

MODELLING OF HETEROGENEOUS - ^{CHEMICAL} HOMOGNEOUS REACTION
SYSTEMS

BY

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For my parents and for Sue.

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ABSTRACT

This thesis reports some aspects of the modelling of reaction systems with both heterogeneous and homogeneous characteristics.

Several systems of this type are identified and classified. Some available models for fixed-bed catalytic reactors are reviewed, together with correlations required to predict transport phenomena within the reactors. Numerical methods are presented for the integration of the models.

Two heterogeneous-homogeneous reaction systems, the thermal decomposition of nitrous oxide and the catalytic air oxidation of methanol, are considered. The models are integrated for a wide range of operating conditions. Instability, originating in the solid-phase energy balance, has been found in some integrations of the two-phase model. In most cases the predictions of a two-phase, two-dimensional model; a one-phase, two-dimensional model and a one-phase, one-dimensional model were significantly different. When a two-phase model is necessary, i.e. when fluid-solid transport resistance is significant, it is important to distinguish between solid-phase and fluid-phase sources.

Considering axial profiles of reactor temperature, cases were found where a reactor appeared stable with respect to the heterogeneous reaction and then became unstable because of the increasing importance of the homogeneous reaction. The differences in activation energies and heats of reaction that promote this situation are typical of many heterogeneous-homogeneous systems.

An investigation of the sensitivity of the two-dimensional models to variations in the heat transfer parameters is reported.

A model has been established for thermal effects during the oxidation of butene over a single pellet of supported tin/antimony oxide. Use of the model, particularly for the prediction of product yields in a fixed-bed reactor where homogeneous reaction may also occur, is discussed.

Simplified models are presented for the prediction of the behaviour of hollow cylindrical catalyst pellets. It is shown that such pellets may be used advantageously in some heterogeneous-homogeneous situations.

Suggestions are made for future work on the modelling of heterogeneous-homogeneous reaction systems.

NOMENCLATURE

- A - pre-exponential factor in rate-expressions.
- chemical species in Chapter 1.
- A' - constant in (6.11)
- A* - chemical species in Chapter 6.
- Ap - external area of catalyst particle (m^2)
- a - degree of hollowing of equivalent hollow sphere
- a' - parameter in (2.43)
- a_s - $4\lambda r^s / R_t^2$ ($Wm^{-3}K^{-1}$)
- a_v - external catalyst surface per unit volume of packed bed (m^{-1})
- B - chemical species in Chapter 1
- B' - constant in (6.11)
- B* - chemical species in Chapter 6
- Bi - Biot Number
- b - external radius of hollow cylindrical catalyst pellet (m)
- C - chemical species in Chapter 1
- concentration ($Kmole\ m^{-3}$)
- C* - chemical species in Chapter 6
- C_Tⁱ -
- C_{T0}ⁱ -
- C_T -
- C_{T1} -
- C_{T2} -
- C_{T3} -
- C_Dⁱ -
- C_D -
- c - dimensionless concentration
- C_p - fluid heat capacity ($J\ kg^{-1}\ K^{-1}$)
- D - chemical species in Chapter 1
- radial mass diffusivity (m^2sec^{-1})
- D' - bulk diffusion coefficient (m^2sec^{-1})
- D_e - equivalent hydraulic diameter of annular tube (m)
- D_{eff} - effective diffusivity of catalyst particle (m^2sec^{-1})
- D_H - radial thermal diffusivity (m^2sec^{-1})
- D_T - external diameter of annular tube (m)
- d - forcing vector in matrix representation of difference equations
- d_m - member of vector d

d_p	- catalyst particle diameter (m)
d_p'	- equivalent catalyst particle diameter - $6V_p/A_p$ (m)
d_t	- reactor diameter (m)
E	- chemical species in Chapter 1
F	- source term in conservation equations (m^{-1}) or (Km^{-1})
F'	- general source term in finite difference equations, (m^{-1}) or ($K m^{-1}$)
F_p	- source term in catalyst particle balance (2.8), ($kg m^{-3} sec^{-1}$)
f	- constant in (1.1)
G	- superficial mass flow rate ($kg m^{-2} sec^{-1}$)
g	- mass fraction (-)
g_m	- parameter defined by (2.52) and (2.53)
H	- heat content ($J kg^{-1}$)
$(-\Delta H)$	- heat of reaction ($J kg^{-1}$)
h	- axial steplength in implicit finite difference method
h'	- axial steplength in explicit finite difference method
h_v	- fluid-solid heat transfer coefficient ($Wm^{-2}k^{-1}$)
h_t	- overall fluid-solid heat transfer coefficient (Chapter 2) ($Wm^{-2}k^{-1}$) - fluid-wall heat transfer coefficient in annulus (Chapter 5) ($Wm^{-2}k^{-1}$)
j_H	- thermal j-factor
K	- $\sqrt{N^f + N^s}$
K_{eff}	- pellet effective thermal conductivity, ($Wm^{-1}K^{-1}$)
k	- radial steplength in finite difference method
k'	- rate constant
k_g	- fluid-solid mass transfer coefficient, ($msec^{-1}$)
k_f	- fluid molecular thermal conductivity, ($Wm^{-1}k^{-1}$)
k_s	- solid thermal conductivity, ($Wm^{-1}k^{-1}$)
L	- reactor tube length, (m)
L'	- mixing length in Chapter 5, (m)
M	- number of radial steps in finite difference equations for the reactor
M_w	- molecular weight, (kg/kmole)
m	- radial index in finite difference equations, Chapter 2
m_s	- shape factor in Chapter 5
N	- dimension less group $h_v a_v R_t^2 / \lambda r$
N_A	- number of axial steps in finite difference equations for the reactor
N_s	- h/h'
N_{sj}	- j^{th} number of a series for N_s
Nu	- Nusselt number
$(Nu)_r$	- Nusselt number for radiation in Chapter 2,
P	- number of steps in difference equations for a catalyst pellet

P_1	- parameter in (2.36)
P_2	- parameter in (2.36)
Pr	- Prandtl number
$(Pe)_{mr}$	- radial mass Peclet number
p	- index in difference equations for a catalyst pellet
Q	- number of iterations in solution of catalyst pellet equations
Q_r	- radial heat flux, (Wm^{-2})
Q_v	- heat removed per unit volume of bed, (Wm^{-3})
Q_w	- heat flux through wall, (Wm^{-2})
R	- universal gas constant
R_t	- reactor tube radius, (m)
r	- radial co-ordinate, (m)
r'	- rate of reaction, ($kgm^{-3}sec^{-1}$) or $kmole\ m^{-3}\ sec^{-1}$)
r_e	- radius of equivalent hollow sphere, (m)
Re_e	- Reynolds number based on D_e
Re_p	- Reynolds number based on dp
Re_p'	- Reynolds number defined by (2.30A)
Re_T	- Reynolds number based on D_T
Sc	- Schmidt number
Sh	- Sherwood number
S_y	- surface area of sphere of radius y (m^2)
s	- number of chemical species
T	- temperature, (K)
T_w	- reactor wall temperature, (K)
t	- dimensionless temperature
U	- overall heat transfer coefficient ($JWm^{-2}K^{-1}$)
u	- modified radial co-ordinate, $u=r^2/R_t^2$
V_p	- volume of catalyst particle, (M^3)
v	- superficial axial velocity, ($M\ sec^{-1}$)
X_s	- heat transfer group in (2.36), ($Wm^{-1}K^{-1}$)
Y	- general state variable
y	- dimensionless radial co-ordinate
z	- axial variable, (m)

GREEK SYMBOLS

α	degree of pellet hollowing
α_w	wall heat transfer coefficient, ($Wm^{-2}K^{-1}$)
α_m	parameter in (2.50)

β	length to external radius ration of cylinder
β_m	parameter in (2.50)
γ	rate term in conservation equations
γ_m	parameter in (2.50)
γ_p	shape factor in Chapter 2
ϵ	effectiveness factor
η	utility factor
θ	dimensionless group in Chapter 5
θ'	Thiele modulus in Chapter 6
Λ	modified Thiele modulus, defined by (6.2)
λ	modified Thiele modulus defined by $\lambda = r \sqrt{k'/D_{eff}}$
λ_r	radial bed conductivity, ($Wm^{-1}K^{-1}$)
v	variable defined by (6.7)
μ	fluid viscosity, ($kg\ m^{-1}\ sec^{-1}$)
ρ	fluid density, ($kg\ m^{-3}$)
ρ_b	bulk density of catalyst pellets
ϕ	bed voidage
	dimensionless group in Chapter 5
ϕ_H	bed voidage with hollow cylindrical pellets
ϕ_S	bed voidage with solid cylindrical pellets
ω_m	parameter defined by (2.52) and (2.53)
χ	dimensionless concentration in Chapter 5

SUBSCRIPTS

A	- referring to species A* in Chapter 5
B	- referring to species B* in Chapter 5
het	- referring to heterogeneous reaction
hom	- referring to homogeneous reaction
in	- referring to reactor inlet conditions
max	- maximum or optimum value
0	- referring to initial conditions
S	- referring to pellet surface

SUPERSCRIPTS

Bd	- referring to butadiene
C	- referring to thermal events in the continuum phase

- F - referring to formaldehyde
- f - referring to thermal events in the fluid phase
- i - referring to the i^{th} chemical species
- M - referring to methanol
- N - referring to nitrous oxide
- NO_2 - referring to nitrogen dioxide
- O_2 - referring to oxygen
- q - referring to the q^{th} iteration
- s - referring to thermal events in the solid phase

CHAPTER 1

INTRODUCTION

- 1.1 Catalytic Chemical Reactors
- 1.2 Non-catalytic Chemical Reactors
- 1.3 Modelling Chemical Reactors
- 1.4 Heterogeneous - Homogeneous Reaction Systems
 - 1.4.1 General
 - 1.4.2 Particular Systems
- 1.5 Aspects of Reactor Modelling relating to Heterogeneous - Homogeneous Systems
- 1.6 Present Work

1.1 CATALYTIC CHEMICAL REACTORS

Catalytic chemical reactors may be found in a number of geometries and configurations. The reactor may contain one, or more, phases and it may be operated either statically, as a batch unit, or continuously, as a flow unit. In this thesis the following working definition of a catalytic chemical reactor will be used.

A catalytic chemical reactor consists of a tube containing a continuous, usually gaseous, phase and an evenly distributed, discrete solid-phase, the catalyst particles. The reactor is operated as a flow unit by passage of the continuous phase through the tube. The reaction takes place on either the external or the internal surfaces of the catalyst particles.

If the reaction occurs on the internal surface of the catalyst particles there are five identifiable stages in the reaction.

- (i) Diffusion of reactants from the fluid to the pellet surface.
- (ii) Diffusion of reactants to the reaction site through the pellet pores.
- (iii) Surface Reaction.
- (iv) Diffusion of products from the reaction site through the pellet pores.
- (v) Diffusion of products from the pellet surface to the fluid.

In general, all of these steps may influence the overall rate of reaction although, under certain conditions, not all of the steps will be rate controlling.

Step (iii) may be quantified in terms of the intrinsic reaction kinetics. Steps (ii) and (iv) may be accounted for by effective diffusivities through the porous material (e.g.1) and steps (i) and (v) may be quantified in terms of film mass transfer coefficients (e.g. 1). Analogous considerations exist for the generation and transfer of heat during the reaction. Petersen (1) has presented criteria enabling the determination of the relative importance of the various steps in the overall reaction rate. The criteria are presented in terms of effectiveness factors for intra-pellet effects and transportation factors for inter-pellet effects. These effects may be referred to as transport phenomena relative to the pellet.

Transport phenomena relative to the reactor are also important. Mass will be transferred radially by turbulent and molecular diffusion

and heat will be transferred by turbulent convection in addition to conduction through the solid and fluid phases and by radiation. An extensive review of these transport phenomena relative to the reactor is given later in Sections 2.5 and 2.6.

1.2 NON-CATALYTIC CHEMICAL REACTORS

A non-catalytic chemical reactor will, in general, differ from a catalytic chemical reactor in that there is no solid phase. Exceptions to this distinction immediately arise in that not only may a non-catalytic reactor contain a distributed solid-phase, possibly to enhance heat removal or to promote radial mixing, but the solid-phase may be absent in a catalytic reactor and the reaction catalysed either by a trace gas or by a liquid phase.

Usually, however, a non-catalytic reactor may be considered as a homogeneous tubular reactor. This type of reactor has received considerable attention in the literature and has been well treated in a text by Levenspiel (2). The reaction occurs throughout the continuous phase and the rate of reaction at a particular point in the reactor will depend on local values of temperature and concentration which will, in turn, depend on transport phenomena relative to the reactor.

An intermediate class of reactor exists which is geometrically similar to the homogeneous reactor but which includes a reaction occurring at the reactor wall. This may, or may not, be in addition to a gas-phase reaction in the bulk of the reactor. Such reactors may have a catalytically coated wall or the wall may act as a quenching surface for radicals during a gas-phase radical chain reaction (see below).

A further hybrid reactor is possible having the exact geometric characteristics of a conventional catalytic chemical reactor, but supporting a gas-phase reaction in the voids between the catalyst particles. This type of reactor forms the basis of the present investigation.

Multiple reactors may also be envisaged to accommodate systems having both heterogeneous and homogeneous properties. For example, a conventional catalytic reactor may be used in series with a conventional non-catalytic reactor so that catalytically formed intermediates may undergo gas-phase reactions to final products.

1.3 MODELLING CHEMICAL REACTORS

The objective in modelling a chemical reactor is to predict the performance of the reactor for a given set of operating variables.

The modelling procedure has two principal stages: the formation of a physical model for the reactor, and the provision of a mathematical model to describe quantitatively the physical model. The two stages are inseparably interlinked as it is possible to generate a physical model of such complexity that its mathematical representation is either insoluble or impossible.

The detailed requirements of a model will vary according to the application. In general the model may be required to reproduce and predict one or more of the following features.

- (i) Outlet conversion.
- (ii) Outlet selectivity.
- (iii) Outlet stream temperature.
- (iv) Maximum temperature existing within the reactor.
- (v) Temperature difference between fluid phase and catalyst particles in catalytic reactors.
- (vi) Radial temperature and composition profiles within the reactor.
- (vii) Axial temperature and composition profiles.
- (viii) Selectivity and conversion profiles throughout the reactor.

The literature is rich with studies of chemical reactor modelling (see Chapter 2.) and, in principle, all of these properties are obtainable. All models, however, suffer from the dual, and sometimes mutually exclusive, problems of accuracy and tractability. However, nature has been provident and some phenomena become unimportant under certain conditions. For example, film, heat and mass transfer resistance between the pellet and the continuous phase becomes unimportant as turbulence develops in the reactor and, when very small catalyst particles are used, the diffusional limitations within the pellet become unimportant.

Thus a further division is introduced into the modelling procedure. The phenomena to be modelled fall into intra-pellet effects and inter-pellet effects, each of which have been the subject of considerable research (e.g. 1). The phenomena are linked by film effects such as fluid-solid heat and mass transfer.

Modelling homogeneous reactors is somewhat simplified by the

absence of the solid-phase and the consequent necessity to consider only bulk phase phenomena. When a non-catalytic reactor contains solids to promote turbulence or to enhance heat transfer, it is only necessary to consider those phenomena, related to the solid-phase, which are concerned with turbulence and heat transfer. Intra-particle diffusion may be neglected.

1.4 HETEROGENEOUS-HOMOGENEOUS REACTION SYSTEMS

1.4.1 General

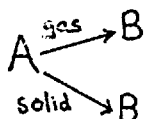
It is becoming increasingly evident that an important class of reaction system is formed when homogeneous reactions occur in the presence of heterogeneous catalytic or non-catalytic reactions. Reports of the occurrence, or possible occurrence of such systems are becoming more frequent. It will be worthwhile to apply some broad ideas concerning the classification of such systems before reviewing the literature of the subject.

The systems of interest will be defined as those in which at least one gas-phase reaction and one surface reaction occur within the same reacting volume. Two major sub-classifications are immediately suggested.

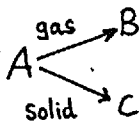
(i) Concurrent Reactions

(ii) Consecutive Reactions

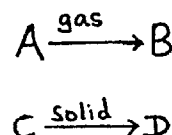
Further subdivision, is, of course, possible. Considering concurrent reactions, these may be divided into dependent-concurrent reactions and independent-concurrent reactions. The three concurrent reactions shown schematically below illustrate the point. Reactions (I) and (II) are examples of dependent-concurrent reactions. In reaction (I) the product is the same for each reaction, whereas in reaction (II) different products are formed during the gas- and



(I)



(II)



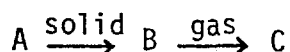
(III)

solid-phase reactions and it is evident that, in principle, the amount of surface present could be used to manipulate the selectivity of the conversion of A to C.

It is probable that the gas- and solid-phase reactions would predominate under different reaction conditions and that a range of conditions might exist in which the two reactions would be of equal importance. Under these conditions there will be competition for the reactant A between the gas- and solid-phase reactions and the two reactions will be interdependent.

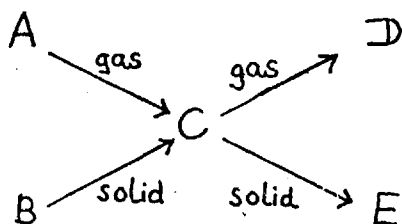
Reaction (III) is an independent-concurrent reaction scheme as may occur when, for example, a reaction mixture is passed over a catalyst. Some reactant might react in the gas-phase and some on the catalyst surface but the reactions would be essentially independent. It should be noted, however, that if thermal effects are present in the reaction space, then the reactions may become inter-dependent by virtue of an increased, or decreased, temperature.

Subdivision of consecutive reactions is also possible. Consider the reaction shown schematically as:



If B is an intermediate towards a desired product C, the reactions may be classified as consecutive-desirable. However if B is the main product and C is essentially a by-product, then the reactions may be classified as consecutive-undesirable.

It is unlikely that all real reaction situations will fall neatly into one of the above classifications. For example, the reactions shown schematically below exhibit the features of all four classifications. In this scheme, E is the desired product.



1.4.2 Particular Systems

Evidence for the occurrence, or possible occurrence, of homogeneous effects in catalytic reaction systems is summarised in Table (1.1). This list is not exhaustive but shows a number of different reactions in which these effects have been reported.

Gorokhovatskii (3) has attempted to identify branched-chain (homogeneous) contributions to heterogeneous systems by varying the catalyst granule size. He studied the following systems:

Oxidation of i) ethylene on silver

ii) propylene on cuprous oxide

iii) acetylene on manganese dioxide

iv) naphthalene on a vanadium oxide catalyst

and synthesis of methanol on a zinc-chromium catalyst.

He found no important homogenous effects for any of these reactions. It will be seen that in at least one case - the oxidation of propylene - this is in disagreement with the findings of other workers (16, 18, 19).

Surface influence of gas-phase free-radical reactions has received much attention in the past and perhaps the work of Hay, Knox and Turner (4) is typical. The surface may affect the overall reaction in two ways. Firstly by the formation at the surface of free radicals that participate in the homogeneous chain reactions, and secondly by surface quenching, where active free radicals recombine to form inert products. Il'chenko et al. (5) have shown that the gas-phase oxidation of hydrogen in the presence of a V_2O_5 catalyst proceeds by a gas-phase chain reaction initiated by H. or OH. radicals formed heterogeneously.

Svintsova et al. (6) have proposed a similar mechanism for Carbon Monoxide Oxidation over platinised catalysts, with heterogeneously formed atomic oxygen acting as the chain initiator. Boldyreva et al. (7) have studied CO oxidation over V_2O_5 and Cr_2O_3 catalysts and propose O. and OH. radicals as the chain initiators. They attribute the source of these radicals to water vapour. Furthermore, they have found that the reaction passes into the gas-phase at a certain temperature. Below this temperature the reaction mechanism is principally heterogeneous, indicating that thermal 'kick-off' of homogeneous reaction mechanisms may be an important effect in industrial situations.

TABLE (1.1)

HOMOGENEOUS EFFECTS IN CATALYTIC REACTIONS

Oxidation of Propylene	Godin and McCain (16) Daniel and Keulks (18) Keulks, Rosynek and Daniel (19)
Oxidation of Butenes	Popova (24) Lozano (26) Schukin (25) Corrie (26)
Partial Oxidation of Benzene to Maleic Anhydride	Brown (33)
Thermal Decomposition of Nitrous Oxide	Halladay and Mrazek (8)
Oxidation of Methane and Methanol to Formaldehyde	Cullis et al. (9) Keene (10) Mann et al. (11, 12, 13)
Oxidation of o-xylene	Irshad and Trimm (21) Satterfield and Loftus (22)
Oxidation of Hydrogen	Il'chenko (5)
Oxidation of Carbon Monoxide	Svintsova (6) Boľdyreva (7)

A good example of a simple dependent-concurrent reaction is the thermal decomposition of nitrous oxide. Halladay and Mrazek (8) have studied the kinetics of the system under conditions where both homogeneous and heterogeneous decompositions occur. They have compared the results with studies for pure homogeneous and pure heterogeneous decompositions and have found good agreement. Consideration of the homogeneous and heterogeneous rate expressions (Section 3.2) shows that, up to about 900K, the heterogeneous reaction occurs almost exclusively and that the homogeneous reaction becomes more important as temperature rises until it predominates at around 1150K. The principal reactions in both phases give the same products although there is a homogeneous reaction of less importance that does not occur heterogeneously.

The oxidation of o-xylene over MoO_3 catalysts has been studied by Irshad and Trimm (21) and Satterfield and Loftus (22) and it has been found that the heterogeneous and homogeneous reactions lead to quite different products. The principal catalytic product is benzoic acid, whereas the homogeneous reaction yields mainly o-tolualdehyde and phthallic anhydride.

Further gas-phase oxidation of formaldehyde during the catalytic oxidation of methane or methanol to formaldehyde may be considered as an example of simple consecutive-undesirable reaction scheme. Cullis et al. (9) have reported gas-phase overoxidation of formaldehyde to CO_2 during the oxidation of Methane over a palladium oxide catalyst. Keene (10) has shown that the overoxidation is a radical reaction and can be quenched by the addition of inert surface. Mann et al. (11, 12, 13) have studied methanol oxidation on different catalysts and considered the variation in the selectivity to formaldehyde with temperature. He has found that the selectivity is constant with temperature up to about 630K, after which the conversion continues to increase while the yield decreases indicating overoxidation of the formaldehyde and again suggesting the possibility of thermal "kick-off" of homogeneous reactions. Gas-phase formaldehyde oxidation has been studied frequently (e.g. 14, 15) and has been established as a branched-chain radical reaction.

Of course, not all heterogeneous-homogeneous reactions schemes can be classified as purely consecutive or purely concurrent. For example, the oxidation of propene over a mixed catalyst proceeds by

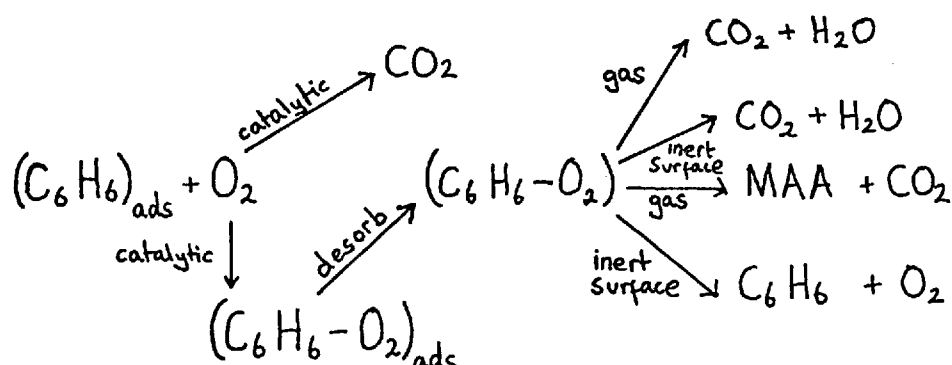
a heterogeneous-homogeneous route which exhibits characteristics of both these classifications (16). In this case a heterogeneously formed product initiates further homogeneous reaction of the reactants. Acrolein has been shown to be the principal reaction product at around 700K(17). Godin and McCain (16) have found propene oxide and acetaldehyde as products at low propene conversions and have considered these to be formed by homogeneous reaction of propene initiated by heterogeneously formed aldehydes. Similar conclusions have been made by Keulks et al. (18, 19). There is evidence that the small amount of acetaldehyde formed heterogeneously may be most important in initiating the homogeneous reaction and it has been shown (20) that acetaldehyde is a more efficient chain initiator than acrolein.

A similar situation appears to exist during the oxidation of n-butenes. Blundell and Skirrow (23) have shown that homogeneous oxidation of butene proceeds readily in the temperature range 560K - 700K. Popova et al. (24) have detected surface initiated homogeneous reactions during the oxidation of n-butenes over copper catalysts. Schukin et al. (25) have studied the oxidation of butene over iron/antimony oxide catalysts and have deduced that the only role of this catalyst is the production of active radicals for initiation of homogeneous reaction. Additionally they have found that the homogeneous reaction only occurs below a certain surface-to-volume ratio, and attribute this to surface quenching of the chain reaction when the surface-to-volume ratio becomes large. It appears that, as for propene, the main chain branching agent is acetaldehyde.

Corrie (26) has observed homogeneous effects during studies of the oxidation of butene to butadiene over single pellets of tin/antimony oxide. A previous kinetic study over packed beds of the same catalyst (27) failed to detect any homogeneous reaction. With a single pellet, the homogeneous reaction appears to be initiated by catalytically formed intermediates, or by thermal effects. Corrie's study was performed at ~22K higher than that of Gabbay (27) and this could be sufficient to cross an explosion limit, which are usually well defined with respect to temperature: Corrie did observe ignition under certain conditions. Lozana (28) found similar effects in a shallow bed of tin/antimony oxide pellets. It is probable that the homogeneous reaction is initiated by acetaldehyde and other

aldehydes, and proceeds by a chain mechanism which can become very sensitive to variations in temperature.

As a final example, the partial oxidation of benzene to maleic anhydride over vanadia-molybdena catalysts may be considered. The mechanism of this reaction is not yet fully understood, but there is a certain amount of evidence that homogeneous effects may be important (29, 30, 31, 32). Brown (33) has proposed the mechanism outlined below.



The route from benzene to maleic anhydride is via the catalytically formed species $(\text{C}_6\text{H}_6\text{-O}_2)$, a benzene-oxygen 'adduct'. This is an example of a consecutive-desirable heterogeneous-homogeneous reaction. Gas-phase decomposition of the adduct to CO_2 is a consecutive-undesirable reaction. Considering just the reactions subsequent to adduct formation, then these are an example of dependant-concurrent reactions. The situation exhibits further complexity in that the products of one of the solid-phase reactions of the adduct are the initial reactants, benzene and oxygen. At later stages in the reactor bed, benzene and the adduct are experiencing independent-concurrent reactions. This example shows how one system can cut across almost all of the classifications for heterogeneous-homogeneous reactions.

1.5 Aspects of Reactor Modelling relating to Heterogeneous-Homogeneous Systems

The existence of simultaneously occurring heterogeneous and homogeneous reactions may present problems in reactor modelling that are not so significant when only pure heterogeneous or pure homogeneous reactions occur.

There has been some attention in the literature to the case where a reaction occurs on the wall of a tubular reactor. Lupa and Dranoff have considered chemical reaction on the wall of an annular reactor (34) and Katz (35) has considered chemical reactions catalysed on a tube wall. Pancharatnam and Homsy (36) have treated a similar situation at high Peclet numbers. Hudson et al. (37, 38) and Maloney and Rabinovitch (39) considered wall reactions in the presence of homogeneous reactions. In the latter case the example considered is wall activation in a thermal unimolecular reaction, the isomerisation of ethyl isocyanide.

Valstar et al. (40) have investigated the dimerisation of butadiene - a gas phase reaction - occurring in a packed bed reactor. They have thus been able to investigate inter-pellet effects free from the complications of intra-pellet effects.

Investigations of purely heterogeneous systems are numerous and are reviewed frequently (e.g. 41). Various models (see Chapter 2) have been compared from the point of view of accuracy and tractability and studies have taken account of such topics as thermal stability theory (42) and the dynamic behaviour of a packed bed (43). Recently investigated topics include the dynamics and control of propagating reaction zones (44).

It appears that there has been no investigation of simultaneously occurring heterogeneous and homogeneous reactions in packed beds.

Before outlining the scope of the present work, possible areas of interest in the modelling of such systems will be considered.

It is well-known that the reaction rates are exponentially dependent upon temperature and that the degree of this dependence is related to E_A , the activation energy. If the rate of reaction is written:

$$r' = f \exp \left(- \frac{E_A}{RT} \right) \quad (1.1)$$

then, considering two reactions with activation energies E_{A1} and E_{A2} the ratio of their reaction rates may be written:

$$\frac{r'_1}{r'_2} = \frac{f_1}{f_2} \exp \left(\frac{E_{A2} - E_{A1}}{RT} \right) \quad (1.2)$$

and the rate of change of this ratio with temperature is given by:

$$\frac{\delta}{\delta T} \left(\frac{r'_1}{r'_2} \right) = - \frac{f_1}{f_2} \left(\frac{E_{A2} - E_{A1}}{RT^2} \right) \exp \left(\frac{E_{A2} - E_{A1}}{RT} \right) \quad (1.3)$$

Thus, as the temperature rises, the reaction with the larger activation energy will be selectively favoured.

Homogeneous reactions tend to have activation energies which are larger than those for heterogeneous reactions, typical values being 30 Kcal/mole for a homogeneous reaction and 10-15 Kcal/mole for catalytic reactions. It must be remembered, however, that these values are only typical and both figures can show wide variation.

Using the theory of absolute reaction rates, Laidler et al. (45) have been able to calculate the difference in activation energies necessary for the heterogeneous and homogeneous reactions to have comparable rates under the same conditions. Generally the activation energy of the heterogeneous reaction must be lower than that for the homogeneous reaction by an amount that depends, amongst other things, on temperature and the amount of surface present. For example, for a surface to volume ratio of 1 sq.cm. per cubic cm. of gaseous reactant the heterogeneous reaction must have an activation energy that is lower by 16.5 Kcal/mole at 300K and by 27.5 Kcal/mole at 500K for the heterogeneous reaction to be as fast as the homogeneous reaction. For instance, gas phase radical recombinations can proceed with zero activation energy and their rates are thus independent of temperature. Nevertheless, in general, temperature increases in the bed will favour homogeneous reactions. It will be noted that all the reactions cited in Table (1.1) are oxidations, and as such are exothermic - leading to temperature increases in the bed. The degree of temperature increase will depend, of course, on local heat transfer conditions. Lozano (28) has observed radial temperature gradients of 40K cm^{-1} . Thus, for $E_{A\text{het}} = 15\text{Kcal/mole}$ and $E_{A\text{hom}} = 25\text{Kcal/mole}$, the difference in reaction rates between the bed centre and the bed wall at 700K would be:

$$\left(\frac{r'_{\text{hom}}}{r'_{\text{het centre}}}\right) : \left(\frac{r'_{\text{hom}}}{r'_{\text{het wall}}}\right) \approx 1.2:1$$

and the selectivity varies by about 20% across the tube radius. This sensitivity to temperature is further compounded when the homogeneous reaction is an overoxidation to products of complete combustion (e.g. Methanol $\rightarrow$ formaldehyde $\rightarrow$ carbon dioxide) as these reactions tend to be very exothermic and lead to increased local heat release, increased homogeneous reaction and a "snow-balling" effect that may lead to local temperature runaway (Section 3.6). For example the heat of reaction for

methanol to formaldehyde is ~ 48 Kcal/mole whilst the heat of reaction for formaldehyde overoxidation is ~ 70 Kcal/mole depending upon the final products.

Such considerations also apply to purely catalytic overoxidation, although in this case the disparity in activation energy may not be so significant. However, the difference in the present situation is that the different reactions, and corresponding heat release, occur in separate phases. In a real situation, heat is transferred by both phases in proportions that depend upon the reaction conditions (46, 47). It would thus seem desirable to study two-phase heat transfer in relation to heterogeneous-homogeneous reactions.

It has been emphasised in Section (1.4) that very small amounts of catalytically formed products, e.g. aldehydes and related species, can lead to large homogeneous reaction effects. Consequently it is important that methods exist for the accurate prediction of minor products in the heterogeneous reaction and for accounting for their transfer to the fluid phase by film mass transfer.

An ultimate test of such an investigation would be the preparation of a model for a heterogeneous-homogeneous system and to test it against experimental results under conditions where:

- (i) the heterogeneous reaction is dominant
- (ii) the homogeneous reaction is dominant
- (iii) both reactions are of equal importance

Condition (ii) above only applies, of course, in the case of concurrent reactions.

1.6 Present Work

Available models for prediction of the behaviour of packed bed catalytic reactors have been reviewed in Chapter 2. Particular attention has been paid to the evaluation of two-phase heat transfer and simplifications that may be made by considering a pseudo-homogeneous reaction medium. Both one-dimensional and two-dimensional models have been considered. Extensions have been made to the models to account for gas phase reactions. In Chapters 3 and 4 these models have been applied to the thermal decomposition of nitrous oxide and to the catalytic oxidation of methanol with gas-phase overoxidation respectively. The decomposition of nitrous oxide is a typical concurrent reaction whilst

methanol oxidation is a typical consecutive reaction. Both reactions exhibit differential activation energies and heats of reaction. The predictions of the models are compared and discussed.

In Chapter 5 the heterogeneous reactions of butene and oxygen over a single tin/antimony pellet have been modelled as part of a continuing study of the butene oxidation system. The catalytic reactions show great complexity, and the principal concern has been the modelling of thermal effects. Nevertheless, it is to be hoped that continued refinement of the model will lead to more accurate predictions of the aldehydic products and, with this in mind, incorporation of the pellet model into a full model for the heterogeneous-homogeneous butene system is discussed. It becomes apparent that, with increasing system complexity, the modelling of homogeneous-heterogeneous systems may become computationally prohibitive.

Anticipating that hollow catalyst pellets may find a role in homogeneous-heterogeneous reaction engineering, existing work on predicting the effectiveness of such a pellet has been reviewed. A simplified model has been advanced and tested against present models.

Chapter 2

PHYSICAL AND MATHEMATICAL MODELS FOR FIXED-BED CATALYTIC REACTORS

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 - 2.7.4 The two-phase model

2.1 INTRODUCTION

In attempting to model the behaviour of fixed-bed catalytic reactors one is faced with conflicting aims - those of tractability and accuracy. The reactor performance is affected by complex interactions of hydrodynamic, kinetic and transport phenomena, and any attempt to account for all possible phenomena would result in mathematical formulations of a prohibitive nature. Consequently there has been much research into effective but representative physical models for the system that could lead to tractable mathematical formulations. A broad classification of available models is presented in Table (2.1).

The distinction between a physical and a mathematical model can be clarified at this stage. A physical model for a system is a collection of phenomena - real, hypothetical or both - which form a system that simulates, in a specified manner, the behaviour of the system to be modelled. A mathematical model is a set of mathematical relationships which represent the physical model for the system.

Ideally, an increase in the significant phenomena considered in the physical model leads to more accurate (and more complex) predictions from the associated mathematical model.

The models are principally divided between one- and two-dimensional models and between one - and two-phase models. Generally, any interphase concentration or temperature differences may be accounted for in two ways. In a two-phase model they will be accounted for by interphase heat and mass flux terms involving the relevant heat or mass transfer coefficient. In a one-phase model such differences are commonly accounted for by effectiveness factors relating the actual rate of reaction within the solid to that which would obtain if all reaction in the solid occurred at bulk phase conditions of temperature and concentration. The evaluation of this factor is a somewhat complicated procedure particularly in the case of fluid-solid temperature and concentration differences. It is necessary in this case to solve the intra-pellet mass and energy conservation equations subject to boundary conditions that express continuity of mass and energy flux at the solid boundary (e.g. 48). The situation is even more time consuming when complex and interacting reactions occur within the pellet.

The most elaborate model that will be considered in this work is the two-dimensional, two-phase model in which distinction is made between solid- and fluid-phase temperatures and concentrations. It will be shown

Table 2.1

Available models for fixed bed catalytic reactors

Phases dimensions	One-Phase	Two-Phase
One-dimension	1-D Continuum Model (Section 2.4)	1-D Heterogeneous Model (Not Considered)
Two-dimension	2-D Continuum Model (Section 2.3)	2-D Heterogeneous Model (Section 2.2)

Table 2.2

Parameters required to describe heat transfer

Model	One-dimension One-phase	Two-dimension One-phase	Two-dimension Two-phase
Heat Transfer Parameters	U -overall heat transfer coefficient	α_w^c -wall heat transfer coefficient λ -effective bed conductivity	α_w^s -solid-wall htc α_w^f -fluid-wall ht λr^s -solid conductivity λr^f -fluid conductivity h_v -solid-fluid htc

in subsequent sections how assumptions may be introduced in order to simplify the model.

The general conservation equations for a two-phase reacting medium may be obtained by considering that the transfer of heat and mass in both axial and radial directions are the result of the superpositions of two processes: a convective flow, and a diffusive flow described by Fick's Law. Convective flow in the radial direction may be neglected so that the conservation equations obtained at steady state are:

$$\text{Component } i: \quad \text{div}\left(\frac{Gg^i}{M_w^i}\right) = - \text{div}\left(-\frac{D^i\rho}{M_w^i} \text{grad } g^i\right) + F^i$$

$i=1 \rightarrow s$

$$\text{fluid phase energy: } \text{div}(C_p G T^f) = -\text{div}(-p C_p D_H \text{grad } T^f) + F^f + h_v a_v (T^s - T^f)$$

$$\text{solid phase energy: } \text{div}(-D_H^s \text{grad } T^s) = F^s - h_v a_v (T^s - T^f) \quad (2.1)$$

If certain assumptions are made, this set of equations may be reduced to the forms used in the fixed-bed reactor models considered in the following sections.

2.2 TWO-DIMENSIONAL, TWO-PHASE MODEL

2.2.1 General description of model

The following assumptions are made in establishing this model.

- (i) No external forces are present
- (ii) The system is at the steady state
- (iii) The pressure drop across the bed is negligible
- (iv) Cylindrical symmetry exists in the bed
- (v) The bed wall is at a constant temperature
- (vi) The properties of the bed and the heat capacity of the fluid are constant
- (vii) The transport parameters are constant throughout the bed
- (viii) The velocity profile is flat
- (ix) There is no heat or mass transferred by diffusion in the axial direction

Assumption (ix) needs closer attention. A great deal of effort has been spent in evaluating axial dispersion in fixed-beds (e.g. 49, 50, 51).

Although Paris and Stevens (41) state that radial diffusional transport may be neglected before axial diffusional transport, their reasoning is not complete. However, a number of authors (52, 53, 54, 55) have shown that the effect of axial mixing can be omitted in commonly operated industrial reactors. This conclusion is, of course, based on a continuum model.

A quantitative assessment of the importance of the effect may be obtained by applying criteria recently developed by Young and Finlayson (56) for non-isothermal reactors. They present a criterion for the bed entrance and also an "a posteriori" criterion which may be used throughout the bed. They show that in at least one case, the moderately exothermic oxidation of sulphur dioxide, axial mixing should not be neglected. However, it is convenient to assume that axial mixing is unimportant for a two-phase model (for both phases), as the introduction of an axial mixing term into the conservation equations results in a two-point boundary value problem which requires iterative solution.

Assumptions (i) to (ix) allow the conservation equations (2.1) to be written in the following form:

$$\text{Mass balance on component } i: \frac{\delta g^i}{\delta z} = \frac{dp\phi}{(Pe)_{mr}} \left(\frac{\delta^2 g^i}{\delta r^2} + \frac{1}{r} \frac{\delta g^i}{\delta r} \right) + F^i(g, T^f, T^s) \quad (2.2)$$

$i=1 \rightarrow s$

$$\text{Energy balance on fluid phase } \frac{\delta T^f}{\delta z} = \frac{\lambda_r^f}{CpG} \left(\frac{\delta^2 T^f}{\delta r^2} + \frac{1}{r} \frac{\delta T^f}{\delta r} \right) + \frac{h_v a_v}{GCp} (T^s - T^f) + F^f(g, T^f) \quad (2.3)$$

$$\text{Energy balance on solid phase } (T^s - T^f) = \lambda_r^s \left(\frac{\delta^2 T^s}{\delta r^2} + \frac{1}{r} \frac{\delta T^s}{\delta r} \right) + F^s(g, T^s) \quad (2.4)$$

The functions F^i , F^f , F^s , are of the following form.

$$F^i \equiv \frac{(\text{rate of change of mass fraction of component } i) \times (\text{fluid density})}{\text{superficial mass flow rate per unit area}}$$

$$F^f \equiv \frac{(\text{rate of heat release in the fluid per unit volume of reactor bed})}{(\text{superficial mass flow rate per unit area}) \times (\text{mass specific heat of fluid})}$$

$$F^s \equiv \text{rate of heat release in solid per unit volume of bed}$$

These functions will be elaborated upon when specific examples are considered.

The initial and boundary conditions for the two-dimensional heterogeneous model are:

mass balance on component i:

$$\begin{aligned}
 z = 0 \quad 0 \leq r \leq R_t \quad g^i &= g_{in}^i \quad i = 1 \rightarrow S \\
 0 < z \leq L \quad r = 0 \quad \frac{\delta g^i}{\delta r} &= 0 \quad i = 1 \rightarrow S \\
 0 < z \leq L \quad r = R_t \quad \frac{\delta g^i}{\delta r} &= 0 \quad i = 1 \rightarrow S
 \end{aligned} \tag{2.5}$$

Fluid energy balance:

$$\begin{aligned}
 z = 0 \quad 0 \leq r \leq R_t \quad T^f &= T_{in}^f \\
 0 < z \leq L \quad r = 0 \quad \frac{\delta T^f}{\delta r} &= 0 \\
 0 < z \leq L \quad r = R_t \quad -\frac{\delta T^f}{\delta r} &= \frac{\alpha_w^2}{\lambda r^f} (T^f - T_w)
 \end{aligned} \tag{2.6}$$

Solids energy balance:

$$\begin{aligned}
 0 \leq z \leq L \quad r = 0 \quad \frac{\delta T^s}{\delta r} &= 0 \\
 0 \leq z \leq L \quad r = R_t \quad -\frac{\delta T^s}{\delta r} &= \frac{\alpha_w^2}{\lambda r^s} (T^s - T_w)
 \end{aligned} \tag{2.7}$$

It will be noted that there is no initial condition given for the solid temperature, and that the boundary conditions for the solid temperature include the equality at $z=0$. It may be intuitively supposed that the solids temperature profile at the reactor entrance - $z=0$ - is flat and equal to the fluid temperature. However this is invalid in that the conservation equation (2.4) is then violated. The profile must be obtained by solution of (2.4) at $z=0$ subject to boundary conditions (2.7).

So far no provision has been made for solid-fluid mass gradients and intra-particle mass and energy gradients. In the general case the following phenomena will also exist in the fixed-bed environment.

- (i) a concentration difference between the bulk fluid and the solid.
- (ii) a temperature gradient within the pellet.
- (iii) a concentration gradient within the pellet.

The first effect may be described by the algebraic relationship:

$$-kg^i a_v (g^i f g^i s)_p = F_p^i(g, T^s) \quad i=1 \rightarrow S \quad (2.8)$$

F_p^i is a measure of the generation of component i within the pellet and will be of the form:

$F_p^i \equiv$ Mass of component i produced per unit volume of pellet per second.

In practice, for the convenience of computation, this effect will be iteratively quantified prior to the calculation of the functions F^i , F^f , F^s . It has been shown (e.g. 1) that in most practical cases the internal solid temperature differences may be neglected as they are likely to be considerably less than the differences existing between the pellet and the bulk fluid (57, 58): the assumption of constant temperature within the pellet will therefore not lead to any great inaccuracies.

In the light of the previous paragraph the third effect may be characterised by a lumped parameter, the isothermal effectiveness factor (e.g. 1) which relates the total rate of reaction in the solid to that which would obtain if the solid reactions occurred under conditions of concentration and temperature existing at the external solid surface.

2.2.2 Previous work on this model

The two-dimensional, two-phase model for the fixed-bed reactor has received relatively little attention in the literature. The work of Wilhelm and Singer (59) relating to heat transfer in a packed tube, considered the presence of two phases. Deans and Lapidus (60) proposed a two-dimensional cell model for the fixed-bed which considers temperature and concentration differences between the bulk fluid and the solid surface. Subsequently McGuire and Lapidus (43) used the model to study the stability of a fixed-bed reactor. A serious drawback encountered in this model is that heat is considered to be transferred radially by the fluid alone. Whilst this might approximate the truth in cases of fully developed turbulence - say $Re_p > 100$ (49, 61) - it restricts the use of the model considerably. Ohki et al. (62) have extended the model to overcome this restriction by considering a cell-to-cell heat transfer coefficient. McGreavy and Cresswell (63) have proposed a diffusional two-phase model but, like Deans and Lapidus, have neglected radial heat transfer by the solid. Carberry and White (64) also consider a two-dimensional two-phase model, but describe the radial heat transfer by using the concept of effective thermal conductivity based on a single lumped phase.

More recently Wasch and Froment (46) have presented a model which distinguishes between both phases but does not have the restrictions of

the previously mentioned models. This model is the basis of the two-phase model used in this work. Olbrich et al. (47, 65) have studied heat transfer in small tubes and other geometries using two-phase transport mechanisms. Their findings are reviewed in Section 2.6.

2.3 THE TWO-DIMENSIONAL, ONE-PHASE MODEL

2.3.1 General description of model

It has been shown that for moderately exothermic heterogeneous reactions, the fixed-bed catalytic reactor may be well represented by a hypothetical continuous phase for which effective transport parameters may be assigned. This concept is valid for reactors when more than 10 particles are packed across the tube and the number of particles exceeds six in the axial direction (42). Thus the radial conductivity of the hypothetical phase is given by λ_r^C and the heat transfer at the wall is characterised by α_w^C . In this model temperature and concentration differences between fluid and solid are neglected, although they may be partly accounted for, as previously described, by the use of a suitably calculated pellet effectiveness factor (e.g. 48). It should be noted, however, that this factor will describe the pellet temperature and fluid-solid temperature and concentration differences relative to the hypothetical continuum phase whereas, properly speaking, they should be described relative to the true fluid-phase.

The preceding paragraph may be summarised by the following additional assumption:

- (x) The continuous (fluid) and distributed (solid) phases existing in the fixed bed may be modelled by a single hypothetical continuous phase.

With this, and the previous nine assumptions, the model may be represented by the conservation equations:

$$\text{Mass balance on component } i: \frac{\delta g^i}{\delta z} = \frac{dp\phi}{(Pe)_{mr}} \left(\frac{\delta^2 g^i}{\delta r^2} + \frac{1}{r} \frac{\delta g^i}{\delta r} \right) + F^i(g, T^C)$$

$i=1 \rightarrow S \quad (2.9)$

Energy balance on continuous phase:

$$\frac{\delta T^C}{\delta z} = \frac{\lambda_r^C}{CpG} \left(\frac{\delta^2 T^C}{\delta r^2} + \frac{1}{r} \frac{\delta T^C}{\delta r} \right) + F^C(g, T^C) \quad (2.10)$$

subject to initial and boundary conditions:

$$\begin{aligned}
 z = 0 \quad 0 < r \leq R_t \quad g_i = g_{in}^i, \quad i=1 \rightarrow S; \quad T^C = T_{in}^C \\
 0 \leq z \leq L \quad r = 0 \quad \frac{\delta g^i}{\delta r} = 0, \quad i=1 \rightarrow S; \quad \frac{\delta T^C}{\delta r} = 0 \\
 0 \leq z \leq L \quad r = R_t \quad \frac{\delta g^i}{\delta r} = 0, \quad i=1 \rightarrow S; \quad -\frac{\delta T^C}{\delta r} = \frac{\alpha_w^C}{\lambda r^C} (T^C - T_w)
 \end{aligned}
 \tag{2.11}$$

The parameters λ_r^C and α_w^C may be deduced from the transfer parameters for the two-phase model (Section 2.6).

2.3.2 Previous work on two-dimensional one-phase model

Wasch and Froment (46) compare the predictions of their two-phase model with the predictions of the one-phase model - this model - for the heterogeneous oxidation of o-xylene to phthalic anhydride and found rather close agreement between the two models. It would appear that there has been no comparison between the two models to date for the case of a homogeneous-heterogeneous system.

The two-dimensional, one-phase model has been considered in extensive detail by Mickley and Letts (66, 67), in reviews by Beek (52), Froment, (68) Paris and Stevens (41) and Hlavacek (42) and in texts by Aris (69), Petersen (1) and Smith (70).

2.4 ONE-DIMENSIONAL, ONE-PHASE MODEL

2.4.1 Description of model

The mathematical representations of the two-dimensional models involve second-order, two-dimensional partial differential equations. It would be attractive to be able to represent the system by ordinary differential equations which are, in general, more easily solved.

This may be achieved by making the assumption:

- (xi) The temperature and composition of the continuous medium are constant across a cross-section of the fixed-bed.

This implies that all radial gradients are neglected and that the transfer of heat from the bed to the wall is characterised by an overall heat transfer coefficient based on the difference between the wall temperature and the mean bed temperature as predicted by the one-dimensional

model.

With this additional assumption the mass and energy balances in the fixed bed reactor may be represented by:

$$\text{mass balance component } i: \frac{\delta g^i}{\delta z} = F^i(\underline{g}, T^C); i=1 \rightarrow S \quad (2.12)$$

$$\text{energy balance:} \quad \frac{\delta T^C}{\delta z} = F^C(\underline{g}, T^C) - \frac{2U}{GCpR_t} (T^C - T_w) \quad (2.13)$$

Subject to the initial conditions:

$$\begin{array}{lll} z = 0 & 0 \leq r \leq R_t & g^i = g_{in}^i \quad i=1 \rightarrow S \\ z = 0 & 0 \leq r \leq R_t & T^C = T_{in}^C \end{array} \quad (2.14)$$

2.4.2 Previous work with the one-dimensional model

The authors referenced at the end of Section 2.3 have considered the one-dimensional model. In particular, Froment (68), considering heterogeneous o-xylene oxidation, has compared the one-dimensional and two-dimensional models.

The 'mean' temperatures predicted by the one-dimensional model are compared with the radial mean temperatures, or flow averaged values, predicted by the two-dimensional model. For the system investigated the agreement between the predicted temperatures was found to be rather good. However, no comparison between predicted product yields or selectivities are given. In general, the one-dimensional predictions for an exothermic reaction will always be low. An extensive treatment of this model was given by Carberry and Wendel (54). Equation (2.13) contains an overall heat transfer parameter U . This has been correlated by Leva (71) and Colburn (72) amongst others. It may also be obtained by amalgamation of the parameters λ_r^C and α_w^C (Section 2.6).

2.5 MASS TRANSFER IN PACKED BEDS

Packed beds are known to be anisotropic with respect to mass transfer effects. As was previously noted (Section 2.2.1) the diffusive contribution to mass transfer in the axial direction may be neglected compared to the convective contribution. It will be assumed that there is no bulk convective flow radially and that radial mass transfer may be represented by an effective diffusion coefficient to describe the radial mass flux

by a Fick's law analogy. Generally, the effective diffusion coefficient will have a molecular diffusion component and a turbulent diffusion component. In practical situations only the second effect is important (41).

The radial mass diffusion coefficient is conveniently correlated as the mass radial Peclet number and as such appears in the conservation equations (2.2) and (2.9). This dimensionless group is defined by:

$$(Pe)_{mr} = \frac{vdp}{D} = \frac{Gdp}{D\rho} \quad (2.15)$$

Several authors have reported values for this group. Bernard and Wilhelm (61) give a semi-empirical correlation, namely:

$$(Pe)_{mr} = \frac{\frac{1.15}{\gamma_p} - 0.15}{0.065 + 17.4\left(\frac{dp}{dt}\right)^{2.7}} Re_p \left(4.28\left(\frac{dp}{dt}\right)^{1.8} - 0.05\right) \quad (2.16)$$

γ_p is a shape factor. The expression is reported valid for $\left(\frac{dp}{dt}\right) < 0.17$ and $(Pe)_{mr} > 2150 dp/D$. This correlation displays a rather complex dependence on particle to tube diameter ratio. Fahien et al. (73, 74) retain a dependance on this ratio when they adopt the group:

$$(Pe)_{mr} / \left(19.4\left(\frac{dp}{dt}\right)^2 + 1\right)$$

as an ordinate in their correlations and find that within reasonable accuracy this group has a constant value of about 8. They have also found that the radial mass Peclet number shows a variation with radial position. This reflects findings by Roblee (75) and Schwarz and Smith (76) who report radial variations in bed porosity and fluid velocity respectively which would both affect the Peclet number.

Although there is some disagreement as to the precise value to be assigned to the radial mass Peclet number, all authors agree that it lies within the range 8 to 14. It has been reported that computed concentration and temperature profiles are insensitive to moderate changes in this parameter (40, 77) and Froment (68) used values of 8 and 10 for $(Pe)_{mr}$ and obtained identical results.

In view of these findings Fahien and Smith's (73) correlation of:

$$(Pe)_{mr} = 8 \left[19.4\left(\frac{dp}{dt}\right)^2 + 1 \right] \quad (2.17)$$

has been used in this work.

2.6 HEAT TRANSFER IN PACKED BEDS

The literature is rich with correlations for the various parameters that may be used to predict the transfer of heat in fixed bed catalytic reactors. Recent reviews by Beek (52) and Smith (78) give a good summary of the correlations presently available. Virtually all correlations refer to the effective transport parameters used when the bed is modelled as a hypothetical continuous phase. Relatively little attention has been paid specifically to two phase heat transfer in packed-beds.

As the physical and mathematical models for the packed bed become more sophisticated, more parameters are required to describe the heat transfer. The basic parametric requirements are shown in Table (2.2) The following sections show how the parameters for the two-phase model may be amalgamated to give the effective parameters for the one-phase model and how these may be subsequently amalgamated to give the overall heat coefficient of the one-dimensional model. The available correlations for the two-phase parameters are also discussed.

2.5.1 Relationship between heat transfer parameters for the three models

In the one-phase model the packed bed environment is represented by a hypothetical continuous medium and the transfer of heat from this medium is calculated from the effective heat transfer parameters α_w^C and λ_r^C .

Considering, first, the effective radial conductivity of the bed, λ_r^C , it has been recommended by Olbrich (47) and Wasch and Froment (46) that the relationship:

$$\lambda_r^C = \lambda_r^f + \lambda_r^s \quad (2.18)$$

adequately describes λ_r^C .

If the total heat flux through the two-phase bed, Q_r^C , is considered to have solid- and fluid-phase components:

$$Q_r^C = Q_r^s + Q_r^f$$

then:

$$\lambda \eta^c \frac{\delta T^c}{\delta r} = \lambda \eta^f \frac{\delta T^f}{\delta r} + \lambda \eta^s \frac{\delta T^s}{\delta r} \quad (2.19)$$

Therefore

$$\frac{\delta T^c}{\delta r} = \frac{\delta T^f}{\delta r} = \frac{\delta T^s}{\delta r}$$

Published radial profiles (46, 47) show that the radial temperature gradient in the solid phase is, in fact, the same as that in the fluid phase over most of the radius. This indicates that the radial conductivities may be regarded as additive.

The situation at the wall is less well understood. It may be surmised that:

$$Q_w^c = Q_w^s + Q_w^f$$

and so:

$$\alpha_w^c (T^c - T_w) = \alpha_w^s (T^s - T_w) + \alpha_w^f (T^f - T_w) \quad (2.20)$$

Thus the wall heat transfer coefficients are only strictly additive if the fluid- and solid-phase temperatures are the same.

If the group $\frac{T^s - T^f}{T^c - T_w}$ is fairly small, then:

$$(T^c - T_w) \approx (T^s - T_w) \approx (T^f - T_w) \quad (2.21)$$

and:

$$\alpha_w^c = \alpha_w^f + \alpha_w^s \quad (2.22)$$

Relationship (2.21) will probably be true in the major part of the bed although it will not be so near to the bed entrance when $T_{in}^c = T_w$. Nevertheless (2.22) provides a useful and straightforward working relationship.

Olbrich et al. (47, 65) have considered the problem of two-phase transfer to the wall and propose the relationship:

$$B_i^s = \frac{\alpha_w^s dp}{\lambda_r^s} \quad (2.23)$$

$$B_i^S = 2.12 \quad (2.23a)$$

for close packed spheres against a flat wall. The solid-phase Biot number, B_i^S , may then be used in the following relationship:

$$\frac{\alpha_w^c}{\alpha_w^f} = \frac{K^3}{B_i^f N^S} \left(\frac{N^f B_i^f + B_i^f K B_i^S + B_i^f N^S}{N^S B_i^S + K^3 + N^f B_i^f} \right) \quad (2.24)$$

Equation (2.23a) gives unacceptably large values for α_w^S despite the assertion (47) that it forms a lower bound for B_i^S . Consequently, (2.24) gives values for α_w^S which are much higher than those reported in the literature (e.g. 52).

However, (2.24) may be used retrospectively. Reasonable correlations are available for α_w^f (79) and α_w^c (52). If (2.22) is assumed to hold, α_w^S may be calculated. If λr^f , λr^S and h_v are known, α_w^c may be predicted from (2.23) and (2.24). This may be compared with the original prediction for α_w^c to assess the error introduced by assuming (2.22) to be true.

The overall heat transfer coefficient, U , is defined by:

$$Q_v = U(T^C - T_w)a_v \quad (2.25)$$

where Q_v is the total rate of heat removal per unit volume of reactor bed.

The relationship between U , α_w^c and λr^c has been considered by Froment (68), Crider and Foss (80) and Beek and Singer (81) who have shown that U may be calculated from:

$$\frac{1}{U} = \frac{1}{\alpha_w^c} + \frac{R_t}{4\lambda r^c} \quad (2.26)$$

2.6.2 Heat transfer parameters for the two-phase model

Singer and Wilhelm (59) and, more recently, Yagi and Kunu (82) have considered the mechanisms by which heat is transferred through a packed bed. Heat transfer, in contrast to mass transfer, occurs through both the fluid- and solid-phases. The following mechanisms for radial heat transfer were considered:

1. Solid Phase

- (a) Conduction through the particle
- (b) Conduction through the particle contact points
- (c) Conduction through stagnant fluid adjacent to particle contact points

(d) Radiation from particle to particle

2. Fluid Phase

(a) Conduction through the fluid

(b) Energy convection by the fluid

(c) Energy transfer from fluid to solid

(d) Radiation from void to void

If each of these mechanisms is assumed to be a heat transfer resistance, their inter-relationship is shown in Figure (2.1).

Application of the methods of Yagi and Kunii yield the following expression for the solid-phase radial conductivity:

$$\lambda_r^S = \frac{(1-\phi)h_t k_s dp}{2k_s + h_t dp} \quad (2.27)$$

The parameter h_t is an overall transfer coefficient between the solid particles and amalgamates the parallel mechanisms transferring heat from pellet to pellet.

It is, however, rather difficult to assign a value to h_t and an alternative approach to the problem is desirable. It has been reported (83) that the solid phase conductivity can in fact be considered as the stagnant conductivity of the bed. Wakao and Kato (84) have calculated the stagnant conductivity from an elaborate model for the packed bed and correlate their results by:

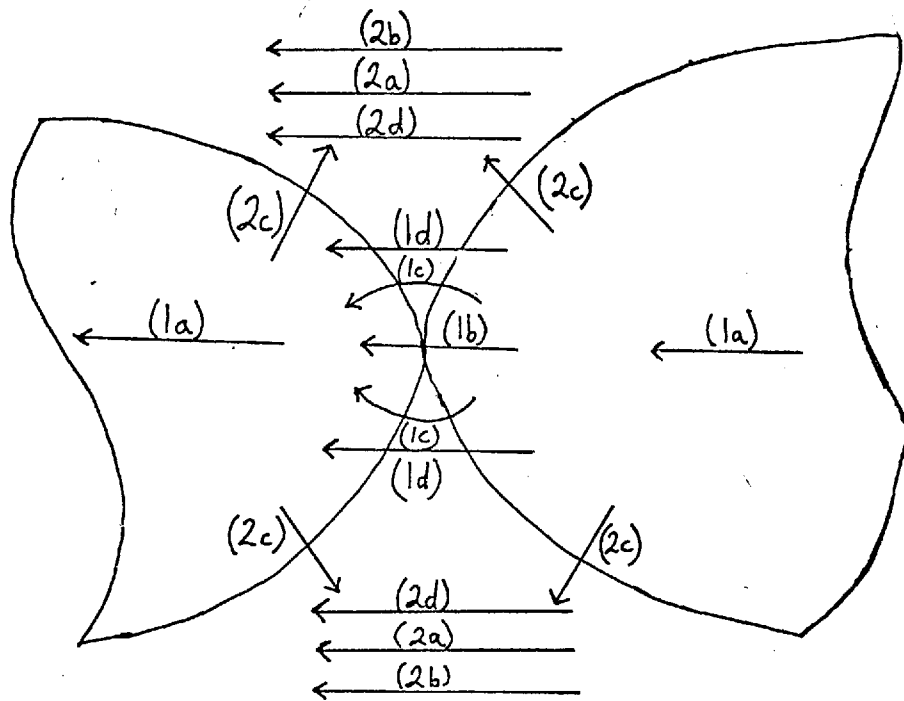
$$\frac{\lambda_r^S}{k_f} = \frac{\lambda_r^S}{k_f (Nu)_r=0} + 0.707 (Nu)_r^{0.96} \left(\frac{k_s}{k_f}\right)^{1.11} \quad (2.28)$$

This expression is a composite of the stagnant conductivity in the absence of radiation added to the radiation effect. The quantity

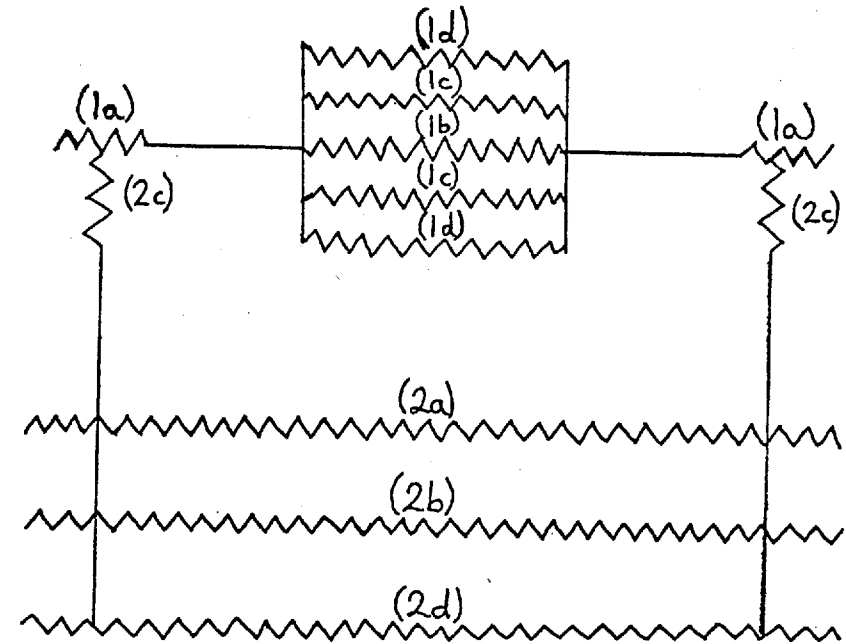
$$\frac{\lambda_r^S}{k_f} (Nu)_r = 0$$

may be obtained from Figure 8. of the paper by Wakas and Kato who also present an expression for $(Nu)_r$, the radiant Nusselt Number. Equation (2.28) is the correlation for λ_r^S used in the present work.

Equations (2.27) and (2.28) have been compared using the data of Froment and Wasch (46). The estimates for the solid-phase conductivity were:



(a) Physical model.



(b) Resistance representation.

Fig(2.1) Radial heat-transfer mechanism in a packed bed.

$$\text{Equation (2.27) (46)} \quad \lambda_r^S = 0.301 \text{ w/m sec K}$$

$$\text{Equation (2.28)} \quad \lambda_r^S = 0.319 \text{ w/m sec K}$$

Thus, there is a discrepancy of only ~5% between the two estimates.

The evaluation of the fluid phase radial conductivity is a relatively straightforward matter. The three mechanisms, namely molecular conduction, convection and radiation operate in parallel and so the fluid phase radial conductivity is given by (78).

$$\lambda_r^f = \phi(k_f + \frac{C_p G d_p}{\phi(Pe)_{mr}} + \frac{4\epsilon\sigma d_p (T^f)^3}{2-\epsilon}) \quad (2.29)$$

ϵ is the particle emissivity and may be assumed to be 0.5 for most catalyst materials (85).

σ is the stefan Boltzman constant, $5.68 \times 10^{-8} \text{ w/m}^2 \text{K}^4$

The Peclet Number for radial mass transfer, $(Pe)_{mr}$, is given by Equation (2.17) for $Re_p > 40$. Also, when $Re_p > 40$ the contribution by molecular conduction becomes negligible (52) and k_f may be removed from Equation (2.29).

The experimental data for the fluid-particle heat transfer coefficient, h_v , has been the subject of a thorough analysis by Whitaker (86). For Reynolds number, based on particle diameter, greater than 40 he proposed the correlation:

$$\frac{h_v d_p' \phi}{k_f (1-\phi)} = \left[0.5 Re_p'^{1/2} + 0.2 Re_p'^{2/3} \right] Pr \quad (2.30)$$

Where d_p' is defined by Whitaker as $d_p' = 6V_p/A_p$ and is thus equal to the particle diameter for a sphere. The modified Reynolds number, Re_p' , is defined by:

$$Re_p' = \frac{G d_p' \phi}{\mu (1-\phi)} \quad (2.30a)$$

Beek (52) has modified the Thoenas and Kramer (87) correlation to heat transfer in proposing an expression similar in form to Equation (2.30).

$$\frac{h_v d_p}{k_f} = 3.22 Re_p^{1/3} Pr^{1/3} + 0.117 Re_p^{0.8} Pr^{0.4} \quad (2.31)$$

Equations (2.30) and (2.31) give similar results over a wide range of

values of the parameters (78). Equation (2.30) has been used in the present work. Whitaker states that the scatter of experimental data about this correlation is at worst 30%. In most cases it is of the order of 10%.

Having discussed the evaluation of λr^S , λr^f and h_v , it remains to evaluate α_w^f and α_w^S . The literature shows much disagreement in the correlation of these parameters (88). When it is required to discriminate between solid-wall transfer and fluid-wall transfer, as in the present case, the situation is even less clear.

Wasch and Froment (88) have correlated the continuum wall heat transfer coefficient, α_w^C , by considering static and dynamic contributions which correspond to α_w^S and α_w^f respectively.

However, the static contributions were determined experimentally and are not generally applicable. Yagi and Wakao (79) report the following correlation:

$$j_H = \frac{\alpha_w^C}{C_p G} Pr^{2/3} = 0.20 Re_p^{-0.20} \quad Re_p > 20 \quad (2.32)$$

The restriction on the particle Reynolds number and the fact that a completely analogous correlation is presented for mass transfer to the wall indicates that (2.32) is more properly written:

$$\frac{\alpha_w^f}{C_p G} Pr^{2/3} = 0.20 Re_p^{-0.20} \quad (2.32a)$$

It might be expected that α_w^S is independent of the Reynolds number and any dependence of α_w^C on Re_p is due to the dependence of α_w^f on Re_p . For α_w^C , Wasch and Froment report a linear dependence on Re_p whereas Calderbank and Pogorski (89) favour an exponent of 0.365, Hanratty (90) a value of 0.5 and Yagi and Kunu (82) a value of unity. These figures illustrate the discrepancy in the literature.

No correlation is available for α_w^S . However, as is shown elsewhere, (2.22) may be used to predict α_w^S , provided a correlation is available for α_w^C .

The correlations for α_w^C also show wide disagreement. Smith (78) recommends that of Beek (52).

$$\text{cylinders } \frac{\alpha_w^C d_p}{k_f} = 2.58 Re_p^{1/3} Pr^{1/3} + 0.094 Re_p^{0.8} Pr^{0.4}$$

$$\text{spheres } \frac{\alpha_w^c dp}{k_f} = 0.203 \text{Re}_p^{1/3} \text{Pr}^{1/3} + 0.220 \text{Re}_p^{0.8} \text{Pr}^{0.4} \quad (2.33)$$

These relationships are of a semi-empirical nature and it will be noted that the conductivity of the solid phase, k_s , is not involved. Nevertheless, they are used in the absence of a better correlation.

For the conditions considered by Wasch and Froment (46), Equation (2.33) predicts a value of $125.4 \text{ Kcal/m}^2\text{hr K}$ which compares favourably with their value of $122 \text{ Kcal/m}^2\text{hr K}$. α_w^f is calculated, for the same conditions, to be $105.6 \text{ Kcal/m}^2\text{hr K}$ and so, from (2.22), α_w^s is $19.8 \text{ Kcal/m}^2\text{hr K}$. These figures differ markedly from those of Wasch and Froment who use:

$$\alpha_w^f = 74.2; \alpha_w^s = 47.8 \quad \text{Kcal/m}^2\text{hr K}$$

Using their figure of $185.5 \text{ Kcal/m}^2\text{hr K}$ for h_v and noting that:

$$a_v = 6(1-\phi)/dp$$

for spheres, it is possible to calculate the following groups for use in Equation (2.24) when $\alpha_w^s = 19.8$ and $\alpha_w^f = 105.6$

$$B_i^s = 0.94 \quad B_i^f = 3.29 \quad N^f = 86.52 \quad N^s = 134.29 \quad K^2 = 220.81$$

resulting in a value of 1.15 for α_w^c/α_w^f which leads to a value of $121.4 \text{ Kcal/m}^2\text{hr K}$ for α_w^c which shows excellent agreement with the two previous values for α_w^c .

Thus the correlations for the two-phase heat transfer parameters are consistent with respect to the wall transfer theory of Olbrich (47).

A summary of correlations used in the present work is given in Table (2.3).

2.6.3 The effect of pellet hollowing on heat transfer in a packed bed

The heat transfer characteristics of a bed of hollow pellets will be expected to differ from those of a bed of similar solid pellets. The greater proportion of less conductive fluid in the bed will lower the amount of radial heat transfer but this will be compensated by increased turbulence and a corresponding increase in the convective transfer. An understanding of the effect of pellet hollowing is best obtained by considering the effective radial conductivity, λ_r^c , to be represented by (52):

TABLE (2.3)

Heat Transfer Correlations

PARAMETER	EQUATION	CORRELATION	REFERENCE
λ_r^s	(2.28)	$\frac{\lambda_r^s}{k_s} = \frac{\lambda_r^s}{k_g} \quad \text{Nu}_r=0 + 0.707 \text{Nu}_r^{0.96} \frac{k_s}{k_g}^{1.1}$	84
λ_r^f	(2.29)	$\lambda_r^f = \phi(k_g + \frac{\text{CpGdp}}{\phi(\text{Pe})_{mr}} + \frac{4\epsilon\sigma d p T^3}{2-\epsilon})$	78
h_v	(2.30)	$\frac{h_v d p' \phi}{\text{Pr } k_g (1-\phi)} = \frac{1}{2} \text{Re}_p^{1/2} + 0.2 \text{Re}_p^{2/3}$	86
α_w^f	(2.32a)	$\frac{\alpha_w^f \text{Pr}^{1/3}}{\text{CpG}} = 0.2 \text{Re}_p^{-0.20}$	79
α_w^c	(2.33)	cylinders $\frac{\alpha_w^c d p}{k_g} = 2.58 \text{Re}_p^{1/3} \text{Pr}^{1/3} + 0.094 \text{Re}_p^{0.8} \text{Pr}^{0.4}$	52
		spheres $\frac{\alpha_w^c d p}{k_g} = 0.203 \text{Re}_p^{1/3} \text{Pr}^{1/3} + 0.22 \text{Re}_p^{0.8} \text{Pr}^{0.4}$	52
α_w^s	(2.22)	$\alpha_w^s = \alpha_w^c - \alpha_w^f$	

$$\lambda r^C = \phi_H K_f + \frac{CpGdp}{(Pe)_{mr}} + \frac{(1-\phi_H)h_t dp k_s}{2k_s + 0.7h_t dp} + \frac{4\epsilon\sigma dp(T^C)^3}{2-\epsilon} \quad (2.34)$$

ϕ_H is the total voidage of the bed of hollow particles. The amount of hollowing is characterised by α which is the ratio of internal to external dimensions of the pellet. When α is zero, the situation is that of a bed of solid particles and when α is 1, it corresponds to an empty tube. The radiation term in (2.34) will be neglected as it is only important at high temperature and is not essential to the argument. Each of the other three terms is affected by pellet hollowing.

If the bed of solid particles has a voidage ϕ_s , then ϕ_H is related to the degree of hollowing, α , by:

$$\phi_H = \phi_s + (1-\phi_s)\alpha^2 \quad (2.35)$$

With the following data:

$$k_f = 0.043 \text{ J/m sec K}; \quad Cp = 1000 \text{ J/kg K}; \quad G = 1.3 \text{ kg/m}^2 \text{ sec} \\ dp = 6Vp/Ap = 0.003\text{m}; \quad k_s = 1.16 \text{ J/m sec K}; \quad \mu = 3.1 \times 10^{-5} \text{ kg/m sec}; \quad \phi_s = 0.4$$

the values of the three contributions to λr^C , for $\alpha=0$, are:

$$\phi_H k_f = 0.017 \text{ J/m sec K}$$

$$\frac{CpGdp}{(Pe)_{mr}} = 0.381 \text{ J/m sec K}$$

$$\frac{(1-\phi_H)h_t dp k_s}{2k_s + 0.7h_t dp} = 0.171 \text{ J/m sec K}$$

The equivalent particle diameter, dp , refers to the solid pellets. The Peclet number, $(Pe)_{mr}$, is calculated from (2.17). These figures indicate the relative importance of the three terms under these, typical, conditions.

The last term, in gross simplification, represents the series addition of the solid conductivity, k_s , and the resistance to particle-particle heat transfer, h_t . This is emphasised by writing the term as:

$$X_s = \frac{(1-\phi_H)h_t dp k_s}{2k_s + 0.7h_t dp} \quad \frac{1}{X_s} = \frac{1}{(1-\phi_H)} \left[\frac{2}{h_t dp} + \frac{0.7}{k_s} \right]$$

or in more general terms:

$$\frac{1}{X_s} = \frac{P_1}{h_t dp} + \frac{P_2}{k_s} \quad (2.36)$$

Gunn (91) has found that the number of particles per unit volume of reactor bed is approximately the same for solid and hollow particles. If the rather more sweeping assumption is made, that the number of particle contact points per unit volume is the same, then it may be argued that the factor P_1 is the same for hollow and solid pellets. However, in a real situation the number of particle contact points will be increased by interpenetration of the particles (see Figure (2.2)) and the particle-particle heat transfer will be enhanced as there is one point of contact between the particles in the solid case and two points of contact in the hollow case. This will result in a lower value for P_1 . The amount of interpenetration will increase as the degree of hollowing increases.

The factor P_2 would be expected to increase in a hollow pellet situation indicating a reduction in the heat transfer through the solid between points of contact. In the example just considered, P_2 has a value of 0.7. If this is doubled, X_s is only reduced by about 10% as this contribution is not the controlling step in the overall transfer process. Furthermore, X_s is decreased by hollowing by virtue of an increase in ϕ_H and a corresponding decrease in $(1-\phi_H)$.

The qualitative arguments of the preceding paragraphs are rather difficult to quantify, particularly the effect of interpenetration. It is therefore assumed that the various effects compensate one another. In any case, this term is smaller than the convective term and the effect of any error in this assumption will be reduced in the overall correlation.

The molecular conduction term, $\phi_H k_f$, is considerably smaller than the other terms, but increases as α increases. In the limiting case of $\alpha=1$ it is the only contribution to radial transfer.

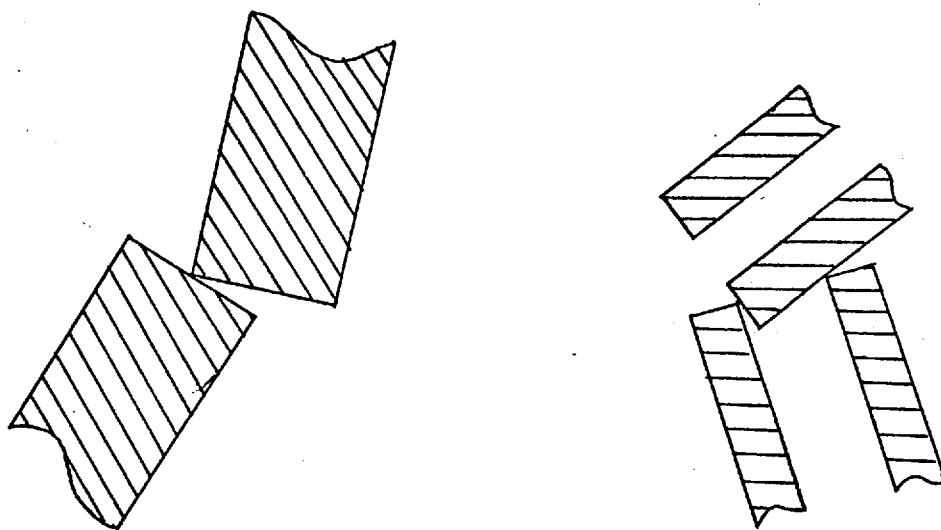
It remains to evaluate the effect of particle hollowing on the convective heat transfer term

CpGdp

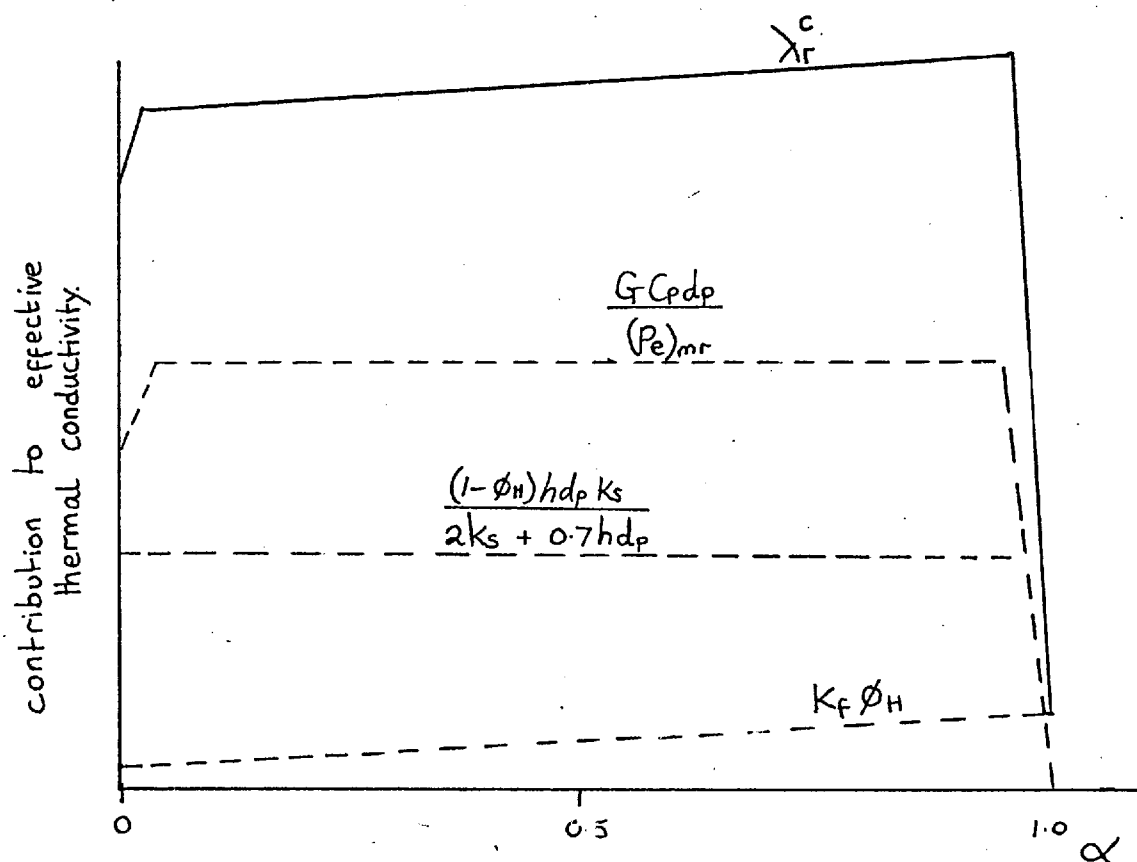
(Pe)_{mr}

one point of contact.

two points of contact.



Fig(2-2) Interpenetration of beds of hollow cylinders.



Fig(2-3) Effect of pellet hollowing on bed heat-transfer.

Gunn (92), discussing dispersion in packed beds, has found that $(Pe)_{mr}$ is reduced for beds of hollow cylindrical pellets compared with beds of similar solid particles and that the amount of the reduction is independent of the degree of hollowing. Thus, for a given Reynolds number, the effect of hollowing is to enhance the radial turbulent mixing. In concept, the turbulence will be maintained as α is increased to the point where the hollow pellet walls are infinitely thin, i.e. $\alpha=1^-$, as long as solid material is actually present.

The form of the dependance on α of these three terms in the correlation for λr^C is shown in Figure (2.3). It may be concluded from these arguments that the heat transfer from a packed bed will be increased by particle hollowing but, provided the hollowing is sufficient to promote increased turbulence, increasing the degree of hollowing will not increase the rate of heat transfer significantly. Furthermore, the increase in rate of heat transfer is confined to the fluid phase so that if a two-phase model is considered, λr^f is increased but λr^s remains constant.

Pellet hollowing should not affect the wall heat transfer coefficient as the geometry close to the wall will not be greatly changed.

2.7 INTEGRATION OF THE MATHEMATICAL MODELS

Each of the three models for the fixed-bed catalytic reactor are described by a set of ordinary or partial differential equations. The behaviour of the reactor is predicted by the integration of subject to their respective initial and boundary conditions.

2.7.1 The one-dimensional model

The model is described by Equations (2.12) and (2.13) subject to initial conditions (2.14). These form a set of S+1 first-order ordinary differential equations which may be solved by the Runge-Kutta-Merson method (42, 93). This is a step-wise integration method requiring five derivative evaluations at each step and providing also an estimate of the truncation error so that step-length variation may be employed as required. A standard library subroutine was used to perform the integration. The subroutine, which was originally developed at the Kjeller computer installation, Norway, is Subroutine D208 in the CERN library.

2.7.2. The two-dimensional models

The one-phase and two-phase two-dimensional models are very similar in their mathematical structure, the only difference being that the two-

phase model has an additional equation, the solid phase energy balance, which is implicit in the solid-phase temperature. Thus the one-phase two-dimensional model will be considered initially and the modifications necessary for the incorporation of the additional equation of the two-phase model will be subsequently discussed.

The one-phase two-dimensional model is described by a set of $S+1$ parabolic partial differential equations, (2.9) and (2.10), subject to boundary conditions (2.11). An analytical integration is not available owing to their highly non-linear and interactive nature. Therefore the equations have been integrated by a procedure based on the finite difference method described by Beek (52).

It will be shown in the following section that the equations are more easily handled if the following variable substitution is made.

$$u = r^2/R_t^2 \quad (2.37)$$

When (2.37) is substituted into (2.9), (2.10) and (2.11) the following set of working equations are obtained.

Mass balance on component i

$$\frac{\delta g^i}{\delta z} = \frac{4dp\phi}{(Pe)_{mr}R_t^2} \left(u \frac{\delta^2 g^i}{\delta u^2} + \frac{\delta g^i}{\delta u} \right) + F^i(\underline{g}, T^C) \quad i=1 \rightarrow S \quad (2.38)$$

Energy balance on the continuous phase:

$$\frac{\delta T^C}{\delta z} = \frac{4\lambda r^C}{C_p G R_t^2} \left(u \frac{\delta^2 T^C}{\delta u^2} + \frac{\delta T^C}{\delta u} \right) + F^C(\underline{g}, T^C) \quad (2.39)$$

Subject to initial and boundary conditions:

$$z = 0 \quad 0 \leq u \leq 1 \quad g^i = g_{in}^i \quad i=1 \rightarrow S$$

$$T^C = T_{in}^C$$

$$0 < z \leq L \quad u = 0 \quad \frac{\delta g^i}{\delta u} = 0 \quad i=1 \rightarrow S$$

$$\frac{\delta T^C}{\delta u} = 0$$

$$\begin{aligned}
 0 < z \leq L \quad u = 1 \quad \frac{\delta q^i}{\delta u} \quad i=1 \rightarrow S \\
 \frac{\delta T^C}{\delta u} = - \frac{\alpha_w^C R_1}{2\lambda r^C} (T^C - T_w) \quad (2.40)
 \end{aligned}$$

2.7.3 Finite difference methods for the solution of partial differential equations

In any finite difference method the region of integration is replaced by a grid of points. The partial differential equations, and, where applicable, their boundary conditions, are represented at each of the points by difference equations involving the values of the dependent variables at that point and at some, or all, of its neighbours. This concept is well known and has been successfully applied to catalytic reactor problems (46, 52, 68, 94). Only those features of the method relevant to the present usage will be discussed.

The difference equations may be established in two ways. If the axial derivative is replaced by a forward difference formula and the radial derivatives by central difference formula calculated on the old profile, an explicit difference scheme is obtained. If the axial derivative is replaced by a central difference formula and the radial derivatives by a central difference formula averaged between old and new profiles, an implicit formulation results. The stability requirements of the explicit method are generally more stringent than for the implicit method, whereas the calculation algorithm for the explicit method is usually simpler than for the implicit method. The grid notation used is as shown in Figure (2.4). The dependent variables are known at points with an axial index of n or less. The relationship between the indices and the independent variables is:

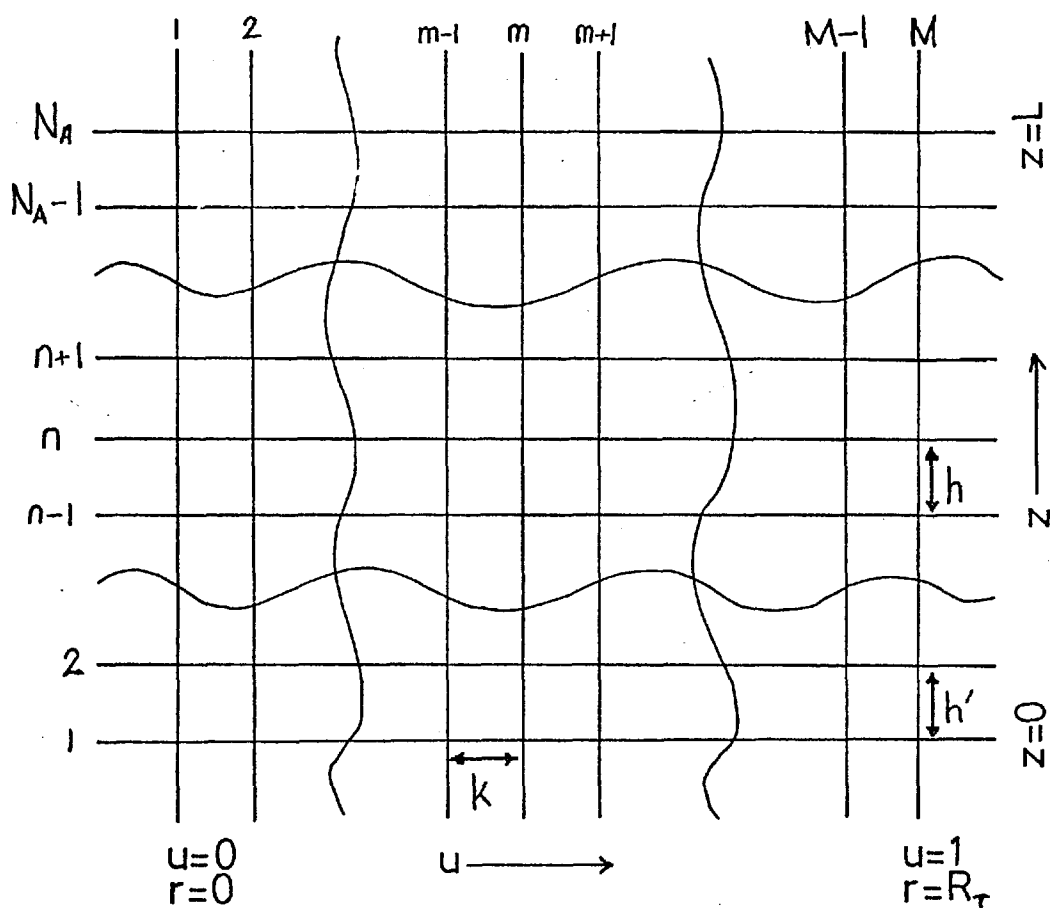
$$\begin{aligned}
 z = 0 \quad , \quad n = 1 \quad ; \quad u = L \quad , \quad n = N_A \\
 u = 0 \quad , \quad m = 1 \quad ; \quad u = 1 \quad , \quad m = M
 \end{aligned}$$

With this notation the derivative substitutions, in terms of a general variable Y , are:

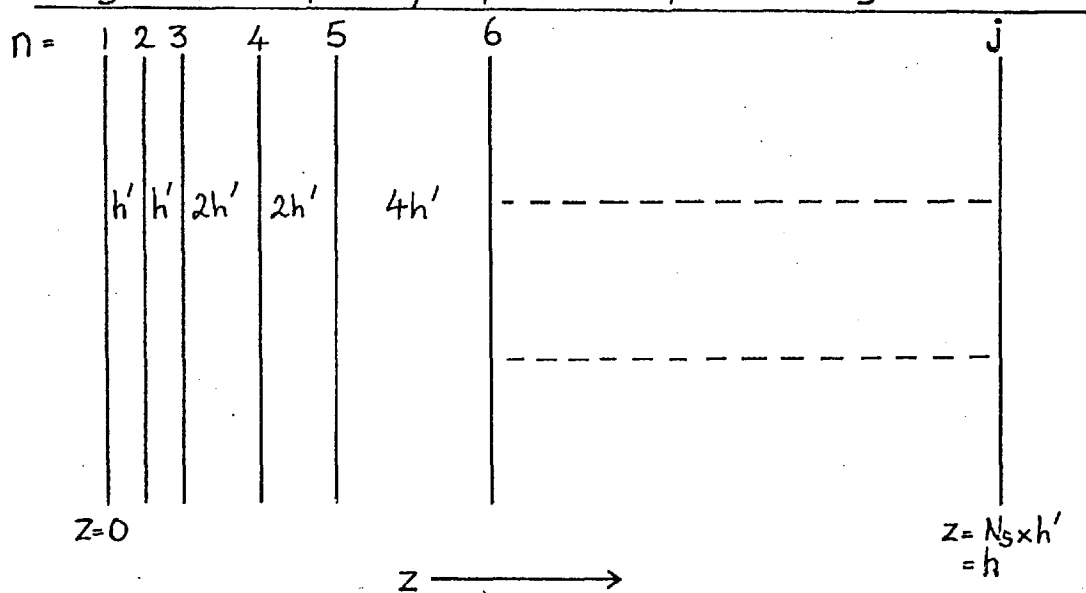
EXPLICIT

$$\frac{\delta Y_{m,n}}{\delta z} = \frac{1}{h} (Y_{m,n+1} - Y_{m,n})$$

Fig(2-4) Finite difference grid notation.



Fig(2-5) Implicit/explicit step doubling scheme.



$$\frac{\delta Y_{m,n}}{\delta u} = \frac{1}{2k} (Y_{m+1,n} - Y_{m-1,n})$$

$$\frac{u \delta^2 Y_{m,n}}{\delta u^2} = \frac{(m-1)}{k} (Y_{m+1,n} - 2Y_{m,n} + Y_{m-1,n}) \quad (2.41)$$

IMPLICIT

$$\frac{\delta Y_{m,n}}{\delta z} = \frac{1}{2h} (Y_{m,n+1} - Y_{m,n-1})$$

$$\frac{\delta Y_{m,n}}{\delta u} = \frac{1}{4k} (Y_{m+1,n+1} + Y_{m+1,n-1} - Y_{m-1,n+1} - Y_{m-1,n-1})$$

$$\frac{\delta^2 Y_{m,n}}{\delta u^2} = \frac{(m-1)}{2k} (Y_{m+1,n+1} - 2Y_{m,n+1} + Y_{m-1,n+1} + Y_{m+1,n-1} - 2Y_{m,n-1} + Y_{m-1,n-1}) \quad (2.42)$$

Substitution of (2.41), into (2.38), (2.39) and (2.40) results in the following set of working equations for the explicit finite difference method (52). The subscripts for F' will be discussed later.

$$Y_{1,n+1} = (1 - \frac{3h'a'}{2k}) Y_{1,n} + \frac{2h'a'}{k} Y_{2,n} - \frac{h'a'}{2k} Y_{3,n} + h'F'_{1,n}$$

$$Y_{m,n+1} = \frac{h'a'}{2k} (2m-3)Y_{m-1,n} + (1 - \frac{2h'a'(m-1)}{k}) Y_{m,n} + \frac{h'a'}{2k} (2m-1)Y_{m+1,n} + h'F'_{m,n}$$

$$1 < m < M$$

$$Y_{M,n+1} = 2h'a'(M-1)^2 Y_{M-1,n} + (1 - 2h'a'(M-1))^2 - \frac{h'Bi'a'}{2} (2M-1) Y_{m,n}$$

$$+ \frac{h'a'Bi}{2} (2M-1)T_w + h'F'_{M,n} \quad (2.43)$$

For a mass balance

$$Y = g^i, \quad i=1 \rightarrow S; \quad a' = \frac{4dp \phi}{(Pe)_{mr} R_t^2}; \quad Bi = 0; \quad F' = F^C(g, T^C)$$

For the energy balance

$$Y = T^C; \quad a' = \frac{4\lambda r^C}{CpGR_t^2}; \quad Bi = \frac{\alpha_w R_t}{\lambda r^C}; \quad F' = F^C(\underline{g}, T^C)$$

When (2.42) is substituted into (2.38), (2.39) and (2.40) the formulae for the implicit finite difference scheme result (52).

$$\begin{aligned} & \left(\frac{3}{4h} + \frac{a'}{k}\right)Y_{1,n+1} - \left(\frac{a'}{k} - \frac{1}{4h}\right)Y_{2,n+1} \\ &= \left(\frac{3}{4h} - \frac{a'}{k}\right)Y_{1n-1} + \left(\frac{1}{4h} + \frac{a'}{k}\right)Y_{2,n-1} + \frac{3}{2}F'_{1,n} + \frac{1}{2}F'_{2,n} \\ & - \frac{a'}{4k}(2m-3)Y_{m-1,n+1} + \left(\frac{1}{2h} + \frac{(m-1)a'}{k}\right)Y_{m,n+1} - \frac{a'}{4k}(2m-1)Y_{m+1,n+1} \\ &= \frac{a'}{4k}(2m-3)Y_{m-1,n-1} + \left(\frac{1}{2h} - \frac{(m-1)a'}{k}\right)Y_{m,n-1} + \frac{a'}{4k}(2m-1)Y_{m+1,n-1} + F'_{m,n} \end{aligned}$$

$$0 < m < M$$

$$\begin{aligned} & - a'2(M-1)^2Y_{m-1,n+1} + \left(\frac{1}{h} + 2(M-1)^2a' + \frac{Bi a'(2M-1)}{2}\right)Y_{M,n+1} \\ &= \left(\frac{1}{h} - 2(M-1)^2a' - \frac{Bi a'(2M-1)}{2}\right)Y_{M,n-1} + 2(M-1)^2a'Y_{m-1,n-1} \\ & + a'Bi(2M-1)T_w + 2F'_{M,n} \end{aligned} \tag{2.44}$$

For a mass balance

$$Y = g^i, \quad i=1 \rightarrow s; \quad a' = \frac{4dp}{(Pe)_{mr}R_t^2}; \quad Bi = 0; \quad F' = F^i(\underline{g}, T^C)$$

For an energy balance

$$Y = T^C; \quad a' = \frac{4\lambda r^C}{CpGR_t^2}; \quad Bi = \frac{\alpha_w R_t}{r^C}; \quad F' = F^C(\underline{g}, T^C)$$

Again, the subscript on F'_n will be discussed later.

The form of the radial profiles indicate the reason for making the substitution (2.37). The radial gradients, for both mass and temperature, change rapidly near to the tube wall and decrease to zero at the tube centre. The accuracy of the difference formulae for the radial derivatives

increases as k decreases, becoming exact as k tends to zero. It would be desirable for the grid spacing with respect to r be small near the tube wall and become large towards the centre of the tube where high accuracy in approximating the radial gradients is less important. Introducing a variable radial steplength into the finite difference scheme results in rather complicated formulations. It is far more straightforward to rewrite the balance equations in terms of the squared radius, u . Equal grid spacing with respect to u results in the desired grid spacing with respect to r .

In the case of implicit finite difference equations the question arises of the proper choice of mesh points where the non-linear source terms in (2.43) and (2.44) should be evaluated. The difference equation may be thought of as an approximation to the corresponding differential equation at a specific point, usually a grid point. From this point of view, the approximation to each term arises naturally from considerations of symmetry or convenience, and just as naturally the error in the approximation can be related to the Taylor expansion of the term in question about the reference point.

In the present formulation the difference equation approximates the corresponding differential equation at the grid point (m,n) . The estimation of all the derivatives are symmetrical about this point and thus the source term is also calculated at this point giving a consistent difference analogue to the differential equation. It is stated by Beek (52) that this formulation is stable in the mathematical sense and is not subject to magnifying fluctuations. This assertion will be tested and discussed in a later section.

Beek also states that a large radiation effect can cause difficulties in this formulation. This is because of the dependence of the radiative conductivity upon temperature, one of the principal dependent variables. These difficulties would appear to be caused by the separation of effective radial conductivity in Beek's formulation into a radiation contribution and an eddy diffusion contribution. The eddy diffusion flux is evaluated at the mean of the $(n+1)^{th}$ and $(n-1)^{th}$ profiles whilst the radiative diffusivity is evaluated at the n^{th} profile. This leads to instability in the solution of the difference equation when the two-terms become comparable. However, in the present formulation, the radiative term occurs on the LHS of the difference equation and, hopefully, will not contribute to instability of this kind. This is particularly important

since at least one of the examples considered in this work has a high radiative contribution. It is not generally possible to predict "a priori" the stability of the scheme. One "a posteriori" check is to repeat the calculations with vastly reduced steplengths and compare results.

A disadvantage of the present implicit/ formulation is that two previous radial profiles are required to calculate a new radial profile. At the beginning of the integration, only one profile, given by the initial conditions, is known. The procedure adopted is to calculate the first new radial profile by an explicit method and then to continue the integration with the implicit method using these two profiles.

The values of h and k , the steplengths in the axial and radial directions respectively are governed solely by the desired accuracy and computation time as the implicit/ method is unconditionally stable. However h' , the axial steplength for the explicit method, has to be chosen with a regard to both accuracy and the stability requirements of the method. The formulation is only stable if, for a particular differential equation (42),

$$h' < \frac{k^2}{2a'} \quad (2.45)$$

Thus (2.45) must be satisfied for all equations in the set. h' will be less than or equal to h in order to satisfy (2.45) and to maintain the desired accuracy. Thus, it is necessary to devise a practical relationship between h' and h and a procedure for changing the steplength after the first explicit calculation. h' is chosen such that (2.45) is satisfied and that the implicit steplength, h , is achieved by successive step doubling. This idea is illustrated in Figure (2.5) and Table (2.4). The step doubling is continued until the integration has proceeded as far as $z=h$. The radial profile is then calculated for $z=2h$, using the known profiles at $z=0$ and $z=h$. The implicit method may then be used row by row with constant steplength until the integration is completed.

Writing the relationship between h' and h as:

$$h' = h/N_s \quad (2.46)$$

and extending (2.45) to:

Table (2.4)

Basic step-doubling and solution procedure for the case where $N_s=10$

Row No	n	Method	Known Rows used n	Row used to Avge. Rad. Grads. n	Row used to evaluate the non linear term n	Step length
1	2	Explicit	1	1	1	h'
2	3	Implicit	1,2	1,3	1	h'
3	4	Implicit	1,3	1,4	3	$2h'$
4	5	Implicit	3,4	3,5	4	$2h'$
5	6	Implicit	3,5	3,6	5	$4h'$
6	7	Implicit	1,6	1,7	6	$10h'=h$

$$\frac{h'}{k^2} < \frac{1}{2a'_{\max}} \quad (2.47)$$

To ensure that all integrations are stable:

$$N_s > \frac{2a'_{\max}h}{k^2} \quad (2.48)$$

However, in order to allow for successive step doubling, N_s may only assume specific values. The admissible values of N_s depend on whether $z=h$ is desired to coincide with an odd or even numbered row (see Figure (2.5)). The choice is arbitrary and, in the present work, even rows have been chosen. The admissible values for N_s are thus:

$$N_s = 1, 4, 10, 22, 46, 94, 190 \dots$$

The j^{th} term of this series is

$$N_{sj} = 3 \times 2^{j-1} - 2; \quad j=1,2,3 \dots$$

N_s is the smallest integer to satisfy (2.45) and so

$$j > 1.443 \log_e \left[\frac{2a'_{\max}h}{3k^2} + 0.67 \right] + 1 \quad (2.49)$$

Thus the required value of j is the smallest integer to satisfy (2.49).

The implicit finite difference formulation yields a set of M linear simultaneous equations at each axial step for each of the partial differential equations. These linear equations form $S+1$ tridiagonal sets which allows them to be solved by a highly efficient algorithm based on Gaussian elimination (95). This is usually referred to, in the American Literature, as the Thomas algorithm (140).

For the dependent variable, Y , the equation (2.44) may be written:

$$-\alpha_m Y_{m-1,n+1} + \beta_m Y_{m,n+1} - \gamma_m Y_{m+1,n+1} = dm \quad (2.50)$$

which, in matrix form, may be written

$$\begin{bmatrix}
 \beta_1 & -\gamma_1 & & & \\
 -\alpha_2 & \beta_2 & -\gamma_2 & & \\
 & -\alpha_3 & \beta_3 & -\gamma_3 & \\
 & & \ddots & \ddots & \ddots \\
 & & & -\alpha_{m-1} & \beta_{m-1} & -\gamma_{m-1} \\
 & & & & -\alpha_m & \beta_m
 \end{bmatrix}
 \begin{bmatrix}
 Y_{1,n+1} \\
 Y_{2,n+1} \\
 Y_{3,n+1} \\
 \vdots \\
 Y_{m-1,n+1} \\
 Y_{m,n+1}
 \end{bmatrix}
 =
 \begin{bmatrix}
 d_1 + \alpha_1 Y_0 \\
 d_2 \\
 d_3 \\
 \vdots \\
 d_{m-1} \\
 d_m + \gamma_m Y_{m+1}
 \end{bmatrix}$$

This system may be solved by the Thomas algorithm provided that:

$$\alpha_m > 0; \quad \beta_m > 0; \quad \gamma_m > 0 \quad (2.51)$$

$$\beta_m \geq (\alpha_m + \gamma_m)$$

Consider the following two-parameter difference relation between Y_{m-1} and Y_m .

$$Y_{m-1} = \omega_{m-1} Y_m + g_{m-1} \quad (2.52)$$

Similarly:

$$Y_m = \omega_m Y_{m+1} + g_m \quad (2.53)$$

Substitution of (2.53) and (2.52) into (2.50) leads to:

$$Y_m = \frac{\gamma_m \cdot Y_{m+1}}{\beta_m - \alpha_m \omega_{m-1}} + \frac{d_m + \alpha_m g_{m-1}}{\beta_m - \alpha_m \omega_{m-1}} \quad (2.54)$$

Comparing (2.53) and (2.54)

$$w_m = \frac{\gamma_m}{\beta_m - \alpha_m \omega_{m-1}}; \quad g_m = \frac{d_m + \alpha_m g_{m-1}}{\beta_m - \alpha_m \omega_{m-1}} \quad (2.55)$$

When $m=1$ it is required that

$$Y_0 = \omega_0 Y_1 + g_0$$

for all Y_1 . Thus:

$$\omega_0 = 0; \quad g_0 = 0 \quad (2.56)$$

and so, from (2.55) and (2.56)

$$\omega_1 = \gamma_1/\beta_1; \quad g_1 = d_1/\beta_1 \quad (2.57)$$

Starting from (2.57) and using (2.55) all the ω_m and g_m may be calculated successively from $m=1$ to $m=M$. When this has been performed for all m , Y_m , for all m , may be calculated by back substitution. In the present case Y_{m+1} is zero and so:

$$Y_M = g_M \quad (2.58)$$

$$\text{and } Y_{m-1} = \omega_{m-1} Y_m + g_{m-1} \quad m = M \rightarrow 1$$

In this way the entire radial profile may be generated. It is necessary to limit ω_m in order to prevent the build up of errors (95). It is necessary that:

$$|\omega_m| \leq 1 \quad (2.59)$$

If (2.51) is satisfied then (2.59) is also satisfied.

2.7.4 The Two-Phase Model

The additional ordinary differential equation required by this model, (2.4), may be represented by a finite difference relationship after making the substitution (2.37) to obtain:

$$a_v h_v (T^S - T^f) = \frac{4\lambda r^S}{R_t^2} \left(u \frac{\delta^2 T^S}{\delta u^2} + \frac{\delta T^S}{\delta u} \right) + F^S(g, T^S) \quad (2.60)$$

Using central difference formulae for the radial derivatives:

$$\begin{aligned} & \left(h_v a_v + \frac{a_s}{k} \right) T_{1,n+1}^S - \frac{a_s}{k} T_{2,n+1}^S \\ &= h_v a_v T_{1,n+1}^f + \frac{3}{4} F_{1,n+1}' + \frac{1}{4} F_{2,n+1}' \\ & - \frac{a_s}{k} \left(m - \frac{3}{2} \right) T_{m-1,n+1}^S + \left(a_v h_v + \frac{2a_s}{k} \right) (m-1) T_{m,n+1}^S - \frac{a_s}{k} \left(m - \frac{1}{2} \right) T_{m+1,n+1}^S \\ &= a_v h_v T_{m,n+1}^f + F_{m,n+1}' \quad 1 < n < M \end{aligned}$$

$$\begin{aligned}
& - \frac{2a_s}{k^2} T_{M-1,n+1}^s + \left(h_v a_v + \frac{2a_s}{k^2} + \frac{Bi a_s}{k} + \frac{Bi a_s}{2k^2} \right) T_{M,n+1}^s \\
& = a_v h_v T_{M,n+1}^f + \left(\frac{a_s Bi}{k} + \frac{a_s Bi}{2k^2} \right) T_w + F'_{M,n+1}
\end{aligned} \tag{2.61}$$

$$\text{where } Bi = \frac{\lambda r^s R_t}{r^s} ; \quad F' = F^s(\underline{g}, T^s) ; \quad a_s = \frac{4\lambda r^s}{R_t^2}$$

The solution procedure for the fluid-temperature and component mass-fraction in the two-phase model is exactly the same as in the one-phase, two-dimensional model, the working equations being (2.43) and (2.44). However, for both equations, the general variables are now defined as:

For a mass balance:

$$Y = g^i, \quad i = 1 \rightarrow S; \quad a' = \frac{4dp\phi}{(Pe)_{mr} R_t^2}; \quad Bi = 0; \quad F' = F^i(\underline{g}, T^f, T^s)$$

For the fluid-phase energy balance:

$$Y = T^f; \quad a' = \frac{4\lambda r^f}{GC_p R_t^2}; \quad Bi = \frac{\alpha_w^f R_t}{\lambda r^f}; \quad F' = F^f(\underline{g}, T^f) + \frac{h_v a_v}{GC_p} (T^s - T^f)$$

When the profiles for fluid temperature and component mass-fraction have been computed at the $n+1^{th}$ axial step, the solid temperature profile may be computed. $F^s(\underline{g}, T^s)$ is unknown in the right-hand side of (2.60) and so an iterative solution is necessary. The initial guessed profile may be either the fluid temperature profile at the $n+1^{th}$ level or the solid temperature profile at the n^{th} level. In both cases the convergence is rapid taking, usually, three or four iterations. Equation (2.61) forms a tri-diagonal system and so it may also be rapidly solved by the Thomas algorithm.

Chapter 3

APPLICATION OF REACTOR MODELS TO THE THERMAL DECOMPOSITION OF NITROUS OXIDE

- 3.1 Introduction
- 3.2 Kinetics and Thermochemistry
- 3.3. Choice of Operating Conditions
- 3.4 Computational Aspects
 - 3.4.1 Source terms in tubular reactor models
 - 3.4.2 Temperature dependence of fluid properties
 - 3.4.3 Temperature dependence of heat transfer parameters
 - 3.4.4 Computer Programs
- 3.5 Stability and Accuracy of Model Integration
- 3.6 Calculations on the Three Fixed Bed Reactor Models
- 3.7 Sensitivity of Reactor Models to Heat Transfer Parameters
- 3.8 Conclusions

3.1 INTRODUCTION

The first system to be studied in the context of heterogeneous-homogeneous reactions was the thermal decomposition of nitrous oxide. This system is suitable for consideration as a typical concurrent reaction system exhibiting both heterogeneous and homogeneous effects.

The reactions, catalysed by gold surfaces, have been the subject of a recent kinetic study by Halladay and Mrazek (8) who have considered simultaneous heterogeneous and homogeneous reaction paths. Their experiments were performed on a gold strip, and the homogeneous contribution was quantified by varying the surface-to-volume ratio. In the present study the reactions are assumed to proceed in the presence of gold coated particles. Thus the system is not complicated by intra-particle diffusional effects.

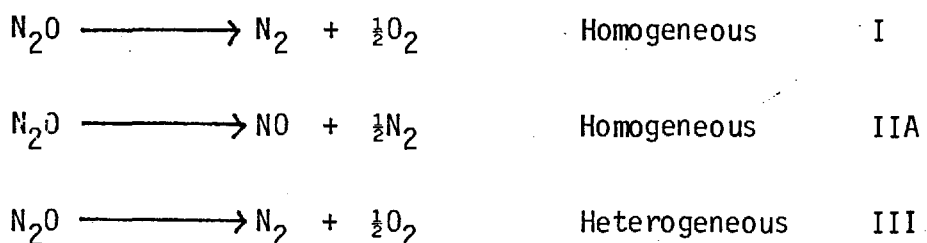
The reasons for considering the thermal decomposition of nitrous oxide are summarised by:

- (i) It is an example of a concurrent heterogeneous-homogeneous reaction scheme.
- (ii) The system has received a kinetic study from the standpoint of heterogeneous-homogeneous effects and kinetic data is available.
- (iii) The effect of heat and mass transfer in a tubular reactor may be studied without the complication of intra-pellet diffusional effects.
- (iv) The activation energy for the homogeneous reaction is approximately twice the value for the heterogeneous reaction. Temperature differences in the bed will thus affect the heterogeneous and homogeneous reactions to different extents.

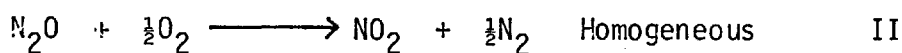
The system was investigated with three aims. Firstly the system was used to investigate the stability and accuracy with respect to radial and axial steplength of the mathematical models for a tubular reactor described in Chapter 2. Secondly, the predictions of these three models were compared for a range of heat transfer conditions and the applicability of the models was investigated. Finally, the sensitivity of the two-phase, two-dimensional model was investigated with respect to the two-phase heat transfer parameters.

3.2 KINETICS AND THERMOCHEMISTRY,

The reactions considered are:



It has been reported (96) that nitric oxide is instantaneously oxidised at room temperature to nitrogen dioxide. The reaction has a zero activation energy (97) and so reaction IIA is replaced by:



For this simplification to be valid there must be sufficient oxygen present in the system to support reaction II, either initially or subsequently produced by reactions I and III.

The rates of the three reactions are given by (8):

$$\begin{aligned}
 r'_I &= k'_I (c^N)^2 / (1 + k'_{Ia} c^N) \\
 r'_{II} &= k'_{II} (c^N)^2 \\
 r'_{III} &= k'_{III} \frac{A_p}{V_p} c^N
 \end{aligned} \tag{3.1}$$

The heterogeneous rate is expressed as a rate of change per unit volume of the solid pellets for direct application to the reactor models.

In a fixed bed of solid spheres the total rate of disappearance of nitrous oxide is given by:

$$\begin{aligned}
 \text{rate} &= \phi k'_I \rho^2 (g^N)^2 / (1 + k'_{Ia} \rho g^N) \\
 &+ \phi k'_{II} \rho^2 (g^N)^2 \\
 &+ \frac{6Rg(1-\phi)}{dp} k'_{III} g^N
 \end{aligned} \tag{3.2}$$

The rate is expressed as rate of disappearance per unit volume of reactor bed. The rate constants are in the $\text{kg-m}^3\text{-sec}$ system of units and g^N is the mass fraction of nitrous oxide in the fluid phase.

R_g is a pellet roughness factor and is defined as:

$$R_g = 1000dp^*$$

The factor was introduced into the analysis to ensure that the relative amounts of heterogeneous and homogeneous reaction at the reactor entrance were not influenced by variations in the pellet size.

The rate constants are given in Table (3.1) and have been converted to the $\text{kg-m}^3\text{-sec}$ system of units from the published values of Halladay and Mrazek.

Similarly, the rate of appearance of nitrogen dioxide is given by:

$$\text{rate} = 1.046\phi\rho^2k'_{II}(g^N)^2 \quad (3.3)$$

The factor 1.046 is the ratio of the molecular weights of N_2O and NO_2 and is necessary because (3.2) and (3.3) are written in mass units.

The heats of reaction for the three reactions were calculated from standard heats of formation and heat capacities (102) and the values obtained at 1000K were:

$$(-\Delta H_I) = 1.98 \times 10^6 \text{ Jkg}^{-1}(\text{N}_2\text{O})$$

$$(-\Delta H_{II}) = 1.05 \times 10^6 \text{ Jkg}^{-1}(\text{N}_2\text{O})$$

$$(-\Delta H_{III}) = 1.98 \times 10^6 \text{ Jkg}^{-1}(\text{N}_2\text{O})$$

3.3 CHOICE OF OPERATING CONDITIONS

The models were integrated for a range of different operating conditions. The choice of operating conditions was such that each of the integrations represented the performance of a tubular reactor under different conditions of heat transfer.

The operating variables that were used to determine the heat transfer characteristics were:

- * because the value of R_g for the smallest pellet considered is unity, which corresponds to a smooth pellet.

Table (3.1)

Rate Constants for Thermal decomposition of N₂O

Rate Constant	Log ₁₀ A	E _A Kcal /gmole
k _I	16.48	81.8
k _{Ia}	6.99	28.4
k _{II}	13.88	72.4
k _{III}	3.55	34.6

$$k' = A \exp \left(\frac{-E_A}{RT} \right)$$

G	mass flow rate per unit area	kg m ⁻² sec ⁻¹
dp	pellet diameter	m
R _t	Reactor Tube radius	K

The temperature was not considered as a primary operating variable in this context although it influences heat transfer through radiative contributions. An allowance for the variation of radiative contributions with temperature has been made. This is described in Section 3.4.

The absolute values of the effective conductivity of the bed and of the wall heat transfer coefficients are governed chiefly by G and dp. Variation of R_t alters the relative importance of bed heat transfer resistance and wall heat transfer resistance.

The heat transfer regime was characterised by three dimensionless groups, namely:

$$\frac{\alpha_w^c R_t}{\lambda r^c}, \quad \frac{\lambda r^f}{\lambda r^s} \quad \text{and} \quad \frac{\alpha_w^f}{\alpha_w^s}.$$

The first group, the continuous phase Biot number, is an indication of the relative importance of the effective heat transfer at the wall and the effective conductivity in the bed. The last two groups represent the relative quantities of heat passed by each phase in the bed and at the wall respectively. For these groups to be strictly comparable it is necessary that the radial gradients in each phase be equal or that the groups be modified to, for example:

$$\frac{\lambda r^f \left(\frac{dT^f}{dr} \right)}{\lambda r^s \left(\frac{dT^s}{dr} \right)}.$$

It has been shown in Section 2.6 that:

$$\frac{\delta T^f}{\delta r} = \frac{\delta T^s}{\delta r}$$

is a reasonable assumption to be made throughout most of the bed and so the groups are satisfactory as first defined.

It would be desirable to be able to define a group which relates h_{va} and λr^f , λr^s , or λr^c . For such a group to be dimensionless, a squared length variable must be introduced. For example, one dimensionless group

might be:

$$\frac{h_v a_v dp^2}{\lambda r^C}$$

However, this group, and other similar groups, have little meaning without reference to fluid-pellet and bed radial temperature gradients which are not, generally, available "a priori".

The heat transfer regimes may be envisaged to encompass the following situations:

- (i) high and low values for bed conductivity
- (ii) high and low values for wall heat transfer coefficients
- (iii) high and low values for fluid-pellet heat transfer coefficients.

Ideally, it would be desirable to consider all possible combinations of these situations leading to $2^3=8$ distinct cases. However, some of the situations are mutually exclusive. For example, it is very difficult to choose a set of conditions such that the fluid-pellet heat transfer coefficient is high but the wall heat transfer coefficients are low.

A 'parameter sweep' was performed over realistic values of the variables G , dp and R_t . Combinations of these variables were chosen to give a reasonable range for the dimensionless groups previously mentioned. Due regard was paid to the requirement that the ratio of tube diameter to pellet diameter should be at least 10 for validity of the assumptions leading to the pseudo-continuous phase model. Seven sets of conditions were chosen and are shown in Table (3.2). The range of values covered for the three dimensionless groups is shown in Figure (3.1) where it may be seen that both the $Bi^C - \lambda_r^f/\lambda_r^S$ space and the $Bi^C - \alpha_w^f/\alpha_w^S$ space are well covered. It is also evident from Figure (3.1) that there is a high positive correlation between λ_r^f/λ_r^S and α_w^f/α_w^S .

3.4 COMPUTATIONAL ASPECTS OF THE THERMAL DECOMPOSITION OF N_2O

3.4.1 Source terms in the tubular reactor models

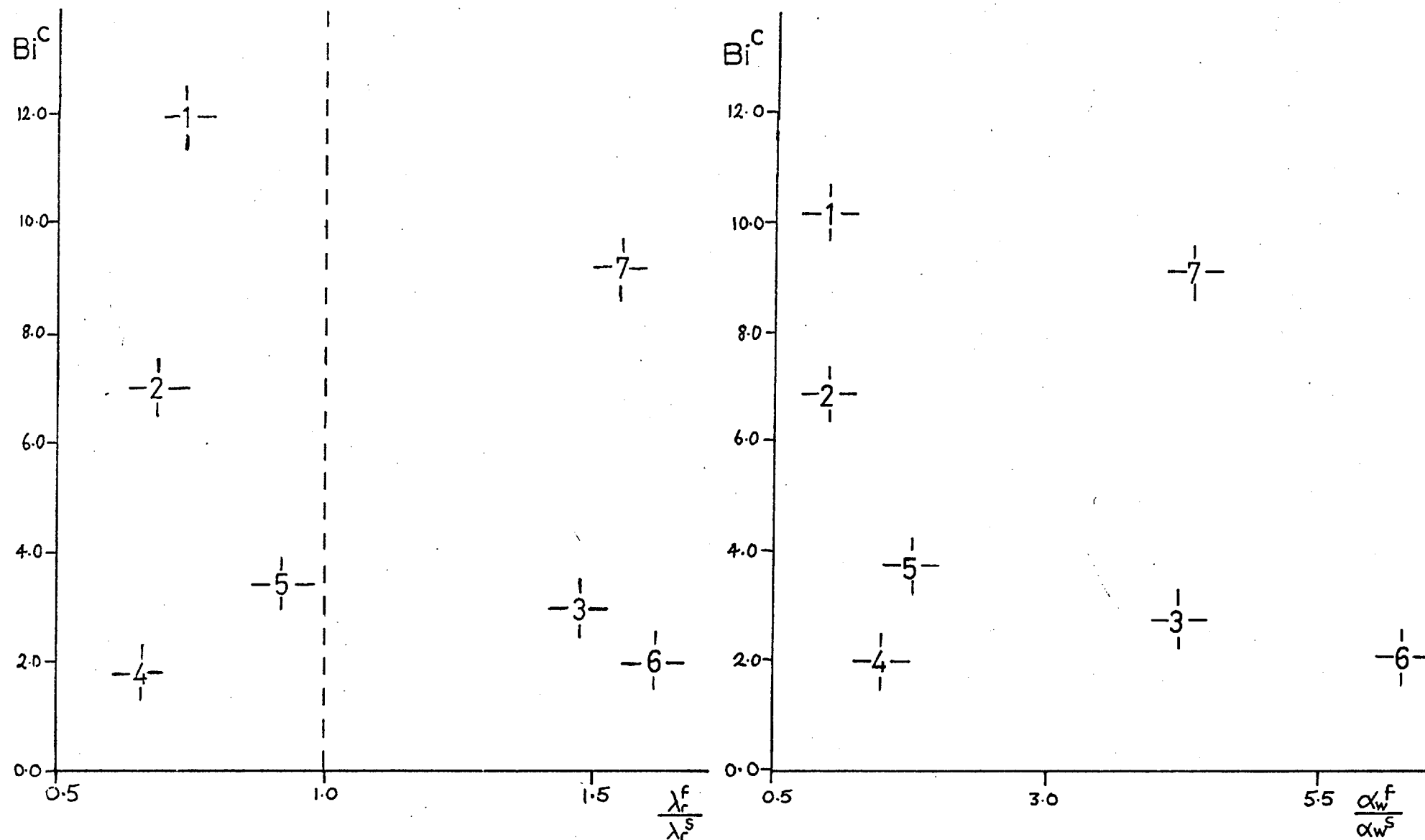
In the integration of this system three dependent variables were considered viz. temperature, mass fraction of nitrous oxide and mass fraction of nitrogen dioxide. By integrating the equations for nitrogen dioxide some indication is available of the role of homogeneous steps in the overall decomposition.

Table (3.2)

Operating Conditions and Heat Transfer Parameters

*Heat Transfer parameters are evaluated at 1075K

No.	G $\text{Kg m}^{-2} \text{sec}^{-1}$	dp m	dt m	Re_p	λr^f	λr^s	α_w^f	α_w^s	λr^c	α_w^c	h_{vav} $\times 10^{-6}$	U	$\frac{\lambda r^f}{\lambda r^s}$	Bi^c	$\frac{\alpha_w^f}{\alpha_w^s}$
1	1.8	0.001	0.03	42.1	0.27	0.35	210.1	210.1	0.62	420.3	1.61	119	0.77	10.2	1.00
2	0.9	0.002	0.05	42.1	0.31	0.44	105.0	105.0	0.75	210.1	0.80	76.6	0.70	77.0	1.00
3	1.7	0.004	0.05	158.9	0.92	0.64	152.3	35.1	1.56	187.4	0.87	107	1.44	3.0	4.34
4	0.5	0.006	0.06	70.1	0.56	0.84	52.7	34.1	1.40	86.8	0.36	59.2	0.67	1.9	1.55
5	1.1	0.003	0.04	77.1	0.50	0.54	113.9	67.0	1.04	180.9	0.76	96.8	0.93	3.5	1.70
6	2.1	0.004	0.04	196.3	1.04	0.64	180.3	26.5	1.68	206.8	0.98	128	1.63	2.5	6.80
7	1.7	0.004	1.155	158.9	1.00	0.64	152.3	35.1	1.64	187.4	0.87	58.3	1.56	8.9	4.34



Fig(3-1) - Heat Transfer Groups.

In the two-phase, two-dimensional model for the fixed-bed reactor, the following source terms must be defined:

- i) Two expressions for F^i , one for N_2O and one for NO_2 .
- ii) An expression for F^f , the rate of heat release in the fluid-phase heat balance.
- iii) An expression for F^s , the rate of heat release in the solid-phase heat balance.

The appropriate expressions are:

$$\begin{aligned}
 F^N &= -\frac{\phi}{G} (k_I' \rho^2 (g^N)^2 / (1+k_{Ia}' \rho g^N) + k_{II}' \rho^2 (g^N)^2) \\
 &\quad - \frac{(1-\phi)6Rg}{Gdp} k_{III}' \rho g^N \\
 F^{NO_2} &= \frac{\phi}{G} \cdot k_{II}' \rho^2 (g^N)^2 \\
 F^f &= \frac{\phi \rho^2}{GCp} (k_I' (-\Delta H)_I (g^N)^2 / (1+k_{Ia}' \rho g^N) + k_{II}' (-\Delta H)_{II} (g^N)^2) \\
 F^s &= \frac{(1-\phi)6Rg}{dp} \rho (-\Delta H)_{III} k_{III}' g^N
 \end{aligned} \tag{3.4}$$

In these expressions k_I , k_{Ia} and k_{II} are evaluated at temperature T^f and k_{III} is evaluated at temperature T^s .

The expression for F^N includes the heterogeneous contribution to the disappearance of nitrous oxide. The use of g^N in this expression implies that there is negligible mass transfer resistance between the bulk phase and the pellet surface.

A mass balance at the pellet surface yields:

$$k_g (g^{N,F} - g^{N,s}) = k_{III}' g^{N,s}$$

where k_{III}' , the rate constant per unit surface area has units ms^{-1} . Film mass transfer resistance will be most evident under conditions of low flow rate and large pellet diameter. In this respect the worst conditions encountered in the present study were:

$$G = 0.5 \text{ kg m}^{-2} \text{ s}^{-1} \quad dp = 0.006 \text{ m}$$

The coefficient, k_g , may be estimated from a suitable j -factor correlation. Using the following typical data at 1100K.

$$\mu = 4 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1} \quad D' = 7.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$$

$$\rho = 0.3 \text{ kg m}^{-3}$$

then $Re_p \sim 75$ and $Sc \sim 1.5$

Using the j-factor correlation of Aris (69) where:

$$j_D = \frac{Sh}{Sc \cdot Re_p} \quad \text{and} \quad Sh = \frac{k_g dp}{D'}$$

the following values were calculated.

$$j_D = 0.12 \quad Sh = 10.3 \quad k_g = 0.13$$

$$\text{and so } \frac{g^{N,f} - g^{N,s}}{g^{N,s}} = 0.002$$

$$\text{or } \frac{g^{N,f}}{g^{N,s}} = 1.002$$

Therefore, to all practical purposes, $g^{N,s}$ is equal to $g^{N,f}$ and (3.4) is validated.

In the one-phase, two-dimensional model F^f and F^s are replaced by:

$$\begin{aligned} F^C = & \frac{\phi \rho^2 (g^N)^2}{GCp} (k'_I (-\Delta H)_I / (1 - k'_{Ia} \rho g^N) + k'_{II} (-\Delta H)_{II}) \\ & + \frac{(1-\phi) 6Rg \rho g^N}{GCpdp} k'_{III} (-\Delta H)_{III} \end{aligned} \quad (3.5)$$

F^{N_2O} and F^{NO_2} remain as before with the exception that all rate constants are now evaluated at temperature T^C .

For the one-phase, one-dimensional model the source terms required are F^N , F^{NO_2} and F^C . In this case F^C is defined by:

$$\begin{aligned} F^C = & \frac{\phi \rho^2 (g^N)^2}{GCp} (k'_I (-\Delta H)_I / (1 + k'_{Ia} \rho g^N) + k'_{II} (-\Delta H)_{II}) \\ & + \frac{(1-\phi) \rho g^N 6Rg}{GCpdp} k'_{III} (-\Delta H)_{III} - \frac{2U}{R_t} (T^C - T_w) \end{aligned} \quad (3.6)$$

All rate constants are, again, evaluated at temperature T^C .

Thus, Equations (3.4), (3.5) and (3.6) are substituted into the

relevant conservation equations (Chapter 2) to yield the mass and energy balances for the two-phase, two-dimensional; one-phase, two-dimensional and one-dimensional tubular reactor models.

3.4.2 Temperature dependence of fluid properties

Most of the fluid properties are, strictly speaking, temperature dependent. The nature of the calculations reported in this chapter is illustrative rather than predictive and it is not essential to use precise values for the fluid properties.

The fluid heat capacity, fluid molecular conductivity and fluid density were assigned values based, loosely, on data for air. The values used were:

$$k_f = 0.04 \text{ W m}^{-1} \text{ K}^{-1} \quad C_p = 10^3 \text{ J Kg}^{-1} \text{ K}^{-1} \quad \rho_{273} = 1.28 \text{ Kg m}^{-3}$$

k_f and C_p were assumed to remain constant with temperature and ρ , the fluid density was assumed to vary linearly with the reciprocal temperature, following the perfect gas laws.

The fluid viscosity was calculated from the linear relationship

$$\mu = 1.05 \times 10^{-5} + 3.08 \times 10^{-8} T$$

This expression, is, again based on data for air. During the calculations the viscosity is used to evaluate Re_p , the particle Reynolds number which is then used to determine the heat transfer parameters. As these parameters are assumed not to vary within the reactor except as described in the following section, the value of viscosity at the reactor inlet was used.

3.4.3 Temperature dependence of heat transfer parameters

Considering the heat transfer parameters to consist of radiative and non-radiative contributions, the non-radiative contributions have been calculated at reactor inlet conditions and have been assumed to be insensitive to temperature. However, the radiative contributions display a third-order temperature dependence which, at the high temperatures encountered during N_2O decomposition, would lead to significant error if neglected. For example, if radiation were to account for 3% of radial heat transfer and there was a 300K temperature rise within the reactor bed to 1400K, then the radial thermal conductivity would be 32% in error at 1400K if the radiative contributions were calculated at 1100K.

Consequently the radiative heat transfer contribution has been updated after each axial step.

3.4.4 Computer Programs

The principal subroutines required for the integration of the models were:

Two-phase, two-dimensional model - SUBROUTINE PHASE2

One-phase, two-dimensional model - SUBROUTINE CONTI2

One-phase, one-dimensional model - SUBROUTINE RKINT

Explanatory details relating to these subroutines are given in Appendix A1.

The following FORTRAN IV subroutines were written in order to obtain the results for this chapter.

SUBROUTINE CMSYS1: This was the controlling subroutine for the model comparison calculations. Its function was to:

- i) Read all input data
- ii) Calculate heat transfer data and set model parameters
- iii) Integrate each of the models for the tubular reactor
- iv) Extract values for the maximum solid and fluid temperatures, the fluid exit temperature and the conversion and selectivity of the reactions and print them.
- v) Assemble the stored profiles for temperature, conversion and selectivity and present them graphically

SUBROUTINE PVSYS1: This was the controlling subroutine for the heat transfer parameter variation calculations. The subroutine was able to perform calculations according to either the one-phase or two-phase models and, having calculated the true heat transfer data once, was able to re-integrate either of the models as many times as was desired for perturbed values of this data.

SUBROUTINE RSSYS1: This calculated source data relating to the solid-phase as required in the two-phase, two-dimensional model. Called by PHASE2.

SUBROUTINE RFSYS1: This calculated source data relating to the fluid-phase as required in the two-phase, two-dimensional model. Called by PHASE2.

SUBROUTINE RCSYS1: This calculated source data relating to both solid- and fluid-phases as required in the one-phase, two-dimensional model. Called by CONTI2.

SUBROUTINE RISYS1: This calculated source and heat removal data relating to the pseudo-continuous phase as required by the one-phase, one-dimensional model.

3.5 STABILITY AND ACCURACY OF MODEL INTEGRATION

The degree of comparison between the performance of a tubular fixed-bed reactor and the predictions of a mathematical model intended to represent the reactor depends on three factors. It will depend on whether the physical model correctly represents the phenomena occurring in the reactor, on the ability of the mathematical model to represent the physical model and, when the mathematical model is to be integrated by finite difference techniques, on the comparison between the solution of the difference equations and the 'correct' solution of the differential equations that they represent. It is this last factor that is to be investigated in this section.

The difference equations representing the two-dimensional models for tubular packed-bed reactors (Chapter 2) include as parameters h , the axial steplength and k , the radial steplength. It is axiomatic of finite difference methods that the error between the difference solution and the 'true' solution tends to zero as h and k tend to zero. In other words, as h and k tend to zero, the difference equations become the exact replica of the original differential equations.

It was decided to study the effect of h and k on the solution of the difference equations for a 'severe' case, i.e. in a reactor exhibiting large thermal gradients. Therefore the reactor modelled in order to assess the accuracy of difference equations had dimensions and was subject to operating conditions as shown for case 4 in Table (3.2). It will be noticed that this set of conditions leads to the lowest value for the overall heat transfer coefficient and that, for similar conversions, other sets of conditions would be expected to yield thermally less severe situations. In that sense the 'worst case' has been investigated. The inlet temperature used was 1100K and nitrous oxide had an inlet mass fraction of 0.667. The steplengths h and k have been characterised by M and N_A which are the number of radial and axial steps respectively. The model predictions at a reactor length of 5cms (0.05m) are shown in Table (3.3). A number of criteria could be used to assess the model predictions. Five reactor characteristics were chosen for comparison. They were:

- (i) Maximum Solids Temperature Rise (MSTR)
- (ii) Corresponding Maximum Fluid Temperature Rise (MFTR)
- (iii) Fluid Exit Temperature Rise (FETR)
- (iv) Conversion of N_2O (C)

Table (3.3)

Variation of model predictions with axial and radial steplength

$$T_{in}^f = T_w = 1100K; \quad g_{in}^N = 0.667; \quad g_{in}^{NO_2} = 0; \quad dp = 0.006; \quad R_t = 0.03m; \quad G = 0.5$$

Reactor length = 0.05m

M radial steps	axial steps N_A	TWO-PHASE MODEL					ONE -PHASE MODEL			
		MSTR	MFTR	FETR	C%	S%	MSTR	FETR	C%	S%
5	39	72.48	69.45	57.75	5.30	3.58	67.74	56.10	5.13	3.63
5	289	72.46	69.44	57.75	5.30	3.59	67.75	56.11	5.13	3.63
11	19	73.03	69.95	57.98	5.31	3.59	67.69	56.13	5.13	3.63
11	109	73.06	69.98	58.02	5.31	3.59	67.77	56.17	5.13	3.63
15	19	73.10	70.02	58.01	5.31	3.59	67.70	56.14	5.13	3.63
15	29	73.13	70.04	58.04	5.31	3.59	67.74	56.16	5.13	3.63
15	109	73.14	70.05	58.05	5.31	3.59	67.77	56.18	5.13	3.63
21	139	73.19	70.09	58.07	5.31	3.59	67.78	56.18	5.13	3.63
31	39	73.21	70.12	58.07	5.31	3.59	67.76	56.17	5.13	3.63
31	89	73.22	70.12	58.08	5.31	3.59	67.78	56.18	5.13	3.63
5	1	70.43	67.43	56.3	5.19	3.42	65.35	54.89	5.05	3.50
5	4	71.50	68.49	57.03	5.24	3.50	66.14	55.29	5.08	3.55
5	6	72.06	69.03	57.41	5.27	3.55	67.02	55.73	5.11	3.59
5	9	72.23	69.21	57.54	5.27	3.56	67.42	55.93	5.12	3.61
5	11	72.34	69.30	57.61	5.28	3.57	67.53	55.99	5.12	3.62
5	14	72.42	69.39	57.69	5.29	3.58	67.61	56.03	5.13	3.62
15	1	71.62	68.55	57.02	5.23	3.47	65.76	55.18	5.07	3.52
15	4	72.08	69.01	57.29	5.25	3.50	66.13	55.38	5.08	3.55
15	6	72.66	69.57	57.69	5.28	3.55	67.02	55.80	5.11	3.59
15	9	72.94	69.85	57.89	5.23	3.57	67.44	56.00	5.12	3.61
15	11	73.01	69.93	57.94	5.30	3.58	67.55	56.06	5.13	3.62
15	14	73.06	69.98	57.98	5.30	3.58	67.63	56.10	5.13	3.63

(v) Selectivity to NO_2 (S)

The conversion of a reactant is defined by:

$$C\% = \frac{\text{amount of reactant reacted}}{\text{amount of reactant originally present}} \times 100\%$$

The selectivity to a particular product is defined by:

$$S\% = \frac{\text{amount of product formed}}{\text{amount of reactant reacted}} \times 100\%$$

FETR, C and S are all flow averaged properties whereas MFTR and MSTR invariably refer to the centreline. For the one-phase model MFTR and MSTR will, of course, be identical and, in the two-phase model, the difference between these values is a measure of the fluid-solid temperature differences existing in the bed.

Table (3.3) shows the results of integrations with M ranging between 5 and 31 and N_A ranging between 1 and 289. It is evident that both models are converging to 'true' solutions as M and N_A become large. Also the two models are converging to different solutions. This implies that any differences in predictions given by the one-phase and two-phase models are due to inherent differences in the differential equations describing the models rather than to differing degrees of accuracy in the solution of the difference equations resulting from the use of finite values of M and N_A .

It is of interest to consider the relative sensitivity of the models to M and N_A . Considering the two-phase model predictions of MSTR for $N_A=39$ and M=5 and 31, a six-fold increase in M has resulted in a 1.01% improvement in the prediction of MSTR. A similar calculation for M=15 and $N_A=6$ and 29 shows that a six-fold increase in N results in a 0.65% improvement in the prediction of MSTR. In each case the upper value of the varying parameter results in a prediction within 0.01 of the converged value. It would thus appear that the two-phase model shows similar sensitivity to M and N_A . Comparative values for the one-phase model are 0.03% and 1.07% respectively. Thus the, one-phase model shows increased, but similar, dependence upon N_A but is very much less dependent upon M. Similar conclusions result from calculations between other pairs of predictions.

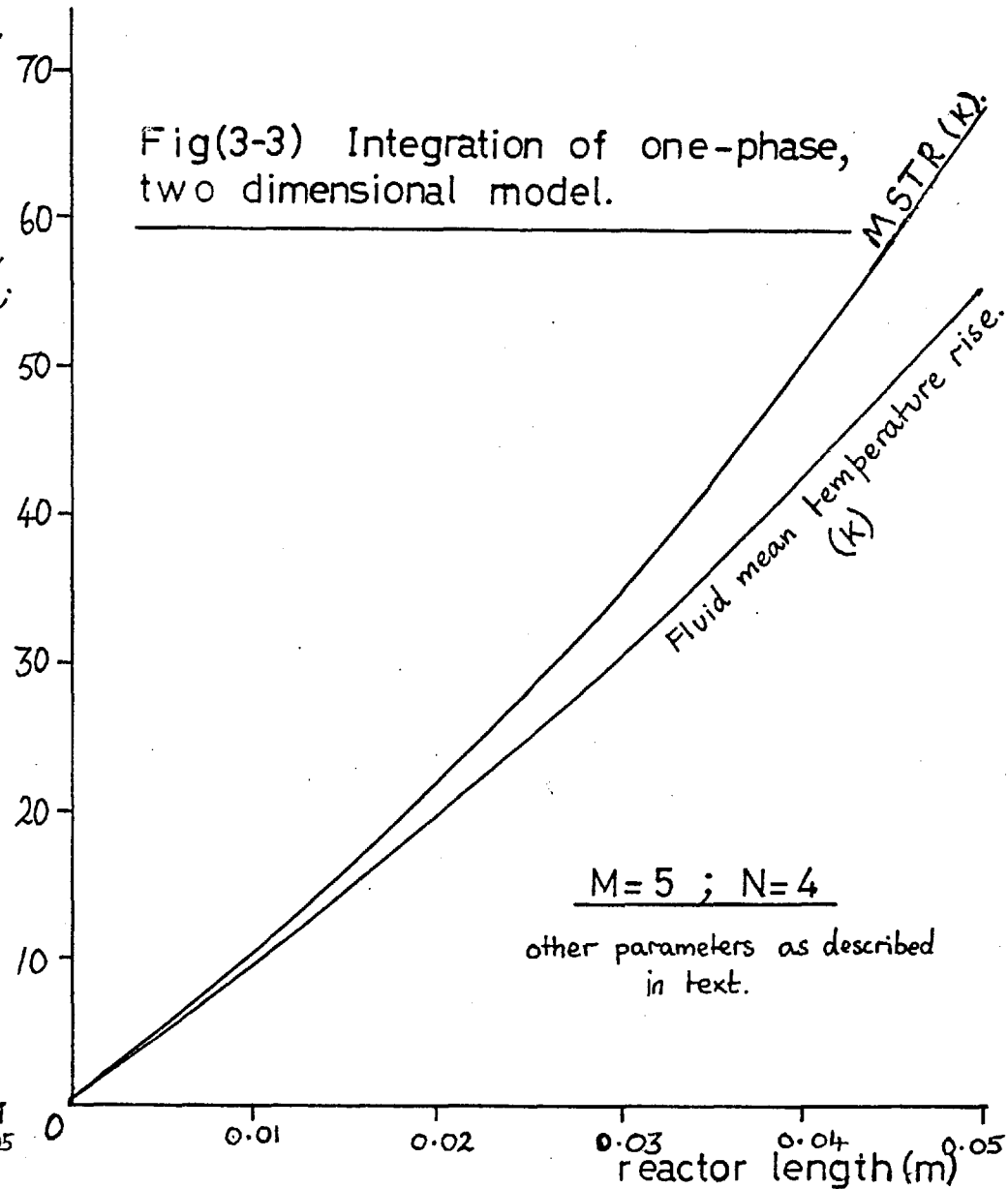
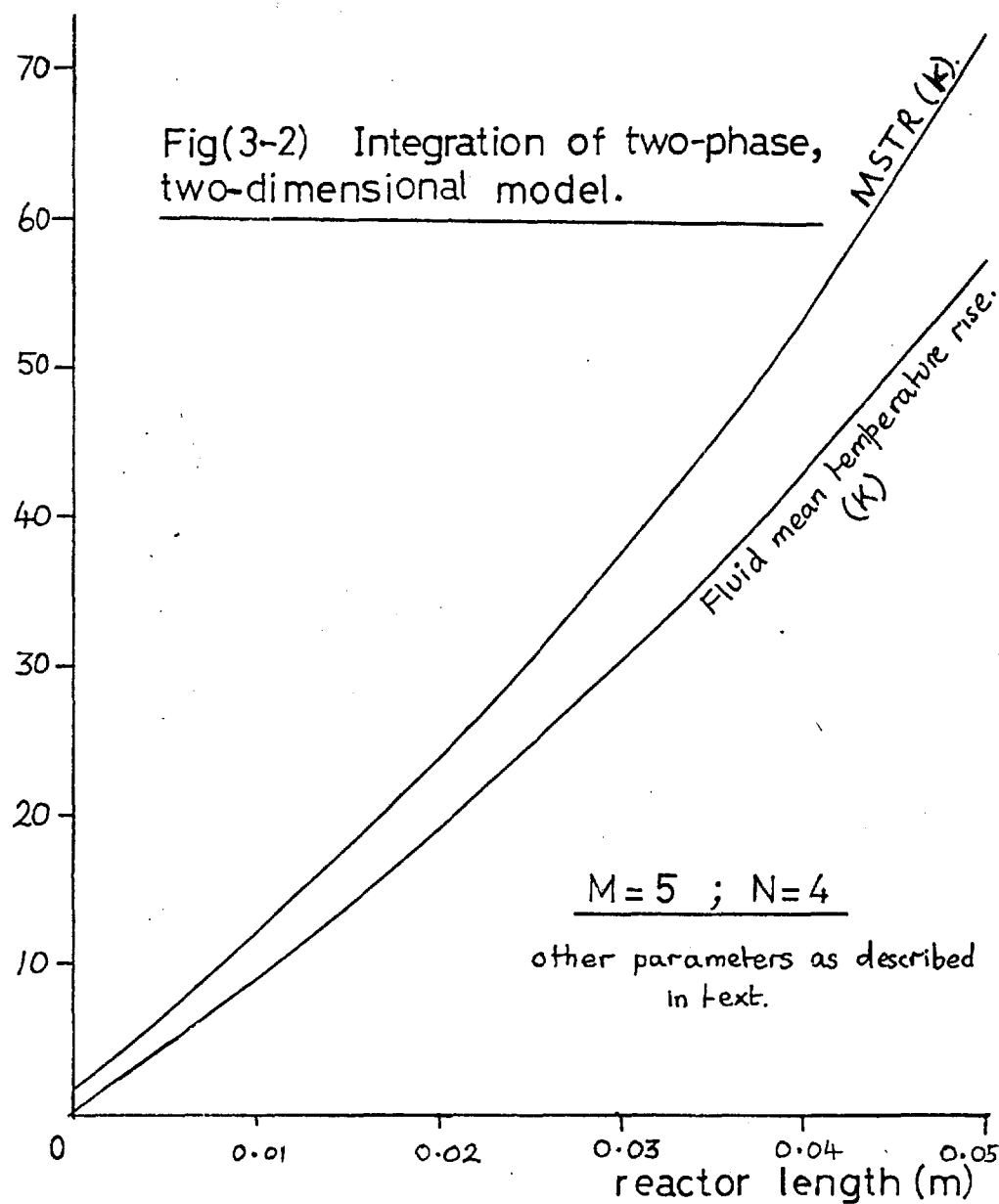
Both models give conservative predictions for temperature rise at lower values of M and N_A . This is to be expected when $\delta T/\delta z$ and $\delta^2 T/\delta z^2$

are both positive, as is the present case.

Instability can appear in the solution of difference equations used to solve partial differential equations, arising from a spurious or satellite solution. A good discussion of this kind of instability is given by O'Brien et al. (98) and a more rigorous treatment is given by Lowan (99). The essential point is that the step from one profile to the next is made by calculating each value on the new profile as a linear combination of the values on old profiles, together with any source term involved. An equivalent representation of a step, then, is to say that the set of values on the old profile is multiplied by a square matrix to get the set of values on the new profile. If the set of values on a profile is thought of as a linear combination of characteristic vectors of the matrix, it may be seen that one contribution to the solution after a large number of steps is the same linear combination of characteristic vectors, each now multiplied by a large power of the corresponding characteristic value. From this value it may be inferred that if any characteristic value of the matrix of coefficients in the difference equation is greater in magnitude than unity, the solution cannot be stable. Beek (52) has stated that the solution of the difference equations for the one-phase model are stable in this sense. The one-phase model and the two-phase model have been integrated to a length of 5cms for $M=5$, $N_A=4$ and $M=5$, $N_A=400$. In the former case the whole of the integration, as monitored by solids temperature rise and radial mean fluid temperature, is shown in Figures (3.2) and (3.3). In the latter case the last ten steps are shown in Figure (3.4).

Instability has not been found in either case for either model.

The model predictions at a reactor length of 10cms (0.10m) are shown in Table (3.4). As N_A is the number of axial steps in the integration, a value of, for example, $N_A=30$ in Table (3.3) and $N_A=60$ in Table (3.4) correspond to the same steplength. By the time the integration has proceeded to a length of 10cms the thermal conditions in the reactor have become very much more severe, particularly at the tube centre. Nevertheless, Table (3.4) shows that the solution still converges as M and N_A grow large. It is apparent, however, that much shorter steplengths are now required, both radially and axially. Figure (3.5) shows MSTR as a function of M at a length of 10cms: 90 Axial steps have been used in this calculation. Convergence with increasing M is clearly demonstrated. Figure (3.6) shows MSTR as a function of N_A at a length of 10cms: 11 radial steps have been used in this calculation. Convergence with N_A is also demonstrated. Figures (3.5) and (3.6) refer to the two-phase two-dimensional model.



Fig(3-4) Progress of last 10 steps of 2-D model integration.

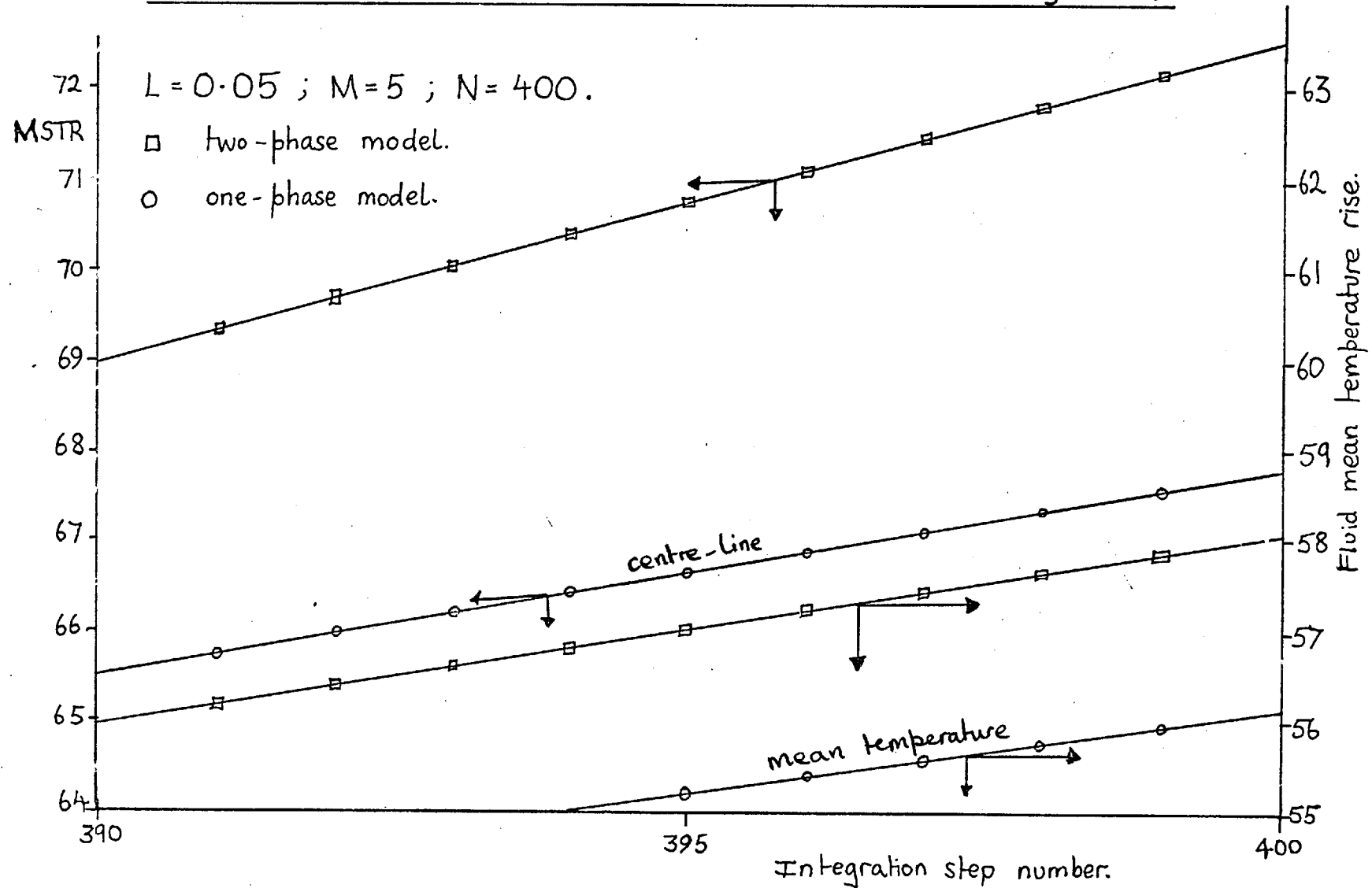
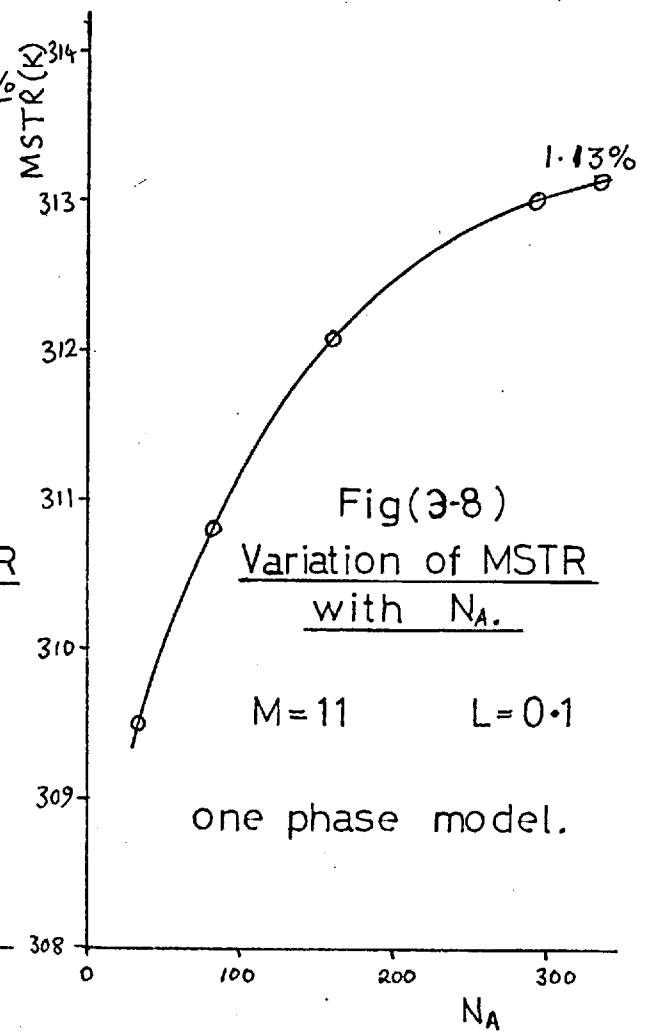
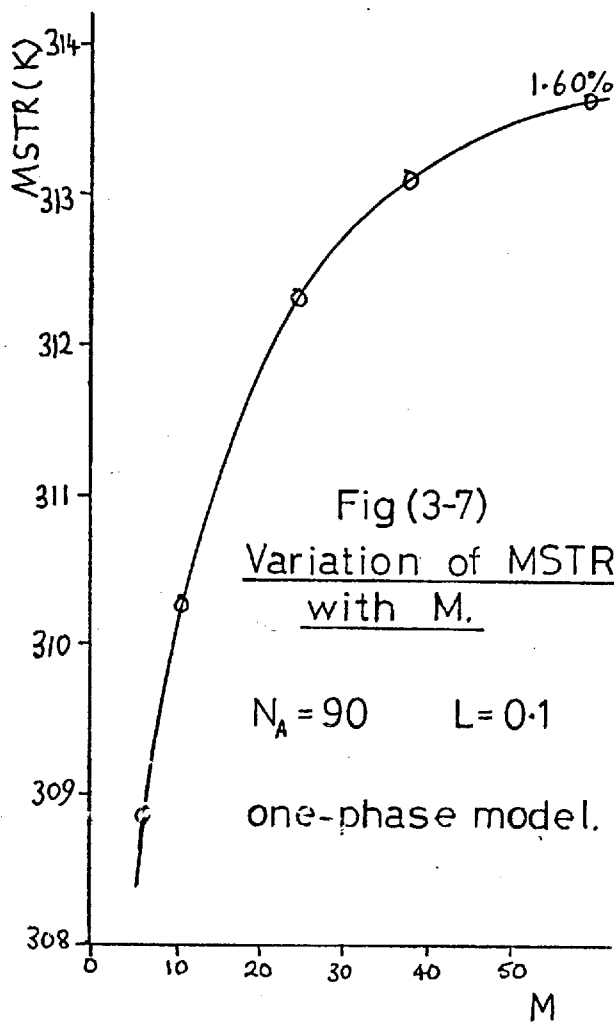
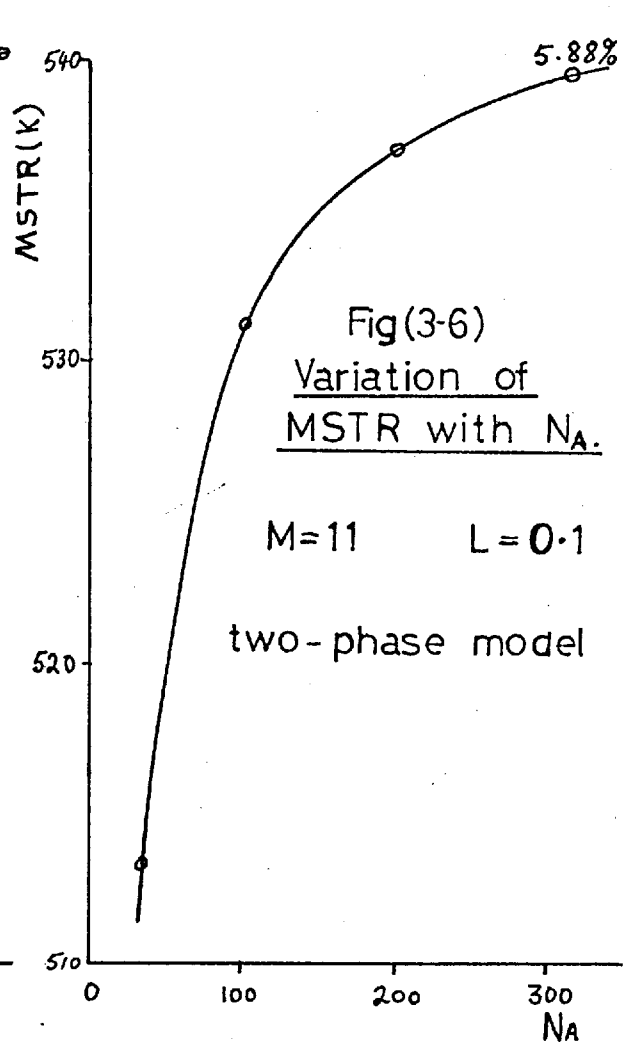
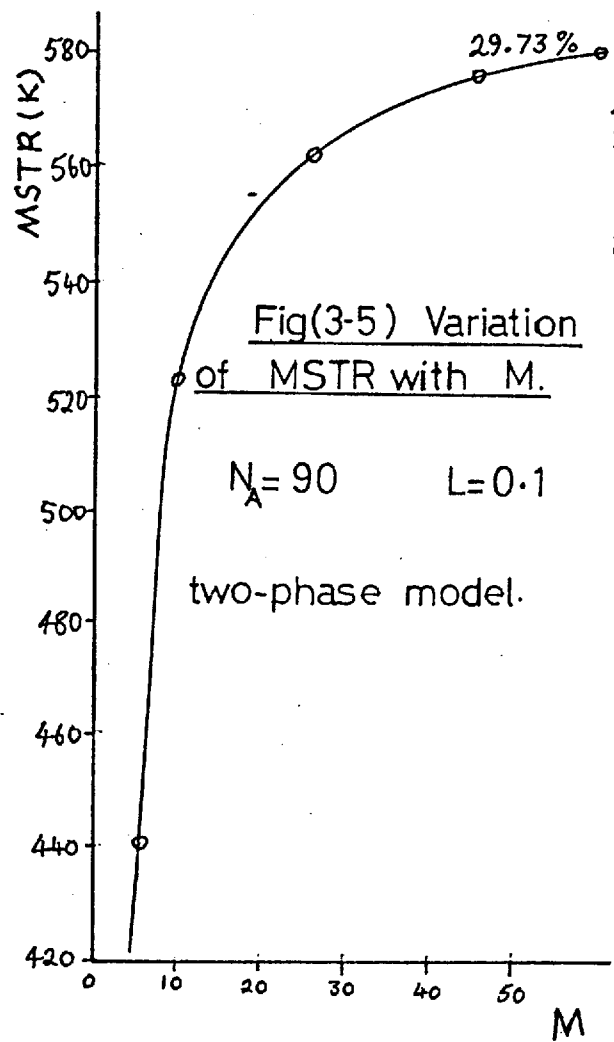


Table (3.4)

Variation of model predictions with radial and axial steplength

$T_{in}^f = T_w = 1100K$; $g_{in}^N = 0.667$; $g_{in}^{NO_2} = 0$; $dp = 0.006m$; $R_t = 0.03$; $G = 0.5$
 Reactor length = 0.1m

M radial steps	N _A axial steps	TWO-PHASE MODEL					ONE-PHASE MODEL			
		MSTR	MFTR	FETR	C%	S%	MSTR	FETR	C%	S%
5	1	226.44	214.77	163.64	16.89	5.77	197.25	153.11	16.02	5.88
5	19	386.51	355.21	242.79	23.99	11.01	288.04	204.59	20.38	9.65
5	60	438.48	399.11	260.55	25.71	12.67	307.17	212.16	21.07	10.42
5	180	447.21	406.83	263.30	25.98	12.99	309.75	213.05	21.15	10.52
5	260	447.33	407.08	263.42	26.00	13.00	309.89	213.10	21.16	10.53
5	360	447.10	406.92	263.40	25.99	13.00	309.93	213.12	21.16	10.53
5	410	447.02	406.86	263.38	25.99	13.00	309.94	213.12	21.16	10.53
7	30	440.68	398.84	258.29	25.34	12.17	300.31	208.94	20.75	10.03
7	180	492.15	441.54	271.50	26.62	13.54	311.33	212.77	21.09	10.44
7	360	492.56	342.03	271.68	26.64	13.57	311.52	212.84	21.10	10.45
11	30	511.65	453.63	273.18	26.65	13.45	309.53	211.78	20.99	10.30
11	180	538.02	475.15	278.25	27.15	14.02	312.64	212.76	20.08	10.41
11	360	539.60	476.56	278.56	27.18	14.06	313.02	212.87	21.09	10.42
11	400	539.52	476.51	278.55	27.18	14.06	313.03	212.87	21.09	10.42
15	4	253.68	238.93	176.73	17.85	6.51	207.01	158.94	16.39	6.32
15	19	426.96	385.48	250.96	24.53	11.34	290.41	204.41	20.32	9.56
15	90	546.07	479.06	278.56	27.13	13.94	312.11	212.45	21.04	10.36
45	60	553.56	481.49	278.14	27.04	13.78	311.44	212.05	20.99	10.31
45	90	576.91	499.18	281.79	27.39	14.18	313.40	212.66	21.05	10.37



Figures (3.7) and (3.8) show the results of similar calculations for the one-phase model. The percentage figure adjoining each line in Figures (3.5) to (3.8) represents the difference between the highest and lowest points on each line and is indicative of the relative importance of M and N_A in the two models. In Figure (3.9) the radial profiles in the plane of the maximum solids temperature are shown with M as a parameter. The profiles are seen to converge to a single, presumably 'true', profile as M becomes large.

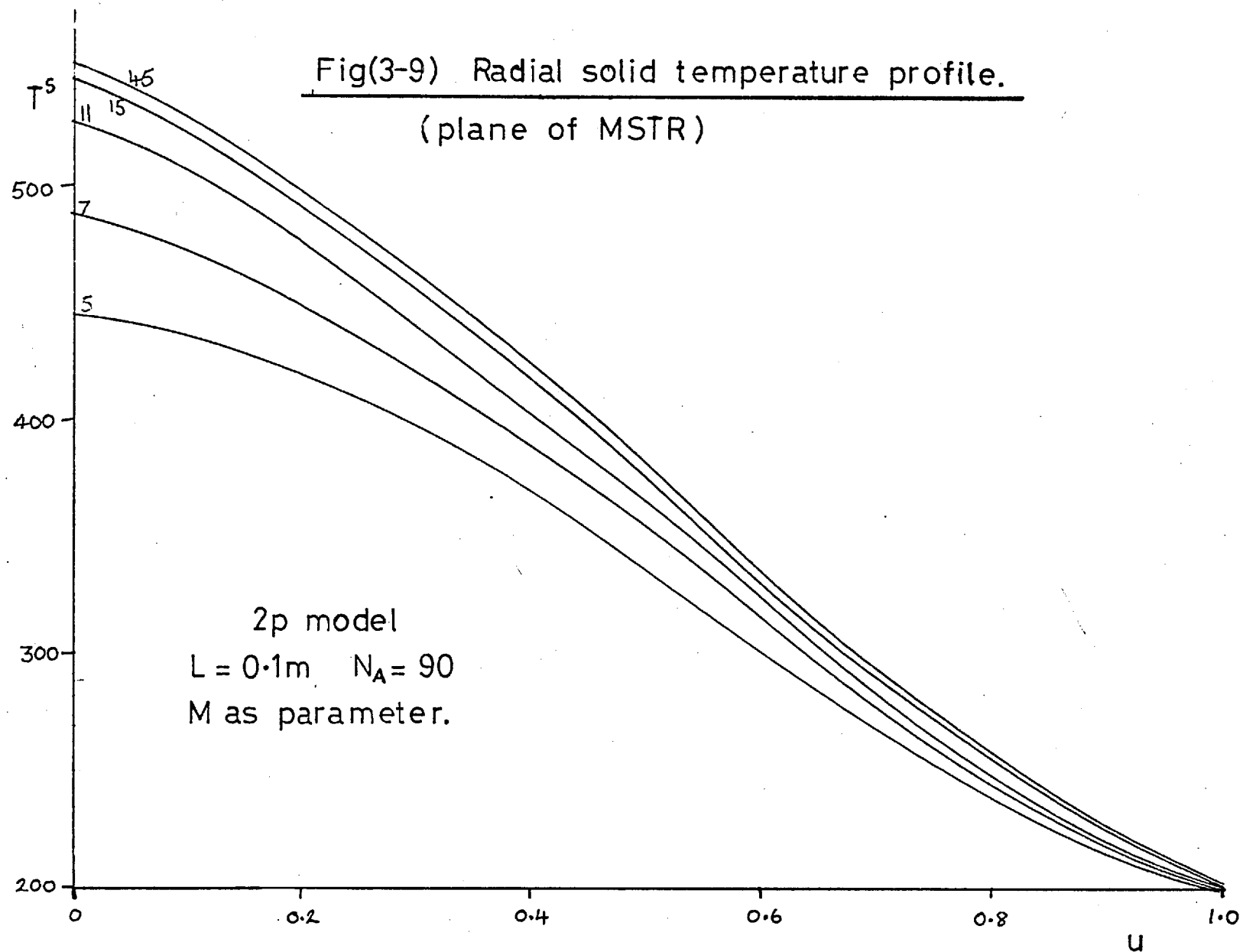
Again, no instability or oscillatory behaviour has been observed during this calculation.

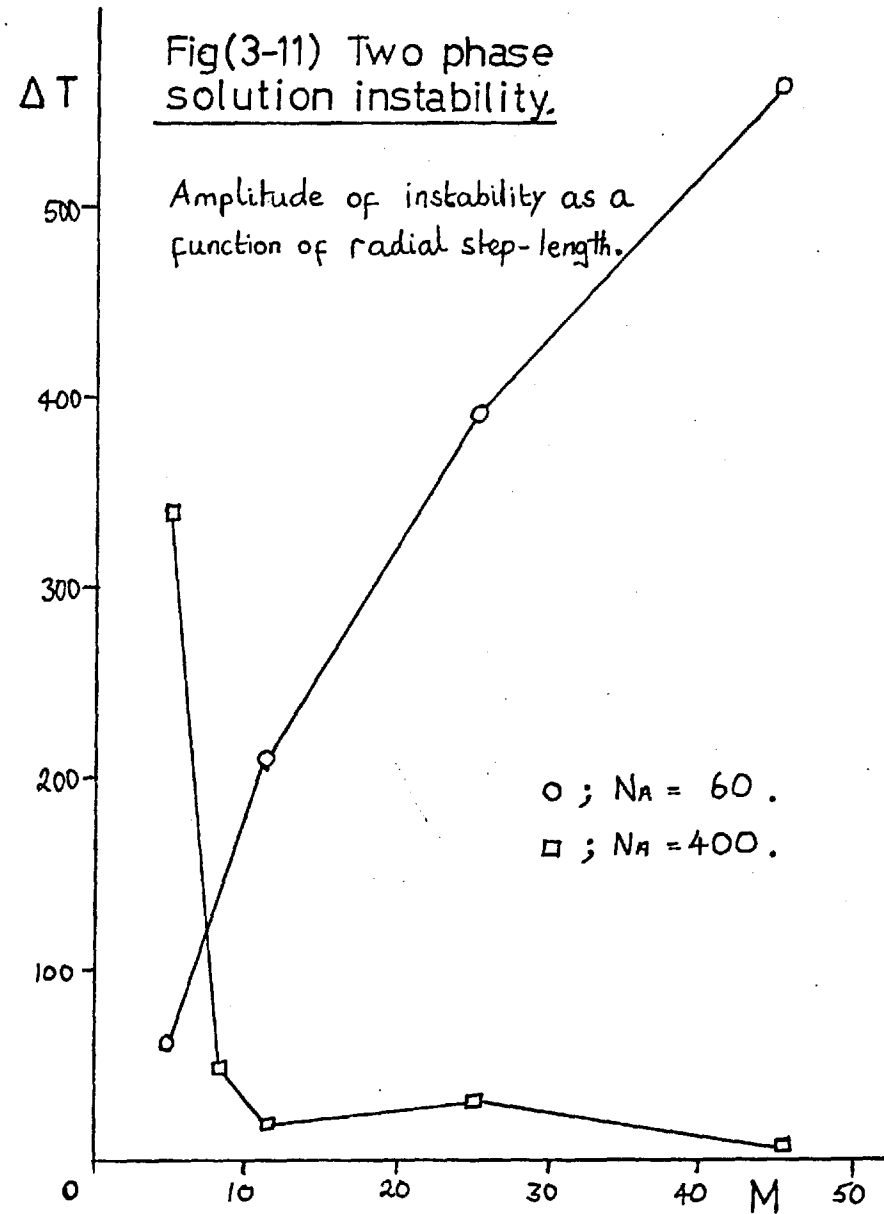
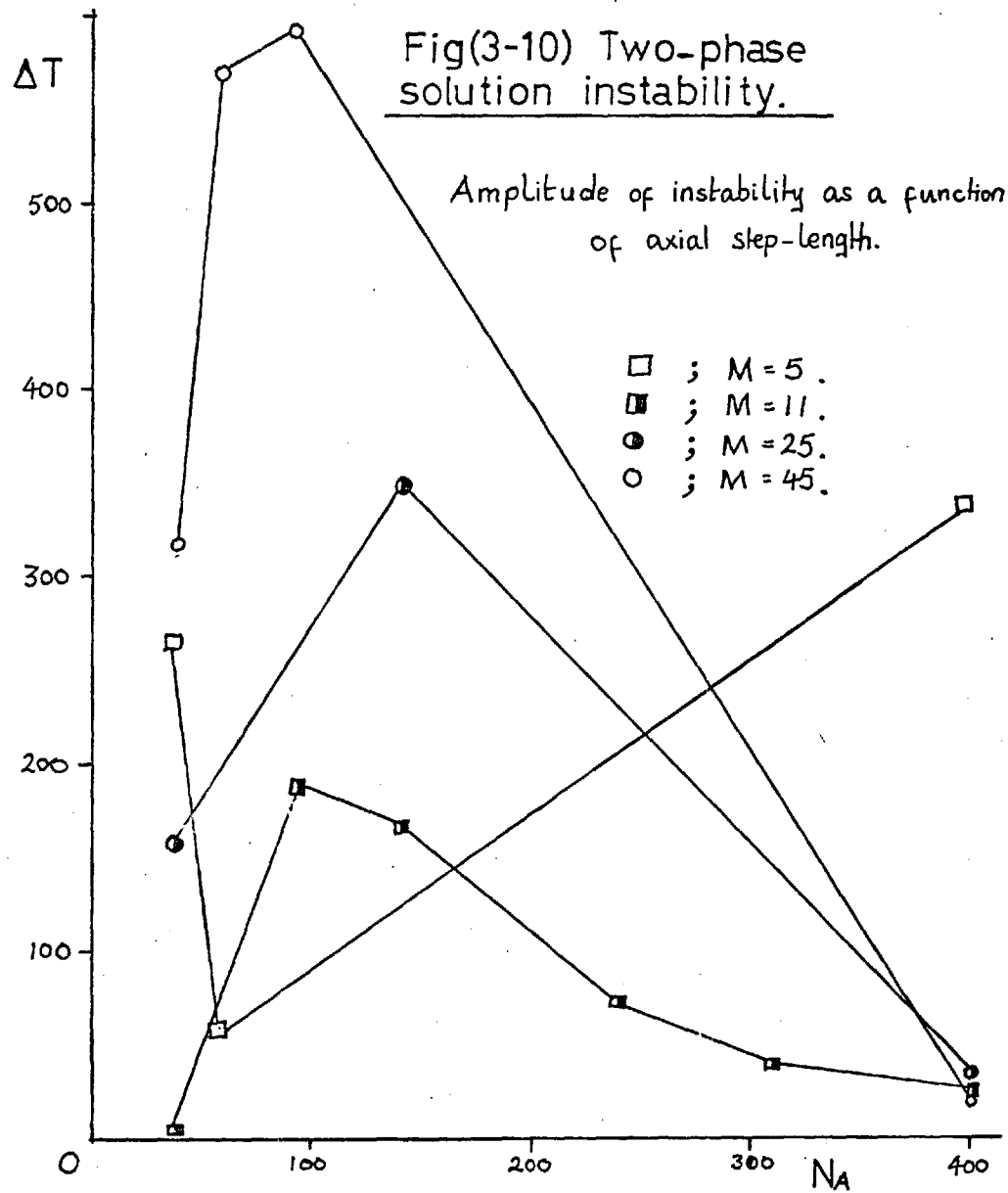
However, if the integration is allowed to proceed a little further, two new features of the mathematical model emerge.

The first feature is that before this length is reached, both models predict a negative value for the mass fraction of nitrous oxide at the centre line. At this point the integration was automatically terminated.

The second, and more significant feature, is that there is evidence of instability in the solution. In this example, the two effects mentioned above seem to become apparent at about the same reactor length and so the nature of the instability is somewhat obscured. Consequently another set of conditions, those of case 1 in Table (3.2), have been integrated in order to study the phenomenon of instability more closely.

For an inlet temperature of 1025K, the solution was found to exhibit oscillatory instability for a range of values of M (5 to 45) and N_A (39 to 399). The effect on the parameters M and N_A on the solution is monitored by the amplitude of the oscillation at a length of 3.75m. The amplitude is shown as a function of N_A with M as parameter in Figure (3.10) and as a function of M for $N_A=400$ and $N_A=60$ in Figure (3.11). The dependence on M and N_A appears complex. However, if the instability were of the type described earlier in this section, the amplitude would be expected to increase monotonically with N_A for a particular value of M . This is clearly not the case for any of the values of M investigated. For $M=11$, 25 and 45 the amplitude at first increases with N_A and then decreases rapidly as N_A increases to large values. It is interesting to note that the solution of the two-dimensional one-phase equations remained stable over the range of values of M and N_A considered and that no instability was found in this solution during the entire investigation of packed bed reactor models. Figures (3.10) and (3.11) indicate that the solutions become more stable as M and N_A increase which reflects the earlier finding that the accuracy





of the finite difference analogies increases with M and N_A . The stability appears to depend upon M to a greater degree than N_A . These considerations lead to the conclusion that the instability originates in Equation (2.61), the solids energy balance, which is independent of N_A , and the variation with N_A merely reflects the accuracy of the solutions.

Anticipating the results shown in Tables (3.5), (3.6) and (3.7) and considering Figure (3.1), instability has only been found in those cases where solid-phase transport is the greater contribution to the radial effective thermal conductivity and this lends further credence to the conclusion that instability originates in the solid phase energy balance.

The curves for $M=5$ in Figure (3.10) and for $N_A=60$ in Figure (3.11) show anomolous behaviour. Inaccuracy in the solution for these relatively low values of M and N_A is a possible explanation of this effect.

A detailed analysis of the stability of the solution procedures used is outside the scope of this thesis. However, it is very important to understand how the solution accuracy is affected by choice of steplength and to recognise that instability can occur under some conditions. During subsequent use of the two-phase, two-dimensional model the solutions have in all cases been checked for stability and accuracy. It will be noticed from Figure (3.9) that radial temperature gradients in the solid-phase need not necessarily be small near the tube centre although, of course, they will fall to zero at the tube centre. This will be particularly true if there is a thermal 'kick-off' of a homogeneous reaction at the tube centre leading to enhanced conversion and, consequently, to heat release in that region. It is apparent, therefore, that the substitution (2.37) described in Section (2.7.2) may not be as beneficial as was at first thought. Indeed, when the substitution is used, for $M=5$ the first radial grid point is at a dimensionless radius of 0.5, and even for $M=45$ the first point is at 0.15. This wide grid spacing near to the tube centre may well be the source of the observed instability. For future use of the two-phase, two-dimensional model it would possibly be safer to revert to the practice of writing the differential equations in terms of the radial co-ordinate rather than its squared value.

3.6 CALCULATIONS ON THE THREE FIXED-BED REACTOR MODELS FOR THE THERMAL DECOMPOSITION OF NITROUS OXIDE

Three models for a packed-bed tubular reactor have been considered viz

the two-phase, two-dimensional (2p) model, the one-phase, two-dimensional (1p) model and the one-phase, one-dimensional (1d) model. For a given set of inlet conditions each model was integrated for a certain length by the numerical methods described in Section (2.7). Forty-five steps were used in the radial direction and up to 500 in the axial direction. The results of these integrations are shown in Tables (3.5) to (3.9). The abbreviations in these tables (e.g. MSTR, FETR etc.) have the meanings given to them in the preceeding section. In order to facilitate comparison and discussion of these results each run is assigned a code. For each set of operating parameters, three integrations, one for each model, constitute a run. The code for each run contains four characters. The first, in this case N, indicates that the results refer to the nitrous oxide system. The second, in this case C, indicates that the results refer to model comparison calculations. The third character, a number between 1 and 7, refers to a particular heat transfer situation as described in Section (3.3) and the final character refers to a particular calculation under those conditions.

Because of the multi-parameter nature of the problem, rigorous comparison of models under different conditions is not possible. Comparison could be made on the basis of same temperature rise, same conversion, same reactor length and so on. A further problem, briefly alluded to in the preceeding section, is that a particular, fairly low, flow averaged exit conversion may not be achievable without reactant exhaustion on, say, the reactor centre line where reaction may be occurring at much elevated temperatures. In order to prevent negative concentrations occurring during the numerical calculation procedure, this situation automatically stops the integration. It is difficult, if not impossible, to predict "a priori" such a situation. A similar problem exists when integrating to a given flow averaged fluid exit temperature. Thus a great many useless integrations may have to be performed to achieve one set of comparable results. In view of the very time consuming nature of the calculations - each run took about 100 seconds of central processor time on a CDC 6400 computer - this is not a desirable approach. Consequently the following policy was adopted in obtaining the results in this section. For runs in which the final digit is 1, 2 or 3 the integration was either stopped automatically by finding negative concentrations or, where a definite 'hump' occurred at the temperature maximum, the integration was stopped after this hump had been passed. Runs terminating in a Figure 3 are at the highest inlet temperature (1110K) and are thus terminated at a shorter length than comparable runs (at 1025K and 1075K) terminating with a figure 1 or 2. Runs terminating in

Table (3.5)

Comparison of 2p, 1p and 1d models

Inlet Temperature = 1075K. $g_{in}^N = 0.667$ $M = 45$ $N_A = 400$

RUN	Length (m)	2p					1p				1d			
		MSTR	MFTR	FETR	C	S	MSTR	FETR	C	S	MSTR	FETR	C	S
NC11	2.2	58.3	58.1	20.3	36.12	2.12	58.0	20.3	36.05	2.12	29.4	19.1	34.98	2.00
NC12	0.31	506.6	493.0	193.7	24.70	9.51	407.9	175.5	22.92	8.17	126.3	126.3	18.94	4.34
NC31	1.0	271.5	269.3	175.6	41.23	6.09	217.9	143.1	36.81	5.22	101.0	101.0	31.44	3.89
NC41	0.149	409.6	382.7	242.5	25.41	9.2	292.0	199.9	21.50	7.4	187.4	187.4	20.51	6.30
NC51	1.0	133.8	133.1	62.1	44.59	3.66	127.1	60.0	43.22	3.58	69.6	49.8	38.91	3.03
NC61	2.5	63.6	63.2	26.8	39.35	2.35	60.3	26.1	38.51	2.32	41.6	25.5	37.90	2.25
NC71	0.41	49.4	48.9	35.8	6.50	2.30	47.7	34.7	6.42	2.30	34.7	34.7	6.43	2.29

Table (3.6)

Comparison of 2p, 1p and 1d models

Inlet Temperature = 1025K $g_{in}^N = 0.667$ $M = 45$ $N_A = 400$ ~ indicates an unstable solution

RUN	Length (m)	2p					1p				1d			
		MSTR	MFTR	FETR	C	S	MSTR	FETR	C	S	MSTR	FETR	C	S
NC12	3.75	~	~	~	~	~	21.7	9.4	25.22	0.80	12.0	9.1	25.07	0.79
NC22	1.6	~	~	~	~	~	94.6	43.3	32.09	1.41	43.9	34.6	29.04	1.18
NC32	1.65	40.2	40.0	26.5	15.19	1.04	39.2	25.9	15.05	1.04	26.1	24.8	14.91	1.01
NC42	1.0	239.8	236.5	170.2	29.82	3.07	209.8	151.8	27.72	2.78	128.2	128.2	25.48	2.25
NC52	1.5	34.6	34.4	19.9	19.80	0.96	34.1	19.7	19.70	0.96	22.2	19.0	19.52	0.95
NC62	3.0	22.4	22.3	13.6	19.02	0.87	21.8	13.3	18.88	0.87	15.5	13.1	18.83	0.87
NC72	0.86	465.5	451.5	173.3	16.75	5.44	390.7	163.7	15.93	4.71	151.3	151.33	14.77	2.66

Table (3.7)

Comparison of 2p, 1p and 1d models

Inlet temperature 1110K, $g_{in}^N = 0.667$

M = 45 $N_A = 400$ ~ indicates an unstable solution

Run	Length (m)	2p					1p				1d			
		MSTR	MFTR	FETR	C %	S %	MSTR	FETR	C %	S %	MSTR	FETR	C %	S %
NC13	1.5	176.7	174.2	29.1	55.28	5.62	170.8	29.4	54.79	5.57	60.6	29.9	46.47	4.07
NC23	0.16	420.9	404.0	177.4	19.42	11.21	342.7	163.0	18.04	11.12	148.0	148.0	16.76	7.44
NC33	0.38	408.4	396.4	224.8	28.1	12.32	314.2	189.6	24.68	10.35	161.8	161.8	22.36	8.00
NC43	0.087	~	~	~	~	~	326.2	219.6	21.31	11.92	211.1	211.1	20.52	10.52
NC53	0.25	282.5	276.6	168.5	23.95	8.96	249.1	154.1	22.42	8.40	133.9	133.9	20.80	6.91
NC63	0.7	233.2	230.2	162.0	35.48	8.20	188.8	132.6	31.58	7.23	110.7	110.7	29.09	6.23
NC73	0.25	267.3	258.3	184.7	16.15	9.97	236.1	172.5	15.13	9.42	181.9	181.9	15.49	9.04

Table (3.8)

Comparison of 2p, 1p and 1d Models

Inlet Temperature = 1075K $g_{in}^N = 0.667$ $M = 45$ $N_A = 400$

RUN	Length (m)	2p					1p				1d			
		MSTR	MFTR	FETR	C	S	MSTR	FETR	C	S	MSTR	FETR	C	S
NC14	1.5	58.3	58.1	25.6	26.84	2.27	58.0	25.6	26.78	2.14	29.4	23.1	24.86	2.04
NC24	0.16	87.9	86.9	54.2	6.57	2.67	86.1	53.7	6.50	2.64	56.5	56.5	6.38	2.56
NC34	0.38	81.2	80.5	56.3	8.40	2.69	78.7	54.8	8.27	2.68	54.7	54.2	8.19	2.59
NC44	0.087	90.9	88.4	69.4	6.97	2.83	85.8	67.4	6.77	2.84	68.3	68.3	6.54	2.73
NC54	0.25	75.3	74.6	50.5	8.41	2.59	73.6	49.8	8.31	2.59	49.5	49.5	8.21	2.44
NC64	0.7	61.7	61.2	44.4	12.26	2.54	58.8	42.4	12.02	2.51	41.1	41.1	11.35	2.41
NC74	0.25	79.4	78.3	63.9	5.62	2.73	77.2	63.0	5.55	2.73	67.4	67.4	5.13	2.41

Table (3.9)

Comparison of 2p, 1p and 1d models

Inlet temperature = 1025K $g_{in}^N = 0.667$ $M = 45$ $N_A = 400$

RUN	Length (m)	2p					1p				1d			
		MSTR	MFTR	FETR	C	S	MSTR	FETR	C	S	MSTR	FETR	C	S
NC15	1.5	21.8	21.7	11.7	11.04	0.87	21.7	11.7	11.03	0.87	12.0	11.2	10.98	0.86
NC25	0.16	30.5	30.3	19.7	2.47	0.91	30.2	19.7	2.46	0.91	19.6	19.6	2.43	0.90
NC35	0.38	28.0	27.8	19.7	3.09	0.92	27.6	19.4	3.08	0.92	18.8	18.8	2.94	0.89
NC45	0.087	31.0	30.4	24.2	2.48	0.93	30.2	24.0	2.46	0.94	23.5	23.5	2.37	0.91
NC55	0.25	26.6	26.4	18.1	3.16	0.91	26.3	18.0	3.15	0.91	17.6	17.6	3.03	0.89
NC65	0.7	22.0	21.8	15.8	4.61	0.90	21.4	15.4	4.59	0.90	15.0	15.0	4.45	0.86
NC75	0.25	28.2	27.9	23.4	2.07	0.92	27.8	23.2	2.06	0.93	24.1	24.1	2.02	0.91

4 and 5 give the model predictions at the same length as comparable runs terminating in 3 at these lower temperatures.

The following questions will be considered in discussing these results.

- (i) How well do the 1p and 1d models approximate the predictions of the 2p model.
- (ii) To what extent are the model predictions influenced by the secondary, homogeneous reactions.
- (iii) To what extent are the predictions of the 2p model influenced by the fact that the reactions occur in different phases.
- (iv) How does the shape of the axial temperature gradients influence the relationship between calculated conversion and calculated MSTR and FETR.

It is evident from the results in Tables (3.5) to (3.9) that there is variation in all cases considered between the predictions of the 2p, 1p and 1d models.

The most significant variation in the predictions of the three models is in the results for temperatures in the fixed bed, particularly the MSTR. The predictions of the models appear to become more disparate as the maximum predicted temperature increases. There is also a strong correlation between the fluid-solid temperature difference (MSTR-MFTR) and the difference between the 2p and 1p models. Indeed, the maximum fluid-solid temperature difference (27K, run NC41) corresponds to the greatest discrepancy between the 1p and 2p models although this run does not have the highest temperature rise (506K in run NC21).

It can be seen that, for the cases investigated, the 2p model predicts that the solid phase temperature is always greater than the fluid-phase temperature for this reaction scheme and that the predicted temperature of both phases is higher than that predicted for the pseudo-homogeneous continuum of the 1p model. That is to say that the continuum temperature is not some mean value of the fluid and solid temperatures. This situation would appear to originate from the boundary conditions that refer to solid, fluid and continuum temperature respectively whereby the solid phase temperature must be greater than T^f or T^c at entry when the heat production in the solid phase exceeds that in the fluid phase. For the present situation a mass fraction of N_2O of 0.67 on inlet requires a temperature of ~1540K before fluid and solid phase heat production becomes equal. This is clearly an unrealistically high temperature achieved during this study only occasionally. This point will be enlarged upon at a later stage of

this discussion.

The predictions for the FETR follow the trends for the MSTR but in general less variation is shown between the models. The maximum discrepancy for MSTR was 40% whereas the value for FETR, a flow averaged value, was 20%. This indicates that a significant part of the disagreement between the models can be accounted for by the efficiency with which they are detecting high temperature events near to the reactor centre. This possibility is supported by the poor predictions of the 1d model (see below). The preceding paragraphs are based principally on Tables (3.5), (3.6) and (3.7). The results in Tables (3.8) and (3.9) are generally less informative in this context, the temperature increases being relatively small and the model predictions consequently similar. Nevertheless, the trends are evident in that a larger fluid-solid temperature difference leads to larger disagreement between the models.

The conversion of N_2O also shows variation in the predictions of the separate models. The maximum discrepancy between 1p and 2p models is ~20% (Run NC41) and the discrepancy shows a greater dependency upon fluid-solid temperature difference than on the overall temperature rise. The conversion figure shown is the flow averaged value at the reactor exit.

S, the selectivity to NO_2 , is also a flow averaged exit quantity and is defined as:

$$S\% = \frac{g_{NO_2} - g_{in, NO_2}}{g_{in, N} - g_{N}} \times 100\%$$

It must be emphasised that this does not show the amount of homogeneous reaction occurring per se, but may be used to indicate this, as NO_2 is totally produced by homogeneous reaction. At 1150K, NO_2 production is 10% of the total homogeneous reaction whereas at 1300K the figure is 75%. A further point must be made. The homogeneous reactions become more significant as the temperature increases for a given fluid concentration of N_2O . However, the homogeneous reactions show a second order dependency on N_2O concentration compared with a first order dependency by the heterogeneous reaction. Thus N_2O depletion as reaction proceeds will adversely affect the rate of homogeneous reaction compared to its effect on the rate of heterogeneous reaction. It is therefore highly unlikely that the system presently under study is capable of producing a situation where homogeneous and heterogeneous reaction proceed with comparable rates of heat release, as a temperature rise of the order

required results in severe N_2O depletion. An inlet temperature of 1540K may be expected to provide the desired effect at some point in the calculation (a greater rate of heat production in the fluid than in the solid) and consequently a fluid temperature that is higher than the solid temperature. This situation would be short lived, as N_2O consumption at this temperature would be very rapid. An attempt to integrate the 2p model under these conditions was unsuccessful due to the very short axial steplengths required.

The only other comparison between 1p and 2p models found in the literature is that given by Wasch and Froment (46) who have considered the oxidation of hydrocarbons using, essentially, the two-phase model formulation used in this thesis. They consider only heterogeneous reaction. A typical value for rate of heat release may be calculated from their data. For temperature of 673K and reactant mass fraction of ~ 0.1 it is about $4 \times 10^5 \text{ W m}^{-3}$. At this rate of heat release they have calculated a film temperature difference of about 2.5°C . Consider Run NC63 as an example. In this run the maximum film temperature difference found is also 2.5°C but the rate of heat release at this point is around $8.9 \times 10^6 \text{ W m}^{-3}$. Thus a vastly increased rate of heat release has resulted in the same film temperature difference. Further calculation for the two models shows that Wasch and Froment's model has a value of $W \text{ m}^{-3}$ of $3.0 \times 10^5 \text{ W m}^{-3} \text{ K}$ whereas our example, from Table (3.8), has a value of $9.8 \times 10^6 \text{ W m}^{-3} \text{ K}$. The quantity

$$\frac{(\text{rate of heat release})}{h_V a_V}$$

thus shows a marked similarity. The N_2O system, whilst experiencing much greater thermal activity, is able to release the heat to the fluid phase more rapidly than the hydrocarbon system of Froment and Wasch. Comparison of Runs NC41, NC72, NC33 which have similar thermal activities - but differing $h_V a_V$ - show this is important.

Results for all runs show that comparison between 1p and 1d models is poor at anything but low conversions. As may be expected, there is a correlation between error in the 1d model relative to the 1p model, and the ratio of centreline temperature and flow averaged temperature in the 1p model. Owing to the variation in temperature rises, conversions and so on it is not possible to determine any strict relationship between the comparison of 1p and 1d models and the Biot Number. Considering, however, runs NC21

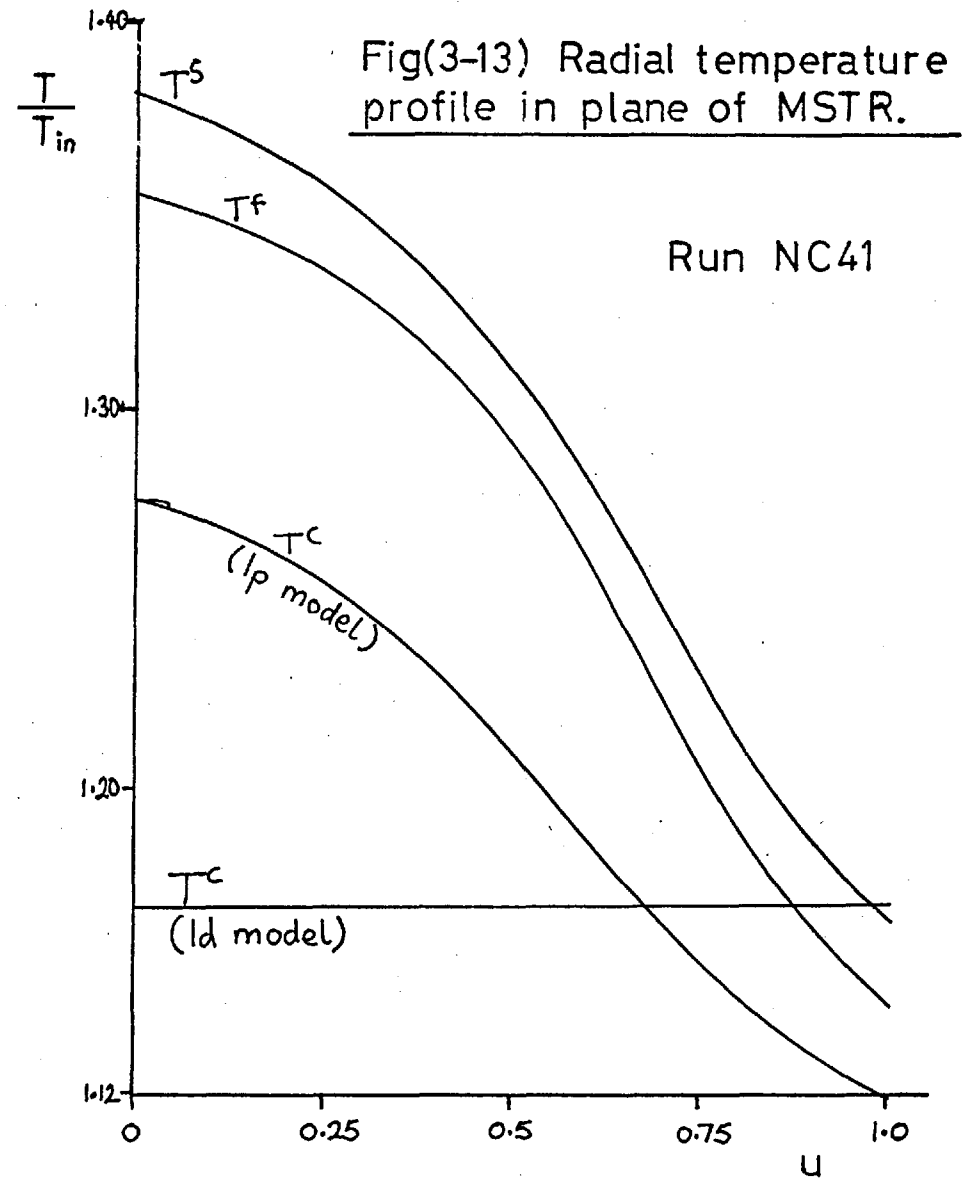
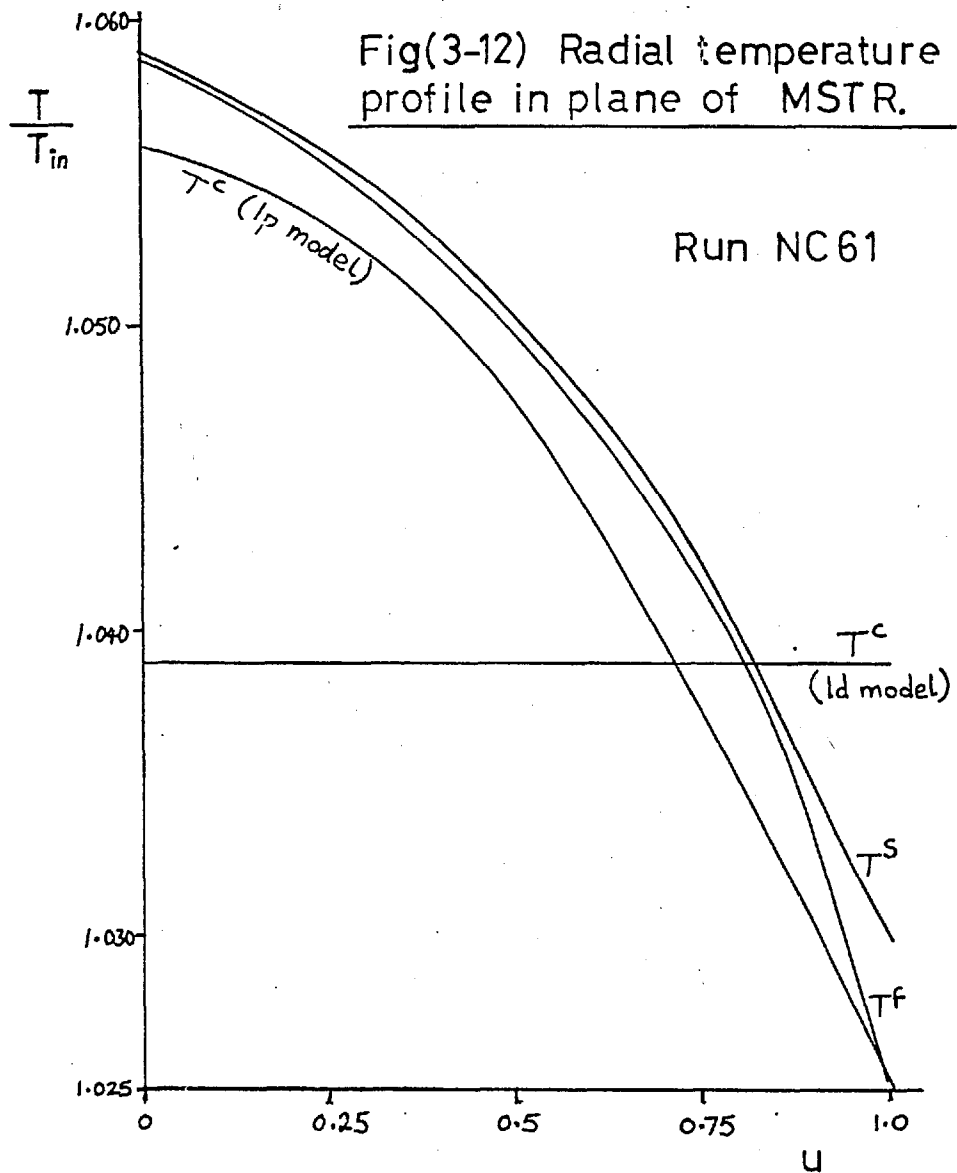
NC42 and NC 43 the discrepancy between the models for prediction of MSTR increases as the Biot number increases. These runs have similar maximum temperatures by the 1d model, and similar conversions. Other sets of comparable runs, e.g. NC32, NC52 and NC11, show the same trends. A low value of the Biot number indicates that the resistance to heat transfer from the bed is lumped at the tube wall which is exactly the assumption made in establishing the 1d model.

Consideration of Tables (3.3) and (3.5), (3.6) and (3.7) reveals that those runs exhibiting the most significant film temperature differences have a low value for $h_v a_v$, the volumetric surface heat transfer coefficient, and are in a heat transfer situation where fluid transport predominates. In contrast heat transfer cases which have a high value for $h_v a_v$ and in which solid phase heat transfer predominates (e.g. NC11, NC21, NC13, NC23) show relatively less significant film temperature differences in view of the elevated temperatures (in, for example, Run NC21) and consequently less significant discrepancy between the 1p and 2p models.

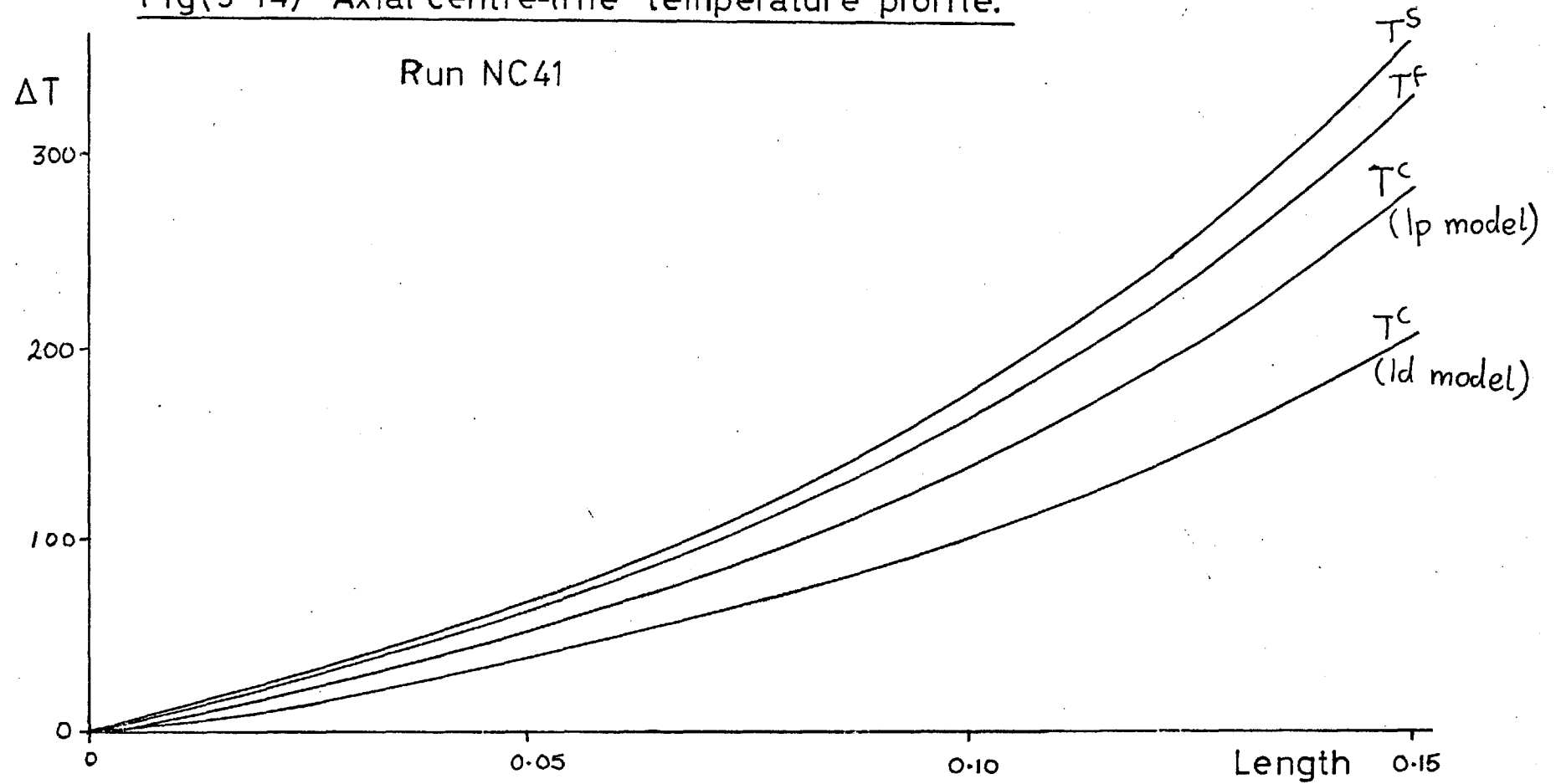
At this stage it has been established that the 1p, 1d and 2p models show wide variation in their predictions. It seems that thermal activity, Biot number and film heat transfer coefficient are parameters that may be used to clarify the variation in the predictions. The role of the homogeneous reactions is not established by the discussion to date. In order to understand the role of these reactions it is necessary to consider axial and radial temperature gradients in the reactor bed.

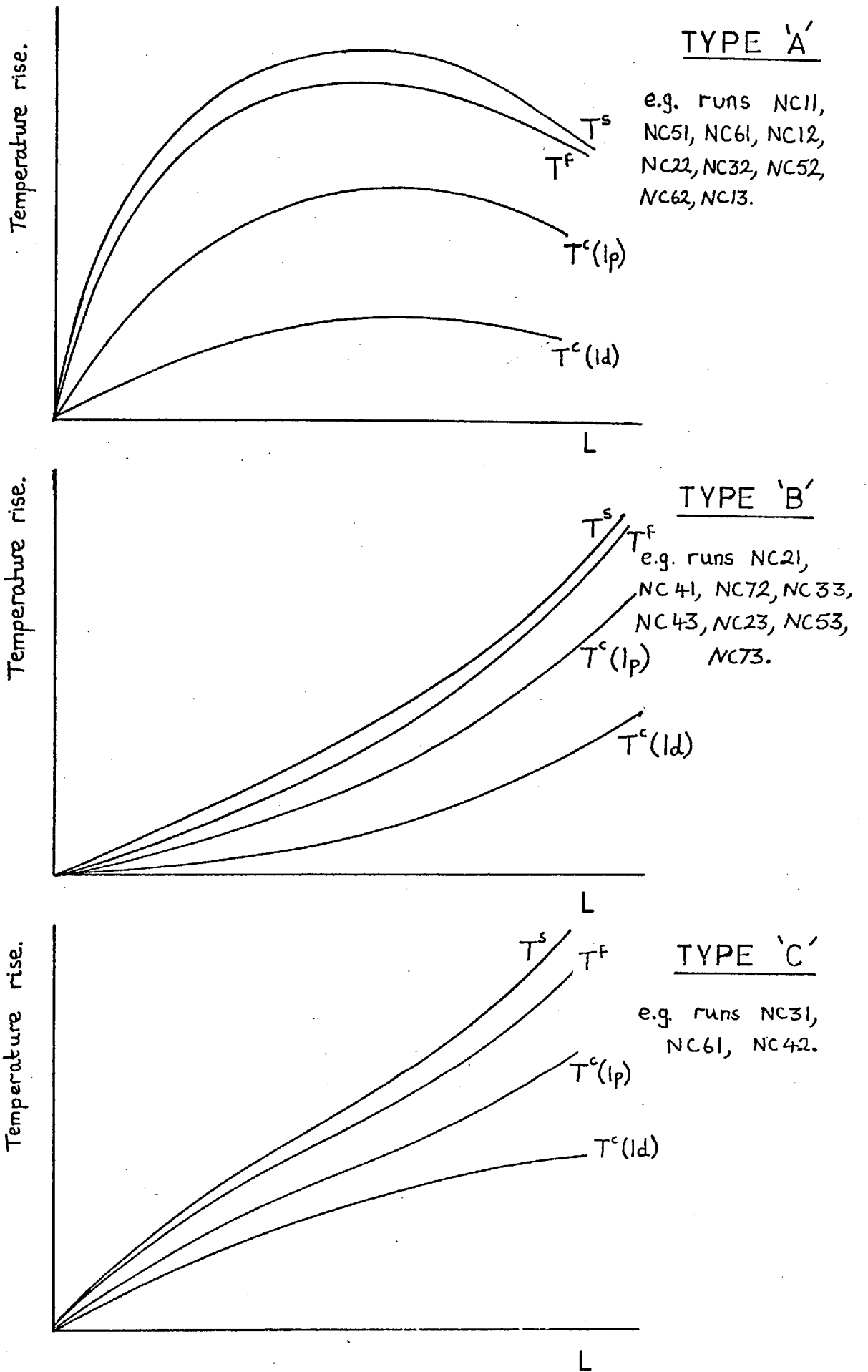
Considering, first, the radial profiles, all runs yield profiles approximately parabolic with respect to the radius and this is so for both models. A typical set of profiles is shown in Figure (3.12) for NC61 and Figure (3.13) for run NC41. The relative behaviour of T^s and T^f near to the reactor wall is clearly shown, as is the significant film temperature difference as the absolute value of the temperature becomes large. The shape of the profiles is in agreement with those published by Olbrich (47). The poor agreement between the three models is emphasised in Figure (3.13).

The calculated axial temperature profiles are more revealing. As an example, that for Run NC41 is shown in Figure (3.14). This shows clearly that the models are in great disagreement, which becomes accentuated as the temperature increases. It would be possible to draw all the profiles obtained, but it is more useful to classify the runs according to the shape of the profiles obtained. In Figure (3.15), four general shapes of axial centre-line temperature profiles are shown and, beside each shape, the runs having that shape are shown. The distinction between types B and C is a



Fig(3-14) Axial centre-line temperature profile.





Fig(3-15) Centre-line temperature profiles.

slight one for the runs considered. More striking examples of this situation have been found during consideration of methanol oxidation (see Chapter 4).

Situations of type A are thermally stable in the sense discussed by such as Hlavacek (42), Adler and Erig (100) and Thomas (101). The profile is everywhere concave.

Situations of type B are thermally unstable and lead, sooner or later, to temperature runaway. The temperature profile is everywhere convex.

Type C is theoretically the most interesting set of profiles. The reactor at first appears to be thermally stable but, at a certain temperature, becomes thermally unstable.

Reference to the results in Tables (3.5) to (3.8) show that runs of type A show little significant difference between the 1p and 2p models, although the 1d model remains a poor approximation. The largest film temperature difference found is 0.7°K in run NC51 although a temperature rise of 133K occurs at the centreline in this run.

In contrast, runs of Type B generally exhibit much larger film temperature differences and consequently predictions of the 1p and 2p models differ by greater amounts. The degree to which this is so, of course, depends considerably upon the final temperature achieved, in all cases much larger than those of type A, that is to say on how far the thermal runaway is allowed to proceed. Again the 1d model performs poorly.

It is emphasised that these arguments apply, at present, to the centreline temperature. When the flow averaged fluid temperature is considered, the same trends are noticeable but the effects are less extreme. For example the knee of the convex curves of Type B is sharper for the centreline temperature than for the flow averaged temperature. As may be expected for a flow averaged property, the 1d model fares rather better in comparison with the 1p and 2p models although agreement is still not good for type B cases.

It is evident, from studying these profiles, that thermal runaway is an important aspect of this system and accounts for some of the apparently anomalous relationships between temperature and conversion occurring in these results.

In generating the results in Tables (3.7) to (3.9) each heat transfer case has been integrated for inlet temperatures of 1110K, 1075K and 1025K respectively. The length of the reactor for the runs in Tables (3.8) and

(3.9) are the lengths corresponding to the same heat transfer case in Table (3.7). The groups of runs that will be considered are NC23, NC24 and NC25: NC53, NC54 and NC55; and NC73, NC74 and NC75.

When conversion is plotted on a logarithmic scale against the reciprocal inlet temperature only slight deviation is observed from the Arrhenius straight line that would result from an isothermal reactor (Figure (3.16)). The slight upturn is due to the non-isothermality of the bed and the mixed kinetics of the three reactions.

An approximate proportionality might be expected between maximum temperature in the bed and the conversion, so that a plot of logarithm of maximum temperature rise against reciprocal inlet temperature might be expected to give only similar slight deviation from Arrhenius behaviour. This is found to be the case.

Returning now to the discussion of the shapes of the axial profiles, the thermal sensitivity analysis of Thomas (101) has been applied to the reactors. At first only the heterogeneous reaction has been considered. Defining the two variables:

$$\text{Adiabatic dimensionless temperature rise, } B_c = \frac{E_{AIII} g_{in}^N (-\Delta H_{III})}{C_p R T_w^2}$$

and,

$$\text{heat transfer parameter, } a = \frac{R T^2 U}{E_{AIII} g_{in}^N (-\Delta H_{III}) \rho A_{III} \exp\left(\frac{-E_{AIII}}{R T_w}\right) R_t}$$

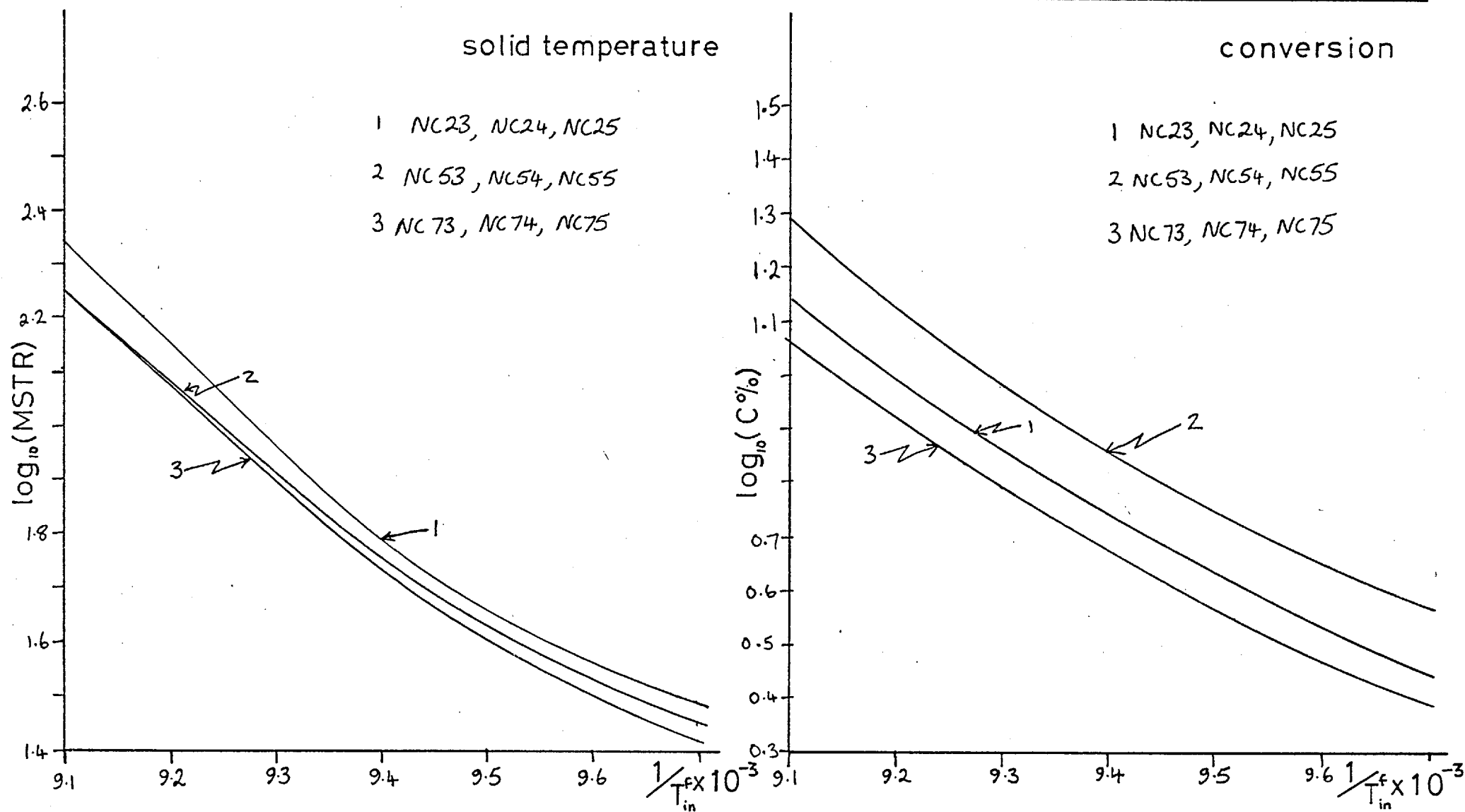
then Thomas shows that the critical value of a , a_{crit} , is:

$$a_{crit} = 2.72 \left(1 - K \left(\frac{1}{B_c}\right)^{0.67}\right)$$

for a first order reaction. In this case $K=3.06$ (42). If a reactor has a value of a greater than a_{crit} then profiles of type A would be expected. Conversely if a is less than a_{crit} profiles of type B would be expected. Table (3.10) shows a and a_{crit} for the groups of profiles found.

The relationship for a_{crit} has been derived on the basis of a one-dimensional reactor model (42) and, as such, may be expected to be only an estimate of the true value. In Figure (3.17) the general behaviour of a fixed bed reactor is shown with a as parameter. Table (3.10) shows that the ratio $a:a_{crit}$ falls into three distinct groups for the runs investigated and that these groups correspond to the types of profile

Fig(3-16) Solid temperature rise and Conversion as a function of Inlet Temperature.



TYPE-A

RUN	NC11	NC51	NC61	NC12	NC22	NC32	NC52	NC62	NC13
a_{crit}	1.59	1.59	1.59	1.66	1.66	1.66	1.66	1.66	1.54
a	1.94	1.18	1.55	3.64	1.40	2.95	2.21	2.94	1.30

TYPE-B

RUN	NC21	NC41	NC72	NC23	NC33	NC43	NC53	NC73
a_{crit}	1.59	1.59	1.66	1.54	1.54	1.54	1.54	1.54
a	0.75	0.47	0.35	0.51	0.69	0.32	0.79	0.13

TYPE-C

RUN	NC31	NC42	NC63
a_{crit}	1.59	1.66	1.54
a	1.04	0.89	1.03

TABLE(3-10) Critical heat transfer.

distinguished in Figure (3.15). The runs which have profiles of Type B all have values of a which are considerably lower than the calculated value $a_{crit} - (a:a_{crit})_{max}=0.51$ - and the thermal instability can be attributed to the heterogeneous reaction alone.

The runs which have profiles of type A are rather less convincing in this respect but, bearing in mind that a_{crit} is only approximate, only run NC51 has a value for a which is significantly lower than a_{crit} . According to Froment (68) the one-dimensional model predicts run-away conditions "too-late" and so the one-dimensional analysis will lead to a value of a_{crit} that is too high.

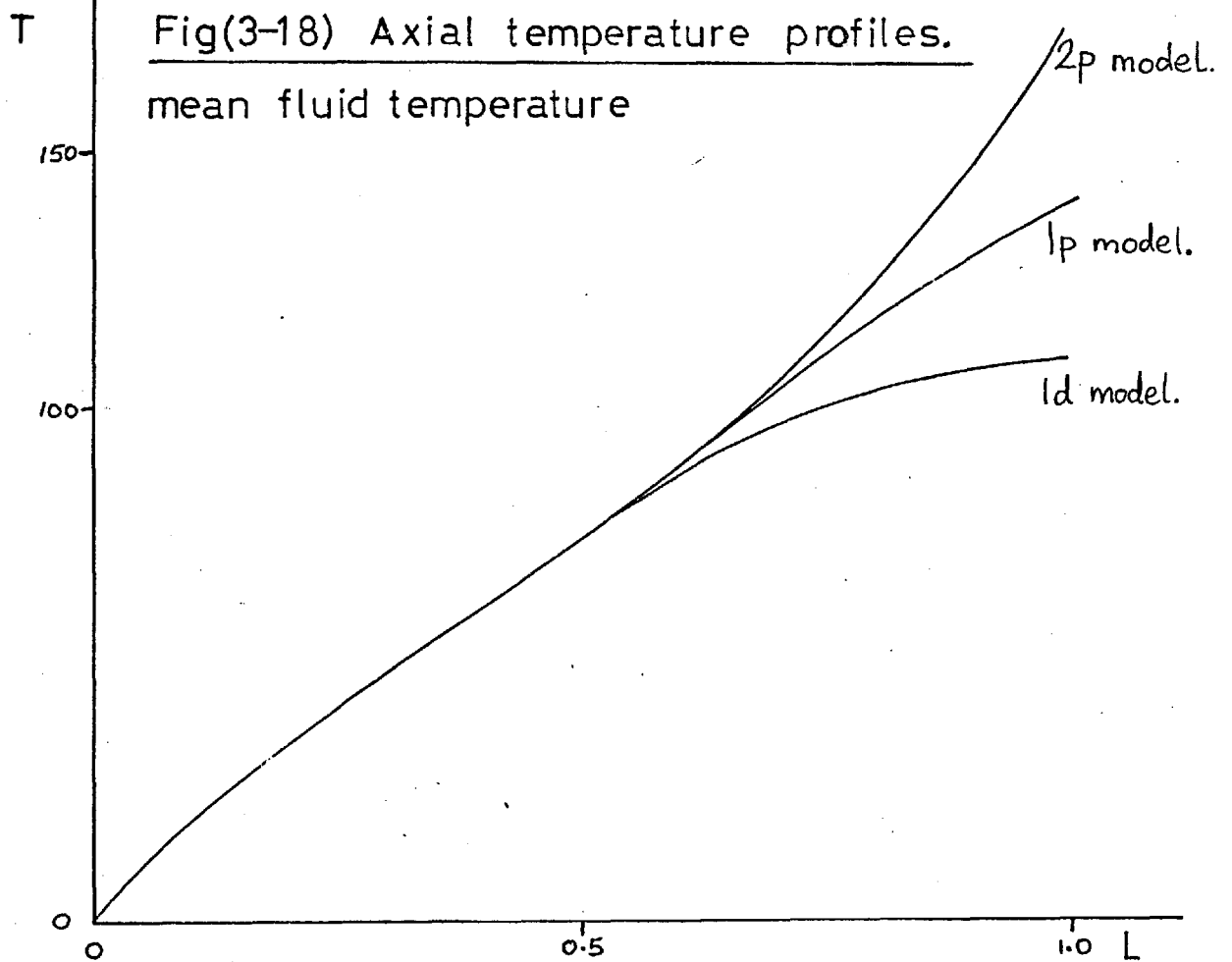
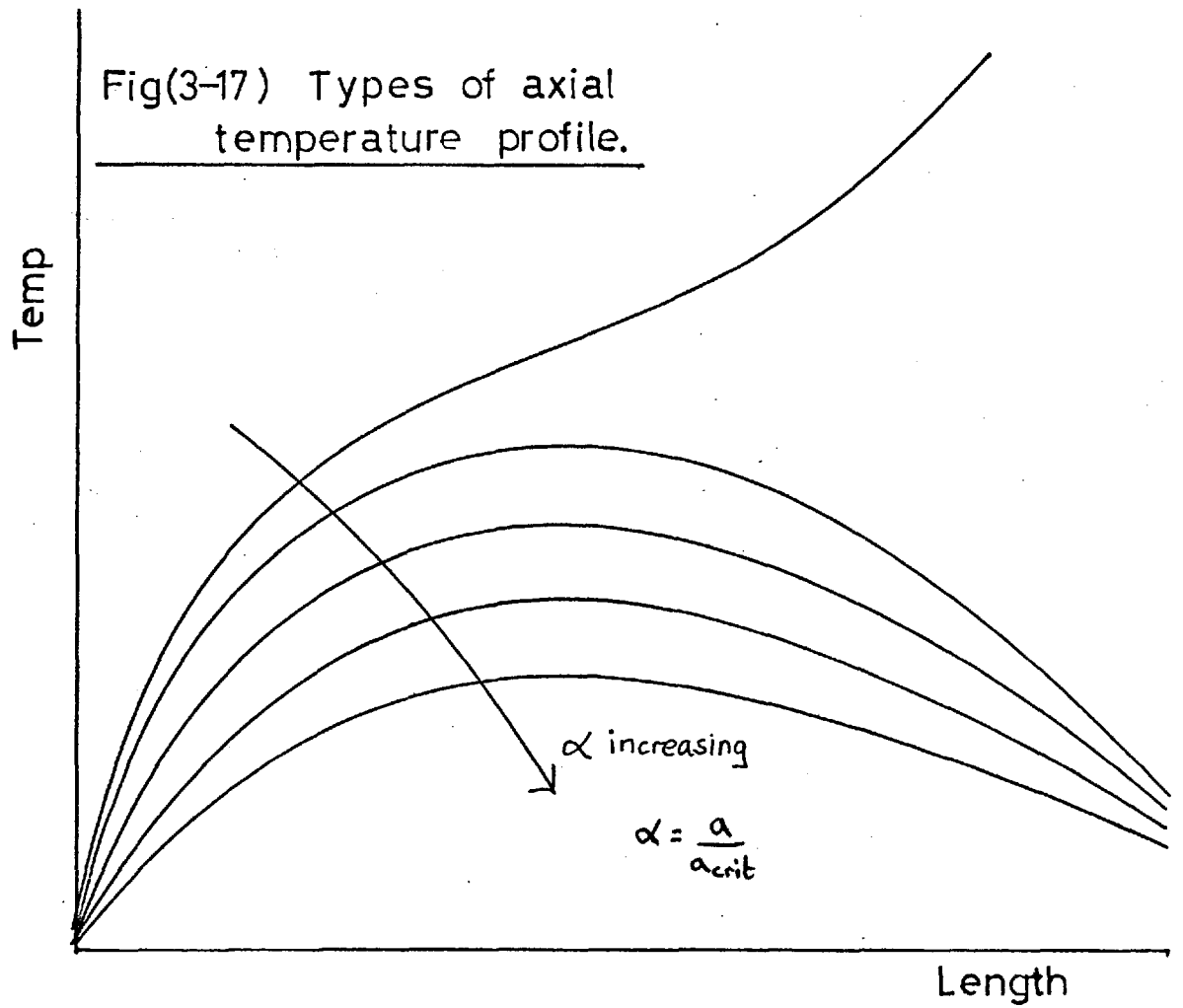
The runs which have profiles of type C have intermediate values of a and ones which, bearing in mind the previous paragraph, must be fairly close to a_{crit} . One explanation for the sigmoidally shaped temperature profiles is that the reactor is thermally stable towards the heterogeneous reaction but is thermally unstable with respect to one or both of the homogeneous reactions.

Figure (3.18) shows the axial, flow-averaged, fluid temperature rise profiles for run NC31. It is interesting to note that whereas eventual thermal instability is predicted by the 2p model, the 1d model has failed to detect this situation and predicts a thermally stable reactor. The 1p model, whilst still predicting a very slightly sigmoidal profile, eventually predicts a stable reactor also.

This leads to a further consideration of the relative values of a and a_{crit} . The parameters a and B_c both include the inlet mass fraction of N_2O . Now, as there is parallel competition between heterogeneous and homogeneous reactions for the consumption of N_2O , the inlet value for g^N is not the correct value to use in evaluating a and B_c . Moreover, as the relative amount of homogeneous and heterogeneous reaction varies with the temperature distribution inside the reactor, it is difficult to assign a correct value to this variable. However, in this case, if g_{in} is reduced by 25% to 0.5, a_{crit} is reduced to 1.57 - a change of only 2% whereas a is doubled. Thus the values of a given are only lower bounds and this helps to explain the apparent anomaly of runs such as NC51 where a is less than a_{crit} and yet the reactor is thermally stable.

Similarly a realistic evaluation of a and a_{crit} with respect to the homogeneous reactions is difficult. It is evident from the values for S in Tables (3.5) to (3.9) that the heterogeneous reaction predominates in the early part of the reactor. Thus for runs with temperature profiles of type C it appears that, whereas the reactors are stable with respect to

Fig(3-17) Types of axial temperature profile.



the heterogeneous reactions, at some point in the reactor the combination of N_2O concentration and temperature is such that the homogeneous reaction becomes significant and the reactor becomes unstable.

The axial profiles for centreline solids temperature are plotted in Figure (3.19) for runs in Table (3.5). The trend in stability with respect to a , shown as a parameter, is evident as is the sigmoidal behaviour of run NC31. The profiles for flow averaged fluid temperature is shown in Figure (3.20) for runs NC31 and NC51 and similar behaviour is found. Runs NC31 and NC51 have very different properties with regard to the ratio of fluid to solid heat transfer and this may account for the reversal of their positions with respect to a .

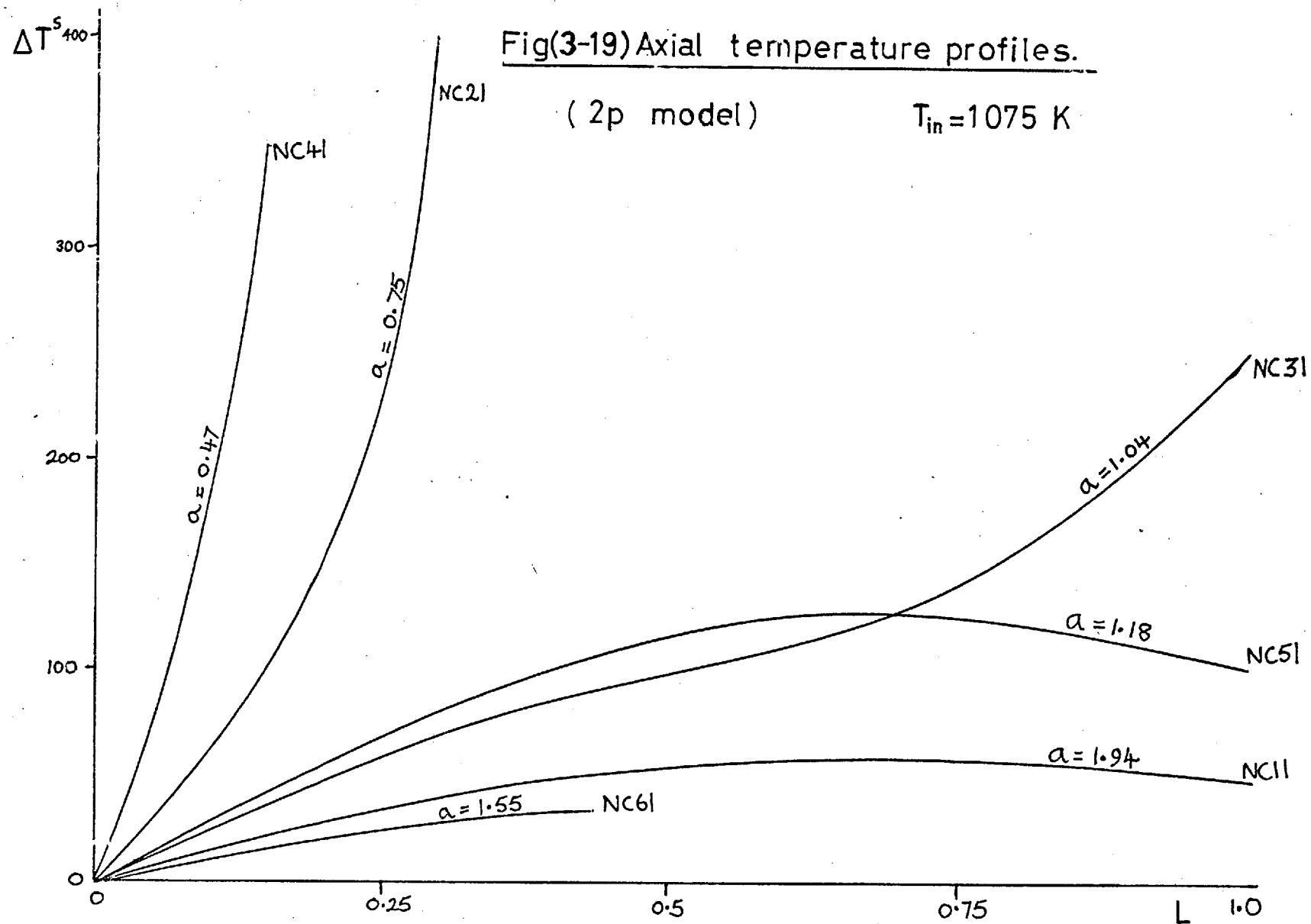
Runs NC11 and NC61 show similar reversal and have similarly disparate properties for the ratio of fluid to solid heat transfer.

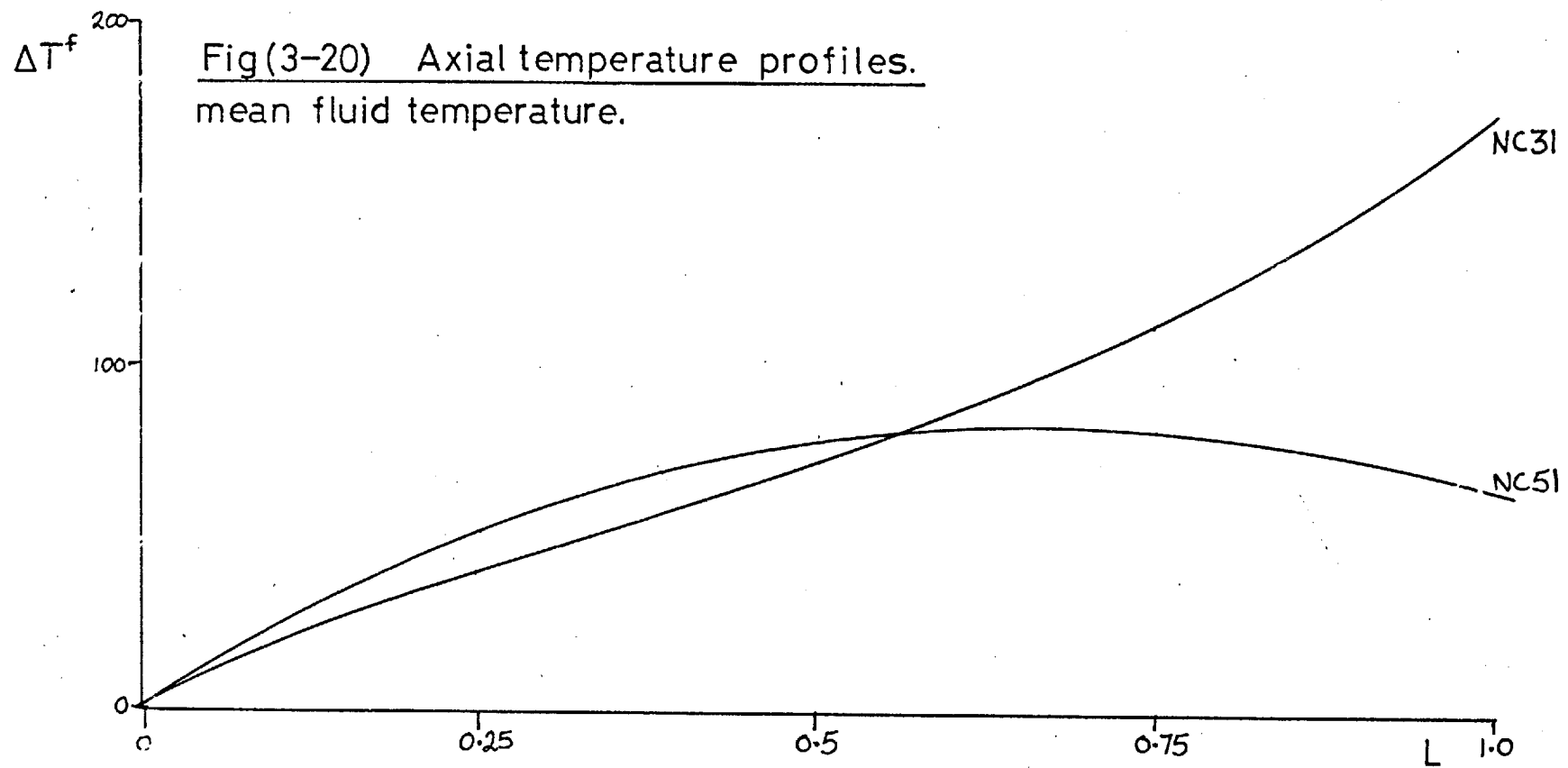
It is not possible, from the figures presented here, to quantify the effect of the distributed nature of the reactions occurring. Obviously, when using a pseudo-homogeneous model, it is not important whether a particular reaction is homogeneous or heterogeneous, providing that proper provision is made to account for the relative amounts of the two-phases in the hypothetical continuum. When the heat is considered to be transferred by separate, parallel, mechanisms (that is, when a two-phase model is used) it is important to specify which phase contains the heat source. In other words, the heterogeneous or homogeneous nature of the reaction, or reactions, must be specified. That this is so may be intuitively appreciated. Table (3.2) shows that the quantity of heat transferred by each phase may differ greatly and that greater heat transfer through the bed may be accompanied by approximately equal fluid-wall and solid-wall transfer. Indeed, as is evident in Case 4 of Table (3.2), the fluid-wall heat transfer may predominate.

Furthermore it will become more important to specify the location of the heat source, or sources, as the film heat transfer coefficient grows smaller. In contrast, as the film heat transfer coefficient approaches infinity, the film temperature difference falls to zero, heat transfer between the two phases is instantaneous and the location of the heat source is unimportant.

3.7 SENSITIVITY OF REACTOR MODELS TO HEAT TRANSFER PARAMETERS

It is an accepted difficulty in the modelling of fixed bed catalytic reactors that one limiting aspect in the sophistication of the models





employed is the accuracy with which the heat transfer data may be predicted. The degree of certainty in this data is not, in general, good (e.g. 68, 78) and this is especially so for two-phase heat transfer data (88). Consequently, it was felt desirable to study the effect of variation of the heat transfer parameters on the predictions of the reactor models. Each of the five heat transfer parameters - λr^f , λr^s , α_w^f , α_w^s and h_v - were varied by $\pm 15\%$ and the 1p and 2p models reintegrated with these values. The models were integrated for the conditions in Table (3.7) and the results in that table are the results of the unperturbed integrations.

The effect upon the predicted MSTR is shown in Table (3.11) for a parameter variation of $+15\%$ and in Table (3.12) for a parameter variation of -15% . As might be expected a low estimate for any of the five parameters leads to an increase in MSTR prediction whereas a high estimate leads to a decrease in MSTR prediction.

The figure of 15% does not represent an extreme uncertainty by any means. In fact uncertainties of 100%, particularly in the film heat transfer coefficient, are not uncommon.

Considering first, the results in Table (3.11), it can be seen that quite considerable error can result from this degree of uncertainty. For runs at high Biot number, e.g. runs NP11, NP21, NP71 variation in the bed conductivities is more significant than variation in the wall coefficients. At low Biot number, e.g. runs NP41, NP61, variation in the wall coefficient is the more significant. The relative importance of variation of λr^f and λr^s reflects the value of $\lambda r^f/\lambda r^s$ shown in Table (3.2). For low $\lambda r^f/\lambda r^s$, variation of λr^s is more significant and vice-versa. The same applies to the relative importance of variation of α_w^f and α_w^s with respect to α_w^f/α_w^s . These remarks apply to both 1p and 2p models and are supported by the results in Table (3.12).

Generally, the 2p model shows greater sensitivity to parameter variation than the 1p model. For parameter increases, i.e. temperature decreases, this brings the predictions of the models closer together but for parameter reductions, the predictions grow further apart.

In no case is this effect large enough to make the model predictions indistinguishable.

The variation of the fluid film heat transfer coefficient has no effect on the 1p model. This is because it does not appear explicitly in this formulation but, rather, is implicit in the correlation for λr^s (see Section (2.6)). Variation of this parameter can have an effect on the

Table (3.11)

Affect of heat transfer Parameter Variation on MSTR
Individual heat transfer parameters increased by 15%
Values given are percentage change in MSTR

RUN	λr^f		λr^S		α_w^f		α_w^S		h_v	
	1p	2p	1p	2p	1p	2p	1p	2p	1p	2p
NP11	-20.0	-20.7	-23.8		-6.7	-6.4	-5.2	-5.9	0	-0.23
NP12	-9.1	-13.1	-13.0	-18.4	-3.1	-4.4	-2.4	-4.1	0	-3.3
NP31	-15.8	-24.8	-14.4	-21.5	-17.2	-25.7	-1.7	-3.7	0	-4.7
NP41	-2.5	-3.8	-4.2	-6.6	-2.6	-4.1	-1.2	-2.4	0	-4.3
NP51	-10.7	-13.0	-12.9	-14.7	-10.1	-11.4	-4.4	-6.1	0	-1.6
NP61	-14.5	-19.3	-11.8	-13.3	-23.6	-28.3	0	0	0	-2.3
NP71	-0.10	-0.16	-0.08	-0.13	-0.01	-0.02	-0.0	-0.0	0	-1.81

Table (3.12)

Affect of Heat Transfer Parameter Variation on MSTR
Individual heat transfer parameters decreased by 15%
Values given are percentage charge in MSTR

RUN	λr^f		λr^S		α_w^f		α_w^S		h_v	
	1p	2p	1p	2p	1p	2p	1p	2p	1p	2p
NP11	48.3		81.2	87.8	9.7	9.4	6.8	8.1	0	0.31
NP12	12.5	22.1	21.3	43.8	3.8	5.8	2.8	5.2	0	5.1
NP31	32.5	64.4	26.3	53.2	42.0	68.3	1.8	4.2	0	7.6
NP41	2.8	4.4	5.0	8.9	3.0	5.0	1.3	2.7	0	7.1
NP51	15.6	21.6	20.4	26.9	15.4	19.1	5.1	7.7	0	2.3
NP61	24.9	44.2	17.5	21.1	70.7	140.4	0	-0.9	0	2.4
NP71	0.07	0.11	0.06	0.10	0.01	0.02	0	0.00	0	2.6

predictions of the 2p model, as might be expected; the effect generally becomes more significant as the unperturbed value of the parameter decreases and the film temperature difference becomes more significant. For example, variation of h_v by 15% results in a change in MSTR of $\sim 4\%$ in run NP41 but only 0.2% in run NP11.

The effect of an increase in a parameter is generally less severe than the effect of a decrease in the same parameter. This is to be expected from the exponential nature of the dependence of reaction rate on temperature.

The variation of the other quantities, FETR, C and S, follow the trends shown in Tables (3.11) and (3.12). Generally, the effect of variation of a parameter is greatest for the MSTR although it has been found that fluid-wall heat transfer coefficient variation results in a larger variation in FETR than MSTR in a number of cases. This is presumably because fluid-wall heat transfer tends to predominate over solid-wall heat transfer and the effect is transmitted through the fluid rather better than through the solid. Cases where this happens tend to have rather high values for $\lambda r^f / \lambda r^s$.

3.8 CONCLUSIONS

- i) The kinetic data of Halladay and Mrazek for heterogeneous and homogeneous stages in the thermal decomposition of nitrous oxide (8) has been incorporated into the three mathematical models for fixed bed catalytic reactors described in Chapter 2.
- ii) The models have been integrated for a wide variety of operating conditions and heat transport situations.
- iii) The accuracy of the finite difference methods used has been investigated. It has been found that the 1p and 2p models converge to definite solutions as the axial and radial steplengths are decreased and that these solutions are in general different.
- iv) Support has been found for the assertion by Beek (52) that the difference equations for the 1p model are stable for any values of the axial and radial steplengths.
- v) The 2p model, which differs in form from the 1p model only by the addition of a radial energy balance in the solid phase, was found to exhibit oscillatory numerical instability under certain conditions. This instability could occur under quite mild thermal conditions and,

converseley, situations were found where severe thermal gradients occurred but numerical instability was absent. Instability was only observed in those situations where solid phase heat transport predominated over fluid phase heat transport. It was not possible to identify the source of the instability but the stability of the 1p model, together with the factors mentioned above, led to a conclusion that inaccuracy in the solid-phase energy balance could lead to this type of instability.

- vi) Wide variations were found between the predictions of the 1p, 2p and 1d models. The variations increased as the thermal activity increased.
- vii) Differences in the prediction of temperature profiles in the bed were found to be the most significant. Differences in the predictions of conversion and selectivity were less but still significant.
- viii) There was a strong correlation between the difference between the 1p and 2p models and the fluid-solid film temperature difference in the 2p model.
- ix) The differences in the 2p and 1p model were discussed in the light of a similar study for a pure heterogeneous reaction (46).
- x) The 1d model was found to be a poor approximation to the 1p and, especially, the 2p models. The best agreement between 1p and 1d models was at low Biot numbers.
- xi) The shapes of the axial temperature profiles calculated fall into three types. The first two types correspond to reactors which are thermally stable or unstable respectively. In the third type, the profile is sigmoidal and indicates that the reactor, whilst being stable with respect to the heterogeneous reaction, is unstable with respect to the homogeneous reaction.
- xii) The situation referred to in (xi) is characteristic of the relative magnitudes of the activation energies of the various reactions, their relative initial rates and the relative kinetic orders of the reactions. It is not characteristic of the fact that the reactions are either heterogeneous or homogeneous in nature.
- xiii) When a two-phase model is considered, and heat is considered to be transported through the fixed bed by parallel mechanisms, it is essential, in complex reaction systems, to distinguish between those reactions occurring homogeneously and those reactions occurring heterogeneously.
- xiv) The sensitivity of the model predictions to variation in the heat

transfer parameters has been studied. Fairly small decreases in heat transfer parameters (15%) lead to quite large (up to 85%) increases in the prediction of MSTR. The effect of varying a particular parameter depends on the heat transfer regime of a particular case.

CHAPTER 4

APPLICATION OF REACTOR MODELS TO THE CATALYTIC OXIDATION OF METHANOL BY AIR

- 4.1 Introduction
- 4.2 Kinetics of the Catalytic Air Oxidation of Methanol
- 4.3 Gas-Phase Kinetics of Formaldehyde Combustion
- 4.4 Overall Rate of Formaldehyde Combustion
- 4.5 Gas Phase Oxidation of Methanol
- 4.6 Choice of Kinetic Model
- 4.7 Computational Aspects of Modelling the Oxidation of Methanol
- 4.8 Calculations on the Three Fixed-Bed Reactor Models for the Air Oxidation of Methanol
 - 4.8.1 Comparison of Models
 - 4.8.2 Axial and Radial Profiles
- 4.9 Conclusions

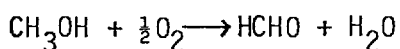
4.1 INTRODUCTION

The reaction scheme considered in the previous chapter was an example of a typical concurrent heterogeneous-homogeneous reaction system. Of more industrial importance are consecutive heterogeneous-homogeneous systems, particularly where catalytically formed products react further in the gas phase. The most obvious examples of this involve catalytic oxidations, where the product suffers further homogeneous combustion to form, eventually, carbon oxides and water. The homogeneous reactions could take place in the voids of the fixed bed or in the riser space following the bed. In the latter case the reaction could be accounted for by the methods of homogeneous reactor modelling (e.g. 2) and, in this chapter, attention will be focused on the possibility of gas phase reaction in the reactor voids. The example chosen for study was the air oxidation of methanol over oxide catalysts.

Mann (11, 12, 13) has worked with this system, and has found that formaldehyde yield passes through a maximum with increasing temperature. The post-maximum decrease in the formaldehyde yield is very rapid. A similar effect has been reported by McConkey and Wilkinson (103) for the air oxidation of methane to formaldehyde. This suggests that overoxidation of formaldehyde occurs above a certain temperature, but gas phase overoxidation has not been specifically cited by these authors.

4.2 KINETICS OF THE CATALYTIC AIR OXIDATION OF METHANOL

The primary formation of formaldehyde can be represented by:



The industrial reaction is widely reported both in the patent literature (104, 105, 106) and in recent studies by Pasquon (107) and Mann (11, 12, 13).

Two types of catalysts (silver metal or metallic oxides, and their mixtures) are used in the manufacture of formaldehyde by methanol oxidation. While silver catalysts employ rich methanol feeds with low conversions, oxide catalysts use lean methanol feeds and operate at high conversions and, providing the temperature is not too great, give high

yields of formaldehyde.

The kinetics over a $MnO_2 - MoO_3$ catalyst are summarised by (11):

$$r' = \frac{k_1' g^m}{1 + k_1' g^m / 2k_2' g^{0.5}} \quad (4.1)$$

where r' is the rate of disappearance of methanol.

The rate constants in (4.1) are:

$$\begin{aligned} k_1' &= 2.71 \times 10^3 \exp(-17.4/RT) \\ k_2' &= 3.09 \times 10^{-8} \exp(14.76/RT) \end{aligned} \quad (4.2)$$

When the catalyst consists of $V_2O_5 - MoO_3$ oxides the rate constants are given by (13):

$$\begin{aligned} k_1' &= 5.93 \exp(-10.8/RT) \\ k_2' &= 1.43 \exp(-9.3/RT) \end{aligned} \quad (4.3)$$

Industrial usage of these catalysts at low methanol air feed ratios allows the use of a pseudo first order rate law. This is confirmed in a recent study by Beskov et al. (108).

There is some ambiguity in the units of the rate constants presented in Mann's work. However, if his graphical results (11, 13) of initial rate vs methanol feed ratio are used, the 'true', pseudo-first order rate constants can be deduced. The activation energies may be extracted without ambiguity. This approach leads to the following rate laws for methanol oxidation.

$$r' = k_{het}' \rho g^m \quad \text{kg m}^{-3} \text{ sec}^{-1} \quad (4.4)$$

For the $MnO_2 - MoO_3$ catalyst the rate constant is:

$$k_{het}' = 8.64 \times 10^7 \exp(-17.43/RT) \text{ sec}^{-1} \quad (4.5)$$

and the for $V_2O_5 - MoO_3$ catalyst it is:

$$k'_{\text{het}} = 2.69 \times 10^6 \exp(-10.8/RT) \text{sec}^{-1} \quad (4.6)$$

This is in good general agreement with values reported by Beskov et al. (108) for methanol oxidation over iron-molybdenum oxide catalysts.

The heat of reaction for methanol oxidation (102) is

$$(-\Delta H)_{298} = 4.9 \times 10^6 \text{ J kg}^{-1} (\text{CH}_3\text{OH})$$

4.3 GAS-PHASE KINETICS OF FORMALDEHYDE COMBUSTION

The gas-phase combustion of formaldehyde has recently attracted much attention (109, 110). Interest in this reaction is partly because of the simple nature of formaldehyde, containing only one carbon atom, but principally because aldehydes are recognised as being instrumental in the initiation of the combustion of many organic materials (110).

The mechanism may be summarised by:

- (i) The oxidation is a degenerately branched chain reaction.
 - (ii) The overall reaction is second-order in formaldehyde and zero-order in oxygen.
 - (iii) The overall activation energy lies in the range 17-25 Kcal/mole.
- The radical mechanism proposed by Hay and Hessam (110) has been used in this study. This kinetic scheme, together with the Arrhenius parameters used, is shown in Table (4.1). The formation of the major products of the reaction, including formic acid and hydrogen peroxide, are explained by this mechanism.

4.4 OVERALL RATE OF FORMALDEHYDE COMBUSTION

It would be desirable to provide a lumped parameter kinetic expression for the formaldehyde oxidation which is consistent with the principal kinetic features of the reaction described in the previous section.

A material balance for each of the important species yields.

$$-\frac{d[\text{HCHO}]}{dt} = k_3' [\text{HCO}_3] [\text{HCHO}] + k_4' [\text{OH}] [\text{HCHO}] \\ + (k_7' + k_8) [\text{HCHO}] [\text{HO}_2] + k_1' [\text{HCHO}] [\text{O}_2]$$

Table (4.1)

Mechanism and Arrhenius parameters for formaldehyde Oxidⁿ.

REACTION		$\log_{10} A$	E_A	Ref
$\text{HCHO} + \text{O}_2 \longrightarrow \text{HCO} + \text{HO}_2$	1	10.65	41.0	109
$\text{HCO} + \text{O}_2 \longrightarrow \text{HCO}_3$	2	8.3	0	111a
$\text{HCO}_3 + \text{HCHO} \longrightarrow \text{HCO}_3\text{H} + \text{HCO}$	3	9.28	7.2	111b
$\text{HCO}_3\text{H} \longrightarrow \text{OH} + \text{products}$	4		30	112c
$\text{HCO} + \text{O}_2 \longrightarrow \text{HO}_2 + \text{CO}$	5	7.78	0	109
$\text{OH} + \text{HCHO} \longrightarrow \text{HCO} + \text{H}_2\text{O}$	6	10.98	0	109
$\text{HO}_2 + \text{HCHO} \longrightarrow \text{OH} + \text{products}$	7	10.06	11	109d
$\text{HO}_2 + \text{HCHO} \longrightarrow \text{H}_2\text{O}_2 + \text{HCO}$	8	10.06	11	109
$2\text{HO}_2 \xrightarrow[\text{solids}]{\text{walls}} \text{termination}$	9	8.78	0	109

Notes:

 E_A is in Kcal mole⁻¹A is in the K mole - m³ - sec system of unitsa) assumed same as $\text{CH}_3\text{CO} + \text{O}_2 \longrightarrow \text{CH}_3\text{CO}_3$ b) assumed same as $\text{CH}_3\text{CO}_3 + \text{CH}_3\text{CHO} \longrightarrow \text{CH}_3\text{CO}_3\text{H} + \text{CH}_3\text{CO}$

c) Pre-exponential factor not found in literature

d) assumed same as reaction VIII: ref. (112)

$$\frac{d[\text{HCO}_3]}{dt} = k_2' [\text{HCO}] [\text{O}_2] - k_3' [\text{HCO}_3] [\text{HCHO}]$$

$$\frac{d[\text{HCO}_3\text{H}]}{dt} = k_3' [\text{HCO}_3] [\text{HCHO}] - k_4' [\text{HCO}_3\text{H}]$$

$$\begin{aligned} \frac{d[\text{HO}_2]}{dt} = & k_5' [\text{HCO}] [\text{O}_2] - (k_7' + k_8') [\text{HO}_2] [\text{HCHO}] \\ & - k_9' [\text{HO}_2]^2 + k_1' [\text{HCHO}] [\text{O}_2] \end{aligned}$$

$$\frac{d[\text{OH}]}{dt} = k_4' [\text{HCO}_3\text{H}] - k_6' [\text{OH}] [\text{HCHO}] + k_7' [\text{HCHO}] [\text{HO}_2]$$

$$\begin{aligned} \frac{d[\text{HCO}]}{dt} = & k_3' [\text{HCO}_3] [\text{HCHO}] - k_5' [\text{HCO}] [\text{O}_2] - k_2' [\text{HCO}] [\text{O}_2] \\ & + k_6' [\text{OH}] [\text{HCHO}] + k_8' [\text{HO}_2] [\text{HCHO}] + k_1' [\text{HCHO}] [\text{O}_2] \end{aligned}$$

In the context of the present work the rate of formaldehyde disappearance is of more immediate concern than the rates of appearance of the various products.

Applying the steady state assumption to species HCO_3 , HO_2 , HCO , OH and HCO_3H , that is;

$$\frac{d[\text{HO}_2]}{dt} = 0; \quad \frac{d[\text{HCO}_3]}{dt} = 0; \quad \frac{d[\text{OH}]}{dt} = 0$$

$$\frac{d[\text{HCO}]}{dt} = 0 \text{ and } \frac{d[\text{HCO}_3\text{H}]}{dt} = 0$$

and if it is assumed that $k_2'^2$ is small and that k_7' is equal to k_8' then, neglecting the initiation reaction, it can be shown that (112):

$$-\frac{d[\text{HCHO}]}{dt} = 18 \frac{k_2' k_8'^2}{k_5' k_9'} [\text{HCHO}]^2 \quad (4.7)$$

This expression successfully represents the second order dependence of the rate on formaldehyde and the zero-order dependence on oxygen.

Expanding (4.7) in terms of Arrhenius Parameters gives

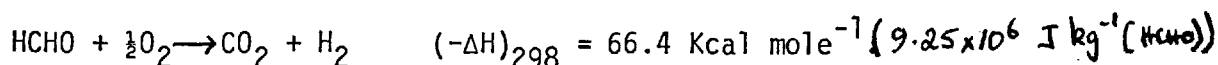
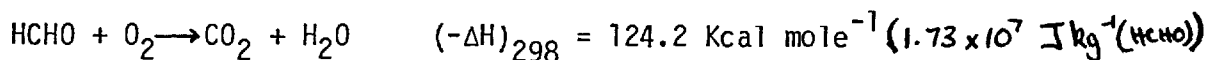
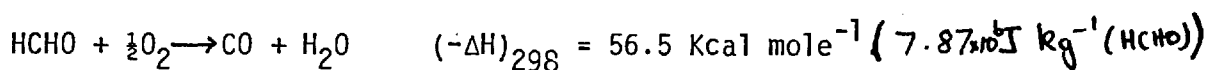
$$-\frac{d[\text{HCHO}]}{dt} = 18 \frac{A_2 A_8^2}{A_5 A_9} \exp \left(- \frac{(E_{A2} + 2E_{A8} - E_{A5} - E_{A9})}{RT} \right) [\text{HCHO}]^2 \quad (4.8)$$

Substituting the values for A and E_A from Table (4.1) into Equation (4.8), the following expression results:

$$-\frac{d[\text{HCHO}]}{dt} = 3.9 \times 10^{14} \exp\left(-\frac{22}{RT}\right) \rho^2 (g^F)^2 \quad \text{kg m}^{-3} \text{ sec}^{-1} \quad (4.9)$$

The value for overall activation energy, 22 Kcal/mole, is within the experimental range of 15 to 27 Kcal/mole.

The heat release during the reaction is calculated on the basis of formaldehyde consumption. The overall reaction of formaldehyde may be described stoichiometrically in three ways.



These three reactions account for all the major products. If the reactions occur in the proportion a:b:c respectively, then the overall heat of reaction is given by

$$(-\Delta H)_{298} = 56.5a + 124.2b + 66.4c$$

The ratios of the product concentrations are:

$$\frac{(\text{CO})}{(\text{H}_2\text{O})} = \frac{a}{a+b}; \quad \frac{(\text{CO}_2)}{(\text{H}_2\text{O})} = \frac{1-a}{a+b}; \quad \frac{(\text{H}_2)}{(\text{H}_2\text{O})} = \frac{1-a-b}{a+b}$$

and, of course, $a+b+c = 1$.

Hessam (112) reports that:

$$\frac{\text{CO}}{\text{H}_2\text{O}} = 0.84; \quad \frac{\text{CO}_2}{\text{H}_2\text{O}} = 0.57; \quad \frac{\text{H}_2}{\text{H}_2\text{O}} = 0.40$$

and so, solving for a, b, and c;

$$a = 0.60 \quad b = 0.11 \quad \text{and} \quad c = 0.29$$

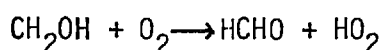
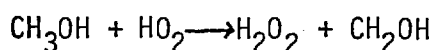
Therefore, the heat of reaction was calculated as (102);

$$(-\Delta H)_{298} = 9.3 \times 10^6 \text{ J kg}^{-1}(\text{HCHO})$$

Beskov et al. (108) include an expression for heterogeneous overoxidation of formaldehyde in their analysis of catalytic methanol oxidation. However, for fairly typical conditions of 1% formaldehyde at 600K, the homogeneous overoxidation rate is more than 2000 times the heterogeneous rate and heterogeneous formaldehyde oxidation can be neglected.

4.5 GAS-PHASE OXIDATION OF METHANOL

There is a possibility that parallel gas-phase oxidation of methanol may occur, and Minkoff and Tipper (113) suggest that the following radical reactions can occur.



However, Mann and Kahn (12) show that the rate of methanol oxidation increases steadily with temperature even when overoxidation of the formaldehyde is almost complete. It would appear that gas-phase overoxidation of methanol is not significant under industrial conditions.

4.6 CHOICE OF KINETIC MODEL

In choosing a kinetic system to model, there is an alternative for both the heterogeneous and homogeneous reactions.

The heterogeneous reaction may be modelled for either a $\text{MnO}_2 - \text{M}_2\text{O}_3$ catalyst or a $\text{V}_2\text{O}_5 - \text{MoO}_3$ catalyst and the two catalysts have very different ^(heterogeneous) activation energies with regard to methanol oxidation. It was decided to use the reaction with the lowest activation energy as this will lead to larger differences between homogeneous and heterogeneous reactions and the variation of the rates of these reactions with temperature will be most disparate.

The homogeneous reaction may be modelled either as a branched chain radical reaction or by using the lumped parameter approximation of

equation (4.9). In the former case a mass-balance for each of the seven species would be included in the reactor model and the conservation equations would be solved for each species.

This approach was discarded at this stage for two reasons. Firstly, this would mean the solution of nine conservation equations, compared to three equations for the lumped parameter model. It has been found, in the previous chapter that, because of the large number of axial and radial steps required to obtain accurate solutions to the conservation equations, the effect of a threefold increase in computational effort, whilst not being prohibitive, would be undesirable. Of more importance, however, was the probability that the number of axial and radial steps required for integration of a system of equations representing a set of radical reactions in a fixed-bed reactor would be very large indeed, as studies of the time-integration of free radical systems have revealed (114, 115) that extremely short steplengths are required for solution stability. The problem could very easily become too large to handle.

Consequently, the lumped parameter model has been used to represent the gas phase oxidation of formaldehyde.

4.7 COMPUTATIONAL ASPECTS OF MODELLING THE OXIDATION OF METHANOL

In the integration of this system, three dependent variables were considered viz. temperature, mass fraction of methanol and mass fraction of formaldehyde.

In the two-phase, two-dimensional model for the fixed-bed reactor the following source terms were defined:

$$\begin{aligned}
 F^M &= \frac{\epsilon k'_{\text{het}} (1-\phi) \rho g^M}{G} \\
 F^F &= \frac{0.9375 \epsilon k'_{\text{het}} (1-\phi) \rho g^M}{G} - \frac{\phi k'_{\text{hom}} (g^F)^2}{G} \\
 F^S &= (1-\phi) \epsilon k'_{\text{het}} c_g^M (-\Delta H)_{\text{het}} \\
 F^f &= \frac{\phi \rho^2}{G C \rho} k'_{\text{hom}} (g^F)^2 (-\Delta H)_{\text{hom}}
 \end{aligned} \tag{4.10}$$

k'_{het} is evaluated at T^S and k'_{hom} is evaluated at T^f . ϵ is the catalyst pellet effectiveness factor given by (1):

$$\epsilon = \frac{3}{h} \left(\frac{1}{\tanh h} - \frac{1}{h} \right) \quad (4.11)$$

where $h = \frac{d_p}{2} \sqrt{\frac{k'_{het}}{Deff}}$

The effective diffusivity of the pellet was taken as $0.1 \times 10^{-5} \text{ m}^2 \text{ sec}^{-1}$. This is the isothermal effectiveness factor and refers to surface temperatures and concentrations. It has been shown in the preceding chapter, that film mass transfer resistance may be neglected, and many recent studies (e.g. 57) have found that intra-pellet temperature differences are small in comparison with film temperature differences. Thus the use of the isothermal effectiveness factor in the two-phase model (2p) is completely justified.

In the one-phase, two dimensional model (1p) F^f and F^S are replaced by:

$$F^C = \frac{1}{GC_p} ((1-\phi)\epsilon k'_{het} \rho g^M (-\Delta H)_{het} + \phi \rho^2 (g^F)^2 k'_{hom} (-\Delta H)_{hom}) \quad (4.12)$$

F^M and F^F remain as before with the exception that all rate constants are now evaluated at temperature T^c .

For the one-phase, one-dimensional model (1d) the source terms required are F^M , F^F and F^c . In this case F is defined by:

$$F^c = \frac{1}{GC_p} ((1-\phi)\epsilon k'_{het} \rho g^M (-\Delta H)_{het} + \phi \rho^2 (g^F)^2 k'_{hom} (-\Delta H)_{hom}) - \frac{2U}{R_t} (T^c - T_W) \quad (4.13)$$

All rate constants are again evaluated at temperature T^c .

Thus, equations (4.10), (4.12) and (4.13) are substituted into the relevant conservation equations to yield the mass and energy conservation equations for the two-phase, two-dimensional; one-phase, two-dimensional and one-phase, one-dimensional models.

The use of ϵ as defined by (4.11) in (4.12) and (4.13) requires further discussion. As defined, the effectiveness factor does not take into account film temperature and mass differences. In the continuum model these are assumed negligible, and the use of this value for ϵ is strictly justifiable.

However, solutions for the internal pellet diffusion problem have been presented which take these differences into account (e.g. 48, 116). Thus it would be possible to use such a representation of ϵ to partially account for solid-fluid temperature differences with respect to reaction rate in the solid. However, evaluation of the effectiveness factor in this way is a time consuming procedure (48) and it is very likely that the solution of the full two-phase model using the isothermal effectiveness factor would be quicker, computationally, than solution of the one-phase model with calculation of a non-isothermal effectiveness factor. This latter approach could possibly be speeded up by neglecting intra-particle temperature gradients, as in the two-phase model, and considering only the film resistances. A future investigation into the evaluation of the effectiveness factor in one-phase and two-phase models would prove advantageous.

The remarks made in Section 3.4 concerning fluid properties and the temperature dependence of heat transfer parameters apply also to this section. As the feed in this system is at least 90% air, the same values for the fluid properties have been used as above (Chapter 3).

The computer subroutines used for obtaining these results were essentially as described in Section 3.4. Subroutine CMSYS2 was used in place of subroutine CMSYS1 etc.

SUBROUTINE CMSYS2. Formally identical to CMSYS1 (Section 3.4)

SUBROUTINE RSSYS2. Calculates F^S , F^{CH_3OH} and heterogeneous contribution to F^{HCHO} in two-phase model.

SUBROUTINE RFSYS2. Calculates F^f , and homogeneous contribution to F^{HCHO} in two-phase model.

SUBROUTINE RCSYS2. Calculates F^C , F^{CH_3OH} and F^{HCHO} for one-phase, two-dimensional model.

SUBROUTINE RISYS2. Calculates F^C , F^{CH_3OH} and F^{HCHO} for one-phase, one-dimensional model.

4.8 CALCULATIONS ON THE THREE FIXED-BED REACTOR MODELS FOR THE AIR OXIDATION OF METHANOL

The operating conditions chosen for investigation for the air oxidation of methanol corresponded to cases 1, 4, 6 and 7 in Table (3.2). These four cases were chosen because, as reference to Figure (3.1) will show, they form extreme cases in the plot of $\lambda r^f / \lambda r^S$ vs Bi^C space. Three

temperatures were considered, viz 383K, 403K and 423K, such that even at the highest of these temperatures, formaldehyde over-oxidation has been found to be unimportant in isothermal reactors (12). The reactor wall temperature is assumed constant and equal to the inlet feed temperature. These temperatures are practically realisable by the use of saturated steam as a cooling medium at 1 bar, 2 bars and 3.5 bars respectively.

The results of these calculations are shown in Tables (4.2) to (4.5). The numbering of the runs is as follows. The first character, M, refers to a calculation on the methanol system. The second character, 1, 4, 6 or 7, refers to a particular heat transfer situation as described in Table (3.2) and the final character, 1, 2 or 3, refers to a calculation at 383K, 403K or 423K respectively. Thus run M62 is a calculation for heat transfer situation 6 with a feed temperature of 403K. All runs were based on an inlet mass fraction of 3.8% methanol.

4.8.1 COMPARISON OF MODELS

It is a noticeable feature of these results that, in contrast to the results for the N_2O system, the three models are generally in rather good agreement. The agreement between the 1p and 2p models reflect the generally smaller fluid-pellet temperature differences, as a result of the fact that when oxidation of formaldehyde becomes important (as indicated by a low value for S, the selectivity to formaldehyde) the rate of heat release in the two phases becomes comparable and, indeed, the rate of heat release in the fluid-phase eventually becomes greater than that in the solid-phase. Thus, from Table (4.2) the following flow averaged exit conditions may be calculated for run M11:

$$g^M = 0.02 \quad g^F = 0.0079 \quad \rho = 0.74 \quad T^F = 478K$$

The rate of heat release in the solid-phase is calculated from (4.10) and (4.11) as $1.1 \times 10^5 J/M^3$ whereas in the fluid-phase heat release calculated from (4.10) leads to a figure of $4.1 \times 10^6 J/M^3$.

At the reactor entry only heterogeneous reaction will occur* and a fluid-solid temperature difference will gradually build up. However, at a certain length along the reactor two effects will cause the homogeneous reaction to become significant: the temperature of the fluid

$$* \text{ as } R_{het} \gg R_{hom}$$

Table (4.2)

Model Predictions for Operating Conditions 1

Run	T_{in}^f	L	2 - p					1 - p				1 - d			
			MSTR	MFTR	FETR	C	S	MSTR	FETR	C	S	MSTR	FETR	C	S
M11	383	0.685	221.8	221.6	95.8	47.7	44.1	213.2	92.6	97.2	45.3	24.0	24.0	39.9	84.9
M12	403	0.265	241.6	241.1	105.7	37.9	39.1	232.2	100.9	36.9	43.7	66.7	66.7	35.2	65.1
M13	423	0.145	230.3	229.1	113.2	34.9	32.4	225.6	110.9	34.5	34.5	121.3	121.3	35.5	25.8

Table (4.3)

Model predictions for Operating Conditions 4

Run	T_{in}^f	L	2 - p					1 - p				1 - d			
			MSTR	MFTR	FETR	C	S	MSTR	FETR	C	S	MSTR	FETR	C	S
M41	383	0.275	209.1	206.9	128.7	39.9	22.2	194.7	121.0	38.5	25.4	141.5	141.5	39.1	13.6
M42	403	0.165	189.3	185.2	118.5	33.6	20.3	176.8	115.0	32.9	21.4	140.6	140.6	34.9	10.0
M43	423	0.110	177.8	171.7	119.2	31.1	14.1	160.1	112.4	29.6	16.1	133.8	133.8	31.4	9.22

Table (4.4)

Model predictions for operating conditions 6

R	T_{in}^f	L(m)	2 - p					1 - p				1 - d			
			MSTR	MFTR	FETR	C	S	MSTR	FETR	C	S	MSTR	FETR	C	S
M61	383	2.3	41.6	41.6	24.0	62.0	48.4	40.2	23.3	61.6	49.4	20.1	19.3	60.8	56.1
M62	403	0.9	143.0	142.6	88.1	54.0	13.3	141.0	87.3	53.4	13.9	88.8	87.0	53.1	13.3
M62	423	0.46	158.6	157.5	101.4	40.6	13.4	153.2	99.4	40.0	14.1	107.6	107.6	41.3	10.8

Table (4.5)

Model predictions for operating conditions 7

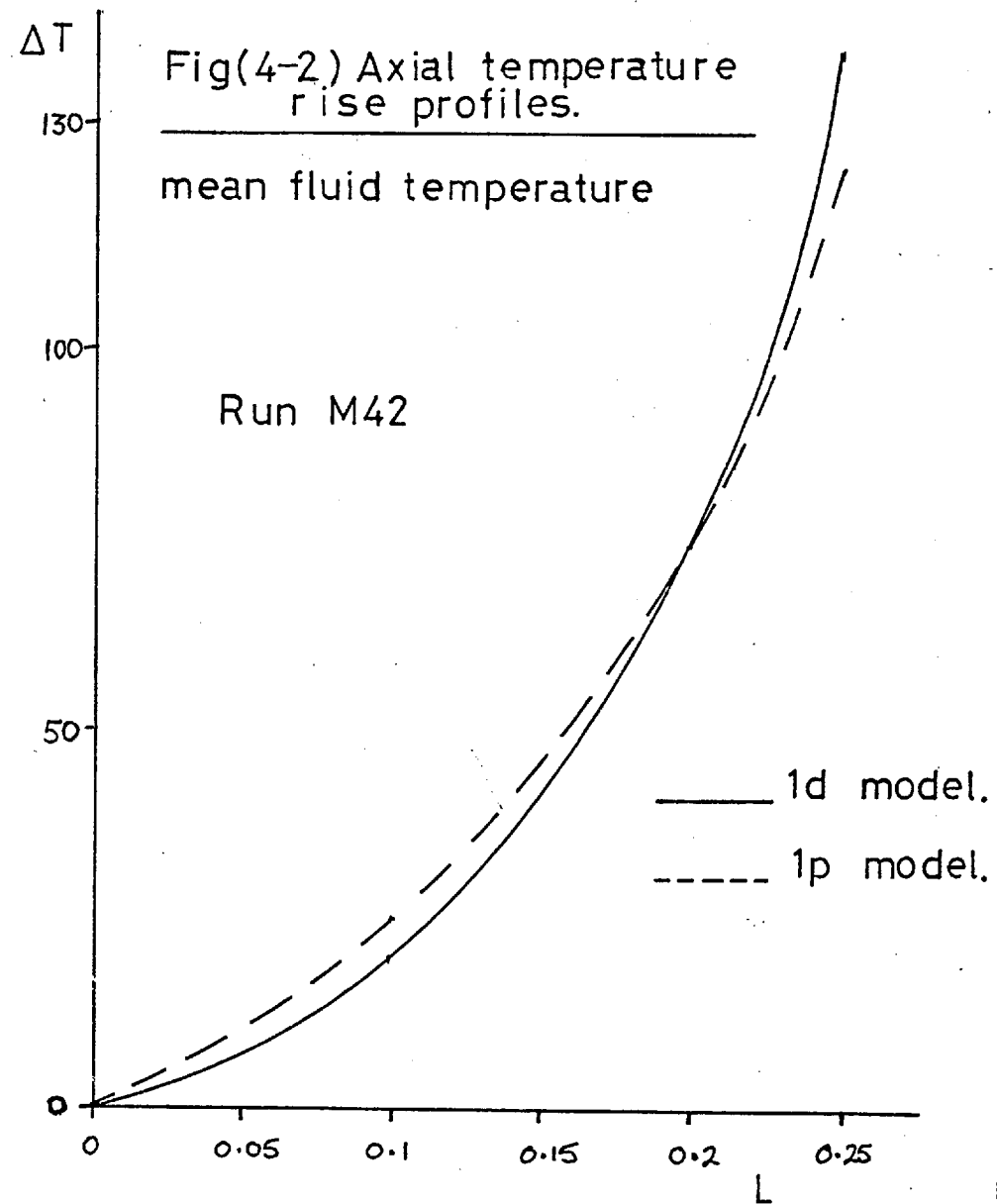
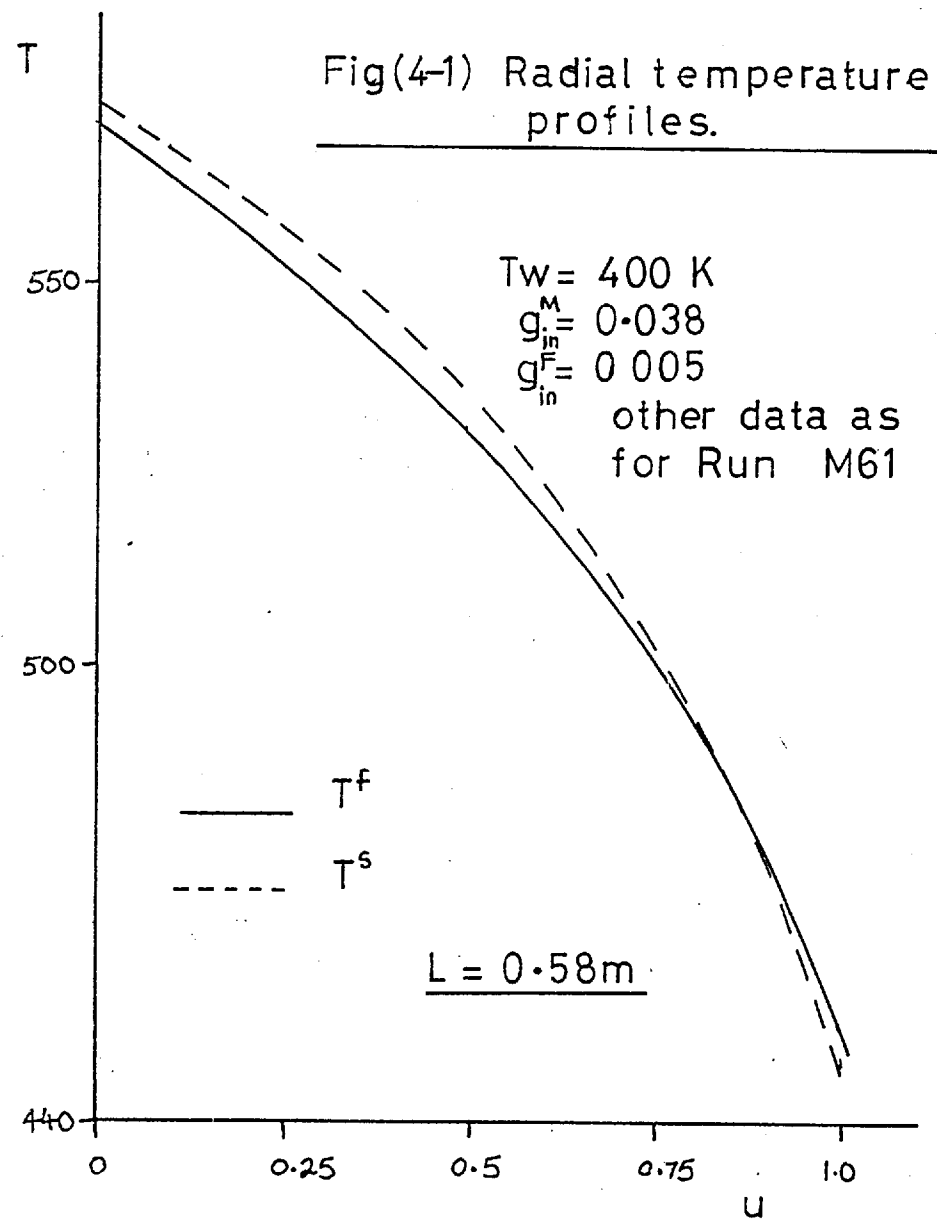
R	T_{in}^f	L(m)	2 - p					1 - p				1 - d			
			MSTR	MFTR	FETR	C	S	MSTR	FETR	C	S	MSTR	FETR	C	S
M71	383	0.59	234.2	231.3	130.7	35.4	30.4	220.4	124.4	34.4	32.4	173.1	173.1	37.2	10.6
M72	403	0.38	197.9	194.8	133.8	33.5	20.7	186.9	130.8	32.6	22.5	172.9	172.9	35.7	7.7
M73	423	0.26	173.4	170.1	135.2	31.1	14.7	163.4	129.9	30.4	16.1	161.1	161.1	32.9	7.6

increases and the mass fraction of formaldehyde in the fluid phase becomes relatively large. Then the heat release in the two-phases becomes comparable and the fluid-solid temperature difference decreases with respect to reactor length. When the overoxidation becomes very significant, the film temperature difference decreases more rapidly with respect to length, to the point where the fluid could become hotter than the solid.

This is not evident from the present results, but to 'force' this theoretical situation, calculations were made for heat transfer conditions 6 considering a feedstock containing formaldehyde (3.8% methanol, 0.5% formaldehyde, temperature 400K). The radial temperature profile at a length of 0.58m is shown in Figure (4.1). It is, at first, somewhat surprising that the 'temperature reversal' has not occurred at the centre line (the hottest part of the reactor) where the homogeneous rate constant is greatest. However, increased activity along the reactor centre-line has led to formaldehyde depletion at this point which, especially in view of the second-order dependence of the homogeneous rate on formaldehyde, causes a lowered rate of homogeneous reaction at this point.

Rather more surprising than the good agreement between the 1p and 2p models is the relationship between the 1p and 1d models. Three situations exist: in the first, the agreement between the models is poor and the predictions of the 1d model are much lower than the predictions of the 1p models. Examples of this situation are runs M11, M12, and M61. In the second situation, good agreement is achieved between the 1p and 1d models. Examples of this situation are runs M13 and M62. It is particularly worthy of note that these runs are at opposite ends of the heat transfer scale with respect to the Biot number, and it was this parameter that principally correlated agreement between 1p and 1d models when the nitrous oxide system was considered.

In the remaining runs, not only is the agreement between the models poor, but the 1d model predicts temperatures and conversions that are greater than those predicted by the 1p model. It will be noticed that this situation only occurs when the pellet diameter is relatively large, or at very high temperatures, and it is concluded that the phenomenon is caused by the influence of the effectiveness factor on the heterogeneous rate. Near the tube centre, the 1d model underestimates the fluid temperature and, therefore overestimates the effectiveness factor. Clearly, a case can be envisaged where the effect of a decrease in effectiveness factor, due to a rise in temperature, will seriously moderate the effect of the increase in the absolute rate constant.



The 'observed' rate may be characterised by the product of rate constant and effectiveness factor. The derivative of the observed rate cannot become negative.

Now,

$$\epsilon k'_{het} = \frac{3}{h} \left(\frac{1}{\tanh h} - \frac{1}{h} \right) \cdot k'_{het} \quad (4.14)$$

The effect described is only likely to be of importance when diffusional limitations are large, that is when h is large. Then:

$$\epsilon k'_{het} = \frac{3k'_{het}}{h} \left(1 - \frac{1}{h} \right) \quad (4.15)$$

and

$$\frac{d(\epsilon k'_{het})}{dT} = \frac{3k'_{het} E_{Ahet}}{2hRT^2} \quad (4.16)$$

which is always positive. If the full expression for $(\epsilon k'_{het})$ is differentiated with respect to temperature, then:

$$\frac{d(\epsilon k'_{het})}{dT} = \frac{3k'_{het} E_{Ahet}}{hRT^2} \left[\frac{1}{\tanh(h)} \frac{h}{2} + \frac{1}{2} - \frac{h \operatorname{Cosech}^2(h)}{2} \right] \quad (4.17)$$

For this to be negative, it is required that:

$$h \sinh(2h) \left[\frac{h}{2} + \frac{1}{2} \right]$$

but this cannot be so for positive h , as $\sinh(h)$ is always greater than h . Thus the effect of intra-pellet diffusion is to reduce the derivative of observed reaction rate with respect to temperature. The derivative cannot, however, become negative and, providing the activation energy is greater than zero, the observed rate will always increase with temperature.

In the two-dimensional model there will also be reactant depletion near the centre-line. That these arguments may explain the relationship between the predictions of the 1d and 1p models for some runs is shown by Figure (4.2), which presents the fluid mean temperature rise as a function of reactor length for run M42. At first the prediction of the 1d model is less than that of the 1p model but, later in the integration, when the 1d model starts to overestimate the heterogeneous reaction near

the reactor centre, and the prediction 'overtakes' the solution of the 1p model. Of course, the 1d model will underestimate the rate of reaction near to the tube wall by an analogous argument. However, the shape of the curve of effectiveness factor against h (e.g. 1) is such that this phenomenon is not pronounced as that occurring near the reactor centre. It may be pointed out that these results are in contradiction to a statement by Froment (68) that the predictions of the mean values of temperature by the 1d model are always low compared to the 1p model. The homogeneous reaction will have a supporting role in this situation, in that the enhanced heat and formaldehyde production predicted by 1d model at the tube centre will lead to a prediction of an enhanced homogeneous reaction.

It may be said at this stage, therefore, that there are differences between the predictions of the 2p, 1p and 1d models when they are used to represent the air oxidation of methanol in a fixed-bed reactor. The differences between the 1p and 2p models are not as pronounced as those found for the decomposition of nitrous oxide, but the greatest discrepancies are, again, found to occur when the film temperature differences, predicted by the 2p model, are greatest. That these temperature differences are not as great in this system as for the nitrous oxide system, despite greater overall thermal activity in this system, is attributed to the fact that heat release is more evenly distributed between the two phases once homogeneous reaction becomes significant.

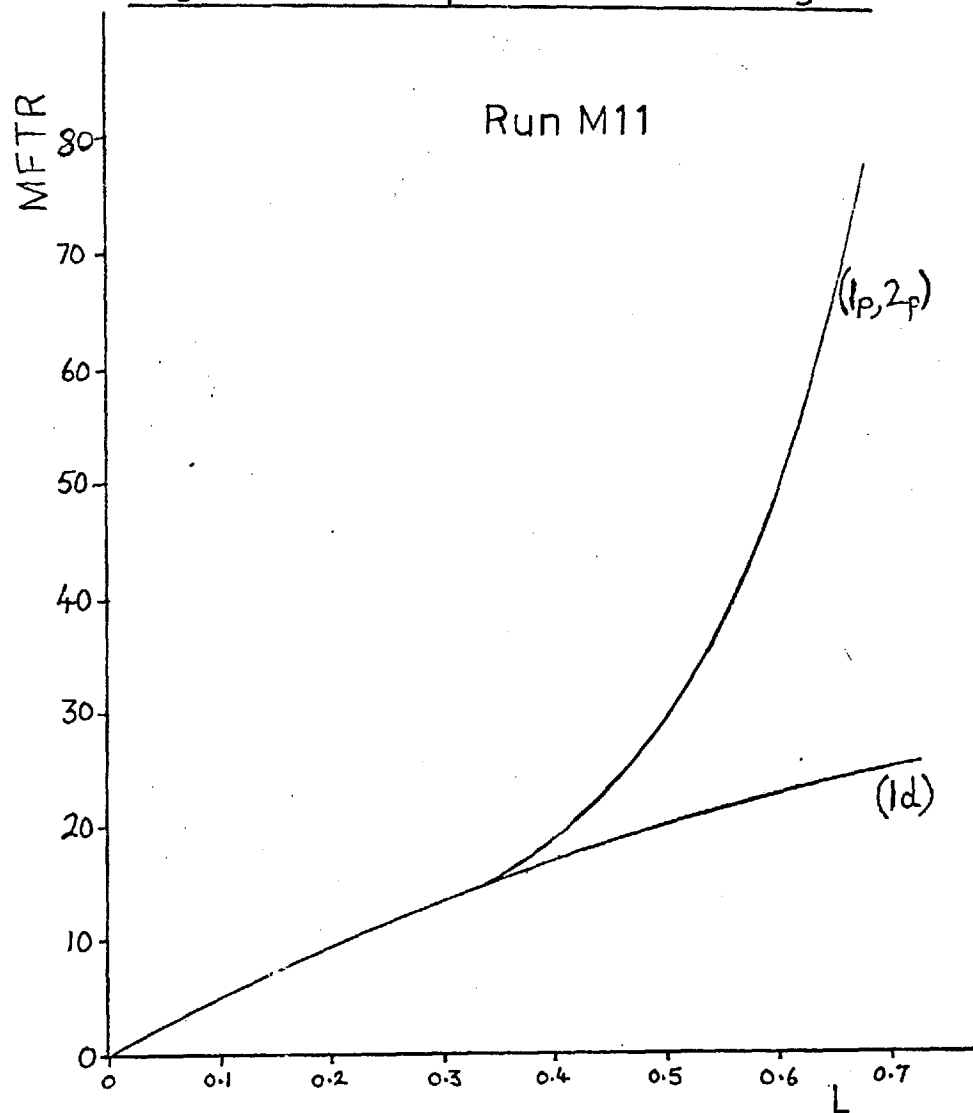
The behaviour of the 1d model relative to the 1p model is different to that found in the nitrous oxide system. The 1d model still provides a poor, conservative estimate of the reactor hot spot temperature (in this case invariably the solids centreline temperature at the exit). However, the 1d estimate of FETR is not always a poor estimate and, more significantly, is not always a low estimate. This situation is attributed to the effect of the variation of pellet effectiveness factor with temperature across a radius of the reactor.

4.8.2. Axial and Radial Profiles

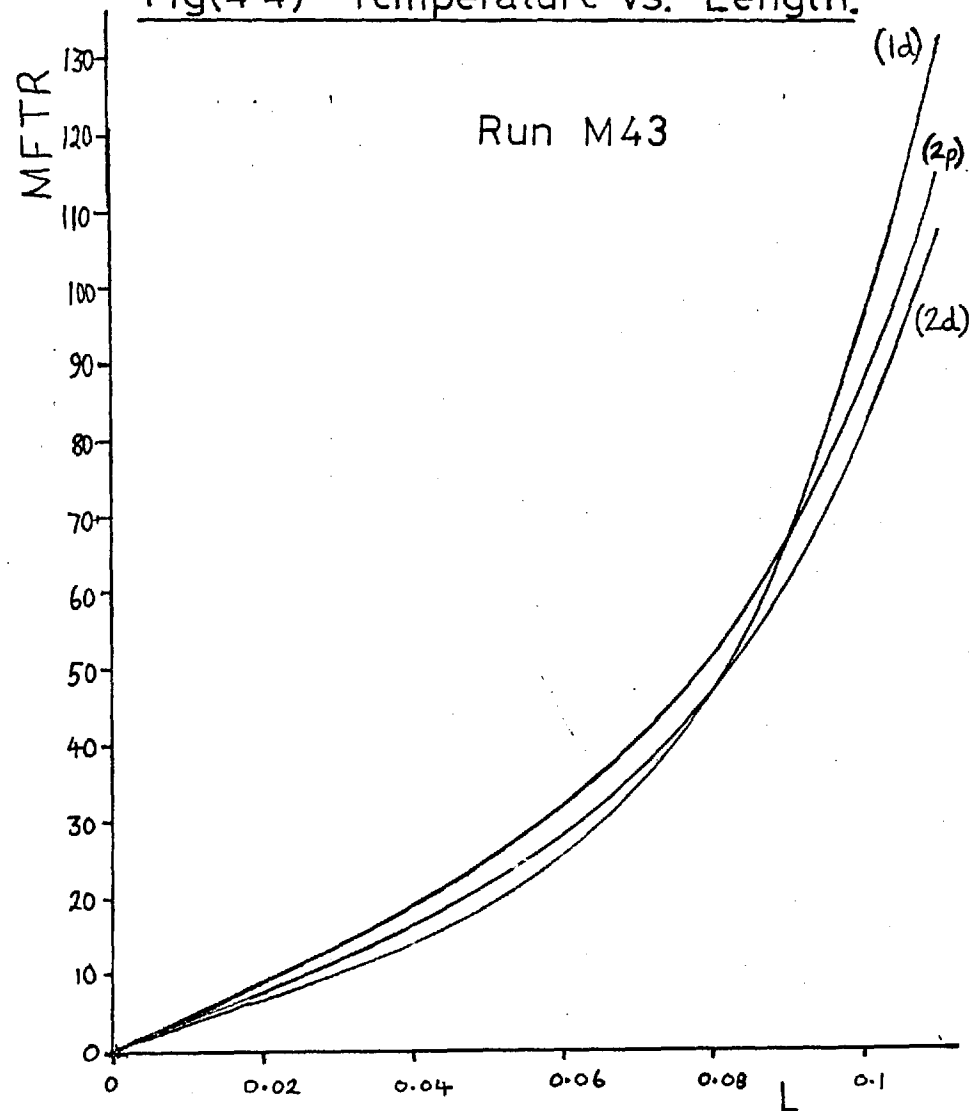
The shape of the axial and radial profiles calculated may now be discussed. The radial profiles were, generally, of the same shape as those found in the N_2O system.

In Figure (4.3) the mean fluid temperature rise is shown as a function of length for the three models in run M11 and, in Figure (4.4), the same curves are drawn for run M43. Figures (4.5) to (4.8) show the

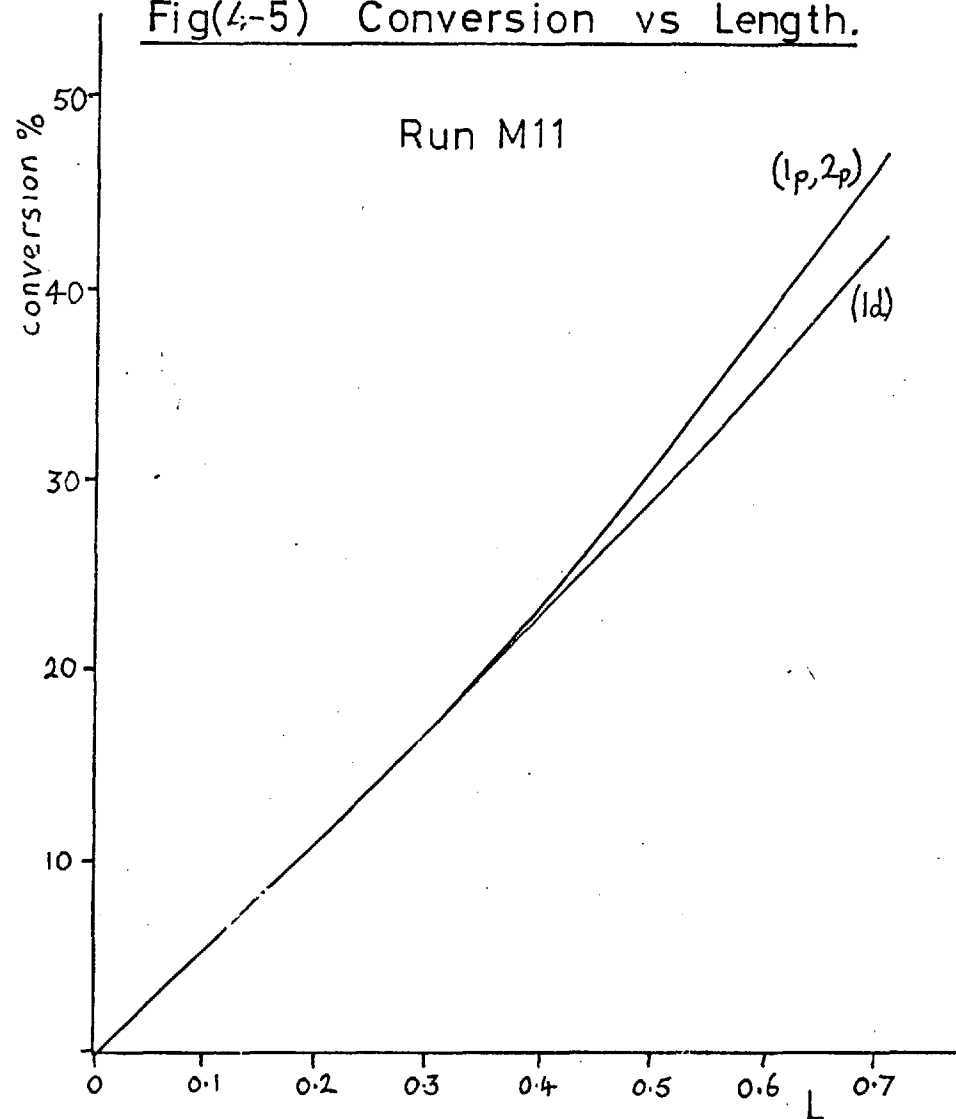
Fig(4-3) Temperature vs. Length.



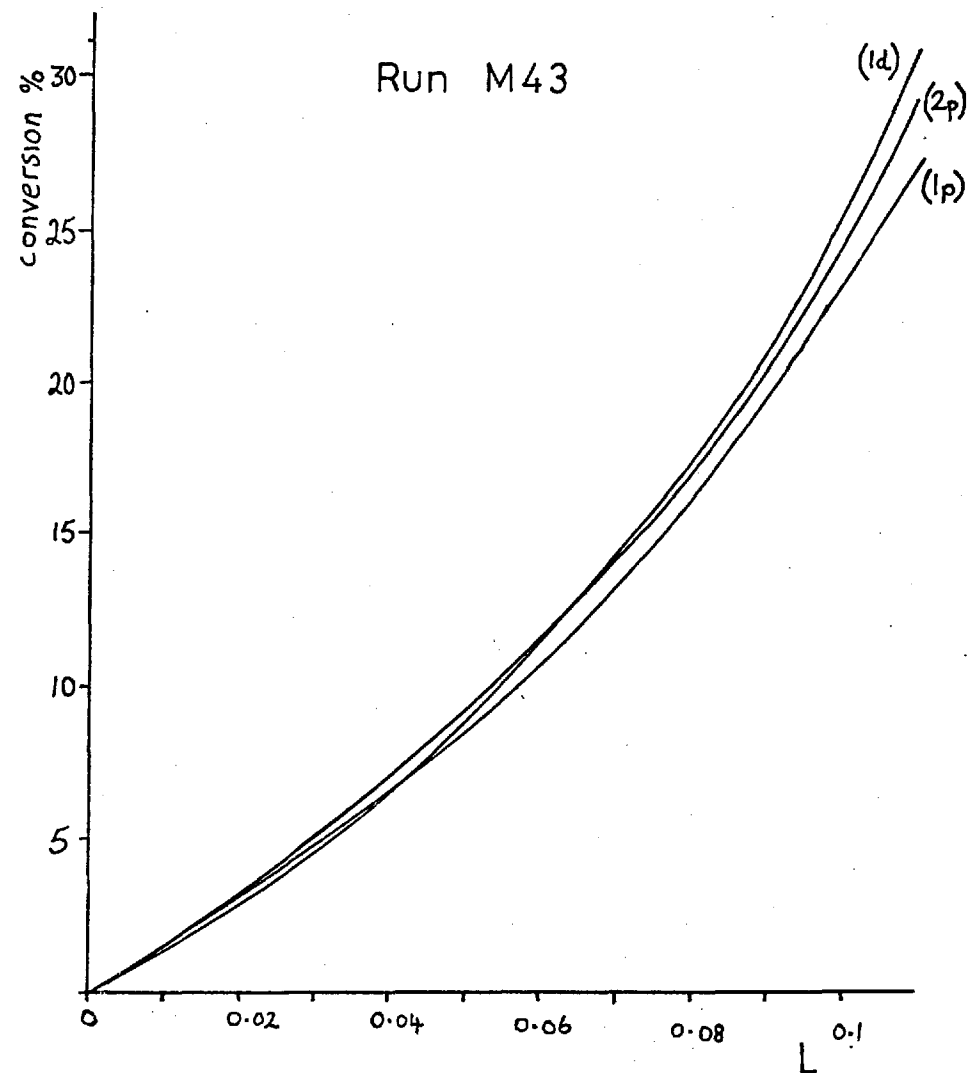
Fig(4-4) Temperature vs. Length.

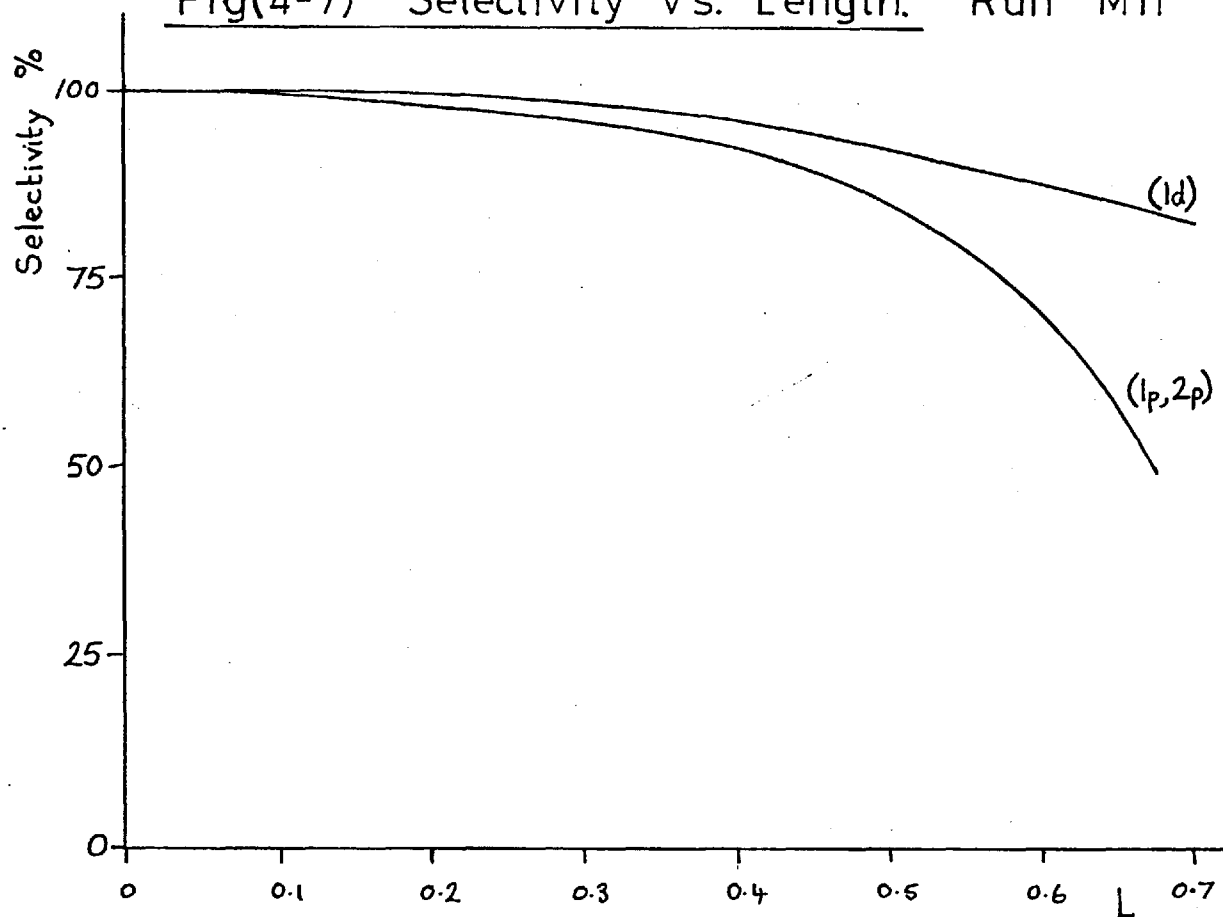
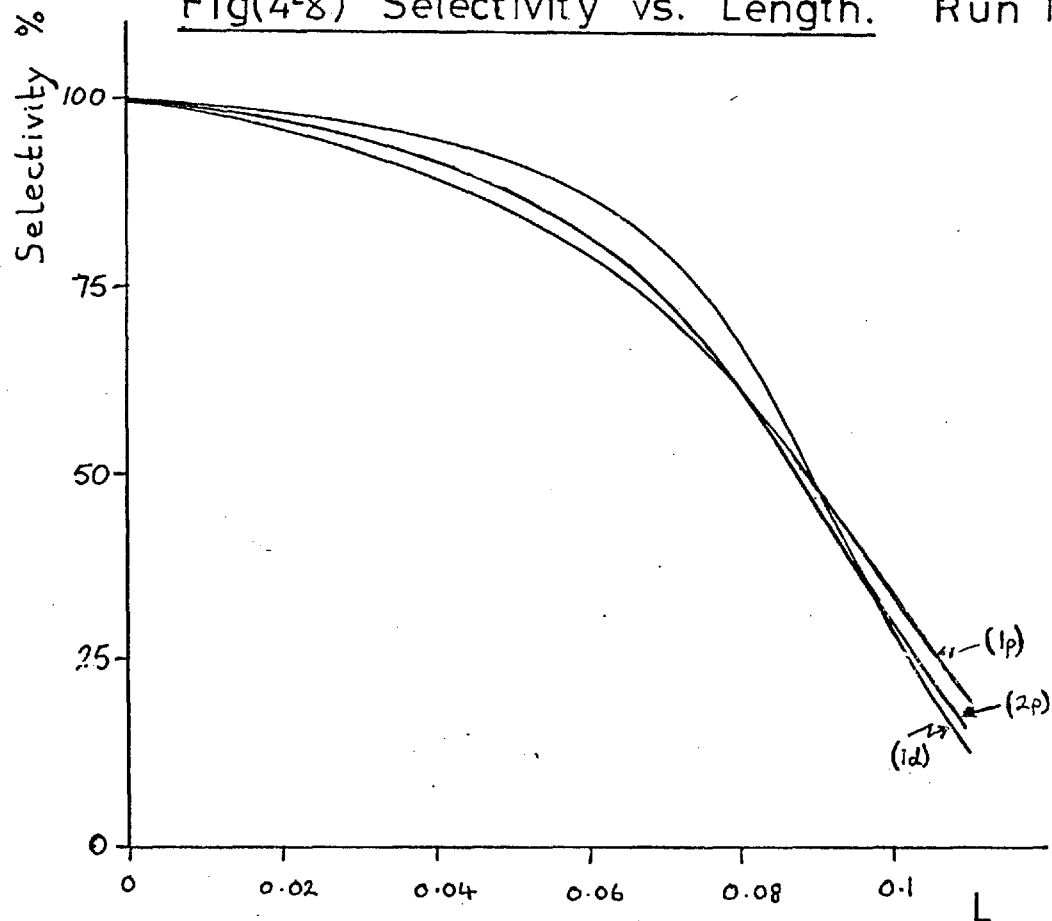


Fig(4-5) Conversion vs Length.



Fig(4-6) Conversion vs Length.



Fig(4-7) Selectivity vs. Length. Run M11Fig(4-8) Selectivity vs. Length. Run M43

conversion and selectivity profiles for these two runs. The agreement between the 1p and 2p models is good in both cases and the curves in Figures (4.3), (4.5) and (4.7) are indistinguishable for these two models. For this run the 1d model appears to be a good approximation, up to the point where the temperature starts to rise significantly, i.e. when the homogeneous reaction becomes significant.

However, for run M43, as shown in Figures (4.4), (4.6) and (4.8), there is a distinguishable difference in the curves for the 1p and 2p models. The behaviour of the 1d model, showing the anomaly previously discussed, is clearly shown.

In this type of situation, where the desired product is converted to worthless combustion products, the prediction of selectivity and of yield is of great importance. It is evident from Figures (4.7) and (4.8), which are typical, that the onset of the homogeneous reaction is a fairly clearly defined phenomenon. Defining

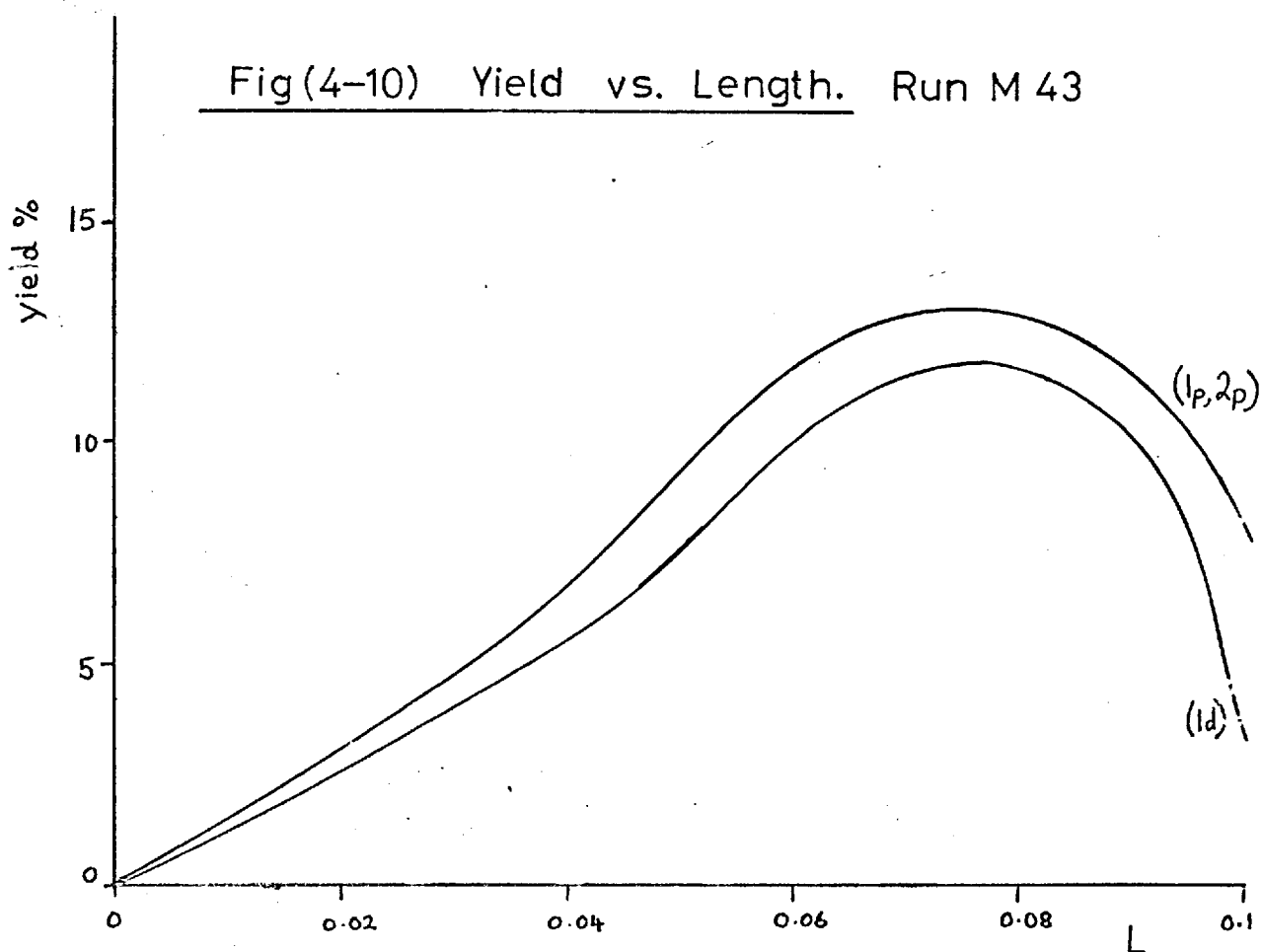
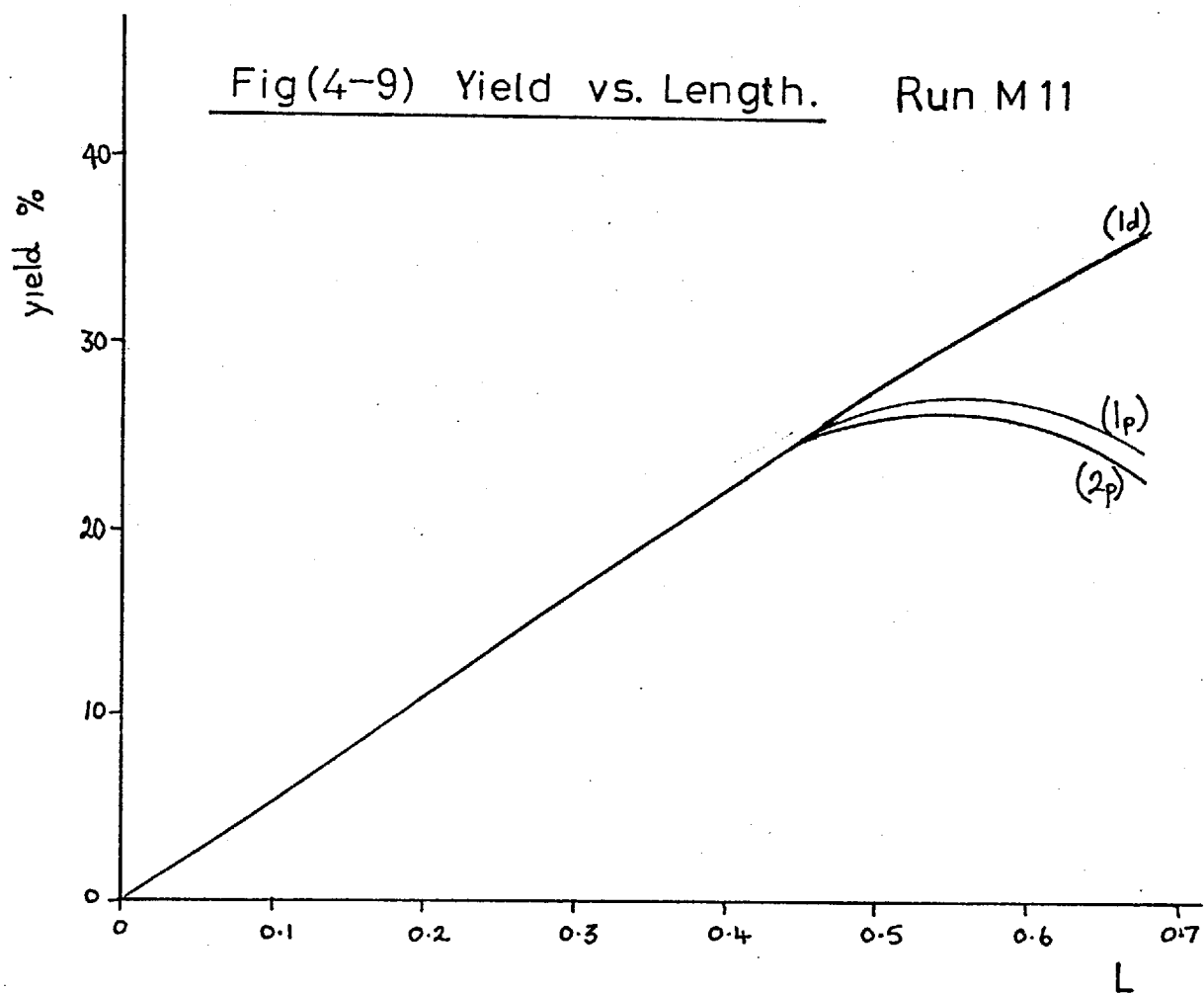
$$\text{yield \%} = \text{conversion} \times \text{selectivity} = \frac{\text{amount HCHO formed}}{\text{amount CH}_3\text{OH consumed}} \times 100\%$$

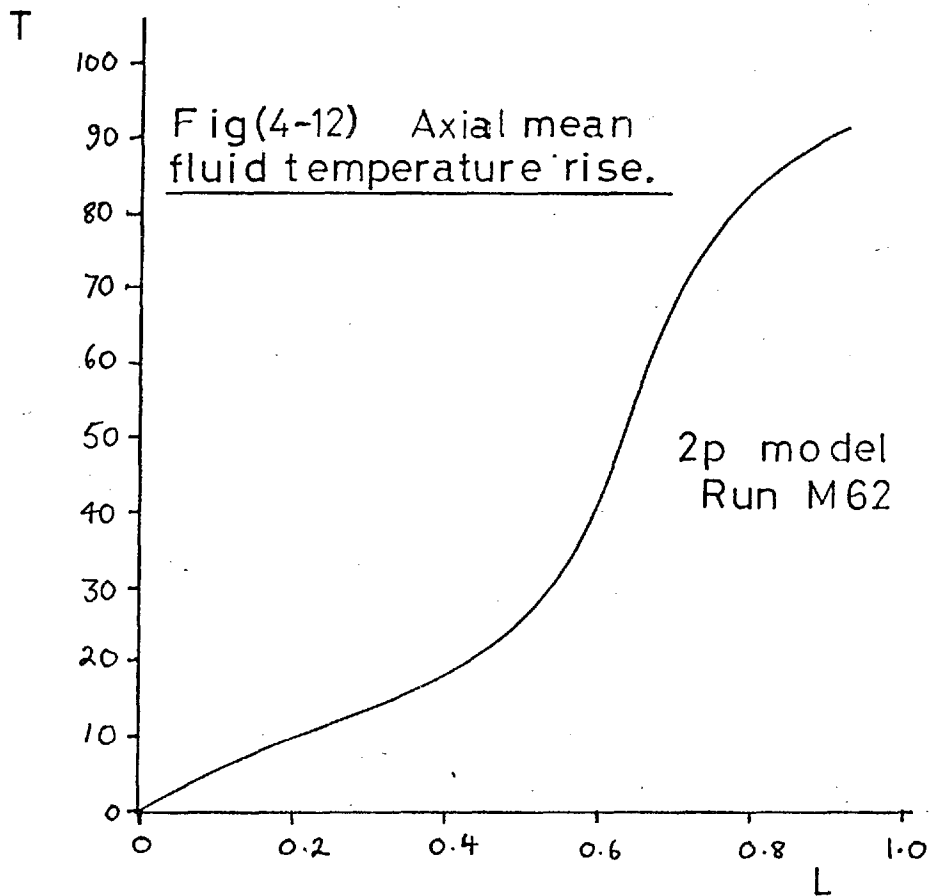
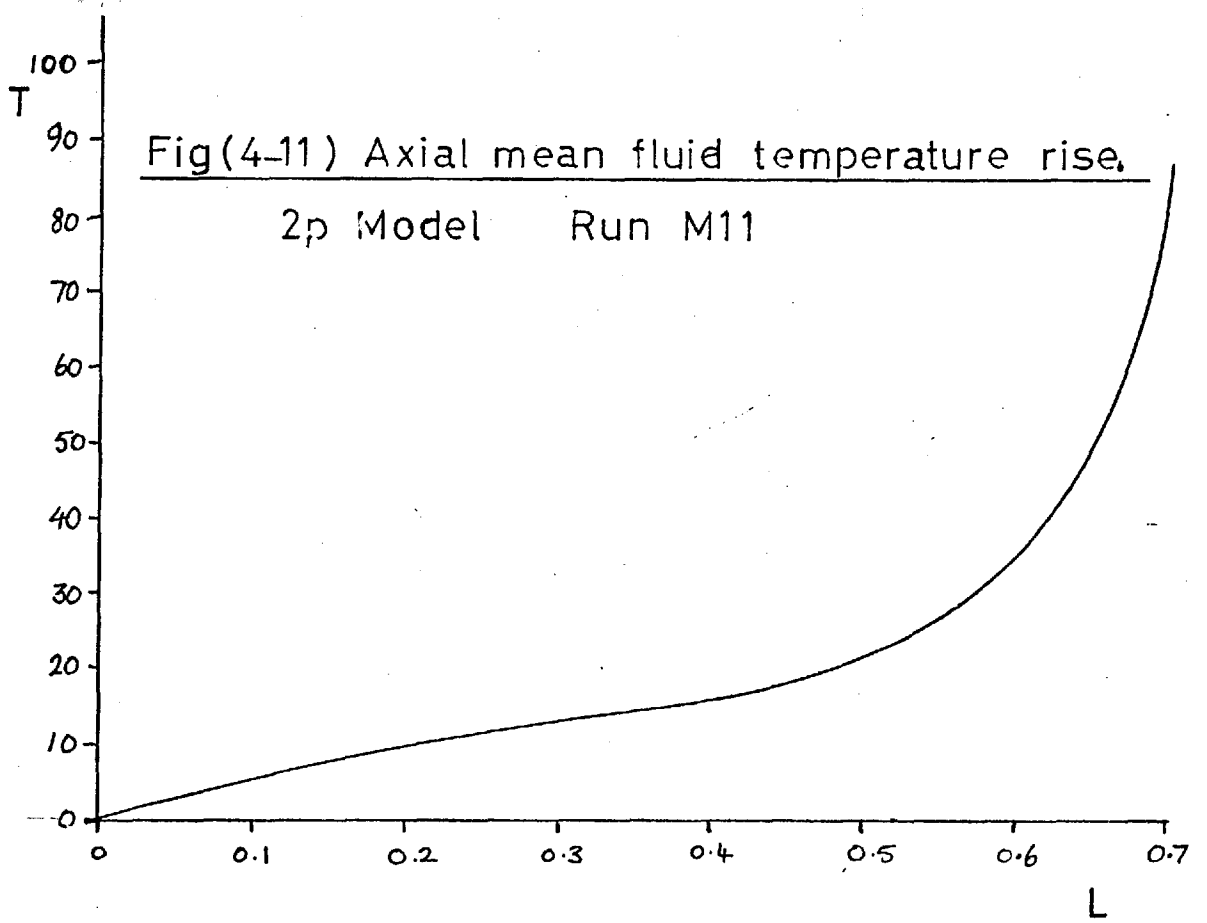
then Figures (4.9) and (4.10) show formaldehyde yield for runs M11 and M43 respectively. For both runs the 1p and 2p models are in close agreement but the 1d model provides a poor estimate of the yield. In the case of run M43, the 1d model gives the same shape of yield-length profile as the two-dimensional models but the use of the 1d model would lead to design errors.

Of much greater importance are the curves shown in Figure (4.9) for run M11. In a disappearing product situation, the maximum, which appears in the 1p and 2p curves, is a normal occurrence. In an industrial reactor design procedure, curves of yield against length would be generated by a suitable mathematical model and the choice of reactor length for a given set of operating conditions would be fixed at this maximum. It may be seen that if the 1d model were used in this procedure for the operating conditions of run M11, no maximum would be found and serious design errors would result. In fact, extrapolating the curves in Figure (4.9) to 0.8m, the yield, predicted by the 1d model, would be in error by more than 100%.

The axial temperature profiles for some runs displayed the sigmoidal character referred to in Section 3.6. The profiles for runs M11 and M62 are shown in Figures (4.11) and (4.12) respectively.

The profile for run M62 is particularly interesting, as it is doubly





sigmoidal. The reactor is, ultimately, thermally stable with respect to both heterogeneous and homogeneous reactors. However, the point at which the homogeneous reaction becomes significant, 0.5m, is readily identifiable and the profile assumes a pseudo-unstable character in this region.

4.9 CONCLUSIONS

(i) A kinetic model for homogeneous and heterogeneous effects during air oxidation of methanol has been incorporated into the three mathematical models for fixed-bed catalytic reactors described in Chapter 2. The models have been integrated for a variety of operating conditions and heat transfer situations.

(ii) The general pattern of agreement between 1p and 2p models is the same as found for the thermal decomposition of N_2O . Differences between these models were less than for the N_2O system because of the comparable heat release in solid and fluid phases.

(iii) The pattern of agreement between 1p and 1d models was, occasionally, not as expected. For some runs the 1d predicts higher temperature rises than the 1p model. This is attributed to the effect of variation with temperature of pellet effectiveness factors.

(iv) Use of the 1d model to calculate formaldehyde yields could result in serious design errors.

(v) The 1p and 2p models generally predict yields in good agreement with each other. However, these models can predict values for the reactor hot spot temperature which are different and this can be important in cases of catalyst poisoning or where thermal limitations exist with respect to catalyst strength.

Chapter 5

MATHEMATICAL MODEL FOR COMPLEX REACTION AND DIFFUSION IN A CATALYST PELLET

- 5.1 Introduction
- 5.2 Mathematical Model for the Catalyst Pellet
- 5.3 Numerical Integration of the Catalyst Pellet Model
- 5.4 Correlation of Experimental Results and Theoretical Predictions
 - 5.4.1 Modelling an Isolated Pellet
 - 5.4.2 Modelling the combined Pellet and Reactor
- 5.5 Conclusions

5.1 INTRODUCTION

The modelling of the interaction of diffusion and chemical reaction in a single catalyst pellet for the butene to butadiene system has been initiated for two reasons. A mathematical model was required for the experimental findings of Corrie (26) who measured temperatures within and around a single pellet of tin/antimony oxide catalysing the oxidative dehydrogenation of butene to butadiene at around 700K. The main requirement of the model was to duplicate experimental observations, to identify sensitive parameters in the system and to obtain some estimate of the order of magnitude of changes caused by variation in these parameters. The second, and parallel, objective was to develop the simplest models for the catalyst pellet that could be used as part of an overall model for reaction and diffusion in a chemical reactor for the butene to butadiene system.

The model must, however, be capable of predicting the formation of the minor products (and particularly the aldehydes) during the reaction, as Corrie has shown that homogeneous reaction can occur in the heterogeneous system under certain conditions. It is probable that homogeneous attack of both butene and butadiene is aldehyde induced at these temperatures (117).

Gabbay (27) has provided a kinetic model for the catalytic system and has fitted his results to a network of thirteen reactions, largely of non-integral kinetics. The reaction scheme, together with kinetic dependence and Arrhenius parameters, are discussed in Appendix A5 at the end of this thesis. It would be very difficult to assign a lumped value for such parameters as the overall heat of reaction or the overall rate of butene or oxygen removal, as the most exothermic reactions are the side reactions, such as the formation of carbon oxides, and the reactions differ greatly in both their activation energies (and thus their temperature dependence) and their kinetic order with respect to the reactant concentrations. Consequently it is not possible to apply a lumped parameter analysis for temperature differences, such as that of Damkohler (118) or its generalisation by Prater (119). Nor is it possible to apply an analysis based on the well-known Thiele modulus because of the highly interactive dependence upon the reactant concentrations.

The situation is further complicated by the possibility of film transfer limitation occurring at the pellet surface. It has been shown (120)

that film resistance is considerably more important than intra-pellet resistance to energy transfer. Thus it might be proposed that the pellet be considered to be isothermal and that the temperature difference between the pellet and the bulk fluid be concentrated at the pellet surface. An energy balance at the pellet surface would then yield:

$$T^S - T^f = \frac{2K_{\text{eff}}}{dp h_v} \left. \frac{\delta T^S}{\delta y} \right|_{\text{surface}}$$

The energy flux across the pellet surface may be related to the equivalent mass flux by:

$$K_{\text{eff}} \left. \frac{dT^S}{dy} \right|_{\text{surface}} = \sum_{i=1}^S D_{\text{eff}}^i H^i \left. \frac{\delta C^i}{\delta y} \right|_{\text{surface}}$$

and so:

$$T^f - T^S = \frac{2}{dph_v} \sum_{i=1}^S D_{\text{eff}}^i H^i \left. \frac{\delta C^i}{\delta y} \right|_{\text{surface}} \quad (5.1)$$

If the surface concentration gradient is known for each component, then the fluid-pellet temperature difference can be calculated. Note, however, that in general T^S will be required to predict reaction rate constants needed to calculate the surface concentration gradients, and some kind of iterative procedure is implied. This question will be considered further when the full mathematical model for the catalyst pellet has been established.

Film mass transfer resistance may also be significant, although this effect is less important than the equivalent energy resistance (121). However, in cases where the mass conservation equations have to be solved by numerical methods - and the present system will prove to be in this category - it is a simple matter to include the film resistance in the solution algorithm without significant increase in computational effort. In this case it is not important to establish when film mass transfer resistance becomes important. It will be useful at this stage to summarise the heat and mass transfer resistances that exist in and near to a catalyst pellet. The principal route for heat transfer within the pellet is through the solid material of the pellet in contrast to mass which is transferred exclusively through the fluid phase in the pellet pores. The principle mode for both heat and mass transfer from the pellet

exterior surface into the bulk gas phase in convection. For mass transfer the intra-pellet resistance is usually the more significant whereas, for heat transfer, the film resistance is usually much more significant than the intra-pellet resistance.

Diffusional limitations within catalyst pellets are often discussed in terms of the effectiveness factor, and physical models of varying degrees of complexity have been considered. Attention has been focussed both on the isothermal (122, 123, 124, 125, 126) and the non-isothermal pellet (127, 128, 129, 130) but, in almost all of the studies, simple first or second order kinetics have been assumed, and complex reactions have received little attention. Butt (131) and Carberry and Wendel (54) have considered consecutive reactions and have used a finite difference method to solve the resulting equations. A general treatment of complex reactions with arbitrary kinetics has been given by Schillson and Amundsen (127). Although suitable for systems of two or three reactions, the treatment becomes unwieldy for larger reaction networks.

There have been several reasonably successful attempts to correlate theoretical predictions of temperature effects in single pellets with experimental measurements. Hughes and Koh (132) have obtained agreement between theory and experiment for the hydrogenation of ethylene on a supported nickel catalyst, but, as film mass transfer was insignificant during their experiments, and as they have used observed surface temperature as a boundary condition for their model there is a degree of interaction between the experiment and the theoretical treatment, preventing the predictive role of the theoretical model for the system. Kehoe and Butt (133) have applied a model similar to that described below, but they consider the hydrogenation of benzene over nickel, a single reaction of integral kinetics. Similar limitations exist with the work of Miller and Deans (134) and of Gunn (135), who has adopted an analytical solution for first order single reaction. None of this work has direct applicability to the present case for one or more of the following reasons:

- i) Only a single reaction is considered
- ii) Film mass and/or energy transfer limitations are neglected
- iii) Non-integral kinetics are not considered
- iv) The system considered is not interactive with respect to the reactants.

The present system consists of a network of parallel and consecutive reactions and an analytical solution to the problem of the interaction of diffusion and reaction in an around a catalyst pellet would appear to be impossible. The remarks made so far are equally applicable whether the

the model is to be used to compare theoretical predictions with experimental results or whether it is to be used in a full reactor model. The film heat and mass transfer coefficients will depend upon the environment of the catalyst pellet.

When the model is to be used to correlate experimental with theoretical predictions the pellet and reactor may be considered to form a set of concentric cylinders with the reacting gas flowing through the annulus thus formed. An estimate for the film heat transfer coefficient is thus required. Kern (136) proposes adaption of the Sieder and Tate correlation for flow in pipes, to give a correlation:

$$Nu = \frac{h_v D_e}{k_f} = 1.86 Pr_e^{\frac{1}{3}} Re_e^{\frac{1}{3}} \left(\frac{L'}{D_e} \right)^{-\frac{1}{3}} \quad (5.2)$$

For air, the Prandtl number may be assumed constant at 0.74 and so (5.2) reduces to:

$$Nu = \frac{h_v D_e}{k_f} = 1.68 Re_e^{\frac{1}{3}} \left(\frac{L'}{D_e} \right)^{-\frac{1}{3}} \quad (5.3)$$

Use of this expression in the present situation is hampered by two considerations. The first, and most serious, is that the correlation has been obtained for tubes. This implies that the heat transfer surfaces were relatively smooth. Kern (136) states that pipes are rougher than tubes and larger heat transfer coefficients will be expected owing to the increased turbulence promoted by the surface roughness. In the present case, the heat transfer surface is the pellet surface, which is considerably rougher than the surfaces of either pipes or tubes. Consequently, the correlation in Equation (5.3) will be a lower limit for the h_v and the actual value will be much larger. The amount by which h_v can be increased by surface roughness is very difficult to estimate. However, increase by a factor of 5-10 would not be unreasonable.

The second difficulty with Equation (5.3) arises from the factor (L'/D_e) . L' is taken to be the length of the annulus, in this case the length of the pellet. However, the length of the pellet is of the same order as the radial dimensions of the annulus and some kind of entrance effect might be expected to influence the heat transfer coefficient. However variation of $(L'/D_e)^{-\frac{1}{3}}$ with L' will be fairly small provided L' does not change too much. If L' is doubled, $(L'/D_e)^{-\frac{1}{3}}$ changes by a factor of only 0.8. L' could be considered as some kind of length of mixing which is of

the same order as the tube length. Thus, this uncertainty will affect the prediction of h_v , but to a lesser degree than the uncertainty introduced by the pellet roughness.

Other correlations are available for heat transfer in an annulus (e.g. 137, 138). They are all substantially of the same form and suffer from the disadvantages mentioned above. The fluid-particle mass transfer in the annulus may be estimated by applying the Chilton-Colburn analogy (see Appendix A5) in the absence of a better correlation.

5.2 MATHEMATICAL MODEL FOR THE CATALYST PELLET

The interaction of diffusion with reaction within a porous catalyst pellet may be represented by the following set of dimensionless conservation equations (e.g. 139). The mass balance is:

$$\frac{d^2 c^i}{dy^2} + \frac{m_s}{y} \frac{dc^i}{dy} = -\phi^i \gamma^i \quad i = 1 \rightarrow 10 \quad (5.4)$$

$$\text{where: } \phi^i = \frac{dp^2 \rho_b}{4D_{eff}^i C^{i,f}}$$

In Equation (5.4) m_s is a shape factor that may be used to account for irregularly shaped particles or for regular particles with finite geometry. Defining m_s by

$$\frac{m_s + 1}{dp} = \frac{A_p}{2V_p} \quad (5.5)$$

Equation (5.4) reduces to the well known forms for the special geometries of a flat slab, an infinite cylinder and a sphere. The corresponding energy balance is

$$\frac{d^2 t}{dy^2} + \frac{m_s}{y} \frac{dt}{dy} = -\theta \sum_{i=1}^{10} \gamma^i H^i \quad i = 1 \rightarrow 10 \quad (5.6)$$

$$\text{where: } \theta = \frac{dp^2 \rho_b}{4K_{eff} T^f}$$

The boundary conditions are:

$$y = 0; \quad \frac{dc^i}{dy} = 0; \quad \frac{dt}{dy} = 0$$

$$y = 1; \quad c^i = 1 - \frac{1}{Sh^i} \frac{dc^i}{dy} \Big|_{y=1}; \quad t = 1 - \frac{1}{Nu} \frac{dt}{dy} \Big|_{y=1}$$

$$Sh = \frac{k_g^i dp}{2D_{eff}^i}; \quad Nu = \frac{h_v dp}{2K_{eff}}; \quad i = 1 \rightarrow 10 \quad (5.7)$$

Following the arguments set out in Section (2.7) the following substitution was made,

$$u = y^2$$

resulting in the mass and energy balances:

$$4u \frac{\delta^2 c^i}{\delta u^2} + \frac{m_s + 1}{2} \frac{\delta c^i}{\delta u} = -\phi^i \gamma^i \quad i = 1 \rightarrow 10 \quad (5.8)$$

$$4u \frac{\delta^2 t}{\delta u^2} + \frac{m_s + 1}{2} \frac{\delta t}{\delta u} = -\theta \sum_{i=1}^{10} \gamma^i H^i \quad (5.9)$$

with boundary conditions:

$$u = 0; \quad \frac{\delta c^i}{\delta u} = 0; \quad \frac{\delta t}{\delta u} = 0$$

$$u = 1; \quad c^i = 1 - \frac{2}{Sh^i} \frac{\delta c^i}{\delta u} \Big|_{u=1}; \quad t = 1 - \frac{2}{Nu} \frac{\delta t}{\delta u} \Big|_{u=1} \quad i=1 \rightarrow 10 \quad (5.10)$$

5.3 NUMERICAL INTEGRATION OF THE CATALYST PELLET MODEL

Equations (5.8) to (5.10) form a two-point boundary value problem comprising a set of non-linear interacting ordinary differential equations. This set of equations was integrated by an iterative finite difference method. The numerical method is first described for the temperature, t , in order to avoid the rather unwieldy notation that would otherwise ensue. The full algorithm for the interacting set will be subsequently discussed. The right hand side of (5.9) is abbreviated to f_H for convenience. Thus

Equation (5.9) is modified to:

$$4u \frac{\delta^2 t}{\delta u^2} + \frac{m_s+1}{2} \frac{dt}{du} = f_H(\underline{c}, t) \quad (5.11)$$

The region of integration, $0 < u < 1$, is divided into $P-1$ sections, equally spaced in the variable u . The value of t at the p^{th} grid point, $1 < p < P$, for the q^{th} iteration is given by t_p^q . The derivatives, and dependent variable, were approximated by the following difference relationships:

$$\frac{dt^q}{du_p} = \frac{t_{p+1}^q - t_{p-1}^q}{2k}; \quad \frac{d^2 t^q}{du_p^2} = \frac{t_{p+1}^q - 2t_p^q + t_{p-1}^q}{k^2}; \quad u_p = (p-1)k \quad (5.12)$$

The source term in Equation (5.11) is non-linear and is handled by the quasi-linearisation technique where the non-linear term at the q^{th} iteration is estimated from the equivalent term at the $(q-1)^{\text{th}}$ iteration. Thus:

$$f_H^q(\underline{c}_p^{q-1}, t_p^{q-1}, t_p^q) = f_H^{q-1}(\underline{c}_p^{q-1}, t_p^{q-1}) + \frac{\delta f_H^{q-1}}{\delta t_p} \cdot (t_p^q - t_p^{q-1}) \quad (5.13)$$

When (5.13) is substituted into (5.11), (5.11) becomes linear provided that $\frac{\delta f_H^{q-1}}{\delta t_p}$ is known.

For the grid points where $1 < p < P$, (5.12) and (5.13) may be substituted into (5.10) to yield the following difference equation.

$$\begin{aligned} & -(p-1 + \frac{m_s+1}{4})t_{p+1}^q + (2(p-1) - \frac{k}{4} \frac{\delta f_H^{q-1}}{\delta t_p})t_p^q - (p-1 - \frac{m_s+1}{4})t_{p-1}^q \\ & = \frac{k}{4} (f_{Hp}^{q-1} - \frac{\delta f_H^{q-1}}{\delta t_p} \cdot t_p^{q-1}) \end{aligned} \quad (5.14)$$

The difference equation for the case of $p = P$ is obtained by substituting (5.10), (5.12) and (5.13) into (5.11) and eliminating the value t_{p+1}^q by the difference equation for the boundary condition. Remembering that $u=1$ when $p=P$ the difference equation obtained is:

$$\begin{aligned}
& -\frac{2}{k^2} t_{p-1}^q + \left(\frac{Nu}{k} - \frac{Nu(m_s+1)}{4} + \frac{2}{k^2} - \frac{1}{4} \cdot \frac{\delta f_H^{q-1}}{\delta t} \right) t_p^q \\
& = \frac{1}{4} \left(f_{H_p}^{q-1} - \frac{\delta f_H^{q-1}}{\delta t_p} \right) + \frac{Nu}{k} - \frac{Nu(m_s+1)}{4}
\end{aligned} \tag{5.15}$$

The difference equation for the case $p=1$ is obtained by localising the difference equation at a dimensionless radius of $\frac{1}{2}k$. Incorporating the boundary condition $\delta t/\delta u=0$ the relationship obtained is:

$$\begin{aligned}
& \left(\frac{1}{2} + \frac{m_s+1}{4} - \frac{k}{4} \frac{\delta f_H^{q-1}}{\delta t_1} \right) t_1^q - \left(\frac{1}{2} + \frac{m_s+1}{4} - \frac{k}{4} \frac{\delta f_H^{q-1}}{\delta t_2} \right) t_2^q \\
& = \frac{k}{8} \left(f_{H_1}^{q-1} + f_{H_2}^{q-1} - \frac{\delta f_H^{q-1}}{\delta t_1} - \frac{\delta f_H^{q-1}}{\delta t_2} \right)
\end{aligned} \tag{5.16}$$

Analogous equations can be obtained in terms of the concentration of the i^{th} species by making the same substitutions into (5.8) and (5.10). In this case the Nusselt number in Equation (5.15) is replaced by Sh^i the Sherwood Number for the i^{th} species. Thus, for example, (5.15) becomes:

$$\begin{aligned}
& -\frac{2}{k^2} c_p^{i,q} + \left(\frac{Sh^i}{k} - \frac{Sh^i(m_s+1)}{4} + \frac{2}{k^2} - \frac{1}{4} \frac{\delta f^{i,q}}{\delta c_p^i} \right) c_p^{i,q} \\
& = \frac{1}{4} \left(f_p^{i,q-1} - \frac{\delta f^{i,q-1}}{\delta c_p^i} \cdot c_p^{i,q-1} \right) + \frac{Sh^i}{k} - \frac{Sh^i(m_s+1)}{4}
\end{aligned} \tag{5.16}$$

When Equations (5.14), (5.15) and (5.16) are written in matrix form, they constitute a tri-diagonal system of equations which may be solved very rapidly. The equations may be written, in generalised form as:

$$\underline{A} \underline{t} = \underline{d} \tag{5.16}$$

$\underline{A}$ is a triadiagonal matrix and $\underline{d}$ is a vector of the right hand sides of the equations. The following relationships define $\underline{A}$ and $\underline{d}$.

$$\begin{aligned}
d_1 &= \frac{k}{8} (f_{H_1}^{q-1} + f_{H_2}^{q-1} - \frac{\delta f_H^{q-1}}{\delta t_1} - \frac{\delta f_H^{q-1}}{\delta t_2}) \\
d_p &= \frac{k}{4} (f_{H_p}^{q-1} - \frac{\delta f_H^{q-1}}{\delta t_p} \cdot t_p^{q-1}) \quad 1 < p < P \\
d_P &= \frac{1}{4} (f_{H_P}^{q-1} - \frac{\delta f_H^{q-1}}{\delta t_P} \cdot t_P^{q-1}) + \frac{Nu}{k} - \frac{Nu(m_s+1)}{4} \quad (5.18) \\
\gamma_1 &= A_{1,3} = \frac{1}{2} + \frac{m_s+1}{4} - \frac{k}{4} \cdot \frac{\delta f_H^{q-1}}{\delta t_1} \\
\beta_1 &= A_{1,2} = \frac{1}{2} + \frac{m_s+1}{4} - \frac{k}{4} \cdot \frac{\delta f_H^{q-1}}{\delta t_2} \\
\alpha_p &= A_{p,p-1} = p-1 - \frac{m_s+1}{4} \\
\beta_p &= A_{p,p} = 2(p-1) - \frac{k}{4} \cdot \frac{\delta f_H^{q-1}}{\delta t_p} \quad 1 < p < P \\
\gamma_p &= A_{p,p+1} = p-1 + \frac{m_s+1}{4} \\
\beta_P &= A_{P,P} = \frac{Nu}{k} - \frac{Nu(m_s+1)}{4} + \frac{2}{k^2} - \frac{1}{4} \cdot \frac{\delta f_H^{q-1}}{\delta t_P} \\
\alpha_P &= A_{P,P-1} = \frac{2}{k^2} \\
\gamma_P &= \alpha_1 = 0 \quad (5.19)
\end{aligned}$$

These definitions are applicable to the variable t . Completely analogous expressions exist for the variable c^i . The ' α, β, γ ' notation has been introduced as a matter of computational convenience, so that the coefficients may be stored in a $3 \times P$ array rather than a $P \times P$ array. Equation (5.17) may be solved very rapidly and efficiently by an algorithm commonly known as the Thomas algorithm (140). The method is described in Section 2.7.

The overall algorithm may now be written for the solution of the mass and energy balances in the catalyst pellet.

1. Read all data and bulk conditions surrounding the pellet.
2. Calculate all quantities that will not vary during the iterative procedure.
3. Solve the energy balance by Thomas's algorithm.
4. Solve the mass balance for each species by the Thomas algorithm.
5. If all solutions have converged stop, otherwise return to step 3.

At all stages in the calculation, the latest information is used. For example, during the q^{th} estimation of the concentration profile of the j^{th} species, the values of d are calculated from t^q ; c^i, q ; i, j ; $c^{i, q-1}$; i, j .

A FORTRAN IV listing of the computer subroutine written to perform these calculations is given in Appendix A5. The following notes explain some of the short-cuts and modifications introduced in an attempt to reduce computing time.

The model requires that the rate of production of each component is calculated at each grid point for each iteration and a value for the rate constants is therefore required at each grid point. Because of the exponentiation required in calculating the rate constants their evaluation was rather time consuming. Consequently any reduction in the number of rate constant evaluations would be advantageous. It was proposed that the rate constants be evaluated only once per iteration and that they should be evaluated at the temperature of the pellet surface. As the average temperature difference between the pellet surface and the pellet centre was of the order of 1 deg K this would appear to be a reasonable assumption. The two approaches were compared and, for a typical set of operating conditions and using a finite difference grid of 40 points, the model simplification afforded a saving in computer time of about one third, whilst the predictions of the two approaches differed by less than half a per cent. It is evident that the amount of time saved will increase as the number of grid points increases. The simplification was thus adopted.

At first sight it would appear to be necessary to solve eleven conservation equations in order to solve the complete problem. This number can immediately be reduced by one if the full temperature solution is not obtained. This will not in any way restrict the usefulness of the model as the solid-fluid temperature difference may still be calculated from Equation (5.1): it has been established that the

temperature drop across the pellet is not sufficiently large to significantly affect the reaction rate constants. If this procedure were adopted it would be necessary to reverse the order of calculation so that the surface temperature is evaluated when all the surface concentration gradients have been calculated. However it is more efficient in practice to compute the full temperature profile within the catalyst pellet as this then allows several of the mass conservation equations to be neglected during the iterative procedure. This may be seen to be possible by considering the independence of the reactions.

The reactions may be represented by:

$$\sum_{j=1}^{13} S_{ij} M_j = 0 \quad (5.20)$$

where the matrix S, whose components are S_{ij} , is the stoichiometric matrix and M represents a chemical species. Schillson and Amundson (127) show that the number of balance equations that need to be solved in order to solve the entire system is given by the rank of the matrix S. The concentrations of the remaining species may then be found by solution of a set of algebraic equations.

The stoichiometric matrix for the present system has a rank of 8. Physical credence may be attached to this figure by considering R1 to R8 (Table (A5.1): Appendix A5) to be independent. The remaining reactions are those describing the oxidation of butadiene, which may be considered to be linear combinations of the oxidation of butene to butadiene and of butene to the produce concerned. For example, it may be seen that $R9 = 2 \times R3 - R1$, thus demonstrating the linear dependence of these three reactions.

This would seem to afford a considerable saving in computational effort, reducing the number of conservation equations to be solved from 11 to 8. The surface concentration gradients would also be related by algebraic equations and so Equation (5.1) could be used to calculate the surface temperature of the pellet. However, in the present system, the most time consuming aspect of the solution procedure is found to be the exponentiation required to calculate the various rates of reaction (Table (A5.1): Appendix A5). The effort devoted to this aspect of the solution procedure is about 50% for a 40 point difference grid. The

necessity for exponentiation cannot be removed by successive multiplication because of the non-integral kinetic dependences. If all the rates are calculated, 18 exponentiations per grid point per iteration are required and it is not possible to choose a set of eight species whose rates involve less than this number of exponentiations. It will be noticed, however, that only three species are involved in the rate expressions. Consequently only four balance equations were solved during the iterative procedure, i.e. those for oxygen, butene, butadiene and temperature. The profiles for the other seven species were not determined at each iteration, although it was necessary to calculate their rates of formation at each grid point in order to calculate the rate of heat release. This involves no significant increase in computational effort as all the quantities involved need to be calculated in order to evaluate the rates of oxygen and butene removal. The concentrations of the inactive products were then determined only after the four primary solutions had converged.

As a result of the present reaction system involving only three reactants participating in thirteen reactions, considerable savings can result from the methods used, as compared to those proposed by Schillson and Arnundson (127). Thus, for example, the computational effort involved in equation solution by the latter methods may be expressed by $8Q$, while the corresponding figure for the approach adopted here is $4Q+7$. If the full model is solved the figure is $11Q$. For Q as low as 5, the saving from the present method is as much as 32% compared with the method of Schillson and Arnundson and 51% compared with the solution of the full model, although the time spent in calculating the reaction rates is the same in all three cases. As Q becomes large, the savings in computation effort reach their limiting values of 50% and 63% respectively.

The effective diffusivities within the pellet, the pellet thermal conductivity and the heat contents of the chemical species have all been evaluated at the bulk fluid temperature.

It is possible, under certain conditions, that oxygen or butene might be totally consumed by the reaction within the pellet and a portion of the pellet might exist where the concentrations of either or both of these reactants is effectively zero. The subroutine used to calculate the reaction rates has been written so that if either of these values falls to zero within the pellet, the reaction rates dependent on this concentration are automatically set to zero without performing the time-consuming exponentiations.

5.4 CORRELATION OF EXPERIMENTAL RESULTS AND THEORETICAL PREDICTIONS

Corrie (26) has published details of temperature measurements in and around a single catalyst pellet. The geometric arrangement may be considered schematically as shown in Figure A5.1. The active pellet was cemented between two inert pellets so as to minimise axial diffusion effects. This has a 'spin-off' advantage for our present purposes in that the flow patterns around the active pellet will be more developed than if the reactant gas stream were to confront the isolated pellet.

In order to apply the model previously described a certain amount of information must be supplied. This information falls naturally into three groups.

(i) Intrinsic rate data.

Thermochemical properties of the reacting species.

Geometric parameters and Flow Rates.

(ii) Bulk diffusivities of the species.

Thermal conductivity of the pellet.

Effective diffusivities in the pellet.

Specific Heats, viscosities and fluid densities.

(iii) Bulk phase temperature.

Bulk phase concentrations.

Film heat and mass transfer coefficients.

The data in group (i) may be said to be known. It was either measured during the experimental runs or has been the subject of extensive specific investigation. The data in group (ii) are subject to a small degree of uncertainty due to extrapolation of correlations, application of single gas data to gas mixtures or application of correlations developed for certain species to different species for which there is no experimental corroboration. The best example of this is the bulk diffusivity data. It would be reasonable to assume that the maximum error in this data is 10%-15%.

The data in group (iii) are subject to a great degree of uncertainty. The reasons for the uncertainty, and how it has been overcome, are described in the next section.

5.4.1 MODELLING AN ISOLATED PELLET

The data in groups (i) and (ii) of the previous section have been

estimated as described in Appendix A5. The experimental data of Corrie is summarised in Table (5.1). In Table (5.1) the mass flow rate and the species concentrations have been calculated assuming the gas mixture to behave as a perfect gas. It is necessary to know the bulk values of temperature and concentration and the film transfer coefficients that pertain to the plane of the pellet containing the thermocouples. The thermocouples, in the present case, are situated in a plane perpendicular to the axis of the pellet and half way along its length. The bulk temperature has been measured independently and is the value given in Table (5.1). The bulk concentrations have not been measured in this plane and it is necessary to estimate their values. If it is desired to predict only the fluid-solid temperature difference then it is only necessary to provide estimates for the bulk phase concentrations of oxygen, butene and butadiene. Experimental values for the inlet and effluent concentrations of butene and butadiene exist but only the inlet value exists for oxygen. Preliminary investigations show that oxygen is always present in excess and is consumed at roughly half the rate of butene. Thus, as an arbitrary first estimate for the bulk oxygen concentration in the plane of the thermocouples, the inlet oxygen concentration has been rounded down to the nearest multiple of $0.25 \times 10^{-3} \text{ kmole/m}^3$.

The concentrations of butene and butadiene in the plane of the thermocouples have been estimated as the arithmetic mean of their inlet and effluent values. This figure is, again, fairly arbitrary but, in the absence of a better estimate, has been used in this section of the work. The effect of varying these concentrations will be discussed later.

It remains to estimate the film transfer coefficients. The basic correlation for the heat transfer coefficient is given by Equation (5.3). This correlation may be expanded to:

$$\text{Nu} = 1.86 C_T (\text{Pr})^{1/3} \left(\frac{D_e}{L'} \right)^{1/3} \text{Re}_e^{1/3} \quad (5.21)$$

The variables C_T and L' are subject to the uncertainties described in Section (5.1). C_T is a measure of the additional turbulence created by the roughness of the pellet surface. Turbulence will also be created by the thermocouple wires in the gas space between the pellet surface and the reactor tube wall. C_T might be expected to depend upon the Reynolds number in some way as it will approach unity as the flow becomes fully turbulent at high Reynolds number. L' is defined as a 'total length of

Table (5.1)

Experimental Data of Corrie (26)

Run	Mass Flow $\times 10^7$ kg/sec	Bulk Temp. K	FEED - kmol/m^3			EFFLUENT Kmol/m^3			Yield Butadiene %	Expt. ΔT K	Rep
			Oxygen $\times 10^3$	Butene $\times 10^3$	Butene $\times 10^3$	Butadiene $\times 10^3$	CO_2 $\times 10^3$	CO $\times 10^3$			
B1	3.15	715.5	1.88	0.93	0.47	0.18	0.78	0.19	19.7	7.5	6.9
B2	3.15	734.5	1.88	0.92	0.40	0.21	0.92	0.20	23.3	10.0	6.9
B3	4.93	735.7	1.83	1.19	0.70	0.25	0.74	0.22	21.4	10.0	10.8
B4	0.985	735.3	1.84	1.04	0.45	0.23	1.28	0.26	20.0	7.5	2.2
B5	4.93	736.1	2.22	0.69	0.32	0.12	0.90	0.18	17.5	9.0	10.8
B6	2.95	738.0	2.15	0.80	0.41	0.17	1.07	0.22	21.0	6.0	6.5
B7	3.15	756.1	1.85	1.23	0.56	0.23	1.03	0.32	18.5	8.5	6.9

 ΔT is the temperature difference between the fluid and the pellet centre

transfer' and as such is rather ambiguous. As a first approximation L' was assumed to be the length of the pellet, 0.0085m, and C_T was assumed to be 2.33. These estimates, particularly for C_T , are somewhat arbitrary but are of a correct order of magnitude as a starting point for the procedure that will follow. The theoretical predictions using these data are shown in the first column of Table (5.2). In Table (5.2) the group C_T' is given by:

$$C_T' = 1.86 C_T (Pr)^{1/3} \left(\frac{D_e}{L'} \right)^{1/3} \quad (5.22a)$$

$$Nu = C_T' Re_e^{1/3}$$

The experimental value for temperature difference has been calculated by smoothing the profiles published by Corrie (26). The value given is the difference between the 'smoothed' pellet centre temperature and the measured bulk fluid temperature. The 'theoretical' value is the difference between the calculated pellet centre temperature and the measured bulk fluid temperature. An example of theoretical and experimental profiles is shown in Figure (5.1).

The fluid-solid temperature difference has been recalculated using values of C_T' of 10.0, 15.7, 25.0, 35.0 and 50.0. The results of these calculations are shown in the subsequent columns of Table (5.2) and the contents of Table (5.2) are shown graphically in Figure (5.2).

From Figure (5.2) the value of C_T' required to correlate experimental measurements and theoretical predictions may be deduced for each run. If all runs are considered C_T' lies between 15 and 40 but, if Run B4 is omitted, the range for C_T' lies between 15 and 30. If Runs B1, B2, B3, and B5 are considered separately the range for C_T' is further reduced to lie between 15 and 20.

This variation in C_T' was attributed to two effects. Firstly the variation of the enhanced turbulence with Reynolds number and secondly, the uncertainty in the bulk concentrations in the plane of the thermocouple.

There is a fairly strong relationship between C_{To}' and Reynolds number as may be seen from Figure (5.3). As Reynolds number increases, C_{To}' decreases. This reflects the assertion that C_{To}' would tend asymptotically to unity as fully turbulent conditions are approached at

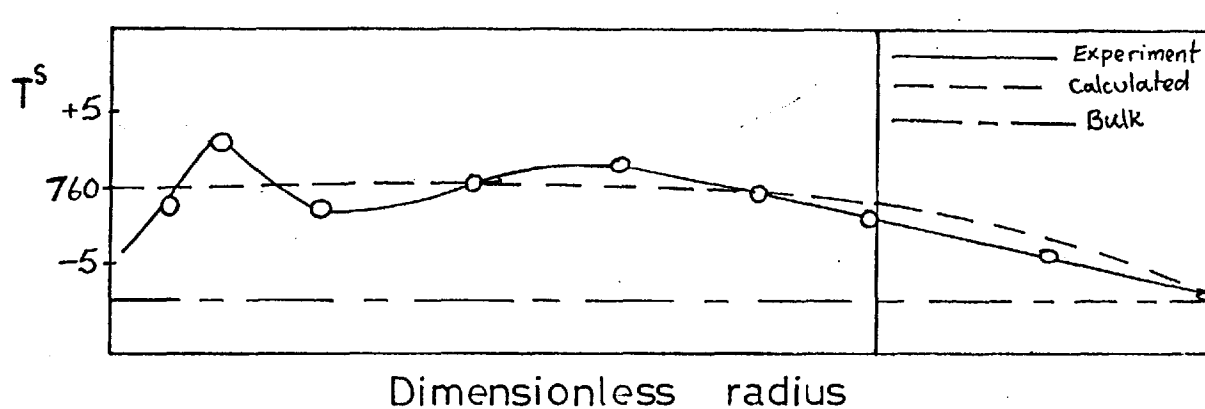
Table (5.2)

Preliminary theoretical predictions of thermal effects in a single catalyst pellet

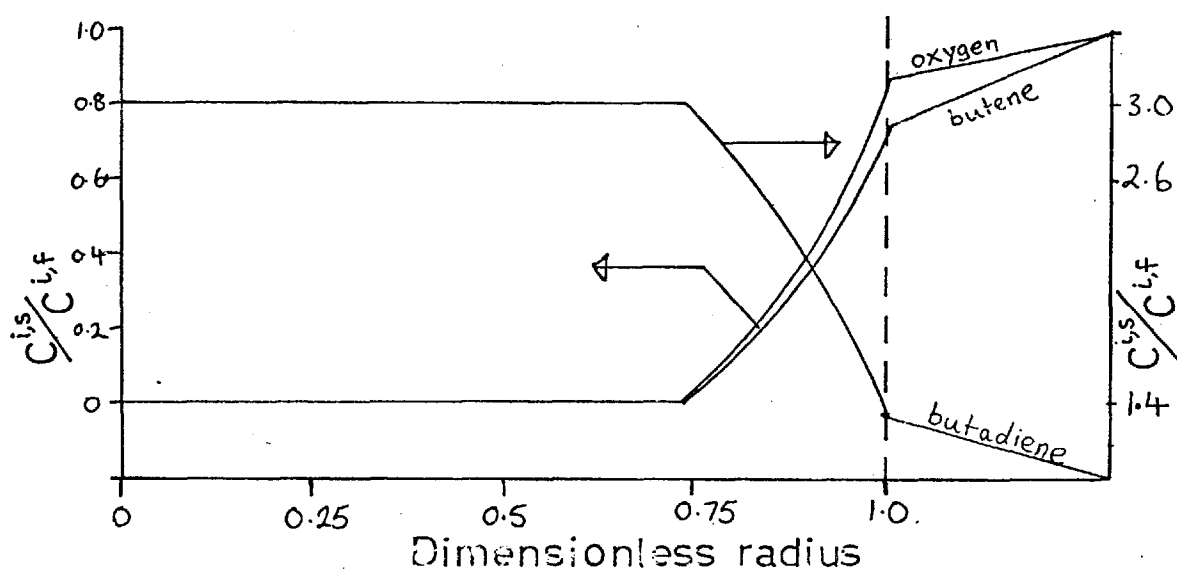
Run	ΔT experimental K	ΔT = Theoretical (K), C_T^1 as a parameter					
		$C_T^1=5.0$	$C_T^1=10.0$	$C_T^1=15.7$	$C_T^1=25.0$	$C_T^1=35.0$	$C_T^1=50.0$
B1	7.5	30.91	13.72	8.65	5.59	4.15	-
B2	10.0	39.36	17.02	10.68	6.78	5.07	-
B3	10.0	44.25	19.20	12.03	7.81	5.88	-
B4	7.5	92.06	30.07	17.80	11.09	8.14	5.75
B5	9.0	28.59	13.01	8.30	5.20	3.91	-
B6	6.0	43.36	18.40	11.51	7.35	5.41	-
B7	8.5	58.25	24.96	15.7	9.86	7.34	5.46

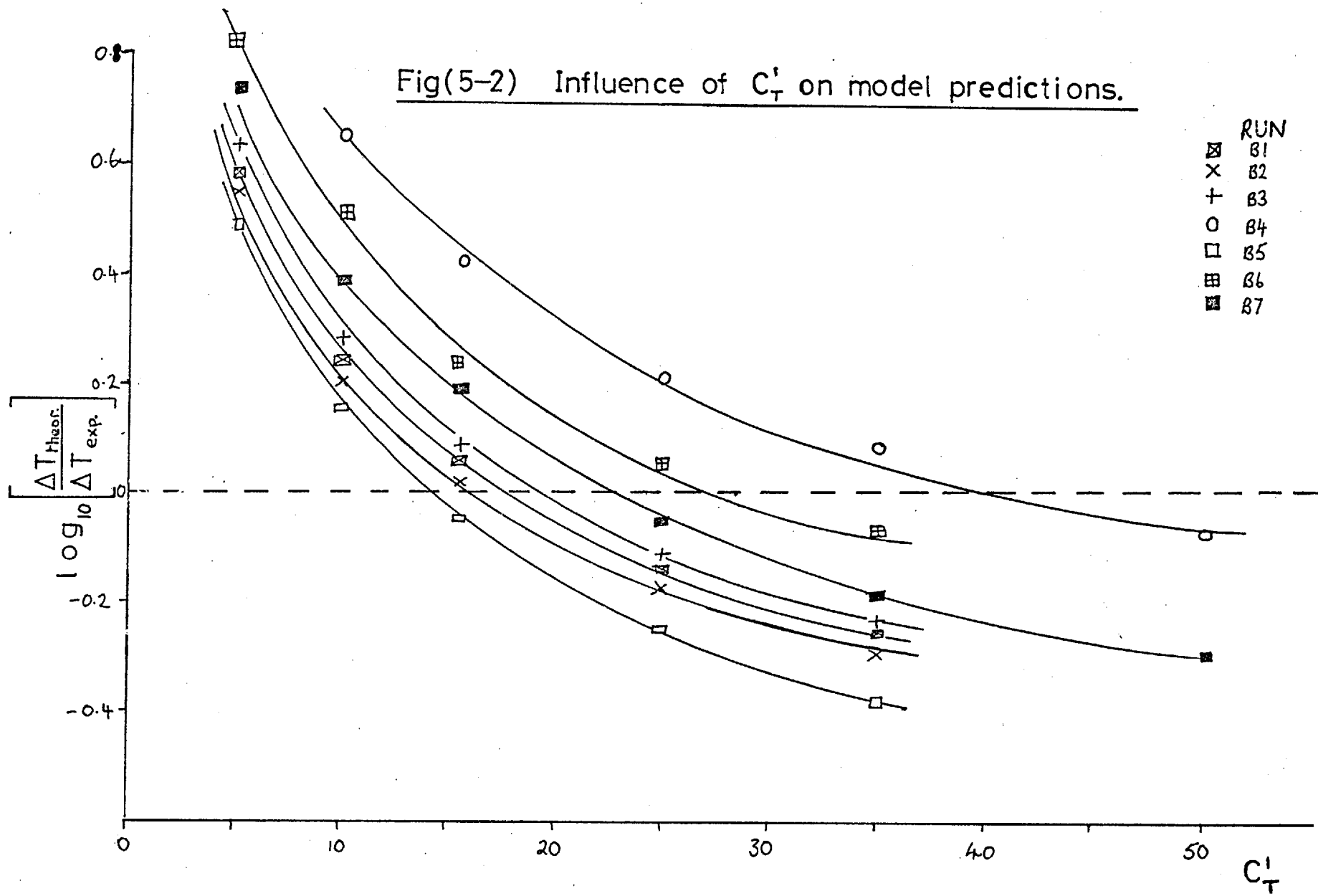
ΔT is the temperature difference between the bulk fluid and the pellet centre

Fig(5-1) Temperature and Concentration profiles in a catalyst pellet.



calculated concentration profiles.





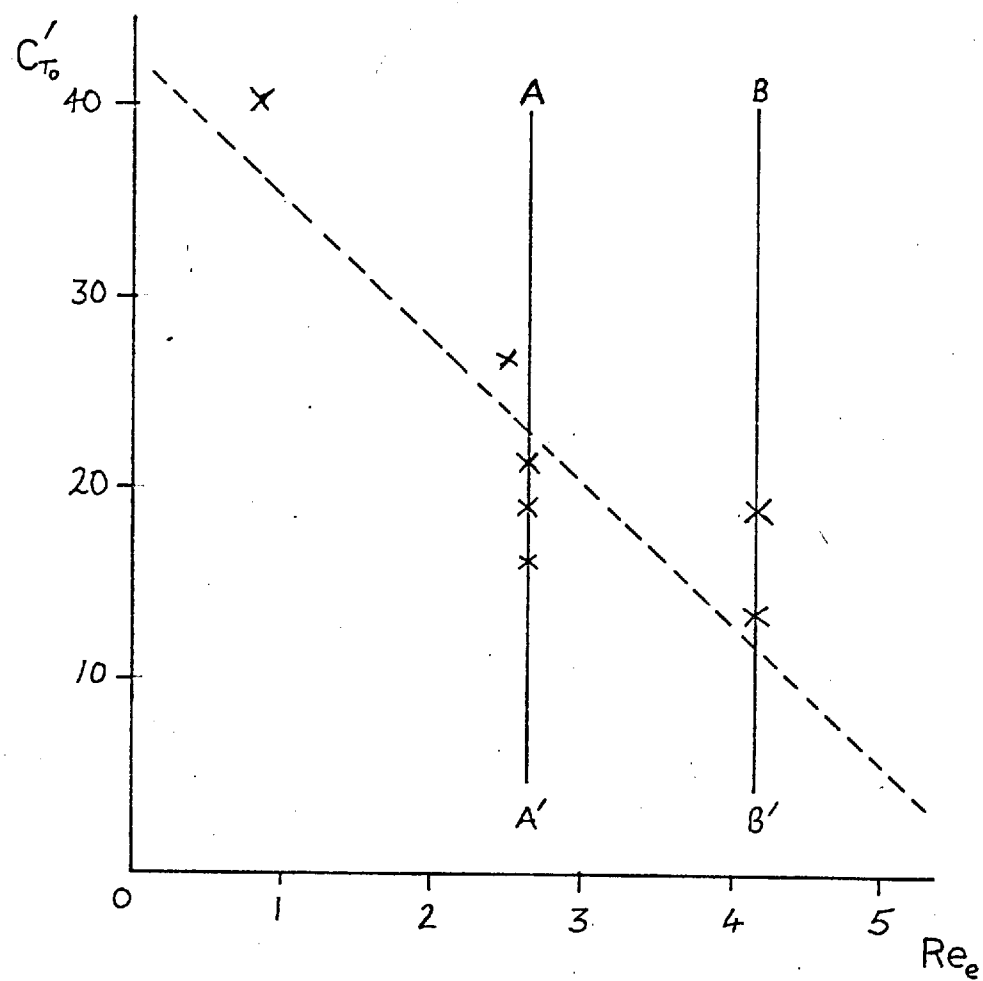
high Reynolds number. The three runs represented in the plane AA' of Figure (5.3) were carried out at temperatures of 715K, 735K and 755K and O_2 /Butene ratios of 2, 2 and 1.5 respectively. The two runs represented in the plane BB' of Figure (5.3) were performed at approximately the same temperatures but have O_2 /Butene ratios of 1.5 and 3.2. It is thus evident that the reaction conditions and, consequently, bulk conditions in the plane of the thermocouple, are a significant unknown factor in the analysis.

Calculations were performed to determine the sensitivity of the predictions to the bulk phase conditions. The results are shown in Table (5.3). It is evident from Figures (5.2), (5.3) and Table (5.3) that errors in the estimated bulk concentrations can account for the spread of points in Figure (5.3). This is demonstrated in Figure (5.4) where the points in Figure (5.3) have been recalculated by varying the bulk concentrations for butene and butadiene by 30% or less. The bulk concentrations were varied in a somewhat arbitrary manner and it must be emphasised that Figure (5.4) is to be regarded as an illustration only. Nevertheless it is very evident that correct estimation of the bulk concentrations in the plane of the thermocouple is essential for successful correlation of theoretical and experimental values.

One feature of Corrie's experimental measurements is worthy of mention. The difference between pellet centre temperature and pellet surface temperature shows good agreement with the theoretically predicted values when the 'smoothed' experimental profiles are considered. The differences are of the order of 1 deg K, which confirms the isothermality of the pellet and the greater importance of film heat transfer resistance compared to the intra-pellet resistances. However, the 'true' experimental profiles show peaks and troughs within the pellet (Figure (5.1)). In particular a peak is usually found near to the pellet surface. Corrie has attributed this effect to the possibility of increased pellet density near to the surface of the pellet caused by case hardening of the pellets during manufacture. The predictions of the pellet model have been recalculated for different values of the pellet bulk density within the range $4.1 \times 10^3 \text{ kgm}^{-3}$ to 4.9 kgm^{-3} . The results of these calculations are shown in Table (5.4) and Figure (5.5). The operating conditions were those already described for Run B6.

The variations predicted were somewhat smaller than the intra-pellet fluctuations measured. Another contributory factor might be the variance of the pellet effective diffusivities near to the surface due to a rearrangement of the pellet pore structure during hardening processes.

Fig(5-3) Best value for C'_{T_0} .



Fig(5-4) Adjustments to bulk values.

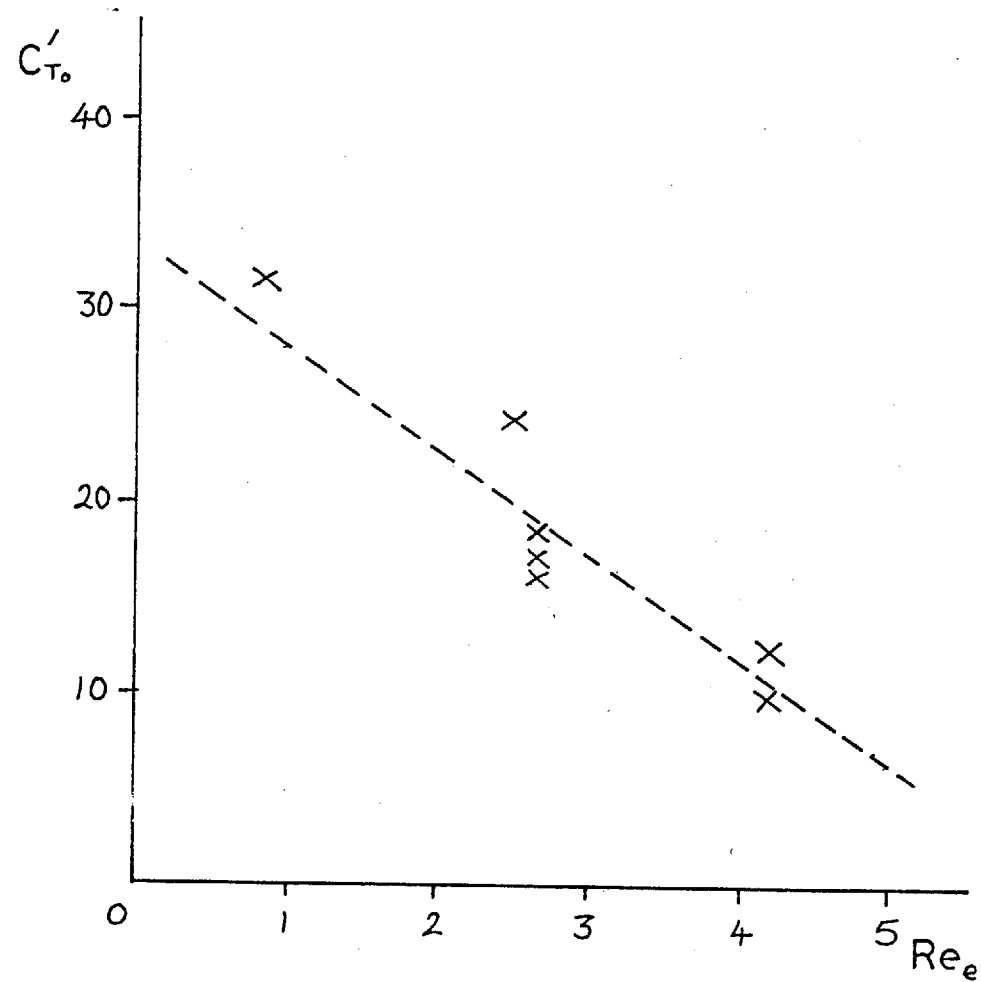


Table (5.3)

Sensitivity of predicted thermal effects to variation in bulk-phase concentrations

Run	(ΔT theoretical/ ΔT experimental)			
	BASE	1	2	3
B1	0.75	0.70	0.66	0.61
B2	0.68	0.65	0.61	0.56
B3	0.78	0.74	0.69	0.64
B4	1.71	1.60	1.48	1.37
B5	0.58	0.56	0.53	0.48
B6	1.13	1.06	1.00	0.92
B7	0.99	0.94	0.86	0.79

$C_T^1 = 25.0$ 'Base' refers to Table (5.2)

Conditions: 1. Butene concentration decreased and Butadiene concentration increased by 10%

2. Butene concentration decreased and Butadiene concentration increased by 20%

3. Butene concentration decreased and Butadiene concentration increased by 30%

It would be an easy matter, from the point of view of computation, to include radial variation of pellet bulk density and effective diffusivities in the pellet model. However it would be very difficult to obtain satisfactory experimental data for this effect.

It has been established, therefore, that the pellet model is reasonably successful in predicting fluid-solid temperature differences. However, it is evident that the model cannot be used in isolation and must be employed in conjunction with satisfactory estimates for the bulk fluid conditions surrounding the pellet and for the film transfer parameters between the pellet and the bulk gas phase.

5.4.2 Modelling the Combined Pellet and Reactor

It was felt that the problems summarised in the previous paragraphs could be most satisfactorily resolved by setting up a mathematical model for the pellet environment. This model will obviously incorporate the previously described pellet model for determination of the source terms.

In modelling the pellet environment, the following assumptions were made for a one-dimensional model.

- (i) The environment is regarded as an annular chemical reactor with the inner surface of the annular space acting as a source for both heat and mass.
- (ii) The heat transfer away from the reactor is represented by an overall heat transfer coefficient based on the temperature difference between the fluid in the annular space and the oven temperature.
- (iii) The fluid in the annulus is in plug flow.

Assumption (iii) is probably the least satisfactory, as the flow is superficially at very low Reynolds number. However, the principal area of interest is the first half of the pellet length and it is in this region that the thermocouple wires are instrumental in breaking up the flow patterns and promoting turbulence.

Adapting the one-dimensional, one-phase model described in Section (2.4) and using the assumptions above, the ^{descriptive} equations may be written as:

Mass balance for each species (See Fig. A5.1):

$$\frac{dC^i}{dz} = \frac{-kg^i dpC^{i,i}(1-c^i)\rho}{G(R_t^2 - dp^2/4)} \quad ; \quad i=1 \rightarrow 10 \quad (5.22)$$

Table (5.4)

Sensitivity of predicted thermal effects to variations in pellet bulk density

P_b	4881	4700	4500	4300	4100
ΔT	7.3	7.2	7.0	6.7	6.5

ΔT is the temperature difference between the bulk fluid and the pellet centre
 Run B6, $C_T^1 = 25.0$

Table (5.5)

Least squares values for C_{T1} and C_{T2}

Run	B1	B2	B3	B4	B5	B6	B7
C_{T1}	7.63	6.91	7.07	11.28	6.50	11.80	11.14
C_{T2}	7.91	15.92	9.05	12.69	6.54	4.92	10.56

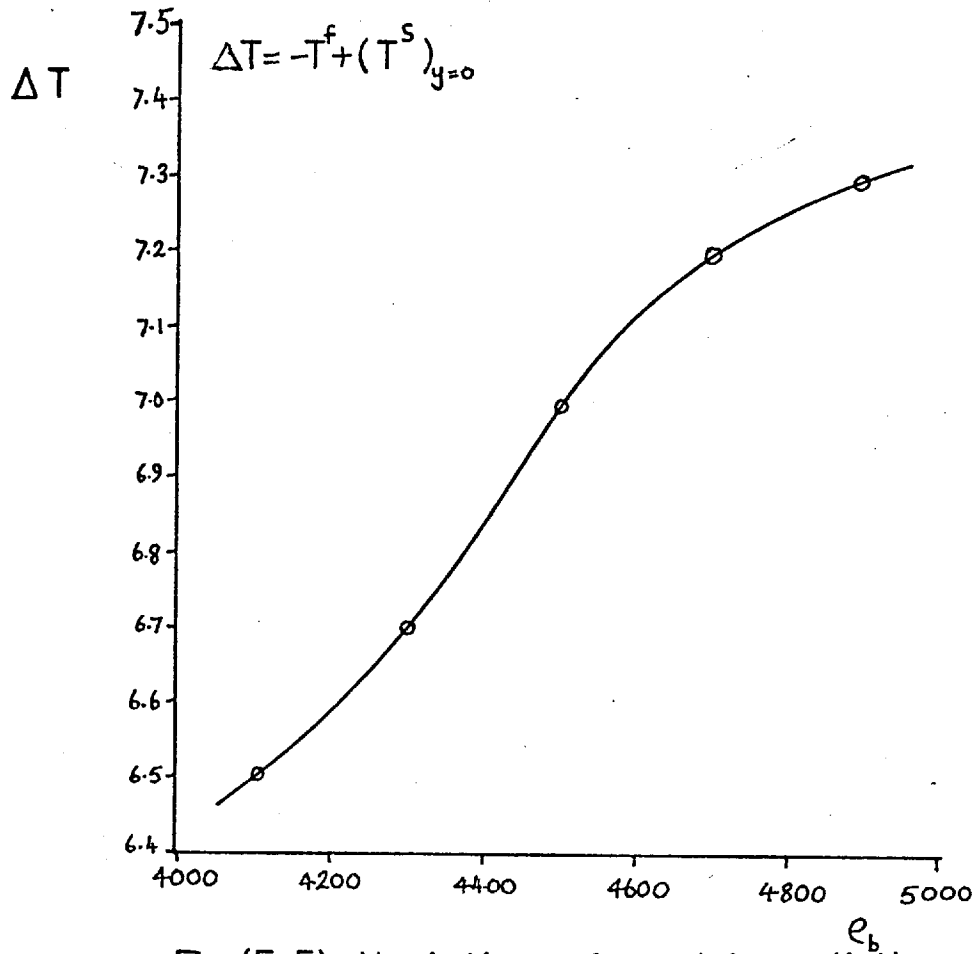


Fig (5-5) Variation of model prediction with catalyst bulk density.

$$\frac{dT^f}{dz} = \frac{2}{GC_p(R_t^2 - dp^2/4)} \left(\frac{dph_v}{2} (T^s - T^f) - R_t U (T^f - T_w) \right) \quad (5.23)$$

with initial condition:

$$z = 0; \quad C^i = C^i_{in}, \quad T^f = T_w \quad (5.24)$$

The parameters that require elucidation in this model are kg^i , h_v and U .

kg^i is eliminated from this discussion by using the Chilton-Colburn analogy to relate it to the parameter h_v . The validity of this assumption will be discussed later.

The pellet-fluid heat transfer coefficient, h_v , is given by equation (5.22a). C_{T1} replaces C_T^i in this expression.

$$\frac{h_v D_e}{k_f} = 1.86 C_{T1} (Pr)^{1/3} \left(\frac{D_e}{L'} \right)^{1/3} Re_e^{1/3}$$

The overall fluid-oven heat transfer coefficient may be similarly correlated as

$$\frac{UD_T}{k_f} = 1.86 C_{T2} (Pr)^{1/3} \left(\frac{D_T}{L'} \right)^{1/3} Re_T^{1/3} \quad (5.25)$$

Re_e is the Reynolds number based on D_e and Re_T is the Reynolds number based on D_T . As before L' has been set at 0.0085m which is the length of the pellet.

It is worth considering the factors contributing to C_{T1} and C_{T2} . C_{T2} consists of two factors. One will estimate the increased turbulence caused by the thermocouple wires in the annulus. The second will be a contribution due to the error in setting L' equal to the pellet length. L' is unlikely to be in error by more than a factor of 3 which, to the power one-third, means that this contribution to C_{T2} will be of the order 1.5. Fully turbulent heat transfer coefficients are of the order of 10 times greater than their laminar equivalents (136). Thus, even if the flow in the annulus does not become fully turbulent, C_{T2} might be expected to lie in the range, say, 3 to 15. C_{T1} will have the same contributory factors and an additional factor caused by pellet surface promoted turbulence. Thus C_{T1} may be expected to be similar to C_{T2} and an

approximate range of 5 to 20 would appear reasonable. When $Pr=0.74$, $D_e=0.00177$, $L'=0.0085$ are substituted into (5.22) a range for C_T' of 11 to 45 is obtained which is in good agreement with the findings of the previous section.

For given values of C_{T1} and C_{T2} , Equations (5.22) and (5.23) may be integrated simultaneously by the Runge-Kutta method.

Care must be taken over a suitable choice of steplength for this method. The two terms on the right hand side of the energy balance, Equation (5.23), are of similar magnitude and opposite sign. Thus, if the step length is chosen too small, the solution will become oscillatory and the results will be meaningless.

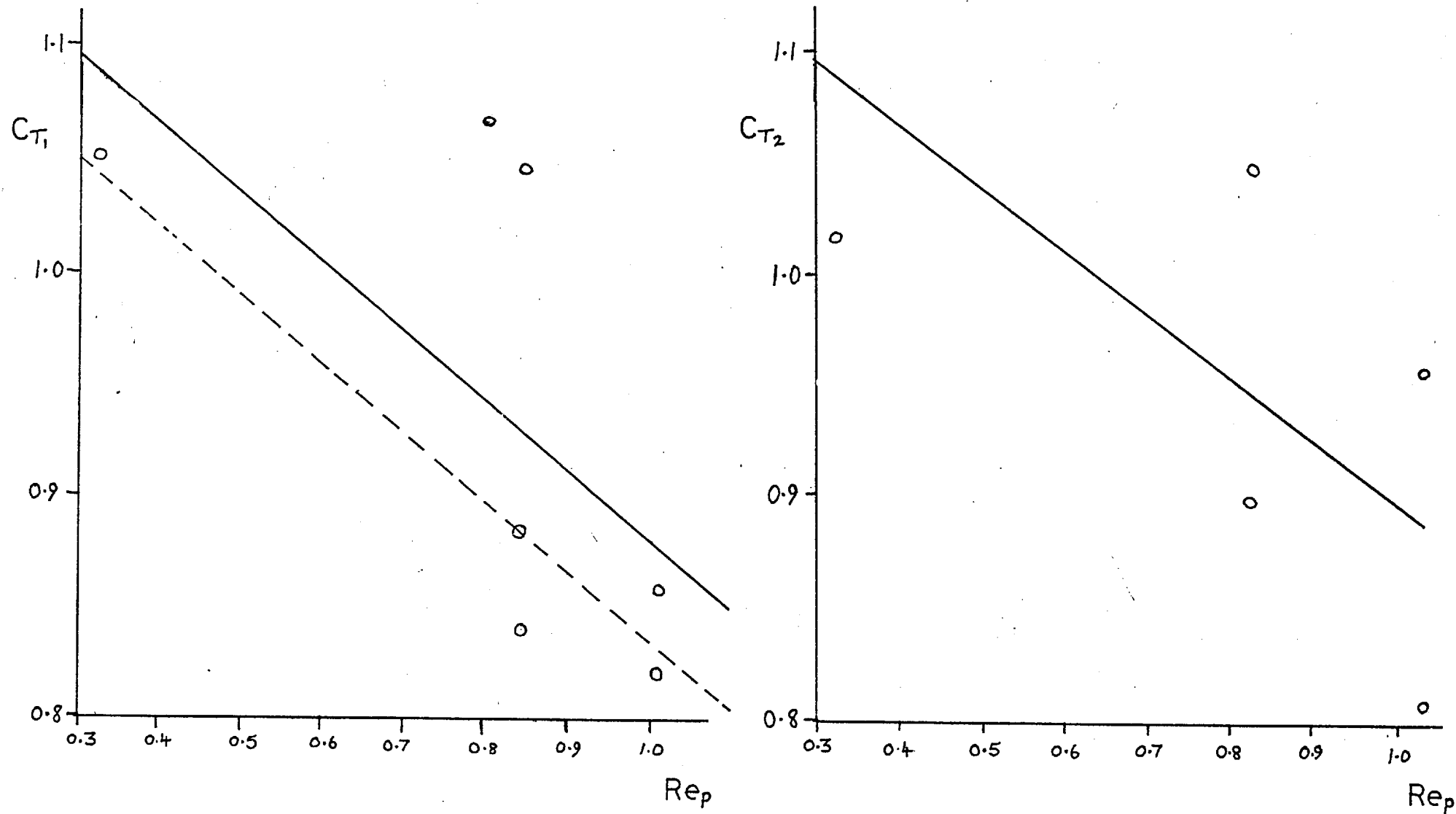
From the work of Corrie (26), values for the temperature of the fluid in the annulus may be extracted for each set of results. For a given pair of values of C_{T1} and C_{T2} , Equations (5.22) and (5.23) may be integrated between $z=0$ and $z=0.00425m$ (the plane of the thermocouples) and theoretical values obtained for this temperature and for the temperature difference between the fluid in the annulus and the pellet centreline.

For each of the seven runs considered in the previous section, values were found for C_{T1} , and C_{T2} which minimised the difference between theoretical and experimental values of these two temperatures. The minimisation procedure was due to Powell (141). Equations (5.22) and (5.23) were integrated by a Runge-Kutta procedure using 75 steps, and 120 grid points were used in SUBROUTINE CAT3A (Appendix A5) for the intra-pellet integration. Decreasing the steplengths below these values did not affect the predictions of C_{T1} and C_{T2} to three significant figures. The values found are shown in Table (5.5). It can be seen that the introduction of the second parameter has reduced the spread of results in C_{T1} .

Considering the proposed contributions towards C_{T1} and C_{T2} , it is a reasonable assertion that these parameters will show a dependency upon the Reynolds number, Re_p . Figures (5.6) shows the dependency of C_{T1} and C_{T2} respectively on Reynolds number. The plots are on log-log co-ordinates. The bold lines show the results of a linear least-squares regression analysis for the two sets of data. The equations for the lines are:

$$C_{T1} = 2.8(Re_p)^{-0.3} \quad (5.27)$$

$$C_{T2} = 2.7(Re_p)^{-0.3} \quad (5.28)$$



Fig(5-6) Best fit of C_{T_1} and C_{T_2} as $f(Re_p)$

The remarkable agreement between these correlations lends considerable support to the arguments for the introduction of these parameters.

Nevertheless, there is still considerable scatter about these correlating lines. In Figure (5.6) the broken line shows the correlation of Runs B1-B5. Run B6 and Run B7 appear to give anomalous results. It can be seen that these five runs show considerably less scatter about the broken line, the equation of which is:

$$C_{T1} = 2.6(Re_p)^{-0.3} \quad (5.29)$$

Note that the index on Re_p is retained.

Possible explanations for the admittedly wide scatter are:

- (i) The nature of the published intra-particle temperature profiles (26) makes estimation of an experimental value for the fluid-particle temperature difference accurate to within only 1 deg K. This is an error of 10% at best.
- (ii) The axial temperature increases in the annulus are very small ($\sim 2-5K$), considering the elevated absolute temperatures and the relatively large fluid-particle temperature differences.
- (iii) A great degree of uncertainty exists in the bulk diffusivity data.
- (iv) The Chilton-Colburn analogy is only established for turbulent condition.

It is probable that the last two explanations are of the greatest importance. It has been found that, whereas the combined pellet/annulus model is capable of predicting the observed thermal effects by suitable choice of C_{T1} and C_{T2} , the comparison between predicted and experimental values of butene conversion and butadiene selectivity is rather poor.

When the integration of the model for the annulus is continued to a length of 0.0085m (the end of the pellet) the theoretically predicted yields are shown in Table (5.6). The yield is defined by:

$$\text{yield \%} = \frac{(\text{moles of product})}{(\text{moles of reactant})} \times \frac{100}{\alpha}$$

$$\text{where } \alpha = \frac{\text{no. of C atoms in reactant}}{\text{no. of C atoms in product}}$$

The discrepancy in the results is partly explained by effects (iii) and (iv) above. Effect (iii) may only be eliminated by specific

Table (5.6)

Theoretical and Experimental Product Yields

RUN	BUTENE		BUTADIENE		CO ₂		CO	
	theor.	expt.	theor.	expt.	theor.	expt.	theor.	expt.
B1	58.7	50.8	36.7	19.7	25.9	20.9	3.6	5.1
B2	52.2	44.1	41.3	23.3	33.8	25.0	4.6	5.4
B3	69.2	58.7	27.7	21.4	20.2	15.7	2.7	4.6
B4	12.9	39.7	70.8	20.0	79.7	28.4	10.5	5.8
B5	62.3	46.5	32.3	17.5	26.1	32.6	3.8	6.7
B7	52.9	45.6	42.9	18.5	36.8	21.0	4.6	6.5

experimental evaluation of the bulk diffusivities of the relevant chemical species at the elevated temperatures employed. Effect (iv) could possibly be resolved by the introduction of a third parameter, C_{T3} say, whereby (A5.4) is modified to:

$$kg^i = C_{T3} \frac{h_v Pr}{C_{pp}} (Sc^i)^{-2/3} \quad (5.30)$$

In this case, C_{T3} is a measure of the validity of the Chilton-Colburn analogy at a given Reynolds number. This approach, although holding promise, was not pursued in the present work because the calculations involved in the two-parameter minimisation, involving two numerical integrations for each pair of parameters tested, was found to be excessively time consuming and it was felt that the further time required for a three parameter minimisation would not provide commensurate returns.

Additionally C_{T1} and C_{T2} should be recalculated after the plane of the thermocouples as the thermocouple wires a major source of the turbulence, are now no longer influencing the flow patterns.

It is possible that homogeneous reaction is occurring in the system. Corrie has observed homogeneous reaction during his investigation although he has not reported it specifically for these runs. Homogeneous reaction has not yet been incorporated into the model.

Referring to Table (5.6), the typical situation is for butene and butadiene yield to be predicted too high and CO yield to be predicted too low. Corrie has reported CO to be the principal product of homogeneous reaction. Thus homogeneous reaction could account for most of the discrepancies in Table (5.6). Run B4 is anomolous, in that too much reaction has been predicted. This run had a considerably lower mass flow rate than the other runs and so probably had the highest error in the prediction of heat and mass transfer coefficients.

5.5 CONCLUSIONS

A model has been set up describing kinetic and transport effects in and around a single cylindrical catalyst pellet within a glass tube. The model has been used to predict thermal effects and the conversion of butene to butadiene over a tin/antimony oxide catalyst and the results have been compared with experimental findings.

It has been found that thermal effects may be predicted with accuracy

by variation of two parameters affecting the film heat transfer coefficients at the two annular surfaces.

The outlet concentrations of butene and butadiene are less well predicted and this is thought to be due to large uncertainties in the bulk mass diffusion data available, to error in the available correlation for film mass transfer coefficients between the pellet and the reacting fluid and to the possibility of homogeneous reaction. It is proposed that these uncertainties are partly responsible for the scatter that exists when the film heat transfer parameters C_{T1} and C_{T2} are correlated with Reynolds Number Re_p .

It is concluded that the primary objective of the study has been successful, in that a model has been proposed which is capable of predicting the thermal effects observed by Corrie (26) during butene oxidation. The secondary objective has only partly been achieved in that no positive demonstration of the ability of the model to predict minor product formation has been given. Indeed the prediction of the major product, butadiene, is poor. Nevertheless, the reasons for this have been outlined and it is thought that the model is a sound basis for development. Future work, both theoretical and experimental, would well be directed to catalyst pellets in fixed bed situations under conditions where uncertainty in film transfer data is not such a serious drawback. Corrie gives no experimental data for aldehyde production and a combined experimental and theoretical investigation centred on this effect, rather than on thermal effects, would prove advantageous, particularly in the context of future use of the model in heterogeneous-homogeneous situations as aldehydes are known to promote gas-phase attack of hydrocarbons.

Chapter 6

DIFFUSION AND CHEMICAL REACTION IN A CATALYST PELLET WITH HOLLOW CYLINDRICAL GEOMETRY

6.1 Introduction

6.1.1 Reasons for Considering Hollow Cylindrical Pellets

6.1.2 Previous Work on Hollow Pellets

6.2 The Equivalent Hollow Sphere Model

6.2.1 Introduction

6.2.2 Equivalence of Spherical and Cylindrical Pellets

6.2.3 Mathematical representation of the model

6.3 Predictions of the Equivalent Hollow Sphere Model

6.3.1 Asymptotic behaviour

6.3.2 Comparison with other models

6.4 Variation of hollow pellet geometry for optimum performance

6.4.1 Single irreversible reaction

6.4.2 Heterogeneous - Homogeneous reactions

6.5 Conclusions

6.1 INTRODUCTION

The interaction of diffusion and reaction in a catalyst pellet has been the subject of extensive research (see below). Little attention, however, has been paid to the case where the catalyst pellet has the geometry of a hollow cylinder.

6.1.1 Reasons for considering hollow cylindrical pellets

The consideration of hollow catalyst pellets is not merely of theoretical interest. In some situations they can have definite advantages over similarly dimensioned solid pellets. Additionally, it may be noted that the manufacture of hollow pellets does not present any great technological problems as they may be produced by extrusion processes. As has been shown in Section (4.7), only the isothermal catalyst pellet need be considered here if the model is to be used in a two-phase model for a chemical reaction.

Generally speaking, the advantage to be achieved by their use is threefold. The maximum usage of catalyst material may be approached by removal of 'dead spaces' in the pellet interior which result from reactant exhaustion (i.e. in cases of rapid reaction or large catalyst pellets). In addition, the use of hollow pellets can result in a reduction in pressure drop across a packed catalytic bed. Thirdly, the heat transfer characteristics of a packed bed may be improved by using hollow catalyst pellets (see Section (2.6)).

In the context of the present research there are further considerations which lead to an interest in this pellet geometry. These arise from the possibility of occurrence of both heterogeneous and homogeneous reactions. Three general cases may be considered.

Concurrent heterogeneous and homogeneous reactions may obviously be selectively controlled by varying the degree of hollowing in a bed of cylindrical pellets, but consecutive reactions may be of two types. Assuming that the heterogeneous reaction is always the first step in the consecutive scheme (i.e. an intermediate is formed on the catalyst), then, if the subsequent homogeneous reaction is desirable, it is possible to have an optimum pellet geometry such that the intermediate production is enhanced whilst simultaneously increasing the amount of space available for the homogeneous reaction. An optimum is clearly reached as the limiting situation of total pellet hollowing results in no reaction at all.

For an undesirable homogeneous reaction (e.g. gas-phase overoxidation

of heterogeneously formed products) a small amount of pellet hollowing may result in an increase in product yield. The actual behaviour will depend strongly on the relative values of the kinetic parameters (see Section 6.4.2).

6.1.2 Previous work on hollow pellets

The problem of predicting the behaviour of hollow cylindrical catalyst pellets has been approached in two ways. Following Petersen (1) and Aris (149), the relative importance of diffusion and reaction in an arbitrarily shaped catalyst pellet may be characterised by a Thiele modulus, Λ , in which the length parameter is the ratio of volume to external surface area of the pellet. The inhibiting effect of intra-particle diffusion is usually expressed as an effectiveness factor. It is shown by these authors that the analytical expression for the effectiveness factor of a flat slab of isothermal catalyst material is applicable to an arbitrarily shaped catalyst pellet if the Thiele modulus is defined in this way.

We may therefore write (1):

$$\epsilon = \frac{\tanh(\Lambda)}{\Lambda} \quad (6.1)$$

where Λ , the modified Thiele modulus, is given by:

$$\Lambda = \frac{(1-\alpha)\beta\theta'}{2(1-\alpha+\beta)}; \quad \theta' = b\sqrt{\frac{k'}{D_{\text{eff}}}} \quad (6.2)$$

This approach will be referred to as the equivalent slab model. It has been specifically applied to hollow cylindrical catalyst pellets by Basmadjian (150), Rester and Aris (151) and Rester, Jouven and Aris (152).

Gunn (153, 154) has provided a rigorous approach to the problem. He has presented an analytical solution to the conservation equation and corresponding boundary conditions for simultaneous reaction and mass transfer in an isothermal anisotropic cylindrical pellet. He considers both solid and hollow cylinders. The effectiveness factor is presented, in the form of charts, for various values of α , β and θ' .

It is felt that the computational requirements of Gunn's approach are such that practical use of the method in packed bed reactor design is precluded. On the other hand the equivalent slab model was thought to provide a rather poor representation of the geometry of the system.

The following theory was developed as a compromise between the two approaches. Comparisons of results from the three models are presented

in Section (6.3).

6.2 THE EQUIVALENT HOLLOW SPHERE MODEL

6.2.1 Introduction

It is proposed that the hollow cylindrical catalyst pellet be modelled by an equivalent hollow sphere assuming that the bulk gas has equal access to the inner and outer surfaces of the sphere.

The choice of this model representation of the system affords the following advantages:

- (i) The problem is reduced from two dimensions to one dimension
- (ii) The balance equation for spherical geometry is handled more easily than that for cylindrical geometry
- (iii) The hollow sphere retains the concept of a finite shape.

6.2.2 Equivalence of Spherical and Cylindrical Pellets

The equivalence of the hollow sphere and the hollow cylinder is specified by:

- (i) Equal external area of sphere and cylinder
- (ii) Equal volume of catalyst material in sphere and cylinder.

These conditions result in the following pair of equations:

$$r_e^2(1+a^2) = \frac{b^2}{2} [(1+\alpha)\beta + (1-\alpha^2)] \quad (6.3)$$

$$r_e^3(1-a^3) = \frac{3b^3}{4} \beta(1-\alpha^2) \quad (6.4)$$

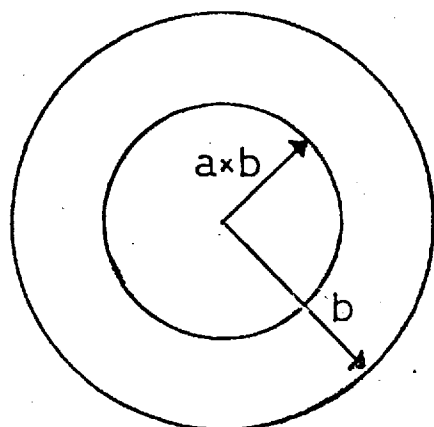
These two equations may be solved simultaneously to yield r_e and a , which specify the equivalent hollow sphere.

6.2.3 Mathematical representation of the equivalent hollow sphere model

Consider a hollow sphere with dimensions as shown in Figure (6.1). It is widely reported (e.g. 1) that the interaction of diffusion and first order isothermal chemical reaction in a spherical catalyst pellet may be represented by:

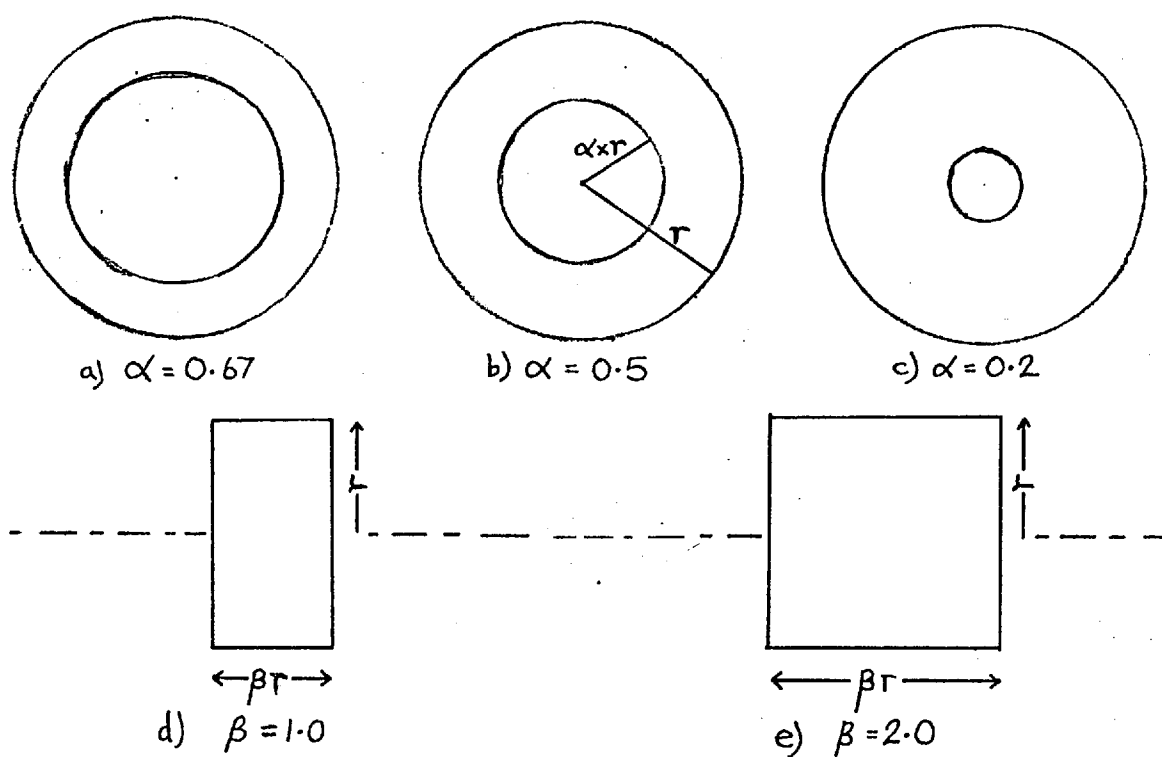
$$\frac{1}{y^2} \frac{d}{dy} \left(y^2 \frac{dx}{dy} \right) - \lambda^2 x = 0 \quad (6.5)$$

Subject to boundary conditions for the hollow sphere:

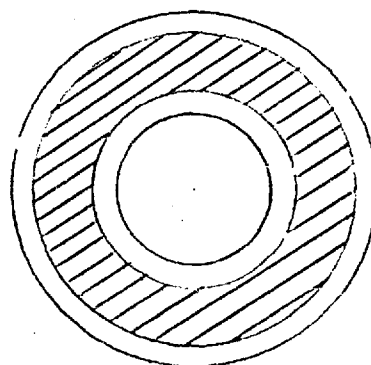
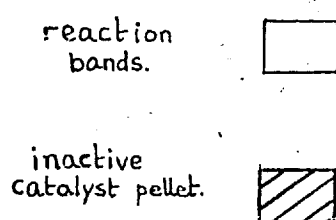


Fig(6-1) Dimensions of "equivalent hollow sphere".

Fig(6-2) Relative dimensions of hollow catalyst pellets.



Fig(6-3) Catalyst usage at high Thiele modulus.



$$\begin{aligned} y &= 1; & X &= 1 \\ y &= a; & X &= 1 \end{aligned} \quad (6.6)$$

Defining a new variable,

$$v = yX \quad (6.7)$$

and substituting (6.7) into (6.5) and (6.6) the following differential equation and boundary conditions are obtained.

$$\frac{d^2 v}{dy^2} - \lambda^2 v = 0 \quad (6.8)$$

$$\begin{aligned} y &= 1 & v &= 1 \\ y &= a & v &= a \end{aligned} \quad (6.9)$$

The general solution to (6.8) may immediately be written as

$$v = A' \exp(-\lambda y) + B' \exp(\lambda y) \quad (6.10)$$

A' and B' are obtained by substitution of (6.9) into (6.10) resulting in:

$$A' = \frac{\exp[(1+a)\lambda] - a \exp(2\lambda)}{\exp(a\lambda) - \exp[(2-a)\lambda]} \quad (6.11a)$$

$$\text{and } B' = \frac{a - \exp[(1-a)\lambda]}{\exp(a\lambda) - \exp[(2-a)\lambda]} \quad (6.11b)$$

Substitution of (6.11) into (6.10) yields the concentration profile in the equivalent hollow sphere:

$$X = \frac{1}{y} \left[\frac{\exp[(1+a)\lambda] - a \exp(2\lambda)}{\exp(a\lambda) - \exp[(2-a)\lambda]} \exp(-\lambda y) + \frac{a - \exp[(1-a)\lambda]}{\exp(a\lambda) - \exp[(2-a)\lambda]} \exp(\lambda y) \right] \quad (6.12)$$

Following normal practice (1) the effectiveness factor is defined by:

$$\epsilon = \frac{\text{actual rate of reaction in catalyst pellet}}{\text{rate of reaction in the absence of diffusional resistance}}$$

We may thus write the effectiveness factor for the hollow sphere as:

$$\epsilon = \frac{3}{4\pi(1-a^3)\lambda^2 b^2} \left[S_1 \frac{dX}{dy} \Big|_{y=1} + S_a \frac{dX}{dy} \Big|_{y=a} \right]$$

and, making the correct substitution for S_1 and S_a :

$$\epsilon = \frac{3}{(1-a^3)\lambda^2} \left[\frac{dX}{dy} \Big|_{y=1} - a \frac{2dX}{dy} \Big|_{y=a} \right] \quad (6.13)$$

The negative sign in (6.13) arises from the opposite sense of the gradients at the two surfaces.

Differentiating (6.12) and reintroducing A' and B' for the sake of convenience:

$$\frac{dX}{dy} = \frac{1}{y^2} \left[B'(\lambda y - 1)\exp(\lambda y) - A'(\lambda y + 1)\exp(-\lambda y) \right] \quad (6.14)$$

Finally, substitution of (6.14) into (6.13) yields:

$$\epsilon = \frac{3}{(1-a^3)\lambda^2} \left[(\lambda - 1)B'\exp(\lambda) + (a\lambda + 1)A'\exp(-a\lambda) - (\lambda + 1)A'\exp(-\lambda) - (a\lambda - 1)B'\exp(a\lambda) \right] \quad (6.15)$$

Thus, for given values of α , β and Θ' ; a , b and thus λ may be calculated from (6.3) and (6.4) and used in (6.15) with (6.11a) and (6.11b) to calculate the isothermal effectiveness factor.

6.3 PREDICTIONS OF THE EQUIVALENT HOLLOW SPHERE MODEL

The predictions of the equivalent hollow sphere model were compared with the predictions of the equivalent slab model and of Gunn's analysis (154).

In order to facilitate comparison between the models a utility factor will be defined as:

$$\eta = \frac{\text{rate of reaction per unit volume of a reactor bed of hollow cylinders}}{\text{rate of reaction per unit volume of a reactor bed of similar solid cylinders without diffusional resistance.}}$$

If it is assumed that the hollow cylinders pack in the same manner as the solid cylinders (154), then the utility factor is simply defined by:

$$\eta = \epsilon(1-\alpha^2) \quad (6.16)$$

where ϵ is the effectiveness factor of the hollow cylinders. Table (6.1) shows the predictions of the three models in terms of utility factors as defined in (6.16) for values of β of 1.0 and 2.0 and for values of α of 0.2, 0.5 and 0.67. It should be emphasised that α is the fraction of hollowing of the hollow cylinder. These values for α and β represent reasonable physical limits to the problem. A value of α greater than 0.67 would probably yield a pellet with rather poor strength characteristics, whereas a value of α of less than 0.12 may hinder bulk diffusion of reactants to the inner surface of the hollow cylinder, thus violating the boundary condition implicit in all three models that the inner surface is at bulk conditions. In fact as α becomes small, the hollow part of the cylinder may effectively be regarded as a macro-pore along the axis of the pellet. The mathematical representation of such a system within the flow situation of a chemical reactor might be expected to be rather difficult to formulate.

Values of β greater than about two result in pellets which may be regarded as thin cylinders: as such they may be expected to have rather loose packing characteristics. Values of β of less than about 1 may be regarded as representing catalyst discs. If arranged "in order", such discs may be packed very tightly with the resulting problems of high pressure drops. If packed randomly, the discs might also be expected to pack loosely. A value for β of 2 might be expected to provide optimum packing characteristics as the pellet is quasi-spherical in shape. Figures (6.2a) to (6.2e) show the relative dimensions represented by these values of α and β .

The utility factors obtained by the equivalent hollow sphere method are shown in Figures (6.4) and (6.5) for β values 1 and 2 respectively.

6.3.1 Asymptotic behaviour of the equivalent hollow sphere model

For low values of the Thiele modulus, the effectiveness factor tends to unity and the utility factor exhibits an asymptote in this region of $(1-\alpha^2)$.

As the Thiele modulus becomes large the curves of Figures (6.4) and (6.5) again approach an asymptote. It is found that these asymptotes are parallel and have a slope of $-\frac{1}{2}$. This value may be deduced analytically by consideration of the equivalent slab model.

From (6.1) and (6.16):

Table (6.1)

Comparison of predictions of equivalent hollow sphere model with other published predictions

η_G utility factor calculated by Gunn (153), (154)

η_A utility factor calculated by equiv. slab model

η_H utility factor calculated by equiv. hollow sphere model

$$\Delta_1 = \frac{\eta_A - \eta_G}{\eta_G} \times 100\%; \quad \Delta_2 = \frac{\eta_H - \eta_G}{\eta_G} \times 100\%$$

$$\Delta_3 = \frac{\eta_A - \eta_H}{\eta_G} \times 100\%$$

β	α	θ^2	η_G	η_A	η_H	$\Delta_1\%$	$\Delta_2\%$	$\Delta_3\%$
1.0	0.5	1.0	0.742	0.743	0.743	0.15	0.10	~
1.0	0.5	10.0	0.658	0.687	0.684	4.48	3.99	0.45
1.0	0.5	31.6	0.536	0.587	0.581	9.59	8.38	1.02
1.0	0.5	100.0	0.373	0.419	0.412	12.33	10.36	1.69
1.0	0.5	316.2	0.229	0.252	0.248	9.92	8.18	1.60
1.0	0.5	1000.0	0.133	0.142	0.141	6.99	5.95	0.71
1.0	0.5	3162.3	0.0769	0.0800	0.0796	4.06	3.49	0.50
1.0	0.5	10000.0	0.0442	0.0450	0.0449	1.81	1.50	0.25
1.0	0.67	1.0	0.547	0.548	0.548	0.23	0.22	~
1.0	0.67	10.0	0.514	0.524	0.524	2.03	1.89	~
1.0	0.67	31.6	0.457	0.476	0.474	4.22	3.81	0.42
1.0	0.67	100.0	0.354	0.376	0.373	6.12	5.27	0.80
1.0	0.67	316.2	0.228	0.244	0.241	6.94	5.89	1.24
1.0	0.67	1000.0	0.133	0.140	0.139	5.53	4.79	0.72
1.0	0.67	3162.3	0.0758	0.0790	0.0787	4.21	3.79	0.38
1.0	0.67	10000.0	0.0432	0.0444	0.0443	2.82	2.59	0.22
1.0	0.2	1.0	0.936	0.944	0.943	0.91	0.71	0.17
1.0	0.2	10.0	0.788	0.828	0.815	5.07	3.47	1.57
1.0	0.2	31.6	0.602	0.652	0.632	8.26	5.04	3.12
1.0	0.2	100.0	0.382	0.422	0.407	10.46	6.60	3.17
1.0	0.2	316.2	0.225	0.243	0.237	7.89	5.25	2.50
1.0	0.2	1000.0	0.130	0.137	0.135	5.08	3.62	1.47
1.0	0.2	3162.3	0.0746	0.0768	0.0762	2.98	2.17	0.79

Table (6.1) CONTINUED

β	α	θ^2	η_G	η_A	η_H	$\Delta_1\%$	$\Delta_2\%$	$\Delta_3\%$
1.0	0.2	10000.0	0.0424	0.0432	0.0430	1.89	1.44	0.46
2.0	0.5	1.0	0.727	0.740	0.740	1.81	1.74	~
2.0	0.5	10.0	0.640	0.664	0.660	3.71	3.16	0.61
2.0	0.5	31.6	0.505	0.540	0.533	6.87	5.64	1.28
2.0	0.5	100.0	0.329	0.362	0.356	9.88	8.18	1.66
2.0	0.5	316.2	0.193	0.211	0.208	9.09	7.79	1.42
2.0	0.5	1000.0	0.112	0.119	0.118	5.88	5.14	0.84
2.0	0.5	3162.3	0.0635	0.0667	0.0664	5.02	4.60	0.46
2.0	0.5	10000.0	0.0360	0.0375	0.0374	4.17	3.94	0.28
2.0	0.67	1.0	0.545	0.547	0.547	0.45	0.43	~
2.0	0.67	10.0	0.505	0.517	0.516	2.37	2.23	0.19
2.0	0.67	31.6	0.436	0.458	0.457	5.08	4.71	0.25
2.0	0.67	100.0	0.320	0.346	0.344	8.08	7.38	0.58
2.0	0.67	316.2	0.200	0.216	0.214	8.00	7.24	0.93
2.0	0.67	1000.0	0.115	0.123	0.122	6.97	6.48	0.82
2.0	0.67	3162.3	0.0659	0.0691	0.0690	4.99	4.72	0.14
2.0	0.67	10000.0	0.0379	0.0389	0.0389	2.66	2.51	~
2.0	0.2	1.0	0.920	0.935	0.932	1.60	1.25	0.33
2.0	0.2	10.0	0.702	0.763	0.745	8.67	6.16	2.40
2.0	0.2	31.6	0.482	0.551	0.531	14.41	10.20	3.70
2.0	0.2	100.0	0.295	0.334	0.323	13.15	9.54	3.35
2.0	0.2	316.2	0.170	0.189	0.185	11.14	8.85	1.93
2.0	0.2	1000.0	0.100	0.106	0.105	6.25	5.02	0.95
2.0	0.2	3162.3	0.0571	0.0598	0.0594	4.64	3.96	0.67
2.0	0.2	10000.0	0.0323	0.0336	0.0335	4.02	3.65	0.30

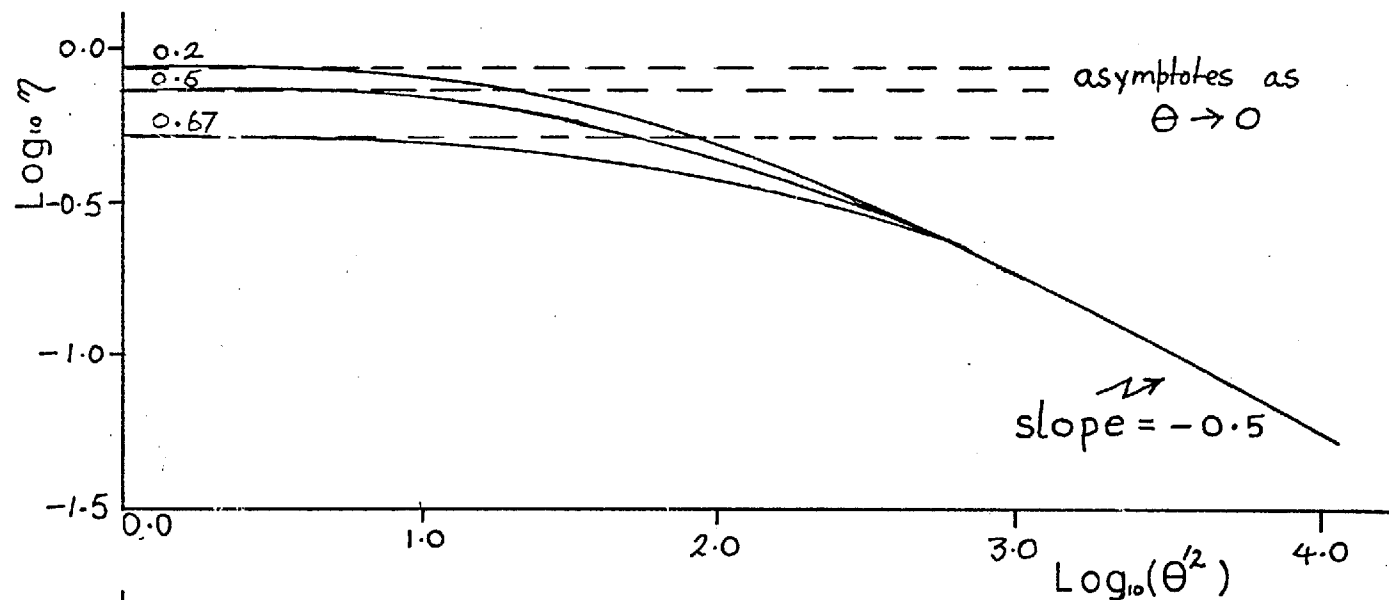


Fig (6-4)

$\log_{10} \eta$ vs. $\log_{10}(\theta^{1/2})$.

α shown as parameter.

$$\beta = 1.0$$

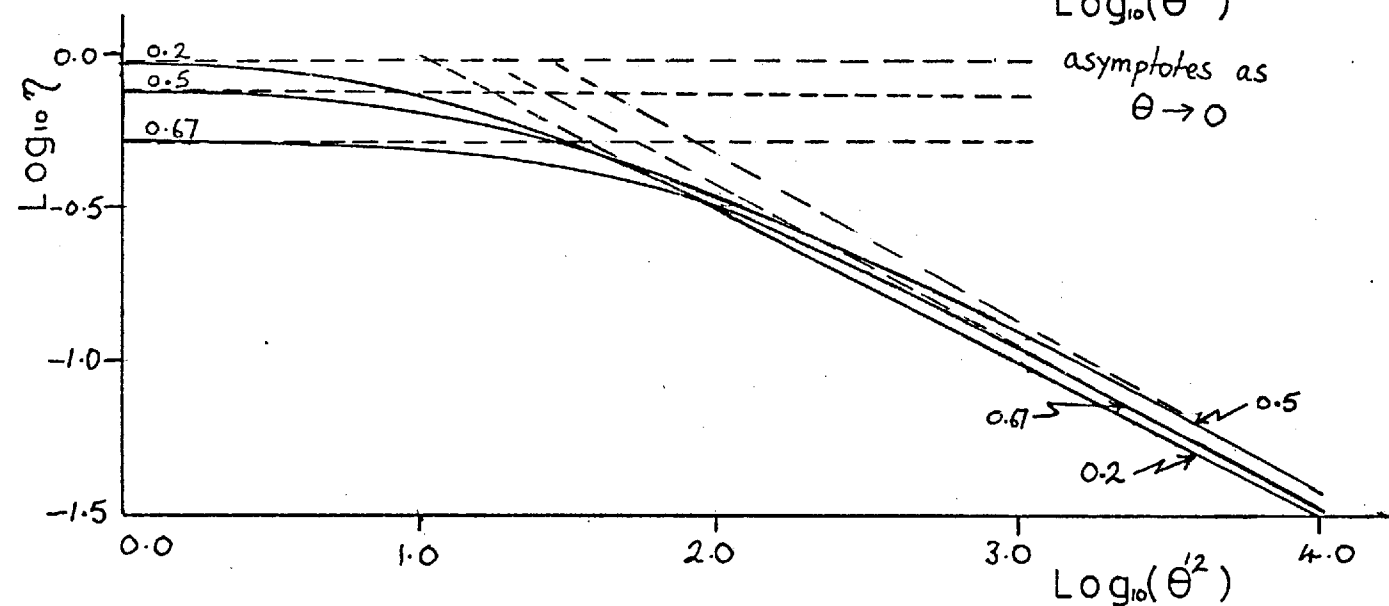


Fig (6-5)

$\log_{10} \eta$ vs $\log_{10}(\theta^{1/2})$.

α shown as parameter.

$$\beta = 2.0$$

$$\eta = \frac{(1-\alpha^2) \tanh(\mathcal{L})}{\mathcal{L}} \quad (6.17)$$

as $\mathcal{L} \rightarrow \infty$, $\tanh(\mathcal{L}) \rightarrow 1$ and (6.17) may be simplified, using (6.2)

$$\eta = \frac{2}{\beta \theta'} (1-\alpha+\beta)(1+\alpha)$$

Taking logarithms and rearranging:

$$\text{Log } \eta = \text{Log } \frac{2(1+\alpha)(1-\alpha+\beta)}{\beta} - \frac{1}{2} \text{Log}(\theta'^2) \quad (6.18)$$

This demonstrates that for large values of $\mathcal{L}$ (i.e. θ'), the graph of $\text{Log } \eta$ against $\text{Log } \theta'^2$ shows an asymptote of gradient $-\frac{1}{2}$. The asymptotes of Gunn's curves (153) also have this slope.

The absolute position of this asymptote is also of interest and may be specified by the value of θ'^2 at the point of intersection of the asymptote and the line $\eta=1$.

When $\eta=1$, $\log \eta = 0$ and (6.18) becomes:

$$\theta' = \frac{2(1+\alpha)(1-\alpha+\beta)}{\beta} \quad (6.19)$$

The positions of the asymptote in Figure (6.5) as $\theta'^2 \rightarrow \infty$ are well represented by (6.19) and (6.19) also predicts that for $\beta=1$, the asymptotes as $\theta'^2 \rightarrow \infty$ for $\alpha=0.2$, 0.5 and 0.67 are almost coincident (see Figure (6.4)).

It may be predicted from these considerations that all three models will provide coincident results as $\theta' \rightarrow \infty$ and as $\theta' \rightarrow 0$.

Closer inspection of Figure (6.5) reveals that the curves "cross over" before reaching their asymptotic forms, which implies that as the Theile modulus becomes larger - i.e. diffusional limitations become more important - the pellet geometry may be optimised with respect to the degree of pellet hollowing.

6.3.2 Comparison of the equivalent hollow sphere model with the predictions of other models

The most elaborate model that exists in the literature for prediction of the behaviour of hollow cylindrical catalyst pellets is that of Gunn (153) and it is of interest to see how well other, less elaborate models reproduce the results of that work.

It should be emphasised that Gunn's predictions must not necessarily be regarded as being correct, as there appears to be no published

experimental data for comparison.

The discrepancies between the three models have been calculated and are presented in Table (6.1). It may be seen that, in all cases considered, the equivalent hollow sphere model is a better approximation to the full solution than the equivalent slab model.

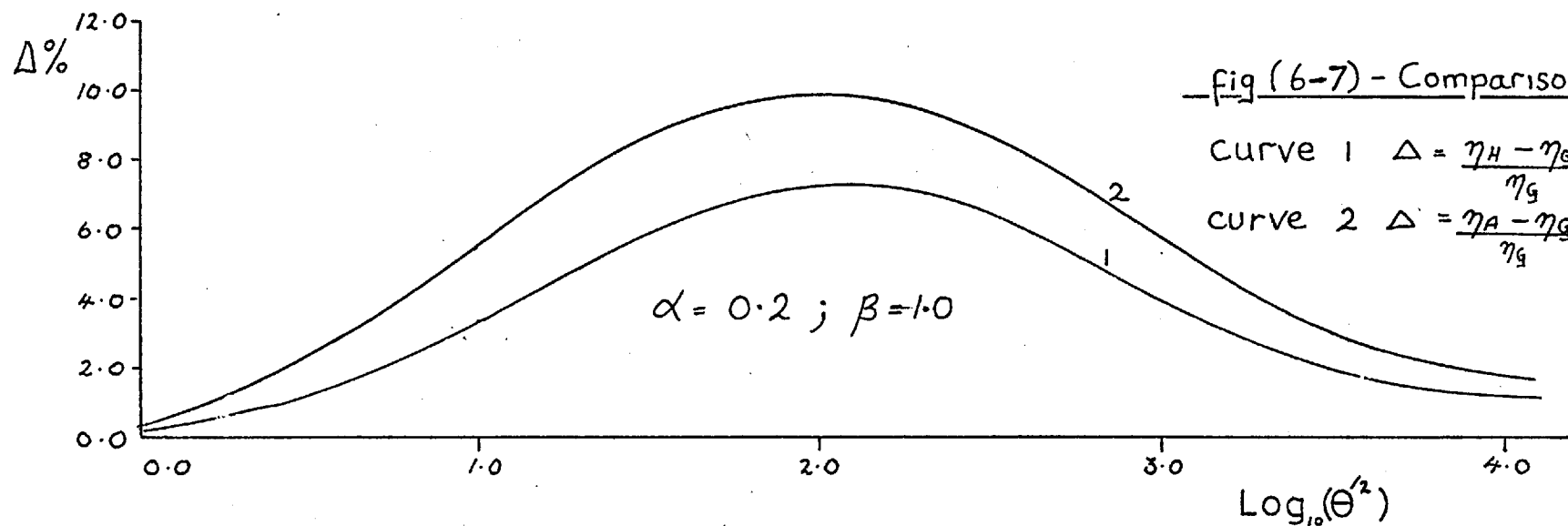
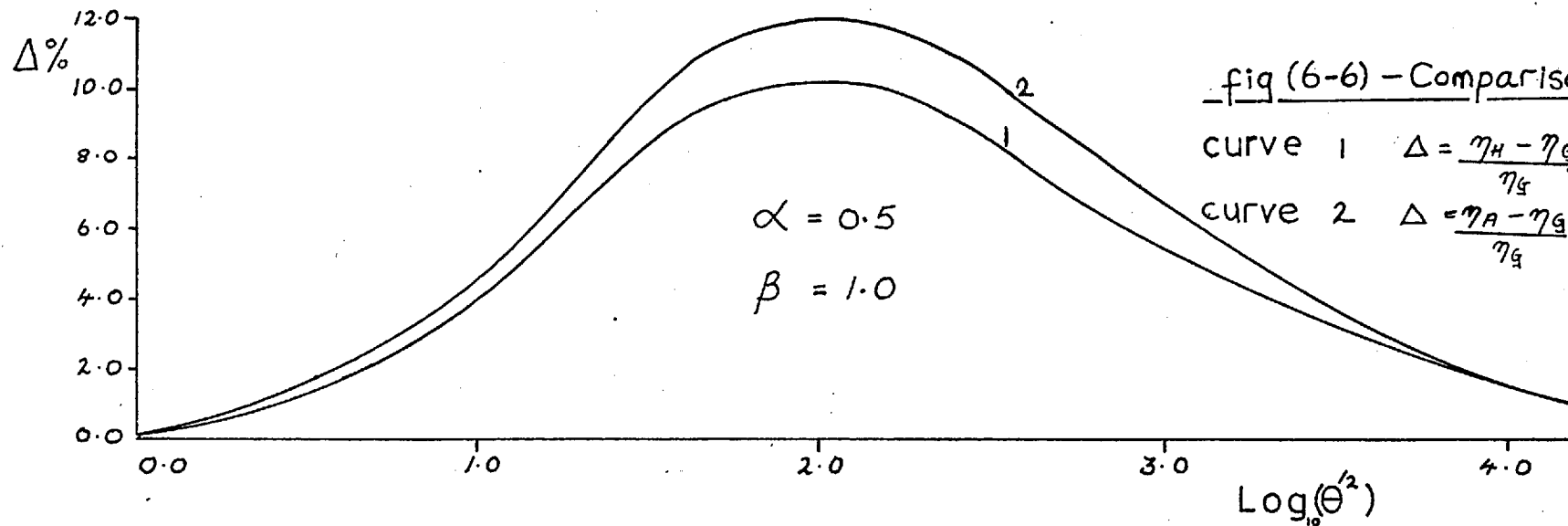
The various discrepancies are plotted against $\log(\theta'^2)$ in Figures (6.6) to (6.11). Each graph shows three distinct regions corresponding to low, intermediate and high values of the Thiele modulus.

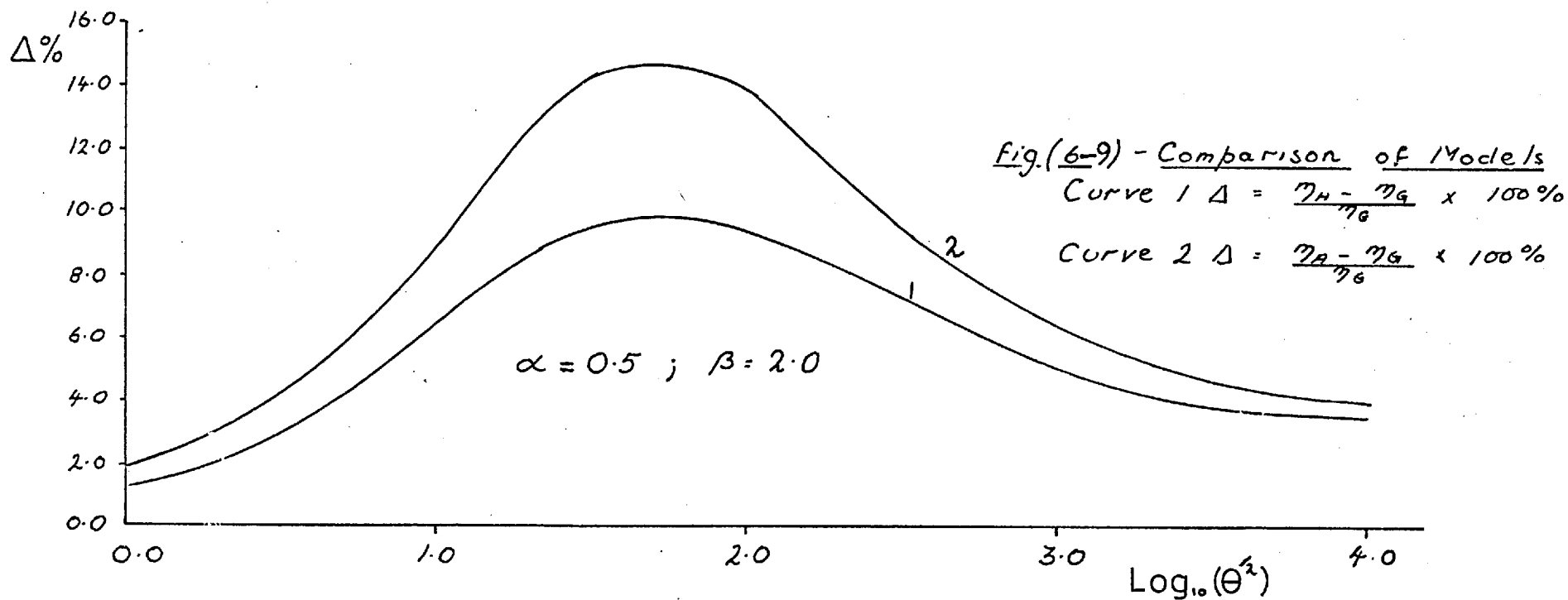
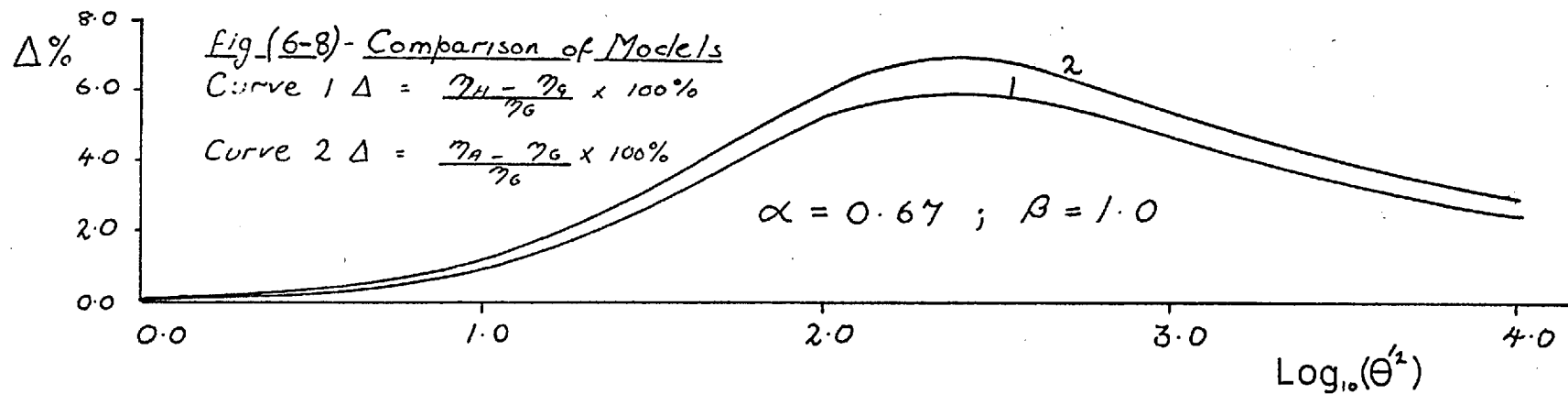
For low values of Thiele modulus ($\theta'^2 < \sim 1$) the diffusional influence is small, and the effectiveness factor tends to unity as θ' tends to zero. The discrepancy between the models is $\sim 1\%$ in this region, which may be termed the kinetic region.

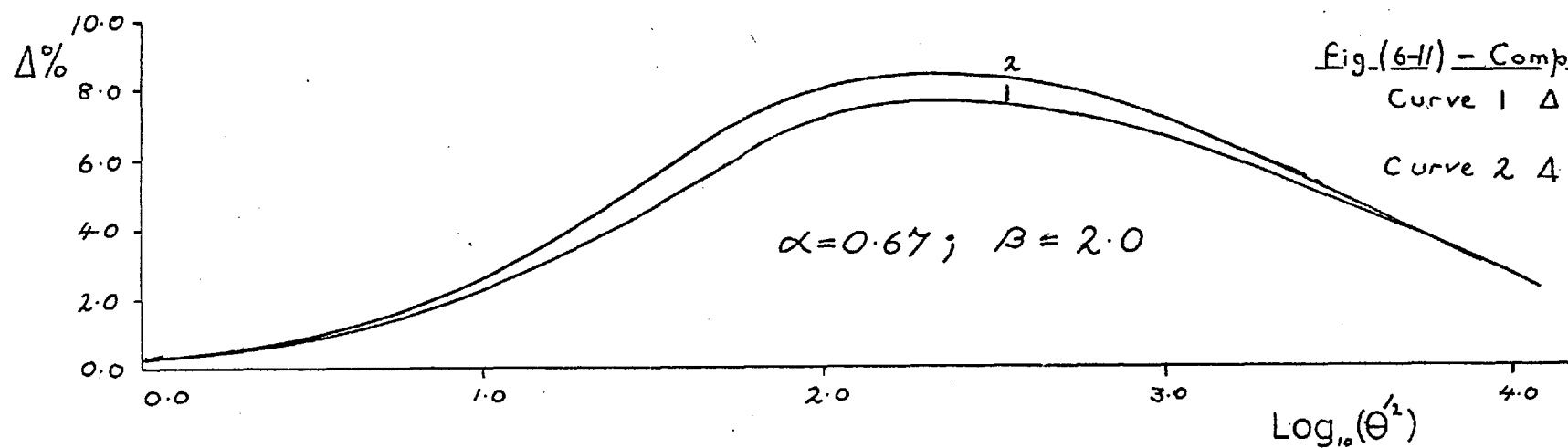
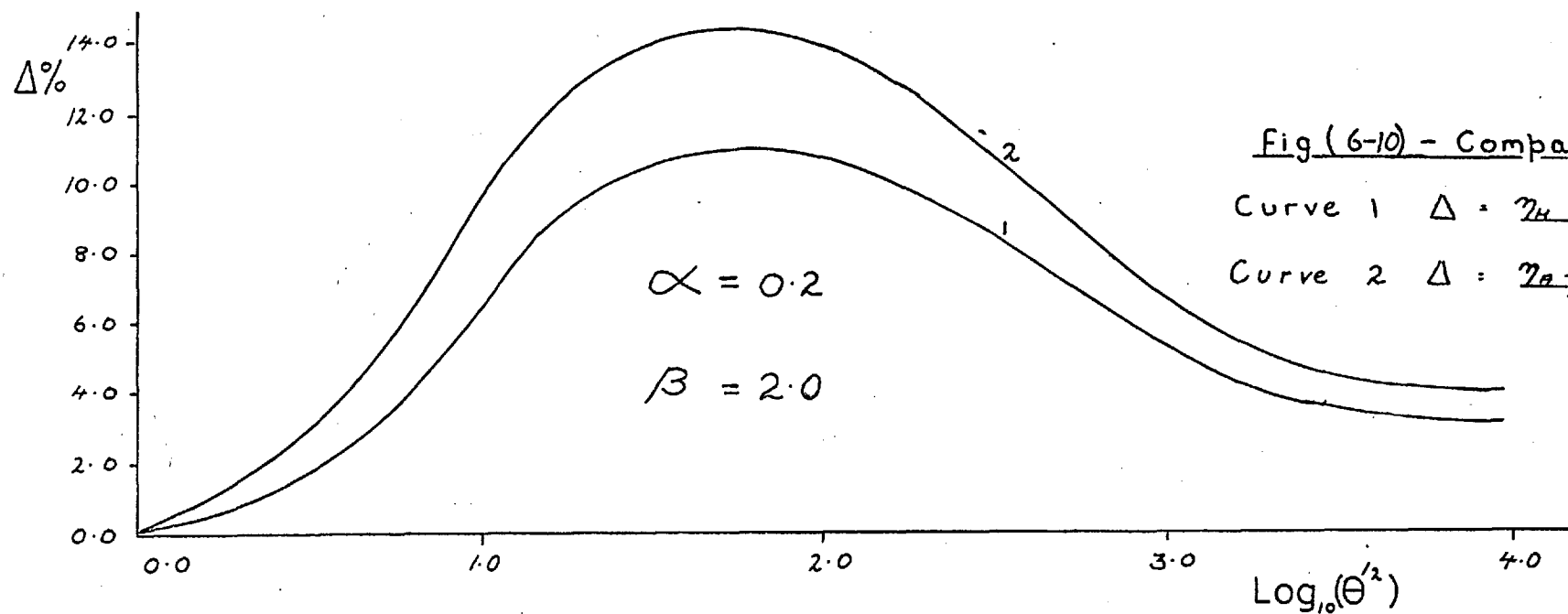
The differences at high Thiele modulus are less well defined. It can be seen that for $\theta'^2 > \sim 3000$, the discrepancy with Gunn's results is, in both cases, at most 5%. However, the difference between this work and the equivalent slab model is in all cases less than $\frac{1}{2}\%$ in this region. This suggests that some of the discrepancy between Gunn's results and other predictions at high Thiele modulus may be attributed to uncertainty in recovery of data from the published form of Gunn's papers.

That fairly good agreement between the models should be achieved at high Thiele modulus is both reasonable and expected. A high value for the Thiele modulus may be caused by large particles, very rapid reactions or a combination of both. A reaction 'band' may thus be envisaged near to the external surfaces of the pellet. This is demonstrated in Figure (6.3). Between the reaction bands the reactant(s) have been consumed and the pellet is not used. As the Thiele modulus tends to infinity, the shape of the band becomes that of a flat slab and all models would be expected to yield identical results. It is evident from Figures (6.6) to (6.11) that in some cases the fall off of the discrepancy to zero is fairly slow. This may possibly be explained qualitatively in that the outer reaction band tends to flat slab behaviour more rapidly than the inner reaction band. Additionally there will be a reaction 'disc' at each end of the cylindrical pellet. Regions of high Thiele modulus may be termed the diffusional regional.

In the intermediate region ($1 < \theta'^2 < 3000$) the phenomena of diffusion and reaction are at their most interactive, and there is less agreement between the three models. Nevertheless the maximum discrepancy between Gunn and this work is 10% and between Gunn and the equivalent slab model is 15%. In







both cases the maximum error is in the region of $100 < \theta^2 < 300$. This is in general agreement with the findings of Rester, Jouven and Aris (152).

Some further observations may be made. Agreement between Gunn and the equivalent hollow sphere model is generally better for high values of α . The thickness of material in the two models is given by $b(1-\alpha)$ and $r_e(1-a)$. It is found that as α increases, r_e and a (given by (6.3) and (6.4)) tend towards b and α respectively and thus the thickness of material (i.e. the distance over which the diffusional resistance acts) becomes more similar in the two models. In the limiting case of $\alpha=1$, the solution to (6.3) and (6.4) is $a=1$, $r_e=b\sqrt{\beta/2}$.

The advantage, if any, to be achieved by use of the equivalent hollow sphere model may be assessed by consideration of the accuracy of its predictions and the comparative computational effort required.

No estimate of the computation time for Gunn's approach is available but it may be expected to be rather high due to (153):

- a) The need to evaluate hyperbolic functions
- b) The inclusion of polynomial approximations to Bessel functions
- c) The need to solve, iteratively, transcendental equations for eigenvalues
- d) The fact that a), b) and c) above are included within infinite series.

The actual time for computation will obviously depend on the number of terms that must be considered in the infinite series before convergence may be assumed. Nevertheless, the computational time may reasonably be expected to be considerably higher than either of the simplified models. The calculations for the two simplified models were performed on a CDC 6400 computer and were found to take 0.15ms for the equivalent slab model and 0.75ms for the equivalent hollow sphere model.

It would thus appear that whereas the equivalent hollow sphere model produces better estimates than the equivalent slab model for the effectiveness factor of a hollow cylindrical catalyst pellet, the increase in computational effort required is disproportionately large. It should be pointed out, however, that in a chemical reactor small errors in any of the rate parameters, e.g. the effectiveness factor, can lead to much larger cumulative errors in conversion, selectivity and temperature rise. As an illustration of this phenomena, two reaction schemes have been integrated in the environment of a one-dimensional pseudo-homogeneous tubular reactor (Section 2.4). The results are shown in Tables (6.4) and (6.5). Scheme A is a simple first order exothermic reaction and scheme B consists of consecutive heterogeneous and homogeneous first order exothermic reactions. In each case the effectiveness factor has been

Table (6.2)

Effectiveness factor calculated by equivalent hollow sphere method

θ^2	β	α	ϵ	θ^2	β	α	ϵ	θ^2	β	α	ϵ
1.0	1.0	0.1	0.979	10.0	2.0	0.6	0.914	1000.0	1.0	0.9	0.621
1.0	1.0	0.3	0.979	10.0	2.0	0.7	0.946	1000.0	2.0	0.1	0.101
1.0	1.0	0.4	0.988	10.0	2.0	0.8	0.973	1000.0	2.0	0.3	0.121
1.0	1.0	0.6	0.992	10.0	2.0	0.9	0.992	1000.0	2.0	0.4	0.136
1.0	1.0	0.7	0.995	100.0	1.0	0.1	0.398	1000.0	2.0	0.6	0.189
1.0	1.0	0.8	0.997	100.0	1.0	0.3	0.456	1000.0	2.0	0.7	0.241
1.0	1.0	0.9	0.999	100.0	1.0	0.4	0.497	1000.0	2.0	0.8	0.345
1.0	2.0	0.1	0.964	100.0	1.0	0.6	0.617	1000.0	2.0	0.9	0.601
1.0	2.0	0.3	0.976	100.0	1.0	0.7	0.705	10000.0	1.0	0.1	0.0420
1.0	2.0	0.4	0.981	100.0	1.0	0.8	0.817	10000.0	1.0	0.3	0.0484
1.0	2.0	0.6	0.991	100.0	1.0	0.9	0.936	10000.0	1.0	0.4	0.0532
1.0	2.0	0.7	0.994	100.0	2.0	0.1	0.308	10000.0	1.0	0.6	0.0698
1.0	2.0	0.8	0.997	100.0	2.0	0.3	0.371	10000.0	1.0	0.7	0.0865
1.0	2.0	0.9	0.999	100.0	2.0	0.4	0.416	10000.0	1.0	0.8	0.120
10.0	1.0	0.1	0.830	100.0	2.0	0.6	0.553	10000.0	1.0	0.9	0.220
10.0	1.0	0.3	0.870	100.0	2.0	0.7	0.658	10000.0	2.0	0.1	0.0321
10.0	1.0	0.4	0.891	100.0	2.0	0.8	0.791	10000.0	2.0	0.3	0.0385
10.0	1.0	0.6	0.935	100.0	2.0	0.9	0.931	10000.0	2.0	0.4	0.0432
10.0	1.0	0.7	0.957	1000.0	1.0	0.1	0.131	10000.0	2.0	0.6	0.0599
10.0	1.0	0.8	0.977	1000.0	1.0	0.3	0.152	10000.0	2.0	0.7	0.0766
10.0	1.0	0.9	0.993	1000.0	1.0	0.4	0.167	10000.0	2.0	0.8	0.110
10.0	2.0	0.1	0.742	1000.0	1.0	0.6	0.219	10000.0	2.0	0.9	0.210
10.0	2.0	0.1	0.742	1000.0	1.0	0.7	0.272				
10.0	2.0	0.4	0.845	1000.0	1.0	0.8	0.374				

Table (6.3)

Utility factor calculated by equivalent hollow sphere method

$\frac{1}{\theta^2}$	β	α	η	$\frac{1}{\theta^2}$	β	α	η	$\frac{1}{\theta^2}$	β	α	η
1.0	1.0	0.1	0.969	10.0	2.0	0.6	0.585	1000.0	1.0	0.9	0.118
1.0	1.0	0.3	0.896	10.0	2.0	0.7	0.482	1000.0	2.0	0.1	0.100
1.0	1.0	0.4	0.830	10.0	2.0	0.8	0.350	1000.0	2.0	0.3	0.110
1.0	1.0	0.6	0.635	10.0	2.0	0.9	0.188	1000.0	2.0	0.4	0.114
1.0	1.0	0.7	0.507	100.0	1.0	0.1	0.394	1000.0	2.0	0.6	0.121
1.0	1.0	0.8	0.359	100.0	1.0	0.3	0.415	1000.0	2.0	0.7	0.123
1.0	1.0	0.9	0.190	100.0	1.0	0.4	0.417	1000.0	2.0	0.8	0.124
1.0	2.0	0.1	0.954	100.0	1.0	0.6	0.395	1000.0	2.0	0.9	0.114
1.0	2.0	0.3	0.888	100.0	1.0	0.7	0.360	10000.0	1.0	0.1	0.0416
1.0	2.0	0.4	0.824	100.0	1.0	0.8	0.294	10000.0	1.0	0.3	0.0440
1.0	2.0	0.6	0.634	100.0	1.0	0.9	0.178	10000.0	1.0	0.4	0.0447
1.0	2.0	0.7	0.507	100.0	2.0	0.1	0.305	10000.0	1.0	0.6	0.0447
1.0	2.0	0.8	0.359	100.0	2.0	0.3	0.338	10000.0	1.0	0.7	0.0441
1.0	2.0	0.9	0.190	100.0	2.0	0.4	0.349	10000.0	1.0	0.8	0.0432
10.0	1.0	0.1	0.822	100.0	2.0	0.6	0.354	10000.0	1.0	0.9	0.0418
10.0	1.0	0.3	0.792	100.0	2.0	0.7	0.336	10000.0	2.0	0.1	0.0318
10.0	1.0	0.4	0.748	100.0	2.0	0.8	0.285	10000.0	2.0	0.3	0.0350
10.0	1.0	0.6	0.598	100.0	2.0	0.9	0.177	10000.0	2.0	0.4	0.0363
10.0	1.0	0.7	0.488	1000.0	1.0	0.1	0.130	10000.0	2.0	0.6	0.0383
10.0	1.0	0.8	0.352	1000.0	1.0	0.3	0.138	10000.0	2.0	0.7	0.0391
10.0	1.0	0.9	0.189	1000.0	1.0	0.4	0.140	10000.0	2.0	0.8	0.0396
10.0	2.0	0.1	0.735	1000.0	1.0	0.6	0.140	10000.0	2.0	0.9	0.0399
10.0	2.0	0.3	0.738	1000.0	1.0	0.7	0.139				
10.0	2.0	0.4	0.710	1000.0	1.0	0.8	0.135				

TABLE(6-4) — Cumulative Error in Reaction Scheme Integration .

Scheme — A

$A \xrightarrow{k_1} B$: catalytic : $(-\Delta H) = 10^6 \text{ J kg}^{-1}$: $k_1 = 10^{5.04} \exp(-7549/T) \text{ sec}^{-1}$.

$G=1.0$; $C_p=1000$; $D_{\text{eff}}=10^{-6}$; $U=90$; $R_T=0.03$; $d_p=0.006$; $\phi_s=0.4$; $\alpha=0.2$; $\beta=0.4$.

Length(m)	Conversion (slab) %	Conversion (sphere) %	ΔConv %	Temp. Rise (slab) K	Temp. Rise (sphere) K	ΔTemp %	ϵ (slab)	ϵ (sphere)	$\Delta \epsilon$ %
0.1	7.2	7.0	2.86	26.8	26.4	1.85	0.441	0.427	3.2
0.2	14.8	14.2	4.22	43.0	42.0	2.4	0.404	0.393	2.8
0.3	22.0	21.2	3.77	51.0	49.0	4.1	0.386	0.377	2.4
0.35	25.6	24.6	4.06	53.2	51.0	4.3	0.382	0.373	2.4
0.4	29.0	27.8	4.34	54.3	51.8	4.9	0.381	0.371	2.7
0.5	35.2	34.0	3.52	52.9	51.1	3.5	0.382	0.372	2.7

TABLE (6.5) Cumulative Error in Reaction Scheme Integration .

Scheme—B

$A \xrightarrow{k_1} B$: catalytic : data as scheme A .

$B \xrightarrow{k_2} C$: gas : $(-\Delta H) = 2 \times 10^4 \text{ J kg}^{-1}$: $k_2 = 10^{7.95} \exp(12560 / T) \text{ sec}^{-1}$

all other data as scheme A.

Length (m)	conversion (slab) %	conversion (sphere) %	Δ Conv. %	Selec. (slab) %	Selec. (sphere) %	Δ Selec. %	Temp. Rise (slab) K	Temp. Rise (sphere) K	Δ Temp %	ϵ (slab)	ϵ (sphere)	$\Delta \epsilon$ %
0.1	7.2	7.0	2.9	93.9	92.9	1.1	31.9	30.5	4.6	0.430	0.417	3.12
0.2	15.4	14.6	5.5	79.1	80.7	2.0	68.6	64.8	5.9	0.351	0.346	1.45
0.3	24.4	23.4	4.3	52.9	56.1	5.7	138.6	126.2	9.8	0.246	0.254	-3.14
0.35	29.8	28.4	4.9	27.5	34.2	19.7	215.4	190.0	13.4	0.176	0.191	-7.9
0.4	36.4	34.4	6.0	6.6	10.1	34.6	293.1	273.9	7.0	0.131	0.138	-5.1
0.5	48.8	47.0	3.8	2.5	2.9	12.3	308.5	303.9	1.7	0.124	0.125	-0.8

estimated by each of the simplified models. It may be seen that quite large errors may accumulate ($\sim 20\%$) even when the discrepancy between the predictions of the effectiveness factor is only $\sim 5\%$.

6.4 VARIATION OF HOLLOW PELLET GEOMETRY FOR OPTIMUM PERFORMANCE

6.4.1 Single irreversible reaction

The optimum pellet performance may be defined in a number of ways. In particular we may define two optimal policies, namely:

- (i) best use of catalyst material
- (ii) best use of reactor volume

Which policy is followed, or whether some combination of policies is preferred, may well be an economic decision. In a situation where the cost of catalyst material is a limiting economic factor, or where low "conversion-per-pass" can be tolerated, then policy (i) would be favoured. However, if a large "conversion-per-pass" is required, or the catalyst material is not particularly expensive in comparison with reactor construction costs, then policy (ii) may prove to be a better proposition.

In order to follow policy (i) it is required to maximise the effectiveness factor. Effectiveness factor has been calculated as a function of α and is shown in Table (6.2). As the effectiveness factor does not exhibit a maximum with respect to α in the range $0 < \alpha < 1$, we must use the greatest convenient degree of hollowing to achieve policy (i). Obviously the amount of hollowing employed must be consistent with the required strength characteristics of the catalyst.

An attempt to achieve policy (ii) presents a more interesting situation. Consideration of Figure (6.12) and the work of Gunn (154) shows that for larger values of the Thiele modulus the utility factor shows a maximum with respect to α and, in general, the greater the value of the Thiele modulus, the greater the degree of hollowing required to reach this maximum. Consideration of Gunn's results (154) shows that:

- (i) for β values < 2 the degree of enhancement, if any, to be achieved by pellet hollowing is small.
- (ii) the degree of enhancement to be achieved with pellet hollowing increases with θ and with β .
- (iii) for $\beta \sim 4$ and $\theta \sim 10,000$ the utility factor for a bed of cylindrical pellets may be increased two-fold by pellet hollowing.

The equivalent slab model would appear to present a relatively straight

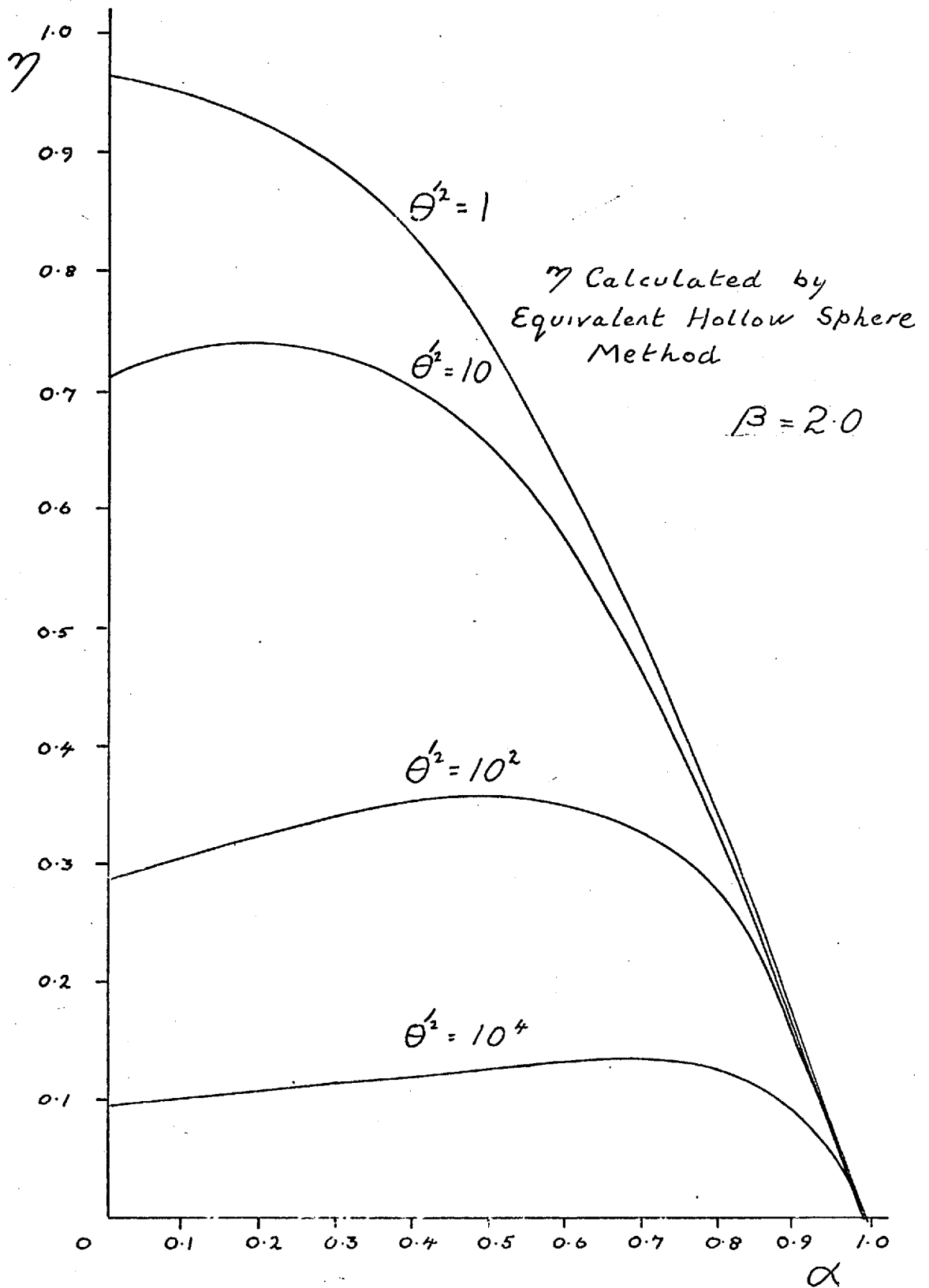


Fig (6-12) Utility factor As A function Of Hollowness Factor

forward basis for a first estimate of the optimum degree of pellet hollowing. Basmadjian (150) has presented curves based on these equations showing the degree of enhancement plotted against Thiele Modulus, with degree of hollowing taken as a parameter. The enhancement is shown to have a limiting value of 1.33.

Differentiating (6.17) with respect to α and using (6.2) yields, for the equivalent slab model,

$$\frac{d\eta}{d\alpha} = \frac{(\beta-2\alpha)(1-\alpha+\beta)\sinh(2\mathcal{L}_m)}{\beta^2\theta'} - (1+\alpha) \quad (6.20)$$

which, for a maximum in η with respect to α , leads to the following implicit relationship for $\alpha_{\max}$:

$$\alpha_{\max} = \frac{(\beta-2\alpha_{\max})(1-\alpha_{\max}+\beta)\sinh(2\mathcal{L}_m)}{\beta^2\theta'} - 1 \quad (6.21)$$

$$\text{where } \mathcal{L}_m = \frac{(1-\alpha_{\max})\beta\theta'}{2(1-\alpha_{\max}+\beta)} \quad (6.22)$$

As before, it is of interest to consider the asymptotic behaviour of the system.

As θ' tends to zero and the effectiveness factor tends to unity, any degree of hollowing will decrease the utility factor and so we may immediately say that, as θ' tends to zero, $\alpha_{\max}$ tends to zero.

As θ' tends to infinity the utility factor may be represented by

$$\eta = \frac{2}{\beta\theta'} (1-\alpha^2+\beta+\alpha\beta) \quad (6.23)$$

Differentiating with respect to α and setting the derivative to zero results in:

$$\alpha_{\max} = \beta/2 \quad (6.24)$$

Thus, as θ' tends to infinity, $\alpha_{\max}$ tends to $\beta/2$. Immediately it appears that (6.24) implies that if β is greater than 2, $\alpha_{\max}$ is greater than 1 and this clearly cannot be the case. This anomaly may possibly be interpreted as stating that for β greater than 2, no maximum in η with respect to α exists in the range $0 < \alpha < 1$. Consideration of Gunn's results

(154) shows this statement to be fallacious and indeed the converse is true; as β becomes larger the maximum in η becomes more pronounced. However (6.22) has no physical meaning for α greater than unity and the analysis leading to (6.24) breaks down for $\beta > 2$.

Having established the asymptotic behaviour of the curve of $\alpha_{\max}$ against Θ' (as predicted by the equivalent slab model) the full curves were generated for different values of β .

The relationship (6.21) was cast in the form:

$$f(\alpha_{\max}) = 0 \quad (6.25)$$

and a solution to (6.25) was obtained by the 'memory' method of Shacham and Kehat (155). Equation (6.25) was found to be rather ill-conditioned towards other methods of solution, including the regular-falsi iteration scheme.

In all cases where β was less than 2, the asymptotic behaviour predicted by (6.24) was found. As an additional check (6.17) was considered and a maximum with respect to α was sought by successive fitting of a cubic in the region of the suspected maximum. The results obtained were identical to three decimal places. The results of these calculations are presented in (Table (6.6)). Calculations were also performed for $\beta=4$ (Table (6.6)) and it was found that (6.25) predicted that $\alpha_{\max}$ tended to unity as Θ' tended to infinity. A value of 2 is predicted by (6.24).

The pellet geometry was also optimised by the equivalent hollow sphere model. For this model, the utility factor is defined by Equations (6.16), (6.15), (6.11), (6.4) and (6.3). Again, the maximum was sought by successive fitting of a cubic in the region of the suspected maximum. The results of these calculations are shown in Table (6.7). Tables (6.6) and (6.7) are presented graphically in Figure (6.13). The maximum discrepancy between the predictions of the two models was $\sim 20\%$, although 10% or less is a more typical figure for the discrepancy. In all cases, the equivalent slab model predicts a lower value for $\alpha_{\max}$ than that predicted by the equivalent hollow sphere model. The prediction of these two models are compared with those of Gunn for $\beta=4$ (Figure (6.14)). It may be concluded that in estimating the optimum degree of hollowing for a single irreversible reaction, the equivalent hollow sphere model affords only slight advantage over the equivalent slab model. However a better estimate of the absolute value of the utility factor at this maximum will

TABLE(6-6) Solution of Equation(6-25).

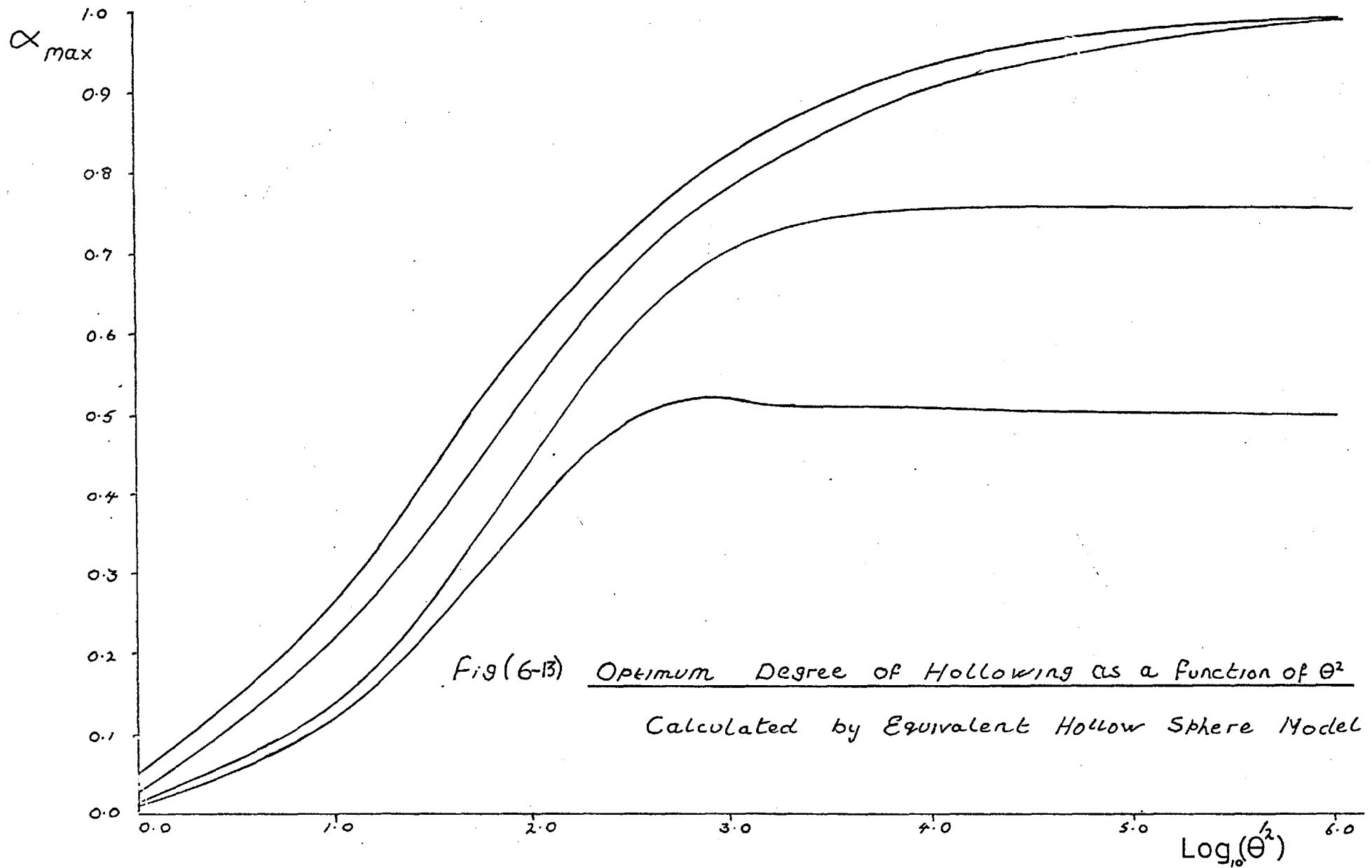
$\bar{\epsilon}$ calculated by the equivalent slab model
value shown is $\alpha_{\max}$.

$\beta \backslash \log_{10}(\theta^2)$	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	4.9
1.0	0.01	0.031	0.085	0.195	0.345	0.465	0.499	0.500	0.500	0.500	0.500
1.5	0.018	0.050	0.132	0.277	0.455	0.610	0.715	0.748	0.750	0.750	0.750
2.0	0.023	0.067	0.167	0.330	0.513	0.670	0.784	0.862	0.913	0.946	0.992
4.0	0.039	0.106	0.237	0.416	0.591	0.729	0.827	0.892	0.933	0.959	0.973

TABLE(6-7) Solution of Equation(6-25).

calculated by the equivalent hollow sphere model
value shown is $\alpha_{\max}$.

$\beta \backslash \log_{10}(\theta^2)$	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	4.9
1.0	0.016	0.045	0.114	0.234	0.380	0.492	0.515	0.509	0.505	0.503	0.502
2.0	0.039	0.099	0.210	0.366	0.535	0.680	0.789	0.864	0.914	0.946	0.963
4.0	0.056	0.134	0.267	0.435	0.600	0.733	0.828	0.892	0.933	0.959	—



Fig(6-13) Optimum Degree of Hollowing as a Function of θ^2
Calculated by Equivalent Hollow Sphere Model

Fig(6-14) Optimum pellet hollowing for a single irreversible reaction. $\beta = 4$.

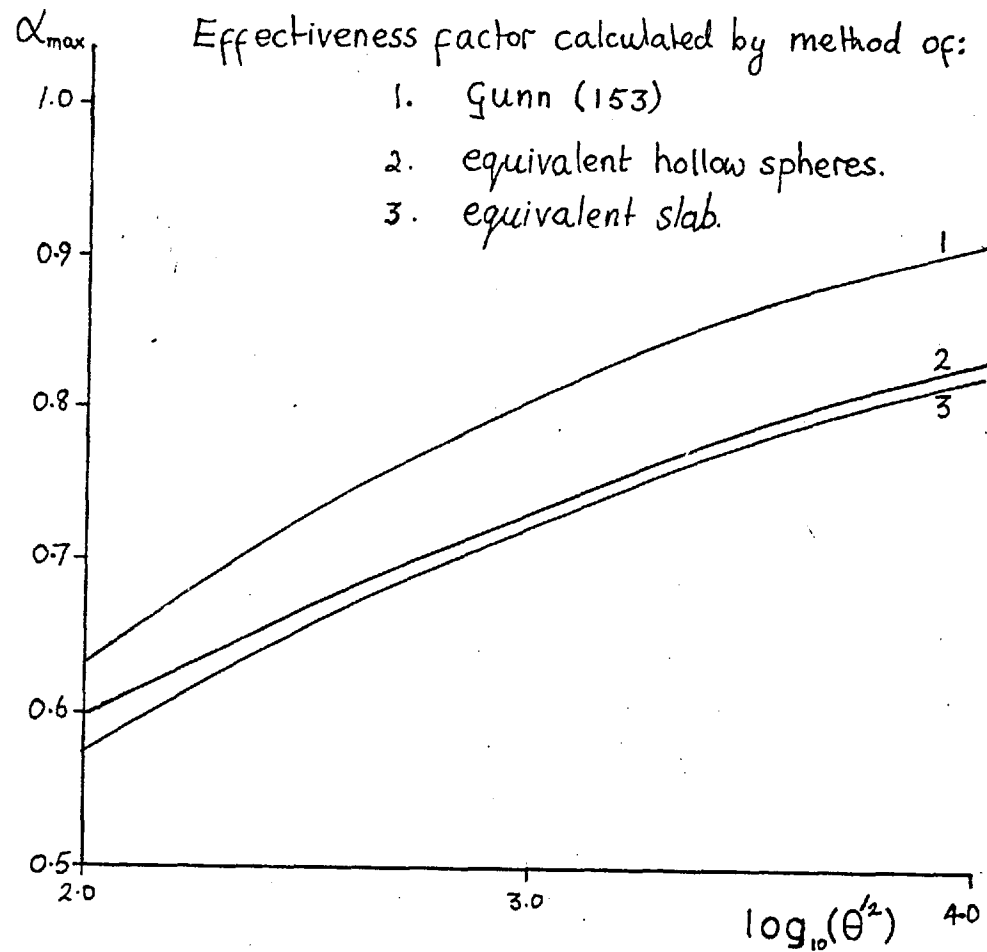
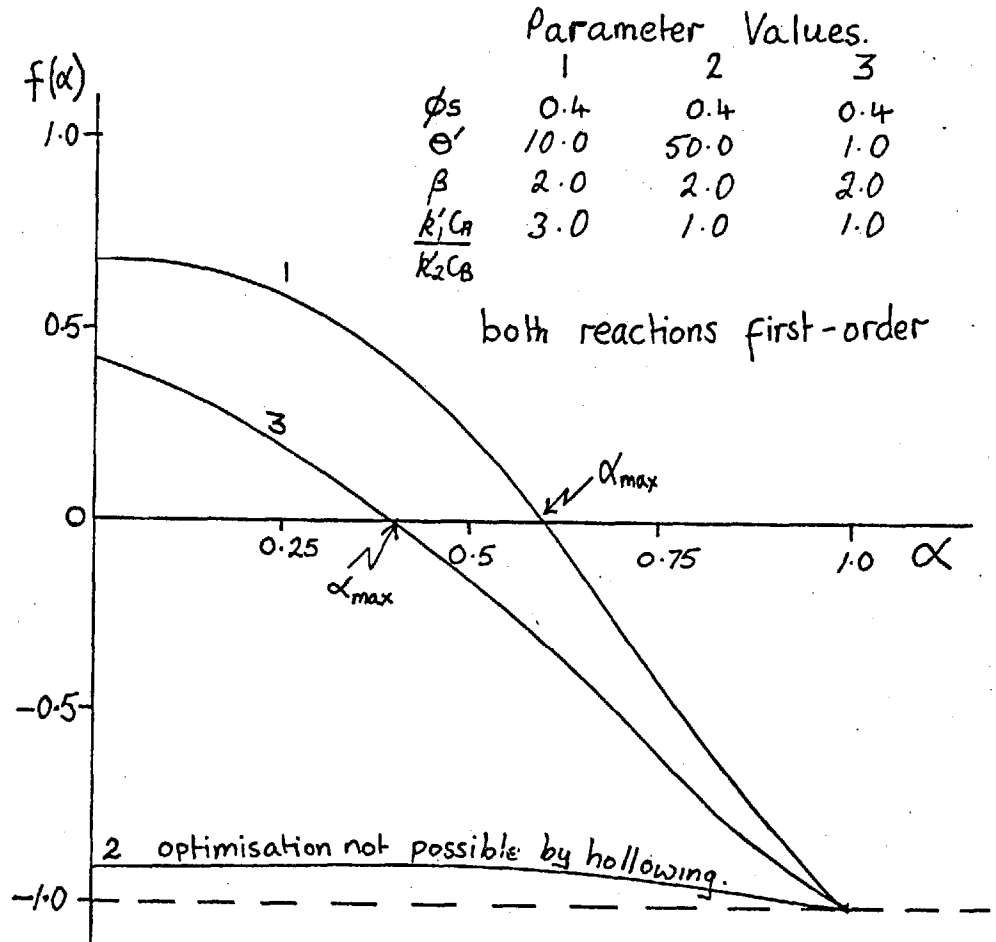


Fig (6-15) Left-hand side of Equation [6-29].



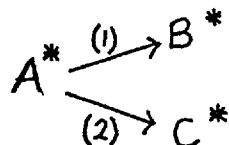
be given by the equivalent hollow sphere model.

Finally it may be noted that both approximate models predict low values for $\alpha_{\max}$. This is significant because consideration of Gunn's curves shows that as α increases at high Thiele modulus, a maximum occurs in the utility factor. Further increase in α rapidly causes the utility factor to fall towards zero. Thus the approximate models provide a 'safe' estimate for $\alpha_{\max}$.

6.4.2 Heterogeneous-homogeneous reactions

As previously noted three general types of heterogeneous-homogeneous systems may be considered; concurrent, heterogeneous with consecutive desired homogeneous reaction and heterogeneous with consecutive undesired homogeneous reaction.

Considering the following, concurrent reaction scheme:



Reaction (1) is a heterogeneous catalytic reaction of order c w.r.t. A^* and reaction (2) is a homogeneous reaction of order g w.r.t. A^* . The relative rates of production of the two products is given by:

$$S = \frac{k_1' \epsilon (1 - \phi_H) C_A^c}{k_2' \phi_H C_A^g} \quad (6.26)$$

which, when c and g are identical, reduces to:

$$S = \frac{k_1' \epsilon (1 - \phi_H)}{k_2' \phi_H} \quad (6.27)$$

ϕ_H , the voidage of a bed of hollow cylindrical pellets, is related to ϕ_S , the voidage of a bed of equivalent solid cylinders, by:

$$\phi_H = \phi_S + \alpha^2 (1 - \phi_S) \quad (6.28)$$

The selectivity of the concurrent reaction scheme will be influenced by pellet hollowing in two ways. An increase in α will increase the effective gas space and will simultaneously enhance the heterogeneous reaction by increasing the pellet effectiveness.

It has already been established that the nature of the dependence

of the effectiveness factor upon the hollowness of the pellet is predicted satisfactorily by the equivalent slab model. This model will be used for a general examination of homogeneous-heterogeneous reaction schemes in beds of hollow cylinders.

Substituting for ϵ and ϕ_H , then:

$$S = \frac{k_1'(1-\phi_s)(1-\alpha^2)(\tanh \mathcal{L}/\mathcal{L})C_A^c}{k_2'(\phi_s + \alpha^2(1-\phi_s))C_A^g} \quad (6.29)$$

The case where it is desired to enhance the production of the homogeneous product is trivial as the pellet may, in principle, be hollowed as much as is desired.

The case where enhancement of the heterogeneous reaction is desired is more difficult. Generally speaking it is necessary to enhance the catalytic reaction by hollowing to an extent greater than that afforded to gas phase reaction by virtue of the increased available gas space. This may be expressed by:

$$\left. \frac{\delta S}{\delta \alpha} \right|_{\alpha} > 0 \quad (6.30)$$

as a condition that further hollowing will selectively increase the yield of heterogeneous product at a particular value of α .

It has already been seen that enhancement of heterogeneous reactions by pellet hollowing is most marked for high values of the Thiele modulus. Under these conditions (6.29) may be written:

$$S = \frac{2k_1'(1-\phi_s) C_A^c}{k_2' C_A^g \theta''} \frac{(1+\alpha)(1-\alpha+\beta)}{(\phi_s + \alpha^2(1-\phi_s))} \quad (6.31)$$

Differentiating:

$$\left. \frac{\delta S}{\delta \alpha} \right|_{\alpha} = \frac{2k_1'(1-\phi_s) C_A^c}{k_2' C_A^g \theta''} \frac{(\phi_s + \alpha^2(1-\phi_s))(\beta - 2\alpha) - 2\alpha(1-\phi_s)(1+\alpha)(1-\alpha+\beta)}{(\phi_s + \alpha^2(1-\phi_s))^2} \quad (6.32)$$

The parameter θ'' is the generalised Thiele modulus for the catalytic reaction of order c and is defined by (1):

$$\theta'' = \theta' \sqrt{\frac{C_A^{c-1}(n+1)}{2}} \quad (6.33)$$

Inspection of (6.32) reveals that $\delta S/\delta \alpha$ is always positive for $\alpha=0$ and thus, at least in principle, the selectivity to the heterogeneous product can always be improved by pellet hollowing. The maximum value of S occurs when $\delta S/\delta \alpha$ is zero. If $\alpha_{\max}$ is the optimum value of δ , then $\alpha_{\max}$ is given by:

$$\alpha_{\max} = \frac{\frac{1}{2} [\phi_s + \alpha_{\max}^2 (1 - \phi_s)] [\beta - 2\alpha]}{[1 - \phi_s] [1 + \alpha_{\max}] [1 - \alpha_{\max} + \beta]} \quad (6.34)$$

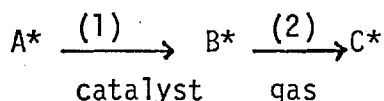
It will be noticed that the position of $\alpha_{\max}$ is independent of Thiele modulus, and kinetics, depending only on β and ϕ_s . However, the amount by which the selectivity is enhanced will depend on all these parameters.

The values of $\alpha_{\max}$ for various values of ϕ_s and β are shown in Table (6.8). The degree to which the heterogeneous selectivity is enhanced at this value of α is shown in Table (6.9). It may be seen from Table (6.8) that the degree of hollowing required to reach an optimum increases with ϕ_s and β . It may be seen from Table (6.9) that the amount of enhancement achieved at the optimum also increases with these parameters.

For low values of the Thiele modulus the full equivalent slab model must be used. Generally speaking, very small values of $\alpha_{\max}$ will be obtained which are lower than the practical values for hollowing that may be considered.

If pellet hollowing is to be employed in order to reduce the pressure drop in a catalytic reactor, calculations, similar to those outlined above, will reveal whether this policy will be significantly detrimental to the desired selectivity.

Attention may now be switched to consecutive reaction schemes, which generally, will be of the form:



Two cases will be considered. Firstly, when B^* is the desired product and secondly when C^* is the desired product.

The former case may be dealt with by an extension of the arguments already advanced for concurrent reaction schemes, for once again it is desired to enhance the catalytic reaction without unduly enhancing the gas-phase reaction. The value for optimum pellet hollowing in this case is identical to that for the concurrent system when the Thiele modulus is

TABLE (6-8)

Value of $\alpha_{\max}$ for optimal heterogeneous selectivity.

$\phi_s \backslash \beta$	1.0	2.0	3.0
0.35	0.104	0.146	0.169
0.45	0.142	0.205	0.237
0.6	0.208	0.312	0.375

TABLE (6-9)

Percentage enhancement at optimum pellet hollowing.

$$\frac{2 K_1^i C_a^c}{K_2 C_a^g \Theta'} = 0.2$$

$\phi_s \backslash \beta$	1.0	2.0	3.0
0.35	2.6	4.9	6.3
0.45	3.6	6.8	8.9
0.6	5.2	10.4	13.9

high, as it has been shown to be independent of both gas- and solid-phase kinetics.

In this case the selectivity to B may be written as:

$$S' = \frac{2k_1'(1-\phi_s)C_A^c}{k_2'C_B^g\theta''} \frac{(1+\alpha)(1-\alpha+\beta)}{(\phi_s+\alpha^2(1-\phi_s))} \quad (6.35)$$

which, in this case, is the ratio of the rate of formation of B* to the rate of gas-phase removal of B*. It is required that $\frac{dS'}{d\alpha}$ is positive for pellet hollowing to improve the selectivity to B*. Thus under given conditions of β and ϕ_s , $\alpha_{\max}$ will have the same value for this consecutive reaction scheme and for the concurrent reaction scheme. However, the actual value for the selectivity will differ between the two schemes as implied by (6.31) and (6.35). The other, more general arguments, also apply.

The latter case, where C* is the desired product, can be tackled by stipulating a number of optimal policies. Only one, fairly arbitrary policy will be considered here in order to demonstrate how an optimum may be achieved by pellet hollowing.

In order to ensure a high yield of C* it is required that a high conversion of A* and high selectivity to B* must be simultaneously achieved. One way this may be done is to attempt to prevent the accumulation of B*, that is to say it is required that the overall rate of production of B* is zero. A negative overall rate of production of B* implies that B* is being converted to C* at the expense of the conversion of A*.

Using the previous notation, this condition may be expressed by:

$$k_1'C_A^c\epsilon(1-\phi_H) = k_2'C_B^g\phi_H$$

$$\text{or } \frac{k_1'C_A^c\epsilon(1-\phi_H)}{k_2'C_B^g\phi_H} - 1 = 0 \quad (6.36)$$

The behaviour of the system may be controlled through the parameters ϵ and ϕ_H although these are not independent, being linked through α .

Using, again, the equivalent slab model, substitution of (6.1), (6.2) and (6.28) into (6.36) yields:

$$\left[\frac{k_1' C_A^c (1-\phi_s)(1-\alpha^2)}{k_2' C_B^g \phi_s + \alpha^2 (1-\phi_s)} \cdot \frac{\tanh \mathcal{L}}{\mathcal{L}} \right] - 1 = 0 \quad (6.37)$$

Solution of (6.37) will yield $\alpha_{\max}$, the optimum value for α in this situation defined by C_A , C_B and the temperature (k_1' , k_2').

The behaviour of the system at the two extremes of $\theta'' \rightarrow 0$ and $\theta'' \rightarrow \infty$ will again be considered.

When the Thiele modulus falls to zero, the effectiveness factor, ϵ , tends to unity and (6.37) reduces to:

$$\frac{k_1' C_A^c (1-\phi_s)(1-\alpha^2)}{k_2' C_B^g \phi_s + \alpha^2 (1-\phi_s)} - 1 = 0 \quad (6.38)$$

As the Thiele modulus tends to infinity, the effectiveness factor tends to its limiting behaviour of:

$$\epsilon = 1/\mathcal{L} \quad (6.39)$$

and (6.37) becomes:

$$\frac{2k_1' C_A^c (1-\phi_s) (1+\alpha)(1-\alpha+\beta)}{k_2' C_B^g \beta \theta'' [\phi_s + \alpha^2 (1-\phi_s)]} - 1 = 0 \quad (6.40)$$

The variation of the L.H.S. of (6.40) for typical values of the pertinent parameters is shown in Figure (6.15).

Limiting behaviour with respect to A^* and B^* may be intuitively determined. As $C_A \rightarrow 0$, $\alpha_{\max} \rightarrow 1$ which confirms that the catalytic reactor bed should be terminated when A^* is totally consumed. As $C_B \rightarrow 0$, i.e. at the bed entrance, $\alpha_{\max} \rightarrow 0$ and, as the gas phase reaction does not occur, pellet hollowing is useless unless the catalytic reaction is significantly enhanced.

6.5 CONCLUSIONS

In the analyses that have been presented it has been assumed that the catalyst pellet is isothermal, i.e., no temperature gradients exist within the pellet. It has been shown (120) that intra-particle thermal

diffusional resistance is usually negligible compared with the inter-particle resistance. If the reactor is represented by a two-phase model as described in Section (2.2), all inter-phase effects are included in the bed conservation equations and a description of the behaviour of the catalyst pellet has only to take account of intra-particle diffusional effects which are only significant for mass diffusion. Thus the ideas presented here have direct application to real chemical reactor problems.

The points made in this chapter may be summarised by:

- a) A prediction of the interaction of diffusion and reaction in a hollow cylindrical catalyst pellet may be obtained by solution of the conservation equations for the system (153, 154). An approximation to the effect of this interaction may be obtained by modelling the hollow cylindrical catalyst pellet by an equivalent flat slab of catalyst material. The maximum discrepancy between this model and the full solution of the conservation equations is 15%. An improved approximation may be obtained by modelling the hollow cylindrical catalyst pellet by an equivalent hollow sphere. This approach exhibits a maximum discrepancy of 10% but requires about six times as much computation as the equivalent slab model. It is suggested that both approximate models afford a considerable computational saving over the solution of the conservation equations.
- b) Small discrepancies in the prediction of effectiveness factors for hollow catalyst pellets can lead to much larger discrepancies in the prediction of temperature rise, conversion and selectivity in fixed beds of hollow catalyst pellets.
- c) Pellet hollowing may be employed to optimise chemical reactor performance for heterogeneous reactions and, for both concurrent and consecutive heterogeneous-homogeneous reaction networks.

In the case of concurrent reaction networks the selectivity to the heterogeneous product may be improved by pellet hollowing providing that the diffusional resistance in the pellet is large enough. This is also the case for a consecutive reaction network in which the intermediate product, heterogeneously formed, is desired. In a consecutive reaction network in which the final, homogeneously formed product is desired, a value for the degree of pellet hollowing may be found such that the yield of this product is maximised.

Chapter 7

CONCLUSIONS

- 7.1 Modelling fixed bed Catalytic Reactors
- 7.2 Modelling catalyst pellets for butene oxidation
- 7.3 Modelling hollow catalyst pellets

A review of the literature has shown that many catalytic systems involve both heterogeneous and homogeneous reactions. A reactant may undergo separate heterogeneous and homogeneous reaction or may be involved in both heterogeneous and homogeneous stages, for example, where a product is formed heterogeneously and then undergoes further homogeneous reaction. Examples of all these types of reaction are given.

7.1 MODELLING FIXED BED CATALYST REACTORS

Some models for fixed-bed, tubular catalytic reactors have been reviewed. Models in one and two dimensions and involving one and two phases have been considered and mathematical representations of each model have been presented.

The parameters required for a two-phase description of heat transfer have been critically reviewed and the relationship between the two-phase parameters and the parameters required for the other models has been established.

The integration of the mathematical models has been considered and a numerical method, based on a finite difference net, has been described.

Published kinetic data for the heterogeneous and homogeneous stages in the thermal decomposition of nitrous oxide has been incorporated into the mathematical models and the models have been integrated for a wide variety of operating and heat transfer variables.

The finite difference methods were found to be convergent with respect to the axial and radial stepsizes and, in a case where radial temperature gradients were severe, the difference equations were found to be more sensitive to changes in the radial stepsize than to changes in the axial stepsize. The three models considered converged, in general, to different solutions.

Wide variation was found in the predictions of the two dimensional, two-phase (2p); two-dimensional, one-phase (1p) and one-dimensional, one-phase (1d) models. The difference between the 2p and 1p models largely reflected the magnitude of the solid-fluid film temperature difference. The most significant differences were in the prediction of bed temperature profiles. Differences in the predictions of conversion and selectivity to nitrogen dioxide were less, but still significant.

The 1d model was found to be a poor approximation to the two-dimensional models. The best agreement between 1p and 1d models was at

low Biot numbers, where wall heat transfer is rate controlling in heat removal. The 1d model assumes that all heat transfer is lumped at the wall.

It was found that a reactor could be thermally stable with respect to the heterogeneous reaction but thermally unstable with respect to the homogeneous reaction. This results in sigmoidally shaped axial temperature profiles. Cases were found where the 1p and 1d models predicted thermal stability while the 2p model predicted thermal instability.

The differences in the predictions of the three models are not directly attributable to the fact that the reactions occur in separate phases. However, it is evident that, when a two-phase model is necessary, it is essential to distinguish between the heterogeneous and homogeneous heat sources. This becomes even more important when λr^f and λr^s differ appreciably.

The 1p and 1d models were found to be numerically stable for all considered values of axial and radial stepsizes. However, numerical instability was found during the integration of the 2p model. The instability appears to originate in the solid phase energy balance, Equation (2.61), which is independent of the axial co-ordinate. Instability was only found in situations where radial heat transfer was predominantly through the solid phase.

The sensitivity of the model predictions to variation in the heat transfer parameters has been studied for the two-dimensional models. Fairly small decreases in heat transfer parameters ($\sim 15\%$) led to quite large (up to 85%) increases in the predicted temperature rises. The effect of varying a given parameter depended on the particular heat transfer situation considered. Generally, a parameter variation resulted in a greater variance in the model predictions for the 2p model than for the 1p model. Because of the exponential dependence of reaction rate on temperature, an increase in a heat transfer parameter led to a smaller variation in predicted temperature rise than a corresponding decrease in the same parameter.

When a kinetic model for heterogeneous and homogeneous effects during the air-oxidation of methanol was incorporated into the three mathematical models, the same general behaviour was found. The differences between the 2p and 1p models were less pronounced than those found in the nitrous oxide system. This was because the quantity of heat released in each phase was of comparable magnitude and thus the fluid-solid film

temperature differences were smaller.

The predictions of the three models are complicated by the existence of "effectiveness factor profiles" within the bed. One result of this is the unexpected comparisons between the 1d and 1p models that were found on occasion.

In a consecutive heterogeneous-homogeneous reaction scheme such as the oxidation of methanol, the yield of the primary product can fall suddenly with increasing reactor length. It has been shown that this characteristic may lead to serious design errors if an inappropriate model for the fixed-bed reactor is used.

7.2 MODELLING CATALYST PELLETS FOR BUTENE OXIDATION

The model that was set up to describe the heterogeneous oxidation of butene over a tin/antimony oxide catalyst pellet was found to be capable of predicting experimentally observed thermal effects. The observed conversions and selectivities were less well predicted, although they showed 'order-of-magnitude' agreement. This was attributed to large uncertainties in the available bulk mass diffusion data, to error in the available correlation for the film mass transfer coefficients and to the possibility of homogeneous reaction.

The capability of the model to predict the formation of aldehydic minor products - important if the model is to be used in a heterogeneous, homogeneous situation - has not been conclusively established. Nevertheless, a sound basis for future development of the model towards that objective has been provided.

7.3 MODELLING HOLLOW CATALYST PELLETS

It has been shown that the use of hollow catalyst pellet geometries may be advantageous in heterogeneous-homogeneous reaction situations.

The interaction of diffusion and reaction in catalyst pellets with such geometries may be described by integration of the conservation for the pellet, taking into account the proper boundary conditions.

A full numerical or analytical integration of these equations is very time consuming, and approximate methods of integration were considered. The agreement between the full solution and the approximate solutions depended strongly on the Thiele modulus. At both high and low values of

Thiele modulus the agreement was excellent. At intermediate values, where diffusion and reaction are equally important in determining the overall rate, the equivalent slab model gave a maximum discrepancy of 15% compared with the full solution. The equivalent sphere model gave a maximum discrepancy of 10% although this model required six times the computational effort required by the slab model.

Small errors in the predictions of effectiveness factors can lead to much larger errors in the prediction of temperature increase and of product yields in beds of hollow catalyst pellets, especially in the case of consecutive heterogeneous-homogeneous reactions.

Pellet hollowing may be employed to optimise reactor performance for heterogeneous reactions and for both concurrent and consecutive heterogeneous-homogeneous reaction networks.

In the case of concurrent reaction networks, the selectivity to the heterogeneous product may be improved by pellet hollowing, provided that the diffusional resistance in the pellet is sufficiently large. This is also true for a consecutive reaction network in which the intermediate product, heterogeneously formed is desired. In a consecutive reaction network in which the final, homogeneously formed, product is desired, a value for the degree of pellet hollowing may be found such that the yield of this product is maximised.

Chapter 8

SUGGESTIONS FOR FUTURE WORK

8.1 Two-Phase Reactor Models

8.2 Use of Hollow Catalyst Pellets

8.3 Investigation of the Oxidation of Butene to Butadiene

8.1 TWO-PHASE REACTOR MODELS

It is suggested that future work with two-phase reactor models be directed towards experimental verification of the model predictions for both heterogeneous and heterogeneous-homogeneous reaction schemes.

Further work is required on the correlation and prediction of two-phase heat transfer parameters particularly for solid-wall and fluid-wall heat transfer coefficients.

In using the models described in this thesis it is recommended that particular attention be paid to the effect of variation of the effectiveness factor within the bed on the overall model predictions.

It would be useful to compare the predictions of the two-phase model with those of a one-phase model employing an effectiveness factor incorporating film resistance to both heat and mass transfer. The comparison should be from the point of view of both the accuracy of the predictions and the computational requirements of the two models as it is expected that such a one-phase model would require a greater computational effort than the two-phase model due to the time consuming calculations necessary to calculate this type of effectiveness factor.

An investigation into the incorporation of a branched-chain homogeneous reaction into the reactor models would also prove useful. The oxidations of formaldehyde, or of butene and butadiene in the gas-phase, would be suitable reactions for this investigation. The results would be of direct relevance to the continuing study of the catalytic oxidation of butene to butadiene.

8.2 USE OF HOLLOW CATALYST PELLETS

The literature does not appear to contain any experimental data concerned with catalytic conversion by pellets with hollow geometries. It is important that this information be collected, preferably for heterogeneous reactions, and compared with the predictions of the models discussed in this thesis.

Experimental verification is also required for the ideas developed on the use of hollow pellets for optimising heterogeneous-homogeneous reaction schemes.

8.3 INVESTIGATION OF THE OXIDATION OF BUTENE TO BUTADIENE

It has been mentioned that the work in this thesis concerned with butene oxidation is part of a continuing study on the system.

Any future work on the system should consider both heterogeneous and homogeneous reactions and it is important to distinguish between these effects. One way to do this would be to use an experimental arrangement similar to that of Brown (33) where a known volume of free space follows the fixed bed. This volume can be varied to determine the proportion of the reaction that is homogeneous. Alternatively, an approach similar to Halladay and Mrarzek (8) could be employed. The amount of effective surface in a fixed-bed could be varied by varying the pellet size and thus the pellet effectiveness factor and the voidage.

Measurements are required on a fixed-bed reactor in which only heterogeneous oxidation of butene is occurring. It is important that the formation of aldehydic products is measured, so that the mathematical model for the catalyst pellet may be finally verified.

This model may then be used as part of an overall model for a fixed bed reactor, the homogeneous stages being described by aldehyde induced radical chain reactions.

APPENDIX A1

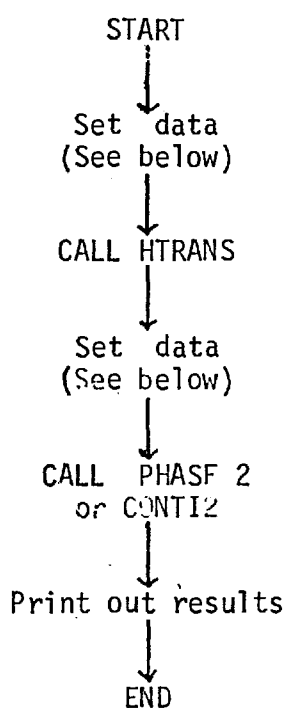
Computer Programs

The following pages show the subroutines that were written to integrate the two-dimensional models. The programs are general in nature and applicable, in principle, to any reaction system, simple or complex, heterogeneous and/or homogeneous, occurring in a fixed bed.

The subroutines listed are:

PHASE 2	-	controls integration of two-phase model
CONTI2	-	controls integration of one-phase model
COMAT2	-	evaluates matrices of coefficients required by ROWNEX
ROWNEX	-	advances implicit finite difference method by one axial step
STDIMP	-	solves the sets of linear equations generated by ROWNEX
ROWONE	-	advances explicit finite difference method by one axial step
SOLIDS	-	solves the solid-phase energy balance
COMAT	-	calculates coefficients required by solids
STDLEQ	-	solves set of linear equations generated by SOLIDS
CHECK	-	checks solutions for negative concentrations
RESULT	-	prints values of radial profiles as integration proceeds
STORE	-	stores axial profiles as integration proceeds
HTRANS	-	calculates heat transfer parameters

The detailed use of these subroutines is specific to the case being studied. Briefly, the calling sequence is:



The data, and FØRTRAN variables, that need to be set before the call of HTRANS are:

<u>Variable</u>	<u>description</u>	<u>units</u>	<u>FØRTRAN symbol</u>
dp	catalyst pellet diameter	m	DP
dt	reactor tube diameter	m	DT
ϕ	bed voidage	-	PØR
G	superficial mass flow rate	$\text{kg m}^{-2}\text{sec}^{-1}$	GF
C_p	heat capacity of fluid	$\text{J kg}^{-1}\text{K}^{-1}$	CP
T_{in}^f	mean fluid inlet temperature	K	TM
k_f	fluid thermal conductivity	$\text{Wm}^{-1}\text{K}^{-1}$	AKCG
k_s	solid thermal conductivity	$\text{Wm}^{-1}\text{K}^{-1}$	AKS
R_t	reactor tube radius	m	RTUBE
Re_p	Reynolds number	-	RE

The main parameters calculated by HTRANS are:

<u>parameter</u>	<u>FØRTRAN symbol</u>
λr^f	AKRF
λr^s	AKRS
λr^c	AKR
α_w^f	AWF
α_w^s	AWS
α_w^c	AW
U	U
h_{va_v}	HVAV
Bi^s	ANBIS
$(Pe)_{mr}$	PE
Bi^f	ANBIF
Bi^c	ANBI

Before PHASE2 or CONTI2 is called the following variables must be set:

Variable	Description	Units	FØRTRAN symbol
-	output control 0 - no output 1 - final profiles printed 2 - profiles printed at each step		IWRITE
-	0 - only current profiles retained 1 - all profiles stored		ISTØRE
N_A	No. of axial steps		N
M	No. of radial steps		M
-	No. of conservation equations		NC
$T^{f,g,i}$	inlet profiles	K or (-)	YS(M,NC)
T_w	wall temperature	K	TW
-	density of fluid at 273K multiplied by 273	kgm^{-3}_K	RHØR
ρ	density of fluid at inlet temp.	kgm^{-3}	DEN
L	reactor tube length		ALT

When a FØRTRAN variable includes NC as a dimension, the first member refers to the fluid temperature and subsequent members to the relevant chemical species.

Additionally, the heat transfer parameters calculated by HTRANS must be incorporated into the following groups.

Group	FØRTRAN symbol
d_t^2	GR1
$d_t^2 C_p G$	GR2
$16d\phi / (Pe)_{mr} d_t^2$	AM
Bi^s	BIS
$16\lambda r^s / d_t^2$	AS
AS x BIS	ASBIS
Bi^f or Bi^c	BIF
$16\lambda r^f$ or $16\lambda r^c / d_t^2$	AF

No further details will be given as each application of these subroutines must, at present, be individually tailored to the situation required.

The out-put of PHASE2 is:

FØRTRAN variable
or array

Description

R3(M,NC)

Radial profiles at reactor exit

TS(M)

Solid-phase radial profile

YST1(2,N)

Centre-line axial profiles of T^f and T^s

YST2(N,N)

Complete 2-dimensional profiles

YST3(2,M)

Solid and fluid radial temp. profiles in the plane of the maximum temperature.

Subroutines for two-dimensional integrations.

```

SUBROUTINE PHASE2(M,N,R1,R2,R3,TS,A,ALT,RATHOM,
XRATHET,IWRITE,NN,F,YS,CM,CS,AD,PELL,FILM,YST1,YST2
X,NC,A1,HF,X,YST3)

```

LIST OF IMPORTANT VARIABLES.

```

C      M      NO. OF RADIAL STEPS.
C      N      NO. OF AXIAL STEPS.
C      NN      N+10
C      NC      NO. OF CONSERVATION EQUATIONS.
C      R1(M,NC) ) PREVIOUS, CURRENT AND FUTURE
C      R2(M,NC) ) RADIAL PROFILES DURING
C      R3(M,NC) ) INTEGRATION.
C      TS(M,NC) RADIAL SOLIDS TEMPERATURE PROFILE.
C      ALT(M,NC) REACTOR LENGTH.
C      RATHOM  SUBROUTINE EVALUATES FLUID SOURCE TERMS.
C      RATHET  SUBROUTINE EVALUATES SOLID SOURCE TERMS.
C      F(M,NC) SOURCE TERMS.

```

ALL OTHER VARIABLES ARE INTERNAL AND MAY BE
REGARDED AS WORKING SPACE.

```

DIMENSION R1(M,NC),R2(M,NC),R3(M,NC),TS(M),A(M),F(M,
XNC),YS(M,NC),CM(3,M,NC),CS(3,M,NC),AD(NC),PELL(M,NC),
XFILM(M),YST1(2,NN),YST2(NC,NN),A1(NC),HF(M),X(NN),
XYST3(2,M)

```

```

COMMON / CONTROL / M1,AK,AK2,ACC
COMMON / FLUID / AF,RIF,AM
COMMON / SOLGAS / HVAV,RHOR,TW,EP
COMMON / SOLID / ASBIS,AS,BIS
COMMON / FACTORS / RADFS,RADFG,RADFC,RADF1
COMMON / RESULT / TSMAX,TFMAX,TCMAX,TIMAX,XMAX,IROW
COMMON / STAR / ISTAR
EXTERNAL RATHET,RATHOM
IF(ISTAR.EQ.1) IWRITE=0
M1=M-1
MT=M1/2

```

```

AK=1./FLOAT(M1)
AA=AK*AK
AK2=AA+AA
AN=ALT/FLOAT(N-1)
ACC=0.00002*FLOAT(M)
IT=0
AL=0.
IPOW=1
TSMAX=0.
DO 5 IM=1,M
DO 5 INC=1,NC
5 R1(IM,INC)=YS(IM,INC)
CALL COMAT
CALL SOLIDS(TS,R1,A,PELL,FILM,HF,RATHET,1,M,NC)
CALL STORE(R1,TS(1),M,IROW,YST1,YST2,NC)
IF(IWRITE.GT.1) CALL RESULT(AL,R1,TS,YST2,M,NC,IROW)
TSMAX=AMAX1(TSMAX,TS(1))
X(IROW)=AL
IF(TSMAX.NF.TS(1)) GO TO 7
TFMAX=YST1(2,IROW)
XMAX=AL
DO 8 IM=1,M
YST3(1,IM)=TS(IM)
8 YST3(2,IM)=R1(IM,1)
7 CONTINUE
ABIG=AMAX1(AF,AM)
AA=0.67*ABIG*AN/AK2
AB=AA+AA+0.67
AC=ALOG(AB)
AI=(AC/0.693142)+1.
IF(AI-1.) 20,20,30
20 AHD=AN
ISUB=1
GO TO 40
30 ISUB=IFIX(AI)+1
AA=2.**((ISUB-1)
ANS=1./((AA+AA+AA-2.))
AHD=AN*ANS
40 CONTINUE

```

```

A1(1)=AF
DO 41 INC=2,NC
41 A1(INC)=AM
CALL ROWONE(AHD,R1,R2,R1F,TW,F,M,NC,A1,PELL,FILM,
XRATHOM)
IROW=2
CALL CHECK(R2,M,IT,NC)
IF(IT.GT.0) RETURN
CALL SOLIDS(TS,R2,A,PELL,FILM,HF,RATHET,2,M,NC)
AL=AL+AHD
CALL STORE(R2,TS(1),M,IROW,YST1,YST2,NC)
IF(IWRITE.GT.1) CALL RESULT(AL,R2,TS,YST2,M,NC,IROW)
TSMAX=AMAX1(TSMAX,TS(1))
X(IROW)=AL
IF(TSMAX.NE.TS(1)) GO TO 42
TFMAX=YST1(2,IROW)
XMAX=AL
DO 43 IM=1,M
YST3(1,IM)=TS(IM)
43 YST3(2,IM)=R2(IM,1)
42 CONTINUE
ICH=ISUB+ISUB
IF(ICH.LT.4) GO TO 90
60 CONTINUE
IF(IROW-ICH) 90,80,70
70 CONTINUE
TMP=R3(MT,1)/R2(MT,1)
TFMP=TMP*TMP*TMP
DO 75 IM=1,M
DO 75 INC=1,NC
R1(IM,INC)=R2(IM,INC)
75 R2(IM,INC)=R3(IM,INC)
GO TO 110
80 CONTINUE
TMP=R3(MT,1)/R2(MT,1)
TFMP=TMP*TMP*TMP
DO 85 IM=1,M
DO 85 INC=1,NC
R2(IM,INC)=R3(IM,INC)
85 R1(IM,INC)=YS(IM,INC)
AHD=AN
GO TO 110
90 IF(IROW.EQ.2) GO TO 105

```

```

IV=MOD(IROW,2)+1
GO TO (70,95),IV
95 CONTINUE
TMP=R3(MT,1)/R2(MT,1)
TFMP=TMP*TMP*TMP
DO 100 IM=1,M
DO 100 INC=1,NC
100 R2(IM,INC)=R3(IM,INC)
AHD=AHD+AHD
GO TO 110
105 TFMP=1.
110 CONTINUE
RSTOR=(1.-RADFS)*AS
ASN=RSTOR+TFMP*RADFS*AS
FACT=ASN/AS
AS=ASN
RIS=RIS/FACT
RADFS=1.-(RSTOR/AS)
RSTOR=(1.-RADFG)*AF
AFN=RSTOR+TFMP*RADFG*AF
FACT=AFN/AF
AF=AFN
R1F=R1F/FACT
RADFG=1.-(RSTOR/AF)
CALL COMAT2(CM,CS,AD,M,NC,AHD,IROW,ICH)
CALL ROWNEX(R1,R2,R3,F,M,NC,CM,CS,PELL,FILM,RATHOM)
CALL CHECK(R3,M,IT,NC)
IF(IT.GT.0) RETURN
IROW=IROW+1
CALL COMAT
CALL SOLIDS(TS,R3,A,PELL,FILM,HF,RATHET,2,M,NC)
AL=AL+AHD
CALL STORE(R3,TS(1),M,IROW,YST1,YST2,NC)
IF(IWRITE.GT.1) CALL RESULT(AL,R3,TS,YST2,M,NC,IROW)
TSMAX=AMAX1(TSMAX,TS(1))
X(IROW)=AL
IF(TSMAX.NE.TS(1)) GO TO 120
TFMAX=YST1(2,IROW)
XMAX=AL
DO 121 IM=1,M
YST3(1,IM)=TS(IM)
121 YST3(2,IM)=R3(IM,1)
120 CONTINUE
IF(ISTAR.FQ.1.AND.IROW.GE.N-5+ICH) IWRITE=2

```

```

IF(IROW.LT.N-2+ICH) GO TO 60
IF(IWRITE.GT.0) CALL RESULT(AL,R3,TS,YST2,M,NC,IROW)
RETURN
END

```

```

SUBROUTINE CONTIP(M,N,R1,R2,R3,ALT,RAT,IWRITE, NN,F,YS
X,CM,CS,AD,X,YST1,YST2,NC,A1,PELL,FILM,TS,YST3)

```

```

DIMENSION R1(M,NC),R2(M,NC),R3(M,NC),F(M,NC),YS(M,NC),
XCM(3,M,NC),CS(3,M,NC),AD(NC),YST1(2,NN),YST2(NC,NN),
XA1(NC),PELL(M,NC),FILM(M),TS(M),X(NN),YST3(2,M)

```

```

COMMON / CONTROL / M1,AK,AK2,ACC

```

```

COMMON / FLUID / AF,RIF,AM

```

```

COMMON / SOLGAS / HVAV,RHOR,TW,EP

```

```

COMMON / FACTORS / RADFS,RADFG,RADFC,RADF1

```

```

COMMON / RESUL / TSMAX,TFMAX,TCMAX,T1MAX,XMAX,IROW

```

```

COMMON / STAB / ISTAR

```

```

EXTERNAL RAT

```

```

IF(ISTAR.EQ.1) IWRITE=0

```

```

TCMAX=0.

```

```

M1=M-1

```

```

MT=M1/2

```

```

AK=1./FLOAT(M1)

```

```

AA=AK*AK

```

```

AK2=AA+AA

```

```

AN=ALT/FLOAT(N-1)

```

```

IT=0

```

```

IROW=1

```

```

AL=0.

```

```

DO 5 IM=1,M

```

```

TS(IM)=0.

```

```

DO 5 INC=1,NC

```

```

5 R1(IM,INC)=YS(IM,INC)

```

```

TCMAX=AMAX1(TCMAX,R1(1,1))

```

```

X(IROW)=AL

```

```

IF(ABS(AL-XMAX).GT.0.1E-10) GO TO 7

```

```

DO 8 IM=1,M

```

```

8 YST3(1,IM)=R1(IM,1)

```

```

7 CONTINUE

```

```

CALL STORE(R1,0.,M,IROW,YST1,YST2,NC)

```

```

ABIG=AMAX1(AF,AM)

```

```

AA=0.67*ABIG*AN/AK2

```

```

AR=AA+AA+0.67

```

```

AC=ALOG(AR)

```

```

A1=(AC/0.693142)+1.

```

```

IF(A1-1.) 20,20,30

```

```

20 AHD=AN

```

```

ISUB=1

```

```

GO TO 40

```

```

30 ISUB=IFIX(A1)+1

```

```

AA=2.**((ISUB-1)

```

```

ANS=1./((AA+AA+AA-2.))

```

```

AHD=AN*ANS

```

```

40 CONTINUE

```

```

A1(1)=AF

```

```

DO 41 INC=2,NC

```

```

41 A1(INC)=AM

```

```

IROW=2

```

```

CALL ROWONE(AHD,R1,R2,BIF,TW,F,M,NC,A1,PELL,FILM,RAT)

```

```

CALL CHECK(R2,M,IT,NC)

```

```

IF(IT.GT.0) RETURN

```

```

AL=AL+AHD

```

```

CALL STORE(R2,0.,M,IROW,YST1,YST2,NC)

```

```

IF(IWRITE.GT.1) CALL RESULT(AL,R2,TS,YST2,M,NC,IROW)

```

```

TCMAX=AMAX1(TCMAX,R2(1,1))

```

```

X(IROW)=AL

```

```

IF(ABS(AL-XMAX).GT.0.1E-10) GO TO 42

```

```

DO 43 IM=1,M

```

```

43 YST3(1,IM)=R2(IM,1)

```

```

42 CONTINUE

```

```

ICH=ISUB+ISUB

```

```

IF(ICH.LT.4) GO TO 90

```

```

60 CONTINUE

```

```

IF(IROW-ICH) 90,80,70

```

```

70 CONTINUE

```

```

TMP=R3(MT,1)/R2(MT,1)

```

```

TEMP=TMP*TMP*TMP

```

```

DO 75 IM=1,M

```

```

DO 75 INC=1,NC

```

```

R1(IM,INC)=R2(IM,INC)

```

```

75 R2(IM,INC)=R3(IM,INC)

```

```

GO TO 110

```

```

80 CONTINUE

```

```

TMP=R3(MT,1)/R2(MT,1)

```

```

TEMP=TMP*TMP*TMP

```

```

DO 85 IM=1,M

```

```

      DO 85 INC=1,NC
      R2(IM,INC)=R3(IM,INC)
85  R1(IM,INC)=YS(IM,INC)
      AHD=AN
      GO TO 110
90  IF(IROW.EQ.2) GO TO 105
      IV=MOD(IROW,2)+1
      GO TO (70,95),IV
95  CONTINUE
      TMP=R3(MT,1)/R2(MT,1)
      TEMP=TMP*TMP*TMP
      DO 100 IM=1,M
      DO 100 INC=1,NC
100  R2(IM,INC)=R3(IM,INC)
      AHD=AHD+AHD
      GO TO 110
105  TEMP=1.
110  CONTINUE
      RSTOR=(1.-RADFC)*AF
      AFN=RSTOR+TEMP*RADFC*AF
      FACT=AFN/AF
      AF=AFN
      RIF=RIF/FACT
      RADFC=1.-(RSTOR/AF)
      CALL COMAT2(CM,CS,AD,M,NC,AHD,IROW,ICH)
      CALL ROWNEX(R1,R2,R3,F,M,NC,CM,CS,PELL,FILM,RAT)
      CALL CHECK(R3,M,IT,NC)
      IF(IT.GT.0) RETURN
      IROW=IROW+1
      AL=AL+AHD
      CALL STORE(R3,0.,M,IROW,YST1,YST2,NC)
      IF(IWRITE.GT.1) CALL RESULT(AL,R3,TS,YST2,M,NC,IROW)
      TCMAX=AMAX1(TCMAX,R3(1,1))
      X(IROW)=AL
      IF(ABS(AL-XMAX).GT.0.1E-10) GO TO 120
      DO 121 IM=1,M
121  YST3(1,IM)=R3(IM,1)
120  CONTINUE
      IF(ISTAB.EQ.1.AND.IROW.GE.N-5+ICH) IWRITE=2
      IF(IROW.LT.N-2+ICH) GO TO 60
      IF(IWRITE.GT.0) CALL RESULT(AL,R3,TS,YST2,M,NC,IROW)
      RETURN
      END

```

```

      SUBROUTINE COMAT2(CM,CS,A,M,NC,AHD,IROW,ICH)
      DIMENSION A(NC),CM(3,M,NC),CS(3,M,NC)
      COMMON / FLUID / AF,RIF,AM
      COMMON / CONTROL / M1,AK,AK2,ACC
      A2=0.25/AHD
      A1=A2+A2+A2
      A3=A1+A2
      A(1)=AF/AK
      A(2)=AM/AK
      DO 5 INC=3,NC
5  A(INC)=A(INC-1)
      NCL=NC
      IF(IROW.GT.ICH)NCL=1
      DO 20 INC=1,NCL
      CM(2,1,INC)=A(INC)+A1
      CS(2,1,INC)=-A(INC)+A1
      CM(3,1,INC)=A(INC)-A2
      CS(3,1,INC)=A(INC)+A2
      CM(1,1,INC)=0.
      CS(1,1,INC)=0.
      DO 10 IM=2,M1
      ACM=FLOAT(IM-1)
      AA=A(INC)*ACM
      CM(2,IM,INC)=AA+AA+A3
      CS(2,IM,INC)=A3-AA-AA
      CM(1,IM,INC)=(ACM+ACM-1.)*0.5*A(INC)
      CS(1,IM,INC)=CM(1,IM,INC)
      CM(3,IM,INC)=(ACM+ACM+1.)*0.5*A(INC)
      CS(3,IM,INC)=CM(3,IM,INC)
10  CONTINUE
      CM(3,M,INC)=0.
      CS(3,M,INC)=0.
      ACM=FLOAT((M-1)**2)
      CM(1,M,INC)=A(INC)*AK*ACM
      CM(1,M,INC)=CM(1,M,INC)+CM(1,M,INC)
      CS(1,M,INC)=CM(1,M,INC)
      CM(2,M,INC)=CM(1,M,INC)+A3
20  CS(2,M,INC)=-CM(1,M,INC)+A3
      TRAN=RIF*AF*0.5*FLOAT(M+M-1)
      CM(2,M,1)=CM(2,M,1)+TRAN
      CS(2,M,1)=CS(2,M,1)-TRAN
      RETURN
      END

```

```

SUBROUTINE STDIMP(C,RN,NC,M)
  DIMENSION C(3,M,NC),RN(M,NC)
  DIMENSION W(100), G(100)
  M1=M-1
  DO 10 INC=1,NC
    W(1)=C(3,1,INC)/C(2,1,INC)
    G(1)=RN(1,INC)/C(2,1,INC)

    DO 20 IM=2,M
      D=C(2,IM,INC)-C(1,IM,INC)*W(IM-1)
      W(IM)=C(3,IM,INC)/D
20    G(IM)=(RN(IM,INC)+C(1,IM,INC)*G(IM-1))/D
      RN(M,INC)=G(M)
    DO 30 IM=1,M1
30    RN(M-IM,INC)=W(M-IM)*RN(M-IM+1,INC)+G(M-IM)
10  CONTINUE
  RETURN
  END

SUBROUTINE ROWNEX(R1,R2,R3,F,M,NC,CM,CS,PELL,FILM,
XSOURCE)
  DIMENSION R1(M,NC),R2(M,NC),R3(M,NC),F(M,NC),
1,PELL(M,NC),FILM(M),CM(3,M,NC),CS(3,M,NC)
  COMMON / SOLGAS / HVAV,RHOR,TW,EP
  COMMON / FLUID / AF,BIF,AM
  M1=M-1
  CALL SOURCE(R2,F,PELL,FILM,M,NC)
  DO 60 INC=1,NC
    F(1,INC)=CS(2,1,INC)*R1(1,INC)+CS(3,1,INC)*R1(2,INC)+
X1.5*F(1,INC)+0.5*F(2,INC)
    DO 50 IM=2,M1
      IM2=IM-2
      F(IM,INC)=F(IM,INC)+F(IM,INC)
    DO 50 IND=1,3
50    F(IM,INC)=F(IM,INC)+CS(IND,IM,INC)*R1(IM2+IND,INC)
60    F(M,INC)=CS(1,M,INC)*R1(M1,INC)+CS(2,M,INC)*R1(M,INC)
      X+F(M,INC)+F(M,INC)
      F(M,1)=F(M,1)+TW*FLOAT(M+M-1)*AF*BIF
      CALL STDIMP(CM,F,NC,M)
    DO 70 INC=1,NC

```

```

DO 70 IM=1,M
70  R3(IM,INC)=F(IM,INC)
  RETURN
  END

```

```

SUBROUTINESOLIDS(TS,ROW,A,PELL,FILM,HF,HETERO,IG,M,NC)
  DIMENSIONTS(M),A(M),ROW(M,NC),PELL(M,NC),FILM(M),HF(M)
  COMMON / CONTROL / M1,AK,AK2,ACC
  COMMON / SOLGAS / HVAV,RHOR,TW,EP
  COMMON / SOLID / ASBIS,AS,BIS
  GO TO (10,30),IG
10  DO 20 IM=1,M
20  TS(IM)=ROW(IM,1)
30  CONTINUE
  DO 40 IM=1,M
40  HF(IM)=(1.-EP)*RHOR/TS(IM)
    CALL HETERO(ROW,TS,PELL,HF,M,NC)
    A(1)=0.75*HF(1)+0.25*HF(2)+HVAV*ROW(1,1)
    DO 50 IM=2,M
50  A(IM)=HF(IM)+HVAV*ROW(IM,1)
      A(M)=A(M)+(ASBIS/AK+ASBIS*0.5)*TW
      CALL STOLEO(A,M)
      ERROR=0.
      DO 60 IM=1,M
        FDR=(A(IM)-TS(IM))/(A(IM)-ROW(IM,1))
60  ERROR=ERROR+ERR*FDR
      DO 70 IM=1,M
        TS(IM)=A(IM)
70  FILM(IM)=(TS(IM)-ROW(IM,1))*HVAV
      IF(ERROR-ACC) 80,80,30
80  RETURN
  END

```

```

SUBROUTINE ROWONE(AHD,R1,R2,BIF,TW,F,M,NC,A,PELL,FILM,
XSOURCE)
  DIMENSION R1(M,NC),R2(M,NC),F(M,NC),A(NC),PELL(M,NC),
XFILM(M)
  COMMON /CONTROL / M1,AK,AK2,ACC
  AA=0.5*AHD/AK
  B=FLOAT(M1*M1)

```

```

CALL SOURCE(R1,F,PELL,FILM,M,NC)
DO 30 INC=1,NC
  A1=A(INC)*AA
  A2=1.-A1-A1-A1
  A3=4.*A1
  A4=2.*AHD*8*A(INC)
  R2(1,INC)=A2*R1(1,INC)+A3*R1(2,INC)-A1*R1(3,INC)
  X=AHD*F(1,INC)
  DO 20 IM=2,M1
    A5=FLOAT(IM-1)
    A6=A5+A5-1.
    A7=A6+2.
  20 R2(IM,INC)=A1*A6*R1(IM-1,INC)+(1.-A5*A3)*R1(IM,INC)
  X+A1/A7*R1(IM+1,INC)+AHD*F(IM,INC)
  30 R2(M,INC)=A4*R1(M1,INC)+(1.-A4)*R1(M,INC)+AHD*F(M,INC)
  AR=A(1)*AA*AK*R1F*FLOAT(M+M-1)
  R2(M,1)=R2(M,1)-AR*(R1(M,1)-TW)
  RETURN
END

```

```

SUBROUTINE COMAT
COMMON / COEFF1 / C(3,200)
COMMON / CONTROL / M1,AK,AK2,ACC
COMMON / SOLID / ASRIS,AS,RI5
COMMON / SOLGAS / HVAV,RHOR,TW,EP
M=M1+1
A1=AS/AK
A2=AS/AK2
DO 10 IM=2,M1
  AMM=FLOAT(IM-1)
  C(1,IM)=A1*(AMM-0.5)
  AA=A1*AMM
  C(2,IM)=AA+AA+HVAV
10 C(3,IM)=A1*(AMM+0.5)
  C(1,1)=0.
  C(3,M)=0.
  C(2,1)=A1+HVAV
  C(3,1)=A1
  AR=A2+A2+A2+A2
  C(2,M)=HVAV+AR+RI5*A1+ASRIS*0.5
  C(1,M)=AR
  RETURN
END

```

```

SUBROUTINE STDLEN(A,N)
DIMENSION W(200),A(N),G(200)
COMMON/COEFF1/ C(3,200)
W(1)=C(3,1)/C(2,1)
G(1)=A(1)/C(2,1)
DO 1 I=2,N
  IM1=I-1
  D=C(2,1)-C(1,1)*W(IM1)
  W(I)=C(3,1)/D
  1 G(I)=(A(I)+C(1,1)*G(IM1))/D
  A(N)=G(N)
  NM1=N-1
  DO 2 I=1,NM1
    J=N-I
    JP1=J+1
    2 A(J)=W(J)*A(JP1)+G(J)
  RETURN
END

```

```

SUBROUTINE CHECK(R3,M,IT,NC)
DIMENSION R3(M,NC)
DO 30 INC=1,NC
  IF(R3(1,INC).LT.0..OR.R3(M,INC).LT.0.) IT=1
30 CONTINUE
  IF(IT.EQ.0) RETURN
  WRITE(6,1000)
  WRITE(6,1001)
  WRITE(6,1002) R3(1,1)
  DO 10 I=2,NC
    WRITE(6,1004) I, R3(1,I)
  10 CONTINUE
  WRITE(6,1003)
  WRITE(6,1002) R3(M,1)
  DO 20 I=2,NC
    WRITE(6,1004) I,R3(M,I)
  20 CONTINUE
  RETURN
1000 FORMAT(1X,48(***)/1X,**NEGATIVE VALUES CALCULATED IN *.
  X*DOWNEX OR ROWONE+*/1X,48(***)/)
1001 FORMAT(1X,48(***)/)
1002 FORMAT(1X,**CENTRE LINE VALUES*/)
1003 FORMAT(1X,**FLUID TEMP */1X,F6.1)
1004 FORMAT(1X,**VALUES AT WALL*/)
1004 FORMAT(1X,**COMPONENT*,12,1X,F6.4)
END

```

```

SUBROUTINE RESULT(AL,ROW,TS,YST2,M,NC,IROW)
  DIMENSION ROW(M,NC),TS(M),YST2(NC,IROW),R(5)
  COMMON / CONTROL /M1,AK,AK2,ACC
  I2=(M+1)/4
  I3=I2+I2
  I4=I3+I2
  WRITE(6,1000) AL
  RS=-1.
  RB=FLOAT(I2)
  R(1)=0.
  R(5)=1.
  DO 40 I=2,4
    RS=RS+RB
    RS=RS*AK
40  R(I)=SQRT(RS)
    WRITE(6,1002) (R(I),I=1,5)
    WRITE(6,1003) TS(1),TS(I2),TS(I3),TS(I4),TS(M)
    WRITE(6,1004) ROW(1,1),ROW(I2,1),ROW(I3,1),ROW(I4,1),R
    XOW(M,1)
    DO 50 INC=2,NC
      IN=INC-1
      WRITE(6,1005) IN,ROW(1,INC),ROW(I2,INC),ROW(I3,INC),
    XROW(I4,INC),ROW(M,INC)
50  CONTINUE
      WRITE(6,1006)
      WRITE(6,1007) YST2(1,IROW)
      DO 60 INC=2,NC
        IN=INC-1
        WRITE(6,1008) IN,YST2(IN,IROW)
60  CONTINUE
      WRITE(6,1009)
      RETURN
1000 FORMAT(1X,110(/**))//1X,*THE FOLLOWING PROFILES WERE CALC
  XA LENGTH OF *.F8.5,*(M*/ )
1002 FORMAT(1X,*RADIUS*,5X,5(1X,F4.2,3X,))
1003 FORMAT(1X,*SOLID TEMP *,5(F6.1,2X))
1004 FORMAT(1X,*FLUID TEMP *,5(F6.1,2X))
1005 FORMAT(1X,*COMP. *,12,2X,5(F6.4,2X))
1006 FORMAT(1H0,*THE EQUIVALENT FLOW AVERAGED FLUID PROPERTII
  X/)
1007 FORMAT(1X,*FLUID TEMPERATURE *,F6.1)
1008 FORMAT(1X,*M,FRAC COMPONENT*,12,1X,F6.4)
1009 FORMAT(///)
  END

```

```

SUBROUTINE STORE(ROW,TS,M,IROW,YST1,YST2,NC)
  DIMENSION ROW(M,NC),YST1(2,IROW),YST2(NC,IROW)
  M1=M-1
  F=2.*FLOAT(M1)
  YST1(1,IROW)=TS
  YST1(2,IROW)=ROW(1,1)
  DO 30 INC=1,NC
    AVGE=ROW(1,INC)+ROW(M,INC)
    DO 20 IM=2,M1
20  AVGE=AVGE+ROW(IM,INC)+ROW(IM,INC)
30  YST2(INC,IROW)=AVGE/F
  RETURN
  END

```

```

SUBROUTINE HTRANS
  COMMON / HTDATA / DP,DT,POR,GF,CP,TM,AKCG,AKS,RE,RTUBE,
  XAKR,AW,AWF,AWS,ANR1,ANR1S,A(RIF,U,HVA,PE,AKRF,AKRS)
  COMMON / FACTORS / RADFS,RADFG,RADFC,RADF1
  COMMON / ROUGH / RGH
  A1=TM*TM*TM*CP
  R=DP/DT
  PE=8.0+155.2*R*R
  AKTD=CP*GF*DP/PE
  AKRAD=7.65F-R*A1
  AKRF=AKTD+POR*(AKRAD+AKCG)
  RADFG=POR*AKRAD/AKRF
  SF=AKS/AKCG
  ANU=6.076F-R*A1/AKS
  R=10.0**((0.3521*ALOG10(SF)+0.25)
  RD=1.3*ANU*SF
  AKRS=AKCG*(R+RR)
  RADFS=RR/(R+RR)
  AKR=AKRF+AKRS
  RADFC=(RADFS*AKRS+RADFG*AKRF)/AKR
  RADF1=RADFC
  AW=AKCG*(2.3*PE**0.33+0.083*RE**0.8)/DP
  AWF=0.25*RE**(-0.2)*GF*CP
  AWS=AW-AWF
  ANR1=AW*RTURF/AKR
  U=AW/(1.+0.25*ANR1)
  ANR1F=AWF*RTURF/AKRF
  ANR1S=AWS*RTURF/AKRS
  REM=RF/(1.-POR)
  DPM=DP*POR/(1.-POR)
  ANUM=0.446*REM**0.5+0.178*REM**0.667
  HV=ANUM*AKCG/DPM

```

/contd.

```

  AV=6.0*RGH*(1.-POR)/DP
  HVA=HV*AV
  RETURN
  END

```

/contd.

Appendix A5

(Appendix to Chapter 5)

DATA FOR BUTENE PELLET MODELLING

- A5.1 Reactor and Pellet Dimensions
- A5.2 Pellet Properties
- A5.3 Thermochemical Properties of Component Species
- A5.4 Kinetic Data
- A5.5 Film Transfer Coefficients
- A5.7 Computer Programs

Note: All data is extracted from PhD Thesis of Corrie (26) unless otherwise stated.

A5.1 REACTOR AND PELLET DIMENSIONS.

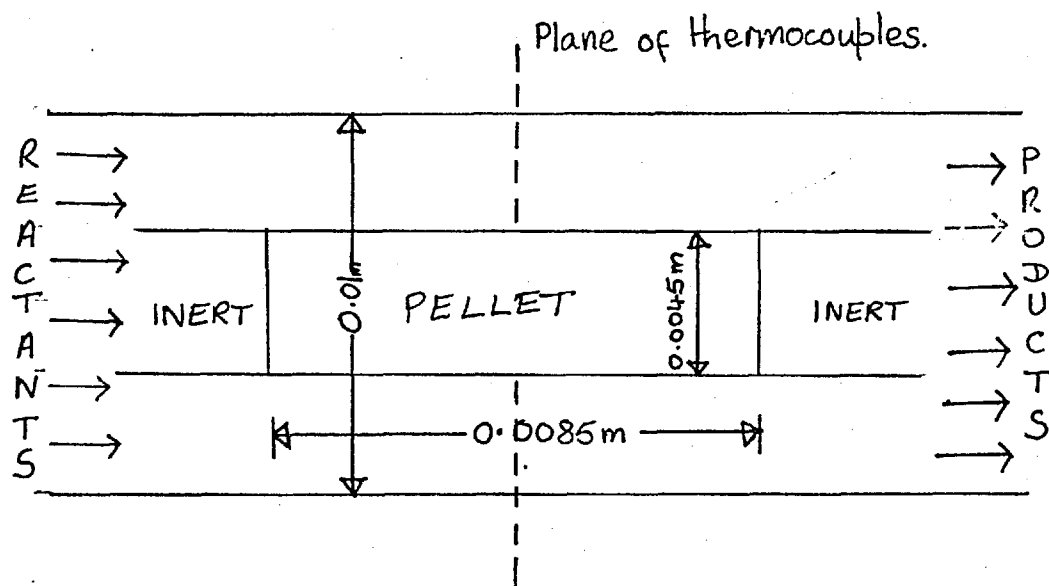


Fig (A5.1) Reactor and Pellet Configuration.

A1.2 PELLET PROPERTIES

(i) Pellet Bulk Density = $\rho_b = \frac{\text{Wt. of one pellet}}{\text{Vol. of one pellet}} = 4881 \text{ kg m}^{-3}$

(ii) Effective Thermal Conductivity of Pellet

$$K_{\text{eff}} = 0.0952 + 0.44 \times 10^{-3} T^5 \text{ Wm}^{-2}$$

(iii) Effective Diffusivities.

Corrie has measured effective diffusivities for oxygen and butadiene at various temperatures. The following polynomials were fitted to his data.

$$D_{\text{eff}}^{\text{O}_2} = -0.1608 \times 10^{-5} + 0.1411 \times 10^{-7} T^f - 0.2771 \times 10^{-10} T^{\epsilon^2} + 0.1942 \times 10^{-13} T^f^3 \text{ m}^2 \text{sec}^{-1}$$

$$D_{\text{eff}}^{\text{Bd}} = -0.3055 \times 10^{-5} + 0.2459 \times 10^{-7} T^f - 0.4831 \times 10^{-10} T^f + 0.3202 \times 10^{-13} T^f^3 \text{ m}^2 \text{sec}^{-1}$$

It was assumed, after Corrie, that Knudsen diffusion predominates in the pellet pores and that the effective diffusivities of the other species will be directly proportional to the Knudsen diffusivity

represented by :

$$D_{\text{eff}}^i = C_D^i \frac{T^f}{M_w} \quad (\text{A5.1})$$

Equation (A5.1) was compared with the fitted value of effective diffusivity at 730K for Oxygen and Butadiene. The values of C_D^i resulting were

$$\text{Oxygen} \quad C_D^{O_2} = 3.3 \times 10^{-7}$$

$$\text{Butadiene} \quad C_D^{\text{Bd}} = 4.2 \times 10^{-7}$$

The difference between these values can probably be attributed largely to the difference in size and geometry of the molecules. Thus, in using (A5.1) to estimate the effective diffusivities of species other than oxygen and butadiene, C_D was taken to be 3.3×10^{-7} for species more similar to oxygen (i.e., Carbon dioxide, carbon monoxide and water) and to be 4.2×10^{-7} for species more similar to butadiene (i.e., butene and all organic products).

(iv) Pellet Shape Factor.

The Pellet Shape Factor is defined by:

$$\frac{m_s + 1}{dp} = \frac{A_p}{2V_p}$$

For a cylindrical pellet of radius 0.00225m and length 0.0085m, m_s is calculated to be 1.53. When a pellet is sandwiched between inactive pellet blanks, as is the case in Corrie's experimental arrangement, axial diffusion is greatly reduced, the situation becomes that of an infinite cylinder and m_s tends to unity.

A1.3 THERMOCHEMICAL PROPERTIES OF THE COMPONENT SPECIES

- (i) Heats of formation at 298K:- $(-\Delta H_f)_{298}^i \text{ J kg}^{-1}$
- | | | | |
|------------------------|---------------------|-----------------------|---------------------|
| Butadiene (142) | $+2.04 \times 10^6$ | Butene (143) | -2.09×10^4 |
| Carbon Dioxide (143) | -8.95×10^6 | Carbon Monoxide (143) | -3.95×10^6 |
| Furan (144) | -9.11×10^5 | Acrolein (143) | -1.53×10^6 |
| n-Butyl aldehyde (143) | -3.05×10^6 | Acetaldehyde (143) | -3.78×10^6 |
| Water (143) | -1.34×10^7 | | |

(ii) Specific Heats

Values for C_p^i the specific heat of component i , were obtained as a function of temperature from polynomial expressions. The data sources used for specific heats were:

ref(143): butene, butadiene, carbon dioxide, carbon monoxide, acetaldehyde, nitrogen and water

ref(145): oxygen, furan, acrolein, n-butyraldehyde

(iii) Heat Contents

The 'heat content' of component i is defined by

$$H^i = (-\Delta H_f)_{298}^i + \int_{298}^T C_p^i dT \quad (A5.2)$$

A5.4 KINETIC DATA

(i) Reaction Scheme

The reaction scheme is essentially that deduced by Gabbay (27). The scheme has been completed by the inclusion of water in the balance and has been simplified by the removal of considerations of isomerisation between butene-1 and cis- and trans-2-butene. The modified scheme that has been used is shown in Table A5.1.

(ii) Arrhenius Parameters and kinetic orders

The rates of reaction have been quantified by Gabbay (27) and are expressed as:

$$\text{rate} = k' x f(\text{concentrations})$$

As the concentrations of only three species are involved, the rate may be expressed as:

$$\text{rate} = k(\text{oxygen})^m (\text{butene})^n (\text{butadiene})^o \quad (A5.3)$$

The values for m , n , and o have been determined by Gabbay by fitting (A5.3) to his experimental results. The rate of reaction is expressed in units of Kmoles per kg catalyst per second and the rate quoted is the rate of production of the primary product of the reaction. In Table (A5.1), the primary product for each reaction is

Table (A5.1)

Overall stoichiometry and kinetics for oxidative dehydrogenation of butene to butadiene

rate = $k(\text{oxygen})^m(\text{butene})^n(\text{butadiene})^0$; $k = A\exp(-E_A/RT)$; E_A expressed in Kcal/g-mole

REACTION	PRIMARY PRODUCT	m	n	0	E_A	$\log_{10} A$
1. $\text{C}_4\text{H}_8 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O}$	C_4H_6	0.44	0.44	0	17.4	1.813
2. $\text{C}_4\text{H}_8 + 6\text{O}_2 \rightarrow 4\text{CO}_2 + 4\text{H}_2\text{O}$	CO_2	1.15	0.8	0	23.8	5.352
3. $\text{C}_4\text{H}_8 + 4\text{O}_2 \rightarrow 4\text{CO} + 4\text{H}_2\text{O}$	CO	1.6	0.9	0	26.3	6.881
4. $\text{C}_4\text{H}_8 + 3/2 \text{O}_2 \rightarrow \text{C}_4\text{H}_4\text{O} + 2\text{H}_2\text{O}$	$\text{C}_4\text{H}_4\text{O}$	0.85	0.33	0	27.5	3.884
5. $\text{C}_4\text{H}_8 + 5/2 \text{O}_2 \rightarrow \text{C}_3\text{H}_4\text{O} + \text{CO}_2 + 2\text{H}_2\text{O}$	$\text{C}_3\text{H}_4\text{O}$	1.2	0.75	0	25.0	2.000
6. $\text{C}_4\text{H}_8 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_3\text{H}_7\text{CHO}$	$\text{C}_3\text{H}_7\text{CHO}$	1	1	0	15.0	1.265
7. $\text{C}_4\text{H}_8 + \text{O}_2 \rightarrow 2\text{CH}_3\text{CHO}$	CH_3CHO	1	1	0	17.5	2.550
8. $\text{C}_4\text{H}_6 + 11/2 \text{O}_2 \rightarrow 4\text{CO}_2 + 3\text{H}_2\text{O}$	CO_2	0.57	0	1	17.0	2.602
9. $\text{C}_4\text{H}_6 + 7/2 \text{O}_2 \rightarrow 4\text{CO} + 3\text{H}_2\text{O}$	CO	0.75	0	1	15.7	2.021
10. $\text{C}_4\text{H}_6 + \text{O}_2 \rightarrow \text{C}_4\text{H}_4\text{O} + \text{H}_2\text{O}$	$\text{C}_4\text{H}_4\text{O}$	1.7	0	0.1	25.0	4.539
11. $\text{C}_4\text{H}_6 + 2\text{O}_2 \rightarrow \text{C}_3\text{H}_4\text{O} + \text{H}_2 + \text{CO}_2$	$\text{C}_3\text{H}_4\text{O}$	1.5	0	0.55	21.0	3.973
12. $\text{C}_4\text{H}_6 + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_7\text{CHO}$	$\text{C}_3\text{H}_7\text{CHO}$	1	0	1.5	10.0	1.342
13. $\text{C}_4\text{H}_6 + 3\text{O}_2 \rightarrow \text{CH}_3\text{CHO} + 2\text{CO}_2 + 2\text{H}_2\text{O}$	CH_3CHO	1	0	1	21.0	2.954

indicated. Table (A5.1) also includes details of the kinetic orders and Arrhenius parameters for the reactions.

A5.5 FILM TRANSFER COEFFICIENTS

The film heat transfer coefficient is predicted by Equation (5.2). The Chilton-Colburn analogy (146) states that:

$$\frac{h_v Pr^{2/3}}{C_{pp}} = kg^i (Sc^i)^{2/3} \quad (A5.4)$$

$$\text{where } Pr = \frac{C_p \mu}{k} \quad Sc^i = \frac{\mu}{\rho D^i} \quad (A5.5)$$

Thus it is required to provide correlations for k , C_p , μ , ρ , and D^i . Simple correlations for μ and ρ were used, assuming them to differ only slightly from the viscosity and density, respectively, of air.

$$\text{Thus } \rho = 353/T^f \text{ kg m}^{-3} \quad \text{and} \quad \mu = 3.2 \times 10^{-5} + 3 \times 10^{-8} (T^f - 673)$$

Both correlations were obtained from data source (145).

The specific heat for each component was calculated as described in Section A1.3 and the specific heat of the mixture was assumed to be the sum of these values weighted by the mass functions of the species concerned.

The thermal conductivity of gases at high temperature are less readily available from the literature. However, use may be made of the fact that Pr is almost constant with respect to temperature and can be used to calculate k for a given temperature, provided that at least one estimate of C_p , μ and k is available at some given temperature.

It only remains to evaluate D^i , the bulk diffusivity of each species in order to use (A5.4). D^i was taken to be the binary diffusion coefficient of the i^{th} species in air. Even the most recent, and extensive, compilation of diffusivity data (148) gives experimental values for only a few of the coefficients. The most conveniently used estimation formula in the literature is due to Gilliland (147) and is of the form:

$$D_i^i = C_D^i T^{1.5} \quad (A5.6)$$

The parameter C_D^i depends on the molecular properties of both air and the i^{th} species. Values for C_D^i have been estimated from data source (145). The values used are:

<u>Gas Pair</u>	<u>C_D^i</u>
Air - Oxygen	3.73×10^{-9}
Air - Butene	1.08×10^{-9}
Air - Butadiene	1.79×10^{-9}
Air - Carbon Dioxide	2.55×10^{-9}
Air - Carbon Monoxide	2.86×10^{-9}
Air - Furan	1.79×10^{-9}
Air - Acrolein	2.00×10^{-9}
Air - n-Butyraldehyde	1.60×10^{-9}
Air - Acetaldehyde	2.22×10^{-9}
Air - Water	3.91×10^{-9}

When T is expressed in degK, Equation (A5.6) yields D^i in $\text{m}^2 \text{sec}^{-1}$.

A1.6 COMPUTER PROGRAMS

A FORTRAN IV listing of the subroutine employed to predict the interaction of diffusion and reaction in and around the catalyst pellet, SUBROUTINE CAT3A, is shown in Figure(A5.2). Those symbols involved in information transfer into and out of the subroutine are explained in Figure(A5.3). Where a variable is subscripted (11), the first location refers to temperature and the remaining locations refer to the species in the following order:

oxygen
butene
butadiene
carbon dioxide
carbon monoxide
furan
acrolein
n-butyraldehyde
acetaldehyde
water

```

SUBROUTINE CAT3A(CC,B,ND)
DIMENSION CC(3,ND,7),B(ND,7)
DIMENSION CN(3),CON(4),AC(11),ACXB(4),HO(10),G(11),
133(11),GD(4)
COMMON / CONT / ITYPE,IFACT
COMMON / SYSTEM / RAD,DP,AS,GMF,IWRITE
COMMON / COEFF2 / SH(11)
COMMON / TWO / AM(10),O(11)
COMMON / ONE / N,XB(11)
COMMON / RESULT / EN(11),XC(11,150),NN
ITER=0
DO 350 I=2,4
IF (XB(I).LE.0.) XB(I)=0.1E-10
350 CONTINUE

```

```

      SET STEPLENGTH AND CALCULATE SHAPE FACTOR.

```

```

      NM1=N-1
      AK=1./FLOAT(NM1)
      AK2=AK*AK
      FS=(AS+1.)*0.25

```

```

      IF NO ESTIMATE OF PROFILES IS AVAILABLE , SET
      PROFILES TO UNITY.

```

```

      GO TO (200,300),ITYPE
200 DO 1 I=1,11
    DO 1 J=1,N
      1 XC(I,J)=1.
300 CONTINUE

```

```

      CALCULATE THE HEAT CONTENTS OF EACH SPECIES AT
      BULK FLUID TEMPERAYURE.

```

```

      CALL HEAT(HO,XB(1),XYZ)

```

```

      IF IT IS DESIRED TO EVALUATE THE EFFECTIVENESS
      FACTORS , CALCULATE THE RATES OF REACTION UNDER
      BULK CONDITIONS.

```

```

      GO TO (30,50),IFACT
30 DO 40 I=1,3
  40 CN(I)=XB(I+1)
    CALL RATEC(XB(1))
    CALL MASSH(CN,GB,HO)
50 CONTINUE

```

```

      CALCULATE EFFECTIVE DIFFUSIVITIES FOR EACH SPECIES
      AND THE EFFECTIVE THERMAL CONDUCTIVITY OF THE
      PELLET.

```

```

      TB=XB(1)
      TB2=TB*TB
      TB3=TB2*TB
      D(1)=0.0952+0.44E-3*TB
      DO 100 I=2,11
      GO TO (130,60,70,80,90,90,70,70,70,90),I
61 D(2)=-0.1608E-5+0.1411E-7*TB-0.2771E-10*TB2
  1+0.1942E-13*TB3
      GO TO 100
70 D(3)=4.2E-7*SQRT(TB/AM(I-1))
      GO TO 100
80 D(4)=-0.3055E-5+0.2459E-7*TB-0.4831E-10*TB2
  1+0.7232E-13*TB3
      GO TO 100
90 D(5)=3.3E-7*SQRT(TB/AM(I-1))
100 CONTINUE

```

Fig(A5-2) Subroutine CAT3A

contd /

CALCULATE FILM HEAT AND MASS TRANSFER COEFFICIENTS.

CALL EXTER2
DO 2 I=1,4

SET CONVERGENCE CRITERIA TO UNITY.

CON(J)=1.

CALCULATE DIMENSIONLESS GROUPS.

AC(I)=RAD*RAD*DP/(XB(I)*D(I))
ACXB(I)=AC(I)*XB(I)

CALCULATE THOSE PARTS OF THE T-D MATRIX THAT
REMAIN CONSTANT DURING THE ITERATIVE
CALCULATION.

CC(3,N,I)=0.
CC(1,1,I)=0.
CC(1,N,I)=2./AK2
DO 13 J=2,NM1
FJ=FLOAT(J-1)
CC(1,J,I)=FJ-FS
CC(3,J,I)=FJ+FS
13 CONTINUE

2 CONTINUE

START OF ITERATION LOOP.
SOLUTIONS ARE OBTAINED FOR TEMPERATURE PROFILE.
OXYGEN PROFILE.
BUTENE PROFILE.
AND BUTADIENE PROFILE.

4 ITER=ITER+1

CALCULATE RATE CONSTANTS AT PELLET SURFACE
TEMPERATURE.

CALL RATEC(XC(1,N)*XB(1))
DO 5 JJ=2,NM1
J=N+1-JJ

CALCULATE REACTION RATES, MATRIX COEFFICIENTS AND
FORCING VECTORS FOR N.GT.J.GT.1.

FJ=FLOAT(J-1)
DO 5 I=1,3
5 CN(I)=XC(I+1,J)*XB(I+1)
CALL MASSRD(CN,G,GD,H0)
DO 5 I=1,4
GDS=G0(I)*ACXB(I)
CC(2,J,I)=FJ+FJ-0.25*AK*GDS
5 B0(I)=AC(I)*G(I)-GDS*XC(I,J))*0.25*AK
DO 7 I=1,3

CALCULATE REACTION RATES, MATRIX COEFFICIENTS AND
FORCING VECTORS FOR J = 1.

7 CN(I)=XC(I+1,1)*XB(I+1)
CALL MASSRD(CN,G,GD,H0)
DO 8 J=1,4
GDS=G0(I)*ACXB(I)
CC(2,1,I)=FS+0.5- AK*0.25*GDS
CC(3,1,I)=CC(2,1,I)
8 B0(1)=0.5*(B(2,1)+(AC(1)*G(I)-GDS*XC(I,1))*0.25*AK)
DO 3 I=1,3

contd /

CALCULATE REACTION RATES , MATRIX COEFFICIENTS AND
J = N.

```

3  CN(I)=XC(I+1,N)*XB(I+1)
   CALL MASSRD(CN,G,GD,HO)
   DO 9 I=1,4
   GDS=GD(I)*ACXE(I)
   CC(2,N,I)=CC(1,N,I)+SH(I)/AK-FS*SH(I)-0.25*GDS
3  B(N,I)=(AC(I)*G(I)-GDS*XC(I,N))*0.25+SH(I)/AK-FS*SH(I)

```

OBTAIN SOLUTION FOR TRI - DIAGONAL SYSTEM
CC * XC = B.

CALL STDIMP(CC,B,4,N)

CHECK FOR CONVERGENCE OF ITERATIVE PROCEDURE .

```

CONVER=0.
DO 14 I=1,4
CON(I)=ABS((B(N,I)-XC(I,N))/B(N,I))
14 CONVER=CONVER+CON(I)
DO 12 J=1,N
DO 12 I=1,4
XC(I,J)=B(J,I)
12 CONTINUE

```

CHECK FOR NEGATIVE VALUES IN SOLUTION FOR
CONCENTRATION PROFILES. IF NEGATIVE VALUES ARE

FOUND , SET THE VALUE TO ZERO.

```

DO 26 I=2,4
DO 26 J=1,N
XC(I,J)=B(J,I)
IF(XC(I,J).LT.0.) XC(I,J)=0.1E-10
26 CONTINUE
IF(ITER.LE.1) GO TO 4

```

STOP CALCULATION IF THE NUMBER OF ITERATIONS
BECOMES LARGE.

IF(ITER.GT.34) GO TO 22

RETURN TO START OF ITERATIVE PROCEDURE IF
SOLUTIONS HAVE NOT CONVERGED.

```

IF(CONVER.GT.0.0010) GO TO 4
GO TO 23
22 WRITE(6,5000) ITER,(CON(I),I=1,4)
23 CONTINUE

```

SOLUTIONS HAVE CONVERGED .

REPEAT CALCULATION TO OBTAIN CONCENTRATION
PROFILES OF THE INACTIVE SPECIES.

```

DO 15 I=5,11
15 A(I)=RAD*RAD*DP/O(I)
DO 18 J=2,NM1
DO 16 I=1,3
15 CN(I)=XC(I+1,J)*XB(I+1)
   CALL MASSH(CN,G,HO)
DO 17 I=5,11
FJ=J-1
CC(2,J,I-4)=FJ+FJ
CC(1,J,I-4)=FJ-FS
CC(3,J,I-4)=FJ+FS
17 B(J,I-4)=AC(I)*G(I)*0.25*AK
18 CONTINUE
DO 19 I=1,3
19 CN(I)=XC(I+1,N)*XB(I+1)
   CALL MASSH(CN,G,HO)

```

contd /

```

DO 21 I=5,11
E(N,I-4)=AC(I)*G(I)*0.25+ XB(I)*(SH(I)/AK -FS*SH(I))
CC(3,N,I-4)=0.
CC(2,N,I-4)=2./AK2 +SH(I)/AK -FS*SH(I)
CC(1,N,I-4)=2./AK2
21 CONTINUE
DO 32 I=1,3
32 CN(I)=XC(I+1,1)*XB(I+1)
CALL HASSH(CN,G,H0)
DO 31 I=5,11
R(1,I-4)=0.5*(B(2,I-4)+AC(I)*G(I)*0.25*AK)
CC(1,1,I-4)=0.
CC(2,1,I-4)=0.5+FS
CC(3,1,I-4)=0.5+FS
31 CONTINUE
CALL SIDIMP(CC,B,7,N)
DO 20 I=5,11
DO 20 J=1,N
20 X(I,J)=E(J,I-4)
IF(IFACT.EQ.1) GO TO 400

      STOP CALCULATION IF EFFECTIVENESS FACTORS ARE NOT
      REQUIRED.

      RETURN
400 CONTINUE

      CALCULATE EFFECTIVENESS FACTORS .

DO 24 I=2,4

24 ESH(I)=SH(I)*(AS+1.)*(XC(I,N)-1.)/(AC(I)*GB(I))
DO 25 I=5,11
EN(I)=SH(I)*(AS+1.)*(XC(I,N)-XE(I))/(AC(I)*GB(I))
25 CONTINUE
EN(1)=SH(1)*(AS+1.)*(XC(1,N)-1.)/(AC(1)*GB(1))
WRITE(6,3001) ITER
RETURN
3001 FORMAT(1X,* CONVERGENCE,*,12,* ITERATIONS.*)
5001 FORMAT(1X,*NO CONVERGENCE AFTER *,12,* ITERATIONS*/
11X,*CONVERGENCE VALUES*,3X,3(F8.5,3X))
END

```

Where a variable is subscripted (10) it refers to the species in the above order. All other symbols are internal to the subroutine and their functions can be deduced from the explanation of the working of the subroutine. A list of subroutines, and their functions, called by SUBROUTINE CAT3A, is given in Figure(A5.4). The subroutines are listed in Figure(A5.5).

One iteration of the calculation procedure took about 25ms of central processor time on a CDC6400 computer. Generally about 20 iterations were required if the dimensionless profiles were initially set to unity. If the profiles from a previous calculation, for fairly similar conditions, were used as a starting point for the next calculation, only about 3 to 6 iterations were required for convergence.

Figure A5.3

Explanation of Symbols in Subroutine CAT3A

SYMBOL	DIMENSION	COMMON BLOCK	UNITS	FUNCTION
ND,N	-	ONE	-	No. of grid points
CC	(3,ND,7)	-	-	T-D MATRICES IN
B	(ND,7)	-	-	FORCING FUNCTIONS IN
I WRITE	-	CONT	-	CONTROLS INITIAL GUESS
I FACT	-	CONT	-	CONTROLS FORM OF RESULTS
RAD	-	SYSTEM	m	Pellet radius
DP	-	SYSTEM	Kg cat/m ³	Pellet bulk density
AS	-	SYSTEM	-	Pellet shape factor
GMF	-	SYSTEM	Kg-Sec	Mass flow rate around pellet
I WRITE	-	SYSTEM	-	Controls writing during calculations
SH	(11)	COEFF2	-	Sherwood Numbers and Nusselt Number
AM	(10)	TWO	Kg/Kmole	Molecular Weight
D	(11)	TWO	m ² /sec	Bulk Diffusivities
XB	(11)	ONE	Kmole/m ³	Bulk fluid concentration
EN	(11)	RESULT	-	Effectiveness Factors
XC	(11,150)	RESULT	-	Dimensionless Concentration Profiles and Dimensionless temperature profile.

Figure A6.4

Support Subroutines called by CAT3A

SUBROUTINES	AUGUMENT LIST	INPUT REQD.	FUNCTION AND OUTPUT
BUTENE	-	-	Sets Arrhenius factors and heats of formation and puts values in common blocks used by 'RATEC', 'MASSH', 'HEAT' and 'MASSRD'.
HEAT	HO(10),XB XYZ	XB	Calculates heat contents and returns them by HO(10)
RATEC	T	Data from BUTENE Temperature	Calculates reaction rate constants
EXTER2	-	XB, Reactor and Pellet Dimensions Flow Rate	Film transfer coefficients in form of Sherwood Nos. and Nusselt Number
MASSH	C(3),G(11), HO(10)	Concn of oxygen Butene and Butadiene	Calculates Rates of Reaction
MASSRD	C(3),G(11), HO(10),GD(11)	As MASSH	As MASSH - also calculates partial rate derivatives

```

SUBROUTINE MASSRD(C,G,GD,H0)
DIMENSION C(3),G(11),H0(10),GD(4)
REAL K(2,8)
COMMON/RATE/ K
IF(C(1)-0.1E-9) 3,3,1
1 CONTINUE
E1=C(1)*0.44
E2=C(2)*1.15
E3=C(1)*1.6
E4=C(1)*0.85
E5=C(1)*1.2
E6=C(1)*0.57
E7=C(1)*0.75
E8=C(1)*1.7
E9=C(1)*1.5
E10=C(2)*0.44
E11=C(2)*0.8
E12=C(2)*0.9
E13=C(2)*0.33
E14=C(2)*0.75
E15=C(3)*0.1
E16=C(3)*0.55
E17=C(3)*1.5
E18=C(2)*0.56
A1=K(1,2)*E10/E1
A2=K(1,3)*E11/E2
A3=K(1,4)*E12/E3
A4=K(1,5)*E13/E4
A5=K(1,6)*E14/E5
A6=K(1,7)*C(2)*C(1)
A7=K(1,8)*C(2)*C(1)
A8=K(2,3)*C(3)*E6
A9=K(2,4)*C(3)*E7
A10=K(2,5)*E15/E8
A11=K(2,6)*E16/E9
A12=K(2,7)*E17/C(1)
A13=K(2,8)*C(3)*C(1)
G(2)=-0.5*(A1+A6+A7+A13/2.)-1.5*(A2+A5)-2.5*A4-2.*A11
1-A10-0.875*A9-1.375*A8-A3
G(3)=-A1-0.25*(A2+A3+A7+A7)-A4-A5-A6
G(4)=A1-0.25*(A8+A9+A13+A13)-A10-A11-A12
G(5)=A2+A8+A5
G(6)=A3+A9
G(7)=A4+A10
G(8)=A5+A11
G(9)=A6+A12
G(10)=A7+A13
G(11)=A1+A2+A3+2.*(A4+A5)+0.75*(A8+A9)+A10+A11-A12
1-1.5*A13
G(1)=0.
DO 2 I=1,10
G(I)=G(I)+G(I+1)*H0(I)
2 CONTINUE
G(1)=0.
G(2)=-0.44*K(1,2)*E10/E6-0.25*C(3)/E1-0.25*C(3)/
12(1)*0.25
G(3)=-0.44*K(1,2)*E1/E18
G(4)=-0.25*(K(2,3)*E6+K(2,4)*E7)
RETURN
3 DO 4 I=1,11
4 G(I)=0.
5 DO 5 I=2,4
5 G(I)=0.
RETURN
END

```

contd /

Fig(A5-5) Support Subroutines

```

SUBROUTINE EXTER2
DIMENSION DB(11)
COMMON / SYSTEM / RAD,DP,AS,GMF,IWRITE
COMMON / ONE / N,XB(11)
COMMON/COEFF2/ SH(11)
COMMON/TWO/ AM(10),D(11)
COMMON/TUBE/ RT
COMMON / REMOVE / TW,U,CPF
COMMON / PARFIT / CT1,CT2
DATA DB /3.73,1.08,1.79,2.55,2.86,1.72,2.,1.6,2.22,3.91
T=XB(1)
TT=T**1.5
RHO=353.2/T
MUJ=(0.032+0.00003*(T-673.))*0.001
AREA=RT**2-RAD**2
TA=3.142*AREA

UAV=GMF/TA
DE=2.*AREA/RAD
RE=DE*UAV/AMU
AL=0.0085
AJ=1.36*CT1*(RE*0.74*DE/AL)**0.3333
TS=CPF*AMU/0.74
AH=AJ*TC/DE
DT=2.*AREA/RT
RET=DT*UAV/AMU
AJT=1.86*CT2*(RET*DT*0.74/AL)**0.3333
U=AJT*TC/DT
SH(1)=AH*RAD/D(1)
DO 20 I=1,10
DBI=DB(I)*TT*1.0E-9
SC=AMU/(RHO*DBI)
F=(0.74/SC)**0.6667
AKC=AH*F/(CPF*RHC)
SH(I+1)=AKC*RAD/D(I+1)
20 CONTINUE
IF(IWRITE.LT.2) RETURN
WRITE(6,1000) RE
WRITE(6,1001) ((I,SH(I)),I=2,11)
WRITE(6,1002) SH(1)
RETURN
1000 FORMAT(1X,*REYNOLDS NUMBER IS *,F8.4/)
1001 FORMAT(1X,*MODIFIED SHERWOOD NUMBER FOR COMPONENT *,I2,
1 * IS *,F8.4/)
1002 FORMAT(1X,*MODIFIED NUSSELT NUMBER IS *,F8.4/)
END

```

```

SUBROUTINE MASSH(C,G,HO)
DIMENSION C(3),G(11),HO(10)
REAL K(2,8)
COMMON/RATE/ K
A1=K(1,2)*C(2)**0.44*C(1)**0.44
A2=K(1,3)*C(2)**0.8*C(1)**1.15
A3=K(1,4)*C(2)**0.9*C(1)**1.6
A4=K(1,5)*C(2)**0.33*C(1)**1.85
A5=K(1,6)*C(2)**0.75*C(1)**1.2
A6=K(1,7)*C(2)*C(1)
A7=K(1,8)*C(2)*C(1)
A8=K(2,3)*C(3)*C(1)**1.57
A9=K(2,4)*C(3)*C(1)**0.75
A10=K(2,5)*C(3)**0.1*C(1)**1.7
A11=K(2,6)*C(3)**0.55*C(1)**1.5
A12=K(2,7)*C(3)**1.5*C(1)
A13=K(2,8)*C(3)*C(1)
G(3)=-A1-0.25*(A2+A3+A7+A7)-A4-A5-A6
G(4)=A1-0.25*(A8+A9+A13+A13)-A10-A11-A12
G(5)=A2+A8+A5
G(6)=A3+A9
G(7)=A4+A10
G(8)=A5+A11
G(9)=A6+A12
G(10)=A7+A13
G(2)=-0.5*(A1+A6+A7+A13/2.)-1.5*(A2+A5)-2.5*A4-2.*A11
1-A10-0.875*A9-1.375*A8-A3
3.1415928*A1+A2+A3+2.*(A4+A5)+0.75*(A8+A9)+A10+A11-A12
1-1.5*A13
G(1)=0.
DO 2 I=1,10
G(I)=G(I)+G(I+1)*HO(I)
2 CONTINUE
RETURN
END

```

cont'd /

```

FUNCTION CP(XB)
DIMENSION XB(11),S(10)
COMMON/TWO/ AM(11),D(11)
T=XB(1)
T2=T*T
T3=T2*T
S(1)=6.148+3.102E-3*T-9.23E-7*T2
S(2)=-1.24+8.65E-2*T-5.11E-5*T2+12.07E-9*T3
S(3)=-1.29+8.35E-2*T-5.583E-5*T2+14.24E-9*T3
S(4)=6.339+10.14E-3*T-3.415E-6*T2
S(5)=6.35+1.811E-3*T-0.2675E-6*T2
S(6)=-0.935+0.12326*T-66.199E-6*T2
S(7)=3.178+91.24E-3*T-31.716E-6*T2

```

```

S(8)=2.566+0.15332*T-79.101E-6*T2
S(9)=4.19+3.164E-2*T-0.515E-5*T2-3.8E-9*T3
S(10)=7.136+2.64E-3*T+0.0459E-6*T2
SN2=6.457+1.39E-3*T-0.069E-6*T2
ANMOL=12.19/T
AMLSUM=0.
DO 1 I=2,11
1 AMLSUM=AMLSUM+XB(I)
AMOLN2=ANMOL-AMLSUM
CPSUM=0.
DO 2 I=1,10
2 CPSUM=CPSUM+S(I)*XB(I+1)/ANMOL
CPSUM=CPSUM+SN2*AMOLN2/ANMOL
AMWT=0.
DO 3 I=1,10
3 AMWT=AMWT+XB(I+1)*AM(I)/ANMOL
AMWT=AMWT+AMOLN2*28./ANMOL
CP=CPSUM*4186.8/AMWT
RETURN
END

```

```

SUBROUTINE STDIMP(C,RN,NC,M)
DIMENSION C(3,M,NC),RN(M,NC)

```

```

PARAMETERS-RN(M,NC) - ENTRY - FORCING VECTOR.
- EXIT - SOLUTION VECTOR.
C(1,M,NC) TRIDIAGONAL
C(2,M,NC)-MATRIX
C(3,M,NC) COEFFICIENTS.

```

M-NO. OF EQUATIONS IN EACH SET.
N-NUMBER OF SYSTEMS.

NOTE----(1)-THE FORCING VECTOR IS DESTROYED DURING
THE CALCULATION.
(2)-EACH SYSTEM MUST CONTAIN THE SAME NUMBER
OF EQUATIONS.
(3)-THE MAX. VALUE FOR M IS 150.
THIS MAY BE INCREASED BY ALTERING THE
DIMENSION STATEMENT FOR W AND G.

```

DIMENSION W(150),G(150)
ML=4-1
DO 10 INC=1,NC

```

CALCULATE THE FACTORS W AND G.

```

W(1)=C(3,1,INC)/C(2,1,INC)
G(1)=RN(1,INC)/C(2,1,INC)
DO 2 IM=2,M
D=C(2,IM,INC)-C(1,IM,INC)*W(IM-1)
W(IM)=C(3,IM,INC)/D
2 G(IM)=(RN(IM,INC)+C(1,IM,INC)*G(IM-1))/D
USE W AND G IN BACK SUBSTITUTION FOR THE SOLUTION.
RN(M,INC)=G(M)
DO 3 IM=1,M1
3 RN(M-IM,INC)=W(M-IM)*RN(M-IM+1,INC)+G(M-IM)
11 CONTINUE
RETURN
END

```

contd /

```

SUBROUTINE HEAT(HO,T,HON2)
DIMENSION HD(10),HO(10)
COMMON/HTFORM/ HF(10)
T1=T-298.
T2=T**2-88804.
T3=T**3-26463592.
T4=T**4-7886150416.
TI=1./T-0.0033557
1  HD(1)=8.27*T1+1.29E-4*T2+1.877E5*TI
2  HD(2)=-0.24*T1+4.325E-2*T2-1.703E-5*T3+3.018E-9*T4
3  HD(3)=-1.29*T1+4.175E-2*T2-1.861E-5*T3+3.56E-9*T4
4  HD(4)=6.339*T1+5.07E-3*T2-1.138E-6*T3
5  HD(5)=6.350*T1+0.906E-3*T2-0.0892E-6*T3
6  HD(6)=-0.935*T1+61.63E-3*T2-22.033E-6*T3
7  HD(7)=3.178*T1+45.62E-3*T2-15.858E-6*T3
8  HD(8)=2.566*T1+76.86E-3*T2-26.367E-6*T3
9  HD(9)=4.19*T1+1.582E-2*T2-1.172E-5*T3-0.93E-9*T4
10 HD(10)=7.136*T1+1.32E-3*T2+0.0153E-6*T3
    HN2=(6.117*T1+0.695E-3*T2-0.023E-6*T3)*149.529
    DO 1 I=1,10
11  HD(I)=(HD(I)-HF(I)*1000.)*4186.8
    RETURN
END

```

```

SUBROUTINE RATEC(T)
REAL K(2,8)
COMMON / KINETX / EE(2,8),AA(2,8)
COMMON/RATE/ K
RT=T*0.001987
DO 1 I=1,2
  IPI=I+1
  DO 1 J=IPI,8
    K(I,J)=AA(I,J)*EXP(-EE(I,J)/RT)
1  CONTINUE
RETURN
END

```

```

SUBROUTINE BUTENE
COMMON/TWO/ AM(10),D(11)
COMMON / KINETX / EE(2,8),AA(2,8)
COMMON/HTFORM/ HF(10)
DATA AM/32.,56.,54.,44.,28.,68.,43.,72.,44.,10./
DATA EE/0.,0.,17.4,0.,23.8,17.0,26.3,15.7,27.5,25.0,
125.0,21.0,15.0,10.0,17.5,21.0/
DATA AA/0.,0.,0.5,0.,0.,2.25E+5,540.,7.6E+6,1.5.,7650.,
13.46E+4,1.E+5,9.4E+3,18.4,22.,355.,900./
DATA HF/0.,0.,28.,26.33,-94.05,-26.42,-14.8,-20.5,
1-52.4,-39.72,-57.8/
X,-2.5,-52.4,-39.72,-57.8 /
RETURN
END

```


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