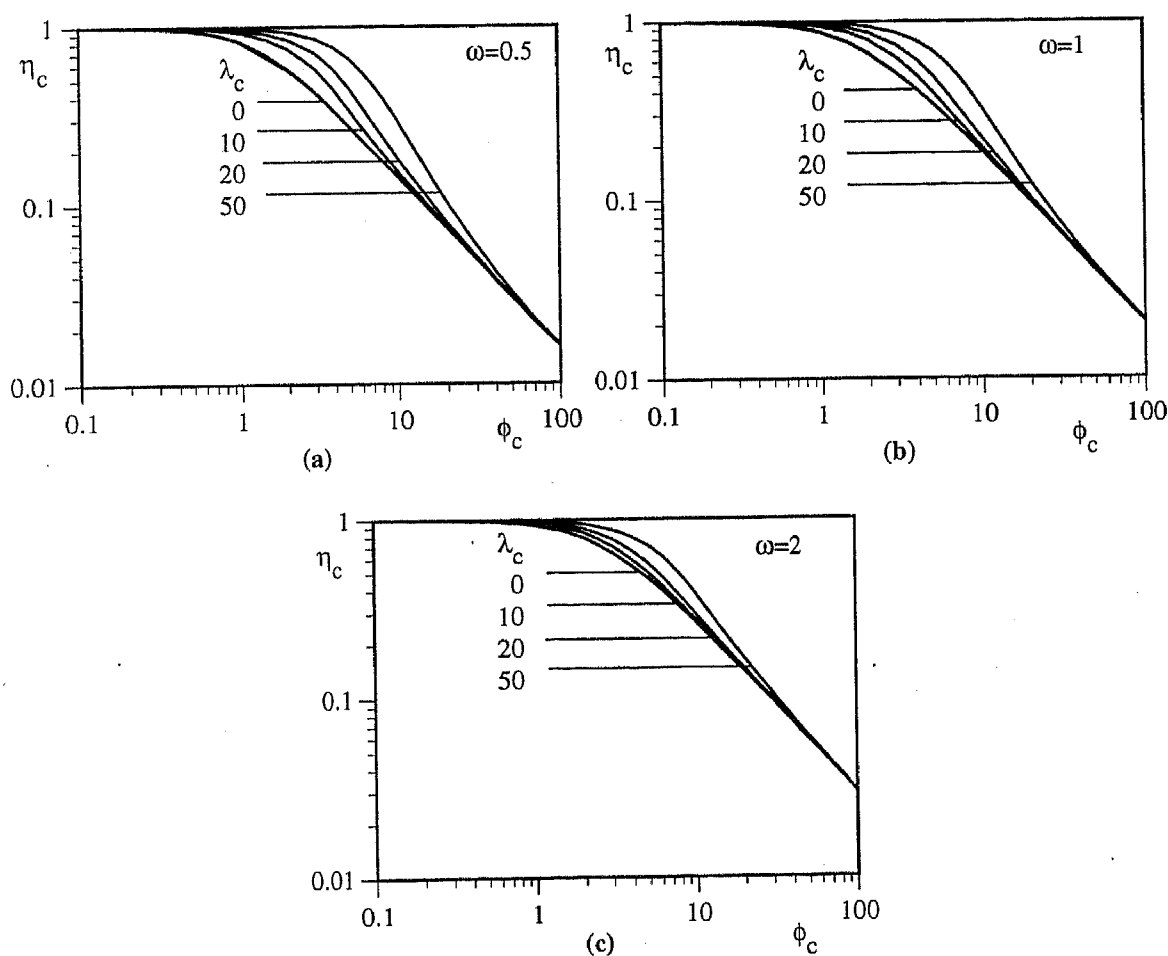


Figure 3.8 Effect of the intraparticle Peclet number, λ_c , on the effectiveness factor, η_c , as a function of the Thiele modulus, ϕ_c , for different aspect ratio values: a) $\omega = 0.5$; b) $\omega = 1$; c) $\omega = 2$.

The observed reaction rate under steady state conditions depends on the effectiveness factor of the catalyst particle. Both the analysis of the augmented diffusivity and of the analogy between characteristic dimensions for different particle geometries can be based on the equivalence of the particle effectiveness factors (Lu *et al.*, 1993). These two questions are addressed in the next two sections.

3.3 AUGMENTED DIFFUSIVITY BY CONVECTION FOR CYLINDER GEOMETRY

If intraparticle convection is not explicitly included in the model equations, the effective diffusivity, D_e , should be replaced by an *apparent* effective diffusivity, $\tilde{D}_e$, which lumps both diffusion and convection, and the species mass balance can now be written as

$$\tilde{D}_e \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) + \frac{\partial^2 C}{\partial z^2} \right) - kC = 0 \quad (3.19)$$

Introducing dimensionless variables and solving this equation subject to the same boundary conditions as before, the apparent effectiveness factor, $\tilde{\eta}_c$, is obtained

$$\tilde{\eta}_c = 1 - \sum_{n=1}^{\infty} \frac{16\tilde{\phi}_c^2}{\alpha_n^2 (\omega^2 \alpha_n^2 + 4\tilde{\phi}_c^2)} \left[1 + \frac{2}{r_0} \left(\frac{1}{\sinh r_0} - \frac{1}{\tanh r_0} \right) \right] \quad (3.20)$$

where

$$r_0 = \sqrt{\omega^2 \alpha_n^2 + 4\tilde{\phi}_c^2} \quad (3.21)$$

and the apparent Thiele modulus is defined as $\tilde{\phi}_c = \frac{L}{2} \sqrt{\frac{k}{\tilde{D}_e}}$.

When $\omega \rightarrow 0$, Equation 3.20 reduces to the well known result for the slab geometry

$$\tilde{\eta}_c = \frac{\tanh \tilde{\phi}_c}{\tilde{\phi}_c} \quad (3.22)$$

The ratio between the augmented intraparticle effective diffusivity, $\tilde{D}_e$, and the intraparticle effective diffusivity, D_e , at steady-state is obtained by imposing that

$$\tilde{\eta}_c = \eta_c \quad (3.23)$$

which leads to a relationship of the type

$$\frac{\tilde{D}_e}{D_e} = F(\phi_c, \lambda_c, \omega) \quad (3.24)$$

This relationship was solved numerically using a standard false position method. Figure 3.9 shows the effect of the aspect ratio, ω , on the diffusivity enhancement factor $\tilde{D}_e/D_e$ as a function of the intraparticle Peclet number, λ_c . As ω decreases the effect of the intraparticle convection becomes more significant, i.e., $\tilde{D}_e/D_e$ increases. For an infinite cylinder placed parallel to flow, $\omega \rightarrow \infty$, intraparticle convection has no effect on the mass transport, i.e., $\tilde{D}_e/D_e \rightarrow 1$. When the cylinder becomes very thin, $\omega \rightarrow 0$, the results are identical to those for the slab geometry (Lu *et al.*, 1993). These results show that the area of the particle facing the external flow plays an important role on the diffusivity enhancement due to intraparticle convection. The effect of the Thiele modulus on the diffusivity enhancement is shown in Figure 3.10, where $\tilde{D}_e/D_e$ is plotted as a function of λ_c .

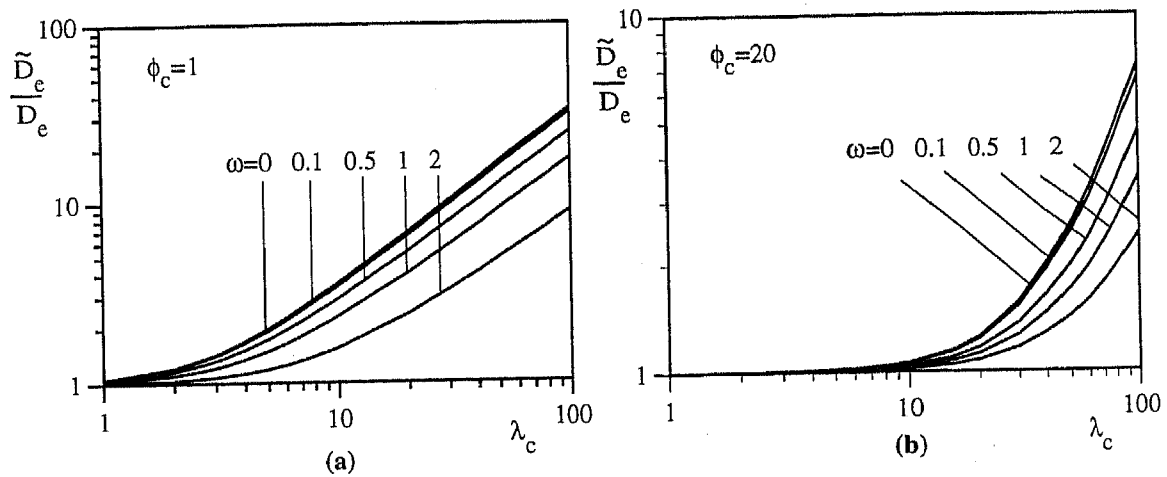


Figure 3.9 Effect of the aspect ratio, ω , on the diffusivity enhancement factor, $\tilde{D}_e/D_e$, as a function of the intraparticle Peclet number, λ_c : **a)** $\phi_c = 1$; **b)** $\phi_c = 20$.

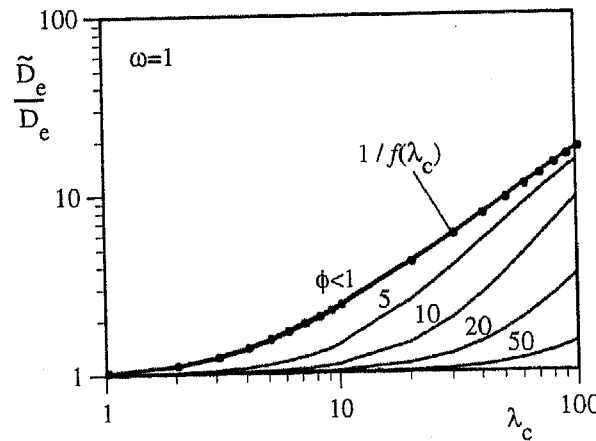


Figure 3.10 Effect of the Thiele modulus, ϕ_c , on the diffusivity enhancement factor, $\tilde{D}_e/D_e$, as a function of the intraparticle Peclet number, λ_c , at $\omega = 1$.

It is observed that the diffusivity enhancement decreases with increasing ϕ_c , and that for large values of ϕ_c and small λ_c values, i.e., in the diffusion controlled region ($\phi_c/\lambda_c \gg 1$), the enhancement is negligible and $\tilde{D}_e/D_e \rightarrow 1$. Nevertheless, the effect of intraparticle convection is significant over a wide range of ϕ_c values. In the kinetic controlled limit, $\phi_c \rightarrow 0$, the diffusivity enhancement can be expressed by the relationship

$$\frac{\tilde{D}_e}{D_e} = \frac{1}{f(\lambda_c)} \quad (3.25)$$

where $f(\lambda_c)$ is given by (see Appendix for details):

$$f(\lambda_c) = \frac{\sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \left[1 + \left(\frac{\cosh \lambda_c}{\sinh \gamma_n} - \coth \gamma_n \right) \frac{2\gamma_n}{\gamma_n^2 - \lambda_c^2} \right]}{\sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \left(1 - \frac{\tanh \zeta_n}{\zeta_n} \right)} \quad (3.26)$$

and

$$\gamma_n = \sqrt{\lambda_c^2 + \omega^2 \alpha_n^2} \quad (3.27)$$

$$\zeta_n = \frac{\omega \alpha_n}{2} \quad (3.28)$$

When $\omega \rightarrow 0$ (slab geometry), Equation 3.25 can be reduced to that derived by Rodrigues *et al.* (1982)

$$f(\lambda) = \frac{3}{\lambda} \left(\frac{1}{\tanh \lambda} - \frac{1}{\lambda} \right) \quad (3.29)$$

Plots of diffusivity enhancement factor, $\tilde{D}_e/D_e$, a function of the Thiele modulus, ϕ_c , for different values of ω and λ_c are shown in Figure 3.11. It can be observed that in the range of small ϕ_c values, $\tilde{D}_e/D_e$ takes constant values, which are equal to those obtained at $\phi_c = 0$. The effect of intraparticle convection for a cylinder with aspect ratio $\omega = 1$ is shown in Figure 3.12. The results are qualitatively similar to those for slab and sphere particles (Lu *et al.*, 1993). Furthermore, from these plots it can be found that Equation 3.26 can be approximately used in the range of $\phi_c = 0 - 1$ for any values of λ_c .

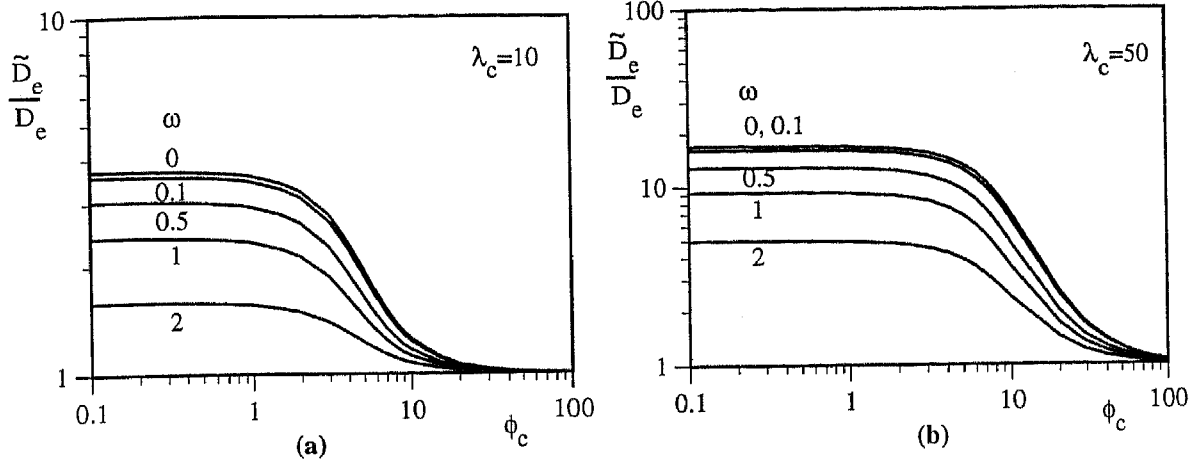


Figure 3.11 Effect of the aspect ratio, ω , on the diffusivity enhancement factor, $\tilde{D}_e/D_e$, as a function of the Thiele modulus, ϕ_c , for different values of the intraparticle Peclet number: a) $\lambda_c = 10$; b) $\lambda_c = 50$.

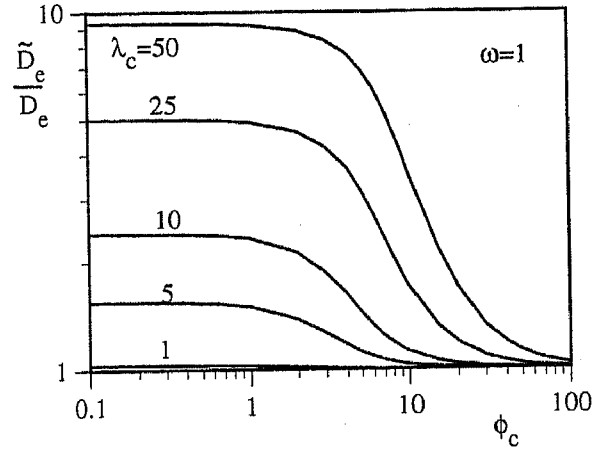


Figure 3.12 Effect of the intraparticle Peclet number, λ_c , on the diffusivity enhancement factor, $\tilde{D}_e/D_e$, as a function of the Thiele modulus, ϕ_c , for $\omega = 1$.

3.4 EQUIVALENCE BETWEEN SLAB AND CYLINDER

The effectiveness factor for a pellet with slab geometry, derived by Nir and Pismen (1977), is given by

$$\eta_s = \frac{1}{\coth r'_1 - \coth r'_2} \left(\frac{1}{r'_1} - \frac{1}{r'_2} \right) \quad (3.30)$$

where

$$r'_{1,2} = \frac{\lambda_s \pm \sqrt{\lambda_s^2 + 4\phi_s^2}}{2} \quad (3.31)$$

and the model parameters, similar to those defined in the case of a cylinder particle, are

$$\lambda_s = \frac{v_o \ell_s}{D_e} \quad (3.32)$$

$$\phi_s = \ell_s \sqrt{\frac{k}{D_e}} \quad (3.33)$$

where ℓ_s is the half thickness of the slab.

Now, imposing the equality of the effectiveness factors for finite cylinder, η_c , and slab particles, η_s , that is,

$$\eta_c = \eta_s \quad (3.34)$$

the ratio between characteristic dimensions for the slab, ℓ_s , and the cylinder, L , is obtained by replacing Equations 3.17 and 3.30 into Equation 3.34, to give a relationship for the equivalent dimensions ratio

$$\frac{\ell_s}{L} = F_c(\phi_c, \lambda_c, \omega) = F_s(\phi_s, \lambda_s) \quad (3.35)$$

Numerical solutions were again obtained with the false position method. Figure 3.13 shows the effect of the Thiele modulus, ϕ_c , on the plots of the ratio ℓ_s/L as a function of the intraparticle Peclet number, λ_c . The Thiele modulus has a significant effect on the equivalent dimensions ratio, λ_c . For large values of ϕ_c and small values λ_c , this ratio is independent of intraparticle convection.

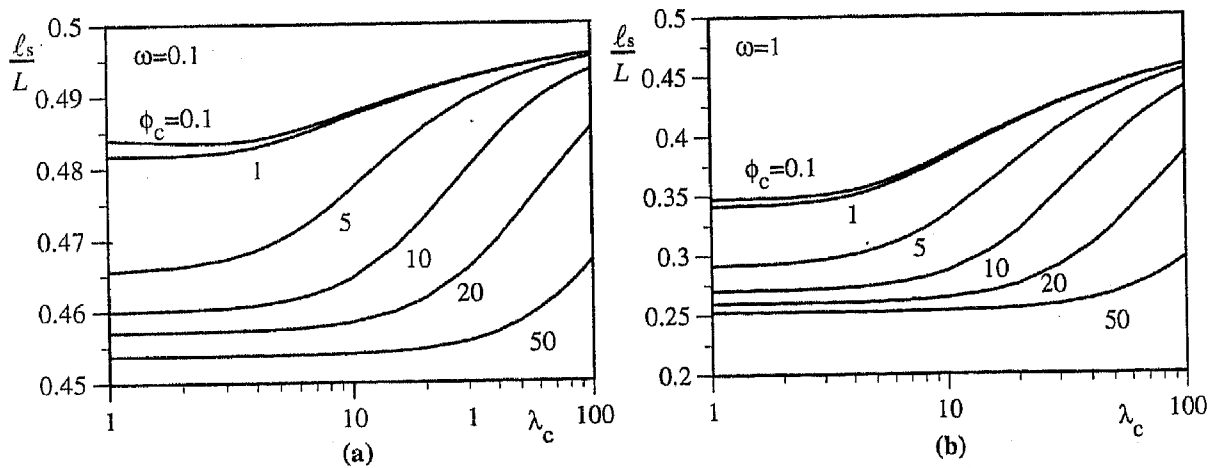


Figure 3.13 Effect of the Thiele modulus, ϕ_c , on the equivalent dimensions ratio, ℓ_s/L , as a function of the intraparticle Peclet number, λ_c , and for different values of the aspect ratio: a) $\omega = 0.1$; b) $\omega = 1$.

The effect of the aspect ratio, ω , on the equivalent dimensions ratio, ℓ_s/L , as a function of λ_c is shown in Figure 3.14. When $\lambda_c < 2$, ℓ_s/L is independent of λ_c , but its value depends on ω . For large values of λ_c , the equivalence ratio approaches a constant value of $\ell_s/L = 0.5$, which is independent of ω and of ϕ_c .

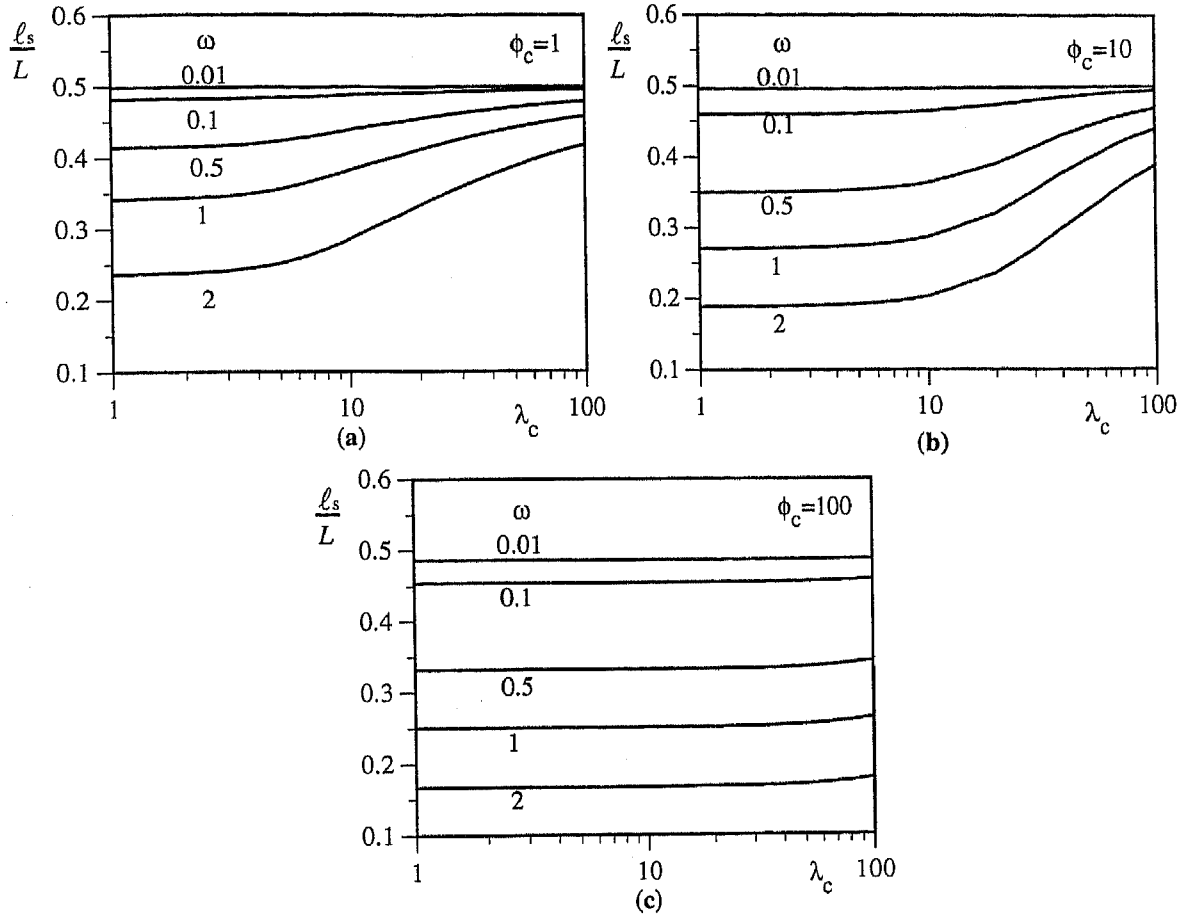


Figure 3.14 Effect of the aspect ratio, ω , on the equivalent dimension ratio, ℓ_s/L , as a function of the intraparticle Peclet number, λ_c , for different values of the Thiele modulus: a) $\phi_c = 1$; b) $\phi_c = 10$; c) $\phi_c = 100$.

Figure 3.15 shows ℓ_s/L as a function of ϕ_c for different values of ω and λ_c . Here some limits for the equivalence ratio can be anticipated. For a fast reaction and insignificant intraparticle convection, $\lambda_c/\phi_c \rightarrow 0$, the effectiveness factor is dependent only on the specific area, and thus comparing the specific areas for the slab and cylinder geometries, an explicit expression can be obtained

$$\frac{\ell_s}{L} = \frac{1}{2(1+\omega)} \quad (3.36)$$

In the limit of $\lambda_c/\phi_c \rightarrow \infty$, the specific area of particle facing the flow becomes the important factor, and the equivalence between two geometries becomes simply

$$\frac{\ell_s}{L} = \frac{1}{2} \quad (3.37)$$

in which case the finite cylinder has the same behaviour as that of a slab.

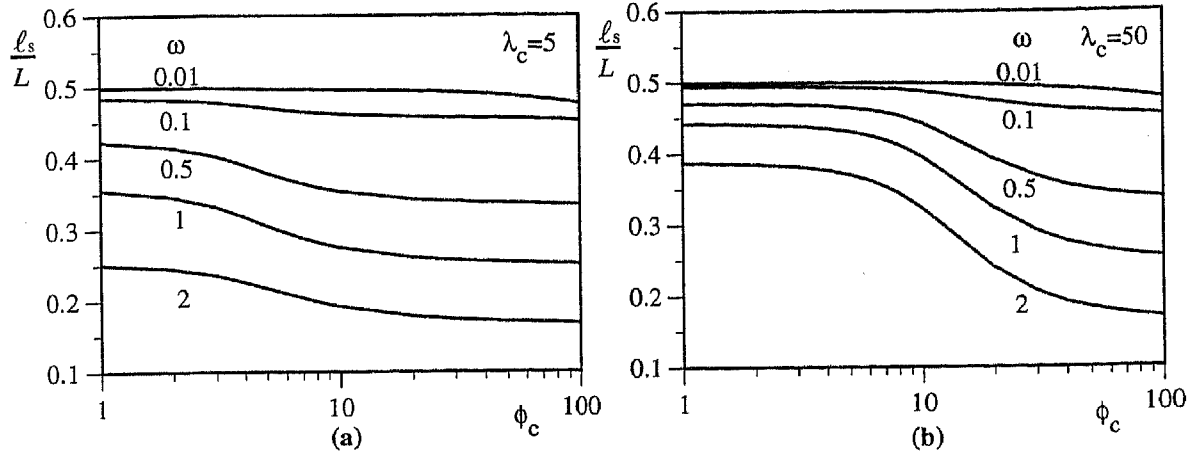


Figure 3.15 Effect of aspect ratio, ω , on the equivalent dimension ratio, ℓ_s/L , as a function of the Thiele modulus, ϕ_c , for different values of the intraparticle Peclet number: **a)** $\lambda_c = 5$; **b)** $\lambda_c = 50$.

If one chooses the radius, R , as the cylinder characteristic dimension, another equivalence between the slab and the finite cylinder can be expressed as

$$\frac{\ell_s}{R} = F_c(\phi_{cR}, \lambda_c, \omega) = F_s(\phi_s, \lambda_s) \quad (3.38)$$

where $\phi = R\sqrt{k/D_e}$. Figure 3.16 shows ℓ_s/R as a function of ϕ for different values of ω and λ_c .

The curve for $\omega = \infty$ and $\lambda_c = 0$ was obtained using the known solution for diffusion and reaction in an infinite cylinder. In this case and for large values of ϕ one observes the expected limiting value of $\ell_s/R = 0.5$. In the limit of small ϕ , the expressions for the effectiveness factor for the slab and for the infinite cylinder may be approximated by

$$\eta_s = \frac{\tanh \phi}{\phi} \underset{\phi \rightarrow 0}{\approx} 1 - \frac{\phi^2}{3} \quad (3.39a)$$

and

$$\frac{1}{\eta_c} = \frac{\phi I_0(\phi)}{2I_1(\phi)} \underset{\phi \rightarrow 0}{\approx} 1 + \frac{\phi^2}{8} - \frac{\phi^4}{192} \quad (3.39b)$$

respectively. Comparing these two expressions one obtains

$$\lim_{\phi \rightarrow 0} \frac{\ell_s}{R} = \sqrt{\frac{3}{8}} \approx 0.612 \quad (40)$$

This value is very close to the value obtained by Miller and Lee (1983) for the shape normalisation factor, valid for $\phi < 1.5$ and $\omega \geq 2$, which, in the notation of this work becomes

$$\frac{\ell_s}{R} = \frac{1}{2} \left(1 + \frac{1}{\omega}\right)^{-1} \left\{ 1 + \left[1 - \frac{1}{2} \left(1 + \frac{1}{\omega}\right)^{-1} \right]^2 \left(1 + \frac{1}{\omega}\right)^{-1} \right\} \quad (41)$$

and taking the limit for large values of ω one obtains

$$\lim_{\omega \rightarrow \infty} \frac{\ell_s}{R} = \frac{5}{8} \approx 0.625 \quad (42)$$

Figure 3.16 also shows that for the finite cylinder, ℓ_s/R decreases with ω , and that for a given value of ϕ , ℓ_s/R increases with λ_c .

In the above discussion of particle equivalence, all figures were drawn with respect to the cylinder parameters. These figures can be easily converted to the slab parameters as it was done by Rodrigues *et al.* (1992).

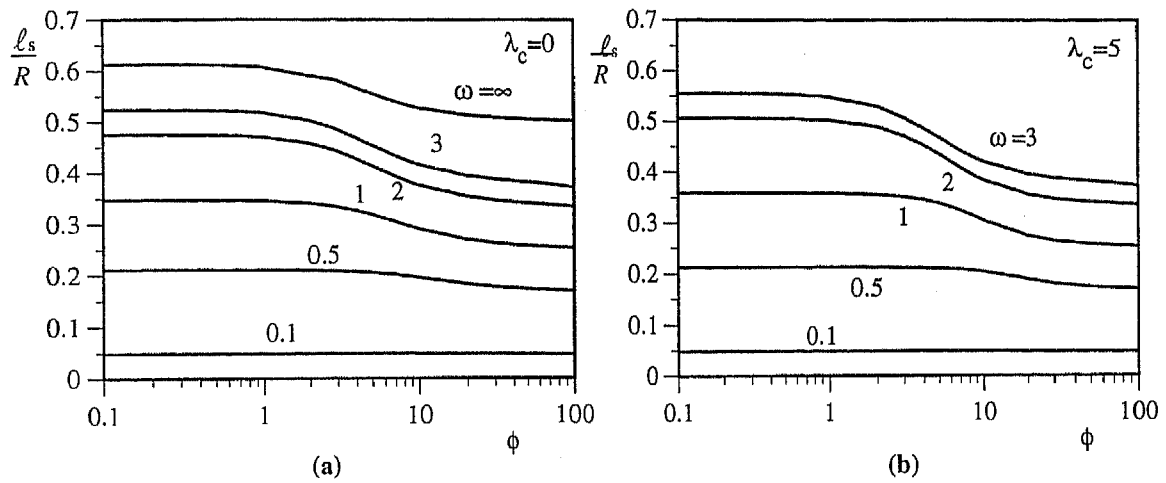


Figure 3.16 Effect of aspect ratio, ω , on the equivalent dimension ratio, ℓ_s/R , as a function of the Thiele modulus, ϕ_{cR} .

3.5 CONCLUSIONS

The relationship for the augmented intraparticle effective diffusivity for the cylinder geometry has been studied for diffusion, convection and reaction problem at steady state. It has been found that the enhancement of effective diffusivity depends not only on the intraparticle Peclet number but also on the Thiele modulus and the aspect ratio. When $\phi_c < 1$, the augmented diffusivity can be estimated approximately by $\tilde{D}_e/D_e = 1/f(\lambda)$. As ω increases the enhancement decreases. This point suggests that, when unsymmetrical catalyst particles are packed in a fixed bed reactor, if the intraparticle convection is present and has a favorite effect, particles should be placed with their larger area sides facing the bulk flow.

An equivalent ratio between the characteristic dimensions of slab and finite cylinder, valid in the whole range of Thiele modulus and in the presence of intraparticle convection, was determined. This ratio, expressed in terms of the half thickness of the slab ℓ_s and the length of the cylinder

L , lies between the bounds $1/2(1 + \omega)$ and $1/2$. The former value is attained in the case of $\lambda_c/\phi_c \rightarrow 0$, and the latter bound is approached when $\lambda_c/\phi_c \rightarrow \infty$. When the intraparticle Peclet number is small, say $\lambda_c < 2$, the effect of intraparticle convection on the equivalent dimensions ratio is negligible. The equivalence between slab and cylinder may also be expressed in terms of the cylinder radius, R , in which case, the infinite cylinder case was derived and compared with previously known analytic solutions.

3.6 NOTATION

C	species concentration, Kgmol/m^3
c	dimensionless species concentration
C_s	species concentration at external surface, Kgmol/m^3
D_e	effective diffusivity, m^2/s
F_n	auxiliary function defined by Equation 3.9
f	$1-c$
f_n	finite Hankel transform defined in Equation 3.5
$g(s)$	particle transfer function
J_0, J_1	zeroth and first order Bessel functions of first kind
k	reaction rate constant, s^{-1}
L	length of cylinder particle, m
ℓ_s	half thickness of slab particle, m
$p_{1,2}$	roots of characteristic equation, defined by Equation 3.A4
R	radius of cylinder particle, m
r	radial coordinate, m
r_0	roots of characteristic equation, defined by Equation 3.21
$r_{1,2}$	roots of characteristic equation, defined by Equation 3.12
$r'_{1,2}$	roots of characteristic equation, defined by Equation 3.31
v_0	superficial intraparticle velocity, m/s
x	dimensionless longitudinal coordinate
z	longitudinal coordinate, m

Greek Symbols

α_n	zero of zeroth order Bessel function of first kind
β_n	auxiliary parameter defined by Equation 3.A6
γ_n	auxiliary variable defined by Equation 3.27
ε_p	particle porosity
ζ_n	auxiliary variable defined by Equation 3.28
η	effectiveness factor
λ	intraparticle Peclet number
μ_n	moment of order n of impulse response
ρ	dimensionless radial coordinate
τ_D	intraparticle diffusion time, s
ϕ	Thiele modulus
ω	aspect ratio of length to radius of cylinder particle

Subscripts and Upperscripts

c	cylinder
s	slab
$\sim$	denotes <i>apparent</i> parameter (intraparticle convection lumped with diffusion)
$-$	denotes Laplace transform domain

3.7 LITERATURE CITED

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APPENDICES

3.A DERIVATION OF $f(\lambda)$ FOR CYLINDER PARTICLES FROM MOMENT METHOD

The unsteady-state differential mass balance equation for intraparticle diffusion and convection in a cylindrical particle is given by

$$D_e \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) + \frac{\partial^2 C}{\partial z^2} \right) - v_o \frac{\partial C}{\partial z} - \varepsilon_p \frac{\partial C}{\partial t} = 0 \quad (3.A1)$$

$$r = R, z = 0 \quad C = C_s \quad (3.A1a)$$

$$r = R, z = L \quad C = C_s \quad (3.A1b)$$

$$r = 0 \quad C = \text{finite} \quad (3.A1c)$$

$$t = 0 \quad C = 0 \quad (3.A1d)$$

Introducing dimensionless variables, defining $\tau_D = \frac{\varepsilon_p L^2}{D_e}$, and taking the Laplace transform

$$\omega^2 \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \bar{C}}{\partial \rho} \right) \right] + \frac{\partial^2 \bar{C}}{\partial x^2} - 2\lambda_c \frac{\partial \bar{C}}{\partial x} - \tau_D s \bar{C} = 0 \quad (3.A2)$$

$$\rho = 1, x = 0 \quad \bar{C} = 1 \quad (3.A2a)$$

$$\rho = 1, x = 1 \quad \bar{C} = 1 \quad (3.A2b)$$

$$\rho = 0 \quad \bar{C} = \text{finite} \quad (3.A2c)$$

Using the finite Hankel transform as before the solution to this problem can be obtained

$$\bar{C} = 1 - 2 \sum_{n=1}^{\infty} \frac{\tau_D s J_0(\alpha_n \rho)}{\alpha_n^2 (\omega^2 \alpha_n^2 + \tau_D s) J_1(\alpha_n)} \left(\frac{e^{p_2} - 1}{e^{p_1} - e^{p_2}} e^{p_1 x} + \frac{e^{p_1} - 1}{e^{p_2} - e^{p_1}} e^{p_2 x} + 1 \right) \quad (3.A3)$$

where

$$p_{1,2} = \lambda_c \pm \sqrt{\lambda_c^2 + (\omega^2 \alpha_n^2 + \tau_D s)} \quad (3.A4)$$

The dimensionless average concentration inside the particle in the Laplace domain is

$$\langle \bar{C} \rangle = 1 - \sum_{n=1}^{\infty} \frac{4 \tau_D s}{\alpha_n^2 (\omega^2 \alpha_n^2 + \tau_D s)} \left[1 + \left(\frac{\cosh \lambda_c}{\sinh \beta_n} - \coth \beta_n \right) \frac{2 \beta_n}{\beta_n^2 - \lambda_c^2} \right] \quad (3.A5)$$

where

$$\beta_n = \sqrt{\lambda_c^2 + (\omega^2 \alpha_n^2 + \tau_D s)} \quad (3.A6)$$

The particle transfer function relating the Laplace transform of the average concentration and the surface concentration is given by

$$g(s) = \langle \bar{c} \rangle \quad (3.A7)$$

and the moments of the impulse response can be obtained by the relationship

$$\mu_n = (-1)^n \left. \frac{\partial^n g(s)}{\partial s^n} \right|_{s=0} \quad (3.A8)$$

The first order moment obtained using Equation 3.A5 results in

$$\mu_1 = 4 \frac{\tau_D}{\omega^2} \sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \left[1 + \left(\frac{\cosh \lambda_c}{\sinh \gamma_n} - \coth \gamma_n \right) \frac{2 \gamma_n}{\gamma_n^2 - \lambda_c^2} \right] \quad (3.A9)$$

where

$$\gamma_n = \sqrt{\lambda_c^2 + \omega^2 \alpha_n^2} \quad (3.A10)$$

On the other hand, if only intraparticle diffusion is taken into account the first moment is given by

$$\bar{\mu}_1 = 4 \frac{\tilde{\tau}_D}{\omega^2} \sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \left(1 - \frac{\tanh \zeta}{\zeta} \right) \quad (3.A11)$$

where

$$\zeta_n = \frac{\omega \alpha_n}{2} \quad (3.A12)$$

Defining

$$f(\lambda_c) = \frac{D_e}{\tilde{D}_e} = \frac{\tilde{\tau}_D}{\tau_D} \quad (3.A13)$$

and comparing Equation 3.A9 to Equation 3.A11 leads to

$$f(\lambda_c) = \frac{\sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \left[1 + \left(\frac{\cosh \lambda_c}{\sinh \gamma_n} - \coth \gamma_n \right) \frac{2 \gamma_n}{\gamma_n^2 - \lambda_c^2} \right]}{\sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \left(1 - \frac{\tanh \zeta_n}{\zeta_n} \right)} \quad (3.A14)$$

4. Effective Diffusivity Measurements by Chromatographic Methods

4.1 INTRODUCTION

Diffusion in porous media is a subject of intensive investigation in chemical engineering due to its important influence on the overall kinetics of heterogeneous catalytic reaction. The effective diffusivity is a complex quantity which often includes contributions from more than one mechanism. It is not always easy to make an accurate prediction of the effective diffusivity since this is strongly dependent on the details of the pore structure. Experimental methods always play an important role in the study of the effective diffusivity of gases in porous media.

Several techniques have been employed to measure the effective diffusivity. Among these, chromatographic measurements are receiving increasing attention as a procedure for measuring rate parameters in fixed bed reactors. The theory of gas chromatography permits the determination of mass transfer resistance such as axial diffusion, interphase diffusion, and intraparticle diffusion in beds packed with catalyst pellets. A carrier gas, which is not adsorbed, is passed continuously through the column. A pulse of a diffusing non-adsorbable component is injected into the stream and some property of the effluent pulse, related with its concentration, is recorded. For linear processes, rapid and simple experiments can provide information about the contributions of each transport mechanism and surface process in gas-solid catalytic reactors. According to the experimental conditions, a set of dynamic equations to describe the system behaviour can be developed. The solution of these equations gives the theoretical responses. The mass transport parameters in the model equations can be obtained by fitting the theoretical to the experimental response values.

Kubin (1965) and Kucera (1965) made the first theoretical contribution by solving the linear chromatographic system where axial dispersion, external diffusion, intraparticle diffusion and adsorption were included, in the absence of reaction. Later, Suzuki and Smith (1970) extended the solution to the case where reaction takes place. Since then, the chromatographic method has been well studied in practice as well as in theory and several laboratory techniques and mathematical methods have been developed (Schneider and Smith, 1968a; Schneider and Smith, 1968b; Gunn and England, 1971; Wakao and Tanisho, 1974; Bashi and Gunn, 1977; Hsu and Haynes, 1981; Cresswell and Orr, 1982; Rodrigues, *et al.*, 1982; Hyun and Danner, 1985; Schneider, 1986).

4.1.1 Experimental Techniques

Experimental techniques of the chromatographic method can be classified in two categories: the fixed bed method and single pellet diffusion cell method.

4.1.1.1 Single Pellet Diffusion Cell Method

The single pellet diffusion cell technique uses a single or a small group of pellets either sealed into or supported in a closed chamber (cell). The concentration of a tracer gas is measured as a function of time at both the cell entrance and exit, following the imposition of a concentration disturbance upstream from the cell. The diffusion cell method is designed primarily to resolve the flow and the diffusive phenomena of interest within the porous medium by eliminating axial dispersion and external mass transfer (Dogu and Smith, 1976). An accurate estimation of the intraparticle diffusivity can be obtained from the first order moment of the response. The earliest diffusion cell were steady state in character, but unsteady state techniques have become increasingly popular in recent years. The disadvantage of this technique is that only catalysts with large particle size can be used.

4.1.1.2 Fixed Bed Method

The fixed bed method offers the attraction of simplicity of design. It can be used for commercial catalyst pellets and can closely reproduce the flow pattern to be met under reactive conditions. Fixed bed systems come in two extreme forms, i.e., the conventional wide-body bed and the single pellet string reactor (SPSR) (Cresswell and Orr, 1982).

In the wide-body bed system the axial dispersion plays a significant role. The model based on the Kubin-Kucera theory requires that the system presents linear behaviour, and that the pressure drop must be a small fraction of the total pressure, in order to keep the carrier gas velocity independent of axial position. However, too low gas velocity and laminar flow introduce external mass transfer resistance. Under these conditions the response of tracer gas is not sensitive to the intraparticle mass transfer (Chou, 1978). For this reason, the single pellet string reactor, which can be operated with high carrier gas velocity, was developed.

The single pellet string reactor was first developed by Scott *et al.* (1974). In this technique, the pellet size is just slightly smaller than the column diameter, that is, the ratio of column diameter to pellet diameter is in the range 1.1 to 1.4, in order to eliminate the possibility of fluid by-passing along the wall. Because of the narrow space between the pellet and the column interior wall, a higher carrier gas linear velocity can be reached under small pressure drop through the column. High carrier gas velocity results in a small external film mass transport resistance. The single pellet string reactor is a preferred type of column for determining intraparticle diffusivity, since the influence of axial dispersion here is limited within manageable range. If the pellet is well arranged inside the column to form an infinite cylinder, a theoretical estimation of the axial dispersion for the coaxial cylinder is possible, no adjustable axial dispersion parameters need to be determined from the experimental data, and more accurate effective diffusivity values can be obtained. Because of its efficiency and simplicity, the single pellet string reactor method has become a dominant method in determining intraparticle diffusivities (Chou, 1978; 1979).

4.1.2 Mathematical Techniques for Parameter Estimation

The dynamic response of a bed packed with porous pellets is influenced by dispersion in the bed, by mass exchange between fluid and pellets, and by intraparticle diffusion. In principle, the measurement of the response of the bed to a known stimulus may be used to provide estimates of the coefficients for each process, but in practical experiments the response may be sensitive to some processes and insensitive to others. A variety of theoretical methods may be used in the analysis of the response.

4.1.2.1 *Minimum Variance Search (Curve Fitting) Method*

In this class of methods, the variance of the experimental measurements about a theoretical curve is calculated, and the values of the parameters are varied so that the variance is reduced and a minimum is found. The values of the parameters associated with the minimum variance are taken to be the best values given by those experiments. The variance may be calculated in the time domain by numerical integration of the partial differential equations, in the transform (Laplace) domain, or in the frequency (Fourier) domain. As described by Hays *et al.* (1967), it can be shown that parameter estimation from minimum variance in the transform and frequency domains is equivalent to that in the time domain. Therefore, the analytical solution of the mathematical model in the Laplace domain can be used directly to make the curve fitting, thus avoiding the complicated inversion of the Laplace transformed expression for the response curve. However, Bashi and Gunn (1977) pointed out that in this method, if the parameters to be estimated are more than one, due to the presence of interaction between the parameters and of experimental errors, the values of parameters can be uncertain.

4.1.2.2 *Moment Method*

This is a simple method compared with the other methods. Theoretical expressions for the moments can be obtained from the model equations which describe the processes occurring in the system. The method then comprises matching the experimentally measured moment with the theoretical expression. In practice, only zero, first, and second order moments are useful since higher order moments can rarely be determined accurately from the experimental response curves. The method is easy to apply because simple relations are usually obtained between the dynamic parameters and the moments.

4.1.2.3 *Analytical Method*

This method uses analytical relationships between the process coefficients and certain integrals of the response in Laplace domain. The functional dependence of the coefficients upon a parameter of the integral is examined, and this simple functional dependence can be used to determine the process coefficients. Since additional information is introduced to remove the interaction between parameters, isolated errors can be identified and the effect of distributed errors may be minimised, it can be concluded that the analytical method is superior to both the

minimum variance search and the moment method (Bashi and Gunn, 1977). Unfortunately, if the solution of the mathematical model in the Laplace or Fourier domains has an intricate expression, it is difficult, or even impossible to get an analytical relationship between the process coefficients and the integral of the responses.

4.1.3 The Objective of the Present Work

Intraparticle diffusion has traditionally been considered as the only mechanism for mass transfer inside catalysts pellets. Since the seventies it has been pointed out that intraparticle convection also contributes to mass transfer in large-pore catalysts (Komiyama and Inoue, 1974; Nir and Pismen, 1977; Cresswell, 1985). It was shown that in the intermediate regime intraparticle convection leads to an improvement of the effectiveness factor of the catalyst. Another significant progress was made by Rodrigues *et al* (1982). An analytical relationship between intraparticle convection and effective diffusivity within the catalyst pellet was obtained. This relationship not only gives a successful explanation of the variation of effective diffusivities with flowrate in the measurement but also makes it possible to quantify intraparticle convection by using the chromatographic method.

The objective of the present work is two folds. First, the establishment of mathematical models for pellets with different geometries - solid cylinder, hollow cylinder and sphere - which are common in industry. All these pellets may have large-pore structures and intraparticle convection will be considered in the models. For the hollow cylinder catalyst an equivalence with slab geometry is developed for first-order reaction. Second, the measurements of the intraparticle diffusivities and the identification of intraparticle convection in such permeable catalysts with these various geometries using the gas chromatographic technique.

4.2 MATHEMATICAL MODEL

4.2.1 Model Equation for Fixed Bed

In a column with length of L packed with porous pellets, the differential mass balance equation for a non-adsorbed tracer and isothermal operation at unsteady-state can be written as

$$\epsilon D_{ax} \frac{\partial^2 C}{\partial X^2} - u_o \frac{\partial C}{\partial X} - \epsilon \frac{\partial C}{\partial t} - (1 - \epsilon) \epsilon_p \frac{\partial \langle C_p \rangle}{\partial t} = 0 \quad (4.1)$$

The boundary conditions are

$$X = 0 \quad C = M\delta(t) \quad (4.1a)$$

$$X = \infty \quad C = \text{finite} \quad (4.1b)$$

and the initial condition is

$$t = 0 \quad C = 0 \quad (4.1c)$$

where ε is the bed porosity; D_{ax} is the axial dispersion coefficient; u_0 is the gas superficial velocity through the column; C is the tracer gas concentration in the bulk phase; X is the axial coordinate in the bed; ε_p is the pellet porosity; $\langle C_p \rangle$ is the average concentration of the tracer in the pore inside the pellet; and t is the time. The concentration pulse is considered as a Dirac function $\delta(t)$, M is the pulse strength.

The solution of Equation 4.1 in the Laplace domain at $X = L$ is

$$\bar{C} = M \exp \left[\frac{Pe}{2} \left(1 - \sqrt{1 + \frac{4N(s)}{Pe}} \right) \right] \quad (4.2)$$

where Pe is the Peclet number defined as

$$Pe = \frac{u_0 L}{\varepsilon D_{ax}} \quad (4.3)$$

and

$$N(s) = [\varepsilon + (1 - \varepsilon)\varepsilon_p \langle \bar{C}_p \rangle] \tau s. \quad (4.4)$$

Here

$$\tau = \frac{L}{u_0} \quad (4.5)$$

is the space time; s is the Laplace transform parameter; $\langle \bar{C}_p \rangle$ is the dimensionless average concentration inside the pellet in the Laplace domain and it can be obtained, for different geometries, from the pellet mass balance equation.

The transfer function for a fixed bed is then obtained

$$G(s) = \exp \left[\frac{Pe}{2} \left(1 - \sqrt{1 + \frac{4N(s)}{Pe}} \right) \right] \quad (4.6)$$

4.2.1 Pellet Model Equations

In order to obtain an expression for $\langle \bar{c}_p \rangle$, it is necessary to know the pellets geometry. Hence the model equations for the hollow cylinder geometry are derived for the first time and equivalence between this geometry and to slab geometry is established. The work for the solid cylinder (finite) geometry and the sphere geometry has been done before (Lu, *et al.*, 1993; Nan, *et al.*, 1995), the main results are presented here.

4.2.1.1 Solid Cylinder Pellet

The unsteady state differential mass balance equation for a solid cylinder pellet is

$$D_e \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_p}{\partial r} \right) + \frac{\partial^2 C_p}{\partial z^2} \right] - v_0 \frac{\partial C_p}{\partial z} - \varepsilon_p \frac{\partial C_p}{\partial t} = 0 \quad (4.7)$$

where the cylinder pellets are placed in parallel to the bulk gas flow. Assuming that the size of the pellet is very small compared to the size of the bed, the assumption that the gas concentration around the pellet is uniform is a reasonable one. Under high bulk gas velocity, the film mass transport resistance can be ignored (Cresswell and Orr, 1982), and the boundary conditions and the initial condition may be written as

$$r = R, \quad \forall z \quad C_p = C \quad (4.7a)$$

$$z = 0 \text{ and } z = \ell, \quad \forall r \quad C_p = C \quad (4.7b)$$

$$r = 0 \quad C_p = \text{finite} \quad (4.7c)$$

$$t = 0 \quad C_p = 0 \quad (4.7d)$$

where D_e is the tracer effective diffusivity within the pellet; C_p is the tracer gas concentration within the pellet; v_0 is the superficial intraparticle flow velocity; r and z are the radial and longitudinal coordinates, respectively. R and ℓ are the pellet radius and length, respectively.

Introducing the following dimensionless variables

$$x = \frac{z}{\ell}; \quad \rho = \frac{r}{R} \quad (4.8)$$

and taking the Laplace transform with respect to the time t , the dimensionless equation in the Laplace domain for the pellet is obtained

$$\omega^2 \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \bar{c}_p}{\partial \rho} \right) \right] + \frac{\partial^2 \bar{c}_p}{\partial x^2} - 2\lambda \frac{\partial \bar{c}_p}{\partial x} - \tau_{Ds} \bar{c}_p = 0 \quad (4.9)$$

with

$$\rho = 1, \quad \forall x \quad \bar{c}_p = 1 \quad (4.9a)$$

$$x = 0 \text{ and } x = 1 \quad \forall \rho \quad \bar{c}_p = 1 \quad (4.9b)$$

$$\rho = 0 \quad \bar{c}_p = \text{finite} \quad (4.9c)$$

and

$$\bar{c}_p = \bar{C}_p / \bar{C} \quad (4.9d)$$

The following dimensionless parameters were introduced

$$\text{The Intraparticle Peclet Number} \quad \lambda = \frac{v_o \ell}{2D_e} \quad (4.10a)$$

$$\text{The Length to Radius Aspect Ratio} \quad \omega = \frac{\ell}{R} \quad (4.10b)$$

$$\text{The Intraparticle Diffusion Time Constant} \quad \tau_D = \frac{\varepsilon_p \ell^2}{D_e} \quad (4.10c)$$

The dimensionless average concentration in the Laplace domain within the pellet is (see Section 3.2.2 for details)

$$\langle \bar{c}_p \rangle = 1 - \sum_{n=1}^{\infty} \frac{4\tau_D s}{\alpha_n^2 (\omega^2 \alpha_n^2 + \tau_D s)} \left[1 + \left(\frac{\cosh \lambda}{\sinh \beta_n} - \coth \beta_n \right) \frac{2\beta_n}{\beta_n^2 - \lambda^2} \right] \quad (4.11)$$

where, α_n are the roots of

$$J_0(\alpha_n) = 0 \quad (4.12a)$$

J_0 is the zero order Bessel functions of the first kind, and

$$\beta_n = \sqrt{\lambda^2 + \omega^2 \alpha_n^2 + \tau_D s} \quad (4.12b)$$

The moment of order n of the pulse response can be obtained from the van der Laan (1958) relationship.

$$m_n = (-1)^n \frac{\partial^n G(s)}{\partial s^n} \Big|_{s=0} \quad (4.13)$$

The first absolute moment (mean retention time) μ_1 and second central moment (variance) μ_2 are given by

$$\mu_1 = \frac{m_1}{m_0} \quad (4.14)$$

$$\mu_2 = \frac{m_2}{m_0} - \mu_1^2 \quad (4.15)$$

From Equation 4.6 the first absolute moment and the second central moment of the response correspondent to the fixed bed are, respectively

$$\mu_1 = [\varepsilon + (1 - \varepsilon)\varepsilon_p]\tau \quad (4.16)$$

$$\mu_2 = \mu_1^2 \frac{2}{Pe} + \frac{4(1 - \varepsilon)\varepsilon_p \tau \tilde{\tau}_D}{\omega^2} \sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \left[1 + \left(\frac{\cosh \lambda}{\sinh \gamma_n} - \coth \gamma_n \right) \frac{2\gamma_n}{\gamma_n^2 - \lambda^2} \right] \quad (4.17)$$

where

$$\gamma_n = \sqrt{\lambda^2 + \omega^2 \alpha_n^2} \quad (4.18)$$

If intraparticle convection is not explicitly taken into account, the effective diffusivity, D_e , should be replaced by the "apparent" diffusivity $\tilde{D}_e$ which lumps both diffusion and convection and the model equations become

$$\tilde{D}_e \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_p}{\partial r} \right) + \frac{\partial^2 C_p}{\partial z^2} \right] - \varepsilon_p \frac{\partial C_p}{\partial t} = 0 \quad (4.19)$$

$$r = R, \quad \forall z \quad C_p = C \quad (4.19a)$$

$$z = 0 \text{ and } z = \ell, \quad \forall r \quad C_p = C \quad (4.19b)$$

$$r = 0 \quad C_p = \text{finite} \quad (4.19c)$$

$$t = 0 \quad C_p = 0 \quad (4.19d)$$

The second central moment is then obtained as

$$\mu_2 = \mu_1^2 \frac{2}{Pe} + \frac{4(1 - \varepsilon)\varepsilon_p \tau \tilde{\tau}_D}{\omega^2} \sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \left(1 - \frac{\tanh \zeta_n}{\zeta_n} \right) \quad (4.20)$$

where

$$\zeta_n = \frac{\omega \alpha_n}{2} \quad (4.21)$$

and $\tilde{\tau}_D$ is the apparent intraparticle diffusion time constant defined as

$$\tilde{\tau}_D = \frac{\varepsilon_p \ell^2}{\tilde{D}_e} \quad (4.22)$$

The relationship between the true diffusivity, D_e , and the apparent diffusivity, $\tilde{D}_e$, for the pellet can be expressed as (Rodrigues *et al.*, 1982)

$$\tilde{D}_e = \frac{D_e}{f(\lambda)} \quad (4.23)$$

and $f(\lambda)$ can be obtained by comparing Equation 4.17 to Equation 4.20

$$f(\lambda) = \frac{\sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \left[1 + \left(\frac{\cosh \lambda}{\sinh \gamma_n} - \coth \gamma_n \right) \frac{2\gamma_n}{\gamma_n^2 - \lambda^2} \right]}{\sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \left(1 - \frac{\tanh \zeta_n}{\zeta_n} \right)} \quad (4.24)$$

Studying the limits of this relationships shows that when λ goes from 0 to ∞ , $f(\lambda)$ changes between 1 and 0, as expected.

Figure 4.1 shows $f(\lambda)$ for different values of the aspect ratio. It can also be shown that as $\omega \rightarrow 0$, $f(\lambda)$ takes the same values as those for the slab geometry.

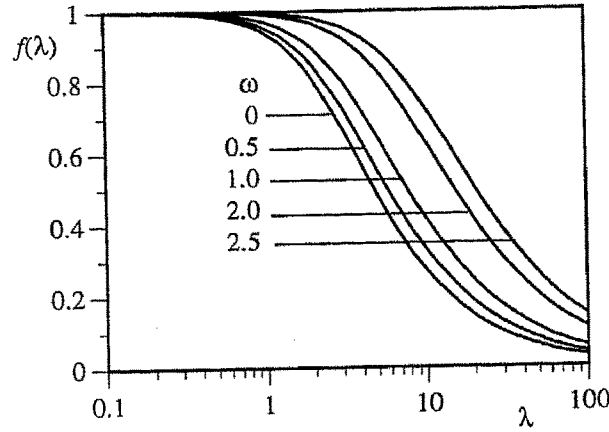


Figure 4.1 The function $f(\lambda)$ for the solid cylinder pellet for different values of the aspect ratio, ω .

4.2.1.1 Hollow Cylinder Pellet

Assuming the hollow cylinder pellets are placed in parallel to the bulk gas flow, the unsteady-state differential mass balance equation for the hollow cylinder pellet is

$$D_e \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_p}{\partial r} \right) + \frac{\partial^2 C_p}{\partial z^2} \right] - v_o \frac{\partial C_p}{\partial z} - \epsilon_p \frac{\partial C_p}{\partial t} = 0 \quad (4.25)$$

with the following boundary and initial conditions

$$r = R_1 \text{ and } r = R_2, \quad \forall z \quad C_p = C \quad (4.25a)$$

$$z = 0 \text{ and } z = \ell, \quad \forall r \quad C_p = C \quad (4.25b)$$

$$t = 0 \quad C_p = 0 \quad (4.25c)$$

here R_1 and R_2 are the internal and the external radius of the hollow cylinder pellet, respectively.

Introducing the following dimensionless variables

$$x = \frac{z}{\ell}; \quad \rho = \frac{r}{R_2} \quad (4.26)$$

and taking the Laplace transform with respect to the time variable t , the mass balance equation becomes:

$$\omega^2 \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \bar{c}_p}{\partial \rho} \right) \right] + \frac{\partial^2 \bar{c}_p}{\partial x^2} - 2\lambda \frac{\partial \bar{c}_p}{\partial x} - \tau_D s \bar{c}_p = 0 \quad (4.27)$$

with the boundary conditions

$$\rho = a \text{ and } \rho = 1, \quad \forall x \quad \bar{c}_p = 1 \quad (4.27a)$$

$$x = 0 \text{ and } x = 1, \quad \forall \rho \quad \bar{c}_p = 1 \quad (4.27b)$$

and

$$\bar{c}_p = \bar{C}_p / \bar{C} \quad (4.27c)$$

The dimensionless parameters are similar to the ones defined in the case of the solid cylinder, except that is now defined with respect to the external radius and an additional parameter is introduced

$$\text{The Length to Radius Aspect Ratio} \quad \omega = \frac{\ell}{R_2} \quad (4.28a)$$

$$\text{The Ratio between Internal and External Radius} \quad a = \frac{R_1}{R_2} \quad (4.28b)$$

The dimensionless average concentration in Laplace domain within the pellet is (see Appendix 4.A for details).

$$\langle \bar{c}_p \rangle = 1 - \sum_{n=1}^{\infty} \frac{2\tau_D s M_n^2}{(1-a^2)(\omega^2 \alpha_n'^2 + \tau_D s) N_n} \left[1 + \left(\frac{\cosh \lambda}{\sinh \beta_n'^2} - \coth \beta_n'^2 \right) \frac{2\beta_n'}{\beta_n'^2 - \lambda^2} \right] \quad (4.29)$$

where α_n' is the root of

$$J_0(a\alpha_n') Y_0(\alpha_n') - J_0(\alpha_n') Y_0(a\alpha_n') = 0 \quad (4.30)$$

and

$$\beta_n' = \sqrt{\lambda^2 + \omega^2 \alpha_n'^2 + \tau_D s} \quad (4.31)$$

$$N_n = \int_a^1 [J_0(a\alpha_n') Y_0(\alpha_n' \rho) - J_0(\alpha_n' \rho) Y_0(a\alpha_n')]^2 \rho d\rho \quad (4.32)$$

$$M_n = \frac{1}{\alpha'_n} \left\{ J_0(a\alpha'_n) [Y_1(\alpha'_n) - aY_1(a\alpha'_n)] - Y_0(a\alpha'_n) [J_1(\alpha'_n) - aJ_1(a\alpha'_n)] \right\} \quad (4.33)$$

Y_0 and Y_1 are the zero and first order Bessel functions of the second kind, respectively.

As before, back substituting Equation 4.29 in Equation 4.6 and using the relationships in Equations 4.13 to 4.15, the first absolute and second central moments of the response are obtained, respectively

$$\mu_1 = [\varepsilon + (1 - \varepsilon)\varepsilon_p] \tau \quad (4.34)$$

$$\mu_2 = \mu_1^2 \frac{2}{Pe} + \frac{2(1 - \varepsilon)\varepsilon_p \tau \tau_D}{(1 - a^2)\omega^2} \sum_{n=1}^{\infty} \frac{M_n^2}{\alpha'^2_n N_n} \left[1 + \left(\frac{\cosh \lambda}{\sinh \gamma'_n} - \coth \gamma'_n \right) \frac{2\gamma'_n}{\gamma'^2_n - \lambda^2} \right] \quad (4.35)$$

where

$$\gamma'_n = \sqrt{\lambda^2 + \omega^2 \alpha'^2_n} \quad (4.36)$$

If intraparticle convection is not expressed in the model equation, the second central moment of the response can be written as

$$\mu_2 = \mu_1^2 \frac{2}{Pe} + \frac{2(1 - \varepsilon)\varepsilon_p \tau \tau_D}{(1 - a^2)\omega^2} \sum_{n=1}^{\infty} \frac{M_n^2}{\alpha'^2_n N_n} \left(1 - \frac{\tanh \zeta'_n}{\zeta'_n} \right) \quad (4.37)$$

with

$$\zeta'_n = \frac{\omega \alpha'_n}{2} \quad (4.38)$$

Similarly, the expression for $f(\lambda)$ now becomes

$$f(\lambda) = \frac{\sum_{n=1}^{\infty} \frac{M_n^2}{\alpha'^2_n N_n} \left[1 + \left(\frac{\cosh \lambda}{\sinh \gamma'_n} - \coth \gamma'_n \right) \frac{2\gamma'_n}{\gamma'^2_n - \lambda^2} \right]}{\sum_{n=1}^{\infty} \frac{M_n^2}{\alpha'^2_n N_n} \left(1 - \frac{\tanh \zeta'_n}{\zeta'_n} \right)} \quad (4.39)$$

Studying the limits of this relationship, shows that when $a \rightarrow 0$, Equation 4.39 has the same form as Equation 4.24.

Figure 4.2 shows $f(\lambda)$ for different values of the aspect ratio, ω , in the case of $a = 0.36$ which is the value for the pellet used in the experimental part of the present work.

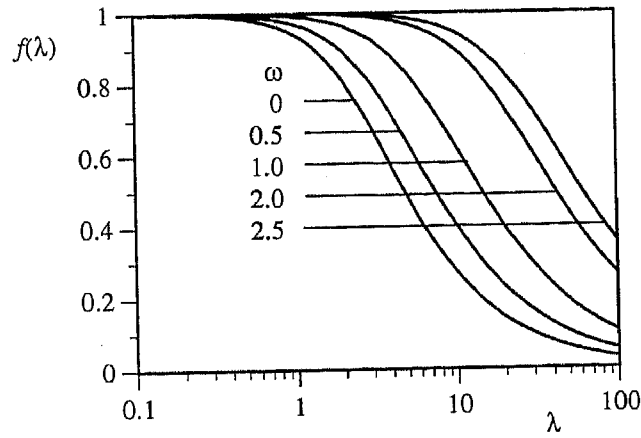


Figure 4.2 The function $f(\lambda)$ for the hollow cylinder pellet for different values of the aspect ratio, ω , and $a = 0.36$.

In Appendix 4.B an equivalence between the hollow cylinder and slab geometries is established using Equation 4.29.

4.2.1.3 Sphere Pellet

The mass balance equation inside the pellet may be written as

$$D_e \nabla^2 C_p = v_0 \cos \theta \frac{\partial C_p}{\partial r} + v_0 \frac{\sin^2 \theta}{r} \frac{\partial C_p}{\partial \cos \theta} + \varepsilon_p \frac{\partial C_p}{\partial t} \quad (4.40)$$

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \cos \theta} \left(\sin^2 \theta \frac{\partial}{\partial \cos \theta} \right) \quad (4.40a)$$

with following boundary and initial conditions

$$r = R \quad C_p = C \quad (0 \leq \theta < 2\pi) \quad (4.40b)$$

$$t = 0 \quad C_p = 0 \quad (4.40c)$$

where r and θ are the sphere spatial coordinates and R is the pellet radius.

Introducing the dimensionless variables

$$\rho = \frac{r}{R}; \quad \mu_\theta = \cos \theta \quad (4.41)$$

and the parameters

$$\lambda = \frac{v_0 R}{D_e}; \quad \tau_D = \frac{\varepsilon_p R^2}{D_e} \quad (4.42)$$

the dimensionless equation in the Laplace domain can be obtained

$$\nabla^2 \bar{c}_p = \lambda \mu_\theta \frac{\partial \bar{c}_p}{\partial \rho} + \lambda \frac{1 - \mu_\theta^2}{\rho} \frac{\partial \bar{c}_p}{\partial \mu_\theta} + \varepsilon_p \tau_{Ds} \quad (4.43)$$

$$\nabla^2 = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial}{\partial \mu_\theta} \left[(1 - \mu_\theta)^2 \frac{\partial}{\partial \mu_\theta} \right] \quad (4.43a)$$

with the following boundary condition

$$\rho = 1 \quad \bar{c}_p = 1 \quad (-1 \leq \mu_\theta \leq 1) \quad (4.43b)$$

and

$$\bar{c}_p = \bar{c}_p / \bar{C} \quad (4.43c)$$

It can be shown that Equation 4.43 has the same form as the steady state mass balance equation for the case of irreversible first order reaction (Nir and Pismen, 1977) by replacing the square of the Thiele modulus, ϕ^2 , by τ_{Ds} . Thus the average dimensionless concentration inside the pellet in the Laplace domain can be written as

$$\langle \bar{c}_p \rangle = \frac{3\pi}{\tau_{Ds} \lambda} \sum_{n=0}^{\infty} (-1)^n (2n+1) I_{n+1/2}^2 \left(\frac{\lambda}{2} \right) \left[\frac{\beta I_{n+3/2} \left(\frac{\beta}{2} \right)}{2 I_{n+1/2} \left(\frac{\beta}{2} \right)} - \frac{\lambda I_{n+3/2} \left(\frac{\lambda}{2} \right)}{2 I_{n+1/2} \left(\frac{\lambda}{2} \right)} \right] \quad (4.44)$$

where $I_{n+1/2}$ and $I_{n+3/2}$ are the modified spherical Bessel function of the first kind and

$$\beta = \sqrt{\lambda^2 + 4\tau_{Ds}} \quad (4.45)$$

It is known that the first absolute moment is independent of the pellet geometry and of the dynamic parameters (Kucera, 1965) and that it has the same form as that in Equations 4.16 and 4.34:

$$\mu_1 = [\varepsilon + (1 - \varepsilon)\varepsilon_p] \tau \quad (4.46)$$

The second moment has been derived by Carta *et al.* (1992) and has the form

$$\mu_2 = \mu_1^2 \frac{2}{P_e} + 2(1 - \varepsilon)\varepsilon_p \tau M'(0) \quad (4.47)$$

where $M'(0)$ is an intricate expression dependent of λ . However, Carta *et al.* (1992) showed that

$$M'(0) = \frac{\tau_D f(\lambda)}{15} \quad (4.48)$$

where $f(\lambda)$ has the same form as that for the slab pellet (Rodrigues *et al.*, 1982) provided that ℓ is replaced by $R/3$, that is

$$f(\lambda) = \frac{3}{\lambda/3} \left(\frac{1}{\tanh \lambda/3} - \frac{1}{\lambda/3} \right) \quad (4.49)$$

The validity of this approximation has been verified by Lu *et al.* (1993).

If intraparticle convection is expressed in the model equation, the second central moment of the response for sphere pellet is well known, and has the form (Ruthven, 1984):

$$\mu_2 = \mu_1^2 \frac{2}{Pe} + \frac{2(1-\varepsilon)\varepsilon_p \tau \tilde{\tau}_D}{15} \quad (4.50)$$

where

$$\tilde{\tau}_D = \frac{\varepsilon_p R^2}{\tilde{D}_e} \quad (4.51)$$

4.3 EXPERIMENTAL WORK

4.3.1 Apparatus Description

A diagram of the experimental apparatus is shown in Figure 4.3. For measurements with cylindrical geometry pellets the single pellet string reactor method was used, while in the case of spherical pellets, the column was randomly packed. Two cylinders of compressed helium and nitrogen were connected to mass flow controllers. The inlet flow rate was accurately controlled by the mass flow controller (HASTINGS MODEL HFC-202, TELEDYNE HASTINGS-RAYDIST, U. S. A). After the mass flow controller, gas nitrogen entered the column as the carrier gas. Gas helium passed through a 6-port two position injection valve with which a pulse of helium was injected into the main nitrogen stream. A tee junction with the main nitrogen line led the reference gas to the detector and the flow rate was adjusted by a needle valve. All of the connecting lines after the injection valve are of 1/16" tube in order to minimise the dead volume. The outlet flow rate from the detectors was measured with a soap film flow meter. Injections and responses of tracer were measured with two micro thermal conductivity detectors (MODEL 40-202, GOW-MAC INSTRUMENT CO., IRELAND). From these detectors the concentration of the tracer gas in the carrier gas was automatically recorded by the data acquisition system which is composed by a computer and an analog to digital conversion board (DT2801 USA). The pressure difference between both sides of the column was measured by an accurate differential pressure transducer (MODEL DPI 260, DRUCK LIMITED, ENGLAND).

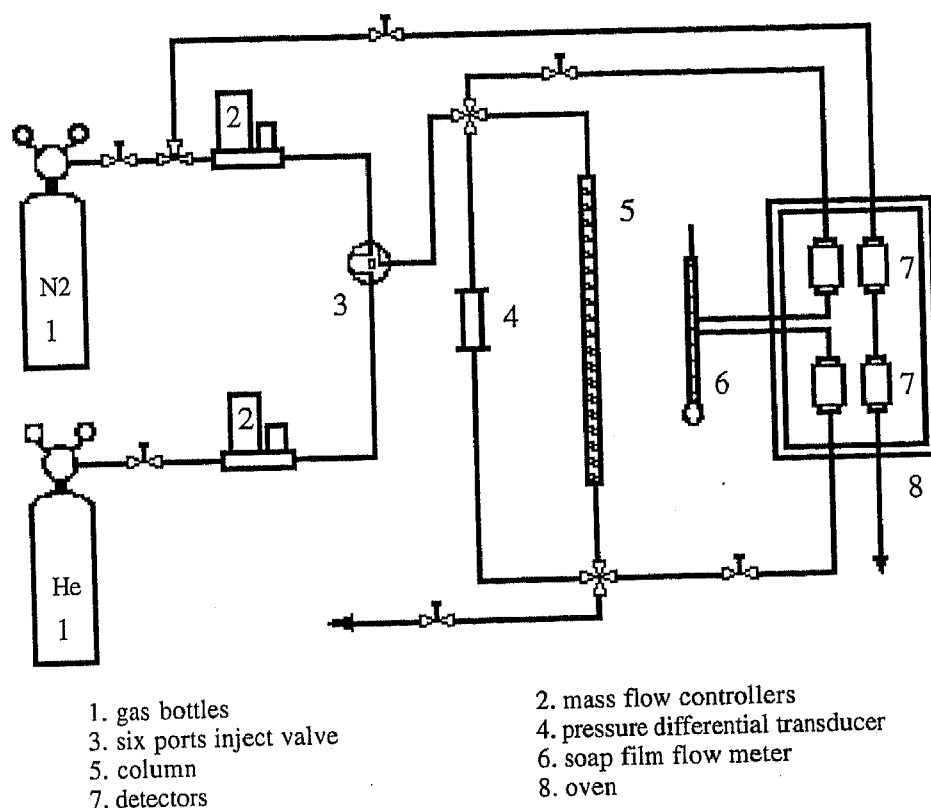


Figure 4.3 Diagram of experimental apparatus for diffusivity measurements.

4.3.2 Experimental Conditions

The experimental conditions are listed in Table 4.1. All experiments were conducted at ambient temperature and atmospheric pressure. In all cases the bed length to pellet diameter ratio is sufficiently large so that the end effects could be safely neglected (Scott, *et. al.*, 1974). The solid cylinder pellets are α -alumina supported steam-reforming catalyst. The hollow cylinder pellets are α -alumina supported ethylene-oxidation catalyst. The sphere pellets are a light weight aggregate (PORAVER expanded glass pellets) supplied by Dennert Poraver Company (Germany). Porosimetry data and photographs of these pellets are shown in Appendix 4.C.

4.3.3 Experimental Procedure

4.3.3.1 Packing the column

The single pellet string reactor technique was used in the cases of the solid and the hollow cylinder pellets. The columns used were a stainless steel tube, for the solid cylinder pellets and a plastic tube for the hollow cylinder pellets, and in both cases the column diameters are slightly larger than the diameters of the pellets (see Table 4.1 and Table 4.2). Two Swagelok reducers were used in both sides of the tubes to connect to the tube of 1/8". At the bottom of the tube a small spring was placed to support the pellets. The solid cylinder pellets were placed one above the other coaxially inside the column. A scheme of this procedure is shown in the Figure 4.4. For the hollow cylinder pellets a thread was placed in the central hole in order to avoid the

possibility of gas by-passing along the hole. The thread is made of a group of fine copper wires. Because the pellets have uneven surfaces, the contact between two pellets is not too tight and gas diffusion at the plate side must be considered.

Table 4.1 Experimental conditions

	solid cylinders	hollow cylinders	large spheres	small spheres
Temperature	$T=293\text{ K}$	$T=293\text{ K}$	$T=293\text{ K}$	$T=293\text{ K}$
Pressure (outlet)	$P=1.194\text{ bar}$	$P=1.194\text{ bar}$	$P=1.194\text{ bar}$	$P=1.194\text{ bar}$
Carrier gas	N_2	N_2	N_2	N_2
Tracer gas	He	He	He	He
Column length	$L=150\text{ cm}$	$L=150\text{ cm}$	$L=150\text{ cm}$	$L=150\text{ cm}$
Column diameter	$d_c=1.4\text{ cm}$	$d_c=1.4\text{ cm}$	$d_c=1.4\text{ cm}$	$d_c=1.4\text{ cm}$
Number of pellets	$n=112$	$n=213$		
Bulk density*			$\rho_b=0.19\text{ g/ml}$	$\rho_b=0.23\text{ g/ml}$
Grain density*			$\rho_p=0.34\text{ g/ml}$	$\rho_p=0.40\text{ g/ml}$
Bed porosity**	$\varepsilon=0.22$	$\varepsilon=0.42$	$\varepsilon=0.441$	$\varepsilon=0.425$
Pellet dimensions	$\ell=1.39\text{ cm}$ $R=0.605\text{ cm}$	$\ell=0.73\text{ cm}$ $R_1=0.14\text{ cm}$ $R_2=0.39\text{ cm}$	$d_p=0.3\text{ cm}$	$d_p=0.17\text{ cm}$
Pellet porosity	$\varepsilon_p=0.517$	$\varepsilon_p=0.498$	$\varepsilon_p=0.645$	$\varepsilon_p=0.800$
Mean pore diameter	$\bar{d}_{pore}=390\text{ \AA}$	$\bar{d}_{pore}=6.1\text{ }\mu\text{m}$	$\bar{d}_{pore}=2.7\text{ }\mu\text{m}$	$\bar{d}_{pore}=2.3\text{ }\mu\text{m}$
Median pore diameter	$\bar{d}_{pore}^{50}=2300\text{ \AA}$	$\bar{d}_{pore}^{50}=5.2\text{ }\mu\text{m}$	$\bar{d}_{pore}^{50}=23\text{ }\mu\text{m}$	$\bar{d}_{pore}^{50}=10\text{ }\mu\text{m}$

* data supplied by the Dennert Poraver Company (Germany)

** $\rho_b = \rho_p(1 - \varepsilon)$

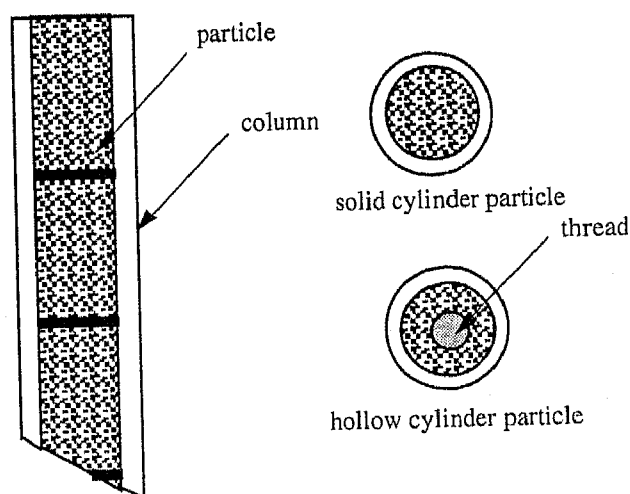


Figure 4.4 Scheme of column packing with the single pellet string method

The experiments with the sphere pellets were conducted using the fixed bed method and the pellets were packed at random in a stainless steel tube.

4.3.3.2 Calibration of volumetric flow rate of carrier gas

The mass flow controller readout must be calibrated with soap film flow meter before starting of experiments. The flow rate in the column can be determined by subtracting the flow rate from the top of the column to the detector from the value given by mass flow controller. The flow rate through the detectors should be as high as possible within their best sensitivity range in order to reduce the effects of the dead volume on the responses.

4.3.3.3 Dynamic determination

Before the column was connected to the detectors, a high velocity gas was introduced to the column and was vented at the bottom of it to blow out the ash, which adheres to the pellets, in order to keep the detector from being contaminated by this ash. Adjusting the gas velocity to a certain value, as the baselines of the thermal conductivity detectors reached constant values, the system is ready for starting the experiment. The sample valve position was quickly changed from the charge position to the injection position. The input and output signals were detected by detectors, recorded and displayed in the computer. The data acquisition period was 1/30 second. The regeneration was performed by changing the sample valve back to its charge position.

4.3.3.4 Data treatment

The dead volume contribution to the responses of both detectors must be subtracted from the corresponding response value to obtain the real response results. The dead volume can be measured from the tube dimensions.

The first absolute moment and second central moment of impulse response of the fixed bed were calculated from experimental data as follows:

$$\mu_1^{exp} = \frac{\int_0^{\infty} t C_o(t) dt}{\int_0^{\infty} C_o(t) dt} \quad (4.52)$$

$$\mu_2^{exp} = \frac{\int_0^{\infty} t^2 C_o(t) dt}{\int_0^{\infty} C_o(t) dt} - (\mu_1^{exp})^2 \quad (4.53)$$

And the contributions of the input pulse and the dead volume should be subtracted from the response peaks. The transfer function was calculated from following relationship:

$$G^{exp}(s) = \frac{\int_0^\infty C_o(t)e^{-st} dt / \int_0^\infty C_o(t) dt}{\int_0^\infty C_i(t)e^{-st} dt / \int_0^\infty C_i(t) dt} \quad (4.54)$$

where C_i is the inlet concentration and C_o is the outlet concentration of the trace gas. In the calculations the concentrations can be replaced by the detector signals, e.g., relative concentrations which are proportional to the actual concentration.

In the numerical integration the Simpson's method was used. In the data fitting, the objective functions were

$$\sum_{i=1}^n (Y_i^{exp} - Y_i^{th})^2 = 0 \quad (4.55)$$

where Y_i^{exp} represent the experimental values, e.g., μ_2^{exp} or $G^{exp}(s)$ and Y_i^{th} represent the theoretical values calculated from Equations 4.6 or 4.20, 4.37 and 4.51.

4.4 RESULTS AND DISCUSSION

4.4.1 First Moment and Pressure Drop

The first absolute moment is the mean retention time of tracer gas passing through the column. It depends on the space time and is not affected by transport phenomena in the system. In the experiments the first absolute moment can be measured at different flow rates. Figure 4.5 shows the plots of the experimental data in μ_1 versus $1/u_0$ for different pellet geometries.

If the column porosity is known, the pellet porosity can be calculated from the first absolute moment. In the case of the solid and hollow cylinder pellets, the column porosity in each case was estimated from the tube and pellet dimensions. For the sphere pellets the column porosity was calculated from the relationship $\rho_b = \rho_p(1 - \varepsilon)$. These values and the pellet porosity calculated from the first absolute moment equations are shown in Tables 4.1 through 4.4. Figure 4.5 shows that the plots μ_1 versus $1/u_0$ result in straight lines passing through the origin, indicating that the porosity values used are good estimates.

The pressure drop across the column were also measured in the experiments and are shown in Figure 4.6. It was found that the pressure drop depends on several factors. For the column packed with cylinder pellets, the width of the annular space ($R_c - R_p$) has a significant effect on the pressure drop. For the column packed with sphere pellets, the pressure drop is strongly influenced by pellet diameter, even when the column diameters are the same.

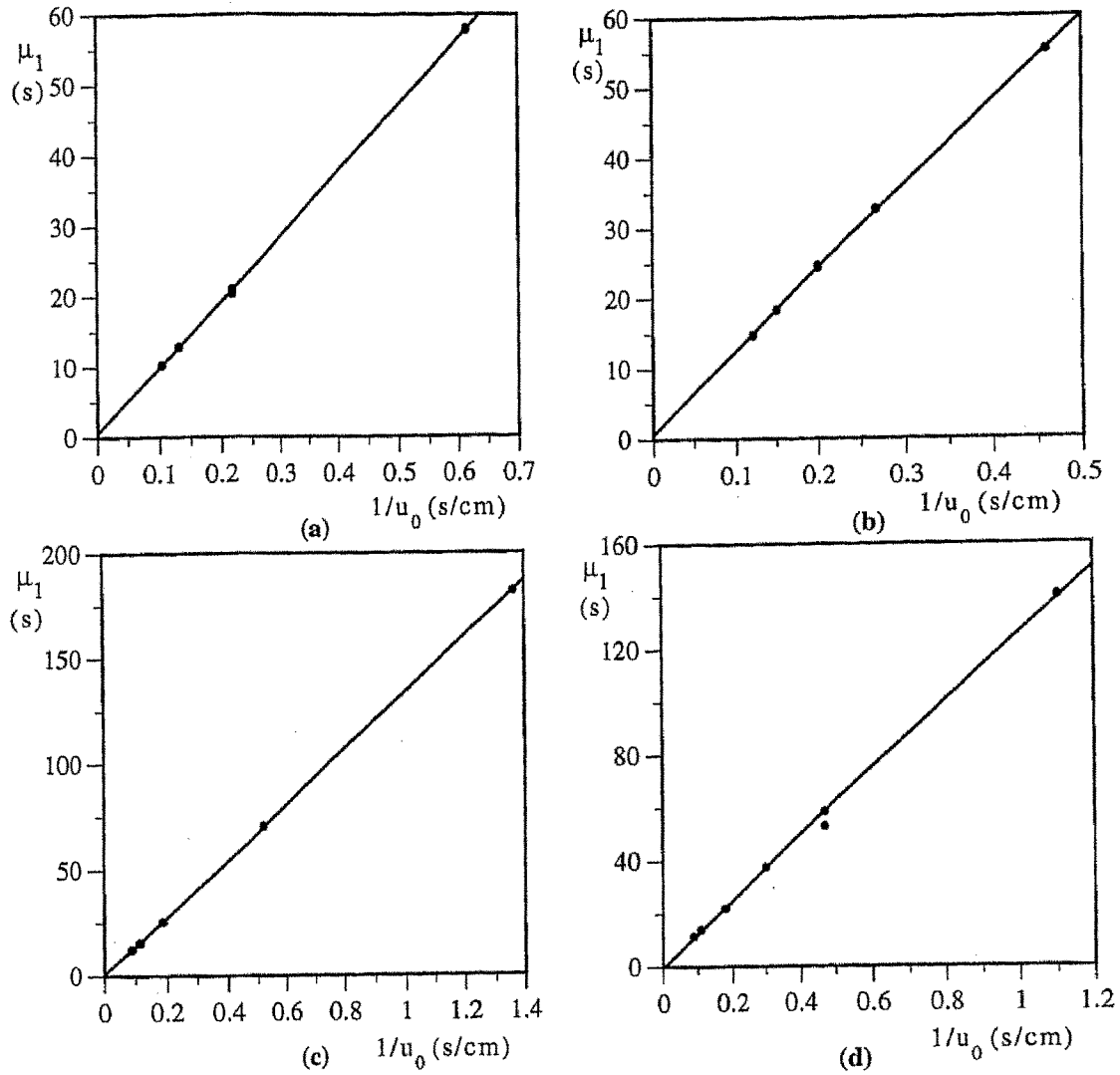


Figure 4.5 The first moment μ_1 versus $1/u_0$ for different pellets **a)** solid cylinder; **b)** hollow cylinder; **c)** sphere $d_p=0.17$ cm; **d)** sphere $d_p=0.3$ cm

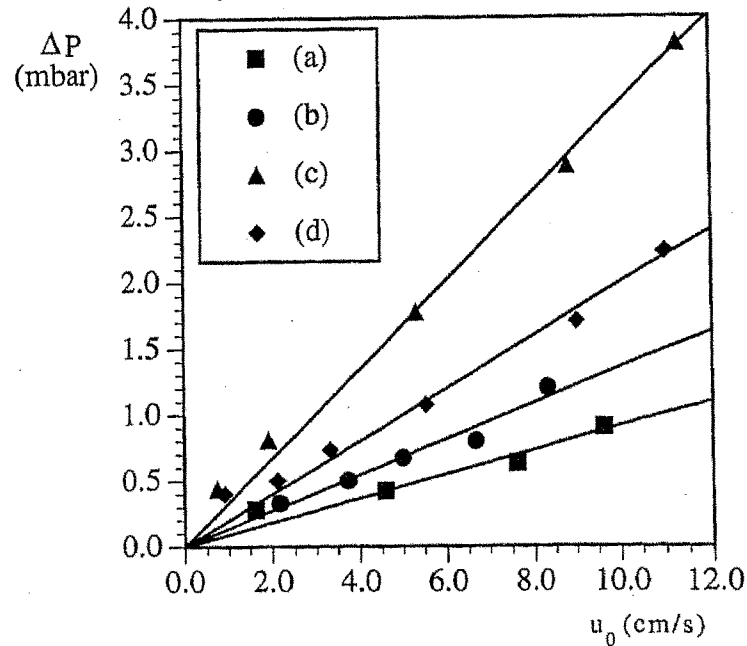


Figure 4.6 The pressure drop ΔP versus superficial velocity u_0 for different pellets **a)** solid cylinder; **b)** hollow cylinder; **c)** sphere $d_p=0.17$ cm; **d)** sphere $d_p=0.3$ cm

4.4.2 Intraparticle Effective Diffusivities

Typical input and output response signals are shown in Figure 4.7. From the shapes of the response curves the sensitivity to the parameters can be predicted. Based on an analysis of the theoretical response curves, Chou (1979) and Haynes (1988) showed that symmetrical response curves indicate that the major contribution to peak broadening is axial dispersion, while skewed response curves are sensitive to intraparticle diffusion. The tailing peaks observed in Figure 4.7 indicate that the experimental conditions were chosen within an acceptable range, and a reliable intraparticle diffusivity measurement can be measured.

There are two parameters involved in this system: one is the axial dispersion coefficient D_{ax} which is expressed in terms of the bed Peclet number, Pe , (Equation 4.3); the other is the intraparticle effective diffusivity, D_e , which may be expressed as the intraparticle diffusion time τ_D . These two parameters can be estimated in two different ways: from the second central moment; or from the transfer function given by Equation 4.6.

In the conventional moment method a set of second central moment values at different flow rates from the experiments is measured, and then, these values are matched with the theoretical expression by using a two parameter optimisation technique. In this case, the gas flow rate is the independent variable in the parameter estimation, thus the effective diffusivity must be independent of it. However, if intraparticle convection is considered, the effective diffusivity is replaced by the apparent effective diffusivity which is dependent on the gas flow rate. With the transfer function method, it has been also found that the two parameters present very strong interactions, making it impossible to get true values of diffusivity and Peclet number by using two parameters optimisation technique. It is then necessary, in both cases, to estimate the bed Peclet number from another independent method.

The estimation of the parameters using the transfer function method is done by choosing a set of values of the Laplace transform parameter, s , which in general may take any positive value. However, the selection of s values has a significant effect on the accuracy of the estimated parameters (Bashi and Gunn, 1977). If s is too big, a large weight is given to the frontal portion of the signal, while Equation 4.54 shows that if s is too small, the transfer function itself has little dispersion effect. Hopkins *et al.*, (1969) studied the effects of s and recommended the range $s = 2/\tau$ to $s = 5/\tau$.

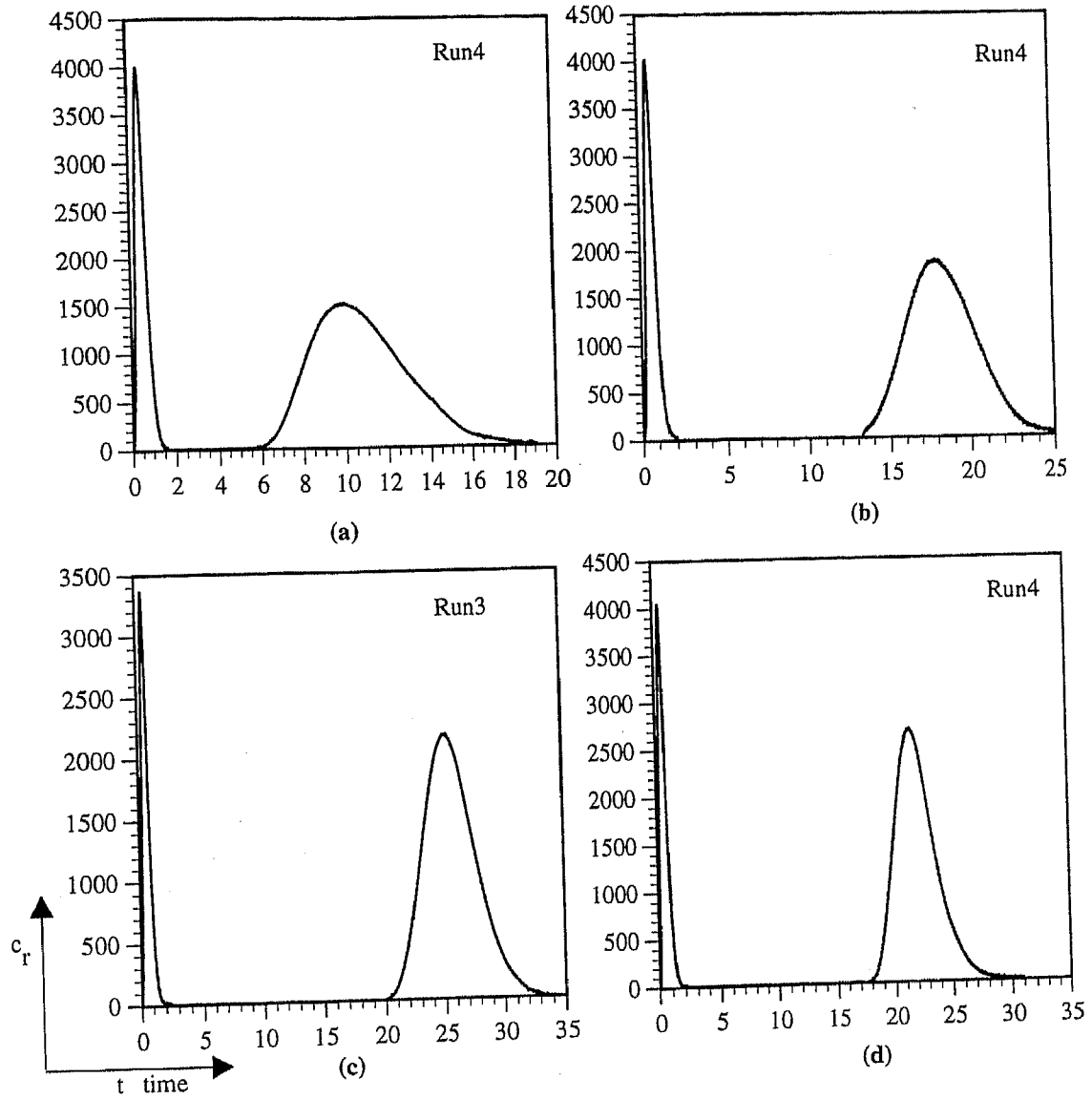


Figure 4.7 The input and output responses signals for different pellets **a)** solid cylinder; **b)** hollow cylinder; **c)** sphere $d=0.17\text{cm}$; **d)** sphere $d=0.3\text{cm}$ (c_r states the relative concentration)

4.4.2.1 Solid Cylinder Pellets

As it has been mentioned above, the packing of the cylinder pellets can be considered as a coaxial cylinder column. According to Aris (1959) the axial dispersion coefficient for a tracer in carrier gas in a coaxial cylinder column can be expressed as (Valus and Schneider, 1985)

$$D_{ax} = D_m + \frac{d^2 u_0^2}{k D_m} \quad (4.56)$$

where d is the width of the annular space ($d = R_c - R_p$); D_m is the molecular diffusivity; and k is a constant which is dependent on the ratio $g = R_p/R_c$. The calculation method for k is given in Appendix 4.D. For an empty tube, $g \rightarrow 0$, the usual value of $k = 48$ is obtained. For a planar slit, $g \rightarrow 1$, $k = 210$.

In this work, a modified chromatographic technique was proposed for the measurement of intraparticle effective diffusivities in the solid cylinder pellets. In order to demonstrate the reliability of this technique the transfer method was used to see if the same results can be obtained from different methods. A finite difference Levenberg-Marquardt algorithm was applied to solve the non-linear least squares problem. The values of $\tilde{D}_e$ obtained from the moment method and the value of Pe obtained from Equation 4.56 was chosen as the initial guesses of the parameter estimation. The results obtained are listed in Table 4.2, and show good agreement with those estimated from moment method. It was also found that parameter estimation is not sensitive to the Peclet number and the results are significantly affected by the initial guesses. An average value (with 95% confidence interval) of $D_e = 0.0418 \pm 0.0137 \text{ cm}^2/\text{s}$ was obtained.

Table 4.2 Experimental results for the solid cylinder pellets.

Run	u_0 cm/s	Pe	ΔP mbar	μ_1 s	μ_2 s ²	ε_p	$\tilde{D}_e^*$ cm ² /s	$\tilde{D}_e^{**}$ cm ² /s
1-1	1.63	1574.8	0.28	57.12	39.55	0.512	0.0322	0.0328
1-2				58.27	41.76	0.514	0.0319	0.0311
1-3				57.79	43.75	0.511	0.0296	0.0295
2-1	4.59	4233.0	0.42	21.34	8.11	0.554	0.0556	0.0509
2-2				19.96	9.60	0.500	0.0438	0.0417
2-3				19.81	8.72	0.495	0.0480	0.0449
3-1	7.62	6639.4	0.63	12.34	6.34	0.521	0.0404	0.0407
3-2				12.29	5.71	0.518	0.0454	0.0446
3-3				12.27	5.07	0.516	0.0497	0.0501
4-1	9.63	7910.7	0.90	9.72	4.32	0.518	0.0480	0.0465
4-2				9.74	4.34	0.520	0.0473	0.0467
4-3				9.87	5.01	0.530	0.0412	0.0420
* transfer function method								

4.4.2.2 Hollow Cylinder Pellets

Table 4.3 shows results for the hollow cylinder pellets where the Peclet number was estimated using Equation 4.56.

Table 4.3 Experimental results for the hollow cylinder pellets.

Table 4.5

Experimental results for the hollow cylinder pellets.

Run	u_0 cm/s	Pe	ΔP mbar	μ_1 s	μ_2 s ²	ε_p	$\tilde{D}_e^*$ cm ² /s	$\tilde{D}_e^{**}$ cm ² /s
1-1	2.17	1224.1	0.33	54.35	16.40	0.502	0.00393	0.00399
1-2				54.19	16.86	0.498	0.00403	0.00377
1-3				54.12	16.52	0.497	0.00384	0.00385
2-1	3.73	2090.9	0.50	31.63	6.36	0.499	0.00552	0.00493
2-2				31.67	6.45	0.500	0.00558	0.00488
2-3				31.63	6.57	0.499	0.00533	0.00474
3-1	4.99	2791.4	0.67	23.58	5.20	0.499	0.00476	0.00413
3-2				23.53	5.16	0.496	0.00470	0.00412
3-3				23.58	5.14	0.498	0.00478	0.00418
4-1	6.66	3691.4	0.80	17.64	4.22	0.495	0.00431	0.00369
4-2				17.69	4.20	0.498	0.00436	0.00375
4-3				17.74	4.09	0.501	0.00451	0.00383
5-1	8.31	4567.4	1.20	14.22	2.32	0.504	0.00663	0.00544
5-2				14.01	2.73	0.485	0.00532	0.00427
5-3				14.10	2.64	0.493	0.00556	0.00456
*				**				
transfer function method				moment method				

One observes that the values of effective diffusivities are one order of magnitude below the values obtained for the solid cylinder pellets. From the knowledge of the pellet pore structure (see Appendix 4.B), these values for the effective diffusivity appear to be under-estimated. One of the causes for these results may be the estimation of Peclet number. Although the hollow cylinder pellets are packed to form of coaxial cylinder column, as for the solid cylinder pellets, in this case the gas also passes through the central hole. This may have a severe effect on the axial dispersion and Equation 4.56 may not be a good approximation in this case. With transfer function method, the interaction between two parameter is so strong that it was impossible to chose a right pair of the parameters. To the best of our knowledge there is no suitable correlation for the Peclet number in a column packed with hollow cylinder pellets, independent experiments were carried out in order to obtain a good estimation of the Peclet number.

The idea behind these experiments is that if non-porous pellets with same dimensions as those of the catalysts pellets are packed in a column, the response of a pulse injection will be determined only by the axial dispersion and the Peclet number can be measured. The contribution to the axial dispersion can be distinguished from the responses of the non-porous

and the original samples and reliable values of the effective diffusivity can be obtained for the porous pellets. For these experiments a hollow glass tube was cut into small pieces with the same dimensions as those of catalysts pellets and the column was packed with these non-porous pellets as single pellet string column. Appendix 4.E shows the experimental conditions and the respective axial dispersion measurements. The results obtained for the Peclet number can be expressed by the correlation equation (Scott *et al*, 1974)

$$\frac{1}{Pe'} = \frac{\gamma'}{Re Sc} + \frac{\alpha'}{1 + \frac{\beta'}{Re Sc}} \quad (4.57)$$

where $Pe' = u_0 d_e / \varepsilon D_{ax}$ is the Peclet number based on the pellet characteristic dimension, $Re = u d_e \rho / \mu$ is the Reynolds number, $Sc = \mu / \rho D_m$ is the Schmidt number, and it takes the value of $Sc = 0.222$. Here, an equivalent diameter of $d_e = 0.83 \text{ cm}$ was used.

The three constants were estimated by data fitting: $\gamma' = 1.55$, $\alpha' = 2.41$ and $\beta' = 24.9$. Figure 4.8 plots the Peclet number as a function of the Reynolds number showing both the experimental data and the respective correlation.

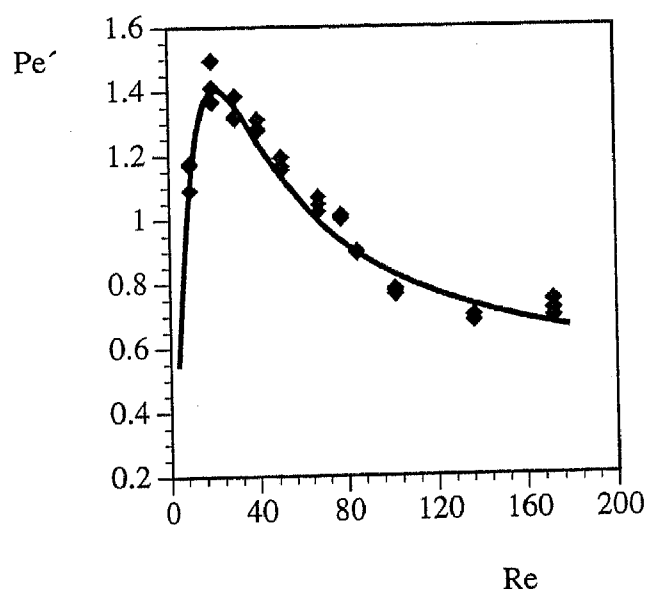


Figure 4.8 Plot of Peclet number, Pe' , versus Reynolds number, Re , for hollow cylinder pellets. Experimental data and correlation are represented by the dots and the solid line, respectively.

Then, under the same conditions, measurements were made with the hollow cylinder catalysts pellets. With the known Peclet number the effective diffusivity was estimated from Equation 4.37 and the results are given in Table 4.4. The poor estimates for the diffusivity for low values of the carrier gas velocity may result from bad experimental conditions. A possible explanation for these results is given below (see Section 4.4.2.3). For the hollow cylinder pellets an average value (with 95% confidence interval) of $D_e = 0.0178 \pm 0.010 \text{ cm}^2/\text{s}$ was obtained.

Table 4.4 Experimental results for the hollow cylinder pellets

Run	u_0 cm/s	Pe^*	μ_1 s	μ_2 s ²	D_e cm ² /s
1-1	1.70	204	74.65	53.02	-0.0175
1-2			74.38	56.24	0.0140
1-3			74.95	60.25	0.00548
2-1	3.42	253	37.08	11.67	0.0175
2-2			37.20	11.47	0.0265
2-3			37.25	11.71	0.0190
3-1	5.14	232	24.87	5.99	0.0142
3-2			24.88	5.81	0.0194
3-3			24.78	5.77	0.0195
4-1	6.89	229	18.46	3.44	0.0150
4-2			18.53	3.45	0.0156
4-3			18.67	3.36	0.0224
5-1	8.63	208	14.69	2.49	0.0135
5-2			14.62	2.44	0.0160
5-3			14.57	2.43	0.0142
6-1	11.56	186	10.78	1.66	0.0103
6-2			11.40	1.65	0.0167
6-3			11.29	1.64	0.0152
7-1	13.32	179	10.07	1.41	0.0131
7-2			9.90	1.41	0.0115
7-3			9.68	1.39	0.0105
8-1	14.51	160	8.86	1.19	0.0159
8-2			8.81	1.10	0.0252
8-3			8.98	1.21	0.0165
9-1	17.42	138	7.25	0.923	0.0171
9-2			7.17	0.870	0.0222
9-3			7.22	0.959	0.0136
10-1	23.35	122	5.41	0.583	0.0199
10-2			5.38	0.589	0.0180
10-3			5.34	0.597	0.0160
11-1	29.43	127	4.26	0.342	0.0291
11-2			4.22	0.334	0.0300
11-3			4.21	0.355	0.0215

* Peclet number values are the average of each three runs measured with the glass pellets.

4.4.2.3 Sphere Pellets

In the column packed with sphere pellets, the axial dispersion coefficient can be obtained by the following expressions (Ruthven, 1984)

$$\frac{1}{Pe'} = \gamma' \frac{D_m \varepsilon}{u_0 d_p} + \frac{1}{Pe'_\infty \left(1 + \beta' \gamma' \frac{D_m \varepsilon}{u_0 d_p} \right)} \quad (4.58)$$

with $\gamma' = 0.73$, $\beta' = 13.0$, $Pe'_\infty = 2.0$ and $Pe' = u_0 d_p / \varepsilon D_{ax}$. Then the Peclet number can be obtained from $Pe = Pe' L / d_p$. In these calculations the diffusivity of helium in air, $D_m = 0.705 \text{ cm}^2 / \text{s}$, was used.

Tables 4.5 and 4.6 show the results for sphere pellets with average diameters of $d_p = 0.17 \text{ cm}$ and $d_p = 0.3 \text{ cm}$.

Table 4.5 Experimental results for the sphere pellets (diameter $d_p = 0.17 \text{ cm}$).

Run	u_0 cm/s	Pe	ΔP mbar	μ_1 s	μ_2 s ²	ε_p	$\tilde{D}_e$ cm ² /s
1-1	0.73	464.05	0.44	180.74	128.36	0.799	-0.00583
1-2				181.12	118.19	0.800	-0.00312
1-3				180.98	111.27	0.802	-0.00242
2-1	1.93	856.29	0.812	69.59	15.53	0.816	0.00654
2-2				69.71	14.44	0.818	0.00893
2-3				70.07	15.34	0.826	0.00711
3-1	5.31	810.66	1.771	25.06	4.71	0.802	0.00316
3-2				25.02	4.46	0.801	0.00344
3-3				25.02	4.07	0.801	0.00397
4-1	8.80	650.12	2.877	14.96	1.90	0.789	0.00500
4-2				14.83	1.90	0.775	0.00494
4-3				15.03	1.90	0.795	0.00502
5-1	11.31	576.62	3.801	11.60	1.53	0.781	0.00443
5-2				11.74	1.56	0.800	0.00435
5-3				11.74	1.60	0.800	0.00418

Table 4.6 Experimental results for the sphere pellets (diameter $d_p=0.3$ cm).

Run	u_0 cm/s	Pe	ΔP mbar	μ_1 s	μ_2 s ²	ε_p	$\tilde{D}_e$ cm ² /s	λ
1-1	0.90	569.1	0.490	138.57	86.38	0.705	0.00612	
1-2				138.95	89.15	0.709	0.00543	3.31
1-3				138.95	89.04	0.709	0.00545	
2-1	2.13	1216.0	0.588	52.27	16.24	0.536	0.00368	
2-2				57.79	13.11	0.676	0.00687	3.97
2-3				57.75	11.99	0.676	0.00812	
3-1	3.33	1413.1	0.732	36.51	6.37	0.659	0.00702	
3-2				37.58	6.97	0.702	0.00620	4.94
3-3				36.63	6.45	0.664	0.00692	
4-1	5.54	1578.7	1.071	21.05	2.74	0.603	0.00867	
4-2				21.10	2.98	0.606	0.00781	7.23
4-3				21.11	3.01	0.606	0.00771	
5-1	9.01	1547.9	1.701	13.18	1.45	0.628	0.00946	
5-2				13.22	1.70	0.632	0.00783	11.48
5-3				13.23	1.77	0.632	0.00753	
6-1	11.01	1502.4	2.226	10.78	1.08	0.626	0.0102	
6-2				10.72	0.86	0.618	0.0134	15.02
6-3				10.71	0.87	0.618	0.0132	

The results for small sphere pellets ($d_p=0.17$ cm) are unexpected, since the calculated effective diffusivities give negative values for low carrier gas velocities. This is mainly due to the experimental conditions, which are not ideal. It is known that in the chromatographic method the dynamic response is influenced by both axial dispersion and intraparticle diffusion. This can be shown in the equation for the second central moment (Equation 4.47). Here, the first term is the contribution of axial dispersion and the second term is the contribution of intraparticle diffusion. To measure the effective diffusivity accurately, Cresswell and Orr (1982) using the criteria that the second term should outweigh the first term, suggested an optimal condition for which they give a lower limit for the product between the carrier gas velocity and the pellet diameter. It is not difficult to see that when the pellet diameter is small, the contribution of the intraparticle mass transfer is smaller, and as the carrier gas velocity is low the contribution of axial dispersion becomes more important. In this case, the experimental condition does not satisfy the above mentioned criteria. Furthermore, under this conditions the value of the first term ($2\mu_1^2/Pe$) on the right hand side of the equations is very close to the term on the left hand side (μ_2). The presence of experimental error may lead to results which are not meaningful, resulting from the subtraction of values which are too close to each other. This is also the reason, in terms of the experimental data treatment, why a high carrier gas velocity, where the dispersion of the inject pulse may have a significant effect on the response peak, is not recommended in the chromatographic method, and pellets with a larger diameter are

recommended in the experiments. However, if the pellet diameter is too big, it leads to a configuration similar to the single pellet string reactor, for which it is difficult to get a large pressure drop along the column, and the measurement of the intraparticle convection is not possible.

4.4.3 Intraparticle Convection

One of the objectives of this work was to study and measure intraparticle convection. The moment equations assuming that intraparticle convection occurs have been obtained for different geometry pellets. From these equations the intraparticle convection can be determined. The intraparticle convection superficial velocity is given by Darcy's law

$$v_0 = -\frac{B_p}{\mu} \frac{\Delta P}{d_p} \quad (4.59)$$

and from the definition of the intraparticle Peclet number, the following expression can be obtained

$$\lambda = -\frac{B_p}{\mu} \frac{\Delta P}{2D_e} \quad (4.60)$$

where B_p is the pellet permeability; Δp is the pressure drop across the pellet and calculated from relationship $\Delta p = \Delta P d_p / L$; μ is the gas viscosity (the viscosity of helium, $\mu = 1.93 \times 10^{-5} \text{ Pa} \cdot \text{s}$, was used in this work).

From the experimental conditions an estimate of Δp can be obtained for the various gas velocities. Substituting Equation 4.60 in the equations of the second central moment leads to a three parameter — Peclet number, Pe , true effective diffusivity, D_e , and pellet permeability, B_p — problem which could be solved using a parameter optimisation technique if a moment equation ($\Delta P/L = au_0 + bu_0^2$, Ergun equation, for instance) is introduced. A simpler method, takes the previous calculation of the apparent intraparticle diffusivity, $\tilde{D}_e$, and uses of the relationship $\tilde{D}_e = D_e / f(\lambda)$ to get both the true diffusivity and the pellet permeability.

In order to observe the effects of intraparticle convection from the experimental data, attention must be paid to the choice of experimental conditions. From Equation 4.60, it can be seen that to get large values of λ , the pellets packed in the column should have high permeability and that a large pressure drop across the pellets is essential. The former one depends on the pellet pore structure and the latter one on the gas velocity. These restrictions lead to difficulties in the estimation of λ in both experimental methods used. In the chromatographic method, the upper limit for the gas velocity is affected by two factors: one is the requirement of linear behaviour of the system, i.e., the pressure drop along the column must be a small fraction of the total pressure; the other is that at high gas velocity, the output signals would be very similar to the input signals, and this would lead to inaccurate results even with small experimental errors. In a

coaxial cylinder column it is difficult to get a enough pressure drop along the column (Valus and Schneider, 1985), and this why, in the case of the cylindrical pellets, an increase of the effective diffusivity with the gas flow rate was not observed.

However, in the case of the large diameter sphere pellet, $d_p = 0.3$ cm, there is an apparent increase of the effective diffusivities with the gas flow rate, as it is shown in Figure 4.9.

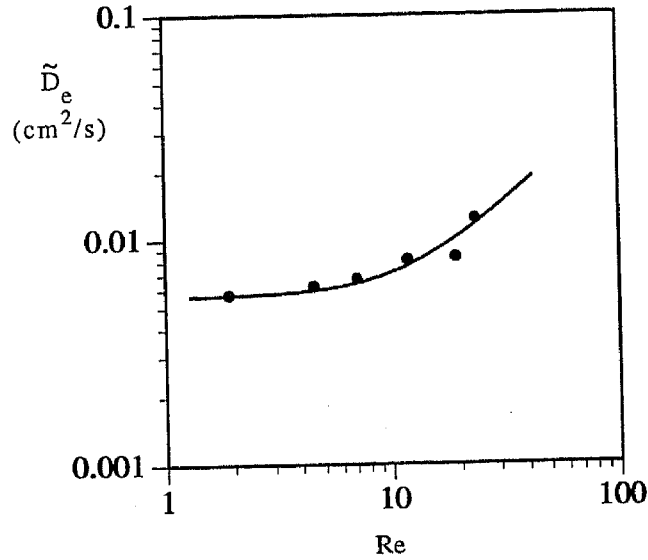


Figure 4. 9 Increase of the apparent effective diffusivities, $\tilde{D}_e$, with the Reynolds number Re .

Taking the equation of $f(\lambda)$ for the sphere pellet (Equation 4.49) and the relationship given by Equation 4.60, the expression of true effective diffusivity is obtained

$$\begin{aligned} \tilde{D}_e &= \frac{D_e}{f(\lambda)} = D_e \left[\frac{3}{\lambda/3} \left(\frac{1}{\tanh(\lambda/3)} - \frac{1}{\lambda/3} \right) \right]^{-1} \\ &= D_e \left[\frac{3}{-\frac{B_p \Delta p}{6\mu D_e}} \left(\frac{1}{\tanh\left(-\frac{B_p \Delta p}{6\mu D_e}\right)} - \frac{1}{\left(-\frac{B_p \Delta p}{6\mu D_e}\right)} \right) \right]^{-1} \end{aligned} \quad (4.61)$$

then from this equation two parameters, B_p , and D_e , can be estimated by optimisation of the objective function

$$\sum_{i=1}^{N_{exp}} \left[\left(\tilde{D}_e \right)_i^* - \tilde{D}_e(B_p, D_e)_i \right]^2 \quad (4.62)$$

where $\left(\tilde{D}_e \right)_i^*$ refers to the value of the apparent effective diffusivity obtained in experiment i , for a particular set of the parameters, $(B_p, D_e)_i$, and N_{exp} is the number of experimental data points.

The values of the pellet permeability and of the true effective diffusivity obtained in this way are the following

$$B_p = 7.2 \times 10^{-6} \text{ cm}^2$$

$$D_e = 5.6 \times 10^{-3} \text{ cm}^2 / \text{s}$$

The corresponding values of the intraparticle Peclet number, λ , calculated using Equation 4.60, are shown in Table 4.9, and the line in Figure 4.9 was determined by replacing these two values in Equation 4.61.

Taking into account this value of the effective diffusivity, and considering the large pore structure of the pellet in which molecular diffusion dominates, the tortuosity factor, T , can be estimated from the relationship

$$D_e = \frac{\varepsilon_p}{T} D_m \quad (4.63)$$

and a value of $T = 81.2$ is obtained.

The values obtained for both the permeability and the tortuosity factor seem to be unreasonably high. Based on the values of the mean and the median pore diameter for this pellet (see Table 4.4) the permeability should be of the order of 10^{-8} cm^2 . Furthermore, an upper limit of $T = 3$ is usually taken as a reasonable value for consolidated pore structures (see for example Dullien, 1979). An explanation for the values obtained, is that this result is due to the special pore structure of the pellets. The light weight aggregate used in present work is made from recycled glass. Its pore structure, resulting from the formation of bubbles formed during the evaporation of some gas, is that of a bi-variate pore structure, composed of large chambers and small channels. Here, to distinguish from normal structure made by compressing small particle, this kind of the pore structure can be called as a "foam structure". This structure can be clearly seen from the SEM photographs shown in Appendix 4.C (Figures 4.12a and b) and from the pore size distribution curves given by mercury porosimetry (Figure 4.10d in Appendix 4.C). In this structure, the range of pore diameters accessible to convection is probably higher than these reported mean and median values, leading to higher permeability values. A permeability of $B_p = 7.2 \times 10^{-6} \text{ cm}^2$ corresponds to diameter of $150 \mu\text{m}$, which is well within the range of diameters in the pore size distribution curve. Furthermore, it is reasonable to think that, it will take longer for the gas to diffuse through such a pellet, and the tortuosity factor has a large value.

4.5 CONCLUSIONS

Mathematical models for the solid cylinder and the hollow cylinder pellets, where the intraparticle convection was considered, have been established and solutions in the Laplace

domain have been obtained. Consequently, the equivalence between the hollow cylinder and the slab characteristic dimensions was presented. A modified chromatographic method has been developed to measure the intraparticle diffusivity for solid cylinder pellets. Parameter estimation is very sensitive to the correlation used for Peclet number calculation. Therefore, in the case of hollow cylinder pellets axial dispersion was independently measured with the column packed with glass hollow cylinder pellets and a correlation equation of Peclet number has been obtained. However, the effects of the intraparticle convection in the pellets is difficult to be quantified. In fact it is not easy to find experimental conditions to measure intraparticle convection with conventional gas chromatographic method. Only in the case of sphere pellets with "foam structure" used for bacterial growth which have a large pore size, conditions are such that we are starting seeing the effect of intraparticle convection. In term of mathematical techniques, it has been found that in the transfer function method, interaction between the parameters to be estimated can not be overcome.

4.6 NOTATION

a	ratio of internal radius to external radius of hollow cylinder pellet
B_p	pellet permeability, cm^2
C	species concentration, gmol/cm^3
c	dimensionless species concentration
$\bar{c}'$	$1 - \bar{c}$
D_{ax}	axial dispersion coefficient, cm^2/s
D_e	effective diffusivity, cm^2/s
$\tilde{D}_e$	apparent effective diffusivity, cm^2/s
D_m	gas molecular diffusivity, cm^2/s
d	diameter, cm
E_n	defined by Equation 4.A17
f_n	finite Hankel transform defined in Equation 4.A7
$G(s)$	bed transfer function
g	R_p/R_c
$I_{n+1/2}$	$n + 1/2$ order modified Bessel function of first kind
$I_{n+3/2}$	$n + 3/2$ order modified Bessel function of first kind
J_0	zero order Bessel function of first kind
J_1	first order Bessel function of first kind
k	reaction rate constant, s^{-1} ; constant in Equation 4.56 and defined in Equation 4.D2
L	length of column, cm
ℓ	length of pellet, cm
ℓ_s	half thickness of slab, cm
M	injection pulse strength
$M'(0)$	parameter given by Carta <i>et al.</i> (1992)
M_n	parameter defined by Equation 4.33
m_n	n -th order moment
N_n	parameter defined by Equation 4.32
$N(s)$	parameter defined by Equation 4.4
P	pressure, bar
Pe	Peclet number, $u_0 L / \varepsilon D_{ax}$
Pe'	Peclet number based on the pellet characteristic dimension, $u_0 d_p / \varepsilon D_{ax}$
R	radius, cm
Re	Reynolds number, $u d_p \rho / \mu$
r	radial coordinate, cm
$r_{1,2}$	roots of characteristic equation, defined by Equation 4.A15
$r'_{1,2}$	roots of characteristic equation, defined by Equation 4.B4
S_{in}	arbitrary parameters given in Equations 4.A19, 4.A20, 4.A28, 4.A29
Sc	Schmidt number, $\mu / \rho D_m$
s	Laplace transform parameter, s^{-1}

T	temperature, K
t	time, s
u_0	superficial velocity, cm / s
v_0	superficial intraparticle velocity, cm / s
X	longitudinal coordinate in column, cm
x	dimensionless longitudinal coordinate
Y_0	zero order Bessel function of second kind
Y_1	first order Bessel function of second kind
z	longitudinal coordinate in pellet, cm

Greek Symbols

α_n, α'_n	zero of zero-th order Bessel function of the first kind and zero of Equation 4.30
β_n, β'_n	parameter given by Equation 4.12 and 4.31
ΔP	pressure drop across the column, mbar
Δp	pressure drop across the pellet, mbar
δ_n	arbitrary parameter stated by Equation 4.A20
$\delta(t)$	Dirac function
ε	porosity
ϕ	Thiele modulus
γ_n, γ'_n	parameter defined by Equations 4.18 and 4.36
η	effectiveness factor
θ	sphere spatial coordinate
λ	intraparticle Peclet number
ρ	dimensionless radial coordinate, gas density, g/ml
ρ_b	pellet bulk density, g/ml
ρ_p	pellet grain density, g/ml
T	tortuosity factor
τ	space time, s
τ_D	intraparticle diffusion time constant, s
μ	gas viscosity, Pa.s
μ_1	first central moment, s
μ_2	second absolute moment, s ²
μ_θ	$\cos \theta$
T	tortuosity
ω	aspect ratio of length to radius of cylinder pellet
ζ_n, ζ'_n	parameter defined by Equation 4.21 and 4.38

Subscripts and Upperscripts

<i>c</i>	column
<i>exp</i>	experimental values
<i>p</i>	pellet
<i>h</i>	hydraulic
<i>hc</i>	hollow cylinder geometry
<i>s</i>	slab geometry
$\sim$	denotes <i>apparent</i> parameter (intraparticle convection lumped with diffusion)
$\bar{f}$	denotes Laplace transform of function $f(t)$

4.7 LITERATURE CITED

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APPENDICES

4.A CONCENTRATION PROFILES INSIDE A HOLLOW CYLINDER PELLET IN LAPLACE DOMAIN

The unsteady-state differential mass balance equation, boundary and initial conditions, for the hollow cylinder pellet are

$$D_e \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_p}{\partial r} \right) + \frac{\partial^2 C_p}{\partial z^2} \right) - v_o \frac{\partial C_p}{\partial z} - \varepsilon_p \frac{\partial C_p}{\partial t} = 0 \quad (4.A1)$$

$$r = R_1, R_2 \quad z = 0 \quad C_p = C \quad (4.A1a)$$

$$r = R_1, R_2 \quad z = \ell \quad C_p = C \quad (4.A1b)$$

$$t = 0 \quad C_p = 0 \quad (4.A1c)$$

Introducing the following dimensionless variables and taking the Laplace transform

$$x = \frac{z}{\ell}; \quad \rho = \frac{r}{R_2} \quad (4.A2)$$

$$\lambda = \frac{v_o \ell}{2D_e}; \quad \omega = \frac{\ell}{R_2}; \quad a = \frac{R_1}{R_2}; \quad \tau_D = \frac{\varepsilon_p \ell^2}{D_e} \quad (4.A3)$$

we get

$$\omega^2 \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \bar{C}_p}{\partial \rho} \right) \right] + \frac{\partial^2 \bar{C}_p}{\partial x^2} - 2\lambda \frac{\partial \bar{C}_p}{\partial x} - \tau_D s \bar{C}_p = 0 \quad (4.A4)$$

$$\rho = a, \text{ and } \rho = 1; \quad x = 0 \quad \bar{C}_p = 1 \quad (4.A4a)$$

$$\rho = a, \text{ and } \rho = 1; \quad x = 1 \quad \bar{C}_p = 1 \quad (4.A4b)$$

with $\bar{C}_p = \bar{C}_p / \bar{C}$ and introducing the variable $\bar{C}_p' = 1 - \bar{C}_p$

$$\omega^2 \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \bar{C}_p'}{\partial \rho} \right) \right] + \frac{\partial^2 \bar{C}_p'}{\partial x^2} - \lambda \frac{\partial \bar{C}_p'}{\partial x} - \tau_D s (\bar{C}_p' - 1) = 0 \quad (4.A5)$$

$$\rho = a, \text{ and } \rho = 1; \quad x = 0 \quad \bar{C}_p' = 1 \quad (4.A5a)$$

$$\rho = a, \text{ and } \rho = 1; \quad x = 1 \quad \bar{C}_p' = 1 \quad (4.A5b)$$

First we choose the associated eigenvalue in ρ

$$\frac{1}{\rho} \frac{d}{d\rho} \left(\rho \frac{df_n}{d\rho} \right) + \alpha_n'^2 f_n = 0 \quad (4.A6)$$

whose solution is

$$f_n = J_0(a\alpha_n') Y_0(\alpha_n' \rho) - J_0(\alpha_n' \rho) Y_0(a\alpha_n') \quad (4.A7)$$

Considering the homogeneous boundary conditions, α_n' can be chosen as the root of

$$J_0(a\alpha_n') Y_0(\alpha_n') - J_0(\alpha_n') Y_0(a\alpha_n') = 0 \quad (4.A8)$$

Now we choose the integral transform

$$f_n(x) = \int_a^1 \bar{c}_p' [J_0(a\alpha_n') Y_0(\alpha_n' \rho) - J_0(\alpha_n' \rho) Y_0(a\alpha_n')] p d\rho \quad (4.A9)$$

According to the Sturm-Liouville theory we can get the inversion of this transform

$$\bar{c}_p'(\rho, x) = \sum_{n=1}^{\infty} \frac{f_n}{N_n} [J_0(a\alpha_n') Y_0(\alpha_n' \rho) - J_0(\alpha_n' \rho) Y_0(a\alpha_n')] \quad (4.A10)$$

The corresponding norm is

$$N_n = \int_a^1 [J_0(a\alpha_n') Y_0(\alpha_n' \rho) - J_0(\alpha_n' \rho) Y_0(a\alpha_n')]^2 \rho d\rho \quad (4.A11)$$

Then Equation 4.A5 becomes

$$\frac{d^2 f_n}{dx^2} - 2\lambda \frac{df_n}{dx} - (\omega^2 \alpha_n'^2 + \tau_{DS}) f_n + \tau_{DS} M_n = 0 \quad (4.A12)$$

$$x = 0, 1 \quad f_n = 0 \quad (4.A12a)$$

where

$$\begin{aligned} M_n &= \int_a^1 [J_0(a\alpha_n') Y_0(\alpha_n' \rho) - J_0(\alpha_n' \rho) Y_0(a\alpha_n')] p d\rho \\ &= \frac{1}{\alpha_n'} \{ J_0(a\alpha_n') [Y_1(\alpha_n') - a Y_1(a\alpha_n')] - Y_0(a\alpha_n') [J_1(\alpha_n') - a J_1(a\alpha_n')] \} \end{aligned} \quad (4.A13)$$

The solution of Equation 4.A12 is

$$f_n = \frac{\tau_{DS} M_n}{\omega^2 \alpha_n'^2 + \tau_{DS}} \left(\frac{e^n - 1}{e^n - e^n} e^{nx} + \frac{e^n - 1}{e^n - e^n} e^{rx} + 1 \right) \quad (4.A14)$$

with

$$r_{1,2} = \lambda \pm \sqrt{\lambda^2 + \omega^2 \alpha_n'^2 + \tau_{DS}} \quad (4.A15)$$

The solution of Equation 4.A5 can be expressed as

$$\bar{c}_p' = \sum_{n=1}^{\infty} \frac{f_n}{N_n} E_n \quad (4.A16)$$

where

$$E_n = J_0(a\alpha'_n)Y_0(\alpha'_n\rho) - J_0(\alpha'_n\rho)Y_0(a\alpha'_n) \quad (4.A17)$$

The dimensionless concentration inside the pellet is

$$\bar{c}_p = 1 - \bar{c}_p' = 1 - \sum_{n=1}^{\infty} \frac{f_n}{N_n} E_n \quad (4.A18)$$

Now we consider the integration in Equation 4.A11. In order to calculate this integral two new functions are introduced

$$S_{1n} = J_0(a\alpha'_n)Y_0(\alpha'_n\rho) - J_0(\alpha'_n\rho)Y_0(a\alpha'_n) \quad (4.A19)$$

$$S_{2n} = J_0(a\delta_n)Y_0(\delta_n\rho) - J_0(\delta_n\rho)Y_0(a\delta_n) \quad (4.A20)$$

where δ_n is a arbitrary parameter. S_{1n} and S_{2n} are, respectively, the solutions of

$$\frac{1}{\rho} \frac{d}{d\rho} \left(\rho \frac{dS_{1n}}{d\rho} \right) + \alpha_n'^2 S_{1n} = 0 \quad (4.A21)$$

$$\frac{1}{\rho} \frac{d}{d\rho} \left(\rho \frac{dS_{2n}}{d\rho} \right) + \delta_n^2 S_{2n} = 0 \quad (4.A22)$$

Multiplying Equation 4.A21 by S_{2n} and Equation 4.A22 by S_{1n} and subtracting one from the other yields

$$\frac{d}{d\rho} \left(\rho \frac{dS_{1n}}{d\rho} \right) S_{2n} - \frac{d}{d\rho} \left(\rho \frac{dS_{2n}}{d\rho} \right) S_{1n} + \alpha_n'^2 \rho S_{1n} S_{2n} - \delta_n^2 \rho S_{1n} S_{2n} = 0 \quad (4.A23)$$

Integrating

$$\int_a^1 (\alpha_n'^2 - \delta_n^2) \rho S_{1n} S_{2n} d\rho + \rho [S_{1n}' S_{2n} - S_{1n} S_{2n}'] \Big|_a^1 = 0 \quad (4.A24)$$

we get

$$\int_a^1 \rho S_{1n} S_{2n} d\rho = - \frac{S_{1n}'(\alpha_n') S_{2n}(\delta_n)}{\alpha_n'^2 - \delta_n^2} \quad (4.A25)$$

Taking the limit when $\delta_n \rightarrow \alpha_n'$

$$N_n = \int_a^1 \rho S_{1n}^2 d\rho = \lim_{\delta_n \rightarrow \alpha'_n} \int_a^1 \rho S_{1n} S_{2n} d\rho = \lim_{\delta_n \rightarrow \alpha'_n} \frac{-S'_{1n}(\alpha'_n) S_{2n}(\delta_n)}{\alpha_n'^2 - \delta_n^2} \quad (4.A26)$$

One can easily get the value of it by using the L' Hôpital rule

$$N_n = \frac{1}{2} S_{3n} S_{4n} \quad (4.A27)$$

with

$$S_{3n} = J_1(\alpha'_n) Y_0(a\alpha'_n) - J_0(a\alpha'_n) Y_1(\alpha'_n) \quad (4.A28)$$

$$S_{4n} = J_1(\alpha'_n) Y_0(a\alpha'_n) + a J_0(\alpha'_n) Y_1(a\alpha'_n) - a J_1(a\alpha'_n) Y_0(\alpha'_n) - J_0(a\alpha'_n) Y_1(\alpha'_n) \quad (4.A29)$$

The average concentration in Laplace domain inside the pellet can be calculated by

$$\langle \bar{c}_p \rangle = \frac{\int_a^1 \int_0^1 2\pi \bar{c}_p \rho d\rho dx}{\int_a^1 \int_0^1 2\pi \rho d\rho dx} \quad (4.A30)$$

Substituting Equation 4.A18 into Equation 4.A30 finally yields

$$\begin{aligned} \langle \bar{c}_p \rangle &= 1 - \sum_{n=1}^{\infty} \frac{2\tau_{DS} M_n^2}{(1-a^2)(\omega^2 \alpha_n'^2 + \tau_{DS}) N_n} \left(1 + \frac{(e^n - 1)(e^{r_2} - 1)}{e^n - e^{r_2}} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \right) \\ &= 1 - \sum_{n=1}^{\infty} \frac{2\tau_{DS} M_n^2}{(1-a^2)(\omega^2 \alpha_n'^2 + \tau_{DS}) N_n} \left(1 + \left(\frac{\cosh \lambda}{\sinh \beta'_n} - \coth \beta'_n \right) \frac{2\beta'_n}{\beta_n'^2 - \lambda^2} \right) \end{aligned} \quad (4.A31)$$

$$\beta'_n = \sqrt{\lambda^2 + \omega^2 \alpha_n'^2 + \tau_{DS}} \quad (4.A32)$$

4.B EQUIVALENCE BETWEEN SLAB AND HOLLOW CYLINDER

For a first order reaction, it can be shown (see Chapter 3) that at steady state the effectiveness factor for a pellet with hollow cylinder geometry is given by Equation 4.29 where $\tau_D s$ is replaced by $4\phi_{hc}^2$, that is

$$\eta_{hc} = 1 - \sum_{n=1}^{\infty} \frac{8\phi_{hc}^2 M_n^2}{(1-a^2)(\omega^2 \alpha_n'^2 + 4\phi_{hc}^2) N_n} \left[1 + \left(\frac{\cosh \lambda}{\sinh \beta_n'^2} - \coth \beta_n'^2 \right) \frac{2\beta_n'}{\beta_n'^2 - \lambda^2} \right] \quad (4.B1)$$

where the Thiele modulus is defined as

$$\phi_{hc} = \frac{\ell}{2} \sqrt{\frac{k}{D_e}} \quad (4.B2)$$

The effectiveness factor for a pellet with slab geometry, derived by Nir and Pismen (1977), is given by

$$\eta_s = \frac{1}{\coth r_1' - \coth r_2'} \left(\frac{1}{r_1'} - \frac{1}{r_2'} \right) \quad (4.B3)$$

where

$$r_{1,2}' = \frac{\lambda_s \pm \sqrt{\lambda_s^2 + 4\phi_s^2}}{2} \quad (4.B4)$$

and the model parameters, similar to those defined in the case of a hollow cylinder particle, are

$$\lambda_s = \frac{v_o \ell_s}{D_e} \quad (4.B5)$$

$$\phi_s = \ell_s \sqrt{\frac{k}{D_e}} \quad (4.B6)$$

where ℓ_s is the half thickness of the slab.

Now, imposing the equality of the effectiveness factors for the hollow cylinder, η_{hc} , and the slab particles, η_s , that is,

$$\eta_{hc} = \eta_s \quad (4.B7)$$

the ratio between the characteristic dimensions for the slab, ℓ_s , and the hollow cylinder, ℓ , is obtained by replacing Equations 4.B1 and 4.B3 into Equation 4.B7, to give a relationship for the equivalent dimensions ratio

$$\frac{\ell_s}{\ell} = F_c(\phi_{hc}, \lambda, \omega, a) = F_s(\phi_s, \lambda_s) \quad (4.B8)$$

Numerical solutions were obtained with the false position method. Figure 4.10 shows plots of the ratio, ℓ_s/ℓ , as a function of the Thiele modulus, ϕ_{hc} , for different intraparticle Peclet numbers, λ . The dimensions of the hollow cylinder pellet, $\omega = 1.87$ and $a = 0.36$, used in the experimental work were chosen as a representative case. Some limits for the equivalence ratio can be anticipated. For a fast reaction and insignificant intraparticle convection, $\lambda/\phi_{hc} \rightarrow 0$, the effectiveness factor is dependent only on the specific area, and thus comparing the specific areas for the slab and hollow cylinder geometries, an explicit expression can be obtained

$$\frac{\ell_s}{\ell} = \frac{1}{2 \left(1 + \frac{\omega}{1-a} \right)} \quad (4.B9)$$

In the limit of $\lambda/\phi_{hc} \rightarrow \infty$, the particle specific area facing the flow becomes the important factor, and the equivalence between the two geometries becomes simply

$$\frac{\ell_s}{\ell} = \frac{1}{2} \quad (4.B10)$$

in which case the hollow cylinder has the same behavior as that of a slab.

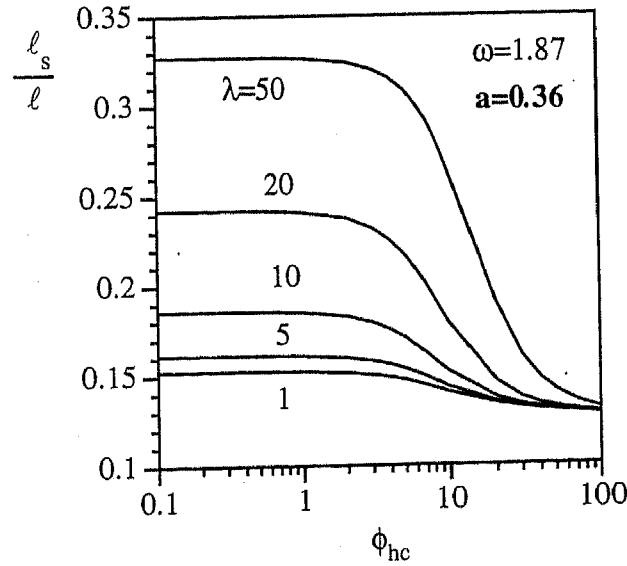


Figure 4.10 The equivalence dimensions ratio ℓ_s/ℓ as a function of the Thiele modulus ϕ_{hc} for different intraparticle Peclet numbers, λ .

4.C PELLET STRUCTURE CHARACTERIZATION

The pore structure for the four types of pellets used in this work was characterized by means of mercury porosimetry data (a Micromeritics Pore Sizer 9320 was used) and SEM photographs.

Figure 4.11 shows the cumulative intrusion curves and the respective incremental histograms for the different pellets, and in Table 4.7 are reported other relevant data that can be extracted from the porosimetry curves.

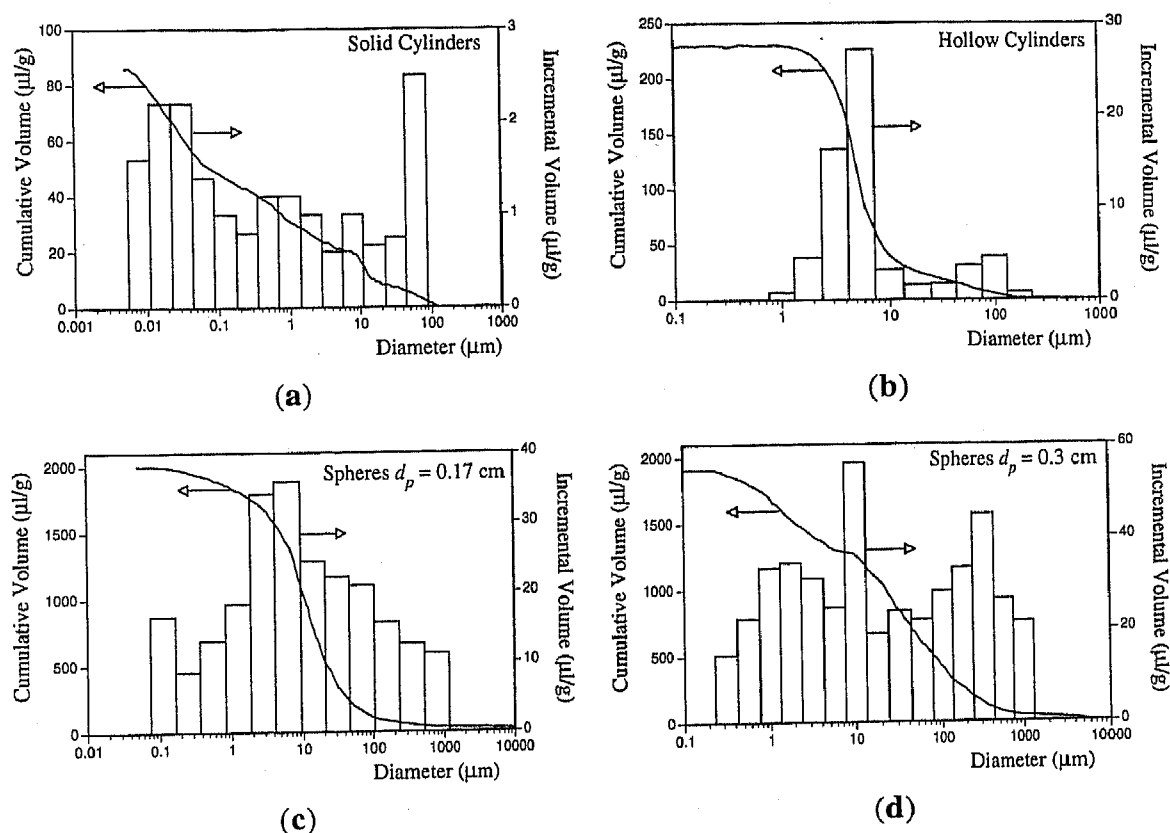
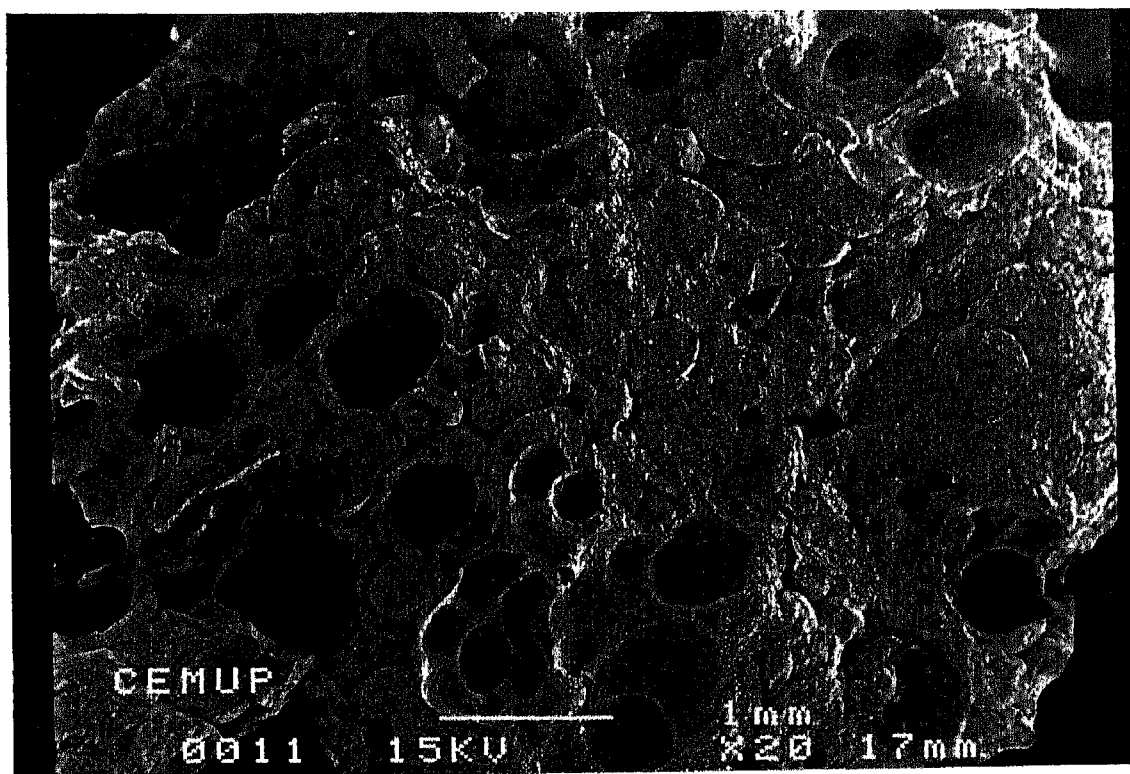


Figure 4.11 Pore size distributions for different geometry pellets: **a)** solid cylinders; **b)** hollow cylinders; **c)** small spheres; **d)** large spheres.

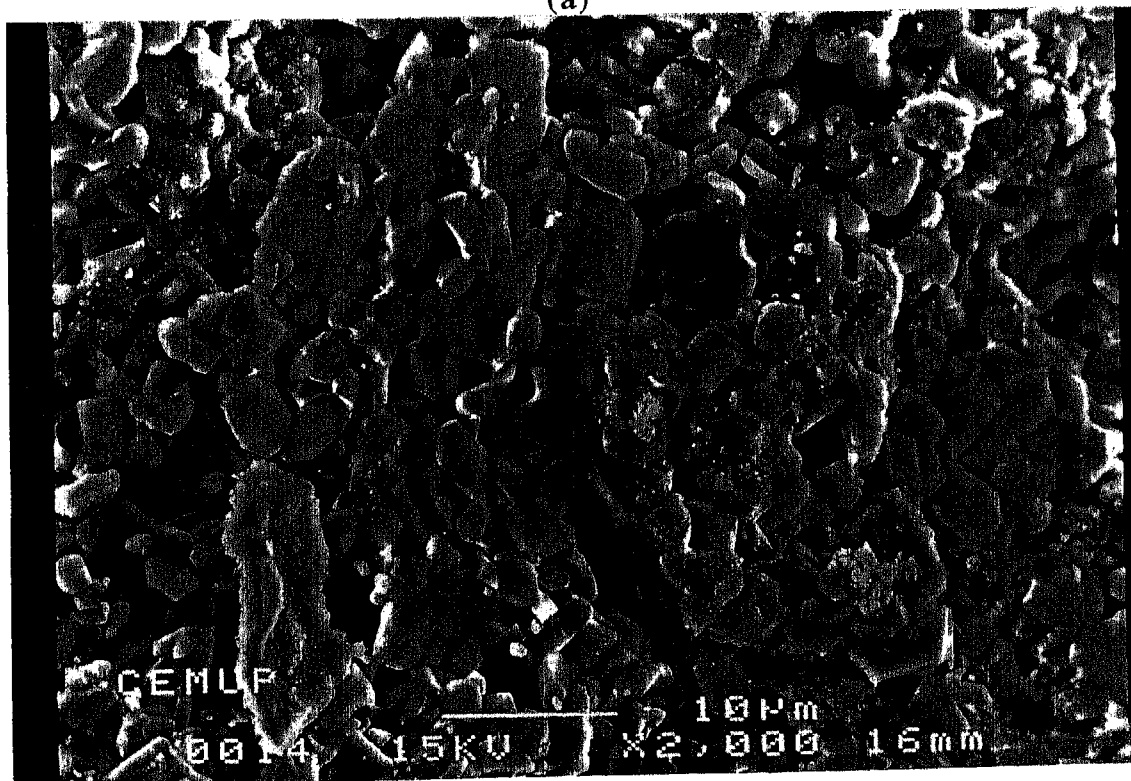
Table 4.7 Summary of mercury porosimetry data for different pellet geometries

Property	Solid Cylinder	Hollow Cylinder	Small Sphere	Large Sphere
Total intrusion volume (ml/g)	0.086	0.229	2.003	1.910
Total pore area (m ² /g)	8.74	0.15	3.50	2.85
Median pore diameter - volume based (μm)	0.230	5.17	10.3	23.2
Median pore diameter - area based (μm)	0.013	45.4	3.28	6.56
Mean pore diameter (μm)	0.039	6.07	2.29	2.68
Grain density (g/ml)	2.84	2.18	0.402	0.382
Skeletal density (g/ml)	3.77	4.35	2.07	1.41
Porosity	0.244	0.501	0.805	0.729

Figures 4.12 through 4.14 show SEM photographs of these four pellets taken at different magnifications, in order to show the pore structure and the crystalline structure for each catalyst.

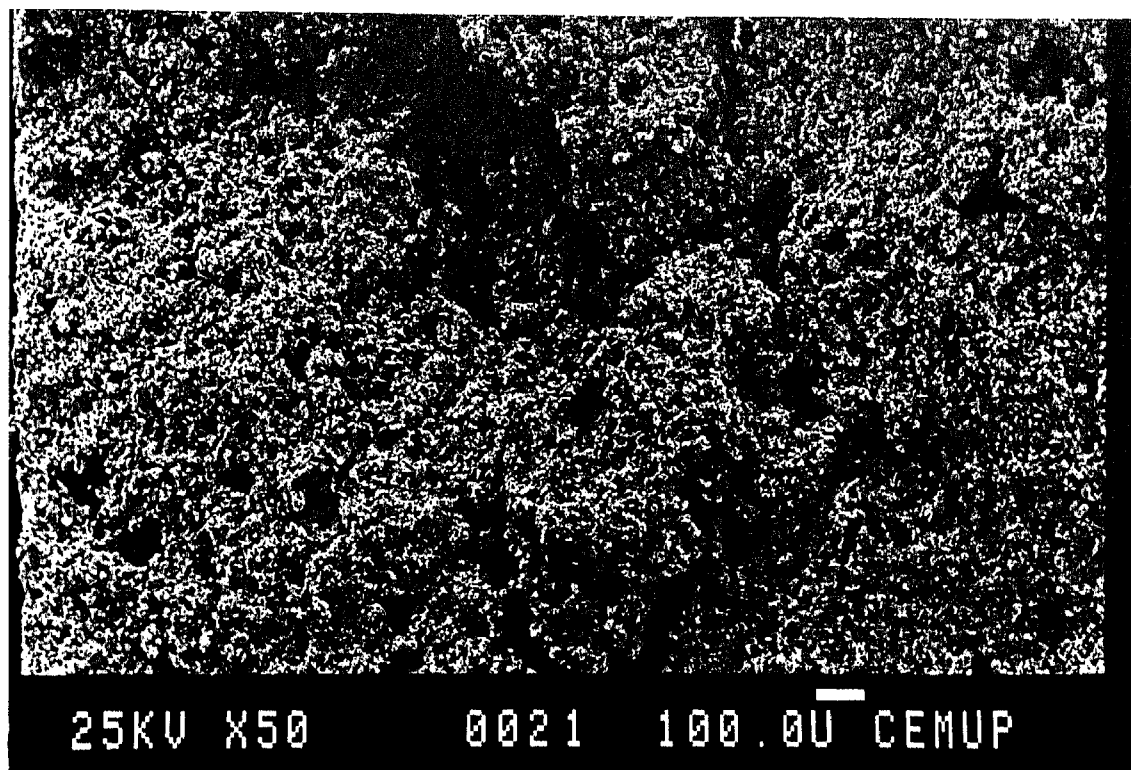


(a)

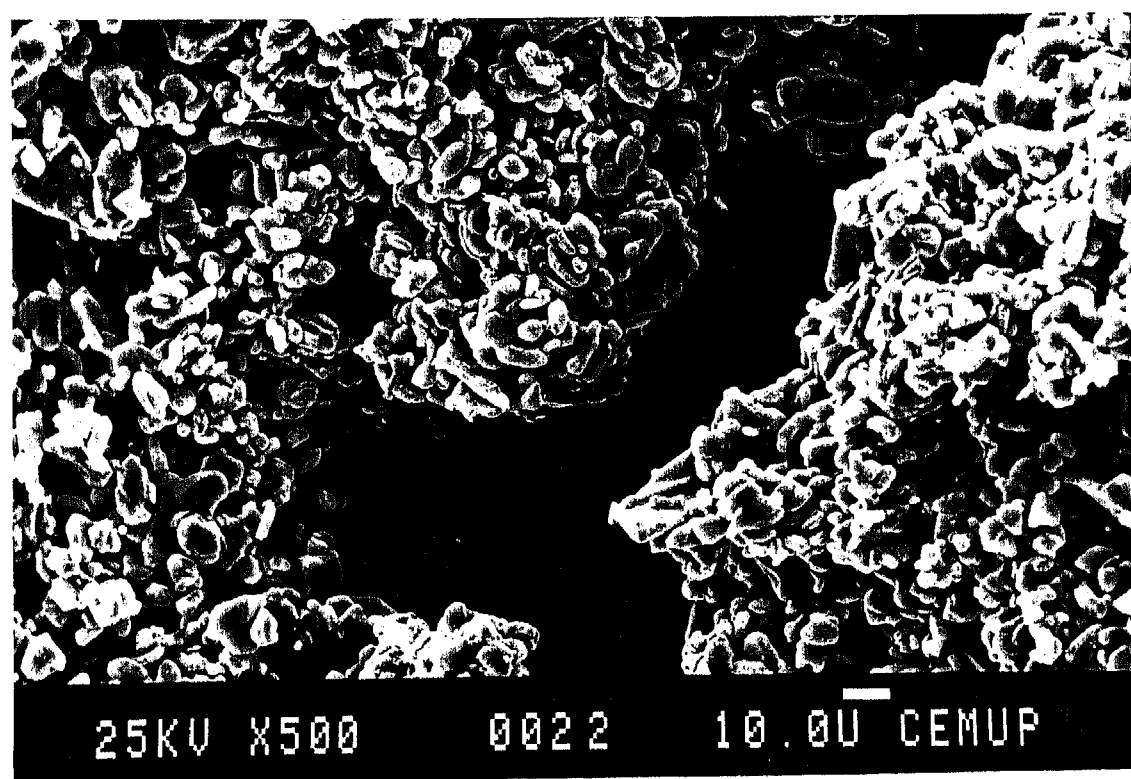


(b)

Figure 4.12 SEM photograph of a solid cylinder pellet at a magnification of: a) 20x; and b) 2000x.

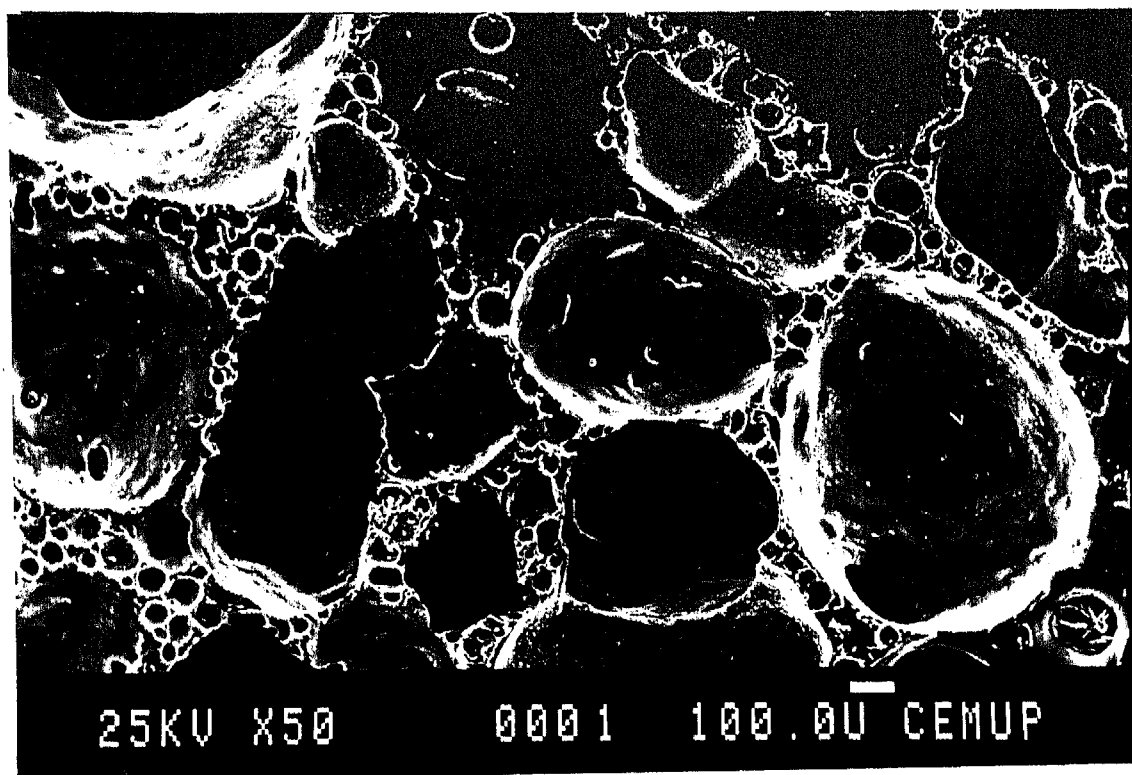


(a)

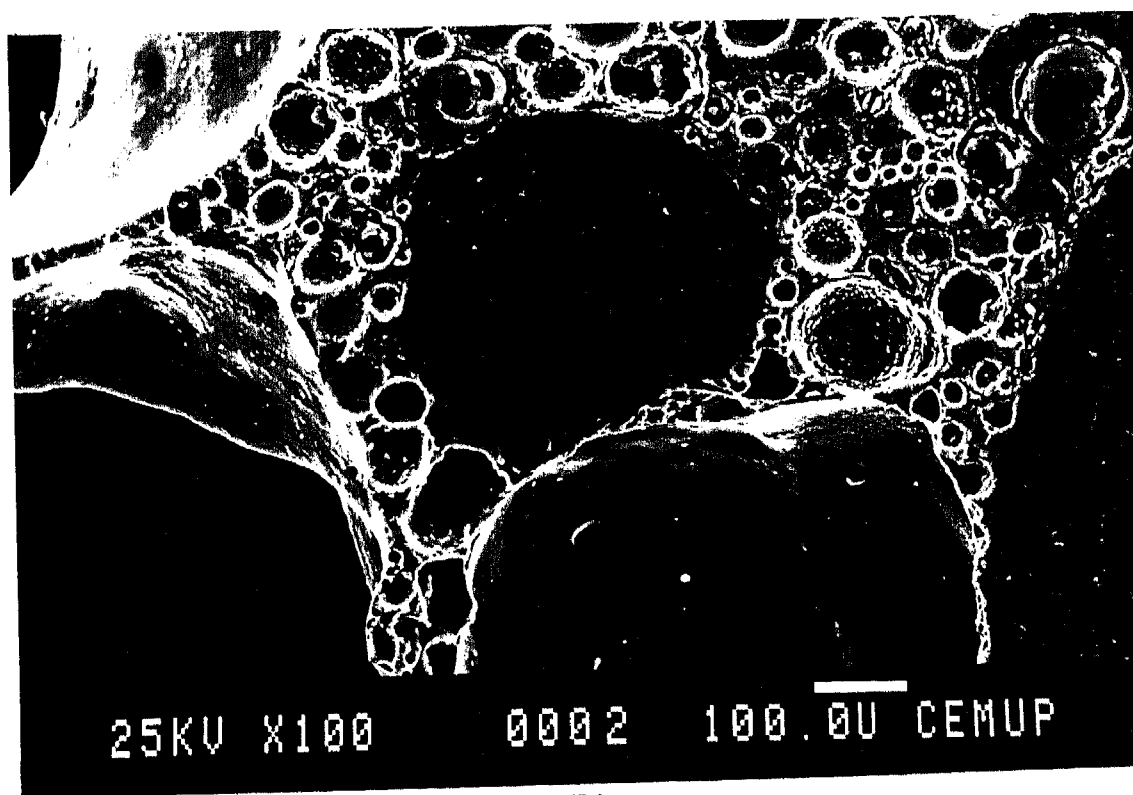


(b)

Figure 4.13 SEM photograph of a hollow cylinder pellet at a magnification of: a) 50 $\times$; and b) 500 $\times$.

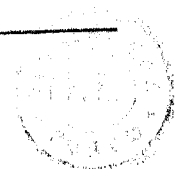


(a)



(b)

Figure 4.14 SEM photograph of a large sphere pellet at a magnification of: a) 50 $\times$; and b) 100 $\times$.



4.D CALCULATION OF AXIAL DISPERSION IN A COAXIAL CYLINDER

Valus and Schneider (1985) derived an expression for the axial dispersion of a tracer in a carrier gas in a coaxial cylinder column

$$D_{ax} = D_m + \frac{d^2 u_0^2}{k D_m} \quad (4.D1)$$

where d is the width of the annular space ($d = R_c - R_p$) and D_m is the molecular diffusivity; The constant k is given by

$$1/k = k_1 - 2k_2 + k_3 \quad (4.D2)$$

$$2k_1 = [(1+g)/(1-g)] \int_{g^2}^1 [\varphi^2(x)/x] dx \quad (4.D3)$$

$$2k_2 = [1/(1-g)^2] \int_{g^2}^1 [\varphi(x)(x-g^2)/x] dx \quad (4.D4)$$

$$2k_3 = [1/(1-g)^2(1-g^2)] \int_{g^2}^1 [(x-g^2)/x] dx \quad (4.D5)$$

$$\begin{aligned} \varphi(x) = & \left\{ 2\ln(g^2) / [(1+g^2)\ln(g^2) + 2(1-g^2)] \right\} \\ & \times \int_{g^2}^x \left\{ 1-x - [(1-g^2)\ln(x)/\ln(g^2)] \right\} dx \end{aligned} \quad (4.D6)$$

$$g = \frac{R_p}{R_c} \quad (4.D7)$$

4.E MEASUREMENTS OF AXIAL DISPERSION IN A COLUMN PACKED WITH HOLLOW CYLINDER PELLETS

Table 4.8 Experimental conditions for the hollow cylinder glass pellets

Temperature	$T=293$ K		
Pressure(outlet)	$P=1.194$ bar		
Carrier gas	N_2		
Tracer gas	H_e		
Column length	$L=150$ cm		
Column diameter	$d_c=1.4$ cm		
Bed porosity	$\varepsilon=0.690$		
Pellet sizes	$\ell=0.72$ cm	$R_1 = 0.14$ cm	$R_2 = 0.40$ cm
Pellet density	$\rho_p=2.13$ g/ml		

Table 4.9 Experimental results of axial dispersion for the hollow cylinder glass pellets.

Run	u_0 cm/s	μ_1 s	μ_2 s ²	P_e
1-1	1.70	61.13	35.66	209
1-2		61.85	36.64	208
1-3		16.19	38.43	194
2-1	3.42	30.39	7.60	243
2-2		30.51	6.96	266
2-3		30.38	7.34	251
3-1	5.14	20.89	3.53	246
3-2		20.56	3.65	232
3-3		21.47	3.97	232
4-1	6.89	15.01	1.99	227
4-2		14.92	1.95	228
4-3		15.09	1.95	233
5-1	8.63	13.11	1.61	212
5-2		13.11	1.67	205
5-3		13.11	1.67	207
6-1	11.56	9.21	0.91	186
6-2		9.17	0.92	182
6-3		9.14	0.89	190
7-1	13.32	7.88	0.69	180
7-2		7.86	0.69	178
7-3		7.87	0.69	179
8-1	14.51	7.14	0.64	159
8-2		7.14	0.64	160
8-3		7.14	0.64	160
9-1	17.42	6.06	0.53	139
9-2		5.95	0.51	138
9-3		6.00	0.53	136
10-1	23.35	4.45	0.33	121
10-2		4.49	0.33	121
10-3		4.49	0.32	124
11-1	29.43	3.67	0.21	132
11-2		3.56	0.20	127
11-3		3.52	0.20	123

5. Kinetic Measurements of Ethylene Oxidation on Silver Catalysts

5.1 INTRODUCTION

Ethylene oxidation is an important reaction in the petrochemical industry. In the thirtieth, the direct oxidation processes for the manufacture of ethylene oxide were used in the industry. Since then, the oxidation of ethylene to ethylene oxide on a silver catalyst, with concurrent formation of carbon dioxide and water as by-products, has been extensively studied. Silver is a unique catalyst for the oxidation of ethylene oxide. The commercial catalysts usually consist of silver supported carriers, promoted with suitable elements. A great number of investigators have studied the kinetics of this process in order to understand its mechanism. However, the mechanism of ethylene oxidation over silver is not certain. It is likely that adsorbed ethylene reacts with adsorbed oxygen. Although on a clean silver surface ethylene is negligibly chemisorbed, data have been collected in favour of adsorption of ethylene under realistic catalytic conditions (Carra and Forzatti, 1977). The most widely accepted pattern is consistent with the following triangular scheme of reaction:

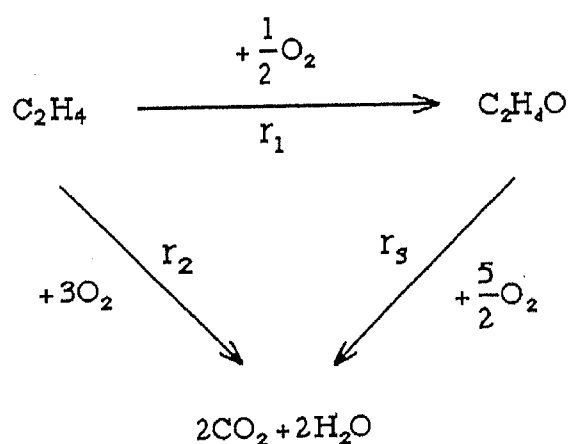


Figure 5.1 Reaction scheme for ethylene oxidation

The ratio $r_3/r_1=0.04-0.08$ has been reported, (Carra and Forzatti, 1977; Ghazali, *et al*, 1983) showing that parallel oxidation of ethylene to CO_2 is more significant than the consecutive oxidation. Most kinetic studies of ethylene oxidation agree on the major importance of direct oxidation of ethylene to CO_2 and water.

Several mechanisms for the oxidation of ethylene over silver catalyst have been proposed, (Petrov, *et al.*, 1985) and, accordingly, various kinetic rate equations have been obtained. Recently, Borman and Westerterp (1995) summarised the reaction rates reported by different authors and a brief survey of the proposed reaction rate equations was presented. A list of these kinetic rate equations is given in Table 5.1.

Table 5.1 Survey of Different Rate Equations for the Oxidation of Ethylene

authors	rate equations
Klugherz and Harriot (1971)	$r_1 = \frac{k_1 P_{ET} P_O^2}{(1 + K_{ET,1} P_{ET} + K_{O,1} P_{ET} + K_{P,1} P_P)^2 (1 + \sqrt{K_{S,1} P_O})^2}$ $r_2 = \frac{k_2 P_{ET} P_O^{3/2}}{(1 + K_{ET,2} P_{ET} + \sqrt{K_{O,2} P_O} + K_{P,2} P_P)^2 (1 + \sqrt{K_{S,2} P_O})^2}$
Metcalf and Harriot (1972)	$r_i = \frac{k_i P_{ET} P_O^{3/2}}{(1 + K_1 P_O^{1/2} + K_2 P_O + K_3 P_{ET} + K_{4PET} P_O^{1/2} + K_5 P_C P_O^{1/2} + K_6 P_W P_O^{1/2})^2}$
Petrov <i>et al.</i> (1985)	$r_i = \frac{k_i P_{ET} P_O}{1 + K_3 P_O + K_4 P_{ET}}$
Ghazali <i>et al.</i> (1983) Park and Gau (1972)	$r_i = \frac{k_i K_{ET,i} K_{O,i} P_{ET} P_O}{(1 + K_{ET,i} P_{ET} + K_{O,i} P_O + K_{EO,i} P_{EO})^2}$
Stoukides and Pavlou (1986)	$r_1 = \frac{k_1 K_{ET} P_{ET} - k_3 K_{EO} P_{EO}^2}{1 + K_{ET} P_{ET} + K_{EO} P_{EO}^2} \quad r_2 = \frac{k_2 K_{ET} P_{ET} + k_3 K_{EO} P_{EO}^2}{1 + K_{ET} P_{ET} + K_{EO} P_{EO}^2}$
Al-Saleh <i>et al.</i> (1987)	$r_1 = \frac{k_1 P_{ET}^{0.6} P_O^{0.5}}{1 + K_{C,1} P_C} \quad r_2 = \frac{k_2 P_{ET}^{0.5} P_O^{0.5}}{1 + K_{C,2} P_C}$

The differences in the rate equations result from assuming different reaction mechanisms. Some of these kinetic models are just empirical formulas (Al-Saleh *et al.*, 1987), while others are based on Rideal-Eley or Langmuir-Hinshelwood type mechanisms. From the results of the different investigations it can be concluded that all components can influence the reaction rates and a maximum has been reported in the reaction rates as function of both the ethylene and the oxygen partial pressures. The orders in ethylene and oxygen partial pressures are reported to vary between -0.3 and 1.5 for oxygen and -0.2 and 1 for ethylene (Force and Bell, 1975; Sachtler *et al.*, 1981; Ghazali, *et al.*; 1983, Petrov, *et al.*; 1985; Haul and Neubauer, 1987). It is likely that each rate equation and mechanism can only be applied to a narrow range of experimental conditions owing to the fact that different conditions produce different surface situations (Carra and Forzatti, 1977).

Borman and Westerterp (1995) experimentally studied the kinetics of the selective oxidation of ethylene over an industrial silver catalyst in a Berty (1974) reactor, and proposed three kinetic models to fit the experimental data. The rate equations for these models are given in Table 5.2. Model I is a dual site Langmuir-Hinshelwood mechanism in which ethylene and oxygen adsorb on different sites and react. Models II and III are Langmuir-Hinshelwood equations in which all

reactants and products compete for adsorption on the same catalytic sites. In Model II molecular adsorption of oxygen is assumed, whereas in Model III dissociative adsorption is assumed.

Table 5.2 Kinetic Rate Equations proposed by Borman and Westerterp (1995)

model	rate equation
I	$r_i = \frac{k_r^i K_{ET}^i P_{ET} P_O^n}{1 + K_{ET}^i P_{ET} + K_C^i P_C + K_W^i P_W + K_{EO}^i P_{EO}}$
II	$r_i = \frac{k_r^i K_{ET}^i K_O^i P_{ET} P_O}{(1 + K_{ET}^i P_{ET} + K_O^i P_O + K_C^i P_C + K_W^i P_W + K_{EO}^i P_{EO})^2}$
III	$r_i = \frac{k_r^i K_{ET}^i \sqrt{K_O^i P_{ET} P_O}}{(1 + K_{ET}^i P_{ET} + \sqrt{K_O^i P_O} + K_C^i P_C + K_W^i P_W + K_{EO}^i P_{EO})^2}$

It was observed that all three models were adequate to fit the experimental data, but the authors recommended Model III, due to its capability to describe the maximum in the reaction rates as a function of the ethylene and oxygen partial pressures.

The direct oxidation processes for the manufacture of ethylene oxide have two type of processes: air process and oxygen process. Oxygen process is dominant in the industry. In the air, under atmospheric conditions the ethylene concentration of the explosion is in the range of 3-36% vol. (Siccama and Westerterp, 1993). In industrial processes, a multi-tubular reactor is usually employed. Typical conditions for the oxygen process are 15 to 25 bar and 200 to 300°C. The oxygen content in the reaction mixture is adjusted to 6-8 %vol and the ethylene to 20-30 %vol, the limits being set outside the flammability levels for ethylene/oxygen mixtures. Under these conditions, the ethylene conversion reaches 8-10% with an ethylene oxide selectivity of 65-70% (Zomerdijk and Hall, 1981).

In most of the previous works the research has been focused on the reaction mechanism with silver catalysts with the objective of obtaining higher selectivity in the industrial process. The object of the present work is to study the kinetics of ethylene oxidation over a supported silver catalyst in a Berty reactor and to propose a kinetic equation of reaction which can be used in further studies in a fixed-bed reactor under specified experimental conditions (see Chapter 6).

5.2 EXPERIMENTAL WORK DESCRIPTION

5.2.1 Apparatus and Materials

5.2.1.1 Apparatus Description

A scheme of the experimental apparatus used in this work is shown in Figure 5.2. A mixture of air and ethylene or air and ethylene oxide is supplied from standard gas cylinders. Gas pressure is reduced with two stage regulators and the flowrate are controlled precisely by mass flow controllers (HASTINGS MODEL HFC-202, TELEDYNE HASTINGS-RAYDIST, USA). After the mass flow controllers, the gases are mixed and the feed stream passes through a three-

way ball valve and then enters either the Berty or the fixed-bed reactor. The product stream passes through a three-way ball valve and then through a tee junction which leads part of the gas stream to the sampling device by way of a needle valve and the remaining gas is vented to the atmosphere. The temperature inside the Berty reactor is controlled by a two-zone temperature controller (MODEL WEST 3810, AUTOCLAVE ENGINEERS EUROPE, UK).

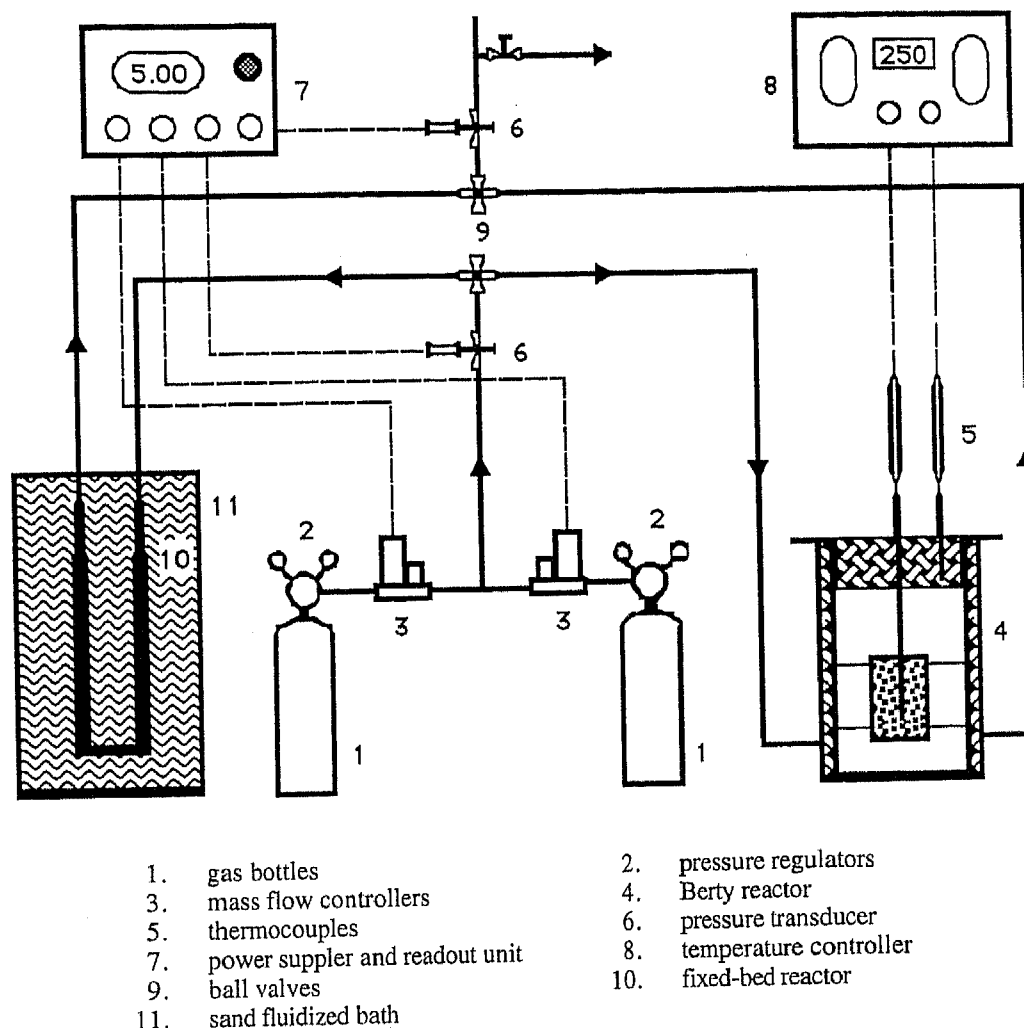


Figure 5.2 Diagram of experimental apparatus for kinetic measurements

5.2.1.2 The Berty Reactor

The Berty reactor is a traditional continuous stirred tank reactor (BOLTED CLOSURE CATALYTIC REACTOR-73 mm ID, 86-1005, AUTOCLAVE Burton Corblin, FRANCE) which can be operated at constant temperature and reactor concentration. The vessel's body is made of stainless steel and the catalyst is held in a basket placed in the centre of the vessel. A jacket-type furnace is furnished with the reactor. This furnace has resistance windings and insulation enclosed in a sleeve-type jacket which slides over the body of the reactor. The furnace is provided with a Type "K" (Chromel-Alumel) thermocouple tack-welded to the inner shell in the middle zone region. This thermocouple permits the furnace temperature to be limited to its maximum recommended value, 600°C, while the reaction temperature is controlled independently and maintained constant, its deviation not exceeding $\pm 1^\circ\text{C}$.

The concentration inside the reactor is maintained uniform by means of a turbine type impeller installed at the bottom of the reactor. The impeller is conducted by a magnet drive which is promoted by a DC motor, whose rotation speed is controlled by a control cabinet. The maximum rotation speed is 3000 RPM.

5.2.1.3 Catalysts

The catalyst is an α -alumina supported ethylene oxidation commercial silver catalyst supplied by Shell Company (SHELL CATALYST S-839). The catalyst pellets are hollow cylinders with length $\ell=0.73$ cm, internal radius $R_1=0.14$ cm and external radius $R_2=0.39$ cm. More information on the catalyst can be found in Section 4.9. In order to eliminate intraparticle mass and heat transfer resistances the catalysts were crushed to a powder of $350\text{-}250\text{ }\mu\text{m}$.

5.2.1.4 Gas Chromatographic Analysis

Ethylene, ethylene oxide and carbon dioxide were analysed on a gas chromatography (GC 1600, GIRA, FRANCE) equipped with a thermal conductivity detector. It was done on a Porapak Q column with dimension $12'' \times 1/8''$ packed with 60-80 mesh particles. Helium was used as the carrier gas at a flowrate of 30 ml ml/min and the temperature was kept at 70°C .

Samples were taken with rubber balloons and the injection was made with a gas-tight syringe with a volume of 1 ml. The detector response was calibrated in moles versus peak area for the pure reagents C_2H_4 , CO_2 and $\text{C}_2\text{H}_2\text{O}$. Integration of the chromatograms was performed with an automatic integrator (SP4270 SPECTRA-PHYSICS, INC., USA).

5.2.1.5 Chemicals

Ethylene with purity $>99.9\%$ was supplied by L'AIR LIQUIDE (France). Ethylene oxide was supplied by CARBUROS METALICOS (Spain), that contains 10% of carbon dioxide and has a purity of $>99.9\%$. A high purity air ($>99.9\%$) was used.

5.2.2 Experimental Conditions

Ethylene oxidation is a strong exothermic reaction and ethylene is a highly reactive and inflammable chemical. The safety of the operation is an important consideration in the choice of the experimental conditions. The reaction feed contains ethylene and air. The composition of ethylene changes in the range of 0.03 to 0.15 (mole fraction). The experiments were carried out at atmospheric pressure and temperature in the range of $230\text{-}285^\circ\text{C}$, which is close to the operation conditions in industrial processes.

5.2.3 Dynamic Determination

The mass flow controller readout was calibrated with a soap-film flowmeter before the starting of the experiments. In order to eliminate any external mass transfer resistances in Berty reactor, the experiments were all performed at the maximum agitation speed of 3000 RPM.

About 30 minutes after the beginning of the operation the temperature readout becomes constant and then after a further 10 minutes interval, the system was considered to be at steady state and ready for sampling. Between experiments and during periods in which the reactor was idle, the system was maintained under the reductive gas ethylene at the temperature required for the next experiment.

Finally, ethylene oxide was introduced in the Berty reactor in order to measure the rate of further oxidation of ethylene oxide to carbon dioxide and water.

5.3 RATE EQUATION AND DATA TREATMENT

There are only two independent reaction routes in the reaction system:



In the first reaction the total mole number changes, but since in these experiments the feed contains a large amount of inert gas, nitrogen, this effect was ignored. From the experimental data, the production rates of ethylene oxide, r_1 , and carbon dioxide, r_2 , can be calculated from:

$$r_1 = \frac{y_{\text{EO}} F^0}{W} \quad (5.3)$$

$$r_2 = \frac{y_{\text{C}} F^0}{W} \quad (5.4)$$

where F^0 is the total mole flowrate, W is the catalyst mass, y_{EO} is the outlet mole fraction of ethylene oxide and y_{C} is the outlet mole fraction of carbon dioxide.

Model III was chosen as the kinetic rate equations. The validity of this rate law also has been proved by other researchers (Carra and Forzatti, 1977). The production rate for reaction i , r_i , is given by

$$r_i = \frac{k_r^i K_{\text{ET}}^i \sqrt{K_{\text{O}}^i P_{\text{ET}}} \sqrt{P_{\text{O}}}}{\left(1 + K_{\text{ET}}^i P_{\text{ET}} + \sqrt{K_{\text{O}}^i P_{\text{O}}} + K_{\text{C}}^i P_{\text{C}} + K_{\text{W}}^i P_{\text{W}} + K_{\text{EO}}^i P_{\text{EO}}\right)^2} \quad (5.5)$$

where k_r^i is the rate constant for reaction i , K_j^i is the adsorption constant for component j in reaction i , and P_j is the partial pressure of component j . The subscripts C, ET, EO and O stand for carbon dioxide, ethylene, ethylene oxide and oxygen, respectively.

The temperature dependence of the kinetic and adsorption constants is expressed as

$$k_r^i = k_r^{i,\infty} \exp\left(-\frac{T_{\text{act}}^i}{T}\right) \quad (5.6)$$

$$K_j^i = K_j^{i,\infty} \exp\left(\frac{T_{\text{ads}}^i}{T}\right) \quad (5.7)$$

where $T_{\text{act}}^i = E_a^i / \mathfrak{R}$, $T_{\text{ads}}^i = \Delta H_j^i / \mathfrak{R}$, E_a^i is the activation energy for reaction i , ΔH_j^i is the heat of adsorption for component j in reaction i , and $\mathfrak{R}$ is the gas constant. The partial pressure P_j of component j is given by

$$P_j = P_0 y_j \quad (5.8)$$

where P_0 is the total pressure.

The estimation of the model constants was done by minimising the objective function

$$\sum_i^n (r_i^c - r_i^e)^2 \quad (5.9)$$

where r_i^c are the theoretical values calculated from Model III and r_i^e are the values from experimental values calculated by Equations 5.3 and 5.4. A Quasi-Newton method was applied to solve the non-linear least-squares problem.

5.4 RESULTS AND DISCUSSION

The experimental data for the ethylene oxidation obtained in the Berty reactor is presented in Table 5.3. The range of variation of the ethylene partial pressure (from 0.03 to 0.15 bar) was not very wide since the experiments were carried out at a total system pressure of 1 bar. Furthermore, it is difficult to enlarge this range due to a problem of temperature control. The reactor used in this work has no cooling system and a large amount of the reaction leads to high reaction heat production, which in turn produces a runaway in the system.

In Table 5.3, r_i^c represent the product rates calculated from Model III with the optimised parameters listed in Table 5.4. In the parameter estimation it was observed that only two sets of parameters, $T_{\text{act}}^i = E_a^i / \mathfrak{R}$, and $T_{\text{ads}}^i = \Delta H_j^i / \mathfrak{R}$ were sensitive to the experimental data, and the parameters were not identical to those reported by Borman and Westerterp (1995). The differences observed could be due to two factors. First the catalysts come from different batches although they were produced in the same company. Second the operating temperatures were different; in the present work the temperatures are in the range of 230-285°C and in Borman and Westerterp's work the temperature range was 181-254°C. They pointed out that one should be cautious in extrapolating to conditions outside the investigated range due to the empirical character of the rate equations.

Table 5.3 Experimental data and reaction rates

Run	Q_{ET} (l/min)	Q_{AIR} (l/min)	T (°C)	F^0 $\times 10^3$ (mol/s)	y_{ET}^0	y_{ET}	y_C	y_{EO}	W $\times 10^3$ (Kg)	r_1^e $\times 10^3$ (mol/s·Kg)	r_2^e $\times 10^3$ (mol/s·Kg)	r_1^c $\times 10^3$ (mol/s·Kg)	r_2^c $\times 10^3$ (mol/s·Kg)
1	0.10	1.5	230	1.19	0.063	0.039	0.0095	0.019	7.1	3.18	1.59	2.38	1.90
2	0.15	1.5	230	1.23	0.091	0.066	0.0097	0.020	7.1	3.46	1.68	2.83	1.89
3	0.20	1.5	230	1.26	0.118	0.095	0.010	0.018	7.1	3.19	1.77	3.07	1.75
4	0.25	1.5	230	1.30	0.143	0.120	0.012	0.017	7.1	3.11	2.20	3.00	1.56
5	0.15	1.5	252	1.13	0.091	0.059	0.021	0.022	7.1	3.34	3.65	4.29	3.86
6	0.10	1.5	285	1.19	0.063	0.028	0.025	0.023	3.8	7.83	7.20	6.95	6.76
7	0.10	3.0	262	1.19	0.032	0.016	0.011	0.012	3.8	3.44	3.76	4.04	3.83
8	0.10	3.0	255	1.19	0.032	0.017	0.012	0.0095	3.8	3.76	2.81	3.68	3.28

Table 5.4 Estimated parameters

(mol/s·Kg)	k_r^∞ (mol/s·Kg)	T_{act} (K)	K_{ET}^∞ (bar ⁻¹)	$T_{ads,E}$ (K)	K_C (bar ⁻¹)	K_{EO}^∞ (bar ⁻¹)	$T_{ads,EO}$ (K)	K_W^∞ (bar ⁻¹)	$T_{ads,W}$ (K)	K_0 (bar ⁻¹)
r_1	4.72×10^{12}	16531	2.05×10^{-7}	9860	83.9	91.8	0	8.25	665	84.8
r_2	1.08×10^8	11461	4.0×10^{-3}	5154	98.5	1.21	0.2	0.19	2910	66.7

Parity plots for Model III are shown in Figure 5.3, and an analysis of the results show that the proposed model is adequate to represent the experimental data. The average error is 14% for the product rate of the ethylene oxide and 10% for the product rate of the carbon dioxide.

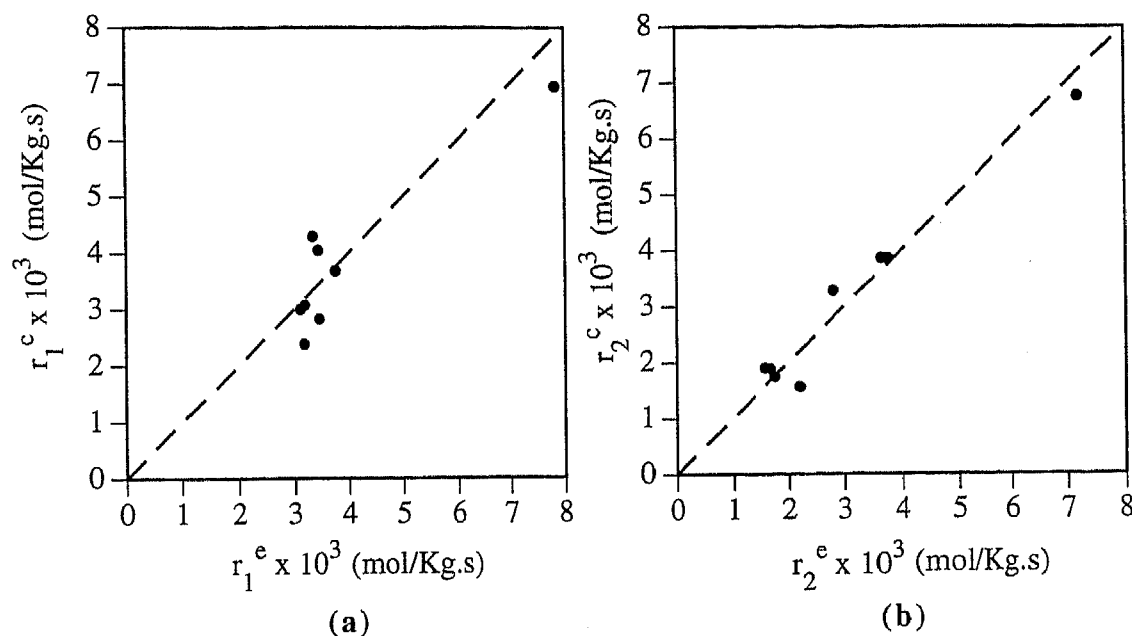


Figure 5.3 Reaction rates calculated according to Model III versus experimentally measured reaction rates a) ethylene oxide product rate, b) carbon dioxide product rate.

To see the importance of further oxidation of ethylene oxide to carbon dioxide and water, ethylene oxide instead of ethylene was introduced to the reactor and the original temperature of the reactor was set in a range of 200-280°C. A temperature increase inside the reactor was not observed, and the analysis showed that the concentrations of ethylene oxide are on the same level both at the outlet and at the inlet. This indicates that further oxidation of ethylene oxide to carbon dioxide is negligible. This point is supported by the works of Stoukides and Pavlou (1985) and of Borman and Westerterp (1995), who found that, under ethylene oxidation conditions, the rate of oxidation of ethylene oxide is very small due to the competitive adsorption of other components on the active surface.

From the rate equations, some of the characteristics of reaction for the ethylene selective oxidation can be predicted. Figure 5.4 shows plots of the reaction rates r_1 and r_2 as a function of the temperature and the partial pressures of each component. Similar plots are obtained using with the parameters given by Borman and Westerterp (1995). As mentioned before one observes that the reaction rates as a function of the ethylene partial pressure go through a maximum. Under the experimental conditions, the partial pressures of ethylene oxide have negligible effect on the product rate of carbon dioxide.

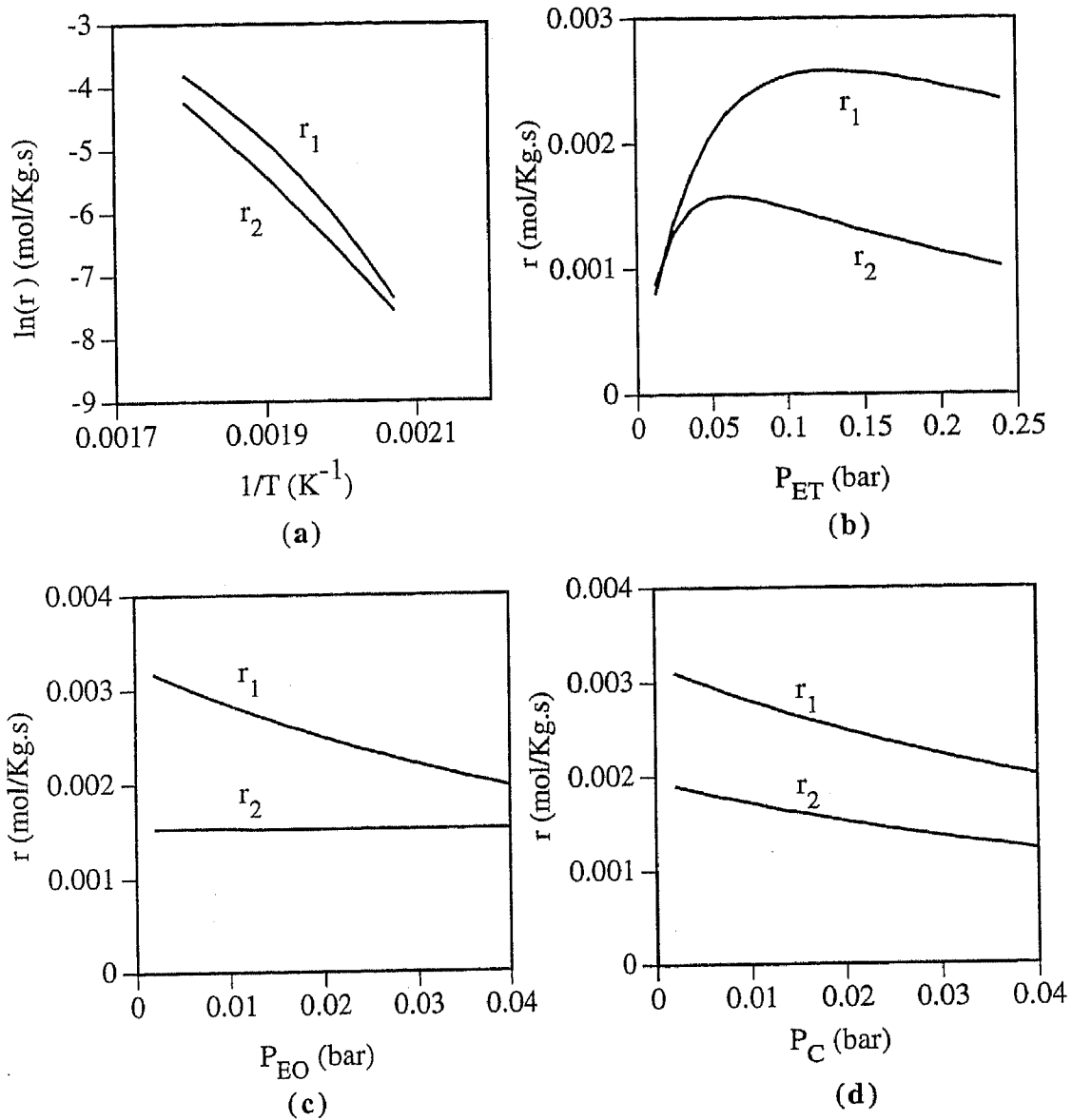


Figure 5.4 Reaction rates calculated from model as function of **a)** temperature; **b)** ethylene partial pressure; **c)** ethylene oxide partial pressure; **d)** carbon dioxide partial pressure. The constants in the calculations are $T=230^\circ\text{C}$, $P_E = 0.09$ bar, $P_{EO} = 0.02$ bar, and $P_O = 0.15$ bar.

Figure 5.5 shows the plot of the experimental data of selectivity versus conversion at a given temperature, $T=230^\circ\text{C}$. Here the yield is defined as the part of ethylene converted to ethylene oxide, that is

$$\rho_{EO} = \frac{F_{EO}}{F_{ET}^0} \quad (5.10)$$

and the conversion is given by

$$X_{ET} = \frac{F_{ET}^0 - F_{ET}}{F_{ET}^0} \quad (5.11)$$

Considering that in the feed a large amount of inert gas is present, in the calculations the mole change was neglected, and the molar flow rates can be replaced by the molar fraction, i.e.,

$$\rho_{EO} = \frac{y_{EO}}{y_{ET}^0} \quad (5.10a)$$

If the selectivity, σ_{EO} , and the relative yield, $\Phi_{EO/ET}$, are defined as

$$\sigma_{EO} = \frac{F_{EO}}{F_{ET}^0 - F_{ET} - F_{EO}} \quad (5.12)$$

$$\Phi_{EO/ET} = \frac{F_{EO}}{F_{ET}^0 - F_{ET}} \quad (5.13)$$

one can find the following relationships

$$\Phi_{EO/ET} = \frac{\rho_{EO}}{X_{ET}} \quad (5.14)$$

$$\sigma_{EO} = \frac{\rho_{EO}}{X_{ET} - \rho_{EO}} \quad (5.15)$$

indicating that the slope of ρ_{EO} versus X_{ET} gives the relative yield, $\Phi_{EO/ET}$, and the slope of ρ_{EO} versus $X_{ET} - \rho_{EO}$, gives the selectivity, σ_{EO} .

Here the experimental data turn Run 3 is taken as an example. Using the data in Table 5.3, the conversion and yield are $X_{ET} = 0.19$ and $\rho_{EO} = 0.15$, respectively. Then the selectivity, $\sigma_{EO} = 3.75$, and the relative yield, $\Phi_{EO/ET} = 0.78$, are calculated by using Equation 5.14 and 5.15 respectively.

With a given feed, temperature and catalyst mass values, combined with the rate equations which have been obtained, the theoretical curves of ρ_{EO} versus X_{ET} and ρ_{EO} versus $X_{ET} - \rho_{EO}$ can be calculated by solving following algebraic equations

$$\frac{y_i F^0}{W} = \frac{k_r^i K_{ET}^i \sqrt{K_O^i P_{ET}} \sqrt{P_O}}{\left(1 + K_{ET}^i P_{ET} + \sqrt{K_O^i P_O} + K_C^i P_C + K_W^i P_W + K_{EO}^i P_{EO}\right)^2} \quad (5.16)$$

$$X_{ET} = \frac{F_{ET}^0 - F_{ET}}{F_{ET}^0} \quad (5.11)$$

where P_j is calculated from Equation 5.8.

In the calculations the inlet composition is $y_{ET} = 0.118$, $y_O = 0.19$ and $y_C = y_{EO} = y_W = 0$. The inlet molar flowrate changes in the range of $F^0 / W = 0.41 - 0.01$. In Figure 5.5 the solid lines are theoretical curves at temperature 230°C. From these curves it can be found that the selectivity, σ_{EO} , and relative yield, $\Phi_{EO/ET}$, decrease as the reaction conversion increases.

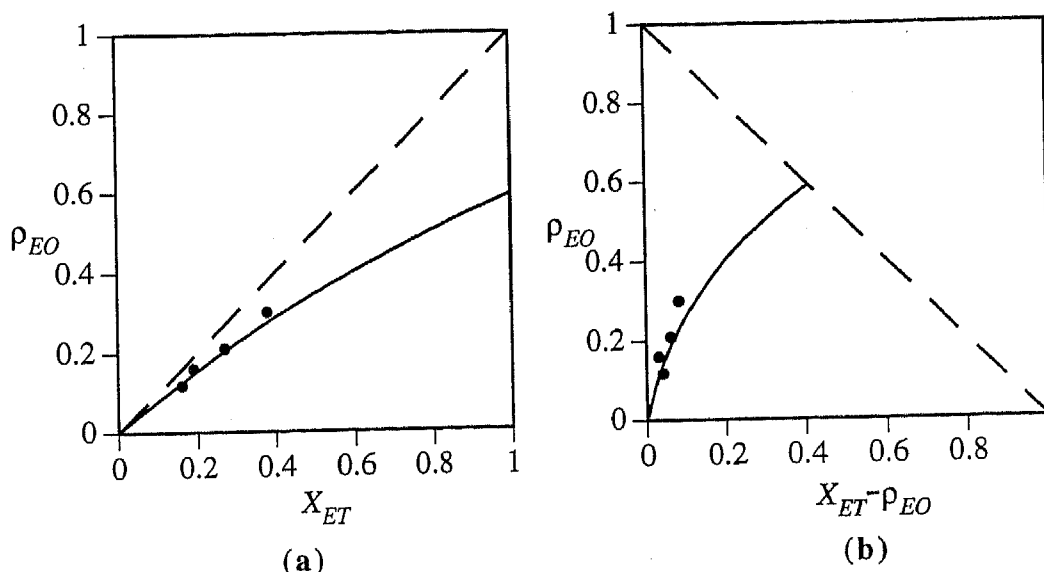


Figure 5.5 Effect of the reaction conversion on the selectivity at $T=230^{\circ}\text{C}$ a) ρ_{EO} versus X_{ET} ; b) ρ_{EO} versus $X_{ET} - \rho_{EO}$

5.5 CONCLUSIONS

The kinetics of ethylene oxidation over α -alumina support commercial silver catalysts has been studied with Berty reactor. Rate equations for the ethylene oxidation for gas mixtures containing excess oxygen have been determined. These rate equations can be used under the experimental conditions of this work. The selectivity of the reaction has been studied. It was found that the selectivity and relative yield decrease with the increasing of the reaction conversion. At conversion of 40% the relative yield is around 75%. The reaction rates change with the increase of the ethylene partial pressure and pass through a maximum. Partial pressures of carbon dioxide inhibit the reaction rates. The partial pressures of ethylene oxide inhibit the ethylene oxide production rate but have negligible effect on the production rate of carbon dioxide. Further oxidation of ethylene oxide to carbon dioxide is not important.

5.6 NOTATION

E_i	activation energy, J/mol
F^0	total molar flowrate of feed, mol/s
F_j	molar flowrate of component j , mol/s
k_r^i	reaction rate constant, mol/s·Kg
k_r^∞	pre-exponential factor, mol/s·Kg
K_j^i	adsorption constant for component j in reaction i , bar ⁻¹
$K_j^{i\infty}$	pre-exponential adsorption factor for component j in reaction i , bar ⁻¹
P_j	partial pressure of component j , bar
Q_{AIR}	standard volume flowrate of air in the feed, m ³ / s
Q_E	standard volume flowrate of ethylene in the feed, m ³ / s
$\mathcal{R}$	ideal gas constant, 8.314 J/Kgmole·K
r_1	product rate of ethylene oxide, mol/s·Kg
r_2	product rate of carbon dioxide, mol/s·Kg
T	temperature, K
T_{act}^i	$= E_a^i / \mathcal{R}$, K
$T_{ads,j}^i$	$= \Delta H_j^i / \mathcal{R}$, K
W	catalyst mass in the reactor, Kg
X_{ET}	reaction conversion defined in Equation 5.10
y_j	mole fraction of component j

Greek Symbols

ΔH_j^i	heat of adsorption for component j in reaction i , KJ/mol
$\Phi_{EO/ET}$	relative yield defined in Equation 5.13
ρ_{EO}	yield defined in Equation 5.10
σ_{EO}	selectivity defined in Equation 5.12

Subscripts and Superscripts

0	inlet
C	carbon dioxide
EO	ethylene oxide
ET	ethylene
i	reaction
j	component
O	oxygen
W	water

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6. Ethylene Oxidation in Fixed-Bed: Simulation and Experiments

6.1 INTRODUCTION

Ethylene oxide is a basic compound in the petrochemical industry for the manufacturing of many products such as detergents, synthetic fibres, paints solvents and pharmaceutical bases. There are two basic manufacturing methods for ethylene oxide, the historical chlorohydrin route and modern catalysed direct oxidation method. As the latter method is now the main industrial process, the selective oxidation of ethylene to ethylene oxide over silver catalysts has been widely studied (Carra and Forzatti, 1977; Sachtler, *et al.*, 1981; Zomerdijk and Hall, 1981; Petrov, *et al.*, 1985). Essentially, ethylene oxide is produced by the careful controlled oxidation of ethylene over a silver catalyst. The reaction conditions are critical: if they are too mild, little oxide is produced; if they are too severe, the reaction runs away and carbon dioxide and water are the only end products. The art of making ethylene oxide is thus to control the oxidation reaction so that while maintaining an adequate production rate, the wasteful production of carbon dioxide and water is severely limited.

In industrial processes, a multitubular reactor is usually employed for the ethylene oxidation. In the reactor shell a liquid coolant or a boiling coolant is applied to remove the heat of reaction. It is not difficult to simulate these conditions in the laboratory and furthermore to use the results to the industrial reactor design. Since the nineties, Westerterp and his co-workers have been doing systematic studies on ethylene oxidation and its behaviour in packed tubular reactors (Westerik, *et al.*, 1990; Borkink and Westerterp, 1992; Borkink and Westerterp, 1994; Schouten, *et al.*, 1994; Borman and Westerterp, 1995). In their studies heat transfer characterisation is the main objective. However, in an heterogeneous catalytic reactor mass transfer is an important factor, and, for most cases encountered in practice, diffusion within the catalyst pellets should be considered (Mears, 1971).

With this in consideration, a chromatographic method has been used with a single pellet string column to measure the effective diffusivity of the catalyst pellets. The results are presented in Chapter 4. Furthermore, with a Berty reactor (CSTR) the reaction kinetics have been studied and the reaction rate equations have been obtained, the results are presented in Chapter 5. The objective of this work is the simulation of the reaction of ethylene oxidation in a fixed-bed reactor packed with silver catalysts supported in α -alumina. The results will be compared with experimental data. A mathematical model in which intraparticle mass transport is considered will be proposed. Finally, the effects of intraparticle convection will be discussed.

6.2 MATHEMATICAL MODEL

The system considered here is a fixed-bed packed with industrial silver on α -alumina catalyst pellets with hollow cylinder geometry.

The reaction system of ethylene oxidation is expressed by two independent reaction equations



In deriving the models, several assumptions are made:

- For the catalyst pellets
 - a. temperature is uniform within the pellets;
 - b. gas composition surrounding the pellet is constant.
- For the bed
 - a. axial dispersion of heat is neglected;
 - b. radial dispersion of both mass and heat are neglected;
 - c. transfer resistance between pellets and bulk gas is neglected.

6.2.1 Model Equations for the Catalyst Pellets

The steady-state differential mass balance equations for the ethylene within the hollow cylinder pellet are

$$D_{eET} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_{ET}^p}{\partial r} \right) + \frac{\partial^2 C_{ET}^p}{\partial z_p^2} \right) - v_o \frac{\partial C_{ET}^p}{\partial z_p} - \rho_p (R_1 + R_2/2) = 0 \quad (6.3)$$

$$D_{eEO} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_{EO}^p}{\partial r} \right) + \frac{\partial^2 C_{EO}^p}{\partial z_p^2} \right) - v_o \frac{\partial C_{EO}^p}{\partial z_p} + \rho_p R_1 = 0 \quad (6.4)$$

$$r = r_1 \text{ and } r = r_2 \quad \forall z_p \quad C_{ET}^p = C_{ET} \quad C_{EO}^p = C_{EO} \quad (6.5a)$$

$$z_p = 0 \text{ and } z_p = \ell \quad \forall r \quad C_{ET}^p = C_{ET} \quad C_{EO}^p = C_{EO} \quad (6.5b)$$

where: D_{ej} is the intraparticle effective diffusivity of component j ; v_o is the gas superficial velocity through the pellet; r and z_p are the radial and longitudinal coordinates, respectively; C_{ET}^p is the concentration of ethylene within the pellet; C_{EO}^p is the concentration of ethylene oxide within the pellet; C_{ET} is the concentration of ethylene in the bulk phase; C_{EO} is the concentration of ethylene oxide in the bulk phase; ρ_p is the pellet density; r_1 and r_2 are the internal and the external radius of the hollow cylinder pellet, respectively; and ℓ is the pellet length. R_1 is the

partial ethylene oxidation rate (Equation 6.1) and R_2 is the carbon dioxide product rate (Equation 6.2). The kinetics rate equations of the reaction have the forms:

$$R_i = \frac{k_{ri} K_E^i \sqrt{K_O^i P_E} \sqrt{P_O}}{\left(1 + K_E^i P_E + \sqrt{K_O^i P_O} + K_C^i P_C + K_W^i P_W + K_{EO}^i P_{EO}\right)^2} \quad (6.6)$$

In the kinetic rate equation, the constants of rate and adsorption are expressed as

$$k_{ri} = k_{ri}^\infty \exp(-T_{\text{act}}^i / T) \quad (6.7)$$

$$K_j^i = K_j^{\text{iso}} \exp(T_{\text{ads } j}^i / T) \quad (6.8)$$

where: k_{ri} is the frequency coefficient for reaction i ; $T_{\text{act}}^i = E_i / \mathfrak{R}$ and $T_{\text{ads } j}^i = \Delta H_j^i / \mathfrak{R}$ for component j in reaction i ; E_i are the activation energies; ΔH_j^i are the adsorption heats of component j ; $\mathfrak{R}$ is the ideal gas constant; and T is the temperature.

These constants have been measured independently (Chapter 5) and listed in Table 6.1.

Table 6.1 Measured kinetic rate constants.

	k_r^∞ (mol/s.Kg)	T_{act} (K)	K_E^∞ (bar ⁻¹)	$T_{\text{ads } E}$ (K)	K_C (bar ⁻¹)	K_{EO}^∞ (bar ⁻¹)	$T_{\text{ads } EO}$ (K)	K_W^∞ (bar ⁻¹)	$T_{\text{ads } W}$ (K)	K_O (bar ⁻¹)
r_1	4.72×10^{12}	16531	2.05×10^{-7}	9860	83.9	91.8	0	8.25	665	84.8
r_2	1.08×10^8	11461	4.0×10^{-3}	5154	98.5	1.21	1680	0.19	2910	66.7

Replacing the concentrations C_j^p by the molar fractions $y_j^p = C_j^p \mathfrak{R} T / P_0$ and introducing the following dimensionless variables

$$z = \frac{z_p}{\ell}; \quad \rho = \frac{r}{r_2}; \quad \xi_j^p = \frac{y_j^p}{y_j} \quad (6.9)$$

the dimensionless model equations become:

$$\omega^2 \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \xi_{ET}^p}{\partial \rho} \right) \right] + \frac{\partial^2 \xi_{ET}^p}{\partial z^2} - 2\lambda \frac{\partial \xi_{ET}^p}{\partial z} - \phi_{ET}^2 (R_1^* + R_2^* / 2) = 0 \quad (6.10)$$

$$\omega^2 \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \xi_{EO}^p}{\partial \rho} \right) \right] + \frac{\partial^2 \xi_{EO}^p}{\partial z^2} - 2\lambda D \frac{\partial \xi_{EO}^p}{\partial z} + \phi_{EO}^2 D R_1^* = 0 \quad (6.11)$$

with

$$\rho = a \text{ and } \rho = 1 \quad \forall x \quad \xi_{ET}^p = 1 \quad \xi_{EO}^p = 1 \quad (6.12a)$$

$$z = 0 \text{ and } z = 1 \quad \forall \rho \quad \xi_{ET}^p = 1 \quad \xi_{EO}^p = 1 \quad (6.12b)$$

The model parameters are

$$\lambda = \frac{v_o \ell}{2D_{eET}}; \quad \phi_j^2 = \frac{\rho_p \ell^2 k_{r1}}{D_{eET} C_j}; \quad D = \frac{D_{eET}}{D_{eEO}}; \quad \omega = \frac{\ell}{r_2}; \quad a = \frac{r_1}{r_2} \quad (6.13)$$

where: λ is the intraparticle Peclet number; ϕ_j are the Thiele modulus; D is the ratio of effective diffusivity of ethylene to that of ethylene oxide; ω is the aspect ratio of the length to the external radius, and a is the ratio of the internal radius to the external radius. The dimensionless reaction rate is defined as:

$$R_i^* = R_i / k_{r1} \quad (6.14)$$

Considering the excess of oxygen it is reasonable to assume that the concentration of oxygen within the pellet is constant and equal to the value at the surface of the pellets.

6.2.2 Model Equations for the Fixed-Bed

In a reactor of length of L packed with porous catalysts where the reaction takes place, the differential mass balance equation for the reactant ethylene and product ethylene oxide at steady-state can be written as

$$\varepsilon D_{ax} \frac{d^2 C_{ET}}{dx_b^2} - \frac{d(u C_{ET})}{dx_b} - \rho_b (\eta_1 R_1^b + \eta_2 R_2^b / 2) = 0 \quad (6.15)$$

$$\varepsilon D_{ax} \frac{d^2 C_{EO}}{dx_b^2} - \frac{d(u C_{EO})}{dx_b} + \eta_1 \rho_b R_1^b = 0 \quad (6.16)$$

where: D_{ax} is the axial dispersion coefficient; ρ_b is the bed density; x_b is the axial coordinate in the bed; C_{ET} and C_{EO} are the concentration of ethylene and ethylene oxide in the bulk phase, respectively; η_i is the effectiveness factor for reaction i ; and u is the gas superficial velocity through the reactor. Considering that the velocity changes along the reactor with the change in temperature, following the relationship

$$u = \frac{u_0 T}{T_0} \quad (6.17)$$

the model equations become

$$\varepsilon D_{ax} \frac{d^2 C_{ET}}{dx_b^2} - \frac{T u_0}{T_0} \frac{dC_{ET}}{dx_b} - \frac{C_{ET} u_0}{T_0} \frac{dT}{dx_b} - \rho_b (\eta_1 R_1^b + \eta_2 R_1^b / 2) = 0 \quad (6.18)$$

$$\varepsilon D_{ax} \frac{d^2 C_{EO}}{dx_b^2} - \frac{T u_0}{T_0} \frac{dC_{EO}}{dx_b} - \frac{C_{EO} u_0}{T_0} \frac{dT}{dx_b} + \eta_i \rho_b R_i^b = 0 \quad (6.19)$$

The effectiveness factors can be obtained from the pellet equations

$$\eta_i = \frac{\int_a^1 \int_0^1 R_i \rho dp dz}{\int_a^1 \int_0^1 R_i^b \rho dp dz} = \frac{2 \int_a^1 \int_0^1 R_i \rho dp dz}{R_i^b (1 - a^2)} \quad (6.20)$$

and combining Equations 6.18 and 19 with Equation 6.20, the following equations can be obtained

$$\varepsilon D_{ax} \frac{d^2 C_{ET}}{dx_b^2} - \frac{T u_0}{T_0} \frac{dC_{ET}}{dx_b} - \frac{C_{ET} u_0}{T_0} \frac{dT}{dx_b} - \rho_b (\bar{R}_1 + \bar{R}_2/2) = 0 \quad (6.21)$$

$$\varepsilon D_{ax} \frac{d^2 C_{EO}}{dx_b^2} - \frac{T u_0}{T_0} \frac{dC_{EO}}{dx_b} - \frac{C_{EO} u_0}{T_0} \frac{dT}{dx_b} + \rho_b \bar{R}_1 = 0 \quad (6.22)$$

where $\bar{R}_i$ is the average reaction rate for reaction i defined as

$$\bar{R}_i = \eta_i R_i^b = \frac{2 \int_a^1 \int_0^1 R_i \rho dp dz}{(1 - a^2)} \quad (6.23)$$

The energy balance equation is

$$G_0 C_{pm} \frac{dT}{dx_b} = \rho_b [\bar{R}_1 (-\Delta H_{R1}) + \bar{R}_2 (-\Delta H_{R2})/2] - \frac{4U}{d_R} (T - T_0) \quad (6.24)$$

where: G_0 is the total mass flow rate; C_{pm} is the heat capacity of the gas; ΔH_{R1} is the reaction heat of partial ethylene oxidation; ΔH_{R2} is the reaction heat of complete ethylene oxidation; d_R is the reactor diameter; U is the overall heat transfer coefficient; and T_0 is the temperature of the cooling medium and it has the same value of that in the inlet gas.

The boundary conditions are

$$x_b = 0 \quad C_{ET} - \frac{\varepsilon D_{ax}}{u_0} \frac{dC_{ET}}{dx_b} = C_{ET0} \quad (6.25a)$$

$$C_{EO} - \frac{\varepsilon D_{ax}}{u_0} \frac{dC_{EO}}{dx_b} = 0 \quad (6.25b)$$

$$T = T_0 \quad (6.25c)$$

$$x_b = L \quad \frac{dC_{ET}}{dx_b} = \frac{dC_{EO}}{dx_b} = 0 \quad (6.25d)$$

Introducing the dimensionless variables

$$x = \frac{x_b}{L}; \quad \theta = \frac{T}{T_0}; \quad c_{ET} = \frac{C_{ET}}{C_{ET}^0}; \quad c_{EO} = \frac{C_{EO}}{C_{ET}^0} \quad (6.26)$$

the dimensionless model equations and the respective boundary conditions become

$$\frac{1}{Pe} \frac{d^2 c_{ET}}{dx^2} - \theta \frac{dc_{ET}}{dx} - c_{ET} \frac{d\theta}{dx} - Da(\bar{R}_1^* + \bar{R}_2^*/2) = 0 \quad (6.27)$$

$$\frac{1}{Pe} \frac{d^2 c_{EO}}{dx^2} - \theta \frac{dc_{EO}}{dx} - c_{EO} \frac{d\theta}{dx} + Da\bar{R}_1^* = 0 \quad (6.28)$$

$$\frac{d\theta}{dx} - Da\Theta_{ad}[\bar{R}_1^* + H\bar{R}_2^*/2] - St(\theta - 1) = 0 \quad (6.29)$$

$$x = 0 \quad c_{ET} - \frac{1}{Pe} \frac{dc_{ET}}{dx} = 1 \quad (6.30a)$$

$$c_{EO} - \frac{1}{Pe} \frac{dc_{EO}}{dx} = 0 \quad (6.30b)$$

$$\theta = 1 \quad (6.30c)$$

$$x = 1 \quad \frac{dc_{ET}}{dx} = \frac{dc_{EO}}{dx} = 0 \quad (6.30d)$$

where $Da = Da_0 \exp\left[-\gamma_0\left(\frac{1}{\theta} - 1\right)\right]$.

The model parameters are

Peclet number

$$Pe = \frac{u_o L}{\varepsilon D_{axET}}$$

Damköhler number

$$Da_0 = \frac{\rho_b \tau_0 k_{r1}^\infty \exp(-\gamma_0)}{C_{ET}^0}$$

Arrhenius number

$$\gamma_0 = \frac{T_{acti}}{T_0}$$

Dimensionless adiabatic temperature rise

$$\Theta_{ad} = \frac{C_{ET}^0 (-\Delta H_1)}{\rho_g C_{pm} T_0}$$

Stanton number

$$St = \frac{a_h UL}{G_0 C_{pm}}$$

Heat transfer area per unit volume of pipe

$$a_h = \frac{4}{d_R}$$

Heats of reaction ratio

$$H = \frac{\Delta H_2}{\Delta H_1}$$

The dimensionless average reaction rates are defined as

$$\bar{R}_i^* = \bar{R}_i / k_r^1 \quad (6.31)$$

and the space time is

$$\tau_0 = \frac{L}{u_0} \quad (6.32)$$

6.2.3 Effective Diffusivity and Heat Capacity

The diffusivities for a binary gas can be predicted from the relationship (Reid, *et al.*, 1987)

$$D_{A-B} = \frac{0.00266 T^{1.5}}{P M_{AB}^{0.5} \sigma_{AB}^2 \Omega_D} \quad (6.33)$$

where σ_{AB} is the molecular characteristic length, and Ω is the diffusion collision integral.

Since in this system there is a large amount of air, it is reasonable to assume that the components only diffuse in the air. Then the diffusivities can be expressed as functions of temperature: for the ethylene $D_{ET-air} = 3.62 \times 10^{-5} T^{1.5}$; and for the ethylene oxide $D_{EO-air} = 3.11 \times 10^{-5} T^{1.5}$.

The effective diffusivity of component j within the pellets can be calculated from the following equation

$$D_{ej} = D_{Aj} \frac{\varepsilon_p}{\tau} \quad (6.34)$$

where the pellet porosity, $\varepsilon_p = 0.50$, and the tortuosity factor, $\tau = 19.6$ (see Chapter 4).

The heat capacities of gases can be estimated from the equation (Reid, *et al.*, 1987)

$$C_{mpi} = a + bT + cT^2 + dT^3 \quad (6.35)$$

where a , b , c and d are constants characteristic of each gas. The first term usually has the major contribution (e.g., for nitrogen $a = 31.15$, $b = -0.01357$, $c = 2.68 \times 10^{-5}$ and $d = -1.168 \times 10^{-8}$), and, therefore, the heat capacity can be considered as a constant along the reactor. In the calculations, the average temperature inside the reactor was used and $C_{mpair} = 1.05 \text{ KJ / Kg} \cdot \text{K}$.

6.2.4 Axial Dispersion

In a fixed-bed packed with catalyst pellets, the axial dispersion coefficient can be estimated by the following expressions (Ruthven, 1984)

$$\frac{1}{Pe'} = \gamma' \frac{D_{ET-air} \varepsilon}{u_0 d_p} + \frac{1}{Pe'_\infty \left(1 + \beta' \gamma' \frac{D_{ET-air} \varepsilon}{u_0 d_p} \right)} \quad (6.36)$$

with $\gamma' = 0.73$, $\beta' = 13.0$, $Pe'_\infty = 2.0$ and $Pe' = u_0 d_p / \varepsilon D_{axET}$. Then the Peclet number can be obtained from $Pe = Pe' L / d_p$. Here, an equivalent diameter of $d_e = 0.56$ cm was used. Strictly speaking, for each component, the axial dispersion coefficient is different due to the different molecular diffusivities. In the model, the axial dispersion coefficients are considered as the same for ethylene and ethylene oxide assuming that the turbulence has a main contribution to the axial dispersion. This will be checked in the calculations below.

6.3 BRIEF DESCRIPTION OF EXPERIMENTAL WORK

6.3.2 Experimental Set-up

The apparatus scheme is indicated in Figure 5.2 (Chapter 5). Air and ethylene or ethylene oxide were supplied from standard gas cylinders. Gas pressure was reduced by a two stage regulator. Flow rates were controlled precisely by mass flow controllers. After the mass flow controllers, the gases were mixed and the feed stream flowed through a three-way ball valve and then entered the fixed-bed reactor. The reactor was immersed in a fluidized bath. The product stream flowed through a three-way ball valve and was vented. A tee junction led gas to the sampling through a needle valve. The temperature inside the reactor was read in the indicator of a temperature controller (more details are given in Chapter 5).

6.3.2 Reactor

The fixed-bed reactor was made of a 20 cm in length of 2 cm I.D. stainless steel tubing. The reactor was immersed in an electrically heated fluidized bath of sand (SBL-2D, TECHNE CAMBRIDGE LTD., UK) to keep the necessary temperature for the reaction. The fluidized bath is a cylindrical stainless steel vessel with 35 cm depth. It provides a uniform temperature and good heat transfer. At 300°C, the temperature difference along the bath is less than 2°C. A clean dry compressed air was used to fluidize the sands. A stainless steel tubing with the same dimension as that of the reactor was connected to the reactor for preheating the entering gases to the reaction temperature. Two type "K" (Chromel-Alumel) thermocouples were placed in both bottom and top of the reactor to measure the inlet and outlet stream temperatures, respectively.

6.4 RESULTS AND DISCUSSION

6.4.1 Experimental Results

The catalyst pellets were packed at random in the tube to form a fixed-bed reactor. The mass of the catalysts was weighed ($W = 40.1$ g) before the packing. From the mass of the catalysts and the length of the bed, the bed density was estimated from the relationship

$\rho_b = 40.1/13.6\pi \times (d_R^2/4) = 0.939 \text{ g/ml}$. The particle density is $\rho_p = 2.18 \text{ g/ml}$. The porosity of the bed was then calculated from the densities of the bed and pellet, $\varepsilon = 1 - \rho_b/\rho_p = 0.57$.

The experiments were carried out with two different lengths of fixed-bed, 2.7 cm and 13.6 cm, respectively. In the experiments the inlet temperature, feed composition and gas flowrate were chosen as the adjustable parameters. A range of flowrate of $Q_0 = 17 - 84 \text{ ml/s}$ was used, corresponding to superficial velocities of $u_0 = 5 - 27 \text{ cm/s}$, and for the 13.6 cm bed length, space times of $\tau_0 = 3 - 0.5 \text{ s}$, which correspond to particle Reynolds numbers, $Re_p = u_0 \rho_g d_p / \mu$, in the range 16-81.

First, the heat transfer coefficient was measured. The catalyst pellets were packed in the preheat tube and two thermocouples were placed at different positions. Then, the following equation was used to determine the overall heat coefficient:

$$G_0 C_{mp} \frac{dT}{dL} = \frac{4}{d_R} U (T_0 - T) \quad (6.37)$$

The heat transfer measurement data is given in Table 6.2. This value of the overall heat transfer coefficient, U , was used in the simulations.

Table 6.2 Data for heat transfer coefficient measurement.

Q_0 (l/min)	T_0 (°C)	T_1 (°C)	T_2 (°C)	L_1 (cm)	L_2 (cm)	U (J/s · cm ² · K)
5	150	133	145	14.08	11.10	0.028
3	150	134	148	14.08	11.10	0.029

The experimental results are listed in Tables 6.3 through 6.6, where the ethylene conversion X_{ET} , yield, ρ_{EO} , and relative yield $\Phi_{EO/ET}$ are defined as

$$X_{ET} = \frac{F_{ET}^0 - F_{ET}}{F_{ET}^0} \quad (6.38)$$

$$\Phi_{EO/ET} = \frac{F_{EO}}{F_{ET}^0 - F_{ET}} \quad (6.39)$$

$$\rho_{EO} = \frac{F_{EO}}{F_{ET}^0} \quad (6.40)$$

Here, F_{ET} is the outlet molar flowrate of ethylene, F_{ET}^0 is the molar flowrate of ethylene in the feed, and F_{EO} is the outlet molar flowrate of ethylene oxide.

Table 6.3 Experimental data for the fixed-bed reactor of length 13.6 cm

Run	Q_{ET} (l/min)	Q_{AIR} (l/min)	T_{in} (°C)	$F^0 \times 10^3$ (mol/s)	y_{ET}^0	y_{ET}	y_C	y_{EO}	T_{out} (°C)	X_{ET}	$\Phi_{EO/ET}$
1	0.10	1.0	220	0.818	0.091	0.028	0.024	0.051	232	0.69	0.81
2	0.15	1.0	220	0.856	0.13	0.081	0.025	0.037	228	0.38	0.75
3	0.20	1.0	220	0.893	0.17	0.13	0.024	0.028	225	0.24	0.71
4	0.10	1.5	220	1.19	0.063	0.023	0.021	0.029	243	0.63	0.74
5	0.15	1.5	220	1.23	0.091	0.035	0.025	0.030	240	0.62	0.78
6	0.20	1.5	220	1.26	0.12	0.082	0.024	0.044	236	0.32	0.68
7	0.10	3.0	220	2.31	0.032	0.012	0.010	0.015	258	0.63	0.76
8	0.10	5.0	220	3.79	0.020	0.0070	0.0073	0.0094	260	0.65	0.72
9	0.20	5.0	220	3.87	0.038	0.010	0.015	0.021	326	0.71	0.74
10	0.45	5.0	220	4.06	0.083	0.038	0.018	0.070	248	0.95	0.94

Table 6.4 Experimental data for the fixed-bed reactor of length 13.6 cm

Run	Q_{ET} (l/min)	Q_{AIR} (l/min)	T_{in} (°C)	$F^0 \times 10^3$ (mol/s)	y_{ET}^0	y_{ET}	y_C	y_{EO}	T_{out} (°C)	X_{ET}	$\Phi_{EO/ET}$
1	0.10	1.0	200	0.818	0.091	0.070	0.027	0.0075	205	0.23	0.36
2	0.15	1.0	200	0.856	0.13	0.081	0.026	0.036	206	0.38	0.68
3	0.20	1.0	200	0.893	0.17	0.13	0.026	0.027	206	0.24	0.27
4	0.10	1.5	200	1.19	0.063	0.047	0.023	0.0045	210	0.25	0.27
5	0.15	1.5	200	1.23	0.091	0.058	0.028	0.019	214	0.36	0.58
6	0.10	3.0	200	2.31	0.032	0.016	0.011	0.011	220	0.50	0.67
7	0.20	3.0	200	2.31	0.063	0.018	0.028	0.031	290	0.71	0.69
8	0.30	3.0	200	2.46	0.091	0.049	0.027	0.029	281	0.46	0.68
9	0.10	5.0	200	3.79	0.020	0.012	0.0009	0.0076	211	0.40	0.75
10	0.20	5.0	200	3.87	0.038	0.013	0.014	0.018	334	0.66	0.73

Table 6.5 Experimental data for the fixed-bed reactor of length 13.6 cm

Run	Q_{ET} (l/min)	Q_{AIR} (l/min)	T_{in} (°C)	$F^0 \times 10^3$ (mol/s)	y_{ET}^0	y_{ET}	y_C	y_{EO}	T_{out} (°C)	X_{ET}	$\Phi_{EO/ET}$
1	0.05	1.5	270	1.15	0.032	0.0089	0.027	0.0096	275	0.72	0.78
2	0.10	1.5	270	1.19	0.063	0.016	0.042	0.026	280	0.75	0.55
3	0.10	3.0	270	2.31	0.032	0.010	0.024	0.010	287	0.69	0.45
4	0.15	3.0	270	2.34	0.048	0.016	0.053	0.0055	306	0.67	0.17

Table 6.6 Experimental data for the fixed-bed reactor of length 2.7 cm

Run	Q_{ET} (l/min)	Q_{AIR} (l/min)	T_{in} (°C)	$F^0 \times 10^3$ (mol/s)	y_{ET}^0	y_{ET}	y_C	y_{EO}	T_{out} (°C)	X_{ET}	$\Phi_{EO/ET}$
1	0.05	1.0	220	0.781	0.048	0.036	0.0022	0.011	225	0.25	0.82
2	0.05	1.5	220	1.15	0.032	0.025	0.0020	0.0060	228	0.22	0.86
3	0.05	2.0	220	1.56	0.024	0.020	0.0006	0.0036	225	0.17	0.93
4	0.10	2.5	220	1.93	0.038	0.030	0.0014	0.0073	297	0.21	0.91
5	0.1	3.0	220	2.31	0.032	0.028	0.0018	0.0031	236	0.14	0.76
6	0.05	1.0	240	0.781	0.048	0.035	0.0064	0.0098	255	0.27	0.75
7	0.05	1.5	240	1.15	0.032	0.022	0.0041	0.0080	255	0.31	0.79
8	0.05	2.0	240	1.53	0.024	0.020	0.0027	0.0027	251	0.17	0.66
9	0.10	4.0	240	3.05	0.024	0.018	0.0043	0.0039	270	0.25	0.64

From these tables it can be seen that the conversion are affected by the feed composition, inlet temperature and gas flowrate. The relative yield is in the range of 0.65-0.80 and shows no significant changes with the conversion.

Figures 6.1 and 6.2 show the experimental data plots of yield versus conversion for different reactor lengths.

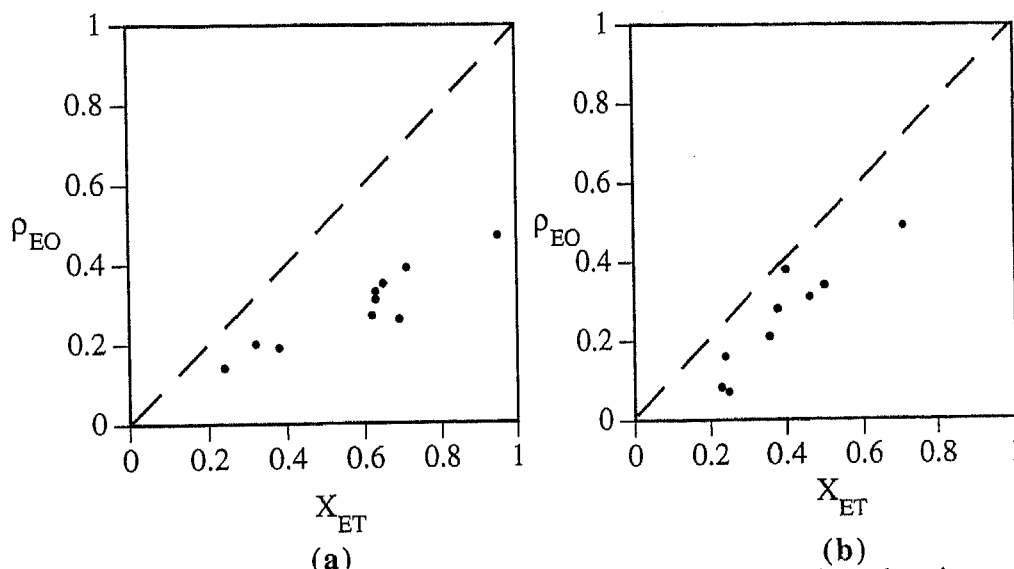


Figure 6.1 Experimental plot of yield versus conversion for the 13.6 cm length reactor: a) inlet temperature $T=220^{\circ}\text{C}$; b) inlet temperature $T=200^{\circ}\text{C}$

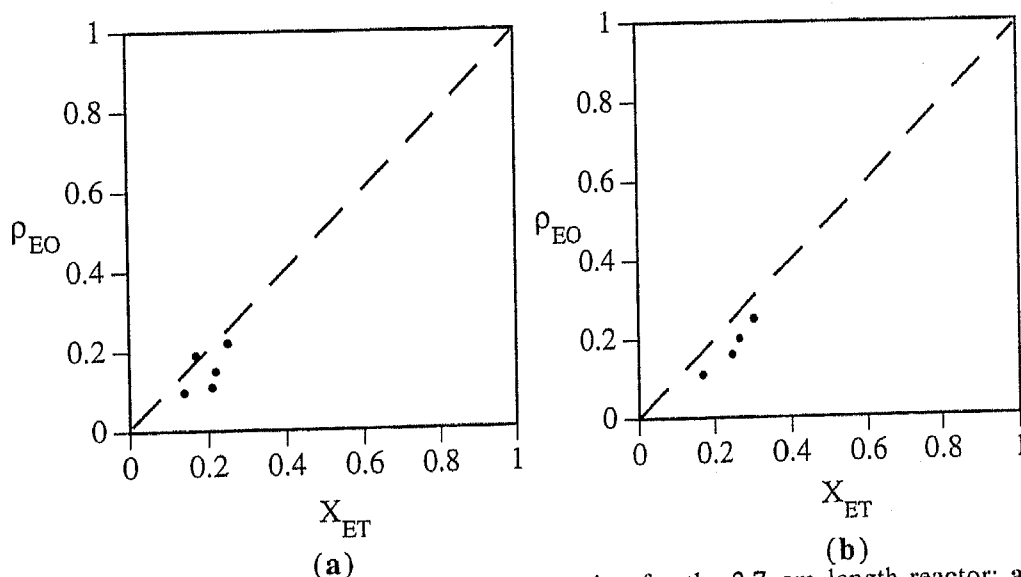


Figure 6.2 Experimental plot yield versus conversion for the 2.7 cm length reactor: a) inlet temperature $T=220^{\circ}\text{C}$; b) inlet temperature $T=240^{\circ}\text{C}$

In the experiments it was found that under certain conditions the reaction ran away, causing the temperature to increase very fast and to very high values. In order to protect the catalyst, when runaway was occurring the feed was cut immediately at temperatures equal or above 350°C . Some of these conditions were recorded and are given in Table 6.7. Comparing the last column in this table with data from Run 4 in Table 6.5, one observes this to be a special case, as the conditions are the same but one of the experiments ran away and the other did not. The

explanation is that this condition may be in the boundary of the runaway limit. At this point even a little disturbance will make reaction run away.

Table 6.7 Conditions for reaction run away.

$T_{in} (^{\circ}\text{C})$	225	250	250	250	250	260	270
$F^0 \times 10^3 (\text{mol/s})$	3.53	7.59	7.66	15.18	15.33	2.38	2.34
y_{ET}^0	0.053	0.020	0.030	0.038	0.029	0.063	0.048

It also was observed that as the feed was introduced to the reactor the outlet temperature goes up, passes through a maximum and finally becomes stable. An example is shown in Figure 6.3.

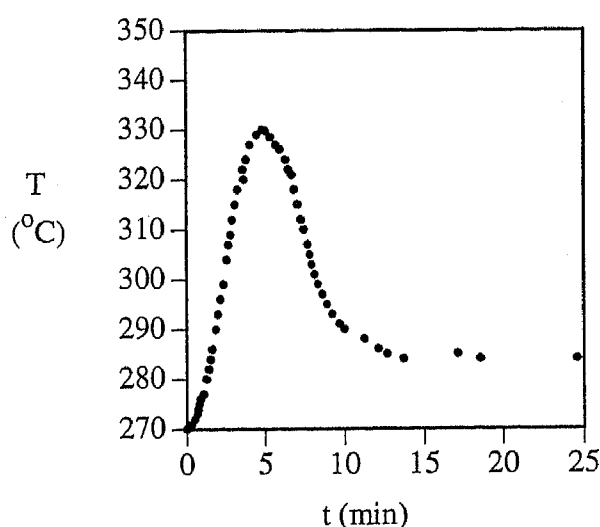


Figure 6.3 Dynamic changes of outlet temperature as a function of time for inlet temperature $T=270^{\circ}\text{C}$ and gas flowrate $Q_0 = 53 \text{ ml/s}$ and ethylene mole fraction $y_{ET}^0 = 0.063$.

6.4.2 Simulations

The partial differential equation for the pellets were solved by using a finite element program of TWODEPEP package (IMSL, 1983). The partial differential equation for the bed were solved by using the PDECOL package (Madsen and Sincovec, 1977). The average reaction rates $\bar{R}_i$ in Equation 6.20 were calculated by using a bicubic spline quadrature method (IMSL, 1982). More details of the numerical solution scheme are given in Appendices 6.A. Simulations for a first order reaction, for which there exists an analytical solution for the pellet equations, are presented in Appendices 6.B.

Figure 6.4 is the plot of concentration and temperature profiles along the reactor at inlet temperature $T=220^{\circ}\text{C}$ with different gas flowrate. The results for the case of inlet temperature $T=240^{\circ}\text{C}$ are shown in Figure 6.5.

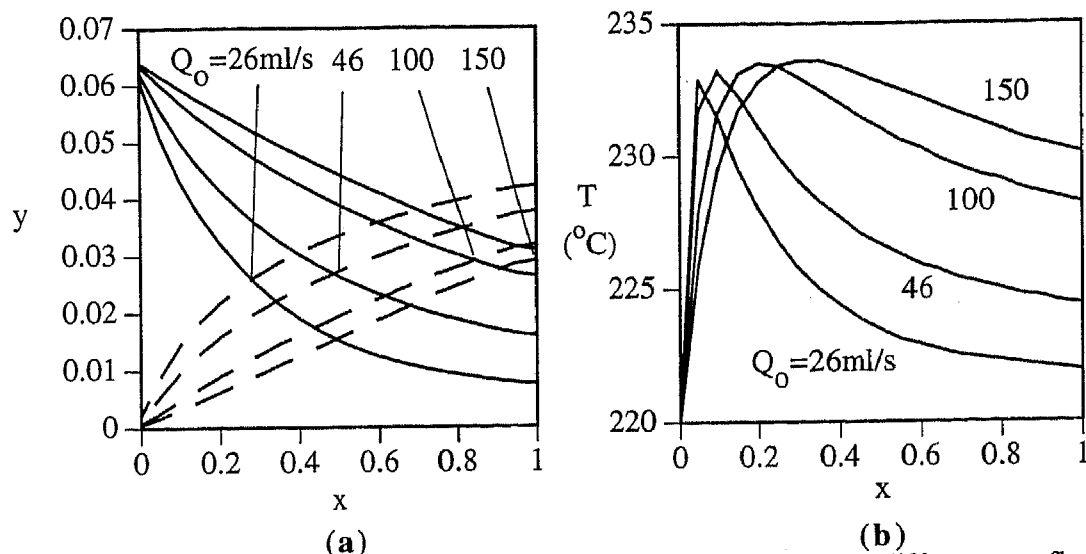


Figure 6.4 Concentration and temperature profiles along the reactor for different gas flowrate with inlet temperature $T=220^{\circ}\text{C}$ and heat transfer coefficient $U = 0.029 \text{ J/s} \cdot \text{cm}^2 \cdot \text{K}$: **a)** concentration (— Ethylene, --- Ethylene oxide); **b)** temperature.

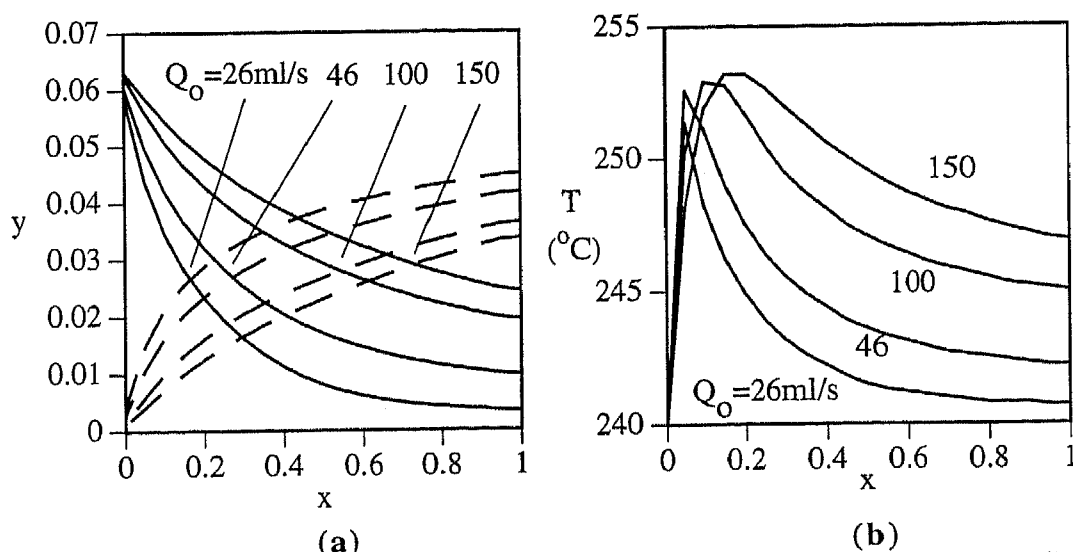


Figure 6.5 Concentration and temperature profiles along the reactor for different gas flowrate with inlet temperature $T=240^{\circ}\text{C}$ and heat transfer coefficient $U = 0.05 \text{ J/s} \cdot \text{cm}^2 \cdot \text{K}$: **a)** concentration (— Ethylene, --- Ethylene oxide); **b)** temperature.

The simulations show that the catalyst is highly active. The hot spot is always near the reactor entrance. The concentration and temperature profiles are strongly dependent on the feed gas flowrate. As the gas flowrate increases the conversion of the reaction decreases and the hot spot goes deeper inside the reactor. Ethylene oxidation is a strong exothermic reaction; in the simulations it has been found that as the inlet temperature goes up to a certain value, $T > 240^{\circ}\text{C}$ the differential equation becomes unsolvable. Physically, this may mean that the reaction runs away at this inlet temperature due to the significant reaction heat. The overall heat transfer coefficient has a significant effect on the temperature profile along the reactor, the simulation results are shown in Figure 6.6.

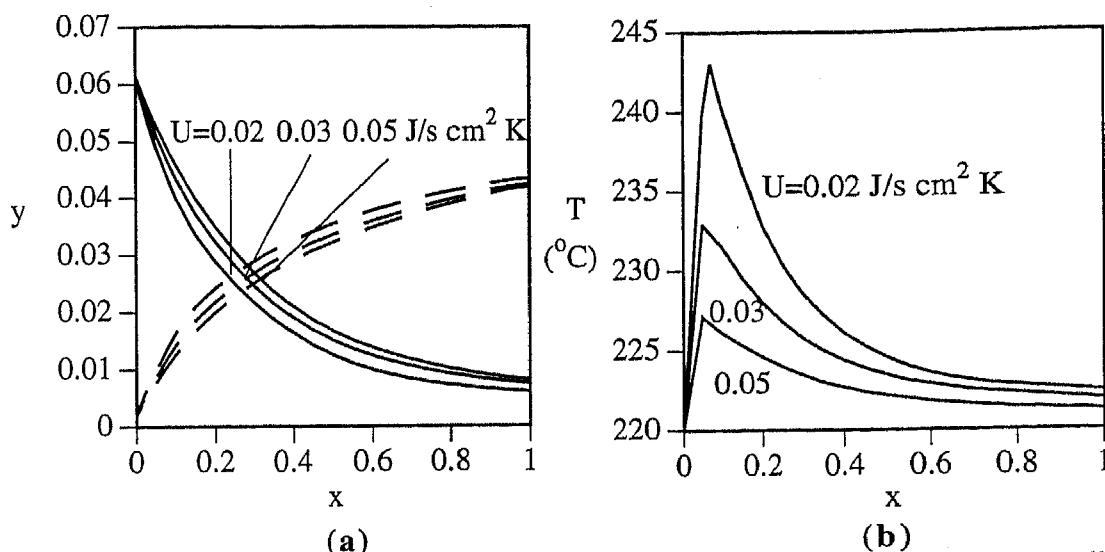


Figure 6.6 Concentration and temperature profiles along the reactor for different overall heat transfer coefficient with inlet temperature $T=220^\circ\text{C}$ and gas flowrate $Q_0 = 26 \text{ ml/s}$. a) concentration (— Ethylene, --- Ethylene oxide); b) temperature.

Figure 6.7 shows the plot of the effectiveness factor profiles inside the reactor. After the hot spot the effectiveness factor goes to a small constant value, $\eta < 0.2$. This value of the effectiveness factor indicates that under these conditions intraparticle mass transfer resistance should not be neglected.

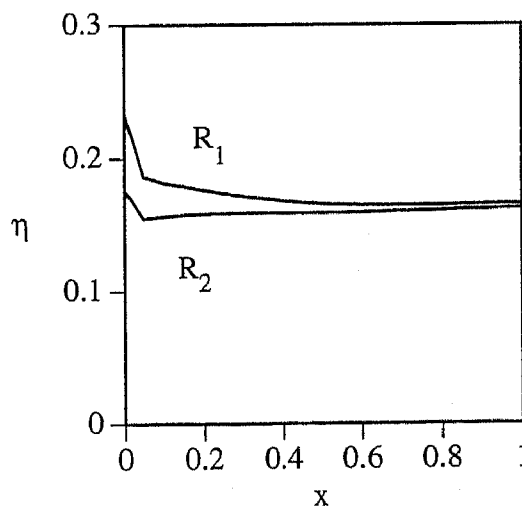


Figure 6.7 Effectiveness factor profiles along the reactor at temperature $T=220^\circ\text{C}$ and gas flowrate $Q_0 = 26 \text{ ml/s}$.

The calculations showed that the Peclet numbers for ethylene ($Pe_{ET} = 65.1$, Run 4 in Table 6.3) and ethylene oxide ($Pe_{EO} = 63.2$) have no significant difference.

6.4.3 Discussion

To check the validity of the model, the experimental data is compared with the simulation results. Run 1, Run 4 and Run 8 in Table 6.3 are taken as examples and the comparison is shown in Table 6.8. The observed deviations are too large to be accepted. These deviations may be attributed to the inaccuracy of the kinetic rates. First, there is deactivation of the

catalyst, as the catalyst pellets for the kinetic measurement and the fixed-bed experiments may have different ages, and present different activities. Second, the rate equations are valid on a narrow range of concentrations, as it has been mentioned in Chapter 5. In fact, the reaction rate equations can only be applied to a narrow range of experimental conditions owing to the fact that different conditions produce different catalyst surface situations (Carra and Forzatti, 1977), and, furthermore, it was found that the experimentally obtained kinetic rate equations are not able to fit the entire range of conversions (Schouten, *et al.*, 1994). Another possible reason is the accuracy of the overall heat transfer coefficient measurement. In the measurement of the overall heat transfer coefficient, its change along the reactor length was not considered.

Table 6.8 Comparison of experimental data and simulation results

		y_{ET}^0	y_{ET}	y_{EO}	T_{out} (°C)
Run 1	Exp.	0.091	0.028	0.051	232
	Simu.	0.091	0.0089	0.061	221
Run 4	Exp.	0.063	0.023	0.029	243
	Simu.	0.063	0.0074	0.042	221
Run 8	Exp.	0.020	0.0070	0.0094	260
	Simu.	0.020	0.0056	0.011	222

For the deactivation of the catalyst, Borman and Westerterp (1995) reported that the changes in the catalyst affect only the magnitude of the reaction rates and not the form of the expressions or the dependence of the rates on partial pressure or temperature. In this case the deactivation of the reactions can be expressed as

$$(r_i)_{t_1} = f_i(r_i)_{t_0} \quad (6.41)$$

where $(r_i)_{t_0}$ and $(r_i)_{t_1}$ are the reaction rates at time t_0 and t_1 , respectively, and f_i is the deactivation coefficient. Then, in the simulations, both overall heat transfer coefficient, U , and the deactivation coefficient, f_i , could be adjusted to simulate the experimental data.

The effect of intraparticle convection on reaction is presented in Figure 6.8. This effect can only be observed for high values of the intraparticle Peclet number, $\lambda > 50$. This result is not surprising, as the hollow cylinder geometry of the catalyst pellets results in an equivalence ratio between the characteristic dimensions of the hollow cylinder and the slab of about $\ell_s / \ell = 0.15$. Thus, since it is known that for a slab, intraparticle convection becomes important for values of the intraparticle Peclet number greater than 10, for the hollow cylinder geometry, this effect should be seen at around $\lambda = 50$.

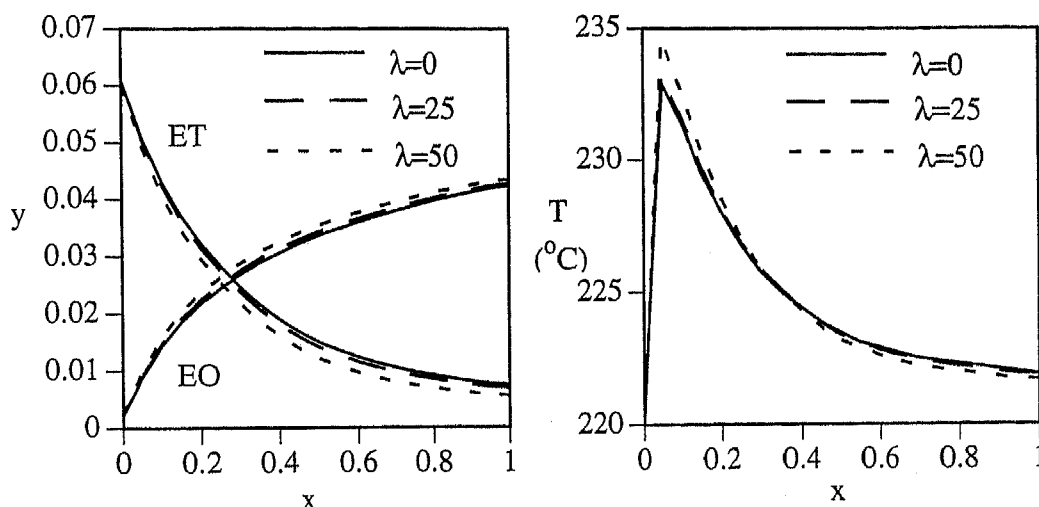


Figure 6.8 Concentration and temperature profiles along the reactor for different intraparticle Peclet number values with inlet temperature $T=220^{\circ}\text{C}$ and gas flowrate $Q_0 = 26 \text{ ml / s}$. a) concentration ; b) temperature .

This effect was not clearly observed in the experiments, although it may exist. In fact, the effect of intraparticle convection is not easily to be observed, due to two main reasons. First, to have significant intraparticle convection, the gas flowrate has to be sufficiently high to generate the necessary pressure drop across the pellet, but by doing this, axial dispersion may decrease, the overall efficiency increase and the effect of intraparticle convection may not be identified. Second, from the plot of the Thiele modulus versus the effectiveness factor it is known that the effect of the intraparticle convection is most important in the intermediate regime, for which the necessary conditions may not be easily reached.

6.5 CONCLUSIONS

Ethylene oxidation has been studied in a fixed-bed reactor. The reaction conversion and yield were analysed. Some conditions for run away were determined. A simulation model was proposed. The concentration and temperature profiles were studied. The effect of the intraparticle convection was discussed. It has been shown that for the hollow cylinder particle the effect of the intraparticle convection can be seen only for high values of the intraparticle Peclet number.

6.6 NOTATION

a	ratio of internal to external radius of pellet
a_h	heat transfer area per unit volume of pipe, cm^{-1}
C_j	concentration of species j , $\text{K mole} / \text{m}^3$
C_{pm}	heat capacity of gas, $\text{KJ/kg} \cdot \text{K}$
c_i	dimensionless concentration defined in Equation 6.23
D	effective diffusivity ratio
D_{AB}	diffusivities for binary gas, cm^2 / s
Da	Damköhler number
D_{ax}	axial dispersion coefficient, cm^2 / s
D_{ej}	effective diffusivity for component j , cm^2 / s
d_p	pellet diameter, cm
d_R	reactor diameter, cm
E_i	activation energy for reaction i , J/mol
f_i	deactivation coefficient for reaction i
G_0	mass flow rate, $\text{Kg}/\text{cm}^2 \cdot \text{s}$
H	reaction heats ratio
K_j^i	adsorption constant for component j in reaction i , bar^{-1}
K_j^{∞}	pre-exponential adsorption factor for component j in reaction i , bar^{-1}
k_r^{∞}	frequency coefficients, $\text{mol/s} \cdot \text{Kg}$
L	reactor length, cm
ℓ	length of the pellet, cm
M_{AB}	mass weight $= 2(1/M_A + 1/M_B)^{-1}$
Pe	Peclet number
P_0	total pressure, atm
P_j	partial pressure of component j , atm
Q	volume flowrate at standard state, ml / min
$\mathfrak{R}$	ideal gas constant
R_i	rate of reaction i , $\text{mol/s} \cdot \text{Kg}$
$\bar{R}_i$	average rate of reaction i within pellet, $\text{mol/s} \cdot \text{Kg}$
$\bar{R}_i^*$	dimensionless average reaction rate, $\bar{R}_i / k_r^1$
r	radial coordinate for the pellets, cm
r_1	product rate of ethylene oxide, $\text{mol/s} \cdot \text{Kg}$
r_2	product rate of carbon dioxide, $\text{mol/s} \cdot \text{Kg}$
St	Stanton number
T	temperature, K
T_{act}^i	$E_i / \mathfrak{R}$ for reaction i , K
$T_{\text{ads},j}^i$	$\Delta H_j^i / \mathfrak{R}$ for component j in reaction i , K
T_0	temperature of cooling medium, K

u	superficial velocity, cm / s
v_0	superficial intraparticle velocity, cm / s
X_{ET}	reaction conversion defined by Equation 6.38
x_b	longitudinal coordinate for the bed, cm
x	dimensionless longitudinal coordinate for the bed
y_j	mole fraction of component j
z_p	longitudinal coordinate for the pellets, cm
z	dimensionless longitudinal coordinate for the pellets

Greek Symbols

γ_0	Arrhenius number
ΔH	reaction heat KJ / mol
ε	porosity
$\Phi_{EO/ET}$	relative yield defined in Equation 6.39
ϕ	Thiele modulus
η	effectiveness factor
λ	intraparticle Peclet number
θ	dimensionless time defined by Equation 6.26
ρ	density, Kg / m ³
ρ	dimensionless radial coordinate
ρ_{EO}	relative yield defined in Equation 6.40
τ	tortuosity factor
τ_0	space time, s
Θ_{ad}	dimensionless adiabatic temperature rise
σ	molecular characteristic length, Å
Ω	diffusion collision intergratal
ω	aspect ratio of length to external radius of pellet
U	overall heat transfer coefficient, KJ/s · cm ² · K
ξ	normalized molar fraction defined in Equation 6.9

Subscripts and Superscripts

b	bulk
EO	ethylene oxide
ET	ethylene
C	carbon dioxide
O	oxygen
i	reaction
j	component
p	pellet
0	inlet
s	slab

6.7 LITERATURE CITED

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APPENDICES

6.A NUMERICAL SOLUTION SCHEME

The numerical integration scheme for the problem at hand is a complex one, as it involves several steps, which will be described below. The problem to be solved can be expressed in the following way. A boundary value, second order, ODE problem corresponding to the fixed-bed model equations

$$F_i\left(x, u_i, \frac{du_i}{dx}, \frac{d^2u_i}{dx^2}; \eta_i(u_i)\right) = 0 \quad i = 1, 2, 3 \quad (6.A1)$$

where x is the bed spatial coordinate, u_i corresponds to the bed ethylene and ethylene oxide dimensionless concentrations, c_{ET} and c_{EO} , and the dimensionless temperature, θ .

The pellet effectiveness factor for each reaction, η_i , which is dependent on the pellet surface conditions, can be obtained by solving the pellet two-dimensional PDE problem

$$G_i\left(\rho, z, v_i, \frac{\partial v_i}{\partial \rho}, \frac{\partial^2 v_i}{\partial \rho^2}, \frac{\partial v_i}{\partial z}, \frac{\partial^2 v_i}{\partial z^2}; f(u_i)\right) = 0 \quad i = 1, 2 \quad (6.A2)$$

where ρ and z are the dimensionless pellet spatial coordinates and v_i correspond to the particle ethylene and ethylene oxide normalised molar fractions, ξ_{ET}^p and ξ_{EO}^p . This problem is coupled with the fixed-bed problem through a reaction term, $f(u_i)$, and through the boundary conditions

$$\text{at pellet surface} \quad v_1 = u_1 \quad v_2 = u_2$$

The solution of this last set of PDE's gives the pellet normalised molar fractions profiles, ξ_{ET}^p and ξ_{EO}^p , which can be integrated over the pellet volume to give the respective efficiency factors, η_i .

The solution of these two coupled problems was accomplished by using two software packages, PDECOL and TWODEPEP, respectively, for the fixed-bed and the particle equations.

PDECOL is a package designed to solve nonlinear partial differential equations (in time and one spatial dimension) and uses finite element collocation techniques with piecewise polynomials for the spatial discretization of the spatial variable and conventional time discretization methods for the temporal integration. This package is used to setup and solve the fixed-bed model equations. In these calculations a third order piecewise polynomial was used (KORD=4) and the number of continuity conditions imposed on the polynomial pieces across all of the interior points was NCC=2. The number of intervals used for the spatial discretization varied from

NINT=10 to 20, according to the difficulty of the problem. This package is used by calling a subroutine named PDECOL which performs the discretization and integration using a set of user-supplied subroutines containing the system of PDE's, the boundary conditions and the initial conditions. Since the problem to be solved here is at steady-state the initial conditions are replaced by an initial guess and each time step corresponds now to an iteration of the non-linear problem.

TWODEPEP is a finite element program which solves elliptic (steady-state) and parabolic (time-dependent) partial differential equation problems in general two-dimensional regions. The finite element used is the standard six-node triangle with quadratic basis functions, with one edge curved when adjacent to a curved boundary, according to the isoparametric method. The resulting algebraic equations are solved by the Newton's method. In these calculations, the number of triangles was set to NTF=100. This package is used by creating an *Input Data Set*, which completely specifies the problem to be solved.

The diagram of Figure 6.9 shows how the interaction between the two packages is done.

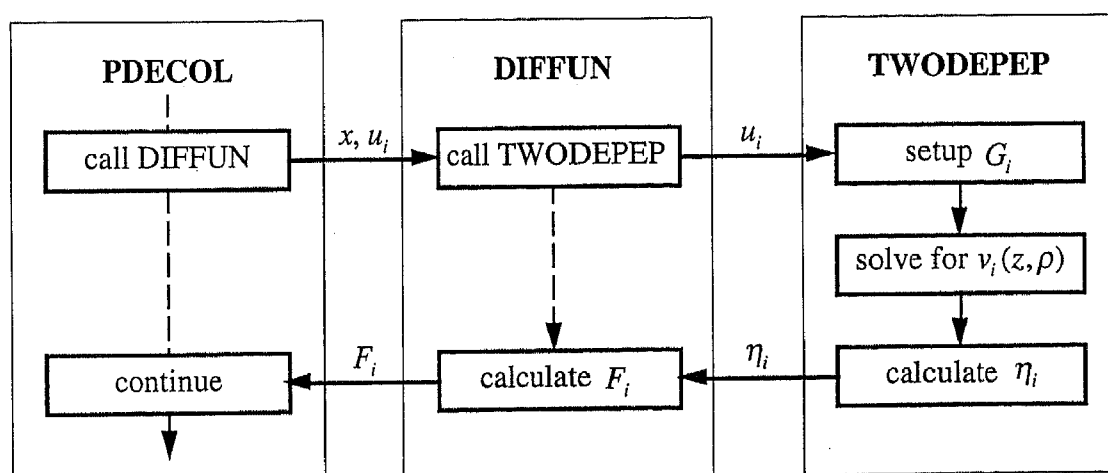


Figure 6.9 Numerical integration scheme.

6.B SIMULATION OF FIRST ORDER REACTION IN FIXED-BED

6.B.1 Model Equations for the Pellets

The steady-state differential mass balance equations for the ethylene within an hollow cylinder pellet are

$$D_e \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_{ET}^p}{\partial r} \right) + \frac{\partial^2 C_{ET}^p}{\partial z_p^2} \right) - v_0 \frac{\partial C_{ET}^p}{\partial z_p} - (R_1 + R_2/2) = 0 \quad (6.B1)$$

$$r = r_1 \text{ and } r = r_2 \quad \forall z_p \quad C_{ET}^p = C_{ET} \quad (6.B1a)$$

$$z_p = 0 \text{ and } z_p = \ell \quad \forall r \quad C_{ET}^p = C_{ET} \quad (6.B1b)$$

where D_e is the intraparticle effective diffusivity of ethylene; v_0 is the gas superficial velocity through the pellet; r and z_p are the radial and longitudinal coordinates, respectively; C_{ET}^p is the concentration of ethylene within the pellet; C_{ET} is the concentration of ethylene in the bulk phase; r_1 and r_2 are the internal and the external radius of the hollow cylinder pellet, respectively and ℓ is the pellet length.

R_1 is the ethylene oxide product rate (Equation 6.1) and R_2 is the carbon dioxide product rate (Equation 6.2). The assumed kinetic rate equations are first order, i.e.,

$$R_i = k_{ri} C_{ET} \quad (6.B2)$$

Here the rate constants are expressed as:

$$k_{ri} = k_{ri}^\infty \exp(-T_{\text{act}i}/T) \quad (6.B3)$$

where k_{ri}^∞ is the frequency coefficient, $T_{\text{act}i} = E_i/\mathfrak{R}$, and E_i is the activation energy for reaction i , $\mathfrak{R}$ is the ideal gas constant and T is the temperature.

Introducing the following dimensionless variables

$$z = \frac{z_p}{\ell} \quad \rho = \frac{r}{r_2} \quad c_{ET}^p = \frac{C_{ET}^p}{C_{ET}} \quad (6.B4)$$

the dimensionless model equation is obtained

$$\omega^2 \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial c_{ET}^p}{\partial \rho} \right) \right] + \frac{\partial^2 c_{ET}^p}{\partial z^2} - 2\lambda \frac{\partial c_{ET}^p}{\partial z} - \phi^2 c_{ET}^p = 0 \quad (6.B5)$$

with

$$\rho = a \text{ and } \rho = 1 \quad \forall z \quad c_{ET}^p = 1 \quad (6.B5a)$$

$$z = 0 \text{ and } z = 1 \quad \forall \rho \quad c_{ET}^p = 1 \quad (6.B5b)$$

The model parameters are

$$\lambda = \frac{v_o \ell}{2D_e}; \quad \phi^2 = \frac{(k_{r1} + k_{r2})\ell^2}{D_e}; \quad \omega = \frac{\ell}{r_2}; \quad a = \frac{r_1}{r_2} \quad (6.B6)$$

where λ is the intraparticle Peclet number; ϕ is the Thiele modulus; ω is the aspect ratio of the length to external radius, and a is the ratio of the internal radius to the external radius.

From the solution of Equation 6.B5, the effectiveness factor can be obtained:

$$\begin{aligned} \eta &= \frac{\int_a^1 \int_0^1 c_{ET} \rho d\rho dz}{\int_a^1 \int_0^1 \rho d\rho dz} \\ &= 1 - \sum_{n=1}^{\infty} \frac{2\phi^2 M_n^2}{(1-a^2)(\omega^2 \alpha_n'^2 + \phi^2) N_n} \left[1 + \left(\frac{\cosh \lambda}{\sinh \beta_n'^2} - \coth \beta_n'^2 \right) \frac{2\beta_n'}{\beta_n'^2 - \lambda^2} \right] \end{aligned} \quad (6.B7)$$

where α'_n is the root of

$$J_0(a\alpha'_n)Y_0(\alpha'_n) - J_0(\alpha'_n)Y_0(a\alpha'_n) = 0 \quad (6.B8)$$

and

$$\beta'_n = \sqrt{\lambda^2 + \omega^2 \alpha_n'^2 + \phi^2} \quad (6.B9)$$

$$N_n = \int_a^1 [J_0(a\alpha'_n)Y_0(\alpha'_n \rho) - J_0(\alpha'_n \rho)Y_0(a\alpha'_n)]^2 \rho d\rho \quad (6.B10)$$

$$M_n = \frac{1}{\alpha'_n} \{ J_0(a\alpha'_n)[Y_1(\alpha'_n) - aY_1(a\alpha'_n)] - Y_0(a\alpha'_n)[J_1(\alpha'_n) - aJ_1(a\alpha'_n)] \} \quad (6.B11)$$

and Y_0 and Y_1 are the zero and first order Bessel functions of the second kind, respectively.

Plots of the effectiveness factor, η , as a function of Thiele modulus, ϕ , for different values of the intraparticle Peclet number, λ , are shown in Figure 6.10. It is observed that intraparticle convection has a significant effect on the effectiveness factor, for values of ϕ around 10 and for large values of the intraparticle Peclet number, say $\lambda \geq 50$. As it was discussed before (see Section 6.4.3) the reason for these high values of λ , compared with the values expected for the slab geometry, $\lambda = 10$, is due to the fact that the equivalence ratio between the slab and the cylinder geometry is around $\ell_s / \ell = 0.15$ (see Chapter 4). If the equivalent length $\ell_s = 0.15 \ell$ is used to define the Thiele modulus, the plots of η versus ϕ should have the same form of those for the slab particle. This is shown in Figure 6.11a. Furthermore, if a specific dimension, defined as the particle volume divided by the external area, $\ell_{norm.} = V_p / A_p = \ell/2[1 + \omega/(1-a)]$,

is used to define the normalised Thiele modulus, the plots in Figure 6.11b show that the shapes are close to those for the slab particle.

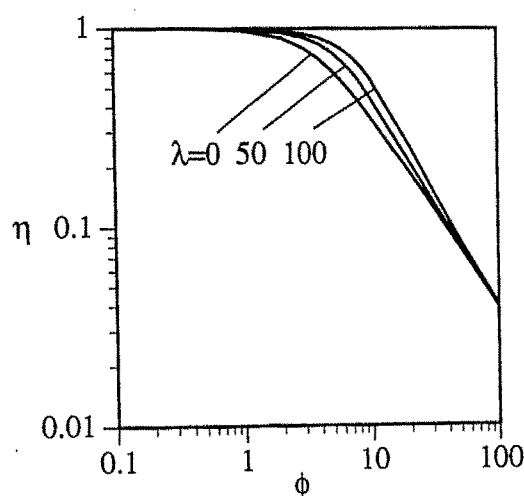


Figure 6.10 Effectiveness factor, η , as a function of Thiele modulus, ϕ , for different values of the intraparticle Peclet number, λ .

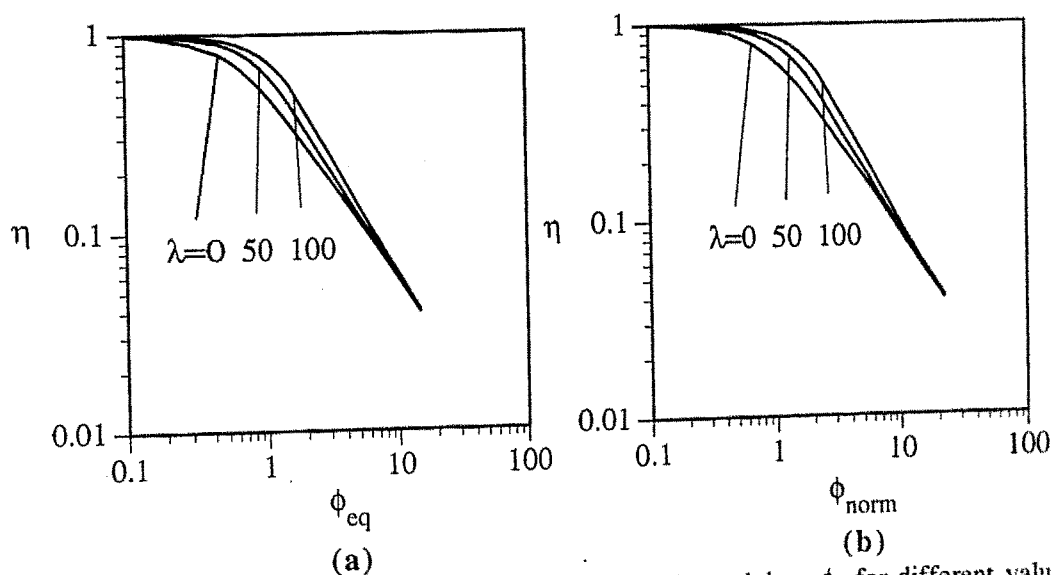


Figure 6.11 Effectiveness factor, η , as a function of Thiele modulus, ϕ , for different values of the intraparticle Peclet number, λ : a) equivalent Thiele modulus; b) normalised Thiele modulus.

6.B.2 Model Equations for the Fixed-Bed

In a reactor of length L packed with porous catalysts where reaction takes place, the differential mass balance equation for the reactant ethylene and product ethylene oxide at steady-state can be written as

$$\varepsilon D_{ax} \frac{d^2 C_{ET}}{dx_b^2} - \frac{d(uC_{ET})}{dx_b} - \eta(1-\varepsilon)(R_1^b + R_2^b/2) = 0 \quad (6.B12)$$

$$\varepsilon D_{ax} \frac{d^2 C_{EO}}{dx_b^2} - \frac{d(uC_{EO})}{dx_b} + \eta(1-\varepsilon)R_1^b = 0 \quad (6.B13)$$

where D_{ax} is the axial dispersion coefficient; ε is the bed porosity; x_b is the axial coordinate in the bed; C_{ET} and C_{EO} are the concentration of ethylene and ethylene oxide in the bulk phase, respectively; η is the effectiveness factor. The gas superficial velocity, u , is a function of the axial position along the reactor due to the temperature profile. Considering that this dependence can be expressed as

$$u = \frac{u_0 T}{T_0} \quad (6.B14)$$

where T_0 is the inlet temperature and u_0 is the inlet gas superficial velocity, the model equations become

$$\varepsilon D_{ax} \frac{d^2 C_{ET}}{dx_b^2} - \frac{T u_0}{T_0} \frac{dC_{ET}}{dx_b} - \frac{C_{ET} u_0}{T_0} \frac{dT}{dx_b} - \eta(1 - \varepsilon)(R_1^b + R_1^b/2) = 0 \quad (6.B15)$$

$$\varepsilon D_{ax} \frac{d^2 C_{EO}}{dx_b^2} - \frac{T u_0}{T_0} \frac{dC_{EO}}{dx_b} - \frac{C_{EO} u_0}{T_0} \frac{dT}{dx_b} + \eta(1 - \varepsilon)R_1^b = 0 \quad (6.B16)$$

The energy balance equation is

$$G_0 C_{pm} \frac{dT}{dx_b} = \eta(1 - \varepsilon)[R_1^b(-\Delta H_{R1}) + R_2^b(-\Delta H_{R2})/2] - \frac{4U}{d_R}(T - T_0) \quad (6.B17)$$

where G_0 is the total mass flow rate, C_{pm} is the heat capacity of the gas, ΔH_{R1} is the reaction heat of partial ethylene oxidation, ΔH_{R2} is the reaction heat of complete ethylene oxidation, d_R is the reactor diameter, U is the overall heat transfer coefficient, and T_0 is the temperature of the cooling medium and it has the same value of that in the inlet gas.

The boundary conditions are

$$x_b = 0 \quad C_{ET} - \frac{\varepsilon D_{ax}}{u_0} \frac{dC_{ET}}{dx_b} = C_{ET0} \quad (6.B18a)$$

$$C_{EO} - \frac{\varepsilon D_{ax}}{u_0} \frac{dC_{EO}}{dx_b} = 0 \quad (6.B18b)$$

$$T = T_0 \quad (6.B18c)$$

$$x_b = L \quad \frac{dC_{ET}}{dx_b} = \frac{dC_{EO}}{dx_b} = 0 \quad (6.B18d)$$

Introducing the dimensionless variables

$$x = \frac{x_b}{L} \quad \theta = \frac{T}{T_0} \quad c_{ET} = \frac{C_{ET}}{C_{ET}^0} \quad c_{EO} = \frac{C_{EO}}{C_{ET}^0} \quad (6.B19)$$

the dimensionless model equations are obtained

$$\frac{1}{Pe} \frac{d^2 c_{ET}}{dx^2} - \theta \frac{dc_{ET}}{dx} - c_{ET} \frac{d\theta}{dx} - Da\eta(1-\varepsilon)(1+k_{r2}/2k_{r1})c_{ET} = 0 \quad (6.B20)$$

$$\frac{1}{Pe} \frac{d^2 c_{EO}}{dx^2} - \theta \frac{dc_{EO}}{dx} - c_{EO} \frac{d\theta}{dx} + Da\eta(1-\varepsilon)c_{ET} = 0 \quad (6.B221)$$

$$\frac{d\theta}{dx} = Da\Theta_{ad}\eta(1-\varepsilon)[1+Hk_{r2}/2k_{r1}]c_{ET} - St(\theta-1) \quad (6.B22)$$

with

$$x=0 \quad c_{ET} - \frac{1}{Pe} \frac{dc_{ET}}{dx} = 1 \quad (6.B23a)$$

$$c_{EO} - \frac{1}{Pe} \frac{dc_{EO}}{dx} = 0 \quad (6.B23b)$$

$$\theta = 1 \quad (6.B23c)$$

$$x=1 \quad \frac{dc_{ET}}{dx} = 0 \quad (6.B23d)$$

$$\frac{dc_{EO}}{dx} = 0 \quad (6.B23e)$$

where $Da = Da_0 \exp\left[-\gamma_0\left(\frac{1}{\theta}-1\right)\right]$, and space time $\tau_0 = \frac{L}{u_0}$.

The model parameters are

Peclet number

$$Pe = \frac{u_0 L}{\varepsilon D_{axET}}$$

Damköhler number

$$Da_0 = \tau_0 k_{r1}^\infty \exp(-\gamma_0)$$

Arrhenius number

$$\gamma_0 = \frac{T_{act}}{T_0}$$

Dimensionless adiabatic temperature rise

$$\Theta_{ad} = \frac{C_{ET}^0 (-\Delta H_1)}{\rho_g C_{pm} T_0}$$

Stanton number

$$St = \frac{a_h UL}{G_0 C_{pm}}$$

The heat transfer area per unit volume of pipe

$$a_h = \frac{4}{d_R}$$

Heats of reaction ratio

$$H = \frac{\Delta H_2}{\Delta H_1}$$

6.B.3 Results of Simulations

The values of the parameters used in these simulations are given in Table 10.

Table 6.10 Summary of parameter values in simulations.

$k_{r2} = 5 \times 10^5 \exp(-60000/\mathcal{R}T) \text{ s}^{-1}$	$k_{r2} = 4 \times 10^5 \exp(-60000/\mathcal{R}T) \text{ s}^{-1}$
$Pe = 100$	$L = 20\text{cm}$
$\Delta H_{R1} = -105\text{kJ/mol}$	$\Delta H_{R2} = -1327\text{kJ/mol}$
$d_R = 2\text{cm}$	$C_{pm} = 1.05\text{kJ/kg} \cdot \text{K}$
$U = 0.5\text{kJ/s} \cdot \text{cm}^2 \cdot \text{K}$	$\varepsilon = 0.57$
$\rho_g = 1.25\text{kg/m}^3$	$D_e = 0.018\text{cm}^2/\text{s}$

It is observed that the concentration and temperature profiles along the reactor depend on the inlet temperature and gas superficial velocity. Figure 6.12 shows the concentration and temperature profiles for different inlet temperatures. For the different gas superficial velocity, the profiles are shown in Figure 6.13.

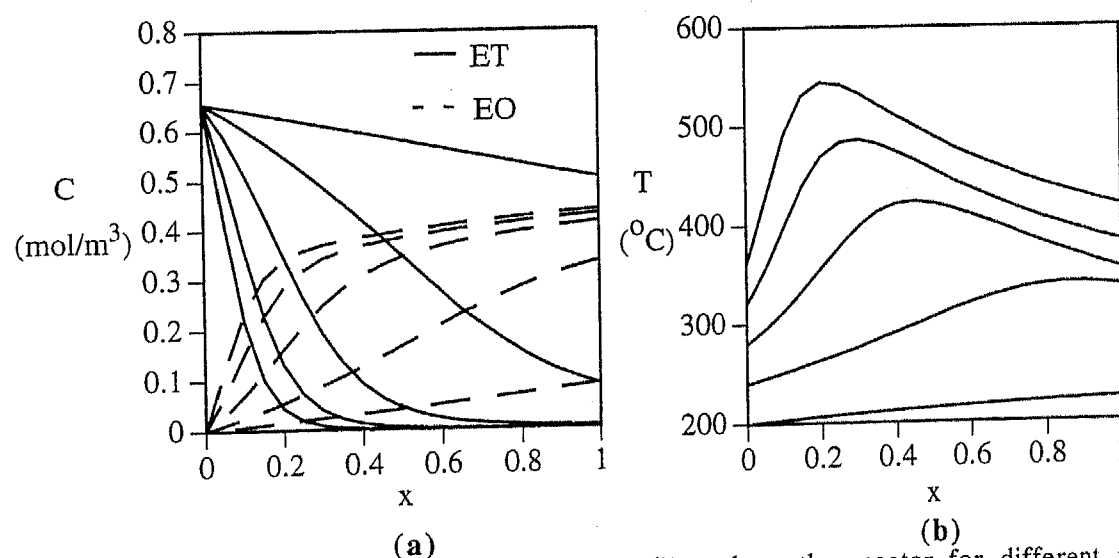


Figure 6.12 Concentration and temperature profiles along the reactor for different inlet temperature with velocity $u_0 = 30 \text{ cm/s}$: a) concentration; b) temperature. Curves from left to right (concentration) or from top to bottom (temperature) correspond to inlet temperatures of 360, 320, 280, 240 and 200 $^{\circ}\text{C}$.

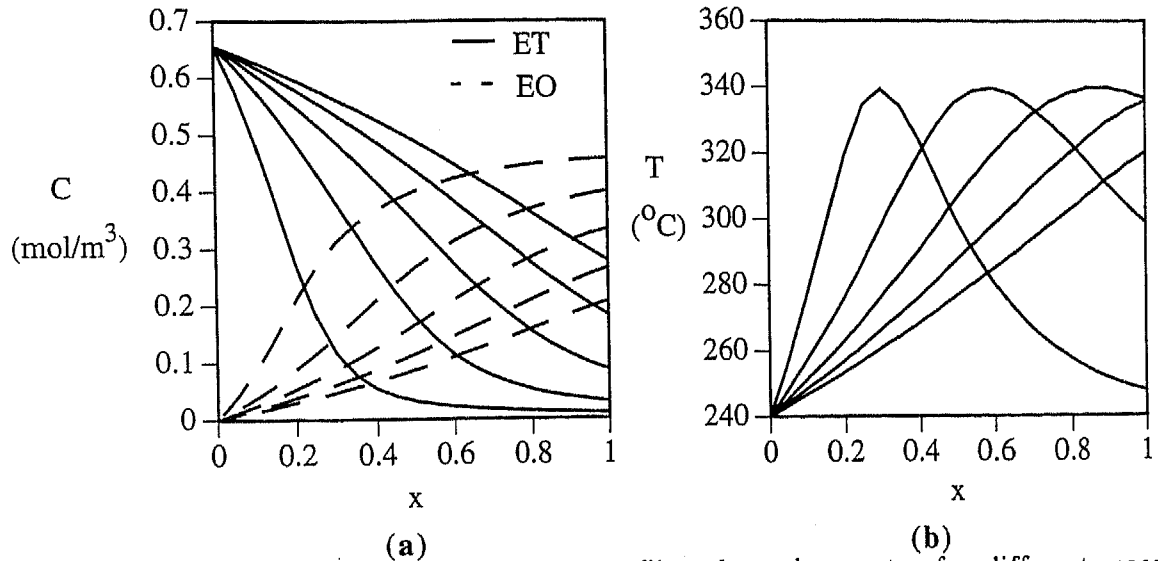


Figure 6.13 Concentration and temperature profiles along the reactor for different mass flowrate with inlet temperature $T=240^\circ\text{C}$: a) concentration; b) temperature. Curves from left to right (concentration) or from top to bottom (temperature) correspond to values of the velocity u_0 of 10, 20, 30, 40, 50 cm/s.

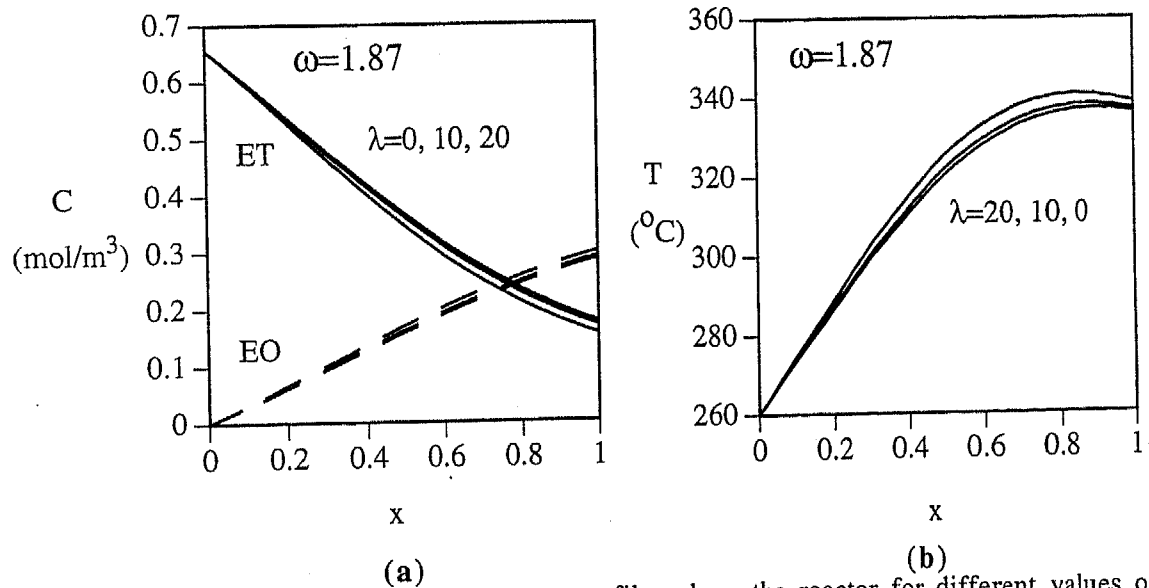


Figure 6.14 Concentration and temperature profiles along the reactor for different values of the intraparticle Peclet number with inlet temperature $T=260^\circ\text{C}$, mass flowrate $u_0 = 30$ cm/s and length radius ratio $\omega = 1.87$: a) concentration; b) temperature.

In the kinetic and diffusion regimes, the effect of intraparticle convection is negligible. In the simulations with the values of parameters given above, the system is near the diffusion controlling regime, i.e., $\phi = 15$ (see Figure 6.10). In order to see the effect of the intraparticle convection, some parameters were adjusted to allow the system to be at the intermediate regime where Thiele modulus is $\phi = 5 - 8$. Here the effective diffusivity is changed from 0.018 to 0.010 cm²/s and the inlet temperature is changed to $T_0 = 260^\circ\text{C}$. With these conditions the effect of the intraparticle convection can be seen. Figure 6.14 and 6.15 show the results of different length to radius ratio. It can be found that as the values of length to radius ratio decrease, the effects of the intraparticle convection become more significant.

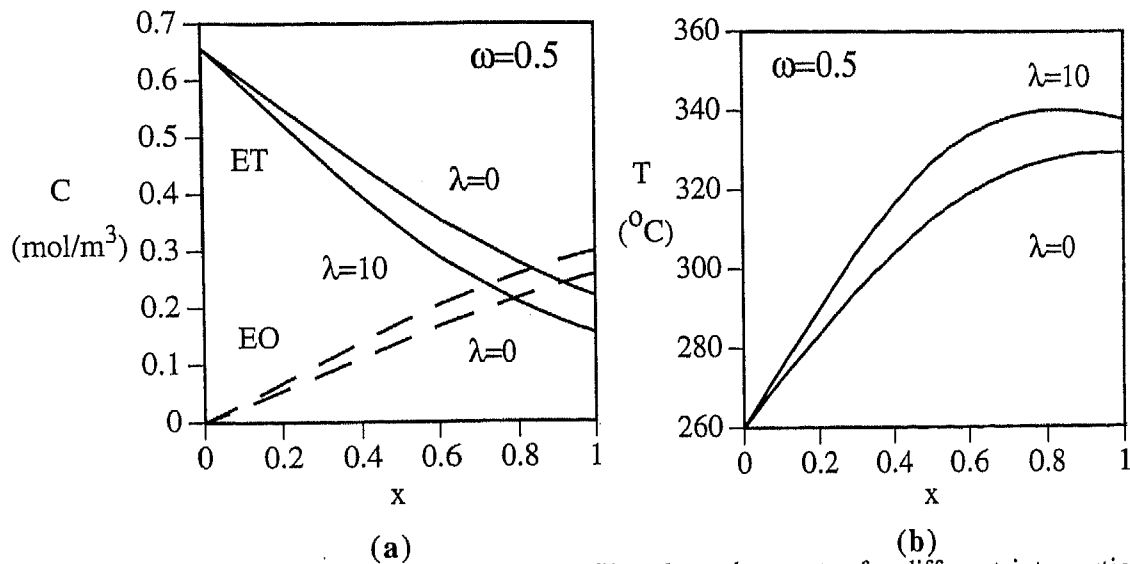


Figure 6.15 Concentration and temperature profiles along the reactor for different intraparticle Peclet number with inlet temperature $T=260^{\circ}\text{C}$, velocity $u_0 = 30 \text{ cm/s}$ and length radius ratio $\omega = 0.5$ a) concentration; b) temperature.

The integration of this problem was done with PDECOL. In order to validate the calculations for the full problem, the calculation of η_i was done both through the analytical solution (Equation 6.B7) and using TWODEPEP as described above. Figure 6.16 shows the plot of the effectiveness factor, η , as a function of Thiele modulus, ϕ , calculated using both methods. For small values of the Thiele modulus, $\phi < 20$, the agreement between the two methods is quite good, but for higher values of ϕ , the numeric method produces erroneous results. This is due to the fact that under these conditions, reactant concentration within the pellet goes down sharply, and TWODEPEP presents integration difficulties.

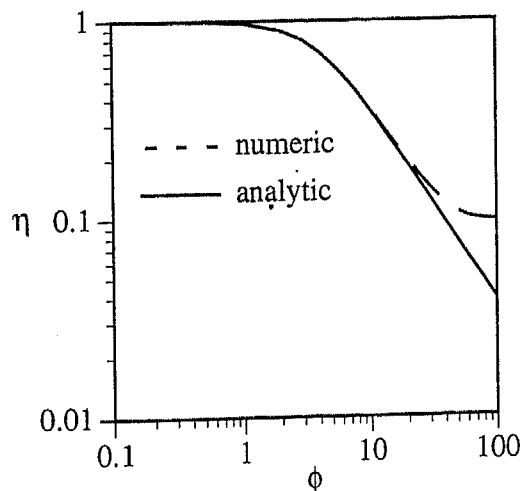


Figure 6.16 Effectiveness factor, η , as a function of Thiele modulus, ϕ , calculated from different methods.

Figure 6.17 shows an example of the use of PDECOL using both the analytical and the numerical methods to calculate the effectiveness factor.

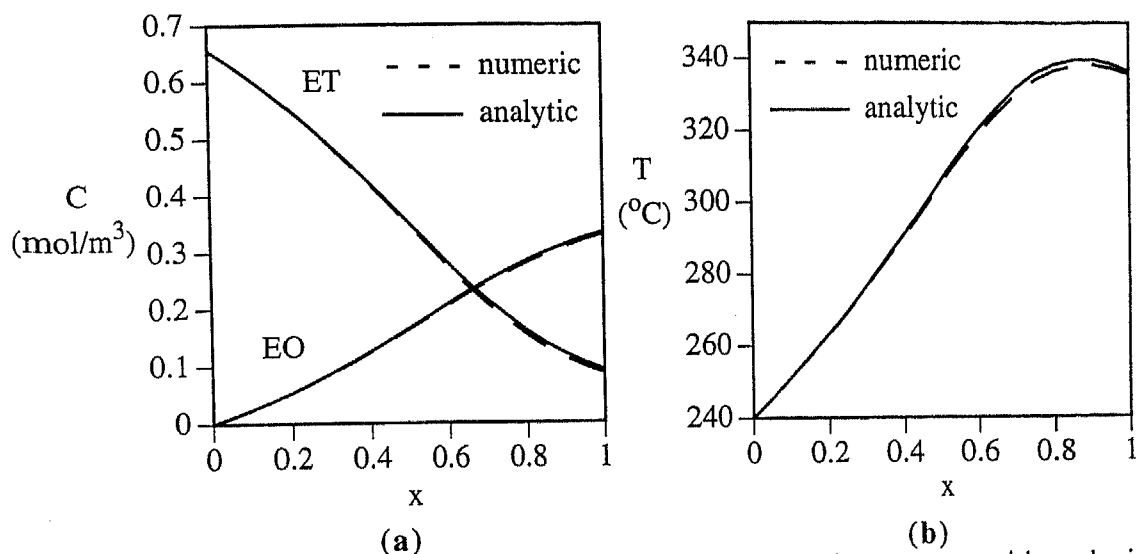


Figure 6.17 Concentration and temperature profiles along the reactor with velocity $u_0 = 30 \text{ cm/s}$ and inlet temperature $T=240^{\circ}\text{C}$ calculated from different methods:: a) concentration; b) temperature.

7. Conclusions and Future Work

7.1 CONCLUSIONS

The effect of intraparticle convection on catalyst performance for irreversible, isothermal first-order reaction with mole changes was analysed. Results show that pressure gradients can exist within the pellet due to both the reaction stoichiometry and the external pressure gradient. The maximum pressure variation is obtained in the Knudsen diffusion regime and its value can be estimated asymptotically. The effectiveness factor is not only dependent on the Thiele modulus and on the change in moles, but it is also dependent on and enhanced by intraparticle forced convection. The intraparticle Peclet number can be used as a criteria for establishing the regime where forced convection is important.

An *augmented* intraparticle effective diffusivity for a finite cylinder geometry pellet and an equivalence ratio between the slab and the finite cylinder characteristic dimensions were studied. It has been found that the enhancement of the effective diffusivity depends not only on the intraparticle Peclet number, λ , but also on the Thiele modulus, ϕ , and the aspect ratio of length to radius, ω . When the Thiele modulus $\phi_c < 1$, the augmented diffusivity can be estimated approximately by $\tilde{D}_e/D_e = 1/f(\lambda)$. As the aspect ratio increases the enhancement decreases. This point suggests that, when non-symmetrical catalyst particles are packed in a fixed bed reactor, if intraparticle convection is present and has a favourable effect, particles should be placed with their larger area side facing the bulk flow.

An equivalent ratio between the characteristic dimensions of slab and finite cylinder, valid in the whole range of Thiele modulus and in the presence of intraparticle convection, was determined. This equivalent dimensions ratio, expressed in terms of the half thickness of the slab, ℓ_s , and the length of the cylinder, L , lies between the bounds $1/2(1 + \omega)$ and $1/2$. The former value is attained in the case of ratio of intraparticle Peclet number to the Thiele modulus $\lambda_c/\phi_c \rightarrow 0$, and the latter bound is approached when $\lambda_c/\phi_c \rightarrow \infty$. When the intraparticle Peclet number is small, say $\lambda_c < 2$, the effect of intraparticle convection on the equivalent dimensions ratio is negligible. The equivalence between slab and cylinder may also be expressed in terms of the cylinder radius, R , in which case, the infinite cylinder case was derived and compared with previously known analytic solutions.

Measurement of intraparticle diffusivities and the identification of intraparticle convection in permeable catalysts with different geometries was carried out using the gas chromatographic technique. The solution of for diffusion and convection in a hollow cylinder geometry pellet was established, and an analogy between hollow cylinder and slab catalysts for first-order reaction was developed. Intraparticle diffusivity in solid cylinder and hollow cylinder pellets was measured in a single pellet string column with chromatographic method. Parameter

estimation is very sensitive to the correlation used for Peclet number calculations. Therefore, in the case of hollow cylinder pellets axial dispersion was independently measured with the column packed with glass hollow cylinder pellets. However, the effects of the intraparticle convection in the pellets is difficult to be quantified. In fact, it is not easy to find experimental conditions to measure intraparticle convection with conventional gas chromatographic method. Only in the case of sphere pellets with "foam structure" used for bacterial growth which have a large pore size, conditions are such that we are starting seeing the effect of intraparticle convection.

The kinetics of ethylene oxidation over α -alumina support commercial silver catalysts has been studied. Rate equations for the ethylene oxidation for gas mixtures containing excess oxygen have been determined. These rate equations can be used under the experimental conditions of this work. It was found that the selectivity and the relative yield decrease with increasing reaction conversion. At conversion of 40% the relative yield is around 75%. The reaction rates change with the increase of the ethylene partial pressure and pass through a maximum. Partial pressures of carbon dioxide inhibit the reaction rates. The partial pressures of ethylene oxide inhibit the ethylene oxide production rate but have negligible effect on the production rate of carbon dioxide. Further oxidation of ethylene oxide to carbon dioxide is not important.

The reaction of ethylene oxidation in a fixed-bed reactor has been measured. The reaction conversion and yield were analysed. Some of runaway conditions were determined. A mathematical model was proposed. The concentration and temperature profiles were studied. The effect of the intraparticle convection was discussed. It has been shown that for the hollow cylinder particle the effect of the intraparticle convection can be seen only if the intraparticle Peclet number have a high value.

7.2 FUTURE WORK

Large-pore materials are widely used in various chemical engineering applications as catalysts in heterogeneous reaction, HPLC packing in protein separation, adsorbents in pressure swing adsorption (PSA). In such supports, mass transfer due to intraparticle convection has to be taken into account. The importance of intraparticle forced convection in large-pore materials has recently received more attention. In most theoretical studies, the flow direction is assumed to be the same as one of the pellet principal axis. However, in industrial applications, the pellets may be randomly directioned and the angle of the flow must be taken into account. This will lead to a problem with difficult mathematical treatment, but, on the other hand this also is a challenge. If the subject concerned in this work is extended to take this factor into account, that is in the models, the curve surface of the cylinder is placed facing the gas flow, it would be an attractive topic.

One of the applications of intraparticle convection is membrane reactors. The problem of reaction with mole-changes treated in Chapter 2 could be easily extended to deal with this type of problems, the main alteration being in the formulation of the boundary conditions.

Chromatography measurement techniques have been successfully applied in chemical engineering to determine the intraparticle effective diffusivity and adsorption equilibrium isotherm. In this work the focus was confined to kinetic studies, intraparticle effective diffusivity measurement. To make full use of this technique, the apparatus used in this work, could be modified in order to determine equilibrium isotherms at high temperature. With ethylene oxidation catalysts the equilibrium isotherm of reactant and product of the reaction can be measured. The data of equilibrium isotherm would be helpful to understand the mechanism of the reaction on the silver catalysts supported α -alumina.

The experimental work done here on the oxidation of ethylene could be followed up, in order to observe the effect of the intraparticle convection on reaction in a fixed-bed reactor. To achieve this, the operating conditions must be considered carefully. First, make sure that the system is in the intermediate diffusion regime, where intraparticle convection has a significant effect. Second a large value of the intraparticle Peclet number is required. To do this a high gas velocity is necessary to obtain sufficient pressure drop across the particle and an high pressure is needed to reduce the effective diffusivity and increase the intraparticle Peclet number.