

CATALYST ACTIVITY PROFILES IN AN INDUSTRIAL SCALE

FIXED-BED REACTOR FOR PARTIAL OXIDATION

by

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Any piece of knowledge I acquire today has a value at this moment exactly proportioned to my skill to deal with it. Tomorrow, when I know more, I recall that piece of knowledge and use it better.

Tout morceau de savoir que j'acquiers aujourd'hui a une valeur en ce moment exactement proportionnelle à ma capacité de l'utiliser. Demain, quand mon savoir se sera accru, je me souviendrai de cette petite partie de savoir et je l'utiliserai mieux. (Traduction)

MARK VAN DOREN, Liberation Education, (1960).

To the Abi's and Tambe's families
and
to all the Ambelle people.

ABSTRACT

An investigation was undertaken to develop a mathematical model suitable for on-line estimation and control of an industrial scale fixed-bed reactor hosting a series of highly exothermic reactions and exhibiting both reversible and irreversible catalyst decay. The main reaction is the partial oxidation of o-xylene to phthalic anhydride over a commercial V_2O_5/TiO_2 catalyst.

Steady state and dynamic experiments carried out on the reactor have shown the existence of steep temperature and concentration gradients which are disparate in both their magnitudes and positions.

In order to tackle the problem of ill-conditioning induced by the steep profiles, the method of orthogonal collocation on finite elements used to solve the model equations was modified. The algorithm developed includes criteria for automatic selection of the sizes and number of finite elements together with the number of interior collocation points in each finite element. Steady state and dynamic simulations show a reduction in computation time which passes through a minimum as the number of finite elements is increased.

In order to account for reversible and irreversible catalyst deactivation in the model, an activity parameter which varied axially along the reactor's length was incorporated into the kinetic model and estimated using both temperature and concentration measurements in the weighted least squares optimization scheme.

Two methods of parameterization of the activity profile were developed and the parameters were estimated at any given time directly and exclusively from current reactor data (temperature and concentration measurements).

The predicted temperature and concentration profiles were generally in very good agreement with the experimental data when both

temperature and concentration measurements were used in the parameter estimation of the activity profile.

When only temperature measurements were used, the estimated activity profile was generally poor; however, by proper choice of temperature measurements, it was possible to predict the final yield of phthalic anhydride but not the composition or temperature profiles. It is noteworthy that the one or two temperature measurements plus exit composition measurement normally found in industrial reactors were found to be insufficient for the estimation of catalyst activity profiles.

The steady state experimental data values were collected for a wide range of operating conditions (168 to 205 gm/hr o-xylene flowrate, 375° to 384°C salt bath temperature and 4 Nm³/hr air flowrate).

Long-run steady state experiments carried out over a continuous period of operation of the reactor for about 13 days (operating conditions 176 gm/hr o-xylene flowrate, 380°C salt bath temperature and 4 Nm³/hr air flowrate) have shown that the partial deactivation of the catalyst is a very slow process and that the time interval required for the re-estimation of the activity profile, in order to predict the steady state behaviour of the reactor at any given time, is in the order of several hours or even days.

Dynamic experiments were performed via step changes in the o-xylene feed concentration and ramp changes in the salt bath temperature. A strong parametric sensitivity to the salt bath temperature was observed even for small perturbations (e.g. 1°C ramp increase) and this has been attributed to changes in the activity profile engendered by local variations in the axial temperature and concentration profiles.

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NOMENCLATURE

A_j	Pre-exponential factor for j^{th} reaction.
$\underline{A}$	$= \{A_{ij}\}$ discretization matrix in Appendix B.
a_1	$= \frac{L}{Ro}$ aspect ratio.
a_2	$= \frac{dp}{Ro}$ aspect ratio.
$\underline{B}$	$\{B_{ij}\}$ discretization matrix (also approximation to Jacobian matrix) in Appendix B.
Bi_w	$= \frac{hwRo}{Ke}$ Biot number at the wall.
C_{AO}	O-xylene concentration at feed conditions (also total concentration of the combustible products to the catalytic combustion tube in Appendix E).
C_n	Homogeneous concentration for species n.
C_p	Heat capacity of gas.
C_{p_s}	Heat capacity of catalyst particle.
De_r	Radial effective mass diffusivity.
dp	Particle diameter
dt	Tube diameter.
E_j	Activation energy for j^{th} reaction
F_{air}	Molar flowrate of diluent air to combustion tube, Appendix E.
F_{AO}	Total molar flowrate of combustible products to the combustion tube, Appendix E.

Fo	Total molar flowrate of reactants to combustion tube.
Fv	Volumetric flowrate of diluent air, Appendix E.
$f_j(X,Y)$	$= \exp \frac{(-Y_1)}{Y} X_j Y$ dimensionless function of rate of j 'th reaction.
g	Acceleration due to gravity (also gradient of the objective function, Chapter 5).
G	Mass velocity.
<u>H</u>	Matrix defined in Chapter 5 and Appendix B.
h	Interface heat transfer coefficient.
hw	Heat transfer coefficient at the wall.
hw _f	Heat transfer coefficient at the wall for the gas-phase.
hw _s	Heat transfer coefficient at the wall for the solid-phase.
<u>J</u>	Jacobian matrix defined in Appendix B.
J _D	J-factor for mass transport at catalyst surface.
J _H	J-factor for heat transfer at catalyst surface.
Ke	Effective thermal conductivity.
Kg	Interface mass transfer coefficient
K _j	Rate constant for j 'th reaction in terms of molar concentration.
K _{rf}	Thermal conductivity of gas-phase.
K _{rs}	Thermal conductivity of solid-phase.
L	Length of reactor bed.
$\bar{M}$	$= (1 + \rho_B C_{P_s} / \epsilon \rho C_p)$ Parameter defined in Eq. 9, Chapter 3.
m _j	$=$ Moles of oxygen consumed per mole of hydrocarbon reacting in reaction j 'th.

NI	Total number of finite elements.
N_K	Number of interior collocation points in a finite element.
NE	Number of finite elements.
$\underline{P}$	Vector defined in Appendix B
P_n	Homogeneous partial pressure for species n.
Pe_{hr}	$= \frac{\epsilon \rho C_p d_p}{K_e}$ radial peclet number for heat transfer.
Pe_{mr}	$= \frac{u d_p}{De}$ radial peclet number for mass transfer.
P_h	$= \frac{Pe_{hr}}{a_1 \cdot a_2}$ parameter defined in Eq. 9, Chapter 3.
P_m	$= \frac{Pe_{mr}}{a_1 \cdot a_2}$ parameter defined in Eq. 8, Chapter 3.
R	Number of reactions in kinetic scheme.
Rep	$= \frac{u \rho d_p}{\mu}$ particle Reynolds number.
R_g	Gas-law constant.
R_j	j^{th} rate of reaction.
R_n	Rate of reaction of species n.
R_o	Reactor radius.
r'	Radial coordinate.
r	$= \frac{r'}{R_o}$ dimensionless radial coordinate.
T	Homogeneous temperature in the reactor.

T_c Coolant temperature in combustion tube.

T_o Reactor inlet temperature.

T_w Temperature at reactor wall.

t' Time.

$t = \frac{t'}{\tau}$ dimensionless time.

U Overall heat transfer coefficient.

u Interstitial velocity.

X conversion

$X_n = \frac{C_n}{C_{AO}}$ dimensionless concentration of species n .

$Y = \frac{T}{T_o}$ dimensionless temperature.

Y_{AO} O-xylene mole fraction at feed conditions.

$Y_w = \frac{T_w}{T_o}$ dimensionless wall temperature.

z' Axial coordinate.

$z = \frac{z'}{L}$ dimensionless axial coordinate.

Greek letters

α activity parameter defined in Eq. 5.2, Chapter 5.

$B_j = \frac{(-\Delta H_j) C_{AO}}{\rho C_p T_o}$ adiabatic temperature rise for j 'th reaction.

$\gamma_j = \frac{E_j}{R_g T_o}$ dimensionless activation energy for j 'th reaction.

$\delta h_j = \frac{\rho_B L A_j R_g T_o \mu_s}{\epsilon \mu}$ parameter defined in Eq. 15, Chapter, 3,
dimensional (Bar. m/sec.)

$\delta m_j = \frac{\rho_B L v_j R_g T_o A_j \mu_s}{\epsilon \mu}$ parameter defined in Eq. 14, Chapter 3,
dimensional (Bar. m/sec.)

$(-\Delta H_j)$ Heat of reaction released by j 'th reaction.

ΔZ_K Length of K 'th sub-interval in axial direction.

ϵ Void fraction of catalyst bed.

θ Degree of coverage of oxygen on the catalyst surface.

μ Gas viscosity.

μ_s Parameter defined in Chapter 2.

ν_{n_j} Stoichiometric coefficient of species n in the j 'th reaction.

ξ Dimensionless axial coordinage defined in Chapter 5.

ρ Gas density.

ρ_B Bulk density.

$\tau = \frac{L}{u}$ residence time in Chapter 3.

Subscripts

A	O-xylene.
B	O-tolualdehyde.
C	Phthalide.
D	Phthalic anhydride.
f	Fluid.
j	$j^{\text{'th}}$ rate of reaction.
K	$K^{\text{'th}}$ sub-interval.
max	Maximum.
n	Chemical specie.
o	Initial or feed conditions.
s	Surface of catalyst particle.
ss	Steady state.
w	Wall.

Superscripts

K	$K^{\text{'th}}$ sub-interval.
o	Feed conditions.
$\wedge$	Molar properties.
-	average value.

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CHAPTER ONE

INTRODUCTION

Fixed-bed catalytic reactors have received considerable attention over the last 30 years not only because of their importance in both the chemical and petroleum refining industries but also because of the daunting operational and simulation problems they pose to Chemical Engineers. The ever increasing capabilities of computers have led to extensive exploration of reactor design and performance, both in the steady and non-steady state and this, in turn, has resulted in the development of highly complex and very sophisticated reactor models.

However, in order to simulate a fixed-bed catalytic reactor, it is necessary to establish the model that best represents the reactor behaviour. The adequacy of a model will depend on the simulation objectives, namely design, control, optimization etc.

For example, a dynamic model for on-line estimation and control of a fixed-bed catalytic reactor must be able to predict the measured experimental effects of the variation of key variables such as jacket temperature, feed flowrate, composition and temperature on the dynamic behaviour of the reactor, yet such a model must be simple enough to be computationally manageable. This, in turn, requires the knowledge of the kinetic and 'effective' transport parameters involved in the model.

Due to the strong interactions between the physical and chemical mechanisms, particularly when catalyst deactivation is present, the parameters estimation problem becomes very difficult. The kinetic parameters are normally obtained from laboratory scale reactors and when used in pilot plant studies have to be tuned [Calderbank et al.

(1977, 1979)] or even re-evaluated [Ramirez et al. (1977)] to obtain reasonable predictions. The transport parameters are estimated either from steady state or dynamic experiments without reaction to obtain approximate values under reaction conditions [Kershenbaum et al. (1982)].

When catalyst deactivation is present, it may be necessary to incorporate a deactivation model into the kinetic model and to estimate the parameters using reactor data and applying either non-sequential estimation schemes [e.g. Seinfeld & Chen, (1971), Lambrecht et al. (1972)] or optimal filters (sequential estimation schemes) [Goldman & Sargent (1971), Ajinkya & Ray (1974)]. Models have been developed to describe the rate of deactivation of a large number of systems exhibiting the various types of deactivation [Hughes (1984)].

Where there is no deactivation model available, as in this reactor-reaction system in which both reversible and irreversible catalyst decay occur with the greater part of the reversible deactivation caused by a combination of low temperatures and high o-xylene concentrations [Calderbank et al. (1977), Lopez-Isunza (1983), Kershenbaum et al. (1984)], it may be necessary to consider an alternative approach of estimating the extent of catalyst deactivation (catalyst activity profiles) directly from reactor data and applying parameter estimation techniques without due consideration to the type of catalyst deactivation. The problems associated with this approach are exacerbated if the catalyst activity profiles vary spatially. On the other hand, to develop a deactivation model for such a system requires an elaborate experimental programme and the time taken for such an exercise may not be justifiable.

The aim of this study was, therefore, to develop a mathematical model capable of predicting both the steady state and dynamic behaviour of the reactor with the spatially varying catalyst activity profiles estimated directly from current reactor operating data. The ultimate objective is to use the model for on-line parameter estimation and control of the reactor.

To my knowledge, since the early work of Gavalas et al. (1972a), there has been no other investigation directed towards the estimation of spatially varying catalyst activity profiles directly from reactor data without the help of a deactivation model. On the other hand, there is considerable advancement in the application of sequential parameter filters to estimate spatially uniform catalyst activity profiles in the absence of a deactivation model [Kuruoglu et al. 1985].

The kinetics of the air oxidation of o-xylene on a V_2O_5/TiO_2 catalyst are presented in Chapter 2, together with a brief review of the existing kinetic schemes that have been proposed in the literature. A brief account of the relevant features of the catalytic system is also given.

The mathematical model and the numerical method of solution employed in this study are presented in Chapter 3 and Appendix B.

The experimental system and operational procedure are discussed in Chapter 4.

In Chapter 5, methods of parameterization of the catalyst activity profile together with the parameter optimization scheme used in this study are presented.

The steady state behaviour of the reactor is presented in Chapter 6, in terms of axial temperature and concentration profiles at different o-xylene feed concentrations and salt bath temperatures. Evaluation of heat transfer parameters from steady state experiments without reaction is also presented. Long-run steady state and transient state experiments are also presented and discussed. In this chapter also, model predictions of both the steady state and dynamic behaviour of the reactor together with catalyst activity profiles estimated directly from reactor data are presented.

Finally, Chapter 7 gives the overall conclusions about this work and presents some recommendations for future work.

CHAPTER TWO

2.0 KINETICS OF THE OXIDATION OF O-XYLENE ON VANADIA CATALYSTS

The importance of deriving a good kinetic model capable of describing the mechanism of the reaction for a specific catalyst in the temperature range of operation, in the development of a reactor model, cannot be over-emphasized. But it suffices to say that a good reactor model necessarily has to have the appropriate kinetic model with suitable parameters.

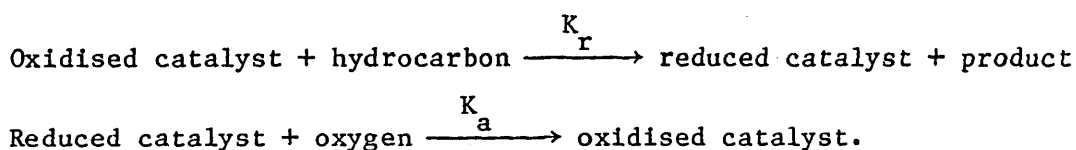
Since the early works of Mars & Van Krevelen (1954), Simard et al. (1955) and Shelstad et al. (1960) which led to the postulation of the steady-state oxidation-reduction model or the REDOX mechanism [Mars & Van Krevelen (1954)] and the steady-state adsorption model [Shelstad, Downie & Graydon (1960)], there has been, in later studies, a growing concern in modelling (or fitting) the kinetics to justify these models. In this respect, the Langmuir-Hinshelwood model has also been tested by a few workers [Juusola et al. (1970) and Skrzypek et al. (1985)]. In most cases, studies have been carried out without due consideration to both catalyst formulation and operating conditions prevailing in industrial practice with the result that several different reaction schemes have been proposed in the literature.

2.1 The Kinetic Models

Mars & Van Krevelen (1954) published a comprehensive study of the oxidation of benzene, naphthalene and anthracene carried out on vanadium pentoxide catalysts using a fluidized bed of 200 to 300 μm catalyst particles. The catalyst contained 9 wt% vanadium pentoxide and 21 wt%

potassium sulphate on silica-gel. From these experiments they proposed a kinetic model based on an oxidation-reduction or "REDOX" mechanism in which "the hydrocarbon to be oxidised reduces the catalyst which was oxidised by oxygen from the air".

The basic rate equations for the formation of a single product, say the oxidation of o-xylene to o-tolualdehyde, can be formulated as follows:



Assuming the reaction rates to be first order with respect to hydrocarbon and proportional to the degree of coverage of oxygen on the catalyst surface θ , it follows that the rate of oxidation of the hydrocarbon may be expressed as follows:

$$R_n = K_n \theta P_n \quad (2.1)$$

The rate of re-oxidation of the surface reduced in the first reaction may be assumed to be proportional to a certain power of the oxygen partial pressure and to the catalyst surface area not covered by oxygen. This can be expressed as follows:

$$R_a = K_a (1 - \theta) P_{O_2}^\alpha \quad (2.2)$$

If, for the oxidation of one aromatic molecule, m molecules of oxygen are required, the following expression holds:

$$R_a = mR_n \quad (2.3)$$

so that for the steady state we may write

$$mK_n \Theta P_n = K_a (1 - \Theta) P_{O_2}^\alpha \quad (2.4)$$

Then, the degree of occupation by the oxygen can be expressed as:

$$\Theta = \frac{K_a P_{O_2}^\alpha}{K_a P_{O_2}^\alpha + m K_n P_n} \quad (2.5)$$

By combining Eqs. 2.1 and 2.5 we find for the reaction rate:

$$R_n = \frac{K_a P_{O_2}^\alpha K_n P_n}{K_a P_{O_2}^\alpha + m K_n P_n} \quad (2.6)$$

Identical values for K_a were found when these hydrocarbons were oxidized at the same temperature on a catalyst containing 9% V_2O_5 , 2.9% MoO_3 and 0.03% P_2O_5 by weight, on corundum.

Similar, somewhat more complicated, expressions can be derived for reaction schemes involving parallel and series reaction steps [Calderbank and co-workers (1977)].

Shortly after the redox model had been proposed, Simard et al. (1955) concluded that "the role of gaseous oxygen in a conventional catalytic oxidation could be a secondary one, with the reaction proceeding through the following steps:

1. Chemisorption of the hydrocarbon on the catalyst surface.
2. Reaction of the chemisorbed hydrocarbon with oxygen ions of the catalyst.
3. Desorption of intermediate or final products.
4. Replenishment of oxygen to the catalyst from the feed air.

Shelstad et al. (1960) studied the oxidation of naphthalene over a vanadium catalyst containing 9.95% V_2O_5 , 0.16% Fe, 14.7% K_2O , 18.6% SO_3 and the remainder mainly silica. They proposed a model in which "the oxygen only is adsorbed on the catalyst surface, and the reaction occurs when the hydrocarbon in the gas phase strikes adsorbed oxygen, then a steady state will be established wherein the rate of removal of oxygen by chemical reaction is equal to the rate of adsorption of oxygen". The resultant rate of reaction for hydrocarbon oxidation, known as the steady state adsorption model or "SSAM", is identical to that for the redox model when $\alpha = 1$, and the re-oxidation rate constant becomes the oxygen adsorption rate constant, and as remarked by Wainwright & Hoffman (1974) reaction kinetic experiments cannot discriminate between these models.

Also in 1960, Hughes & Adams, studying the oxidation of phthalic anhydride came to an analogous equation to 6; however, it does not contain the oxygen partial pressure.

Juusola and co-workers (1970) studied the oxidation of o-xylene and o-tolualdehyde and as Shelstad et al. (1960) tried the Langmuir-Hinshelwood model where both the aromatic and oxygen molecules are reversibly adsorbed onto the catalyst.

$$R_n = \frac{K P_n P_{O_2}}{(1 + K_a P_{O_2} + K_n P_n)^2} \quad (2.7)$$

For Shelstad's work, the Langmuir-Hinshelwood model gave a slightly better fit. However, the extra complexity of the model was not considered to be practicable and both groups of workers settled for the SSAM.

This model has recently been tested by Skrzypek et al. (1985) who carried out their experiments of the gas-phase oxidation of o-xylene over commercial V_2O_5 - TiO_5 catalyst in a fixed bed non-isothermal reactor containing 0.2 dm^3 of catalyst and 0.5 dm^3 of inert carrier. The bath temperature range was between 360 and 390°C and o-xylene conversions between 0.04 and 0.53 . They observed that the rate of o-xylene disappearance with respect to initial o-xylene concentration passed through a maximum and suggested that the Langmuir-Hinshelwood model, Eq. 2.7, describes this reaction rate behaviour precisely. They further observed that at lower bath temperatures there was a drop in the total o-xylene conversion but at higher bath temperatures the disappearance increased in proportion to the initial o-xylene concentration and that the redox model failed to interpret the experimental data.

This phenomenon has also been observed by other workers [Calderbank and co-workers (1974, 1977), Lopez-Isunza (1983), Kershenbaum et al. (1984) and in this work (Chapter 6)] and has been attributed to reversible catalyst deactivation. Calderbank (1974) suggests that it is possible that vanadium oxide is reduced to a lower valence state of less catalytic activity at high o-xylene concentrations. The amount of lower oxide determined by the o-xylene/ O_2 ratio. Boreskov (1980) [in Skrzypek et al. (1985)] suggests that the effect of reaction mixture composition on catalyst properties is taken into account.

Boreskov emphasizes that it is assumed indirectly in the kinetics of heterogenic reaction that the catalyst is still the same "independently of reaction mixture composition".

This assumption is usually improper in most cases. Hence, the relationship of reaction rate versus concentration of reagents shall comprise two functions: Kinetic $f(C_j, \theta_j)$ (hitherto used as only one) and $\rho(C_j)$, which bears in mind the effect of changes in a reaction mixture composition on catalyst properties:

$$R_n = Kf(C_j, \theta_j), \rho(C_j)$$

This approach by Boreskov will possibly be fruitful in the case of o-xylene oxidation to phthalic anhydride since experimental evidence suggests that high o-xylene concentrations at low temperatures effect the catalyst so as to reversibly deactivate it [Lopez-Isunza (1983)].

2.2 Industrial catalysts

There are two types of catalysts commonly used in the industry; the German type, consisting of V_2O_5 promoted with potassium oxides and/or sulphates and supported on SiO_2 or TiO_2 (anatase), and the American type, consisting of V_2O_5 supported on SiC or alundum.

A comprehensive review of the role of the various components of these catalysts is given by Wainwright & Foster (1979) and therefore the review presented here will be brief and selective.

2.2.1 Catalytic behaviour of vanadium oxides

There is still a great deal of uncertainty regarding the active valence states of vanadium for particular reactions.

Tamura et al. (1976) have suggested that for the oxidation of sulphur dioxide, V^{4+} may be more active than V^{5+} , despite the claim by

Frazer & Kirkpatrick (1940) that it is impossible for V^{4+} to be present in the catalyst at any stage under normal SO_2 oxidation conditions.

Simard et al. (1955) presented their study of the catalytic behaviour of unpromoted vanadium oxides. Their conclusions are summarised as follows:

1. Vanadium in an unpromoted vanadium oxide catalyst during catalyst oxidation is in V^{4+} and V^{5+} states.
2. In bulk, these states are associated with oxides in three crystalline forms - V_2O_4 , $V_2O_{4.34}$ and V_2O_5
3. The relative proportions of these oxides are dependent on the hydrocarbon/air feed ratio; the changes with time of operation observed were in a direction to establish a characteristic (oxides) composition.
4. V_2O_4 and V_2O_3 are not catalytically active and the active portion of the catalyst is confined to V_2O_5 , $V_2O_{4.34}$ and to intermediate structures which may exist on the catalyst.

Schaefer (1967) has investigated the oxidation of benzene to maleic anhydride. Pure vanadium oxides in the range of composition $VO_{2.5}$ to $VO_{1.5}$ were studied under non-stationary conditions using microcatalytic techniques. The results were as follows:

1. In the presence or absence of molecular oxygen the maximum specific activity for benzene oxidation was observed with $VO_{2.0}$. With oxygen in the reaction mixture, benzene reacted 75-100 times faster in the presence of $VO_{2.0}$ than in the presence of $VO_{2.5}$.
2. The reaction of benzene is slower in the absence of oxygen than in its presence.

3. In the presence of oxygen no great differences in the oxidation rate for maleic anhydride were observed in the range of catalyst composition studied. $\text{VO}_{2.0}$ showed not only the maximum activity but also the maximum selectivity for maleic anhydride formation in the presence of oxygen.

Shaprinkaya et al. (1970) investigated the catalyst properties of V_2O_5 , V_6O_{13} , V_2O_4 and V_2O_3 for the oxidation of naphthalene. The activity sequence of the oxides was found to be $\text{V}_6\text{O}_{13} > \text{V}_2\text{O}_3 > \text{V}_2\text{O}_4 > \text{V}_2\text{O}_5$, using high space velocities and temperatures between 340 and 415°C. At 390°C, the specific effectiveness (total moles converted per minute per sq. m) of V_6O_{13} and V_2O_5 differed by a factor of 9, while the effectiveness with respect to the formation of phthalic anhydride differed by a factor of 13.5. They also observed that samples based on V_6O_{13} partially oxidised to V_2O_5 were twice as active as species of V_2O_4 oxidised to V_2O_5 to the same extent.

These findings are not compatible with the observations made by Butakova et al. (1975) that the activity of vanadia catalysts is proportional to the ratio of V_2O_5 to total vanadium.

Ushakova et al. (1957) have shown that although V^{4+} possesses high activity for the oxidation of naphthalene, the yield of phthalic anhydride is low because the reduced oxide also has a high activity for oxidising phthalic anhydride. Hughes & Adams (1960) also observed this high activity of reduced vanadia for the oxidation of phthalic anhydride.

Wainwright & Foster (1979) concluded from experimental evidence that large oxygen to hydrocarbon ratios are necessary to obtain high selectivity to phthalic anhydride. Presumably, low oxygen levels

enable the catalyst to become partially reduced, thus increasing the selectivity to total oxidation products.

2.2.2 The role of the support material

The role of the support material for the catalytic oxidation of o-xylene is not well understood. From a review of articles published by a Japanese research group which has carried out studies on the oxidation of o-xylene and naphthalene using silica-gel, titanium dioxide, gypsum and carborundum supported catalysts, Wainwright & Hoffman (1974) reported the following findings.

1. The support material has very little effect on the yields of phthalic anhydride for a naphthalene feedstock whereas a marked difference is noted when o-xylene is oxidised.
2. A silica-gel supported catalyst yielded 103 wt% phthalic anhydride and 15 wt% phthalic anhydride when the feedstocks were naphthalene and o-xylene respectively. The corresponding yields on TiO_2 supported catalysts were 98 and 93 wt%.
3. Selectivities to phthalic anhydride increased in direct proportion to the oxygen adsorption per unit surface area (the oxygen adsorption ratio of the four catalysts was measured and Langmuir-type isotherms were obtained) and that the difference between the selectivities for the different catalysts arose because of their different affinities for oxygen.

Juusola et al. (1970) and Mann et al. (1968) have also reported similar low selectivities of phthalic anhydride in a silica-gel supported catalyst for the oxidation of o-xylene.

Wainwright & Hoffman (1974) have investigated the oxidation of o-xylene on a number of commercial vanadia catalysts in an isothermal

packed bed reactor. The data showed that phthalic anhydride selectivities of up to 85 mol% could be obtained on a catalyst consisting of 84% TiO_2 , 6% V_2O_5 , 2% K_2O , 2% SO_3 and 6% Sb_2O_3 by weight. The catalyst was obtained from the research laboratories of W.R. Grace. A catalyst containing a similar percentage of V_2O_5 (6.1%), promoted by potassium sulphate but supported on silica-gel produced a maximum yield of 29% phthalic anhydride under similar conditions.

Wainwright & Hoffman (1977) carried out further studies and from the experimental results suggested that TiO_2 in TiO_2 -supported catalysts takes an active role in the reaction unlike SiO_2 in SiO_2 -supported catalysts. They further observed that whereas the activity of the SiO_2 -supported catalyst is reduced some twenty fold after 300 hrs on stream, the TiO_2 -supported catalyst exhibited less than a 20% reduction under similar conditions.

2.2.3 The role of promoters

The role of promoters (alkali metal sulphates) and the influence of SO_3 on catalyst properties of supported vanadia catalysts has been investigated, among others, by Tandy (1956) for the oxidation of SO_2 and Vorlow et al. (1985) for the oxidation of CO and benzene. A comprehensive review is given by Wainwright & Foster (1979). The promoting effect of alkali sulphate or pyrosulphate is thought to be due to:

1. The formation of a melt with V_2O_5 , thereby dispersing the active oxygen sites through the support [Tandy (1956), Wainwright & Hoffman (1977)].
2. The reduction of the overall activity of vanadium oxides in the

catalyst, thereby increasing the selectivity of partial oxidation products.

3. The sulphate distributing itself so as to change the orientation of oxygen on the catalyst surface, thus placing the surface oxygen in positions of greater steric availability to particular hydrocarbon groups resulting in higher selectivity.
4. The sulphate forming pyrosulphates and thus providing a source of SO_3 in the active matter. The interaction of the SO_3 , alkali metal, and vanadium oxide is thought to result in a stable molten phase capable of maintaining vanadium in a highly oxidized state [Frazer & Kirkpatrick (1940), Tandy (1956), Wainwright & Foster (1979), Vorlow et al. (1985)].

The industrial practice for potassium sulphate-promoted catalysts is to add small amounts of SO_2 or sulphur compounds, in an optimum ratio (between 0.1 to 1.5 wt% based on o-xylene feed) to promote higher yields of phthalic anhydride and to maintain constant the activity of the catalyst [Wainwright et al. (1979)]. Changes in the activity and selectivity of these catalysts, seem to be associated with the loss of SO_3 , as noticed from long term catalyst deactivation effects in a number of studies on hydrocarbon oxidations, as sulphur compounds were not included in the feed [Wainwright & Foster (1979)]. However, Wainwright & Hoffman (1977) have reported catalyst deactivation even when SO_2 was added to the feed. Sometimes instead of a continuous feed of SO_2 to maintain catalyst activity, periodic regeneration of the catalyst is performed by purging the reactor with air containing 5 to 7% SO_2 at 420° to 450°C . This practice succeeds only if the loss of sulphate groups from the catalyst is not greater than 30-35%.

2.3 Kinetic schemes

Many kinetic schemes have been proposed for the oxidation of o-xylene on vanadia catalysts. This is due to the fact that various researchers in the field have used catalysts of different compositions and have conducted experiments at varying operating conditions (some of them well below the normal operating range of industrial reactors). For example, Wainwright & Foster (1979) remarked that "much of the work on o-xylene oxidation networks is complicated by the fact that silica-supported catalysts were used, thereby limiting the extent of the oxidation of intermediate compounds to phthalic anhydride and resulting in excessive total oxidation at high conversions".

Herten & Froment (1968) and Wainwright & Foster (1979) presented a generalised kinetic scheme as shown in Fig. 2.1 to represent the various networks that have been postulated. The scheme includes the most probable steps and the review of each investigation will be presented with respect to the general case. Fig. 2.1 is actually obtained from Wainwright & Foster (1979). In Herten & Froment (1968), maleic anhydride is not included as a product of total oxidation.

The following abbreviations are used in Fig. 2.1 and are applied throughout in this thesis:

OX = o-xylene; OT = o-tolualdehyde; PT = phthalide; PA = phthalic anhydride; MA = maleic anhydride; COM = CO + CO₂ + H₂O.

Simard et al. [in Dixon & Longfield (1960)] studied the oxidation of o-xylene on a SiC-supported V₂O₅-catalyst at conversions below 25%. For feed o-xylene concentrations in air of 0.4 to 1.4%, contact times of 0.1 to 0.06 sec. at 400°C to 450°C, the kinetic scheme proposed comprises of steps 1, 3, 4, 8 and 9. The total oxidation products, maleic anhydride, CO and CO₂ were formed only from o-xylene and no

phthalide was observed. Steps 1 and 8 were found to be first order with respect to o-xylene and o-tolualdehyde respectively, while the rest of the steps 3, 4 and 9 were all zero order. All reactions were found to exhibit a square root dependence on oxygen partial pressure. Yields of o-tolualdehyde varied from 10-40 mole%, depending upon the initial o-xylene concentration. Unfortunately conversion levels were too low to get more information about the kinetics.

Novella & Benloch (1962) studied o-xylene oxidation using a K_2SO_4 -promoted catalyst in a fluidized bed in the temperature range 310° to 370°C. They obtained the same reaction products as Simard and co-

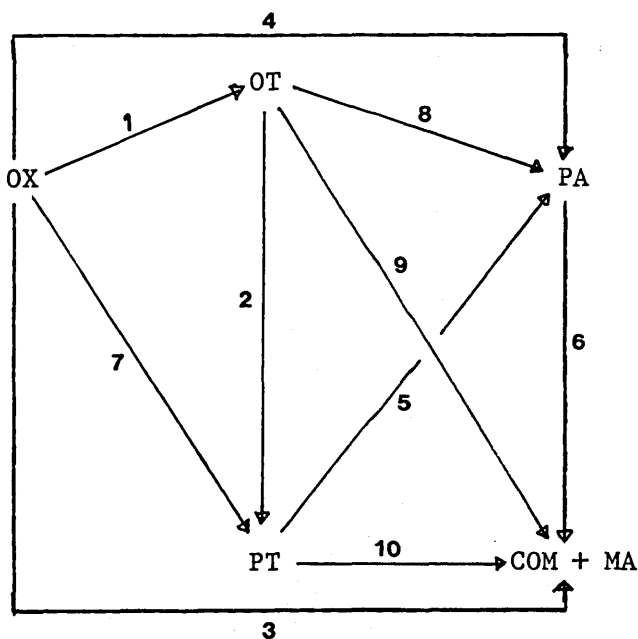


Fig. 2.1 Generalised reaction network for o-xylene oxidation [From Wainwright & Foster (1979)]

workers but proposed the formation of the oxides of carbon from o-tolualdehyde and phthalic anhydride as well as from o-xylene. Again no phthalide was detected in the reaction products. All steps were found to be first order with respect to hydrocarbon.

Bernardini & Ramacci (1966) studied the oxidation of o-xylene and phthalic anhydride and all its possible intermediates on a $V_2O_5-SiO_2$ supported catalyst, using a non-isothermal fixed bed reactor, operating in the range 360°C to 510°C. As phthalic anhydride was formed when all these intermediates (o-methyl benzyl alcohol, o-tolualdehyde, o-toluic acid and phthaldehyde) were oxidised with molar yields in the range 65% to 87%, a complex kinetic scheme was proposed. No attempt was made to model the kinetics using the network postulated.

Herten & Froment (1968) studied the gas-phase oxidation of o-xylene on a doped $V_2O_5-SiO_2$ supported catalyst. Kinetic measurements were made in the temperature range 325° to 402°C for a wide range of feed compositions and residence times. No details of the catalyst composition were given. The reaction scheme proposed is the same as that shown in Fig. 2.1 with the exception that no maleic anhydride was isolated in the reaction products. They concluded that the conversion of o-tolualdehyde into phthalide is probably not important (contrary to most other studies) and that even phthalic anhydride does not decompose easily into CO and CO₂ except when residence time becomes excessive. They successfully correlated their data by using the redox and the power law models. The order with respect to oxygen was nearly constant (0.29 to 0.37) for all temperatures, but the apparent order with respect to o-xylene was found to be temperature dependent and varied from 0.195 to 0.74.

Juusola et al. (1970) using a differential reactor, studied the oxidation of o-xylene and o-tolualdehyde on a V_2O_5 - K_2SO_4 - SiO_2 catalyst, at very low conversions (less than 7%) in the temperature range 290°C to 325°C. At these temperatures and conversion ranges, product distribution is far from being representative to that in an industrial reactor. They compared the goodness of fit of five different models and concluded that the SSAM best described their data.

Boag et al. (1975) using a recirculation reactor, carried out the oxidation of o-xylene using the same catalyst as Juusola et al. (1970), over a wide range of conversion, in the temperature range of 310°C to 330°C. The proposed scheme is similar to that postulated by Herten & Froment (1968) with the exception that phthalide is considered to be a final product and not an intermediate in phthalic anhydride formation. With reference to Fig. 2.1, steps 5, 7 and 10 are absent. This study shows that an extended form of the SSAM (and hence the redox model) suitably describes the reaction scheme, as they were able to represent reasonably well their data with this model.

McLean et al. (1980) performed the oxidation of o-xylene and o-tolualdehyde using a multi-stage tubular reactor. The catalyst was the same as Boag et al. (1975) and was used in its inactive state, but pretreatment was different in order to achieve constant activity over the experimental program. The network proposed differed from that of Boag et al. (1975) in that Maclean found significant amounts of maleic anhydride in the reaction gases.

Lyubarskii et al. (1973) studied the oxidation of o-xylene and its identified partial products (OT, PA and MA) using a recirculation reactor on a "high temperature" promoted V_2O_5 catalyst (presumed supported on SiC). They found, from the oxidation of partial products, the rate

of maleic anhydride oxidation to be independent of oxygen concentration, and the oxidation of phthalic anhydride to $\text{CO} + \text{CO}_2$ to be independent of PA concentration. In the presence of o-xylene, complete stability of phthalic anhydride was observed, and in the presence of phthalic anhydride, oxidation of maleic anhydride is strongly inhibited. The oxidation of o-xylene was performed in the temperature range 380° to 460°C . For the concentration range studied, there was no effect of oxygen partial pressure on the hydrocarbon rates of oxidation. The proposed scheme is the same as that by Simard et al. (1960). The absence of phthalide in both studies, an intermediate normally detected in industrial reactors, is remarkable.

Wainwright & Hoffman (1974, 1977) carried out studies of the oxidation of o-xylene on several commercial vanadia catalysts, some of them K_2SO_4 -promoted and SiO_2 -supported, others K_2SO_4 - SbO_3 -promoted and TiO_2 -supported including one from Von Heyden (Catalyst W0) of unknown composition. Kinetic data were obtained under transient and steady-state conditions in a quasi-isothermal fixed-bed reactor in the temperature range 350° to 390°C and in a transported bed reactor in the temperature range 233° to 242°C . To maintain constant a constant activity of the catalyst they added 0.01 volume percent SO_2 , and no appreciable long term decay of catalyst could be attributed to this effect. Their findings can be summarised as follows:

1. There is a dramatic decrease in the activity of fully oxidized vanadia catalysts just after they begin to participate in the o-xylene oxidation reaction and that selectivity of these catalysts to partially oxidised products is highest while the vanadia is in the highly oxidised state.

2. The lattice oxygen rather than chemisorbed oxygen is likely to be responsible for the direct oxidation of the hydrocarbon.
3. The catalyst supported material, including other reaction-moderating substances, has a marked effect on product distribution although the rates of partial oxidation of o-xylene are of the same order for both silica and titania supported catalysts.
4. The difference between both supported catalysts is that the titania takes an active role in the reaction, making its activity and selectivity to phthalic anhydride higher than those from the silica supported catalyst.
5. Despite the addition of SO_2 in the feed, long term deactivation of the TiO_2 supported catalyst occurred depending upon how much above 400°C the reaction temperature was taken.
6. For TiO_2 -supported catalysts, the original oxidation state could be restored after about 6 hours, suggesting that the oxidation/reduction reactions of the catalyst are completely reversible.
7. For TiO_2 -supported catalysts, the rate of o-xylene oxidation had little or no temperature dependency in the range 350°C to 390°C ; this was attributed to catalyst deactivation.

The proposed kinetic scheme for the titania-supported catalyst included steps 1, 2, 3, 5 and 9 of Fig. 2.1. For the silica-supported catalyst both phthalic anhydride and phthalide were taken as end products. In both kinetic schemes the formation of the total oxidation products, CO , CO_2 and H_2O were not considered and no maleic anhydride was detected except for the von Heyden catalyst.

A multi-step redox model was used to model the kinetics. However, the use of an "active site parameter" to account for a loss in

catalyst activity for the TiO_2 -supported catalyst is questionable. Selectivities of 85 mole% were obtained at 100% conversion of o-xylene.

Calderbank et al. (1970, 1972) using a promoted V_2O_5 on SiC-supported catalyst, performed kinetic measurements using a spinning catalyst basket reactor (SCBR) in the temperature range 390°C to 430°C . The catalyst was evaluated in a pilot plant non-isothermal reactor for a molten salt bath temperature range 370°C to 454°C and 0.5 to 1.5 mole% o-xylene in the feed. A constant selectivity of 58-64%, independent of both bath temperature or flowrate, was observed.

Yields of phthalic anhydride obtained with the isothermal SCBR were much lower than those from the fixed bed reactor. A maximum selectivity of 55% was obtained in the SCBR. They suggested that phthalic anhydride undergoes total oxidation under SCBR conditions in contrast to its great stability in the fixed bed, as residence time in the latter is at least ten times smaller than in the SCBR. In agreement with Lyubarskii et al. (1973) they found phthalic anhydride to be remarkably resistant to further oxidation from the fixed-bed experiments. From experiments with the SCBR, the catalyst was reversibly deactivated at o-xylene partial pressures over 0.016 atm (~ 1.5 mole%).

Ellis (1972) [in Lopez-Isunza (1983)] performed an extensive study of the oxidation of o-xylene in 2.5 cm and 5.0 cm I.D. pilot plant non-isothermal fixed bed reactors, on a promoted V_2O_5 on SiC-supported, 0.63 cm diameter catalyst particles. The salt bath temperature range was 410° to 490°C for an o-xylene feed range of 1 to 1.5 mole% in air (34N lt/min). "Approximate" axial conversion profiles allowed for the determination of a kinetic scheme involving steps 1, 2, 5, 6 and 7. The maximum overall selectivity to OT, PT and PA was about 80%; and to phthalic anhydride 70%. The selectivities were virtually independent

of temperature. Increasing the o-xylene inlet concentration from 1.0 to 1.5 mole% resulted in deactivation of the catalyst, in the region of the hotspot. No reactivation of the catalyst was reported. It was observed, working at extreme conditions, that the yield of phthalic anhydride was independent of salt bath temperature over the range 410°C to 490°C (maximum hotspots of 490°C and 590°C respectively). However, homogeneous combustion of phthalic anhydride was also noticed. Lopez-Isunza (1983) further reported that Ellis observed a change in apparent activation energy of the o-xylene oxidation rate at approximately 440°C, from the kinetic evaluation of the catalyst using diluted catalyst beds (quasi-isothermal conditions) in the temperature range 375°C to 465°C and inlet o-xylene partial pressure range 0.0014 to 0.012 atm (0.16 to ~1.3 mole%). It was suggested that this phenomena cannot easily be explained in terms of intraparticle diffusion control in porous solid as a surface coated promoted catalyst on SiC support was used, but perhaps in terms of a reduction in specific area and a change in the lattice structure, due to the formation of a liquid layer of molten catalyst. This explanation has also been suggested by the experiments of Tandy (1956), who found that liquid pyrosulphate- V_2O_5 -mixtures were formed above 440°C, using alkali metals, and the experiments by Butt & Kenny (1977) who observed that a catalyst containing 39% V_2O_5 and 61% K_2SO_4 by weight, forms an eutectic with a sharp melting-point of 433°C. They found the rate of naphthalene oxidation falls with increasing temperature between 400°C and 440°C and the selectivity for phthalic anhydride formation to decrease.

Ramirez & Calderbank (1977,1982) have observed a similar reduction in apparent activation energy, in the temperature range 425°C to 450°C, for the benzene oxidation on a V_2O_5 - MoO_3 - P_2O_5 catalyst. Calderbank

(1974) studied the oxidation of o-xylene and phthalic anhydride using an unpromoted V_2O_5 on SiC catalyst in an SCBR, where the basket and the chamber were made of titania. He found the o-xylene reaction rate to be first order up to nearly 1 mole% o-xylene. At higher concentrations, the catalyst was reversibly deactivated. His findings of a low activation energy for o-xylene rate of disappearance above 440°C agrees with that of Ellis (1972) and "explains the absence of strong parametric sensitivity of the fixed bed reactor". A nearly constant overall selectivity of about 75% was obtained in the SCBR at temperatures below 440°C for up to 100% o-xylene conversion, but this diminishes at higher temperatures. He proposed a 5-step kinetic scheme comprising of steps 1, 2, 3, 4 and 5.

Calderbank et al. (1977) carried out a study of the oxidation of o-xylene over various commercial V_2O_5 and $TiO_2-V_2O_5$ catalysts using an SCBR. A "catalytic-tube-wall reactor" (CTWR) made of titania and internally coated with catalyst ($TiO_2-V_2O_5$) was used to determine selectivities without the influence of metals. They found the results to be generally applicable to commercial catalysts despite variations in the ratio of total to superficial area for the various catalysts, the rate constants being reported for the superficial areas only.

Their findings can be summarised as follows:

1. O-xylene disappears at low concentrations by first order reaction with respect to o-xylene with an apparent activation energy falling from 109KJ/mol between 370°C and 440°C to about 54.5 KJ/mole between 440°C to 550°C , provided thermal deactivation does not take place in the latter range.
2. Rates of reaction at temperatures between 370°C and 440°C are almost completely independent of oxygen partial pressure becoming

- increasingly dependent on the latter as the temperature is raised.
3. At high temperatures and high o-xylene concentration, the reaction tends towards a zero order with respect to o-xylene and first order with respect to oxygen.
 4. At low temperatures and high o-xylene concentrations, reversible deactivation takes place.
 5. O-tolualdehyde and phthalide disappear with the same first-order rate constants as does o-xylene above 440°C.
 6. The reaction selectivity to C_8 (PA and precursors) at low conversions is constant and independent of temperatures above 370°C varying between 0.75 and 0.82 for different catalysts.
 7. Phthalic anhydride undergoes total oxidation relatively slowly on the catalysts examined.
 8. The reaction rate decreases sharply at temperatures below 370°C and the hydrocarbon disappearance rate becomes first-order with respect to oxygen being independent of o-xylene partial pressure.

They claimed that V_2O_5 - TiO_2 catalysts deactivate almost completely and irreversibly when heated above about 500°C and that experimental data at higher o-xylene concentrations in the feed (1.5%) show partial deactivation of the catalyst, probably due to crystalite sintering and loss of area at the hot-spot where the temperature is predicted to rise initially to about 600°C. The proposed kinetic scheme comprises steps 1 to 6.

No maleic anhydride was detected.

During the parameter estimation stage to fit Ellis' (1972) data obtained from the pilot plant fixed bed reactor, they found the activation energy for catalyst re-oxidation to be zero and step 6 to be kinetically negligible.

Chandrasekharan et al. (1978, 1980) studied the oxidation of o-xylene in a TWCR. Two catalysts were used; one of pure V_2O_5 and the second one, 95% TiO_2 - 5% V_2O_5 by weight. The same products were obtained with both catalysts. Although small quantities of phthalide and maleic anhydride were also formed, particularly at high conversions of o-xylene and temperatures above $420^\circ C$, the kinetic scheme that "adequately represented the product distribution" comprised of steps 1, 3, 4 and 8.

Recently, Skrzypek et al. (1985) studied the oxidation of o-xylene over a commercial V_2O_5 - TiO_2 catalyst in a fixed bed non-isothermal reactor with o-xylene conversions between 0.12 to 0.71 and salt bath temperatures between 360° and $390^\circ C$. They proposed a kinetic scheme which includes all the steps in Fig. 2.1 except steps 8 and 10. However, maleic anhydride detected was considered to be formed directly from o-xylene. The reaction network is very similar to that presented by Calderbank et al. (1977, 1979) and Ljubarskii (1973). In Calderbank's reaction network no maleic anhydride is present while in Ljubarskii's network there is no phthalide at all.

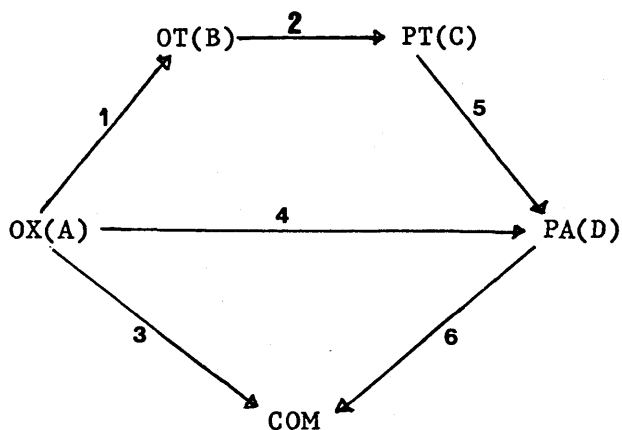
2.4 The kinetic model used in this study

From the review of the work that has been carried out so far on the oxidation of o-xylene using vanadia catalysts, it is apparent that most of the experiments were conducted under conditions that do not conform with industrial practices. Since one is constrained to consider only those kinetic data that have been obtained at reaction conditions similar to those encountered in the industry, there is only a very limited choice of kinetic models available.

The kinetic model used in this study is, therefore, based on the work of Calderbank and co-workers (1977) because, as remarked by Lopez-Isunza (1983), "it is the only one known which satisfies the following criteria:

1. the kinetics were evaluated for a conversion range of nearly 100%, in the temperature range of industrial reactor, i.e. 370° to 550°C, using both laboratory scale reactors and a pilot plant fixed bed reactor;
2. the results were found to be generally applicable to commercial V_2O_5 and V_2O_5/TiO_2 catalyst, despite variations in the ratio of total to superficial surface area".

In the present study a V_2O_5/TiO_2 catalyst of unknown composition was used in an industrial scale reactor operating in the temperature range 370° to 590°C for the reaction scheme



At low o-xylene feed compositions (~ 1 mole), the redox kinetic model for each species gives

$$R_A = -\mu s(K_1 + K_3 + K_4) P_A$$

$$R_B = \mu s(K_1 P_A - K_2 P_B)$$

$$R_C = \mu s(K_2 P_B - K_5 P_C)$$

$$R_D = \mu s(K_4 P_B + K_5 P_C - K_6 P_D)$$

or simply

$$R_n = \sum_{j=1}^R \nu_{nj} R_j$$

where:

$$\mu s = \frac{K_a P_{O_2}}{K_a P_{O_2} + (M_1 K_1 + M_3 K_3 + M_4 K_4) P_A + M_2 K_2 P_B + M_5 K_5 P_C + M_6 K_6 P_D}$$

and n stands for OX, OT, PT, PA and

$$R_j = \mu s K_j P_n = \mu s A_j \exp(-E_j/RgT) P_n$$

are the individual steps of reaction, and ν_{nj} is the stoichiometric coefficient of species n in the j^{th} reaction.

A problem associated with the above kinetics is that they do not include the formation of maleic anhydride, a normal by-product from industrial reactors (0.06 Ton of maleic anhydride are produced per 1 ton of phthalic anhydride [Nicholl (1985)]).

2.4.1 The kinetic parameter values

The kinetic parameter values presented by Calderbank et al. (1977) are given in Tables 2.1 and 2.2. The values presented in Table 2.1 were obtained from an S.C.B.R. In order to satisfactorily fit axial temperature and concentration profiles from Ellis' (1972) work on the fixed bed reactor, Calderbank et al. (1977) made a further "tuning" of the parameters leading to the values given in Table 2.2.

The kinetic parameters in Table 2.2 were then used in this work for the simulation of the reactor.

TABLE 2.1

Step	T < 440°C		T = 440°C	
	A _j	E _j	A _j	E _j
1	9841	113.6	0.729	56.8
2	2.515	56.8	2.515	56.8
3	8484	113.6	0.629	56.8
4	15612	113.6	1.156	56.8
5	2.466	56.8	2.515	56.8
6	1381	127.7	1381	127.7

A_j in (Kmol/kg.sec.bar) and E_j in (KJ/mole)

TABLE 2.2

Step	A _j	E _j	
1	3.903	61.4	Step 6 kinetically insignificant and: $K_{aO_2} P_{O_2} \sim 0.722 \times 10^{-5} \neq f(T)$ [in (Kmole/Kg.sec.)]
2	0.567	46.5	
3	0.365	51.2	
4	1.391	54.5	
5	3.253	57.9	

2.5 CONCLUSIONS

Much of the work in the literature that has been carried out on the oxidation of o-xylene on vanadia catalysts was conducted under conditions that are different from those that prevail in the operation of industrial reactors. As remarked by Wainwright & Foster (1979), "the failure of researchers to operate catalysts at reaction conditions similar to those encountered industrially has led to the publication of kinetic data which, if used for design purposes, would lead to erroneous and sometimes disastrous results". The kinetic scheme proposed by Calderbank et al. (1977) was used in this work because the data were obtained within the range of industrial conditions and the results were found to be generally applicable to commercial V_2O_5 and V_2O_5/TiO_2 catalysts.

The exact mechanism of o-xylene oxidation on vanadia catalysts is still not known. There are shortcomings in each of the kinetic models that have been proposed. The redox mechanism [Mars & van Krevelen (1954)], has been extensively used by many workers but it is unable to account for certain phenomena that occur during the oxidation process. For example, the decrease in the rate of o-xylene disappearance with high o-xylene concentrations and low salt bath temperatures cannot be explained using either the redox model or the S.S.A.M. Skrzypek et al. (1984) suggest that this behaviour can be accounted for by the Langmuir-Hinshelwood model but it is unlikely that this model can explain the abrupt change in the kinetics of oxidation of o-xylene on vanadia catalysts occurring at a temperature of about 440°C with the apparent activation energy falling from 109 KJ/mole between 370° and 440°C to about 54.5 KJ/mole between 440° to 550°C [Calderbank et al. (1977)]. However, the kinetic parameters estimated by Skrzypek et al.

(1985) were for temperatures lower than 440°C and for low o-xylene conversions ($<.53$). It is important that the kinetic parameters be evaluated to cover the whole range of industrial reactor temperatures, preferably using both isothermal and non-isothermal reactors.

In any case, this Langmuir-Hinshelwood model has already been rejected by Shelstad et al. (1960) and Juusola et al. (1970) because its complexity cannot be justified by the marginal improvement of the experimental data fit obtained by Shelstad et al. (1960).

In this work, we chose to use the redox model whose kinetic parameters have been evaluated for a conversion of nearly 100%, in the temperature range of industrial reactors, i.e. 370° to 550°C, using both Laboratory scale reactors and a pilot plant fixed bed reactor [Calderbank et al. (1977), Chandrasekharan et al. (1979)]. It has been suggested that a deactivation model used in conjunction with the redox model is a viable approach in modelling the kinetics of this complex reactor-reaction system [Lopez-Isunza (1983), Kershenbaum et al. (1984)]. This is in line with the approach advocated by Boreskov (in Skrzypek et al. (1985)] that the effect of changes in a reaction mixture composition on catalyst properties be taken into consideration when modelling the kinetics of heterogenic reactions. It is known that the catalyst reversibly deactivates at high o-xylene concentrations and low temperatures [Calderbank et al. (1974, 1977), Lopez-Isunza (1983)] and as such there is bound to be spatially varying catalyst activity profiles present in this reactor-reaction system.

It is therefore the aim of this work to estimate such activity profiles using reactor data in order to predict both the steady state and dynamic behaviour of the fixed bed reactor.

CHAPTER THREE

3.0 MATHEMATICAL MODELS OF FIXED BED REACTORS

Mathematical models of chemical reactors are useful for predicting the conversion and temperature profiles in packed bed reactors. While very general models can be written down, these are not often used either because of the computational complexity or because it is difficult or impossible to estimate the parameters in the model.

The models can be grouped into two broad categories: pseudo-homogeneous and heterogeneous models.

In the pseudo-homogeneous model, the basic assumption is that the gas- and solid-phases are lumped together into a single continuous phase with properties expressed in terms of 'effective' transport parameters.

In the heterogeneous model, the two phases are considered separately but are linked together via heat and mass balances at the gas-solid interface.

Froment (1972) classified the model within each category in an order of growing complexity as shown in Table 3.1.

TABLE 3.1

Fixed-bed Reactor Models

A	Pseudo-Homogeneous	B	Heterogeneous Models
I	plug flow	I	interfacial gradient
II	+ axial dispersion	II	+ intraparticle gradient
III	+ radial dispersion	III	+ radial dispersion

Recently, Martinez et al. (1985) separated the kinetic and pellet models (a pellet model represents the intraparticle phenomena) from the reactor models and reclassified the models, together with the associated heat transfer parameters, as shown in Fig. 3.1.

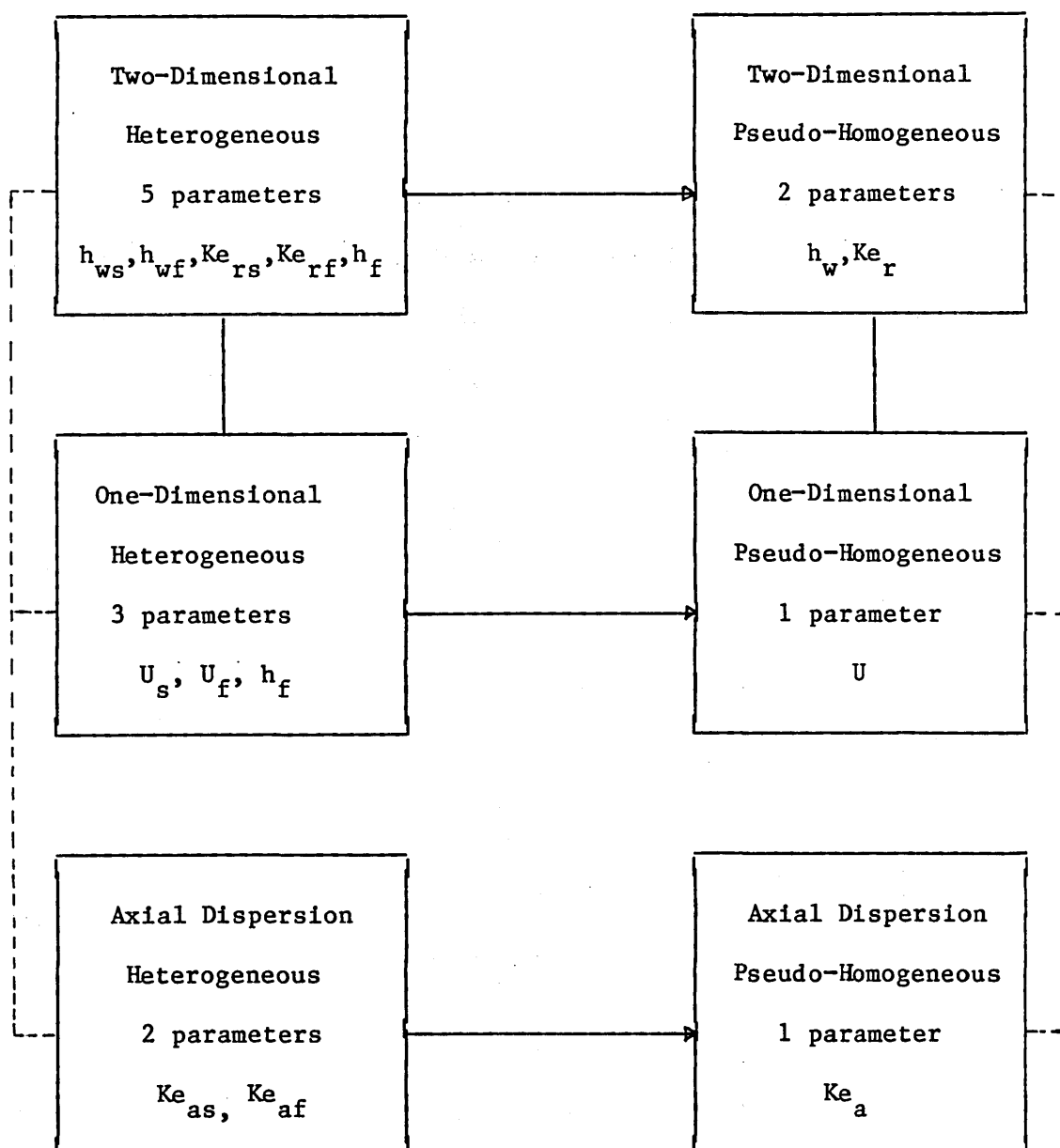


Fig. 3.1 Fixed-bed reactor models and heat transfer parameters

Eight basic models can be established from Fig. 3.1, four with and four without axial dispersion, which correspond to the combination of the one- and two-dimensional versions of the pseudo homogeneous and heterogeneous models. These basic models are related among themselves, and, under simplifying assumptions, the simpler models can be derived from the more complex ones.

The simplest model considered involves a single heat transfer parameter, the overall heat transfer pseudo-homogeneous coefficient. The more complex model involves seven heat transfer and three mass transfer parameters, if the mass balance is also considered.

The whole spectrum of the theoretical and experimental work on fixed bed reactors in the last 30 years has been reviewed, among others by Beek (1962), Amundson (1970), Hlavacek (1970), Froment (1974), Carberry & Butt (1974), Hofmann (1979) for the steady-state behaviour and Ray (1972), Schmitz (1979), Giles (1976), Endo et al. (1978) and Hlavacek et al. (1981) for the dynamic behaviour.

From these reviews it is evident that a large amount of theoretical as compared to experimental work has been done, especially in the case of the dynamic behaviour of chemical reaction systems and in particular, of industrial fixed bed catalytic reactors. In the case of industrial fixed bed reactors for the partial oxidation of o-xylene, there is a considerable amount of both theoretical and experimental work that has been done. A recent review by Lopez-Isunza (1983) points out the various mathematic models that have been applied to model this type of highly exothermic reactor-reaction system. The review is therefore not repeated here.

3.1 The mathematical model selected for this work

Models are developed in order to represent the actual behaviour of a system. The problem that normally confronts workers is how to justify the degree of sophistication of the model used.

In addressing the problem, Froment & Bischoff (1979) proposed that the model should depend on the process, that is, on the reaction scheme and its sensitivity to perturbations in the operating conditions.

Perhaps the main limitation is the existence and accuracy of the experimental data. Any prediction that can be made will be as exact as the physical and chemical data that are introduced in the model. When there are not enough data available, once the model is proposed, the whole effort has to be concentrated on a more precise estimation of the parameters in already known models. The desired accuracy in the knowledge of the parameters depends to a certain extent, on their influence on the overall process [Martínez et al. (1985)]. It follows that the more accurate parameters are needed when their influence is greater and that a simple existing model whose parameters are well known (or can be estimated from reactor data) could be much more useful than a complex one whose parameters are being estimated from correlations that do not very well extrapolate to the operating conditions of the reactor system under study.

This is particularly the case with this reactor-reaction system where the distributed activity parameter plays a very dominant role both in the steady state and dynamic behaviour [Lopez-Isunza (1983) and in this work]. The uncertainty in the activity far outweighs any consideration of using a very complex model. It is an objective of this work to estimate activity profiles from both temperature and concentration measurements.

In selecting between one-dimensional and two-dimensional models, Pereira-Duarte (1984) observed that the performance of a one-dimensional model depends mainly on the maximum difference between the mean radial temperature and the salt bath ($\bar{T} - T_w$) and the dimensionless mean activation energy ($\bar{\gamma}$). Similar results have been obtained by Foss and co-workers [Crider (1966); Sinai (1970); Hoiberg et al. (1971)] and Hlavacek & Marek (1967). They recommended a one-dimensional model for a reactor under low thermal sensitivity conditions.

The above consideration precludes the use of a one-dimensional model in simulating this type of highly exothermic reactor-reaction system where temperature differences between the hot spot and salt bath could go as high as 140°C and above under normal operating conditions.

When the choice is between pseudo-homogeneous and heterogeneous models, it is necessary to evaluate the importance of interphase gradients [Martinez et al. (1985)]. Recently, Pereira-Duarte & Lemcoff (1984) developed a criterion for predicting the deviations between the models as a function of the inlet conditions. They concluded that without axial dispersion, pseudo-homogeneous models can be applied for a ratio $dt/dp > 10$. For small ratios, the decision will depend on the reaction sensitivity to the interfacial gradients, which in turn depend on the adiabatic temperature rise, activation energy, reaction order, and difference between inlet and wall temperatures.

In a previous study of this reactor-reaction system, Lopez-Isunza (1983) used heterogeneous models to simulate both the steady state and dynamic behaviour. This work is in fact a continuation of the work by Lopez-Isunza (1983). He observed that unless catalyst activity profiles were considered, the dynamic model was far from predicting the observed behaviour. It is therefore considered in this work that a

simpler model which takes into account catalyst activity profiles may be adequate. In order to evaluate the importance of interface gradients, the mass and heat transfer coefficients (K_g , h) in Lopez-Isunza's heterogeneous model were set to very high values. This has the same effect as reducing the model to a pseudo-homogeneous model. K_g and h were calculated from correlations by Petrovic & Thodos (1968) and Aerov & Todos (1968) respectively (see Appendix A.2). For the operating conditions considered in this study ($4 \text{ Nm}^3/\text{hr}$ of air), the values were $0.21158 \text{ cm sec}^{-1}$ ($21.158 \text{ cm sec}^{-1}$) and $595.5 \text{ W/m}^2\text{K}$ ($1.4179 \times 10^{-2} \text{ cal/cm}^2 \text{ sec } ^\circ\text{C}$) respectively.

It was observed that the hotspot temperature and the temperature and concentration profiles in the gas-phase were insensitive to interphase gradients. Increasing the values of both K_g and h only resulted in the reduction of the catalyst surface hotspot temperatures and a shift of the temperature and concentration profiles towards the predictions of the gas-phase. The predictions of both the heterogeneous and the homogeneous models are compared in Fig. 3.2.

This insensitivity to interphase gradients was also observed by Chandrasekharan & Calderbank (1978) who used a one-dimensional heterogeneous model to estimate kinetic and transport parameters in a fixed bed reactor for the partial oxidation of o-xylene. They found that the predicted hotspot temperature and the temperature profiles were insensitive to increasing values of K_g and h , up to infinity, in spite of a maximum predicted temperature difference of 32°C between the catalyst surface and the bulk phase. However, they observed that the predicted hotspot temperature was very sensitive to the overall heat transfer coefficient. When they decreased U by 23%, the predicted hotspot temperature increased by 28°C .

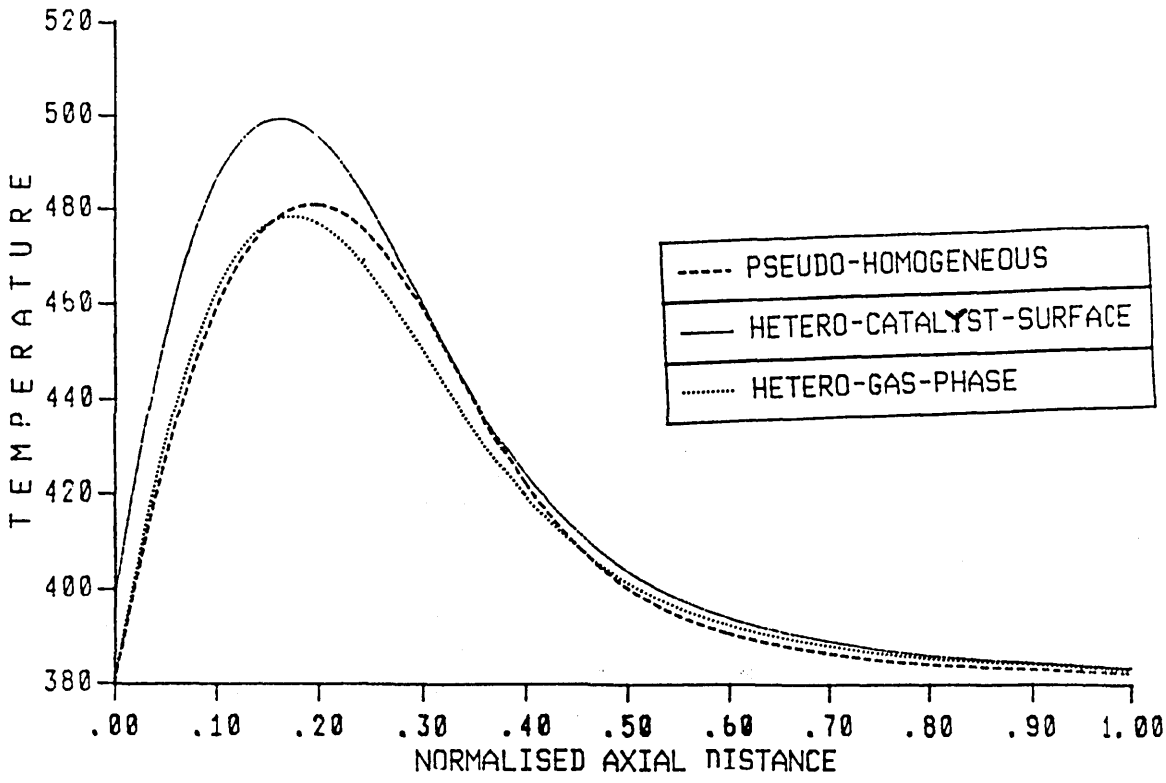


Fig. 3.2a Predicted temperature profiles of the pseudo-homogeneous and heterogeneous models compared.

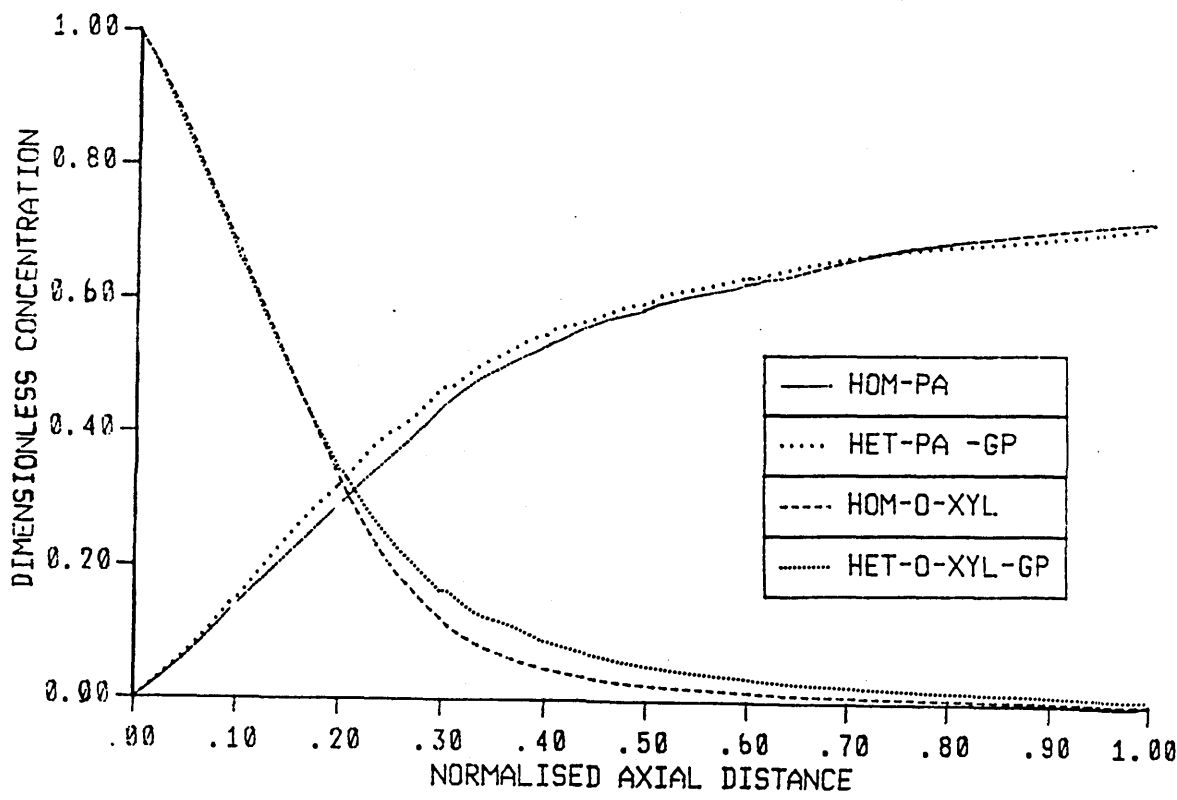


Fig. 3.2b Predicted concentration profiles of o-xylene and phthalic anhydride obtained from the pseudo-homogeneous and heterogeneous models compared.

The question as to whether to include or exclude axial dispersion has received considerable attention over the years [Wicke (1972, 1975), Dixon et al. (1979), Young & Finlayson (1973), Hlavacek & Marek (1966), Votruba et al. (1975), Carberry (1963, 1976), Paterson & Carberry (1983)]. It is important to determine under which conditions axial dispersion is negligible, since this complicates to a large extent the numerical solution of the model equations. Based upon experimental evidence, Wicke (1972, 1975) has shown that axial dispersion of mass is negligible as compared to axial dispersion of heat, for the case of a highly exothermic reaction.

Earlier criteria for neglecting axial dispersion terms based on reactor length to particle diameter ratio, $L/d_p > 150$ [Carberry (1963, 1976)] or also involving the axial peclet number for mass $Pe_{ma} L/d_p > 100 - 400$ [Hlavacek & Marek (1966)], have been questioned by Young & Finlayson (1973), who developed a more fundamental criteria for non-isothermal reactor (independent of reactor length) in terms of the maximum temperature and conversion gradients. If axial dispersion is to be negligible, the next conditions must be satisfied.

$$\max_{z'} \left| \frac{1}{Pe_{ma}} \frac{dX}{d(z'/d_p)} \right| \ll 1 \quad \max_{z'} \left| \frac{1}{Pe_{ha}} \frac{dY}{d(z'/d_p)} \right| \ll 1$$

where $X = 1 - C/C_0$ is the fractional conversion, $Y = (T-T_w)/(T_0-T_w)$ is a dimensionless temperature; z' is the axial position and Pe_{ha} and Pe_{ma} are peclet numbers for heat and mass respectively. The above is in agreement with the observations of Hlavacek & Van Rompay (1981) who noted that due to steep profiles in long packed beds, the axial dispersion term for heat cannot easily be neglected.

This is particularly true for this type of reactor-reaction system where most of the chemical reaction takes place in a short length of the bed. It is generally accepted that high flowrates do decrease the importance of axial dispersion [Young & Finlayson(1973), Mears (1976)].

The particular characteristics of this system, i.e. high particle Reynolds number ($Re_p \sim 750$), very short residence time ($\tau < 1$ sec), $L/d_p \sim 320$ and $dt/d_p \sim 3$ suggest that axial dispersion may be negligible but this has been found not to be the case [Lopez-Isunza (1983), and this work, Chapter 6].

3.1.1 Further considerations and conclusions

Experiments performed by Fieguth & Wicke (1971), Kehoe & Butt (1972) and Karanth & Hughes (1974), during which very high interface temperature gradients were measured, support the use of a heterogeneous model for this type of highly exothermic fixed-bed reactor system, although for our case it was not possible to measure gas and solid temperatures as the reactor is not suited for this kind of fundamental research.

In this type of system, temperature measurements are considered as a sort of "gas-solid averages" and this makes it extremely difficult to obtain reasonable estimates of all the heat transfer parameters in a fully heterogeneous model. To avoid introducing larger uncertainties in estimating these parameters, Lopez-Isunza (1983) used a pseudo-heterogeneous dynamic model - in the sense of Carberry & White (1969).

However, in most cases, a pseudo-homogeneous model, which makes no distinction between the fluid and solid temperatures, is used to analyse temperature measurements in a packed bed [Dixon & Cresswell (1979)]. Accordingly, Dixon et al. (1978b) have shown that a two-

dimensional pseudo-homogeneous model, comprising both radial and axial heat dispersions, with its effective parameters provide a statistically adequate description of the temperature distribution in a packed bed. This model was therefore chosen for this work.

Although axial heat dispersion has been found to be very important especially during the dynamic behaviour of this reactor-reaction system [Lopez-Isunza (1983) and this work, Chapter 6], it was not considered because of computational complexity in the solution of the model equations. Since it is intended to use the model for on-line estimation and control of the reactor, it is essential that the model be as simple as possible in order to allow for low computation times.

Radial temperature measurements obtained by Lopez-Isunza (1983) have shown that this reactor exhibits steep radial gradients with the maximum temperature difference between the salt bath and the maximum temperature in the region of the hotspot within the range 40 to 50°C. It was therefore very important that radial heat dispersion be considered in the model.

The two-dimensional pseudo-homogeneous model, with axial heat and mass dispersions excluded, used in this work is presented in the next section (Section 3.2). It is a very popular model which has been used by many other workers in similar studies [e.g. Finlayson (1970), Jutan et al. (1977) and Baiker & Bergougnan (1985)].

3.2 The pseudo-homogeneous two-dimensional model

The following set of parabolic partial differential equations describing the mass and energy balances represent the dynamic behaviour of the reactor.

Mass balance

For the nth component

$$\epsilon \frac{\partial C_n}{\partial t'} = - \epsilon u \frac{\partial C_n}{\partial z'} + \epsilon De_r \left(\frac{\partial^2 C_n}{\partial r'^2} + \frac{1}{r'} \frac{\partial C_n}{\partial r'} \right) + \rho_B \sum_{j=1}^R v_{nj} R_j(C, T) \quad (3.1)$$

Heat balance

$$M \frac{\partial T}{\partial t'} = - \epsilon u \rho C_p \frac{\partial T}{\partial z'} + Ke \left(\frac{\partial^2 T}{\partial r'^2} + \frac{1}{r'} \frac{\partial T}{\partial r'} \right) + \rho_B \sum_{j=1}^R (-\Delta H_j) R_j(C, T) \quad (3.2)$$

where $M = \epsilon \rho C_p + \rho_B C_{p_s}$.

The initial and boundary conditions are:-

$$@ \quad t' = 0 \quad C_n(r', z', 0) = C_n(r', z')_{ss} \quad (3.3)$$

$$T(r', z', 0) = T(r', z')_{ss}$$

$$@ \quad r' = 0 \quad (0 < z' < L) \quad (3.4)$$

$$\frac{\partial C_n}{\partial r'} = \frac{\partial T}{\partial r'} = 0$$

$$@ \quad r' = R_o \quad (0 < z' < L) \quad (3.5)$$

$$\frac{\partial C_n}{\partial r'} = 0$$

$$- Ke \frac{\partial T}{\partial r'} = hw(T - T_w)$$

$$@ \quad z' = 0 \quad (0 < r' < R_o) \quad (3.6)$$

$$C_{n_o}(r', 0, t') = C_{n_o}(t')$$

$$T(r', 0, t') = T_o(t')$$

Eqs. 1 to 6 are expressed in the following dimensionless form, using the dimensionless parameters and variables, described in the nomenclature.

Mass balance

$$\frac{\partial X_n}{\partial t} = - \frac{\partial X_n}{\partial z} + \frac{1}{P_m} \left(\frac{\partial^2 X_n}{\partial r^2} + \frac{1}{r} \frac{\partial X_n}{\partial r} \right) + \sum_{j=1}^R \delta_{m,j} f_j(\underline{X}, Y) \quad (3.8)$$

Heat balance

$$\bar{M} \frac{\partial Y}{\partial t} = - \frac{\partial Y}{\partial z} + \frac{1}{P_h} \left(\frac{\partial^2 Y}{\partial r^2} + \frac{1}{r} \frac{\partial Y}{\partial r} \right) + \sum_{j=1}^R \beta_j \delta_{h,j} f_j(\underline{X}, Y) \quad (3.9)$$

with boundary conditions

$$@ \quad t = 0 \quad X_n(r, z, 0) = X_n(r, z)_{ss} \quad (3.10)$$

$$Y(r, z, 0) = Y(r, z)_{ss}$$

$$@ \quad r = 0 \quad (0 < z < 1)$$

$$\frac{\partial X_n}{\partial r} = \frac{\partial Y}{\partial r} = 0 \quad (3.11)$$

$$@ \quad r = 1 \quad (0 < z < 1)$$

$$\frac{\partial X_n}{\partial r} = 0$$

$$(3.12)$$

$$- \frac{\partial Y}{\partial r} = Bi_w (Y - Y_w)$$

$$@ \quad z = 0 \quad (0 < r < 1)$$

$$X_n(r, 0, t) = X_{n_0}(t)$$

$$(3.13)$$

$$Y(r, 0, t) = Y_0(t)$$

3.3 The model parameters

The parameters of the model P_m , P_h , Bi_w , β_j 's, K_j 's, δm_j 's and Sh_j 's are defined in the nomenclature.

The first two parameters P_m and P_h are derived from the aspect ratios, which involve the reactor's geometry in terms of d_p , L and R_o , and the peclet numbers for mass and energy in the radial direction respectively. The third parameter Bi_w , is the wall Biot number, involving the effective thermal conductivity and heat transfer coefficient at the wall. There exists an enormous amount of experimental and theoretical work on the evaluation of these parameters which has been comprehensively reviewed by Beek (1962), Froment (1972), Smith (1970, 1973), Schlünder (1978), Dixon et al. (1978, 1979), Hlavacek & Votruba (1977), Li & Finlayson (1977), Kulkarni & Doraiswamy (1980) and Wellauer et al. (1982). A common feature of the experimental work is that heat transfer studies were almost invariably made on tubes of large diameter by measuring radial temperature profiles [Specchia et al. (1980)].

Recently, however, Wellauer et al. (1982) carried out extensive experimental determinations of overall heat transfer coefficients over packed reactor tubes, of diameters 21 mm and 28 mm, suitable for selective oxidation. Using the experimental data obtained, they compared the various models in the literature and came to the conclusion that the two-phase continuum model, incorporating combined conduction, convection and radiation gave best results (to within $\pm 10\%$). In this work, the correlations based on the two-phase continuum model were used to evaluate the parameters, and they are presented in Appendix A.

The parameters β_j 's are the adiabatic temperature rise for all the reactions, and are well known from thermodynamic data. Their values are given in Appendix A.

The set of Kinetic parameters $\underline{K} = \{k_j\}$ are given in Chapter 2. See the nomenclature for the definition of the parameter sets $\delta m = \{\delta m_j\}$ and $\delta h = \{\delta h_j\}$ which are closely related to the kinetic parameters.

3.4 NUMERICAL SOLUTION OF THE MODEL EQUATIONS

The majority of chemical reaction engineering problems ultimately require the solution of sets of nonlinear partial differential equations by numerical techniques. Some of the techniques that have been successfully applied are the finite difference methods with either explicit [Liu, (1969)] or implicit schemes [von Rosenberg et al. (1962)], which have been reviewed by Hlavacek (1970), and the method of orthogonal collocation [Finlayson (1971, 1974), Hansen (1971, 1973) and Villadsen (1970)].

To cut down on computation time and storage requirements, these methods are continuously being modified and adapted to tackling specific problems. For example, the modified Crank-Nicolson Technique [Eigenberger & Butt (1976)] and the method of orthogonal collocation on finite elements [Finlayson (1980)] also called global spline collocation [Villadsen et al. (1978)] have been used and they prove to be very efficient in solving problems involving highly exothermic reactions in which steep temperature and concentration profiles are encountered.

In this work, some modifications were carried out on the method of orthogonal collocation on finite elements, which has hitherto been used in solving boundary value problems [Carey & Finlayson (1975), Pederson

& Tanoff (1982)], to solve an initial value problem exhibiting steep temperature and concentration profiles. A brief description of the method of orthogonal collocation, together with relevant details, is given in Appendix B.

3.4.1 Model reduction - radial collocation

The model Eqs. 3.8 to 3.13 are not easy to solve because of their two-dimensional character (spatial dimensions). Model reduction attempts to retain all the basic details but employs techniques for incorporating all the intrinsic features in a lower dimensional model [Jutan et al. (1977)].

One such technique which is widely used is the method of orthogonal collocation [Finlayson (1980), Villadsen et al. (1970)]. The partial differential equations were reduced from parabolic to hyperbolic by applying the method in the radial direction.

The following assumptions based upon experimental evidence were made in order to carry out further reductions of the model equations.

- a) With typical residence times less than 1 second, particle Reynolds numbers of about 800 and tube-to-particle diameter ratio of 3, one would expect small values of the wall Biot number [Finlayson (1971)]. Thus, a small number of radial finite difference (or collocation) points should be adequate.

In this work, one interior collocation point was used.

- b) The time constants associated with changes in concentration are very small compared with those for temperatures. Hence the dynamic term for the accumulation of concentration was set to

zero (quasi steady state approximation) [Lopez-Isunza (1983), McGreavy et al. (1977), Jutan et al. (1977)]

The model equations then become:

Mass balance

$$0 = - \frac{\partial X_n}{\partial z} + \sum_{j=1}^R \delta_{m,j} f_j(\underline{X}, Y) \quad (3.14)$$

Heat balance

$$\bar{M} \frac{\partial Y}{\partial t} = - \frac{\partial Y}{\partial z} + \left(\frac{6 \text{ Biw/Ph}}{3 + \text{Biw}} \right) (Y_w - Y) + \sum_{j=1}^R \beta_j \delta_{h,j} f_j(\underline{X}, Y) \quad (3.15)$$

with initial conditions

$$\begin{aligned} @ \quad t = 0 \quad X_n(z, 0) &= X_n(z)_{ss} \\ Y(z, 0) &= Y(z)_{ss} \end{aligned} \quad (3.16)$$

$$\begin{aligned} @ \quad z = 0 \quad X_n(0, t) &= X_{n_0}(t) \\ Y(0, t) &= Y_0(t) \end{aligned} \quad (3.17)$$

It is important to bear in mind that Eqs. 3.14 to 3.17 still retain a two-dimensional character as radial temperature profiles can be reconstructed by using the original boundary conditions [Eqs. 3.11 and 3.12].

It is possible to further reduce Eqs. 3.14 and 3.15 to a system of nonlinear algebraic equations and ordinary differential equations respectively, by applying orthogonal collocation in the axial direction. Axial collocation has been used by Michelsen et al. (1973), Sørensen (1976) for adiabatic reactors and Jutan et al. (1977) for a non-adiabatic reactor. In all the cases the solution profiles were well approximated by relatively low-order polynomials. Michelsen et al. (1973) used six collocation points.

In the present reactor-reaction system, most of the reaction takes place on a small length of the catalytic bed and as a result both the temperature and concentration profiles have very steep gradients. There also exists a disparity in the magnitude and position of these steep gradients for the various solution profiles. Global collocation using high order orthogonal polynomials of up to 20 interior points were used in the axial direction and, for the steady state case, the resulting system of non-linear algebraic equations were solved iteratively using Broyden's method [Broydon (1965), Paloschi & Perkins (1981)]; convergence was not obtained.

Perhaps, the idea of using very high-order polynomials is futile in dealing with problems of this nature because numerical ill-conditioning induced by the collocation weights may begin to swamp the error [Michelsen et al. (1973)] and the polynomial may even start to ripple along the curve [Jutan et al. (1977)]. Moreover, the increased amount of computation time and storage requirements can hardly be justified by the accuracy obtained from using a much high-order polynomial.

It was therefore necessary to look for an alternative method which is capable of overcoming the problem outlined above.

3.4.2. Orthogonal collocation on finite elements

The method of orthogonal collocation on finite elements [Finlayson (1980)] also called global spline collocation [Villadsen et al. (1978)] was then modified and used in the axial direction. This method is particularly useful when the solution has steep gradients [Finlayson (1980)]. Trial functions are defined only over part of the region and adjacent functions are pieced together to provide an approximation over

the whole domain. In order to improve the approximation small regions are utilized near the steep gradients. See Fig. 3.3.

The entire domain $0 < z < 1$ was divided into several sub-intervals and orthogonal collocation applied at interior points within these sub-intervals. The size and number of sub-intervals and the number of interior collocation points at each sub-interval were chosen to suit the steepness of the temperature profile obtained. Generally, 4 to 7 sub-intervals, with 2 to 6 interior points in each one, were used for the whole reactor length.

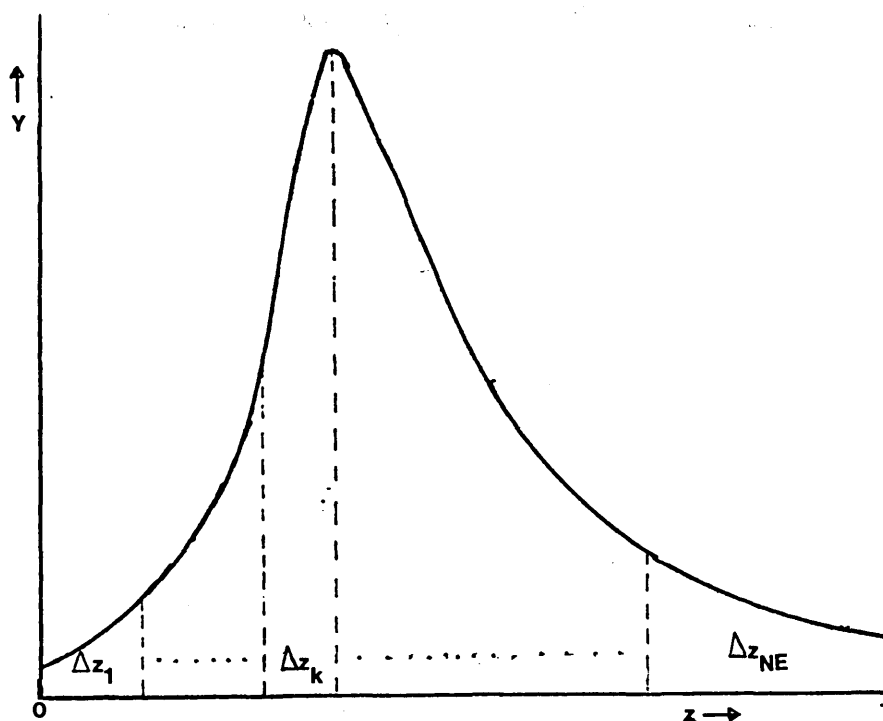


Fig. 3.3. Schematic diagram of finite elements

For the K^{th} subinterval the model equations become:

Mass balance:

$$0 = - \frac{1}{\Delta z(k)} \sum_{j=1}^{N_K+2} A_{ij} X_{nj} + \sum_{\ell=1}^R \delta m_{\ell}(\underline{X}, \underline{Y}) \quad (3.18)$$

Heat balance:

$$\frac{dY_i}{dt} = - \frac{1}{\Delta z(k)} \sum_{j=1}^{N_K+2} A_{ij} Y_j + \frac{6 Bi_w/Ph}{3+Bi_w} (Y_w - Y_i) + \sum_{\ell=1}^R \beta_{\ell} \delta h_{\ell} f_{\ell}(\underline{X}, \underline{Y}_{\ell}) \quad (3.19)$$

$i = 1, N_K+2$

with initial conditions

$$\begin{aligned} @ t = 0 \quad 0 < z < 1 \\ X_n(z, 0) &= X_n(z)_{ss} \\ Y(z, 0) &= Y(z)_{ss} \end{aligned} \quad (3.20)$$

$$\begin{aligned} @ z = 0 \quad t > 0 \\ X_n(0, t) &= X_{n0}(t) \\ Y(0, t) &= Y_0(t) \end{aligned} \quad (3.21)$$

and requiring continuity of functions at the boundaries of the finite elements.

$$X_n, N_K+2 = X_{n1}^{K+1} \quad (3.22)$$

$$Y_{N_K+2}^K = Y_1^{K+1}$$

where $\Delta z(k)$ is the size of the finite element and N_K is the number of interior collocation points.

Eqs. 3.18 to 3.22, comprising a set of nonlinear algebraic equations (NLAE's) and one ordinary differential equation (ODE), were solved by a fourth-order Runge-Kutta method and an implementation of Broyden's method [Broyden (1965), Paloschi & Perkins (1981)].

3.4.3. Size and number of finite elements

The choice of the size and number of finite elements is very important especially if low-order approximation polynomials are to be used. Generally, the location of the steep gradients may not be known a priori and the process of sub-dividing the domain into finite elements could be time-consuming if carried out by trial and error simulations. The problems are compounded if the solution profiles move with time as it is the case with this reactor-reaction system. There would be great convenience in having the task carried out in some automatic manner.

Carey & Finlayson (1975) applied orthogonal collocation on finite elements and used the residual to place new elements where they were needed to achieve the best solution. They used the same order of polynomial in all the elements. Pederson & Tanoff (1982) solved a set of partial differential equations representing a mixing-diagonal competitive-consecutive chemical reaction problem with initial discontinuities in the concentration profiles. They used a fixed number of finite elements chosen freely and manually, with a relatively small element around the location of the discontinuity in order to highlight the solution at that particular sub-region. Their algorithm allowed for a difference in the number of interior points in the finite elements.

Eigenberger & Butt (1976) developed a method to undertake readaptation of grid points based on approximating the function under study by parabolic interpolation and on analysing the discrepancies between the interpolated values produced by two parabolas neighbouring the study point (one staying mainly on the left and the other mainly on the right hand side of the point).

Carlos (1982) calculated the values of the curvature of the function on the points of the existing grid and integrated the curvature function over the domain being studied in order to redistribute the grid points so as to grant that the interval associated to each point on the new grid may share the same contribution for the integral.

In Carey & Finlayson (1975), the finite elements were first chosen at random since the position of the steep gradients was not known a priori. However, by examining the residual everywhere over the entire domain to insert additional elements where it was large, after a given calculation, they were able to eventually cluster enough finite elements around the regions where the solution has steep gradients, to achieve the best solution.

The method developed here places more emphasis on the importance of dividing the domain into suitable finite elements right from the beginning. This is so because it is understood that once the elements have been obtained to reflect the shape of steep profiles, low-order polynomials can be used to approximate the solution with a high degree of accuracy, a reduction in computation times and storage requirements. This entails an accurate pre-knowledge of the characteristics of the solution profiles (temperature and concentration profiles) which is not possible else there will be no need trying to solve the problem in the first place. However, a rough estimate of the profiles can be obtained and used to divide the domain into finite elements as described as follows.

As a first approximation, orthogonal collocation was applied in the axial direction over the entire domain ($0 < z < 1$) using a high order polynomial (say, 15 interior collocation points). In this case, the solution did not converge even with much higher order polynomials

up to 20-order. However, the approximate temperature profile obtained was used in order to divide the domain into finite elements and the apparent location of the maximum temperature was taken as a pivot for this exercise. The temperature profile was chosen because it exhibits the steepest gradients.

The gradient of the temperature profile was calculated at the interior points and at $z = 0, 1$ and compared at adjacent points. The gradient was calculated by making use of the forward difference method as follows:

For the i^{th} interior point the gradient (Grad_i) is given by

$$\text{Grad}_i = \frac{Y_{i+1} - Y_i}{z_{i+1} - z_i} \quad i = 2, N_k+1$$

and at the ends of the domain the gradient is given by

$$\text{at } z = 0, \text{ Grad}_1 = \frac{Y_2 - Y_1}{z_2 - z_1}$$

$$\text{at } z = 1, \text{ Grad}_{N_k+2} = \frac{Y_{N_k+2} - Y_{N_k+1}}{z_{N_k+2} - z_{N_k+1}}$$

The absolute value of the ratio of the gradient at adjacent points was compared against a certain specified minimum value and finite element boundary points (Bpt) or spline points [Pedersen & Tanoff (1982)] were generated whenever this minimum value (C) was exceeded.

In addition to boundary points at $z=0$ and 1 , $z_{\text{max}-1}$, z_{max} and $z_{\text{max}+1}$, were automatically set to emphasise the solution around the region of the maximum temperature. It is important to note that the

position of the apparent hot spot temperature, $z_{\max}$, is dependent upon the order of the initial polynomial. The order of the polynomial should be high enough to ensure that $z_{\max}$ is as close as possible to the true position of the maximum temperature.

The rest of the boundary points (Bpts) were then generated from:

$$\text{if } \left| \frac{\text{Grad}_i}{\text{Grad}_{i-1}} \right| > C \quad \text{Bpt} = z_i \quad 2 < i < \max - 1$$

$$\text{if } \left| \frac{\text{Grad}_{i-1}}{\text{Grad}_i} \right| > C \quad \text{Bpt} = z_i \quad \max + 1 < i < N_K + 1$$

$$\text{where } 0 < C < \infty$$

A schematic diagram of the finite elements is shown in Fig. 3.4

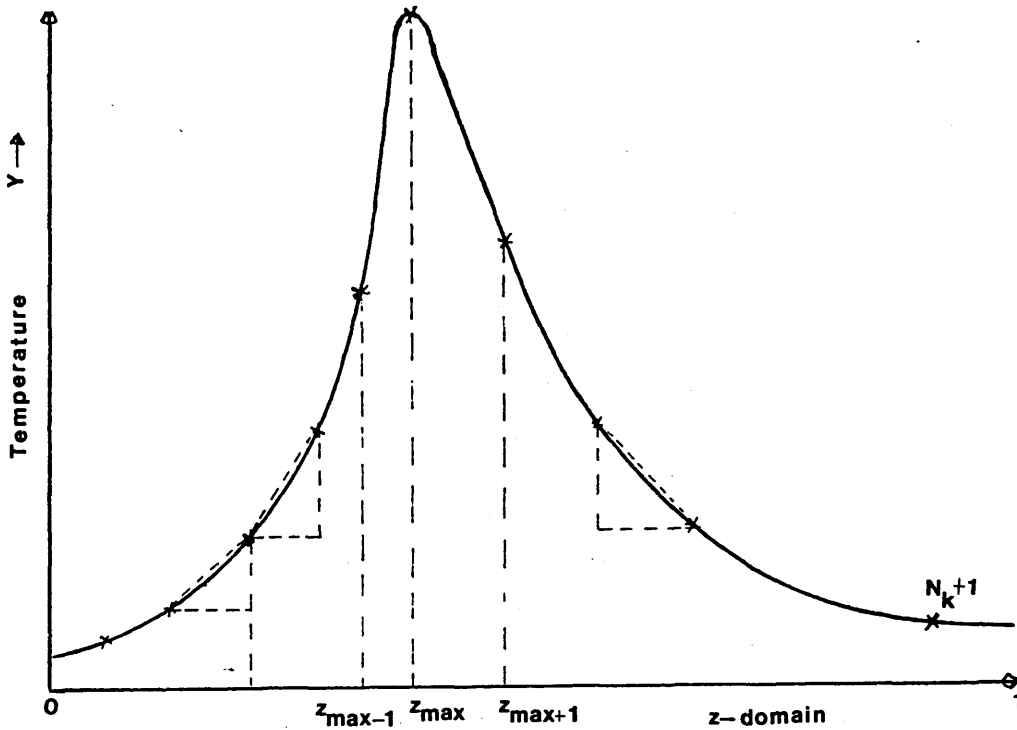


Fig. 3.4 Schematic diagram of finite elements obtained by comparing gradient of the temperature profile at adjacent interior points

The number of finite elements (NI) was automatically defined by fixing a value for C.

An infinite number of finite elements results when the value of C tends to zero. On the other hand, by setting the value of C to infinity the number of finite elements obtained is 4 (the minimum possible number), which corresponds to the finite elements generated by the two boundary points at the end and those at $z_{\max-1}$, $z_{\max}$ and $z_{\max+1}$

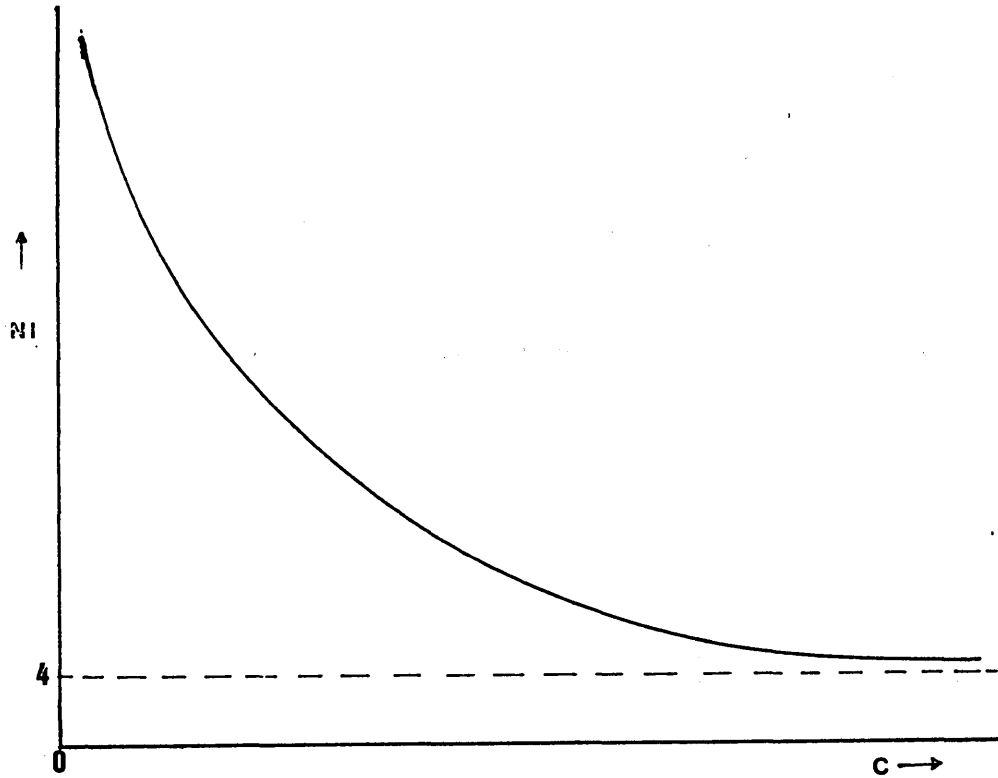


Fig. 3.5 Variation of number of finite elements (NI) with C

An alternative approach is to specify the number of finite elements (NI) required and work backwards to determine the value of C and hence the sizes of the finite elements.

3.4.4 Automatic increase in the number of collocation points

Even if the partitioning of the domain into finite elements is properly done as described in Section 3.4.3, the process of finding a

low-order polynomial to approximate the solution, fairly accurately, could be much more demanding if done manually. Moreover, the same order of polynomial may not be suitable for all the sub-regions.

In situations where the displacements of the solution profiles are not very significant following small perturbations to input variables during transient operation or gradual internal disturbances such as catalyst decay, it might not be necessary to repartition the domain. The same numbers of finite elements could be used but it might be necessary to change the order of the approximating polynomial in all or some of the finite elements.

It was therefore necessary to develop and incorporate a criterion into the algorithm which allows for automatic and sequential increase in the order of the polynomial in each finite element. This criterion was developed with the understanding that the best polynomial should lead to fast convergence of the solution within a few number of calls to the Broyden sub-routine (usually 100 calls were specified).

However, for large perturbations and for large deviations of the solution profiles it is necessary to repartition the axial domain in order to keep the order of the polynomial low.

The Algorithm

Briefly, the algorithm outlined in Sections 3.4.3 and 3.4.4 involves the following steps:

1. Apply orthogonal collocation in axial direction over the entire domain using a high order polynomial to obtain a first approximation to the solution.
2. Locate the collocation point at the maximum temperature in order to set the three boundary points at $z_{\max-1}$, $z_{\max}$ and $z_{\max+1}$. Boundary points are also set at $z = 0, 1$.

3. Calculate the slope of the temperature profile at the interior points and at $z = 0, 1$.
4. Set a low value for C , say 1.
5. Set the maximum number of finite elements required.
6. Calculate the rest of the boundary points using the criterion given in Section 3.4.3 and hence determine the number of finite elements.
7. If necessary increase the value of C by a step change of about .01 and go back to step 6 until the number of finite elements calculated is less than or equal to the set value.
8. Calculate the sizes of the finite elements and assign an initial number of interior collocation points to each finite element (say, 2 interior points).
9. Start with the first element and automatically and sequentially increase the order of the polynomial until convergence is obtained within the specified number of calls to Broyden (say 100 calls). The program is stopped if the number of interior points exceeds a specified maximum.

The algorithm makes an extensive use of Global Collocation sub-routines that are available in Villadsen & Michelsen, (1978), and Finlayson, (1980). A general routine JCOBI [(Villadsen et al. (1978)] is given to locate the zeroes of a Jacobi polynomial that are the collocation points in a normalised region. A second routine PLANAR is given by Finlayson (1980), to evaluate the discretization elements or collocation matrices A_{ij} and B_{ij} at the collocation zeros. Steps 1 and 9 involve the use of these two sub-routines while steps 2 to 8 are performed in a single sub-routine provided by the user.

3.5 SIMULATION RESULTS AND DISCUSSIONS

The algorithm described in Sections 3.4.3 and 3.4.4 was used to simulate the steady state and dynamic behaviour of the reactor. In the steady state case, the dynamic term of Eq. 3.19 was set to zero and the resulting set of non-linear algebraic Eqs. 3.18 to 3.22 were solved iteratively using Broyden's method [Broyden (1965), Paloschi & Perkins (1981)]. A fourth-order Runge-Kutta method combined with Broyden's method were used in the dynamic simulations.

As already pointed out in Chapter 2, a common problem in the operation of industrial reactors is the existence of catalyst deactivation which makes the description of the reactor's behaviour more difficult. In this reactor-reaction system, the maximum or hotspot temperature, in a typical experimental temperature profile, is normally preceded by an inflection on the curve around the reactor inlet and this could be very prominent when o-xylene inlet concentrations are high (~1 mole%) and salt bath temperatures low (see Fig. 3.6a and Chapter 6). This shape of the profile is attributed to partial deactivation of the catalyst [Lopez- Isunza (1983), Kershenbaum et al. (1984)].

The reactor was simulated with and without catalyst activity profile consideration as described in Sections 3.5.1 and 3.5.2.

3.5.1 Steady state without activity profile

The simulations here highlighted the inadequacy of the kinetic model given in Chapter 2. Since no account is given of the activity of the catalyst in the kinetics, it was impossible to model this extremely complex system. An effort to match model predictions with experimental data by "tuning" both the key heat transfer parameters (Bi_w and P_h) and the kinetic parameters (A_j 's and E_j 's) proved futile. Neither the

shape of the temperature profile nor the position of the hotspot temperature could be predicted in this fashion. However, it was relatively easy to predict the magnitude of the hotspot temperature, the outlet selectivity to phthalic anhydride and o-xylene concentration to within a few degrees by adjusting only the values of the pre-exponential factors. The model predictions compared with typical experimental profiles obtained under the same operating conditions are shown in Fig. 3.6. In this case, the value of the pre-exponential factor of each reaction rate equation was increased by a factor of 4, keeping the activity of the catalyst uniform throughout the fixed-bed reactor.

Despite the limitations of the model, it is interesting to find out how the algorithm works. Table B.4.1a (Appendix B.4) shows the number and size of each finite element, the number of interior collocation points used in each element and the total computation time as a function of the total number of finite elements specified. It was observed that, with just four finite elements, the solution did not converge at the last element even when up to 14 interior points were used. The reason is partly due to the size of the element which is relatively large ($\sim 69\%$ of the entire domain) and partly because of the existence of a temperature difference of 62°C per axial distance of about 40 cm. By specifying 6 finite elements, the large element was broken into three smaller ones and this resulted in convergence of the solution in all the finite elements with relatively low-order polynomials (4 to 6 interior points when initially 4 interior points were set in all the elements). With 8 finite elements, there was a further reduction in size of some of the elements with convergence obtained using the minimum number of interior points. The computation time also reduced by about 50%. The computation time passed through a

minimum with further increase in the number of finite elements specified. As shown in Fig. 3.6, the solution was independent of the number of finite elements in so far as convergence was attained.

To take full advantage of fast convergence with increase in the number of finite elements, the initial number of interior points set was reduced to 2. This resulted in even further reduction in computation times as shown in Table B.4.1b. No significant difference between the results obtained using 4 interior points and 2 interior points, in all the finite elements, was observed.

3.5.2 Steady state with activity profile

In order to reflect the effect of catalyst deactivation on the reactor model, an activity parameter which varied axially along the reactor length was incorporated into the kinetic model. The activity of the catalyst was arbitrarily made to increase linearly from zero at the reactor inlet to about 0.065 at a normalized axial distance of 0.25 with a jump, at that point, to 1.0 for the remaining part of the catalytic bed. With the activity profile incorporated, both the shape of the temperature profile and the magnitude of the hotspot were simulated to within a few degrees though the position of the hotspot temperature was still 10 cm away downstream from that observed experimentally. The experimental value for the conversion of o-xylene at the outlet of the reactor was about 99.95% with selectivity to phthalic anhydride between 72 to 78. The simulated values were 100% and 80 to 81 respectively. The model predictions are compared with typical experimental profiles obtained under the same operating conditions in Fig. 3.7, and it is found that they are very close. There is no doubt that these results can further be improved if an appropriate activity profile is fitted.

Table B.4.2 (Appendix B.4) shows the number and size of the finite elements, the number of interior collocation points used in each element and the total computation time when the activity profile is incorporated. This time, with four finite elements specified, the integration did not even proceed past the first finite element; no convergence was achieved even when 14 interior points were used. Although, specifying a higher number of finite elements led to convergence of the solution in all the elements with relatively low-order polynomials used and a reduction in computation time, especially when the number was increased to 10, the solution around the vicinity of the discontinuity was questionable. Fig. 3.7a shows a slight drop in temperature around the discontinuity which, perhaps, could be attributed to ill-conditioning of the problem in that region. A slight increase in the o-xylene concentration around the region is shown in Fig. 3.7b.

In order to eliminate the ongoing problem, an additional boundary point (Bpt) or spline point [Pedersen & Tanoff (1982)] was placed at the point of discontinuity of the activity profile. The description of the finite elements, including the computation times, is presented in Tables B.4.3a and B.4.3b for the two cases when the initial number of interior points in each finite element was set to 4 and 2 respectively. Again, it is seen that the computation time passes through a minimum with increase in the number of finite elements. The minimum computation time was obtained when the sizes of the finite elements were such that the minimum number of interior points was used in every sub-region. Figs. 3.8a to 3.8c show the temperature and concentration (for o-xylene and phthalic anhydride) profiles compared with typical experi-

mental profiles. The results are exactly the same as before except that this time the profiles are smooth around the point of discontinuity of the activity profile.

3.5.3 Dynamic simulation with constant activity profile

With the activity profile introduced in the previous section the sensitivity of the model with respect to step changes in some of the input variables (say, salt bath temperature and inlet o-xylene concentration) was investigated. This exercise was also aimed at testing the robustness of the algorithm in coping with small and large displacements of the temperature and concentration profiles with time.

It was observed that the model was not very sensitive to small perturbations of the salt bath temperature and o-xylene inlet concentration; only a marginal displacement of the solution profiles (temperature and concentration profiles) was observed, with the result that convergence of the solution at each time step was attained using virtually the same number of interior points as in the case of the steady state. Even for large perturbations, the displacement of the position of the hotspot temperature with time was not very significant although a proportional increase in its magnitude with respect to the degree of perturbation was noticed. Fig. 3.9 shows the temperature and concentration profiles obtained by applying a 10°C step increase in the salt bath temperature, and the number of interior collocation points used at the various time intervals compared with those initially employed in the steady state simulation are presented in Table B.4.4. It can be observed that despite the fact that the magnitude of the hotspot temperature increases by about 10°C in 120 sec, there is only a slight

increase in the number of interior points in some of the finite elements. The number of interior points in the majority of finite elements does not change with time.

3.5.4 Dynamic simulation with time-varying catalyst activity profile

Dynamic experiments carried out by Lopez-Isunza (1983) and in this work (cf Chapter 6) have shown that the reactor presents a strong parametric sensitivity to feed concentration and salt bath temperature. Lopez-Isunza (1983) concluded that this type of behaviour is due to the oxidation-reduction or "redox" dynamics of the catalyst activity profile and that catalyst re-oxidation during transient period is a strong function of the local temperature and therefore of axial dispersion of heat. A good dynamic model must therefore allow for the variation of catalyst activity with time as well as with axial position.

In order to simulate an increase in catalyst activity due to an increase in the rate of catalyst re-oxidation (or a reduction of catalyst activity due to partial deactivation) the activity parameter, α_{ij} $= \alpha(t_i, z_j)$, was allowed to vary at regular time intervals t_i , between the limits $0 < \alpha_{ij} < 1$.

Fig. 5.10 shows the predicted dynamic response to a 10°C step increase in the salt bath temperature when 10 finite elements were specified in the steady state simulation. It can be observed that there is a significant displacement of profiles with time and that the response is in qualitative agreement with the experimental profiles (cf Chapter 6 where it was noted that the hotspot moved towards the upstream end of the reactor when a ramp increase in the salt bath temperature of 1°C was applied). In this case, the activity (α) at any given point within the inlet region where $0 < \alpha < 1$ was made to

increase at a rate of 0.001 per a time step of ~ 12 secs. Table B.4.5 (Appendix B.4) compares the number of interior collocation points used at the various time intervals and at steady state, for the various number of finite elements initially specified. It can be seen that the algorithm still converges with relatively a small number of interior points in each finite element. In most finite elements, there is no change in the number of interior points at all.

3.5.5. Comments on the accuracy of the solution method

No error analysis was performed to verify the accuracy of the results since it was not possible to obtain an analytical solution of the equations. However, from Figs 3.6 to 3.8c it is found that the results are the same no matter the number of finite elements used so far as there is convergence. To ascertain the exact location of the maximum temperature and hence further verify the accuracy of the method, the partitioning of the axial domain into finite elements was done manually inserting boundary points away from the hotspot location. From Fig. 3.11 it is seen that there is no difference between the solution obtained by selecting the elements manually or automatically.

It was also found that the solution was independent of the number of interior collocation points used so far as convergence was achieved, although a very low number might lead to poor interpolation of results between collocation points. This is evident in Figs. 3.8a and 3.11 where a 'blip' on the temperature profile around the hotspot region is indicated for the case when the solution converged with only 2 interior points in each finite element.

The computation times reported were from a CDC Cyber 855 computer system. The computer code was in single precision and the error criterion for convergence was set at 1.0×10^{-10} .

3.6 SUMMARY

The method of orthogonal collocation on finite elements originally developed and used for solving two-point boundary-value problems [Carey & Finlayson (1975), Pederson & Tanoff (1982)] has been modified and extended for use in solving initial-value problems which exhibit steep solution profiles.

By applying radial collocation and assuming negligible axial dispersion of heat and mass in the pseudo-homogeneous model, the two-dimensional boundary-value problem was reduced to a one-dimensional initial-value problem.

From a first approximation of the solution using a fairly high-order orthogonal polynomial the reactor axial domain was partitioned into subregions or finite elements, automatically, by comparing the gradient of the temperature profile at adjacent collocation points.

Each finite element was considered independently in order to apply axial collocation within the normalised distance and the resulting system of first order differential equations were integrated with initial conditions taken as the output values of the previous element, or in the case of the first element the reactor inlet conditions.

The method allows for small size elements in which the solution can be approximated using low-order polynomials with a reduction in computation time, which passes through a minimum, when the number of finite elements is increased.

By allowing for sequential and automatic increase in the order of the approximating polynomial in each element, the method can be used repeatedly without axial repartition for small perturbations to process variables or small axial displacements of the solution profiles during the dynamic behaviour of the system.

However, for large perturbations or large displacements of the solution profiles it might be necessary to redive the whole domain in order to keep low both the order of the approximating polynomial and the computation time.

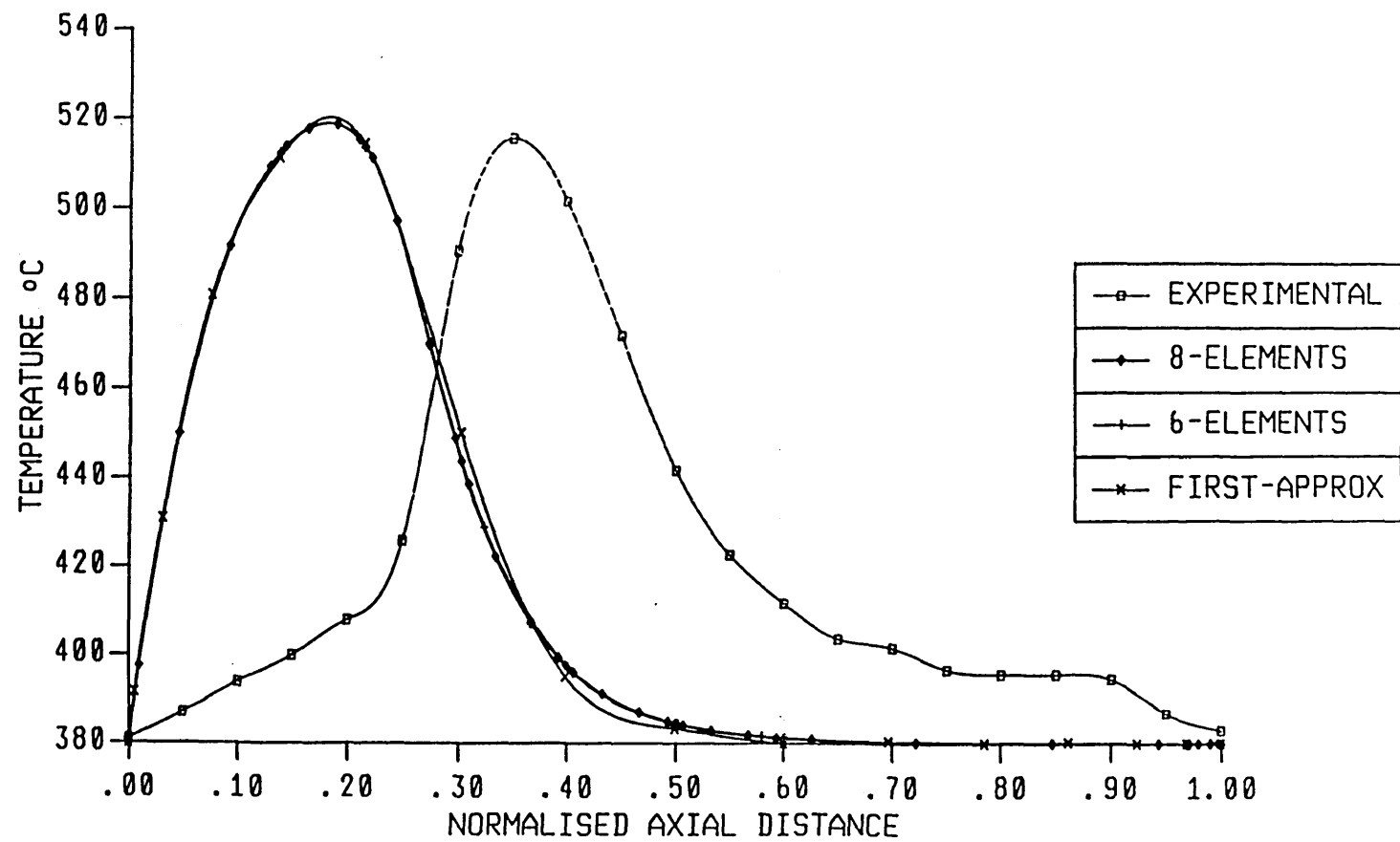


Fig. 3.6a Simulated steady state temperature profiles obtained by assuming spatially-uniform catalyst activity compared with a typical experimental profile.

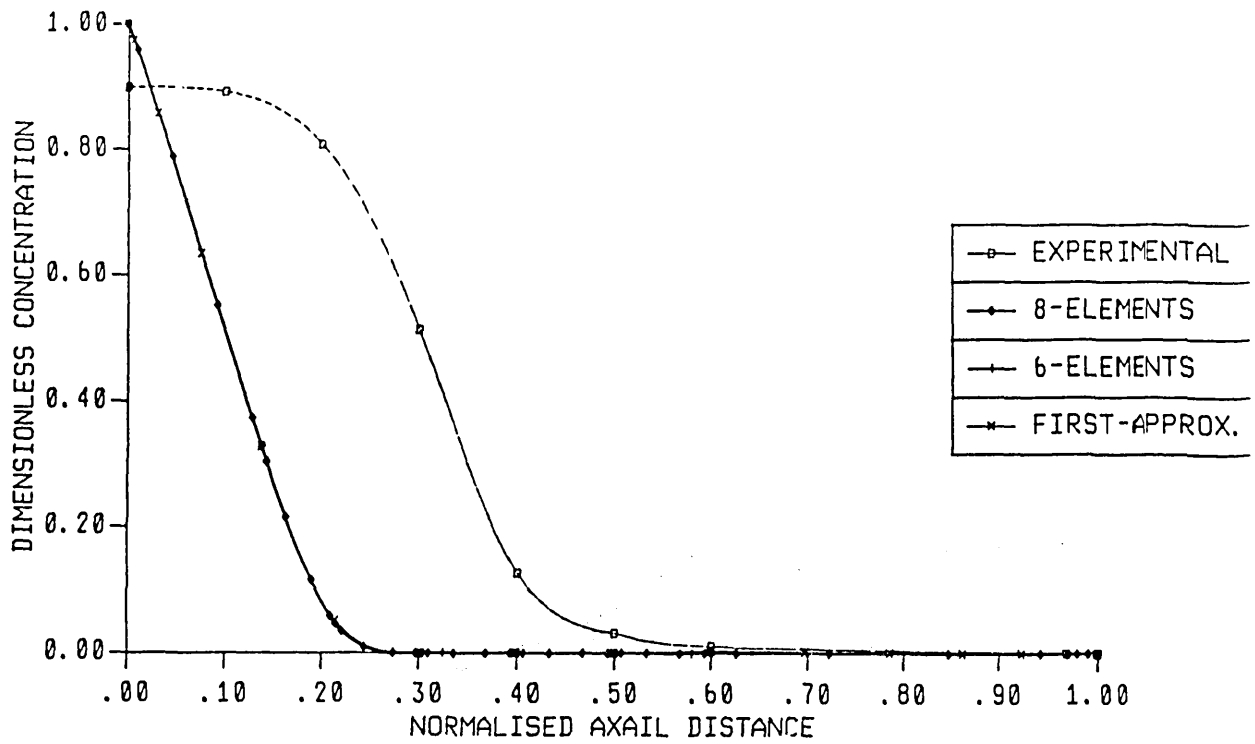


Fig. 3.6b O-xylene concentration profiles corresponding to the temperature profiles in fig. 3.6a

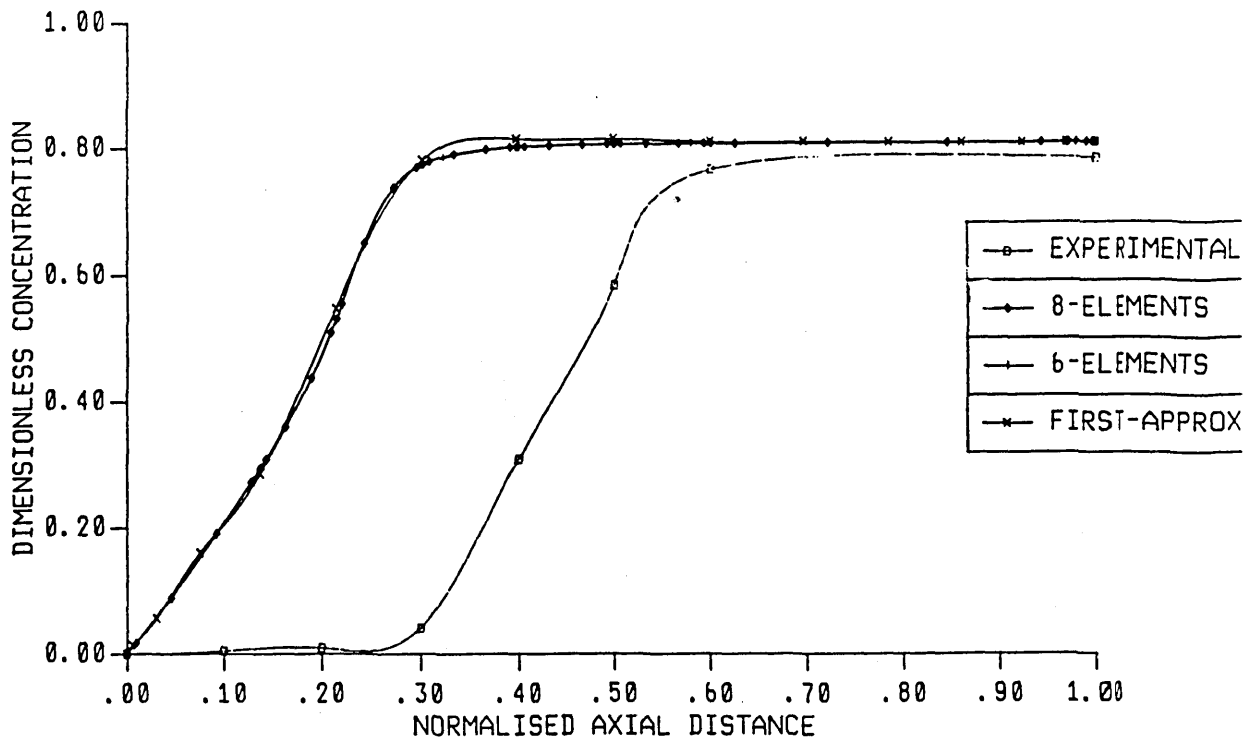


Fig. 3.6c Phthalic anhydride concentration profiles corresponding to the temperature profiles in fig. 3.6a

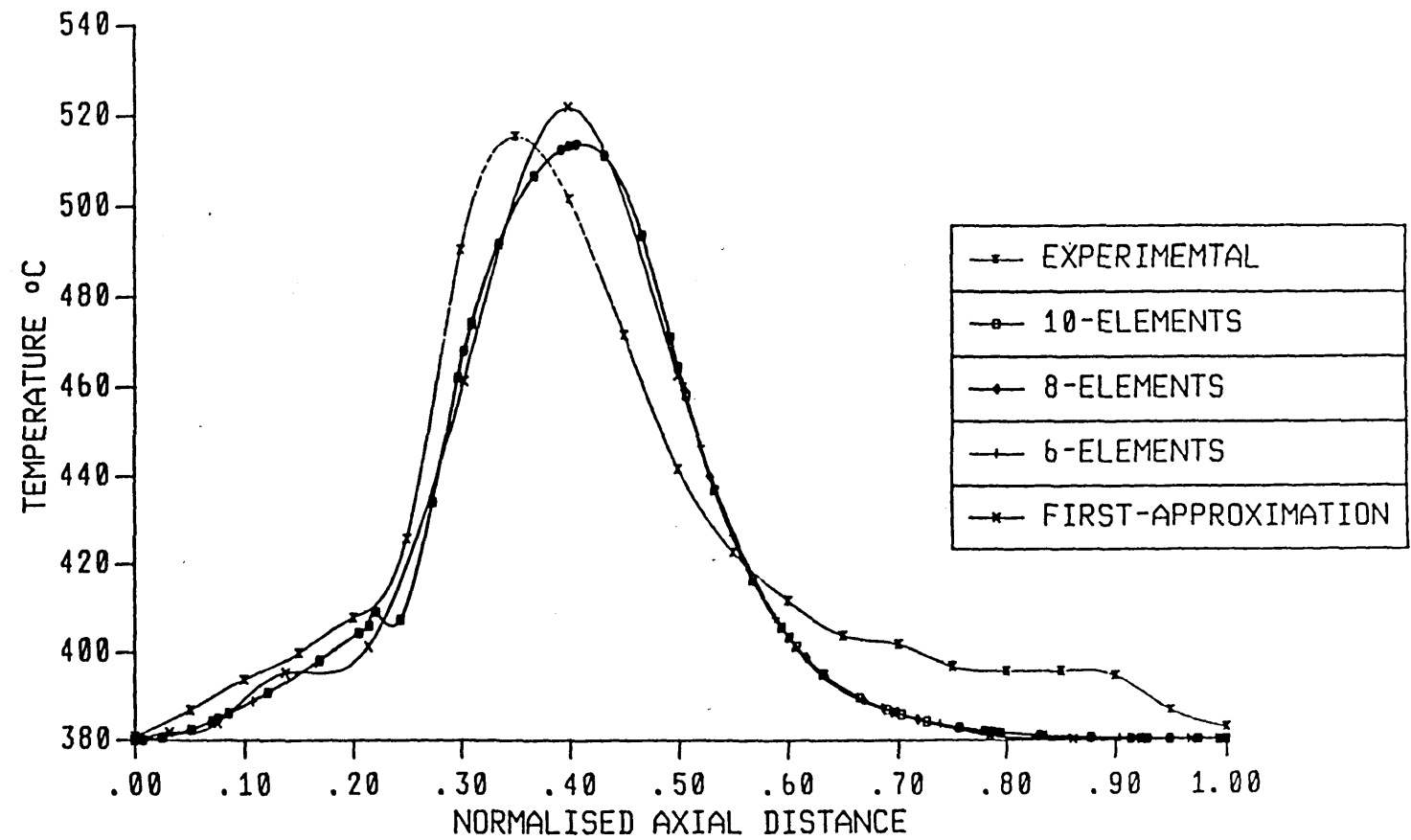


Fig. 3.7a Simulated steady state temperature profiles with spatially-varying catalyst activity profile compared with a typical experimental profile

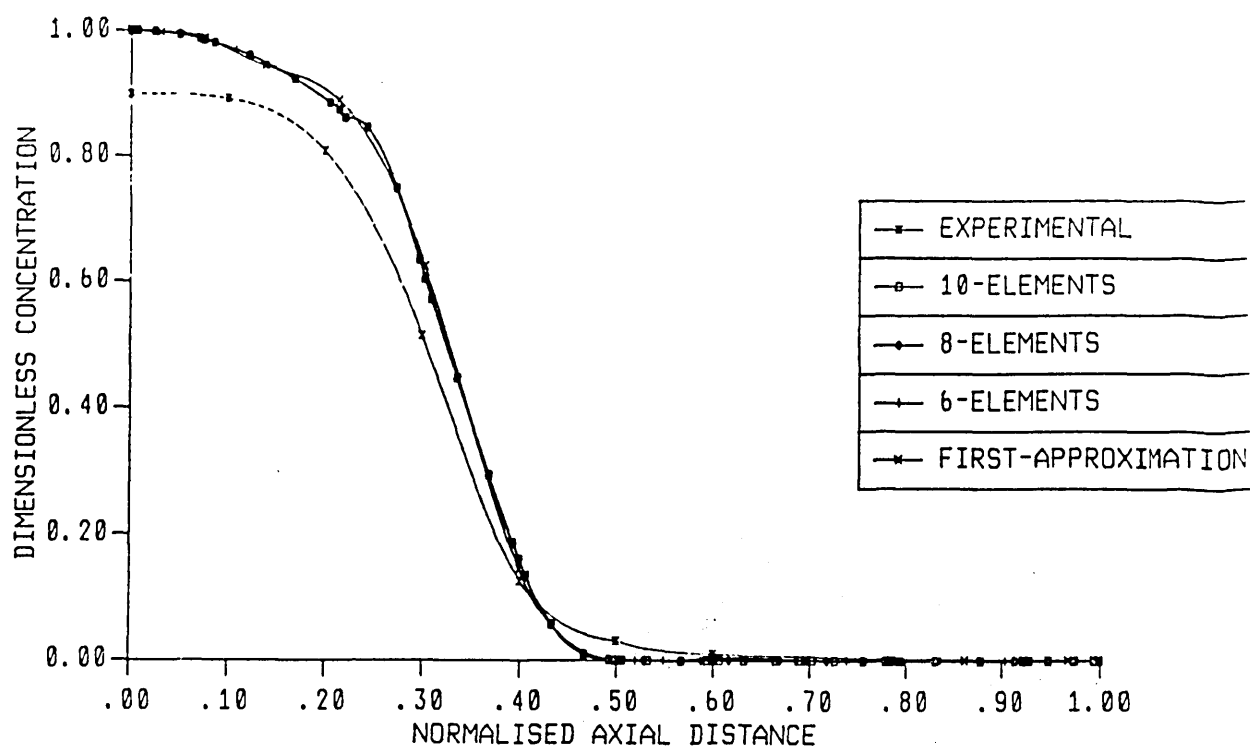


Fig. 3.7b O-xylene concentration profiles corresponding to the temperature profiles in fig 3.7a.

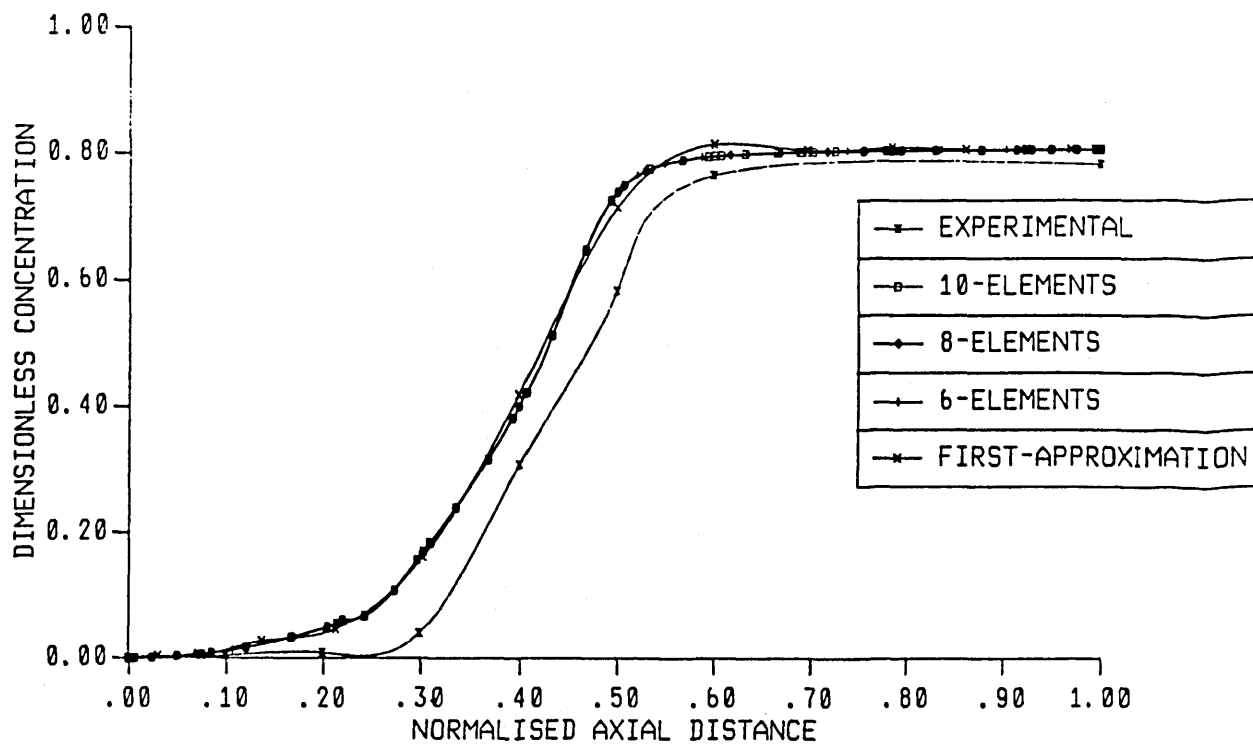


Fig. 3.7c Phthalic anhydride concentration profiles corresponding to the temperature profiles in fig. 3.7a.

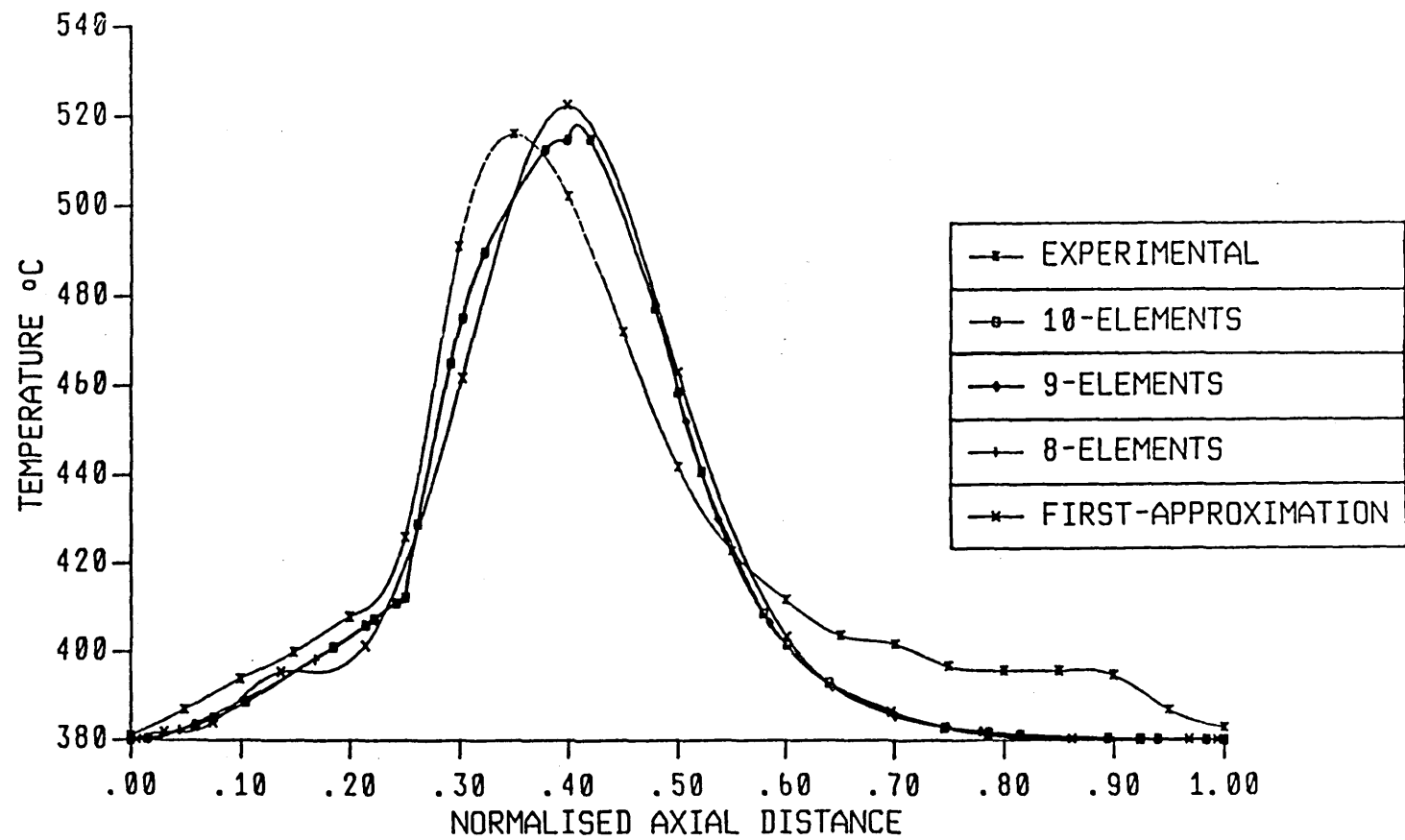


Fig. 3.8a Simulated steady state temperature profiles, with an additional spline point inserted at the point of discontinuity of the activity profile, compared with a typical experimental profile.

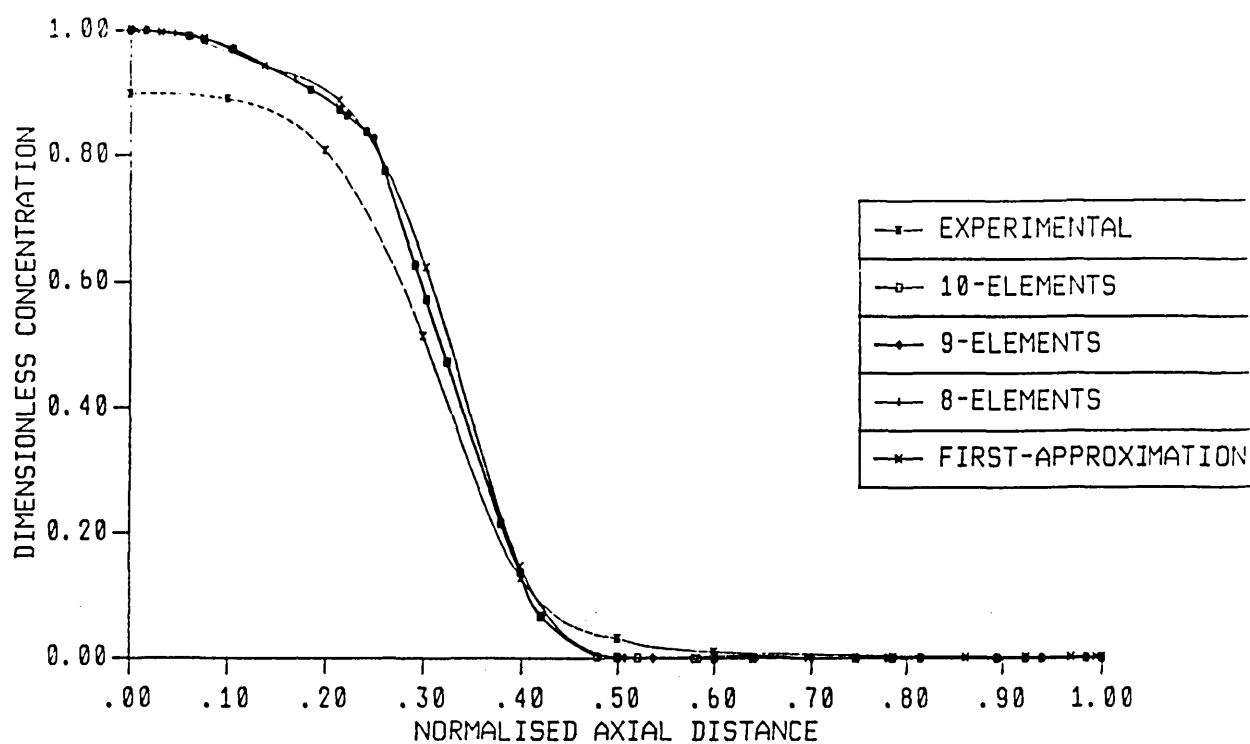


Fig. 3.8b O-xylene concentration profiles corresponding to the temperature profiles in fig. 3.8a

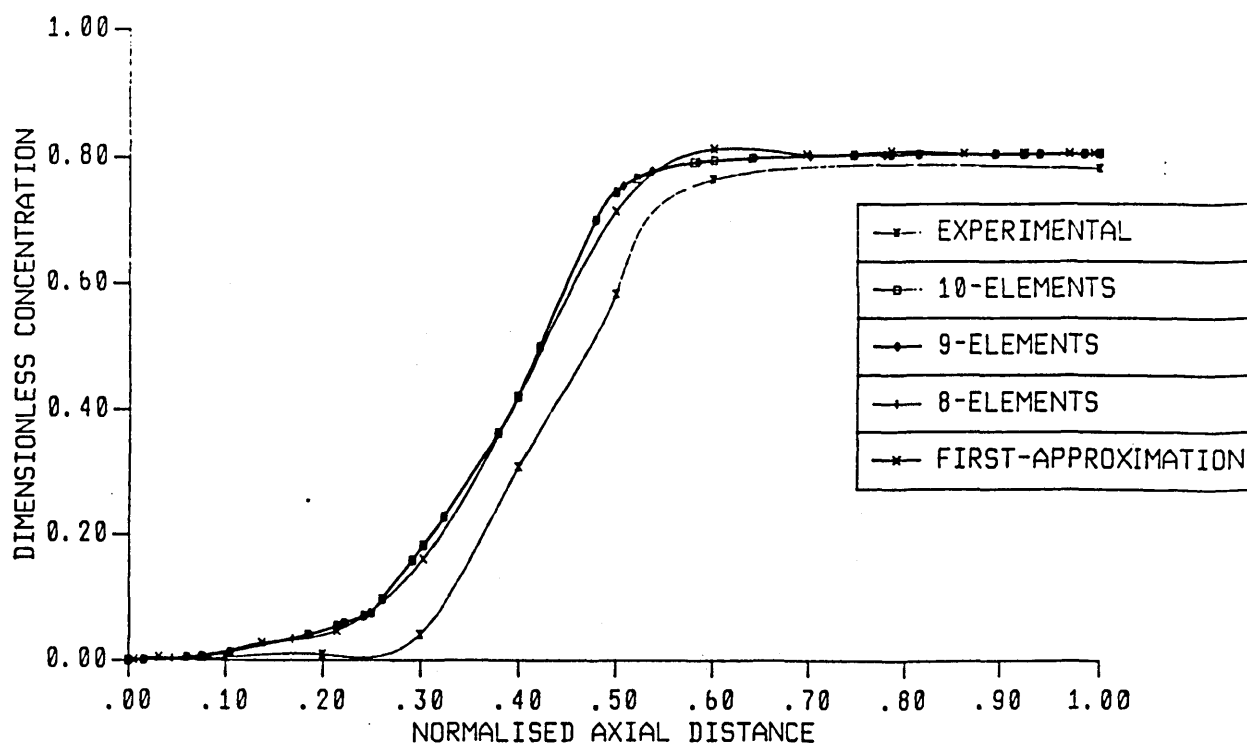


Fig. 3.8c Phthalic anhydride concentration profiles corresponding to the temperature profiles in fig. 3.8a.

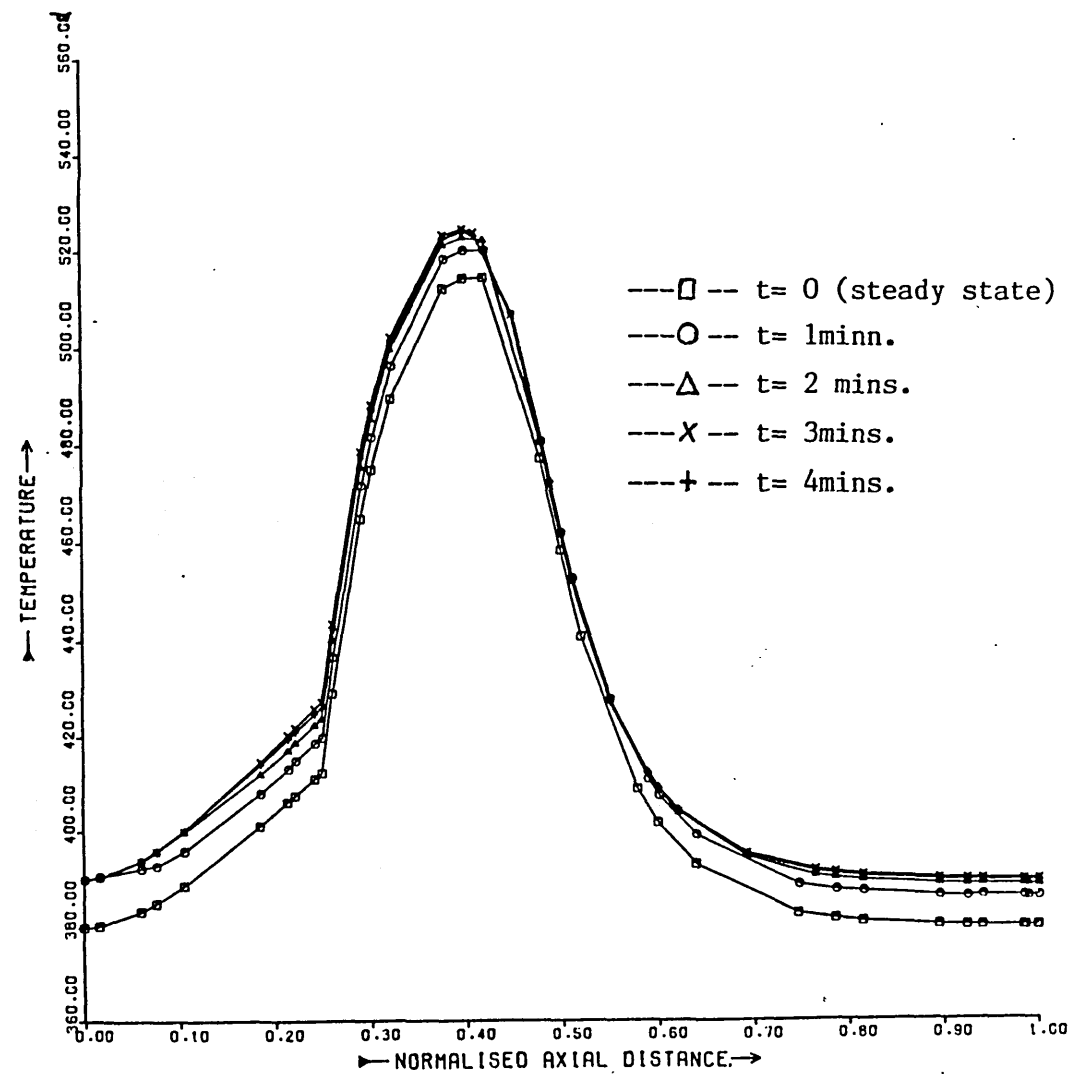


Fig. 3.9a Dynamic simulation temperature profiles for a 10°C step increase in the salt bath temperature and time-constant activity profile.

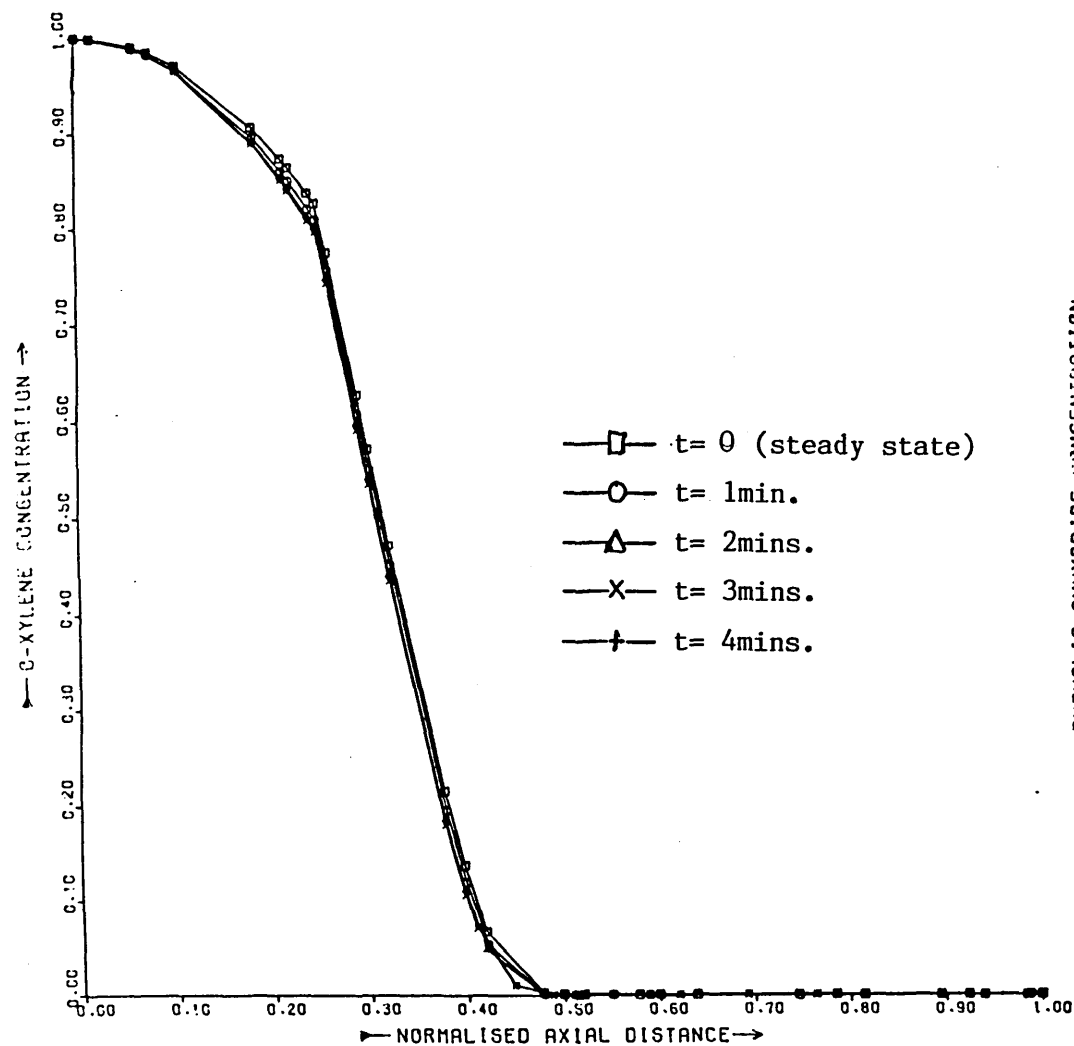


Fig. 3.9b O-xylene concentration profiles corresponding to the temperature profiles in fig. 3.9a

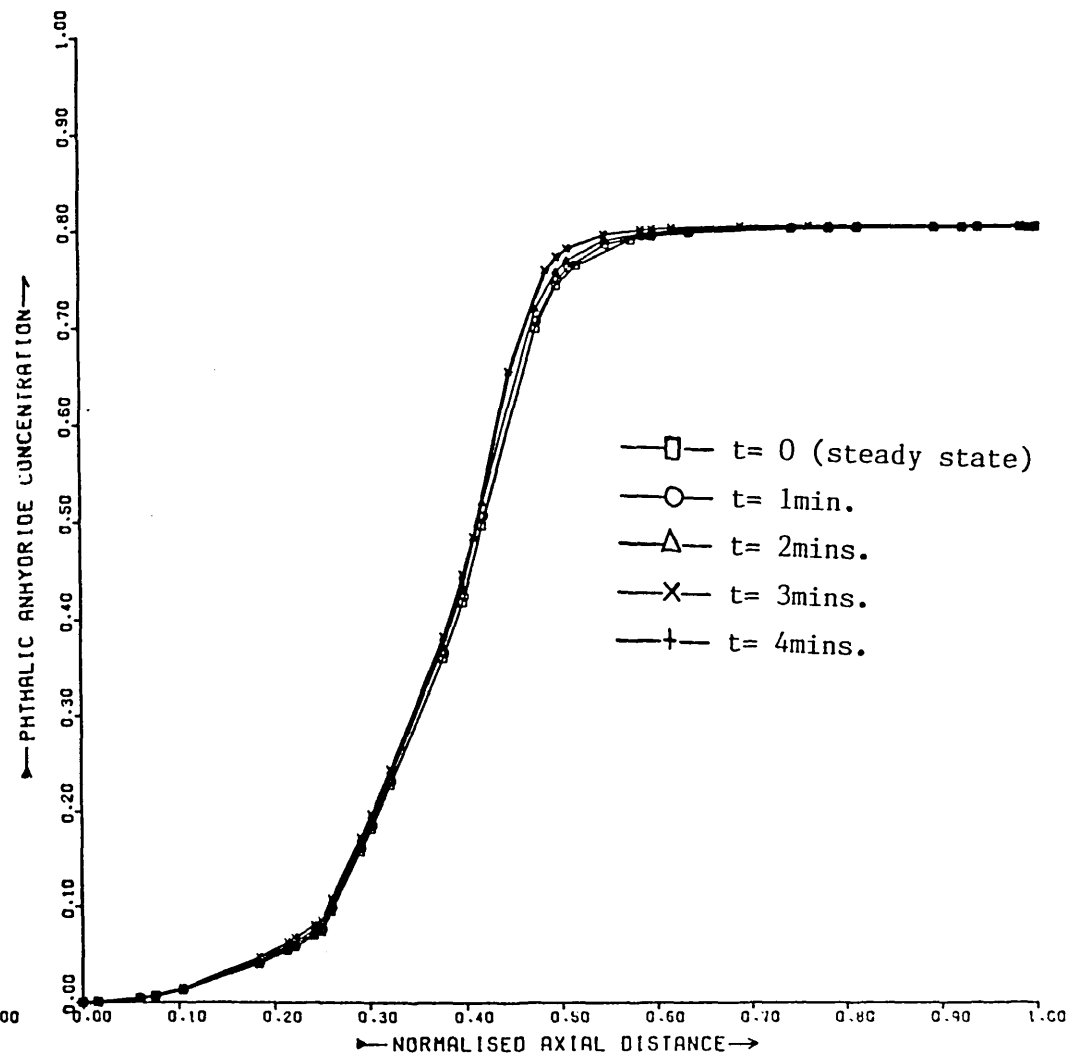


Fig. 3.9c Phthalic anhydride concentration profiles corresponding to the temperature profiles in fig. 3.9a.

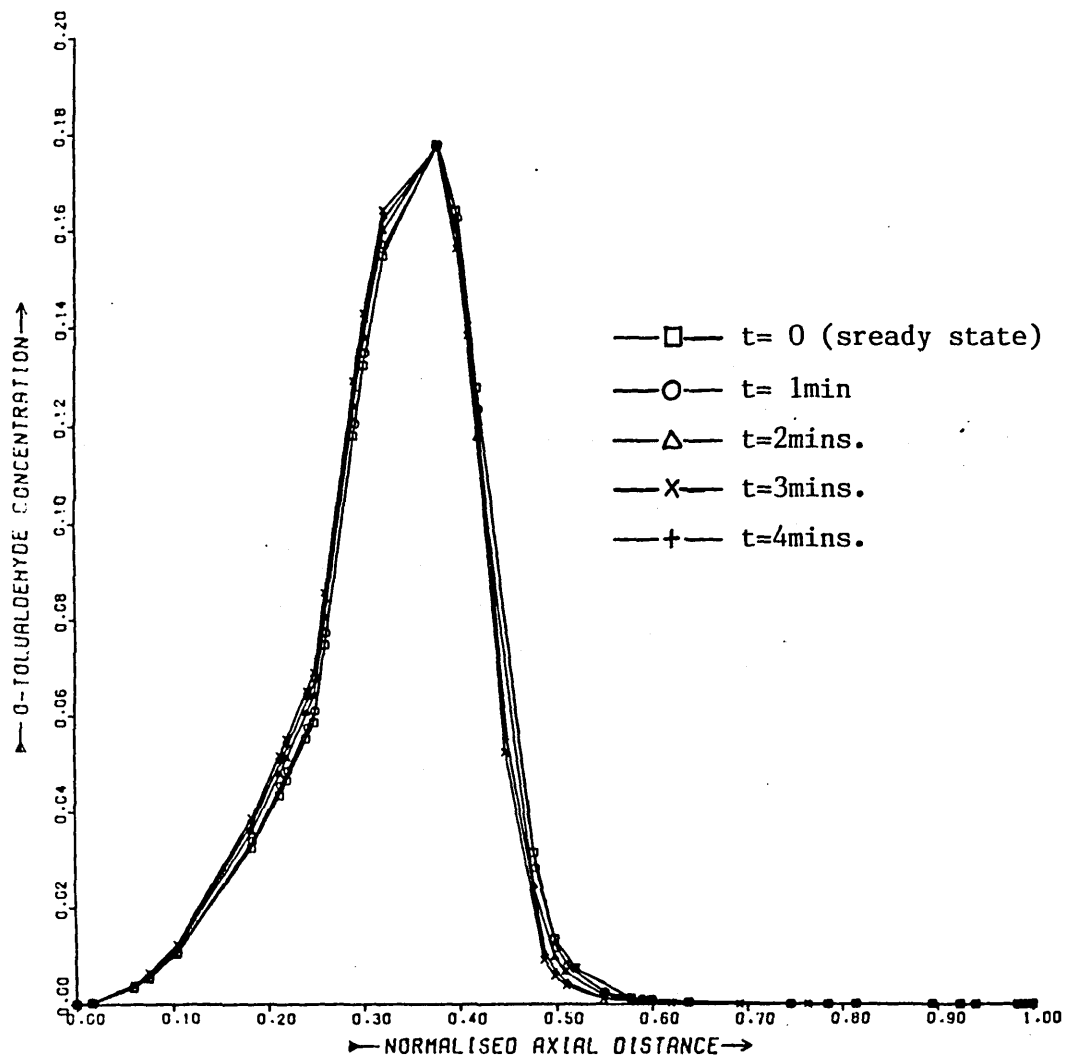


Fig. 3.9d O-tolualdehyde concentration profiles corresponding to the temperature profiles in fig. 3.9a

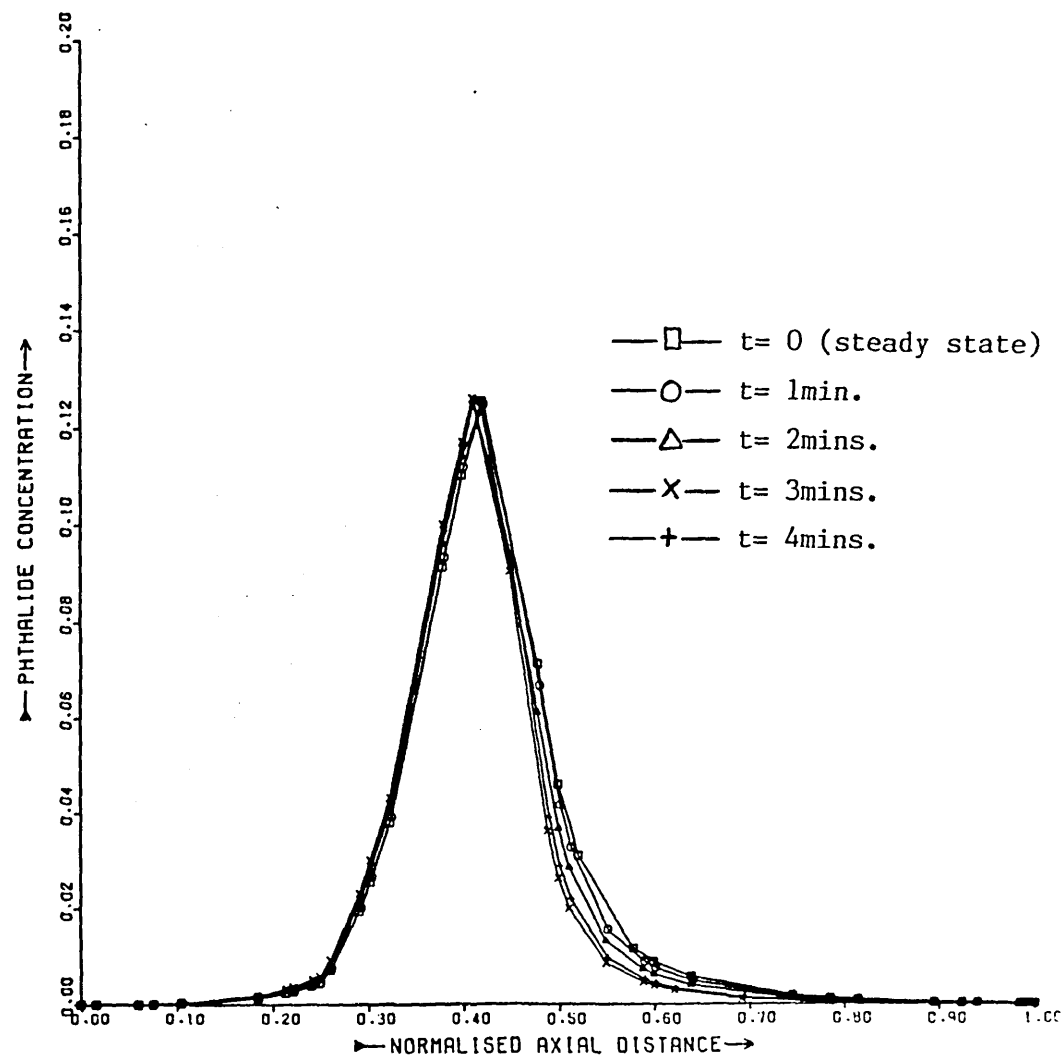


Fig. 3.9e Phthalide concentration profiles corresponding to the temperature profiles in fig. 3.9a

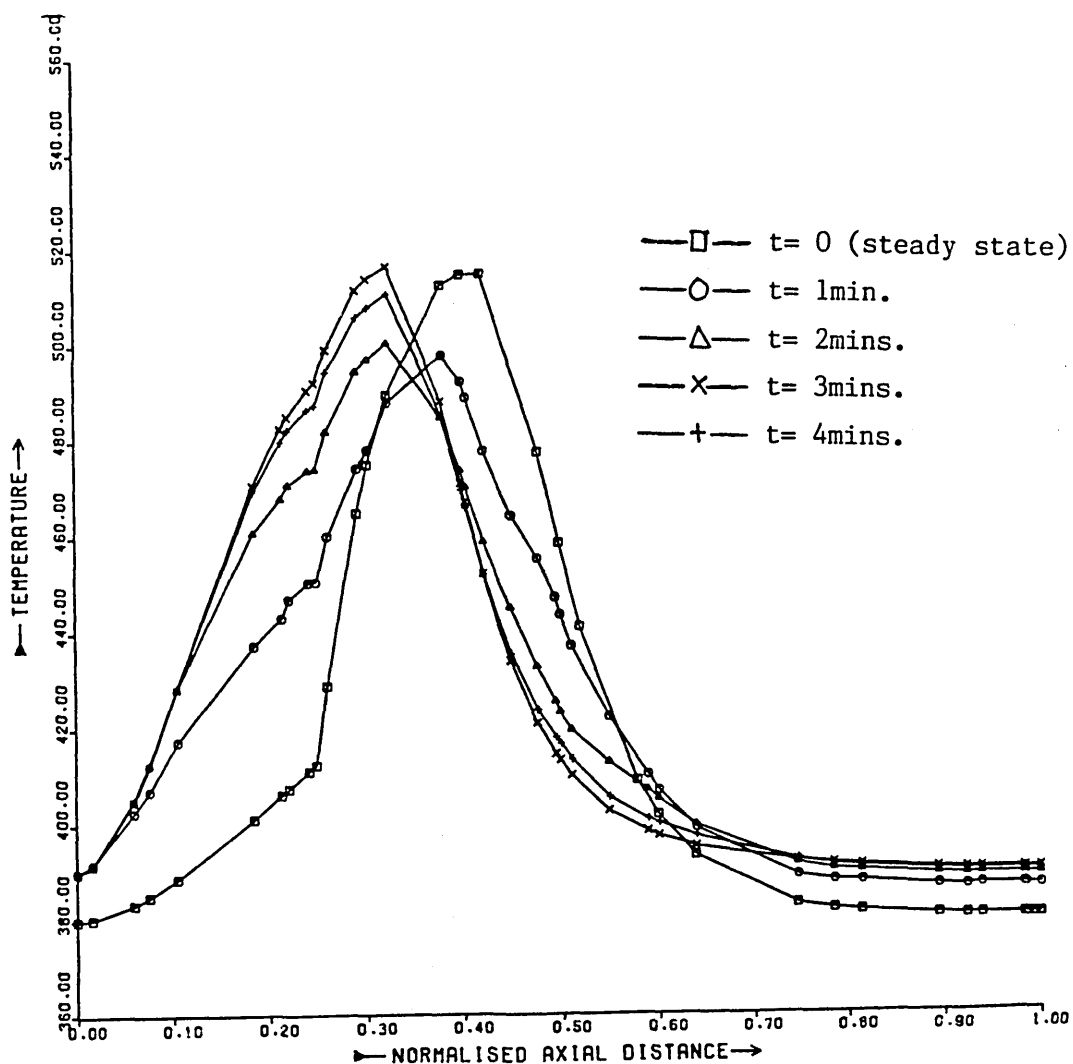


Fig. 3.10a Dynamic simulation temperature profiles for a 10°C step increase in the salt bath temperature and time-varying activity profile.

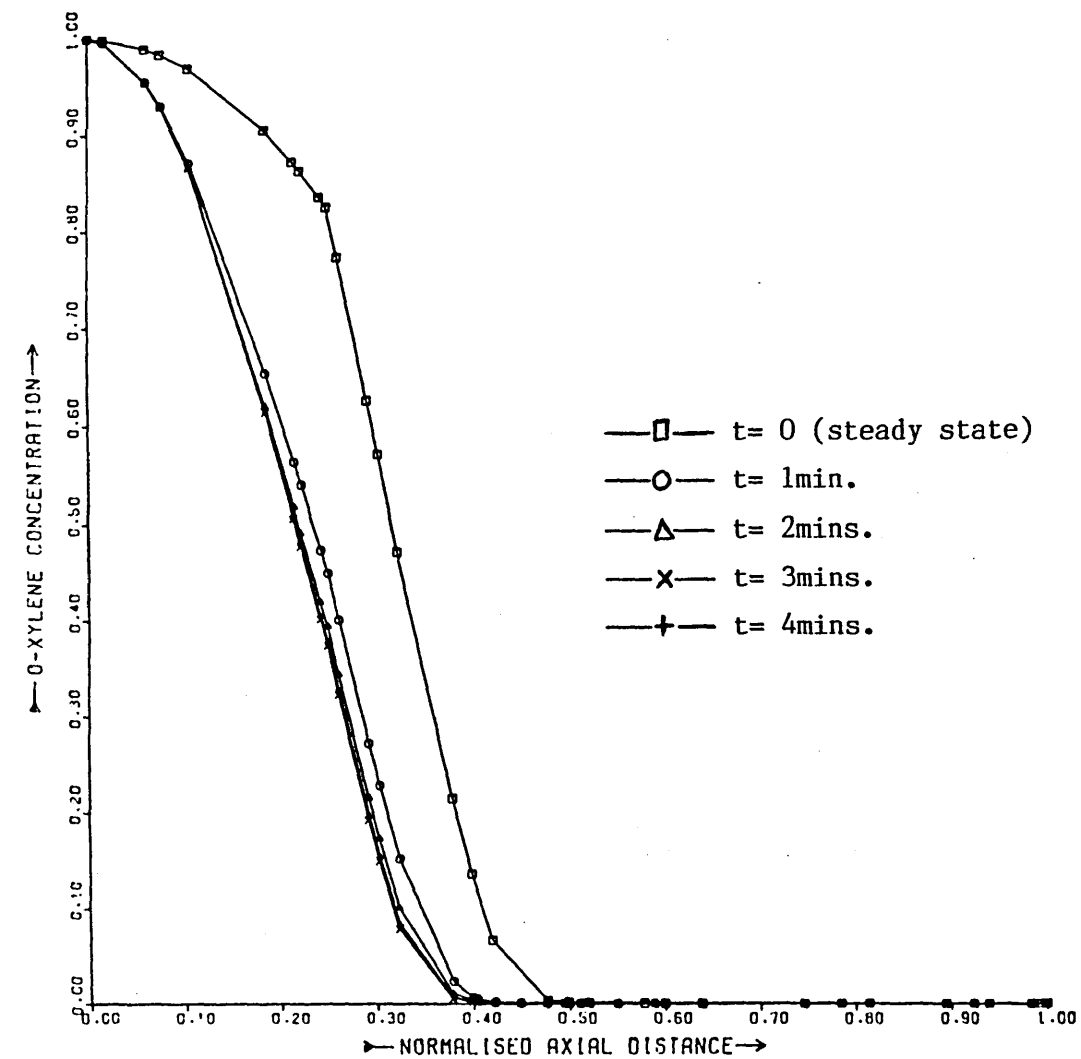


Fig. 3.10b O-xylene concentration profiles corresponding to the temperature profiles in fig. 3.10a

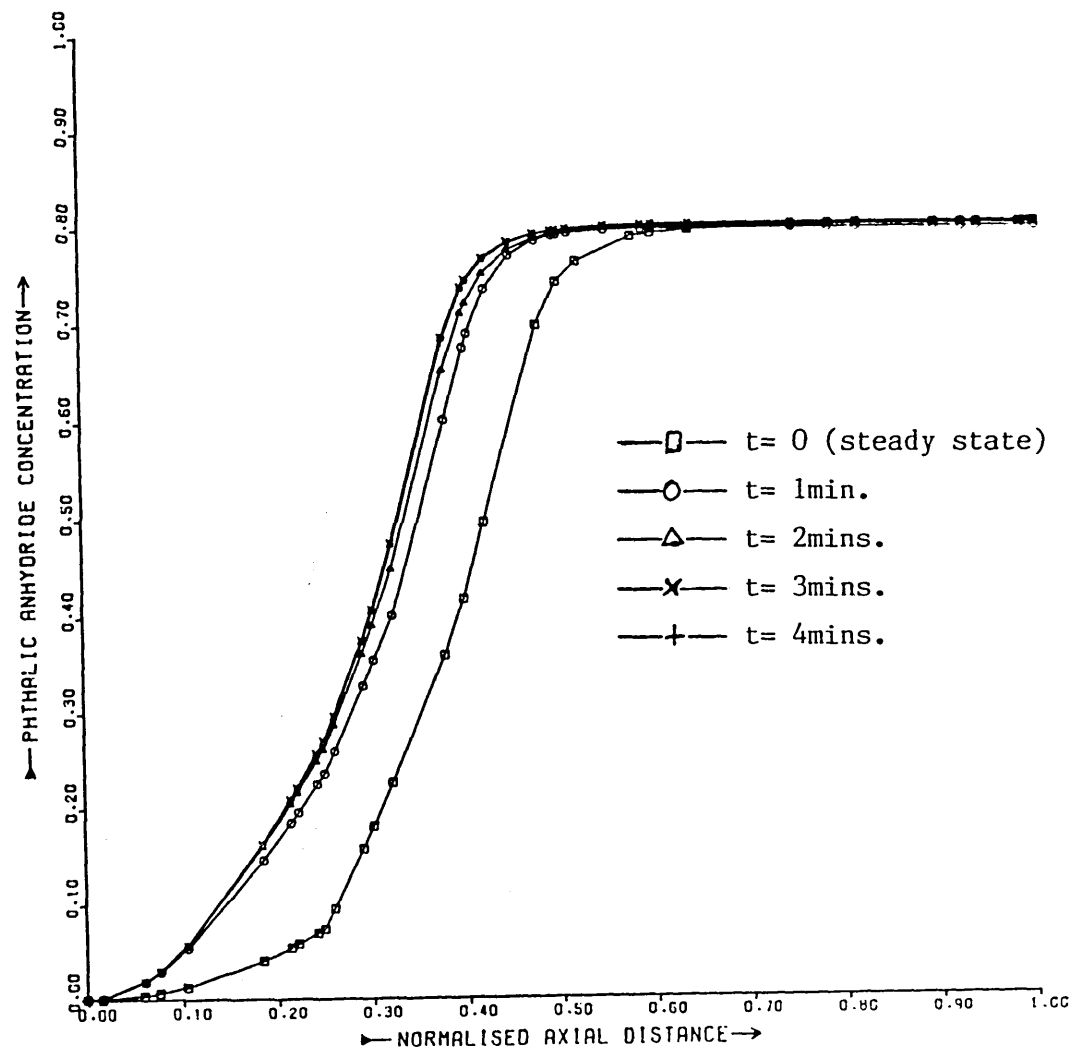


Fig. 3.10c Phthalic anhydride concentration profiles corresponding to the temperature profiles in fig. 3.10a.

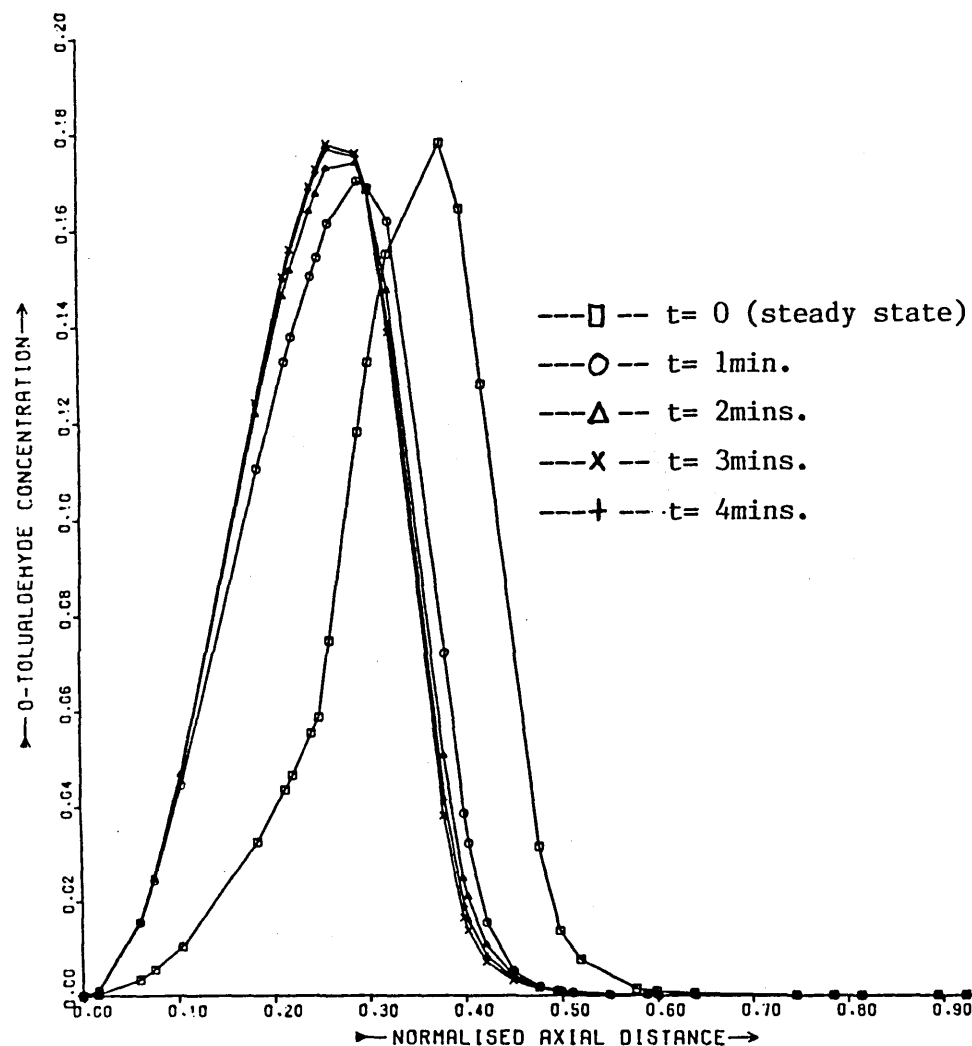


Fig. 3.10d 0-tolualdehyde concentration profiles corresponding to the temperature profiles in fig. 3.10a.

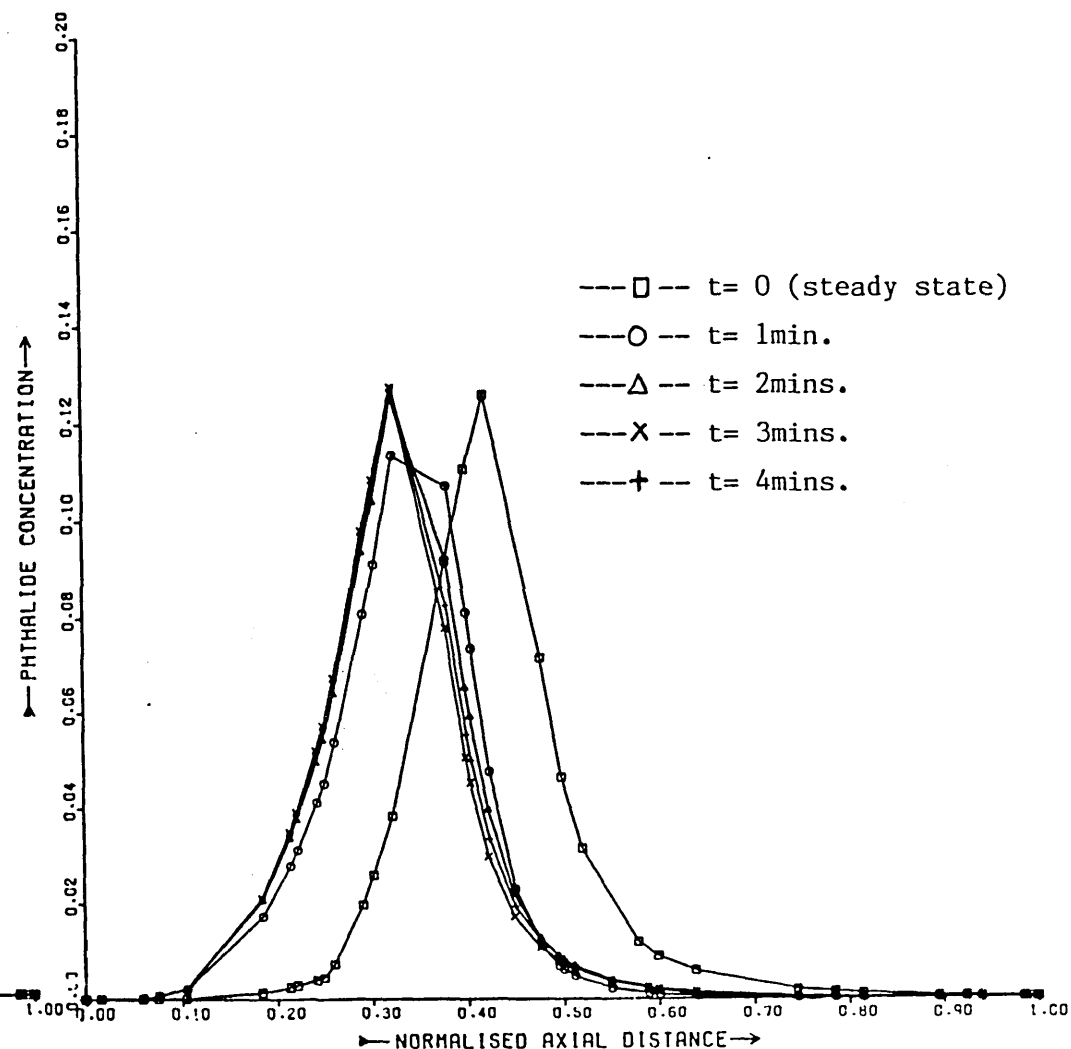


Fig. 3.10e Phthalide concentration profiles corresponding to the temperature profiles in fig. 3.10a.

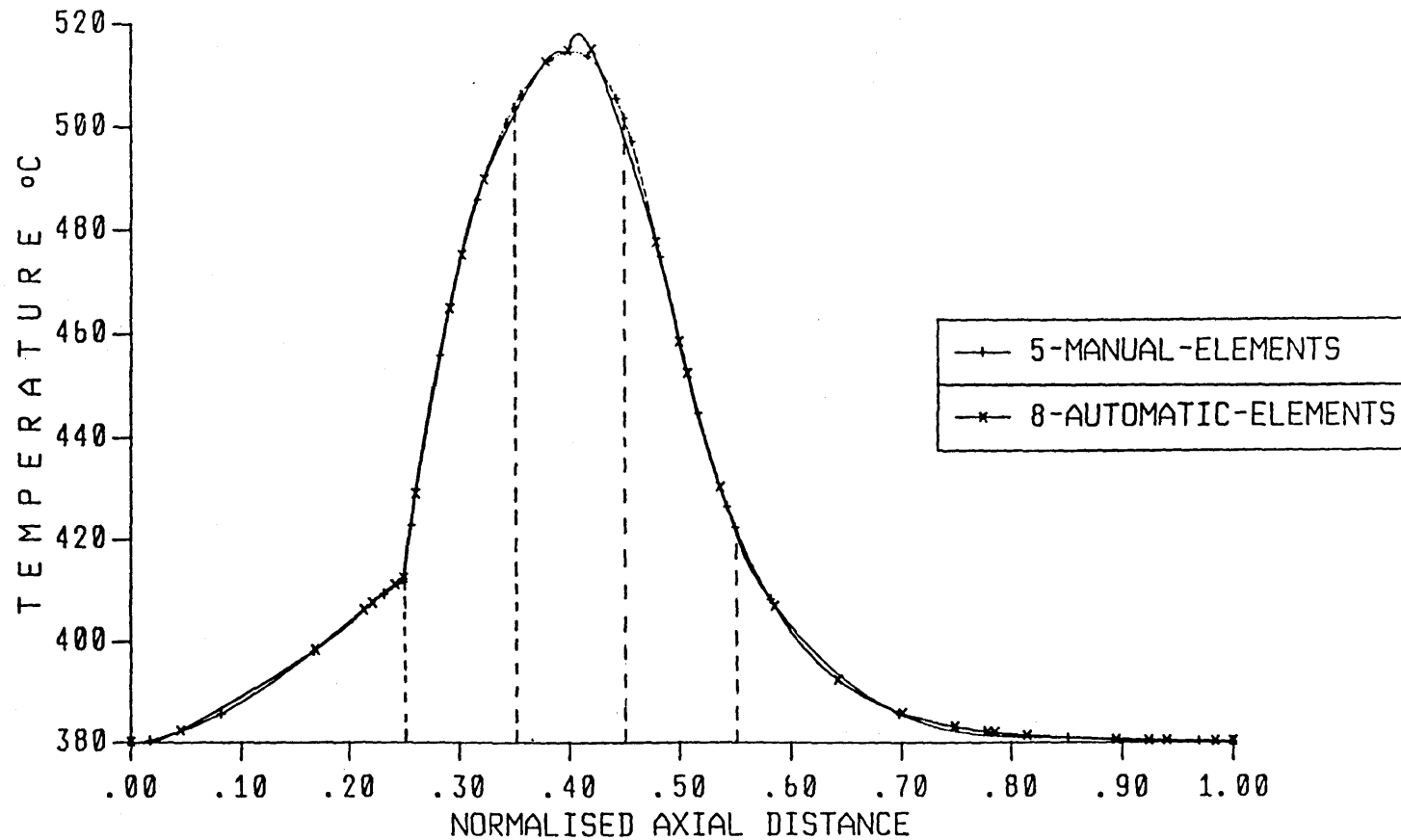


Fig. 3.11 Comparison of the solution of the model using 5-manually and 8-automatically selected finite elements. The broken vertical lines depict the boundaries of the manually selected elements.

CHAPTER FOUR

4.0 THE EXPERIMENTAL SYSTEM AND OPERATIONAL PROCEDURE

This Chapter deals with the experimental system and the operational procedure. A description of the pilot plant, together with the reactor and catalyst characteristics, is presented in Section 4.1. Temperature and concentration measurements are discussed in Section 4.2. Measurements Limitations and Catalyst and Chemicals are presented in Section 4.3 and 4.4 respectively. An outline of the experimental program is given in Section 4.5 while the experimental procedure is presented in Section 4.6.

Finally, a brief description of an auxillary catalytic reactor (combustion tube), incorporated into the experimental system for total oxidation of the reaction products, is given in Section 4.7.

4.1 Description of the pilot plant

The schematic diagram of the pilot plant is as shown in Fig. 4.1, the reactor and catalyst characteristics together with operational conditions are presented in Table 4.1.

Liquid o-xylene was fed from a feed tank by a metering pump to the required flowrate and compressed dry air adjusted to the required volumetric flowrate (Nm^3/hr) using a rotameter. The reactant mixture, consisting normally of ~1 mole% o-xylene in air, was raised to a temperature of 105°C - 110°C by a vaporiser located upstream of the reactor, before entering the top of the bed. The reactor is a single tube of 25 mm internal diameter, 2.5 mm wall thickness and 3.35 m long. 2.6 m of the length of the tube is packed with $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst pellets.

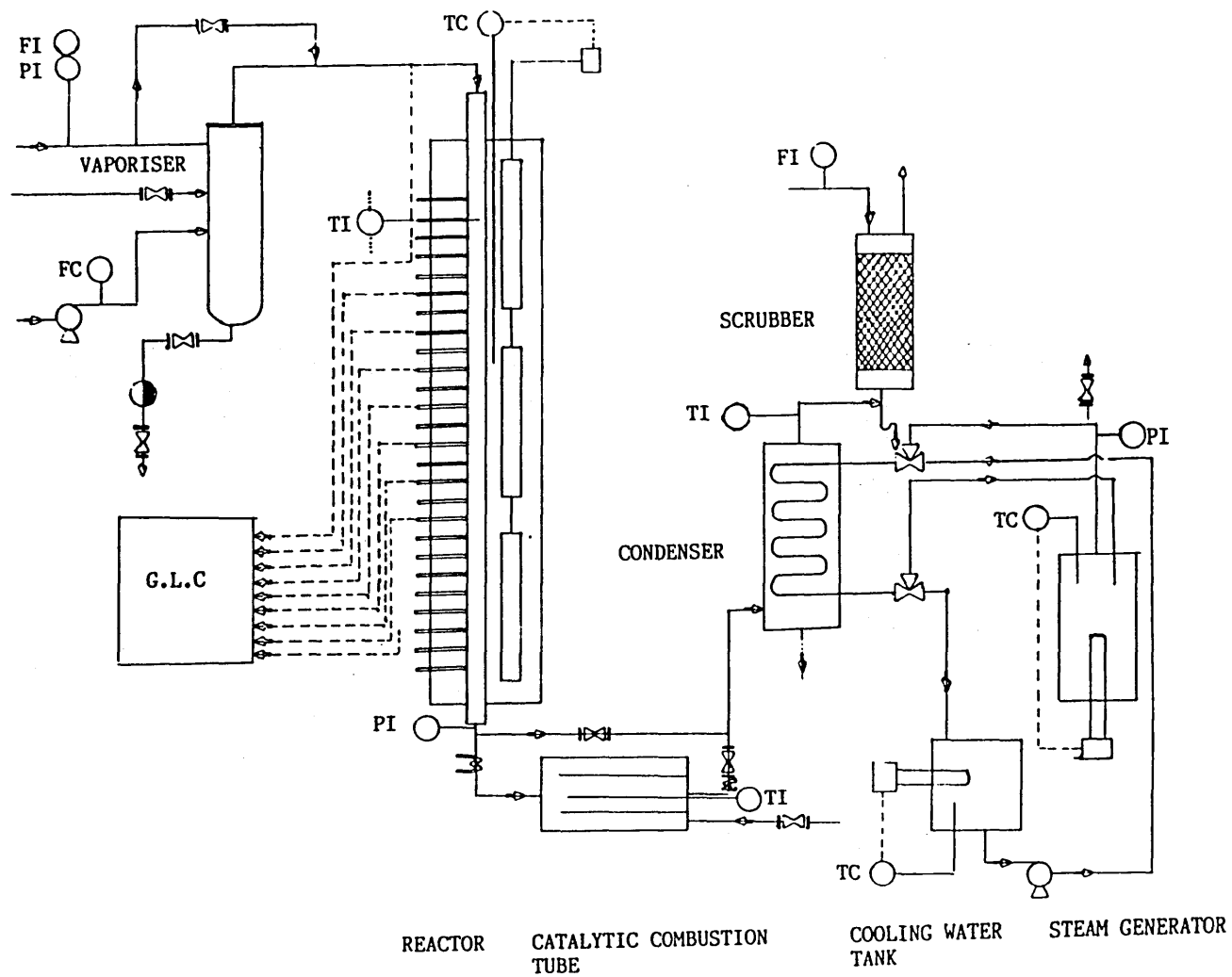


Fig. 4.1 Schematic diagram of the pilot plant.

TABLE 4.1

Reactor and Catalyst CharacteristicsReactor geometry

Total length	3.350 m
Diameter	0.025 m
Wall thickness	0.0025 m
Packed length	2.60 m
Fixed bed void fractions	0.5
Fixed bed bulk density	1312 Kg/m ³

Catalyst (V₂O₅/TiO₂ from Von Heyden)

Diameter	8.2 mm
Pellet density	2000 Kg solid/m ³ solid
Specific heat [*]	1.134 KJ/Kg°K
Thermal conductivity [*]	0.1047 W/m°K

Operating conditions[#]

Salt bath temperature	Tw	=	375 - 410°C
O-xylene feed concentration			0.68 to 1.2 mole%
Air flowrates			2 - 4 Nm ³ /hr
Inlet pressure			1.4 bar

* Estimated values [Lopez-Isunza (1983)]

All physical properties for the reacting mixture were those of air, as the mixture contains ~99% air.

The reactor was immersed in an air-agitated bath of molten salt (originally a mixture of 59 wt% potassium nitrate and 41 wt% sodium nitrite) acting as a heat transfer medium. The effluent from the reactor passed either directly to a condenser where the phthalic anhydride sublimated and was later removed by melting or via an auxiliary catalytic combustion reactor for total oxidation. In either case, the residual gas was conveyed to a scrubber where the organic material was washed out before being vented into the atmosphere. The condensers were cooled by cooling water whose temperature was kept constant between 45° and 55°C by a thermostat in the cooling water tank.

The salt bath was heated by a three-stage heater and controlled by a PID controller. Stirring-air was injected into the salt bath in order to promote good mixing and to keep the temperature within $\pm 0.5^\circ\text{C}$ from the set point along most of the bath. However, despite the good mixing conditions, increases of ~ 2 to 4°C were inevitable around the hotspot region. Full details about the pilot plant instrumentation and control are reported elsewhere [Wardlaw (1976), Whitfield (1983)].

The plant is supplied with a large condenser which is capable of lasting for 10 hrs of continuous operation, and an emergency condenser which can only operate for a period of 4 hrs, before crystals of phthalic anhydride begin to block the entrance of the condenser, and cause the pressure to rise. To melt the product in the condenser, 16 bar steam was supplied by the steam generator. After a period of about 3 hrs, the condenser was ready to be used again.

4.2 Temperature and concentration measurements

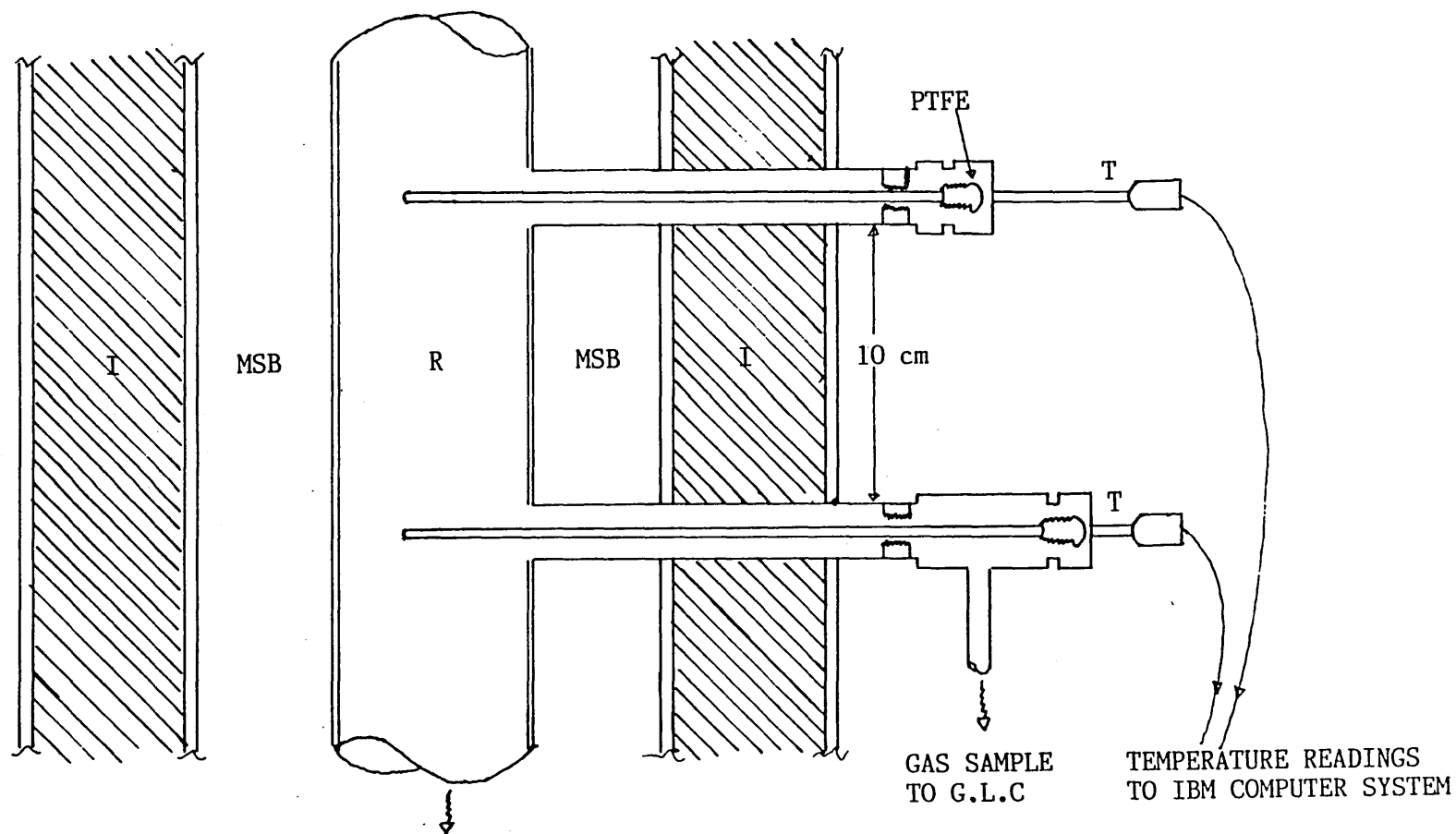
The reactor was provided with 25 axial sampling points which consist of steel tubings welded on one side of the reactor and arranged

in 0.1 m intervals with the catalyst bed beginning just above the first sampling point. 8 sampling locations were used for measuring both temperature and concentration, and they are positions 6, 8, 10, 12, 14, 16, 18 and 24 corresponding to axial distances of 0.5, 0.7, 0.9, 1.1, 1.3, 1.5, 1.7 and 2.3 m respectively. The rest of the sampling positions were for temperature measurements only. An illustration of how the sampling locations are constructed and arranged is shown in Fig. 4.2.

The concentration measurements were taken via sampling lines of 3 mm diameter copper tubing and maintained at about 160°C by a steam jacket to prevent any possible condensation of gaseous products. 9 sampling lines, including one for the feed, were connected to a ten-port multiposition valve, via 1/16th inch couplings, installed in a precision oven. The 10th port was not connected to any sampling line and was used as the resting position for the valve when no samples were being taken.

The outlet of this valve was connected to an air activated gas sampling valve (0.68 ml sampling loop) also located in the same oven. Manipulation of the multiposition valve permitted flow through a single sampling line, at a time, into the sampling loop and out to the vent. The sample was then introduced into a flame ionization detector chromatograph operated at either 190°C or 230°C by manipulating the air activated gas sampling valve.

The chromatographic column (0.00625 m o.d. x 2.0 m length) was 10% XE 60 silicone gum on chromosorb-w AW-DMCS. The carrier gas was nitrogen, and hydrogen and air were used for the flame ionization detector.



R = Reactor
 MSB = Molten Salt Bath
 I = Insulation
 T = Thermocouple(chromel-alumel)
 PTFE = PTFE ferrule

4.2 Fig. Schematic diagram of the reactor showing measurements arrangements

Both liquid- and vapour-phase calibrations were carried out in situ on the chromatograph with the column maintained at 190°C and/or 230°C.

In the former, standard liquid samples with acetone as solvent, for o-xylene, o-tolualdehyde, phthalide and phthalic anhydride were injected into the chromatograph with the column temperature maintained at either 190°C or 230°C. The molar relative response of each component with respect to o-xylene was computed from the ratio of the peak height of the component to that of o-xylene, except in the case of phthalic anhydride when the peak area, approximated by the product of the peak height and the width at half the peak height, was used instead. Absolute calibrations for o-xylene were made by sampling known air-o-xylene mixtures before they entered the reactor.

Vapour phase calibrations were carried out to improve upon the liquid phase calibrations of phthalic anhydride at column temperature of 230°C. The sampling line for the feed was connected to the multi-position valve via a vaporiser (bubbler), placed in the precision oven, containing liquid phthalic anhydride in equilibrium with its vapour at the oven operating conditions. Air was slowly bubbled through the liquid to saturate it with phthalic anhydride at the operating conditions. By varying the oven temperature, the mole fraction of phthalic anhydride in the air also changed and this was reflected on the chromatogram.

Operating the column at a higher temperature of 230°C resulted in narrower peaks and a reduction in retention times of the various components. This was particularly useful during the dynamic experiments when it was required to inject samples at a faster rate. Unfortunately-

ly, the resolutions of some of the peaks was marred especially in the case of phthalic anhydride and phthalide. The retention times for the various species at 190° and 230°C are presented in Table 4.2.

TABLE 4.2

Retention times of the components at 190° and 230°C

Component	Retention time (Sec.)	
	190°C	230°C
O-xylene (OX)	65	48
O-Tolualdehyde (OT)	116	65
Phthalic anhydride	363	153
Phthalide	417	167

A second chromatograph was used to analyse the compositions of CO and CO₂. The analysis of CO and CO₂ was done in order to obtain an independent check on the selectivity of o-xylene to phthalic anhydride and the other partial oxidation products.

Gas samples were occasionally taken from the vent of the sampling valve using a 100 ml glass tube fitted with a septum and analysed using a thermal conductivity detector.

The thermal conductivity chromatograph consisted of two columns: a molecular sieve column which separated oxygen, nitrogen and carbon monoxide with the carbon dioxide being permanently retained, and a Porapak column which separated carbon dioxide with o-xylene, nitrogen

and carbon monoxide appearing as one peak on the chart. Both columns were maintained at room temperature and the carrier gas was hydrogen.

Calibration of these components was done relative to nitrogen by injecting gas samples of known compositions of CO and CO₂ in nitrogen and also of pure air.

A further check on the selectivity of o-xylene to phthalic^{anhydride} was obtained by melting and weighing the amount of phthalic anhydride produced in the condenser over a given period of time.

Temperature measurements were performed using 1.5 mm o.d. chromel-alumel sheathed thermocouples which were free to move radially within the reactor. For temperature readings and data acquisition, the thermocouples were interfaced into the IBM computer system along with two other pilot plants in the Department of Chemical Engineering at Imperial College.

4.2.1 The IBM computer system

Three levels of computer system are used in the data acquisition, control, display facilities and overall management of the plants.

At the lowest level, an Analogics 4400 computer system serves as an interface to the plants, converting all the plant measurements to suitable digital form and, conversely, in the case of the other two plants, sending the required analogue signals to the control valves and digital signals to pumps and motors.

At the next highest level, the IBM Series 1 minicomputer serves as an intermediary between the Analogics system and the mainframe computer system.

The mainframe is an IBM 4341 computer and is, in fact, located remotely. All of the control calculations are carried out on the 4341 and the resulting control action is passed on to the plants via the Series 1 and Analogics. The 4341, however, is also used for other "stand alone" activities not associated with the pilot plants.

Communication with the computer (and hence with the plants) is done by three work stations, one for each plant. Each work station consists of three IBM 3279 colour-graphics terminals which are able to display (among other things) plant schematic diagrams, past and current plant data, details of the control system configuration and details of plant performance. In addition, hard-copy output diagrams and data are available on IBM dot-matrix and multicolour line printers.

The primary software used in controlling and monitoring the plants is the IBM Advanced Control System (ACS). This package allows the operator quick and vivid display of all relevant plant information.

4.3 Measurements limitations

Among other factors, the accuracy of temperature and concentration measurements depends on the inherent limitations of the instruments used.

It is important to bear in mind that all measurements were subjected to variations in the salt bath temperature which were in the range of $\pm 0.5^{\circ}\text{C}$.

The detector and amplifier of the chromatograph (Pye Unicam) had a maximum unseable sensitivity of about 1 ppm [Jordan (1977), Lopez-Isunza (1983)].

The multipoint digital indicator used with thermocouples in obtaining independent temperature readings of the salt bath, the

precision oven, inlet cooling water to the condensers as well as the combustion tube, allowed readings up to 1°C .

Liquid phase calibrations were accurate up to 0.2 mass% while the accuracy of the vapour phase calibrations very much depended on the multipoint digital indicator with its inherent error of $\pm 1^{\circ}\text{C}$. Calibration curves are shown in Appendix C. Sample chromatograms for the column operated at 190° and 230°C are also shown in Appendix C.

Radial temperature measurements carried out on the reactor [Lopez-Isunza (1983)] have shown large distortions of the profiles due to conductive heat losses along the sampling tubes welded to one side of the reactor. This posed a major problem in deciding where to place the thermocouples for measuring axial temperatures. The mathematical model assumes that the profiles are symmetrical about the centre of the reactor and does not take into account the presence of the sampling tubes.

However, from preliminary calculations using the radial temperature measurements, it was decided that the best possible location of the thermocouples was at the single radial interior collocation point. The thermocouples were placed at this point with the help of a caliper. However, measurement errors of $\pm 2^{\circ}\text{C}$ were still recorded when the reactor was run under static conditions (no air passed through the reactor but the salt bath stirrer was switched on) in order to obtain a uniform temperature profile throughout the reactor. These errors were probably due to some of the thermocouples making contact with the solid particles. See Appendix D for the details involved in calculating the best position to locate the thermocouples.

4.4 Catalyst and chemicals

The catalyst used was developed by Chemische Fabrik Von Heyden, and consisted of an inert spherical carrier of about 8.2 mm diameter, covered with a thin active coating containing V_2O_5 and TiO_2 [Chemische Fabrik Von Heyden (1974)]. Industrial grade o-xylene was supplied by British Petroleum through the courtesy of Dr. J.M. Allen of B.P. Chemicals Limited, Hull works.

4.5 Experimental program

The experiments were designed to be carried out in four stages.

The first stage was the initial start-up which involves packing the reactor with fresh catalyst and operating the plant continuously, at normal operating conditions, for a period of two to three weeks in order to allow the catalyst to stabilise its activity. Unfortunately, this stage turned out to be most difficult and lasted longer than it was envisaged since it was not possible to operate the plant continuously as stipulated following a breakdown in the emergency shutdown control system of the pilot plant. However, the reactor was eventually packed with fresh catalyst and the plant operated continuously for three weeks. Before starting up the plant, the catalyst was pretreated with SO_2 , to improve its selectivity to phthalic anhydride, by passing 0.01 mole% SO_2 in air for 24 hrs with the salt bath temperature maintained at $380^\circ C$.

In the second experimental stage, steady state experiments with reaction were carried out. Temperature and concentration readings at various salt bath temperatures and o-xylene initial concentrations were taken.

The dynamic experiments were conducted during the third experimental stage and they involved ramp changes in salt bath temperature and step changes in inlet o-xylene concentrations.

During the fourth and last experimental stage the reactor was run continuously, at steady state, for 13 days with temperature measurements taken after every 20 minutes and concentration measurements carried out every 12 hrs. Some steady state experiments without reaction were carried out and axial temperature measurements taken in order to evaluate heat transfer parameters.

4.6 Operational procedure

Except for the initial start-up, every other start-up was preceded by a period of about 30 to 40 hours of catalyst regeneration or reactivation. It is believed that the catalyst deactivates because it is reduced by a rich hydrocarbon environment at low temperatures [Lopez-Isunza (1983), Kershenbaum et al. (1984)] (see Chapters 5 and 6). To activate the catalyst the salt bath temperature was raised to 400°C or 410°C and the air flowrate set to about 2 Nm³/hr for a period of 30 to 40 hrs.

The start-up procedure itself was exactly the same for all the experiments. The salt bath temperature was set to the desired value by manipulating the controller's setpoint. O-xylene pump was then started to deliver about 75% of the total o-xylene flowrate while monitoring the axial temperature profile which normally starts to develop after 3 minutes. Once the steady state was reached, step increases in o-xylene flowrate were performed every 10 minutes until the desired o-xylene/air ratio was reached.

Various displays of the axial temperature profile on the colour-graphics terminals were used to determine, at any given moment, whether the system was at steady state or not. The displays were updated every 8 seconds but reports to be printed were not updated until after every minute. It was also possible to print 6 minute temperature averages, at any given moment, for the last 8 hours. Hourly and daily averages were also available but were hardly used.

4.7 The auxillary catalytic combustion reactor

For prolonged continuous operation of the plant over several days it was convenient to incorporate an after-burner to completely oxidize the reactor effluents before passing them to the condensers and to the vent. Perhaps the greatest advantage of this burner was derived during the first start-up when the main reactor was packed with fresh catalyst and the plant was run continuously for three weeks. The larger condenser was then able to withstand four to five days of continuous operation before there was any indication of a back pressure. This prevented many sleepless nights.

The burner consists of an inner tube 0.1 m diameter .58 m long packed with about 18% active Co_3O_4 catalyst in inert. This is surrounded by an outer tube of about .15 m diameter and .625 m long; the annulus between the two tubes packed with inert packing. The temperature of the reacting mixture (effluents from the main reactor) was raised above 300°C by two electric heaters, connected in parallel, tracing the pipeline between the two reactors. Two thermowells placed at radial positions .02 m and .04 m from the centre were used for measuring axial temperatures along the reactor.

Compressed dry diluent air metered by a rotameter was passed counter-currently from the exit end of the burner via the outer packing and mixed with the reacting mixture at the inlet end before entering the inner tube. Temperatures as high as 900°C and above were recorded with fresh catalyst and diluent air of more than $10.5 \text{ Nm}^3/\text{hr}$ was used to bring the hotspot temperatures below 800°C . The penalty for using such a large amount of diluent air was a slight increase in back pressure in the main reactor.

However, the catalyst gradually deactivated with time and it was possible to operate the burner stably and safely with hotspot temperatures below 800°C without passing any diluent air. Most of the experiments were performed without diluent air.

Typical axial temperature profiles measured at radial position .02 m from the centre for a diluent air flowrate of 6 Nm³/hr are shown in Fig. 4.3.

These temperature measurements were taken for experiments carried out after the original experimental program outlined in Section 4.5.

Typical CO conversions were about 58% obtained by analysing gas samples at the exit of the partial oxidation reactor (axial position 24) and at the inlet to the scrubber. Phthalic anhydride conversion was estimated to be between 88 to 91%. This was obtained by melting and weighing the amount of phthalic anhydride produced in the condenser after 96 hours of continuous operation.

The design and construction of the burner, together with catalyst characteristics and operational procedure, are given in Appendix F.

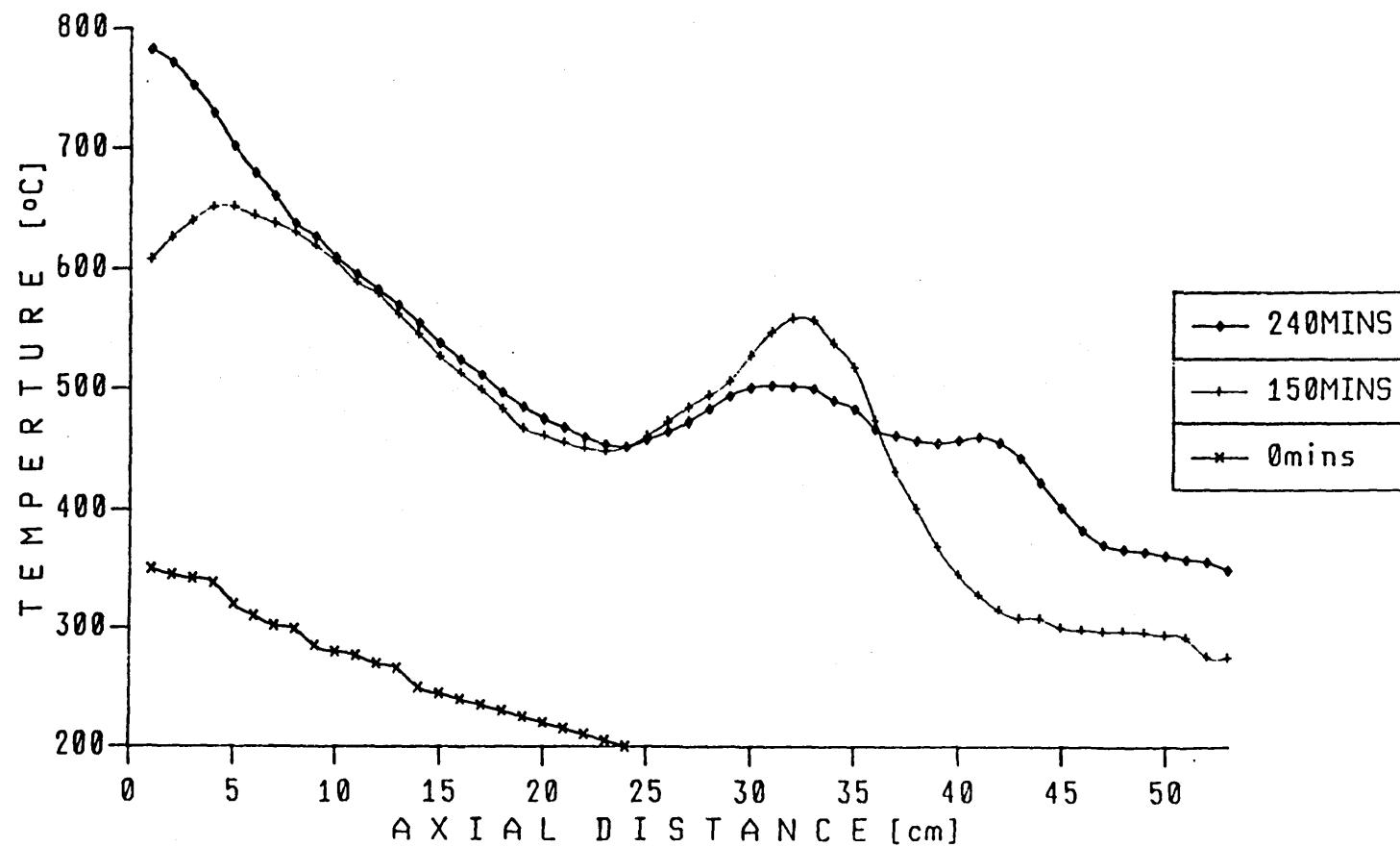


Fig. 4.3 Typical axial temperature profiles measured at radial position .02m from the centre; diluent air flowrate $6\text{Nm}^3/\text{hr}$.

CHAPTER FIVE

5.0 CATALYST ACTIVITY PROFILES

The phenomenon of both reversible and irreversible catalyst decay is very common in catalytic chemical reactors. The decay may be due to poisons (when impurities are contained in the reactant feed), to sintering (when the catalyst surface area is reduced by physical deterioration due to high operating temperatures), or to fouling (when coke or high polymeric material is deposited on the catalyst [Ogunye & Ray (1971)]). A fixed bed catalytic reactor would normally have activity profiles as a result of catalyst decay.

Mathematical models which represent the time and spatial history of catalyst decay have been developed for a large number of systems exhibiting the various types of deactivation [Voorhies (1945), Froment et al. (1961), Jackson (1965), Szepe et al. (1968), Osawa et al. (1968), Butt et al. (1968)]. They have been reviewed by Hughes (1984).

There are two different activity profiles involved in this reactor-reaction system; one is a surface profile associated with structural changes, which develops during the operation of the reactor and which changes rather slowly and irreversibly around the region of the hotspot temperatures [Sedlmeier (1982) and Lopez-Isunza (1983)]. The other is an oxidation-reduction profile which is reversible, but needs several days for adjustment to new reaction conditions. It is suggested that a major cause of reversible deactivation is due to a combination of high o-xylene concentrations (1 to 1.5 mole%) and low temperatures [Calderbank et al. (1974, 1977), Lopez-Isunza (1983), Kershenbaum et al. (1984)].

Calderbank (1974) carried out experiments on the partial oxidation of o-xylene on a V_2O_5 -SiC catalyst using a spinning catalyst-basket reactor with the basket and chamber made of titanium and arrived at the following conclusions:

- The disappearance kinetics of o-xylene were first-order up to nearly 1 mole% o-xylene concentration.
- At higher concentrations the catalyst was reversibly deactivated (see Fig. 5.1).

He suggested that it is possible that vanadium oxide is reduced to a lower valence state of less catalytic activity at high o-xylene concentrations.

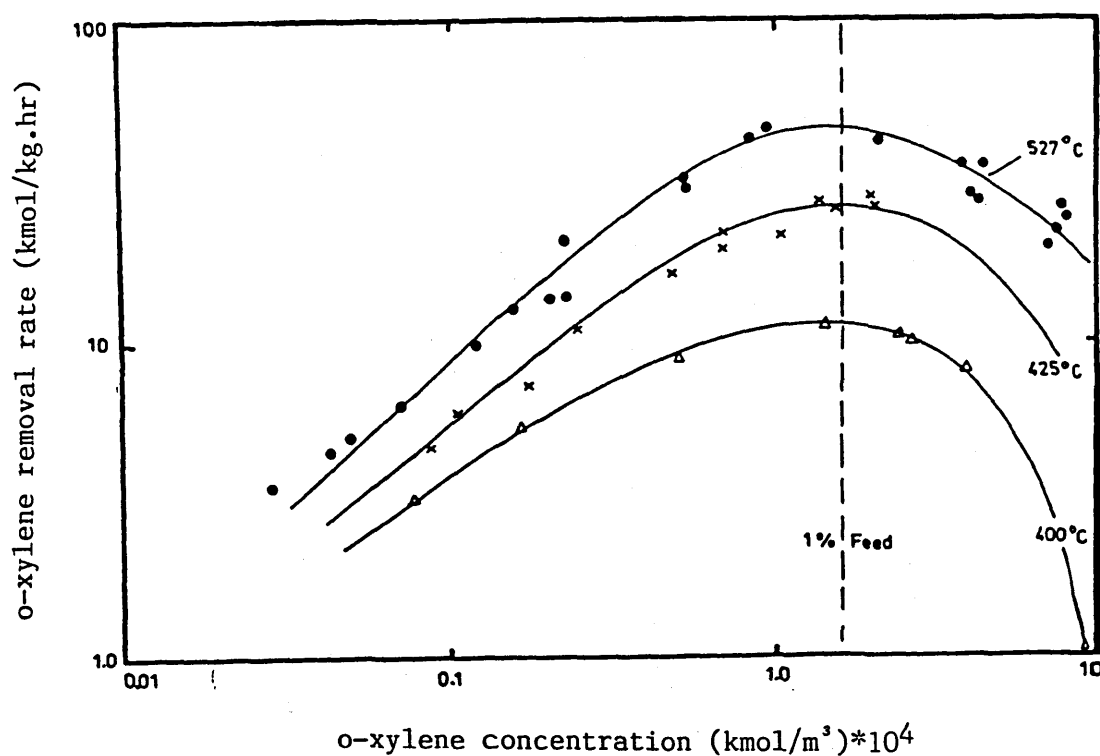


Fig. 5.1 Oxidation rate of o-xylene with air in the CSTR
(from Calderbank, 1974).

Further evidence of reversible deactivation of the catalyst by o-xylene at high concentrations and low temperatures is provided by experiments performed by Lopez-Isunza (1983) on a V_2O_5 - TiO_2 catalyst employed in this reactor-reaction system.

Lopez-Isunza (1983) performed three different experiments on three consecutive days, for a period of about 10 hours/day under the same operating conditions but with the catalyst subjected to different levels of re-oxidation (regeneration) and with or without pretreatment with o-xylene. He arrived at the following conclusions:

- a. The catalyst was reversibly deactivated when a large amount of o-xylene was allowed to leave the reactor without reacting.
- b. The activity of the catalyst was fully restored, allowing for reproducibility of experimental results when the catalyst was regenerated or re-oxidized for a period of about 40 hrs by passing only air at $2 \text{ Nm}^3/\text{hr}$ and maintaining the salt bath temperature constant at 410°C .

Fig. 5.2 shows the temperature profiles obtained by Lopez-Isunza (1983) for the three experiments. The profile labelled 'A' was obtained during the first experiment which was preceded by a 40-hour period of catalyst regeneration. The profile labelled 'B' was obtained on the second day when no further regeneration of the catalyst was done before the start-up of the experiment.

Lopez-Isunza reported a near extinction of the reaction when he lowered the salt bath temperature by 10°C at the end of the second day, as the hotspot moved to the reactor's exit and its magnitude changed to about 440°C at axial position 26. "At these conditions a large amount of o-xylene left the reactor without reacting and consequently, deactivating the catalyst."

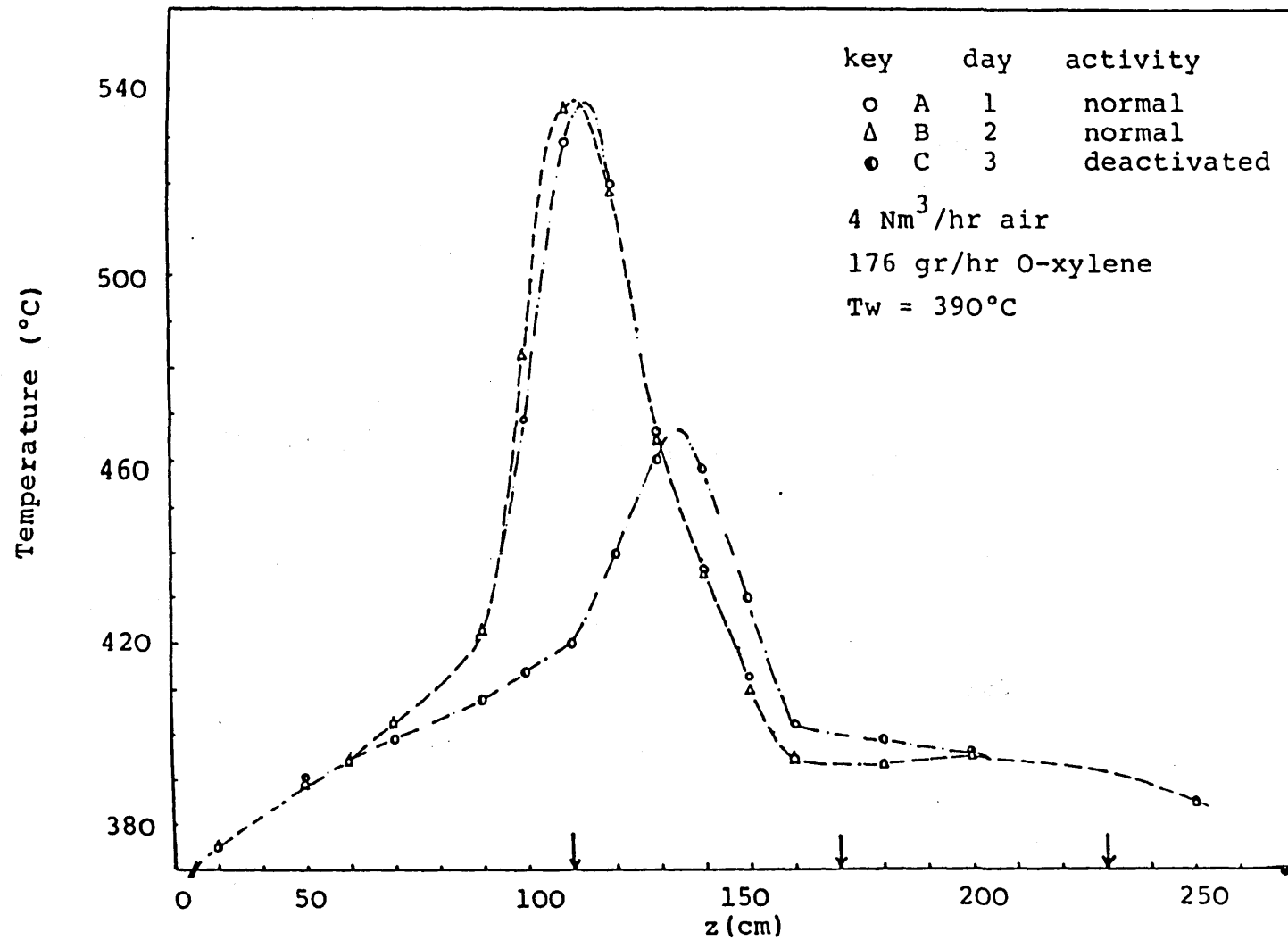


Fig. 5.2 Experimental steady state axial temperature profiles for different catalyst activity profiles (from lopez-Isunza,1983).

The profile labelled 'C' in Fig. 5.2 was obtained on the third day during the third experiment performed after a short re-oxidation period of 6 hr in air at 390°C.

All the three temperature profiles show the characteristic inflection at the inlet region of the reactor, suggesting that even when the catalyst is operating at normal activity the inlet region is reversibly deactivated due to high o-xylene concentrations and low temperatures within that region. For the reversibly deactivated catalyst (profile 'C'), both the inflection point and the hotspot were displaced further to the downstream end of the reactor.

Dynamic experiments carried out by Lopez-Isunza (1983) and in this work (cf Chapter 6) have shown that there is a strong correlation between partial deactivation of the catalyst (changes in the activity profile) and parametric sensitivity during the dynamic behaviour of the system. For example, experiments performed for a ramp increase in salt bath temperature show that the system's dynamic response is affected by the relative contributions of the rate of catalyst re-oxidation and axial dispersion of heat.

All these observations point to the difficulties involved in modelling this type of reactor-reaction system. It is suggested that, perhaps the only best way to adequately model this system, in the light of several limitations particularly with the kinetic model, is to consider catalyst activity profiles incorporated into the kinetic model via a deactivation model (Lopez-Isunza (1983)]. Such a model can either be mechanistic or empirical but should be able to describe the oxidation-reduction of the catalyst during the dynamic behaviour of the reactor and also take into account the effect of o-xylene concentrations on the surface of the catalyst. The parameters of the model can

then be evaluated from early pilot plant reactor data. This requires extensive temperature and concentration measurements during steady state and dynamic experiments and such a process might not be justifiable especially when there is a time limitation.

It was therefore appropriate to seek alternative methods of determining the extend of catalyst deactivation, at any given time, without recourse to a deactivation model. The approach adopted in this work was to estimate catalyst activity profiles, at any given time, directly from current reactor data, in order to predict the behaviour of the reactor, without due consideration to the type of deactivation model.

Although off-line measurements are used in this work the ultimate aim is to be able to estimate catalyst activity profiles from on-line measurements in order to predict the reactor behaviour and if possible control it.

5.1 Parameter estimation of catalyst activity profiles

Since the system under study is characterised by Partial Differential Equations (PDE's), the parameter estimation of activity profiles is treated under the general heading of Distributed System Parameter Identification Problem (DSPIP).

Before proceeding any further, the following definitions for parameter identification are in order [Goodson & Polis (1974)].

- a. The parameter identification problem is the determination from experimental data of a set of unknown parameters in a mathematical model of a physical process such that over a desired range of operating conditions, the model outputs are close, in some well defined sense, to the process outputs when the two are subject to analogous inputs.
- b. A Distributed System is defined as a system where the variables of importance are related by transformations or mappings which depend on local spatial variations as well as time.
- c. Parameters are defined as functions or constants other than the dependent variables, which appear explicitly in the mathematical model.

A step by step procedure to solve DSPIP is outlined by Goodson & Polis (1974); it is as follows.

- i Write the mathematical description, containing unknown parameters, of the physical system under consideration.
- ii Choose a method to solve the mathematical description of the distributed system.
- iii Decide on measurement location(s) in the spatial domain.
- iv Choose a criterion of performance.

- v Perform a sensitivity analysis.
- vi Choose an optimisation scheme.
- vii Perform an error analysis.

There exists a wealth of results on the estimation of parameters in distributed systems which have been reviewed, among others, by Seinfeld (1970), Goodson & Polis (1974) and Ray (1978).

Recent developments in the estimation of catalyst activity from packed-bed reactors have been directed towards on-line, real time estimation using non-linear filtering. In almost all the work reported catalyst activity was considered uniform throughout the reactor and applications range from lumped parameter filters [Gavalas et al. (1969, 1972), Goldman & Sargent (1971)] to distributed parameter filters (where the spatially distributed states are considered as parameters together with the lumped activity parameter) [Ajinkya & Ray (1974)]. Very recently, Kuruoglu et al. (1985) derived two filters; a steady state estimator for the spatially distributed states with fast dynamics (for concentration and temperature) and a time-varying lumped parameter estimator for catalyst activity.

When the catalyst activity is a function of spatial variations as well as time, the estimation problem becomes much more difficult. Goldman & Sargent (1971) first fitted the activity profile to a given functional form and sequentially determined the parameters.

In their case [Goldman & Sargent (1971)] the activity profile was approximated by a linear function of the axial distance as:

$$\alpha(z,1) = \alpha_0 - t.C_1T(o,t) - C_2z$$

where $\alpha_0 = \alpha(z,0)$; initial activity uniform throughout the catalytic bed. C_1 and C_2 constants which were estimated along with α_0 .

A functional form of activity profile for this reactor-reaction system would be more complex and certainly not linear with respect to axial distance. Such an activity profile would also be a function of local variations in temperature and concentration of o-xylene throughout the catalytic bed. The expected profile would be S-shaped considering the type of approximate activity profile used in Chapter 3 to simulate the steady state behaviour of the reactor.

The method developed in this work deals exclusively with the problem of estimating activity profiles from current operating reactor data without using any functional form. A similar approach was adopted by Gavalas et al. (1972) who approximated the activity profile by parameterization and used a few measurements along the reactor to estimate the parameters.

The problem is formulated here along the guidelines given by Goodson & Polis (1974).

5.1.1 Mathematical model with catalyst activity parameter

Due to the partial activation of the catalyst, the rate of reaction of the j^{th} reaction step (cf Chapter 2) can be expressed as:

$$(R_j)_d = \alpha(z,t) \mu A_j \exp(-E_{j/RT}) P_n \quad (5.1)$$

where $\alpha(z,t)$ is the catalyst activity parameter which is a function of both time and space and is given by

$$\alpha(z,t) = \frac{(R_j)_d}{(R_j)_f} \quad [\text{Wheeler (1955)}] \quad (5.2)$$

the subscripts d and f denoting deactivated and fresh catalyst respectively. The activity parameter was assumed to be the same for all the reactions.

The mathematical model in dimensionless parameters and variables (cf Chapter 3) can then be rewritten with the kinetic model replaced by Eq. 5.1 thus:

$$\frac{\partial X_n}{\partial t} = -\frac{\partial X_n}{\partial z} + \frac{1}{P_m} \left(\frac{\partial^2 X_n}{\partial r^2} + \frac{1}{r} \frac{\partial X_n}{\partial r} \right) + \alpha(z, t) \sum_{j=1}^R \delta_{mj} f_j(\underline{X}, Y) \quad (5.3)$$

$$\bar{M} \frac{\partial Y}{\partial t} = -\frac{\partial Y}{\partial z} + \frac{1}{P_h} \left(\frac{\partial^2 Y}{\partial r^2} + \frac{1}{r} \frac{\partial Y}{\partial r} \right) + \alpha(z, t) \sum_{j=1}^R \beta_j \delta_{hj} f_j(X, Y) \quad (5.4)$$

$$\frac{\partial \alpha}{\partial t} = f(z, X, Y) \quad (5.5)$$

with boundary conditions

$$\begin{aligned} \text{at } t = 0 \quad X_n(r, z, 0) &= X_n(r, z)_{ss} \\ Y(r, z, 0) &= Y(r, z)_{ss} \\ \alpha(z, 0) &= \alpha(z)_{ss} \end{aligned} \quad (5.6)$$

$$\begin{aligned} \text{at } r = 0 \quad (0 < z < 1) \\ \frac{\partial X_n}{\partial r} = \frac{\partial Y}{\partial r} &= 0 \end{aligned} \quad (5.7)$$

$$\begin{aligned} \text{at } r = 1 \quad (0 < z < 1) \\ \frac{\partial X_n}{\partial r} &= 0 \\ -\frac{\partial Y}{\partial r} &= Bi_w (Y - Y_w) \end{aligned} \quad (5.8)$$

$$\begin{aligned} \text{at } z = 0 \quad (0 < r < 1) \\ X_n(r, 0, t) &= X_{n0}(t) \\ Y(r, 0, t) &= Y_0(t) \\ \alpha(0, t) &= \alpha_0(t) \end{aligned} \quad (5.9)$$

In this case, Eq. 5.5 is not used since the function $f(z,X,Y)$ is not known.

5.1.2 Method of solution of the distributed parameter system

Eqs. 5.3 to 5.9 were solved by the method of orthogonal collocation on finite elements as modified for the solution of initial-value problems (cf. Chapter 3). However, in order to integrate the equations at any given time (t), a complete knowledge of the activity profile $\alpha(z)$ is required. An estimation of the complete profile $\alpha(z)$ requires an infinite number of temperature and concentration measurements along the reactor length which is impractical. However, for practical purposes, an approximation of the activity profile was made.

Gavalas et al. (1972) used two simple parameterization methods to approximate the activity profile as shown in Figs. 5.3a and 5.3b. In the first, the activity profile $\alpha(z)$ was approximated by a curve $\alpha(z;P_1,P_2,P_3)$ consisting of two segments of straight lines and including three parameters P_1, P_2, P_3 . The parameters were then determined simultaneously by minimizing the sum of squared errors.

$$J = \sum_{j=1}^M [\bar{g}(z_j) - \phi(z_j; P_1, P_2, P_3)]^2$$

where $\bar{g}(z_j)$ is a function of measurements,

$\phi(z_j; P_1, P_2, P_3)$ is obtained from integration of the governing equations and m is the number of measurement.

In the second method, the activity $\alpha(z)$ was approximated by a piecewise constant function, Fig. 5.3b.

$$\alpha(z) = \bar{\alpha}_j \quad z_{j-1} < z < z_j$$

$j = 1, \dots, m$ are the measurement points.

The parameter $\bar{\alpha}_j$ were then determined by the minimization of the quantity

$$J = \sum_{j=1}^m [\bar{g}(z_j) - \phi(z_j; \bar{\alpha}_j)]$$

where, $\bar{g}(z_j)$, $\phi(z_j; \alpha)$ and m are as defined previously.

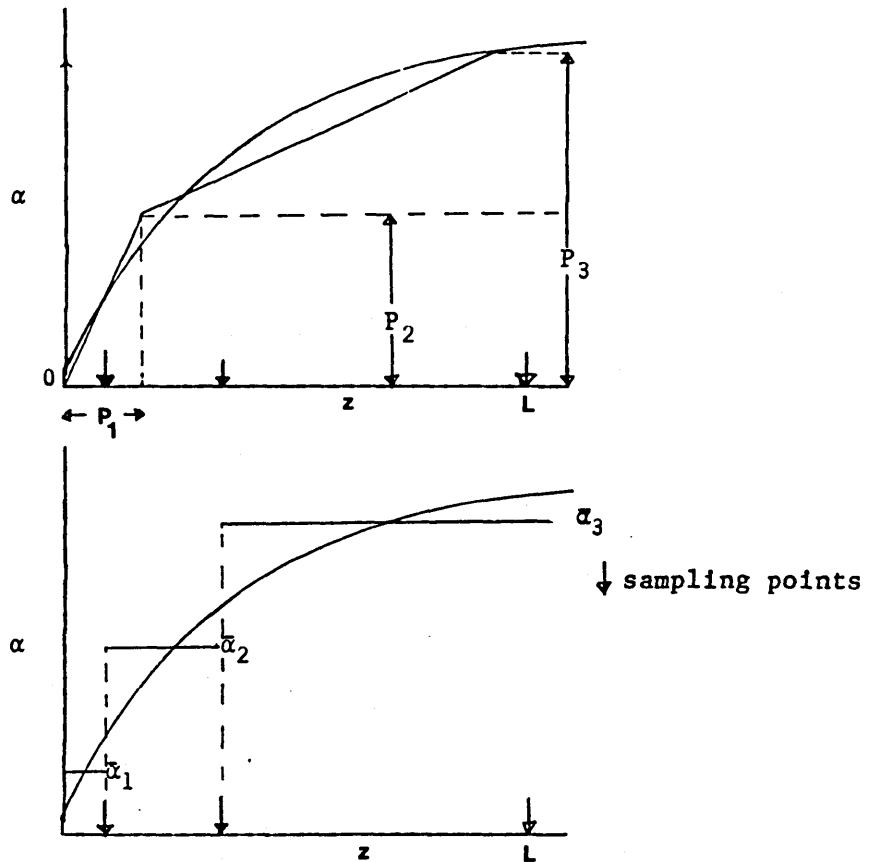


Fig. 5.3 Two parameterizations of a catalyst activity profile (Gavalas et al. (1972))

Gavalas et al. (1972) considered a simple case where only one ordinary differential equation was required to be integrated at any given time and therefore the amount of computation times used were moderate. For a more complex problem, like the one considered in this work involving the solution of several coupled non-linear differential equations, estimating the parameters simultaneously can involve prohibitively a large amount of computation times.

Fortunately, for an initial-value problem like the one considered in this work, it is possible to modify both methods so that the parameters can be determined separately and sequentially at any given time (t). The two methods developed here take advantage of the fact that the entire domain can be divided into a series of finite elements such that the governing equations can be integrated in each finite element sequentially by specifying only the inlet conditions which are, in fact, the output values of the previous finite elements or in the case of the first element the inlet conditions to the reactor.

In the first method, the global activity profile $\alpha(z)$ was assumed to be continuous linear with break points at the boundaries of the finite elements such that the activity profile in the j 'th finite element was approximated by a straight line $\alpha_j(z; z_j, C_j, P_j)$ where:

$$\alpha_j(z) = C_j + P_j(z - z_j); \quad z_j < z < z_{j+1} \quad (5.10)$$

$$j = 1, \dots, n$$

and n is the number of finite elements.

For this reactor-reaction system, the value of $C_1 = 0$ can be assumed up to axial position 6 (.50 m from the reactor inlet). This is because, under normal operating conditions of the reactor, very little reaction occurs within this region of the catalytic bed, probab-

ly because of very low temperatures and high o-xylene concentrations (see Chapter 6).

∴ For $C_1 = 0$, and $z_1 = 0$ (see Fig. 5.4a)

$$\alpha_1(z) = P_1 z; \quad z_1 < z < z_2 \quad (5.11)$$

Eqs. 5.7 and 5.8 can be rearranged so that the activities at the end of each finite element (C_{j+1} 's) instead of the slopes of the straight lines (P_j 's) are estimated since

$$P_j = (C_{j+1} - C_j)/(z_{j+1} - z_j) \quad (5.12)$$

Substituting Eq. 5.12 into Eq. 5.10 we have

$$\alpha_j(z) = C_j + \left(\frac{z - z_j}{z_{j+1} - z_j} \right) (C_{j+1} - C_j); \quad 0 < C_j < 1 \quad (5.13)$$

Similarly Eq. 5.11 becomes

$$\alpha_1(z) = \frac{z}{z_2 - z_1} C_2 \quad (5.14)$$

Hence, starting with the first finite element the C_{j+1} 's are estimated sequentially by minimizing the objective function defined at the corresponding finite elements.

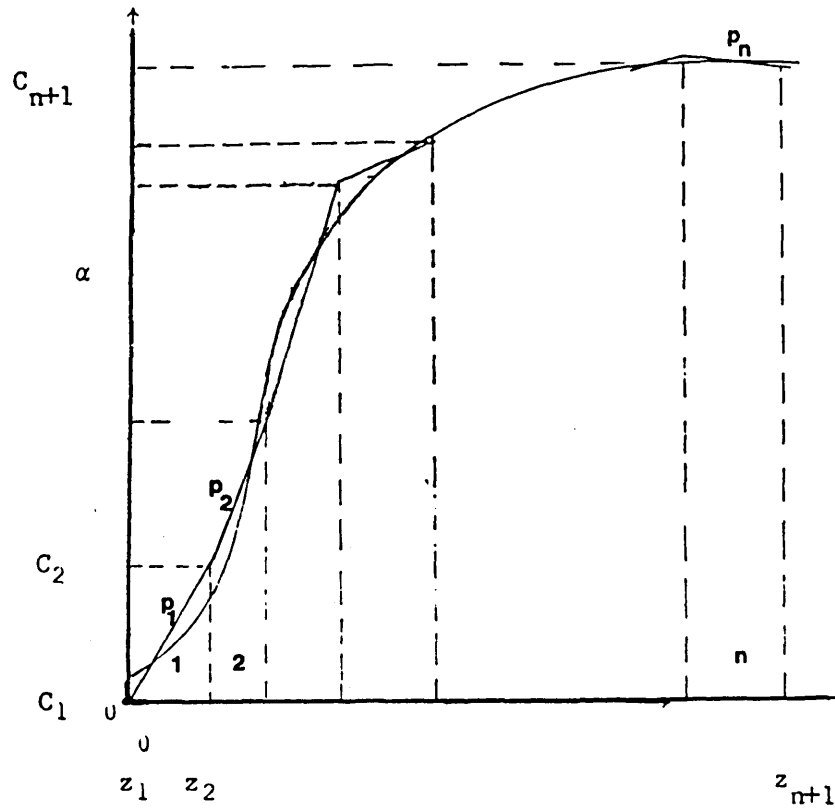


Fig. 5.4a Approximation of catalyst activity profile
by straight lines

In the second method, Fig. 5.4b, the activity profile $\alpha(z)$ was approximated by a piecewise constant function with each finite element having a uniform activity $\bar{\alpha}$

$$\alpha_j(z) = \bar{\alpha}_j; \quad z_j < z < z_{j+1} \quad (5.15)$$

$$j = 1, n$$

The $\bar{\alpha}_j$'s were estimated sequentially by minimising the objective function defined at the corresponding finite elements.

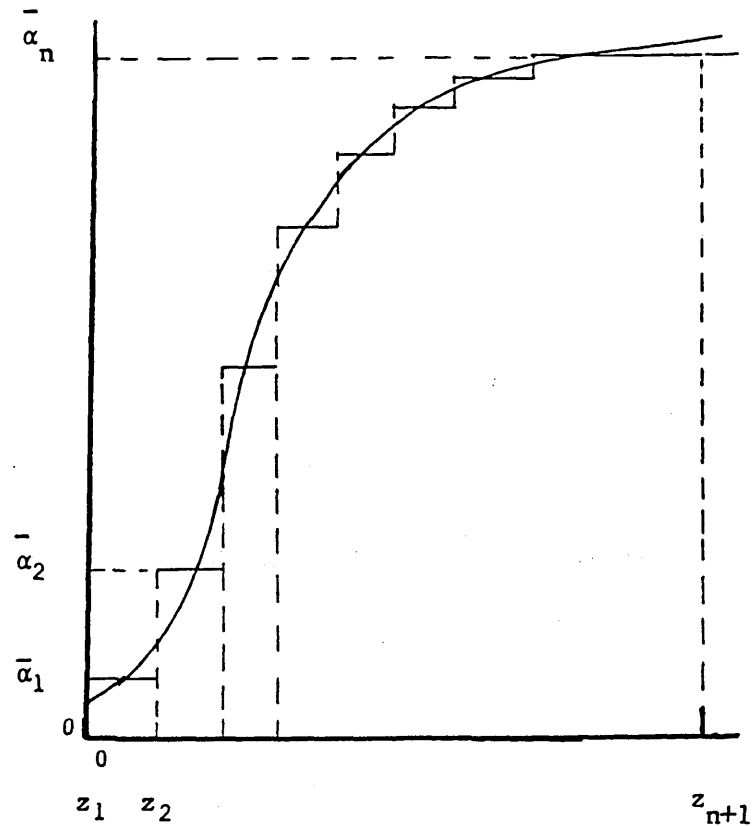


Fig. 5.4b Approximation of a catalyst activity profile
by a piecewise constant function

5.1.3 Location of measurements in the axial direction

All the 25 measurement points were available for use for the estimation of activity profiles. The location of the sampling points for concentration measurements at axial positions 6, 8, 10, 12, 14, 18 corresponding to axial distances of 0.50, 0.70, 0.90, 1.10, 1.30, 1.50 and 1.70 m was very convenient for the partitioning of the reactor into sub-reactors since the experimental hotspot temperatures were normally within that vicinity. Under normal operating conditions of the reactor, very little reaction was observed within the first 0.50 m of the catalytic bed (i.e. about the 6th sampling point). Hence, the temperature and concentration measurements at that point were taken as the

inlet conditions to the reactor. Also the activity of the catalyst was assumed to be very close to zero at that point; so effectively, only 20 measurement points were used.

The reactor was divided into a series of sub-reactors such that at least one sampling point for concentration was present within each sub-reactor. Each sub-reactor constituted a finite element and the minimum number of measurements were 2 for temperature and 1 for concentration. The sizes and number of finite elements were determined by the shape of the experimental temperature profile. Fig. 5.5 shows how a typical experimental profile could be used to divide the axial domain into finite elements.

Once the finite elements were obtained, the activity profile in each one was estimated using temperature and concentration measurements located in the corresponding finite element, and the partial differential equations were then integrated as described in Chapter 3.

Although the finite elements here were determined manually, as opposed to the method used in Chapter 3, the interior collocation points in each finite element were still obtained automatically.

5.1.4 Criterion of performance

The choice of the objective function used in parameter estimation should incorporate the specific error structure of the experimental data if the best fit of the data is to be achieved [Biegler et al. (1986)]. A simple objective function was used in this work and the following relationship was assumed:

$$\zeta_1 = \zeta_1(\alpha) + \varepsilon_1$$

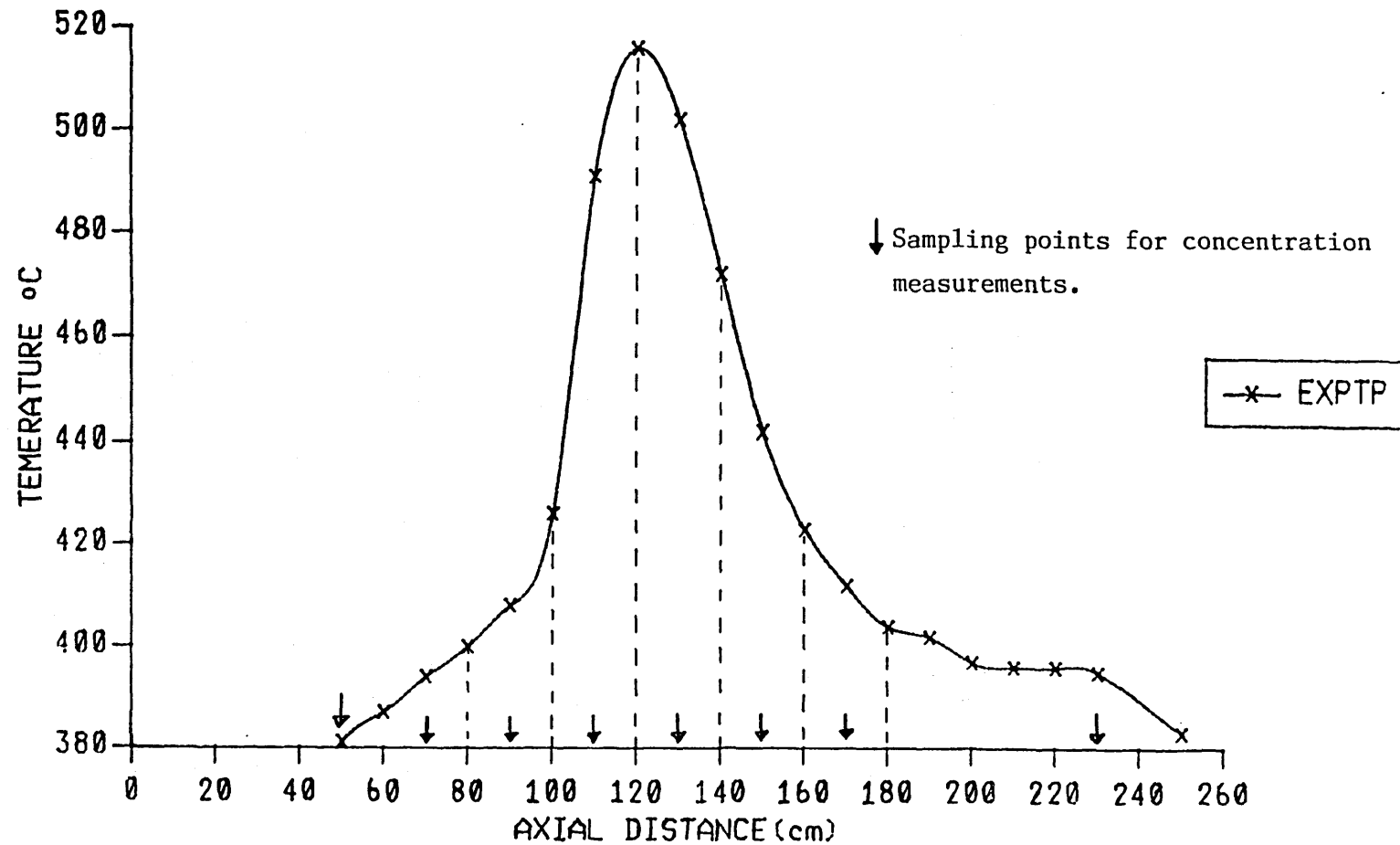


Fig. 5.5 An illustration of how the finite elements may be obtained using the shape of a typical experimental profile and the concentration sampling points.

where ζ_i = measured value for component i
(temperature or concentration)

$\zeta_i(\alpha)$ = computed value of component i from model ($\zeta_i(\alpha)$
is either temperature or concentration)

α = vector of adjustable model parameters (in this case α
is a scalar variable of the activity parameter)

ϵ_i = residual error, assuming the model is correct.

Also, the following error structure of the measured values was assumed.

- a. Observations errors are independent of axial position, for a given component.
- b. The measured variables are independent so that the covariance matrix is diagonal.
- c. Each measured variable has a known variance.

The objective function defined in each finite element was then given by:

$$J(\alpha) = \sum_{j=m}^{NC} \sum_{i=1}^{NE-1} (x_{ij} - \hat{x}_{ij})^2 w_i + \sum_{\lambda=2}^{NT} (y_{\lambda} - \hat{y}_{\lambda})^2 w_{NE} \quad (5.11)$$

where m is the first axial concentration measurement point in the finite element; NC and NT , the total number of concentration and temperature measurements respectively. NE , the total number of components (1 temperature and 4 concentrations). w_i 's are the least squares weightings, the diagonal elements of the inverse of the covariance matrix, which reflect the accuracy attached to the measurements.

For the concentration measurements, the weightings were calculated from the inverse of the mean square error about regression of the calibration lines (Appendix C). The scaled values were 0.333, 1.0, 0.2

and 0.1667 for o-xylene, o-tolualdehyde, phthalide and phthalic anhydride respectively. These values were obtained by dividing the inverse of the mean square error about regression of each component by that of o-tolualdehyde which was the largest, in this case. For the temperature measurements the value was adjusted through preliminary simulations to 1.7.

5.1.5 Optimization scheme

There are a number of gradient-based algorithms which are capable of using the above class of objective functions to find optimal parameters [Gill et al. (1981)]. The important steps of these algorithms are the calculation of a search direction and determination of the step length to take along this direction. The iteration step for the optimization variable, α , can be expressed as

$$\alpha_{k+1} = \alpha_k + \delta H^{-1}g$$

where δ = step length

H = Hessian matrix (second derivatives) of the objective function or its approximation

g = gradient of objective function.

Here the parameters to be estimated, α , do not appear explicitly in the objective function. Thus, calculation of the gradients of the objective function with respect to the model parameters cannot be determined analytically if the model predictions are not solved explicitly from the model.

The various gradient-based optimization schemes differ from one another in the way the gradient and second derivatives are calculated.

A quasi-Newton optimization scheme was employed in this work. The theory of quasi-Newton methods is based on the fact that an approximation to the curvature of a non-linear function can be computed without explicitly forming the Hessian matrix.

Let δ_k be the step taken from α_k , and consider expanding the gradient function about δ_k in a Taylor series along δ_k :

$$g(\alpha_k + \delta_k) = g_k + H_k \delta_k$$

The curvature of the objective function along δ_k is given by

$$\delta_k^T H_k \delta_k \approx (g(\alpha_k + \delta_k) - g_k)^T \delta_k$$

The first derivatives (g_k) are themselves calculated by finite differences or otherwise.

The subroutine E ϕ 4JAF (obtained from NAG library) employed in this work is an easy-to-use quasi-Newton algorithm for finding a minimum of a function subject to fixed upper and lower bounds of the independent variables.

The subroutine is capable of handling several parameters at a time. This particular feature was exploited by combining two to three finite elements so that the activity parameters in them could be estimated simultaneously. The solution obtained by combining the finite elements in this way was not significantly different from that obtained when the activity parameters were estimated sequentially. Moreover, the time taken to determine two to three parameters simultaneously could not be justified at all by the marginal improvement in the predicted results (see Chapter 6, Section 6.3.2).

Hence, in almost all the simulations carried out in this work the activity parameters were estimated sequentially and independently.

5.1.6 Example: Estimation of activity profiles using simulated measurements

In order to test the optimization algorithm, it was appropriate to apply it to a situation where the catalyst activity is well known. Hence simulation measurements obtained by introducing an arbitrary catalyst activity profile were used.

Using the activity profile introduced in Chapter 3 for the steady state simulation of the reactor, the solution of the model equations at the measurement locations was obtained by polynomial interpolation of the values at the collocation points. A special subroutine INTRP which uses the roots and the first derivatives of the orthogonal polynomials to calculate the interpolation weights, and is available in Villadsen & Michelsen (1978), was used extensively for this purpose. The simulated measurements, solution values at the measurement points, were then used to estimate the activity profile using the two methods of approximation of an activity profile described in Section 5.1.2 (continuous linear with breakpoints and piece-wise constant function).

The simulated and estimated profiles of catalyst activity, temperature and concentration of the various chemical components are compared in Figs. 5.6 and 5.7 for the case when both temperature and concentration measurements were used in the optimization scheme.

As expected, the prediction using the first method was better up to the point of discontinuity of the activity profile as shown in Fig. 5.6. The predicted profiles were shifted to the right after that

point because the method failed to predict the discontinuity in the simulated activity profile.

The second method gave a better overall prediction of all the profiles as shown in Figs. 5.7a to d. This was probably because the method predicted the discontinuity in the activity profile. However, Fig. 5.7 shows ripples on the estimated temperature and concentration profiles in the region prior to the discontinuity of the simulated activity profile. The reason for these ripples is due to the inherent limitations of this method of approximation of the activity profile. Since the method allows for discontinuities in the rate of reaction engendered by the fact that the activity profile is discontinuous from one finite element to the next, there is bound to be discontinuity in the slopes of the estimated temperature and concentration profiles.

When only temperature measurements were used to estimate the activity profiles, the first method failed to predict the activity profile after the hotspot and gave poor estimates of both the temperature and concentration profiles (see Fig. 5.8a to d). This is so because the estimated activity after the hotspot was very low. In this case, the second method still gave good estimates of the profiles but only when the upper fixed bound of the activity was strictly imposed (see Figs. 5.9a to d). When the bound was removed or reset to a higher value, the activity of the catalyst was over estimated. Of course, this is not a realistic approach since in a real situation the activity of the catalyst is not known a priori.

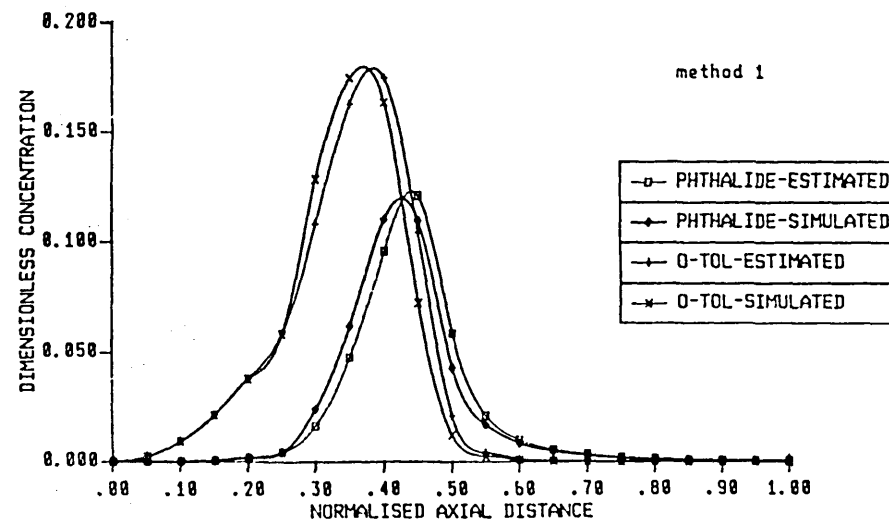
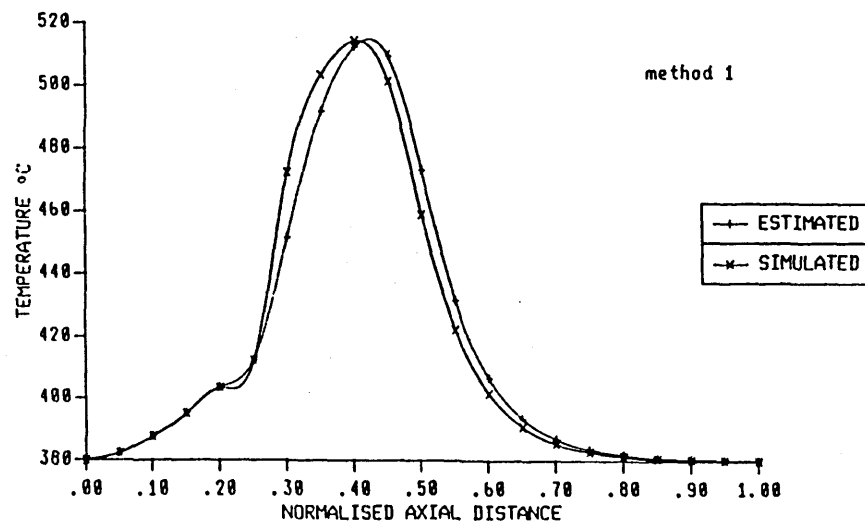
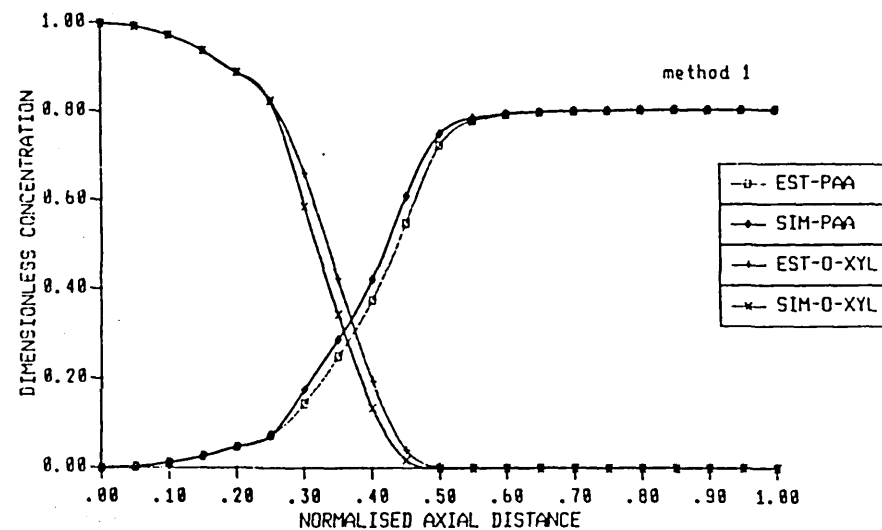
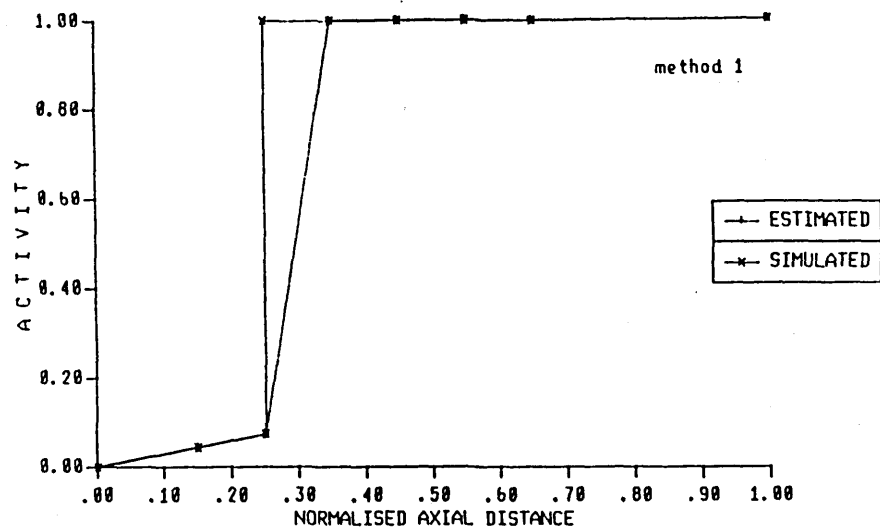


Fig. 5.6 Estimated temperature and concentration profiles compared with simulated data; activity profile approximated by method 1 and estimated using both simulated temperature and concentration measurements.

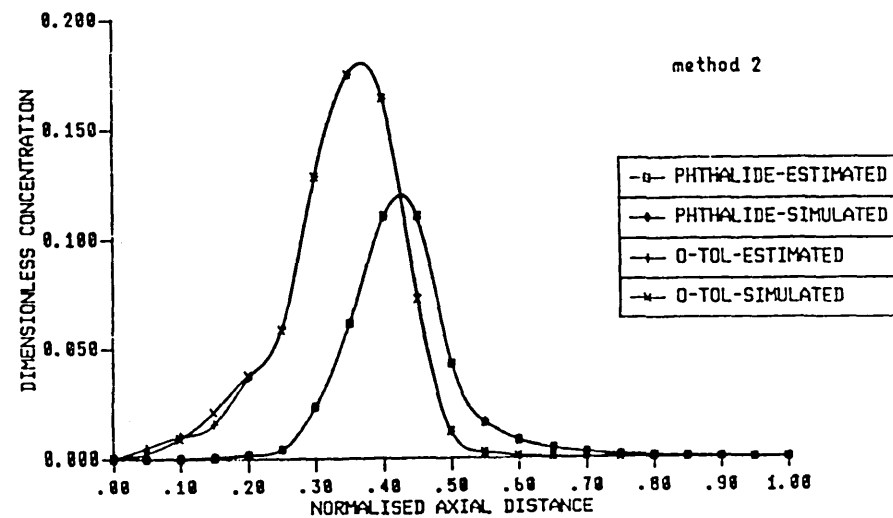
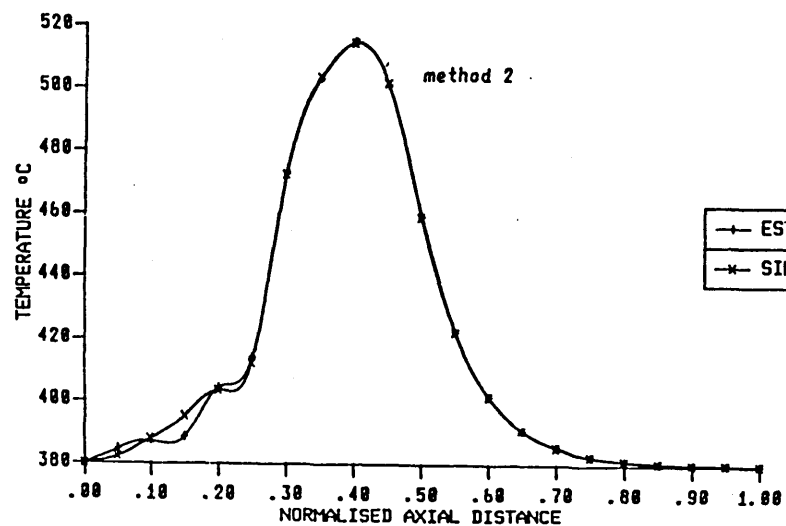
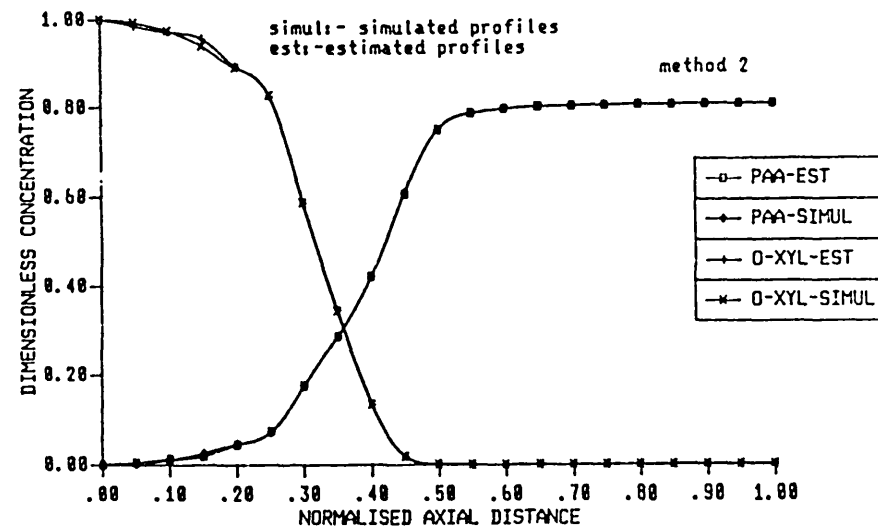
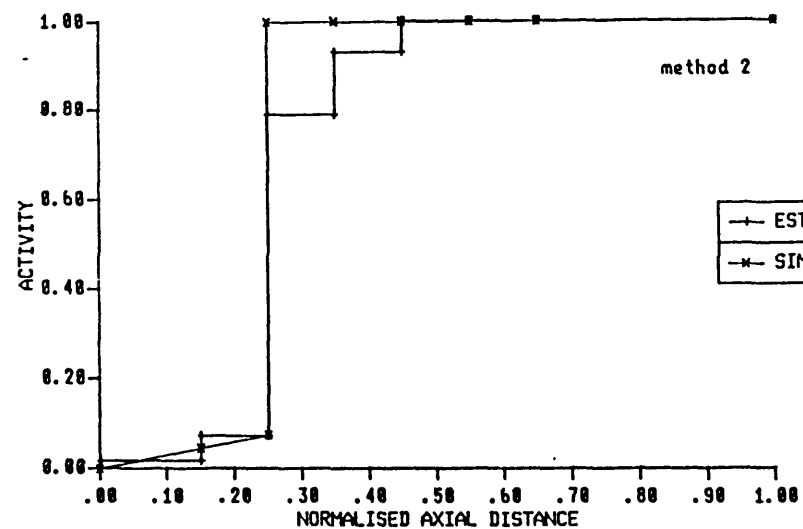


Fig. 5.7 Estimated temperature and concentration profiles compared with simulated data; activity profile approximated by method 2 and estimated using both simulated temperature and concentration measurements.

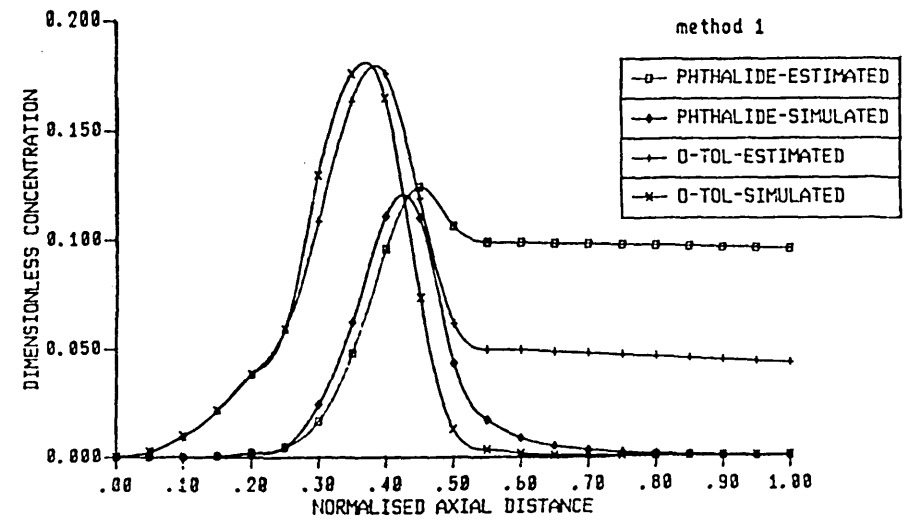
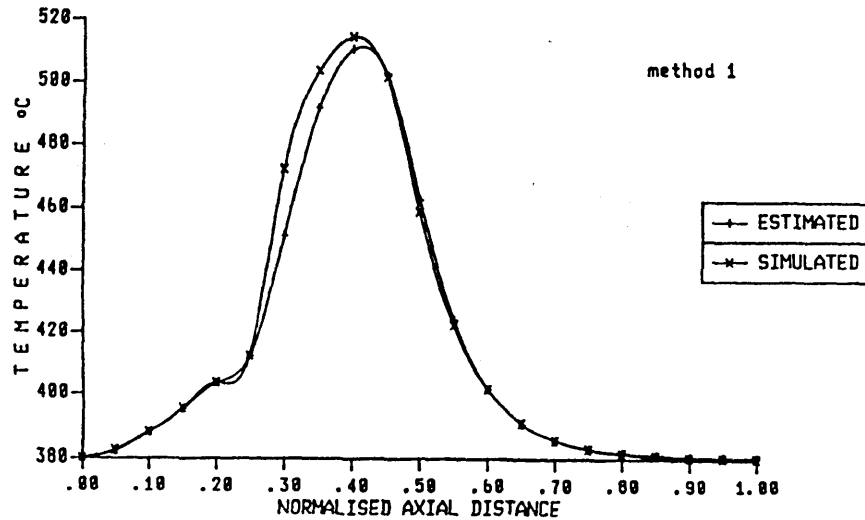
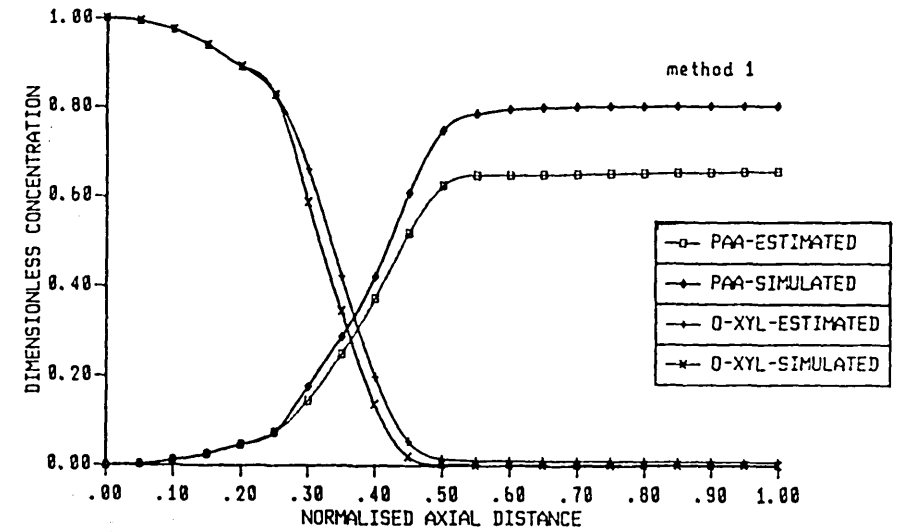
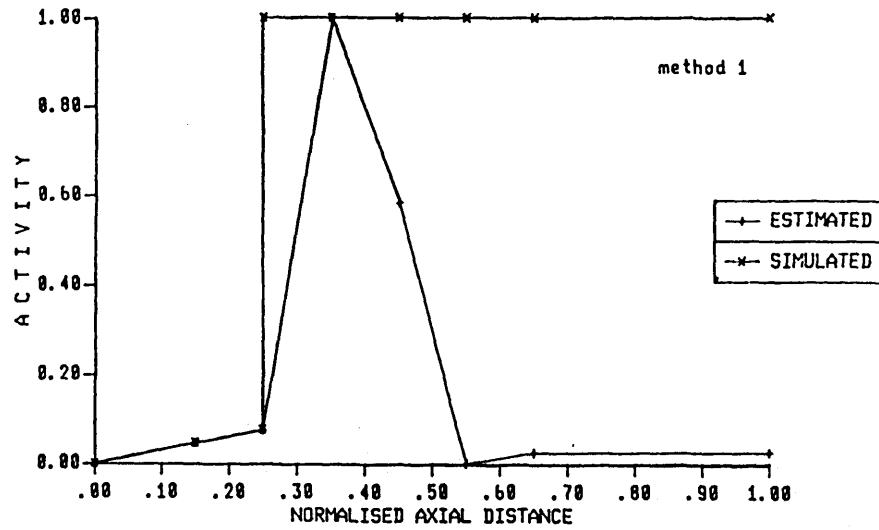


Fig. 5.8 Estimated temperature and concentration profiles compared with simulated data; activity profile approximated by method 1 and estimated using only simulated temperature measurements.

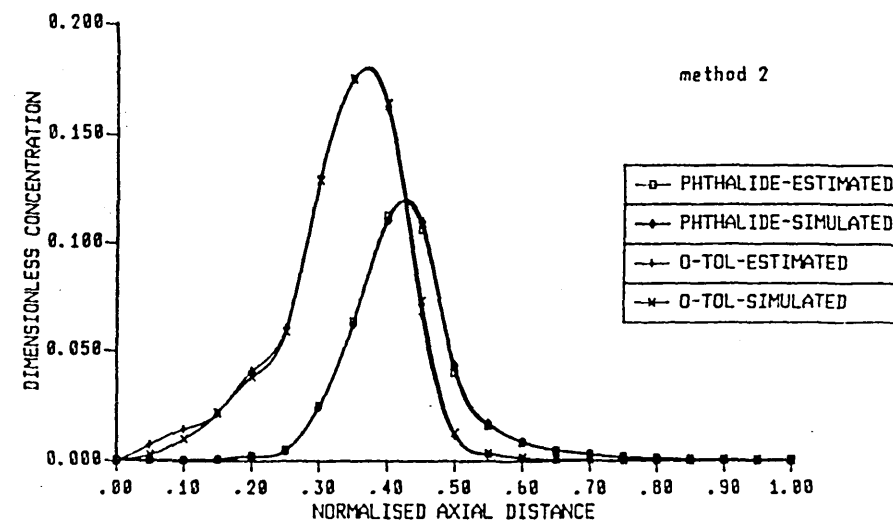
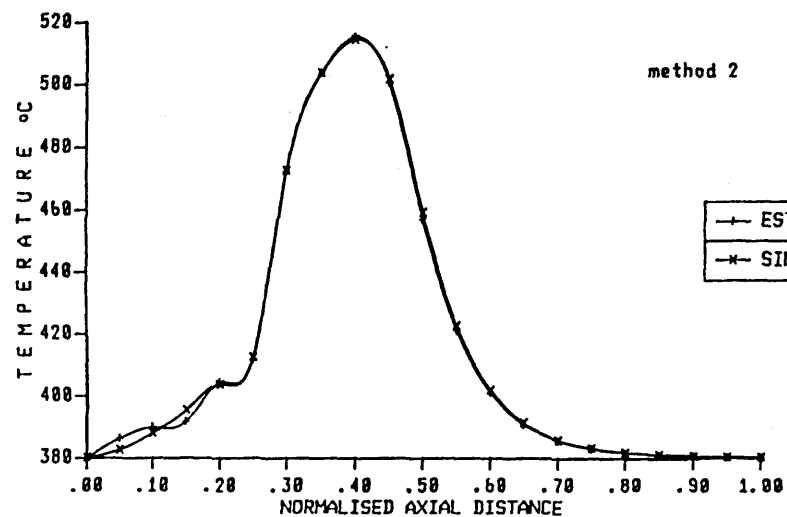
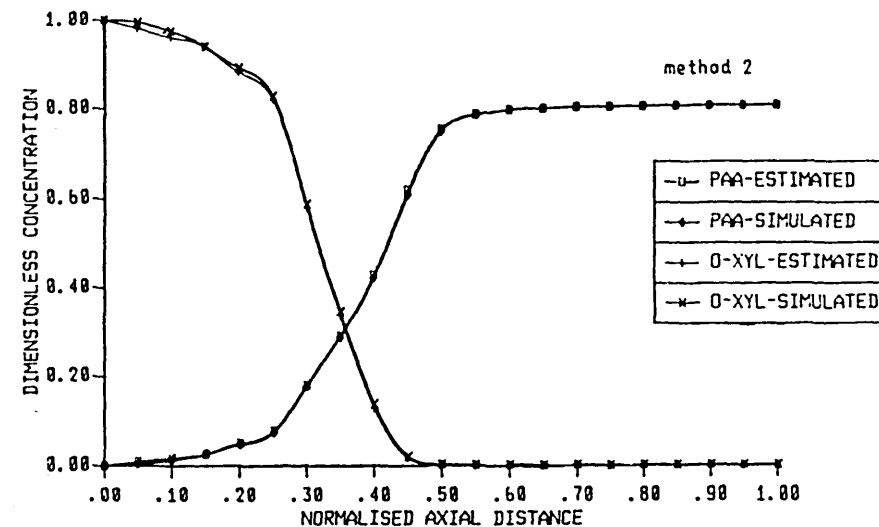
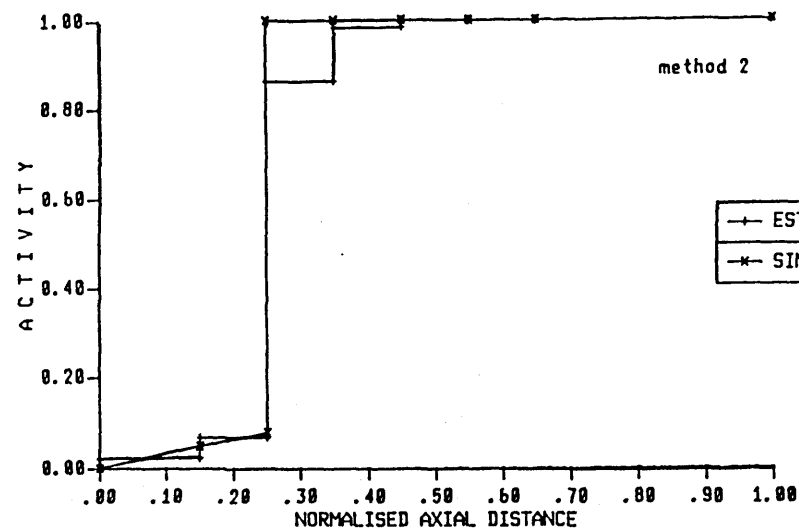


Fig. 5.9 Estimated temperature and concentration profiles compared with simulated data; activity profile approximated by method 2 and estimated using only simulated temperature measurements.

5.2 CONCLUSIONS

The presence of catalyst deactivation in this complex reactor-reaction system makes it extremely difficult to model. It is suggested that, perhaps the best approach to model the system, in the light of several limitations (e.g. with the existing kinetic model), is to incorporate catalyst activity profiles into the kinetic model via a catalyst deactivation model whose parameters can be estimated using early pilot plant reactor data.

Due to time limitations, it was not possible to derive such a model for this system. Instead, two methods of parameterization of an activity profile have been developed so as to estimate the activity parameters directly, at any given time, from current reactor data.

The first method approximates the activity within each finite element by a straight line so that the global activity profile is continuous linear with break points. For the second method, the activity within each element is assumed to be uniform and the resulting global activity profile is a piece-wise constant function.

Both methods have been used to estimate the arbitrary activity profile introduced in Chapter 3 to simulate the steady state behaviour of the reactor; an activity profile which has a discontinuity at the point of inflection of the simulated temperature profile.

In both cases, the activity parameters were estimated sequentially by minimizing the square of deviations of the model solution from simulated measurements by applying a quasi-Newton optimization scheme which is capable of handling several parameters at a time. Such a powerful optimization scheme was probably not necessary for only a one-dimensional search but it was used because it was appropriate at some stage

to estimate several activity parameters simultaneously for comparison of results (cf Chapter 6).

The second method gave a better overall estimate of both the simulated temperature and concentration profiles but there were ripples on the profiles at the upstream end of the reactor caused by discontinuities in the rate of reaction from one finite element to the next. The first method predicted a slight shift of the profiles towards the reactor's exit, possibly because the nature of the simulated activity profile made the situation rather awkward for this method.

However, both methods were used to estimate catalyst activity profiles using experimental reactor data in order to predict the reactor behaviour but the second method was extensively used because it gave closer predictions of both the magnitude and position of the hot-spot temperature (from preliminary calculations using real reactor data) especially when both temperature and concentration measurements were used in the estimation (see Chapter 6 for details).

CHAPTER SIX

6.0 RESULTS AND DISCUSSION

In this chapter, steady state experimental results are presented and discussed in Section 6.1. Section 6.2 deals with the evaluation of heat transfer parameters while the important topic of predicting the steady state behaviour of the reactor using experimental data to estimate catalyst activity profiles is treated in Section 6.3. In Section 6.4 long-run steady state experimental results are presented and discussed. Finally, in Section 6.5 the results of the dynamic behaviour of the reactor comprising step changes in the o-xylene feed concentration and a ramp increase in the salt bath temperature are presented and discussed. Also in this section, an attempt is made to predict the dynamic behaviour of the reactor by estimating catalyst activity profiles using only temperature measurements.

6.1 STEADY STATE EXPERIMENTS

The experiments were carried out to investigate the behaviour of the reactor when subjected to the various steady state operating conditions for a period of about 10 to 12 hrs per day per set of operating conditions. But for a few exceptions, every start-up was preceded by a period of about 30 to 40 hrs of catalyst regeneration during which time the salt bath temperature was maintained between 400 and 410°C and 2Nm³/hr of air passed through the reactor. This process ensured the reproducibility of experimental results.

The operational procedure has already been outlined in Chapter 4, Section 4.6. For a given set of operating conditions, steady state

was achieved after about 3 hours of continuous operation. The axial temperature and concentration measurements were then taken during the steady state period and were later used for estimation of catalyst activity profiles.

A summary of the various operating conditions considered in this work is presented in Table 6.1. The experiments were carried out in two different periods of the catalyst life.

The first period was immediately after the end of the first start up, just when the catalyst had attained normal activity. Only experimental run 1 (Table 6.1) was carried out during this period.

At the end of the three weeks of continuous operation to normalise the activity of the catalyst, the reactor was shut down and the catalyst regenerated by passing only air at $2 \text{ Nm}^3/\text{hr}$ with the salt bath temperature maintained at 405°C for a period of about 40 hrs. After catalyst regeneration, the reactor was run for 3 consecutive days for a period of about 10 to 12 hrs per day with the air flowrate $4 \text{ Nm}^3/\text{hr}$, o-xylene flowrate 176 gm/hr and salt bath temperature 384°C . By the third day the catalyst had sufficiently partially deactivated especially around the inlet region of the reactor. Only measurements taken on the third day were analysed and the results are shown in Fig. 6.1. Despite the fact that the catalyst was reversibly deactivated, a maximum selectivity to phthalic anhydride of about 81% was observed. Other workers have also recorded high selectivities. Wainwright & Hoffman (1974, 1977) reported 85 mole% for 100% conversion, Calderbank et al. (1977) observed 75 to 82 mole%.

Fig. 6.1a shows a steep axial temperature profile with a temperature difference of about 112°C within an axial distance of just about

TABLE 2
STEADY STATE OPERATING CONDITIONS

Run	Figure	Air Flowrate (Nm ³ /hr)	O-xylene Flowrate (gm/hr)	Saltbath Temperature (°C)	Inlet Pressure (Bar)	Pressure Drop (Bar)	Hotspot Tempera- ture (°C)	Yield of Phthalic Anhydride mole%	O-xylene Final Conversion (%)
*1	6.1	4	176	384	1.33	.1914	512	81	99.91
2	6.2	"	168	375	1.33	.278	495	63.62	99.73
3	6.3	"	168	380	1.33	.278	497	66.94	99.87
4	6.4	"	168	384	1.33	.278	511	72.99	99.96
5	6.5	"	176	375	1.33	.278	490	68.30	99.71
6	6.6	"	176	380	1.33	.278	516	72.73	99.91
7	6.7	"	176	384	1.33	.278	531	69.46	99.95
8	6.8	"	205	375	1.33	.278	531	69.46	99.85
9	6.9	"	205	380	1.33	.278	558	64.28	99.92

* A pre-reversibly deactivated catalyst.

20 cm. The hotspot is located very close to axial position 14 (~130 cm downstream of the reactor). This position is also the point of intersection of the concentration profiles of o-xylene and phthalic anhydride as shown by Fig. 6.1b.

The rest of the experiments, runs 2 to 9, were carried out during the second period after a three-month shutdown of the reactor which resulted in a slight reduction in the selectivity of the catalyst to phthalic anhydride, probably due to irreversible catalyst deactivation. During this period, it was found that changes in the overall yield of phthalic anhydride and the total conversion of o-xylene with respect to variations in the operating conditions, within the ranges considered, were only marginal. Similar conclusions have been reached by other workers [Calderbank et al. (1970, 1972, 1979), Ellis (1972)].

Calderbank et al. (1970, 1972) obtained a constant selectivity of 58-64% under the operating conditions 370 to 454°C salt bath temperature and 0.5 to 1.5 mole% o-xylene in feed. Ellis (1972) [in Lopez-Isunza (1983)] obtained a maximum PA selectivity of 70% independent of the salt bath temperature within the range 410 to 490°C. However, both groups of workers used a promoted V_2O_5 on SiC-supported catalyst.

For the TiO_2 -supported catalyst used in this work, the selectivity measured was between 63 to 74% under the operating conditions 375 to 384°C salt bath temperature, 168 to 205 gm/hr o-xylene flowrate and 4 Nm^3/hr air flowrate. For this same catalyst, Lopez-Isunza (1983) obtained a selectivity of 67 to 77% under the operating conditions 390 to 400°C salt bath temperature, 129 to 242 gm/hr o-xylene flowrate and 3 to 4 Nm^3/hr air flowrate.

All the experiments were carried out with the air flowrate maintained at $4\text{Nm}^3/\text{hr}$. Figs. 6.2 to 6.4 were obtained for o-xylene flowrate of 168 gm/hr and salt bath temperatures of 375 , 380 and 384°C respectively. The results depicted by Figs. 6.5 to 6.7 were obtained for o-xylene flowrate of 176 gm/hr and salt bath temperatures of 375 , 380 and 384°C respectively, whereas for Figs. 6.8 and 6.9 the o-xylene flowrate was 205 gm/hr and salt bath temperatures 375 and 380°C respectively. It must be emphasized that these conditions are well within industrial practices.

A common feature of Figs. 6.2 to 6.9 is the steepness of the axial temperature profile. In just about 20 to 25 cm axial distance a temperature rise of about 100°C is indicated. There is also a remarkable coincidence between the point of intersection of the concentration profiles of o-xylene and phthalic anhydride and the position of the hotspot temperature shown by these figures. At that point, almost invariably, about 70% of the o-xylene has disappeared and about 30 mole% of the phthalic anhydride produced. Figs. 6.2 to 6.9 show that the rest of the phthalic anhydride was produced within an axial distance of about 40 cm after the hotspot. These observations are consistent with those made by Lopez-Isunza (1983) who remarked that for 70 to 84% o-xylene conversion, about 28% PA, 4% OT, 0.3% MA and 2 to 3% PT were produced. However, he used only a few concentration measurements to construct his profiles and therefore their accuracy is very much questionable.

Traces of maleic anhydride were observed only at the outlet of the reactor, axial position 24, when o-xylene conversions were almost 100%. However, it is difficult to say precisely whether maleic anhydride was present in the other sampling points or not since there was very poor

resolution between peaks of maleic anhydride and o-tolualdehyde in the chromatograms. It is possible that maleic anhydride, a final product, could have been present in some or all the other sampling points but its peak was overshadowed by that of o-tolualdehyde which is an intermediate product, and only came visible at the outlet where almost all the o-tolualdehyde has disappeared. At this juncture it is difficult to say whether maleic anhydride was produced only from the overoxidation of phthalic anhydride [Wainwright & Foster (1979)] or was a total oxidation product formed only from o-xylene [Simard *et al.* {in Dixon & Longfield (1960)}].

It can also be observed from Fig. 6.1 to 6.9 that the rate of reaction around the inlet region of the reactor is very low for temperatures lower than 415°C and for high o-xylene concentrations (~1%). This temperature may be regarded as the ignition temperature since the rate of reaction immediately after that is very high as manifested by the steep temperature gradients. The axial position at which this temperature was attained was dependent upon the salt bath temperature and the inlet o-xylene concentration, on the one hand, and on the state (activity) of the catalyst, on the other hand.

The influence of catalyst deactivation on the positions of the ignition and hotspot temperatures can be very much appreciated if Figs. 6.1 and 6.7, obtained from experiments carried out under the same operating conditions, 384°C salt bath temperature and 176 gm/hr o-xylene flowrate, are compared. It can be seen that for the reversibly deactivated catalyst, Fig. 6.1a, the ignition and hotspot temperatures are located at an axial distance of about 110 and 135 cm whereas for a regenerated catalyst, Fig. 6.7a, the two are located at about 70 and 105 cm respectively from the reactor inlet. Similar observations can

be made for the influence of salt bath temperature and o-xylene initial concentration on the steady state behaviour of the reactor. Figs. 6.2a and 6.5a show that for a salt bath temperature of 375°C and o-xylene flowrate of 168 or 176 gm/hr, the ignition and hotspot temperatures are located at axial distance of about 110 and 150 cm whereas for a salt bath temperature of 384°C and o-xylene flowrate of 168 gm/hr (Fig. 6.4a) the two are located at 75 and 100 cm, respectively, from the reactor inlet.

The ignition temperature itself was dependent upon the state of the catalyst. For a fresh catalyst (very active) it was found that the reaction was capable of starting at temperatures as low as 350°C. Lopez-Isunza (1983) reported an even lower ignition temperature of 290°C for a fresh catalyst.

The measured selectivity of o-xylene to CO and CO₂ at the reactor's exit (axial position 24) was within the range 19 to 22%. This is in agreement with the value of 21.7% for phthalic anhydride selectivity of 74% reported by von Heyden (1974). Detailed experimental results of CO/CO₂ analysis are reported in Appendix A.

6.1.1 Conclusions

Steady state experiments have demonstrated the existence of steep axial temperature and concentration gradients caused by partial deactivation of the catalyst especially in the inlet region of the reactor where o-xylene concentrations are high and temperatures low.

The temperature at which the reaction started (the ignition temperature) was found to be a function of the state of the catalyst; for a very fresh catalyst the reaction was able to start at temperatures as

low as 350°C while for a catalyst whose activity has been normalised little or no reaction occurred at temperatures lower than 415°C.

The axial position at which the steep temperature and concentration gradients were located was found to be partly dependent upon the activity of the catalyst on the one hand and on the salt bath temperature and o-xylene initial concentration on the other hand. For a freshly regenerated catalyst whose activity has been stabilised and provided the salt bath temperature was sufficiently high (380-384°C), the hot-spot was generally located at the upstream end of the reactor between axial positions 11 and 14 while for a reversibly deactivated catalyst and for low salt bath temperatures (~375°C) it was usually located further downstream between axial positions 14 and 16.

These observations highlight the importance of a catalyst deactivation model to be incorporated into the kinetic model if it is intended to develop a suitable reactor model for this type of reactor-reaction system. The existence of spatially varying catalyst activity profiles is caused by the fact that the deactivation process is not uniform throughout the catalytic bed.

One may therefore conclude that if such an activity profile could be estimated, it may be possible to predict the reactor behaviour reasonably well.

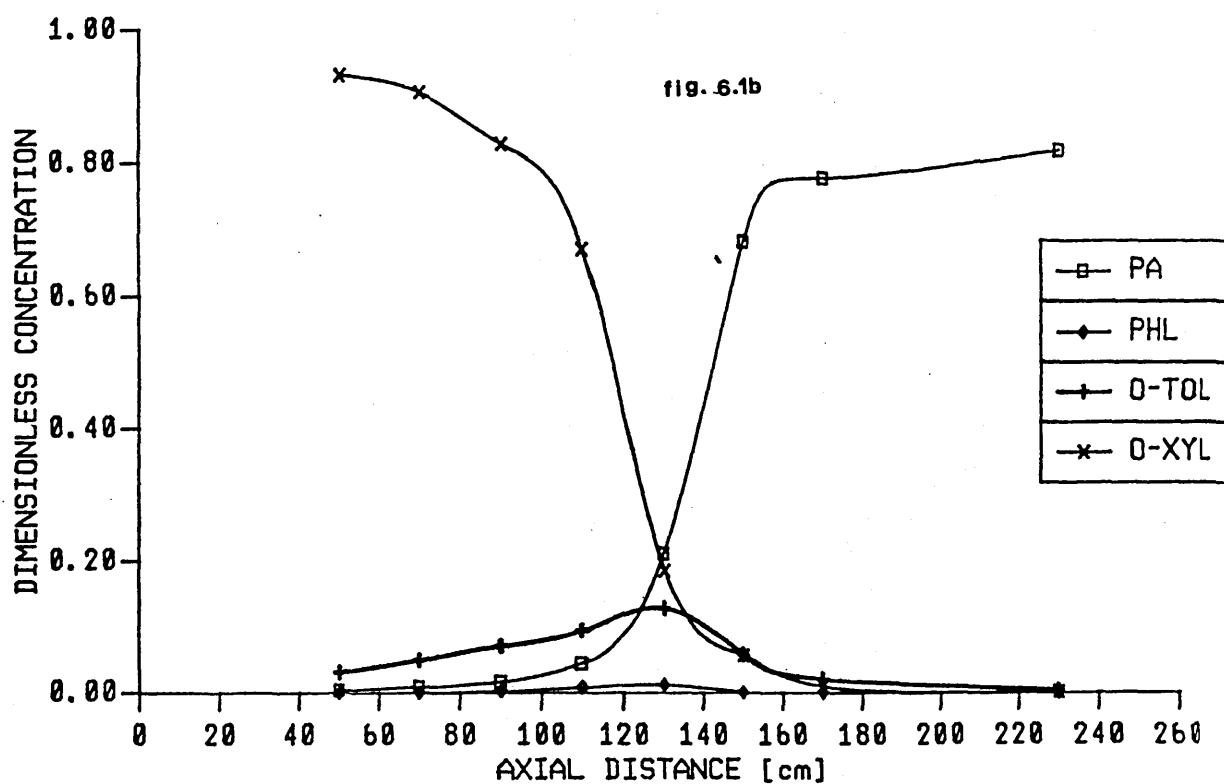
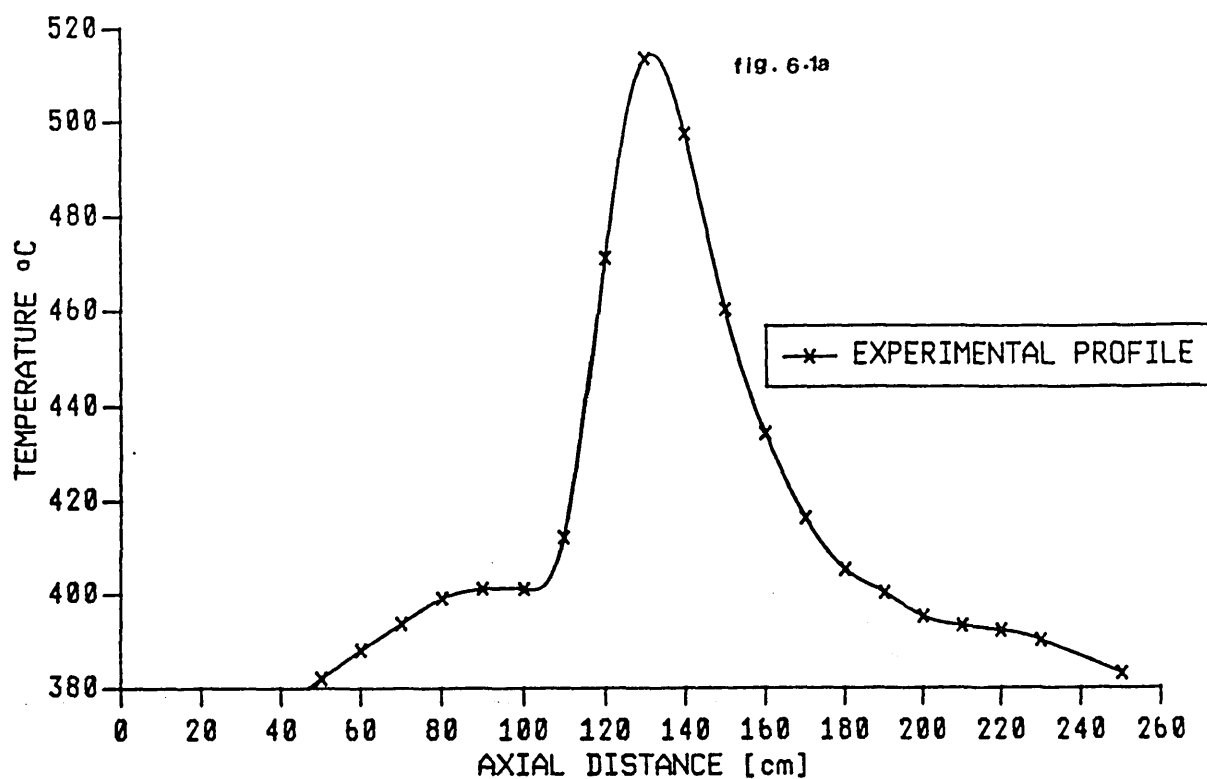


Fig. 6.1 Experimental steady state axial temperature and concentration profiles for a pre-reversibly deactivated catalyst; salt bath temperature 384°C and o-xylene flowrate 176gm/hr(see table 6.1)

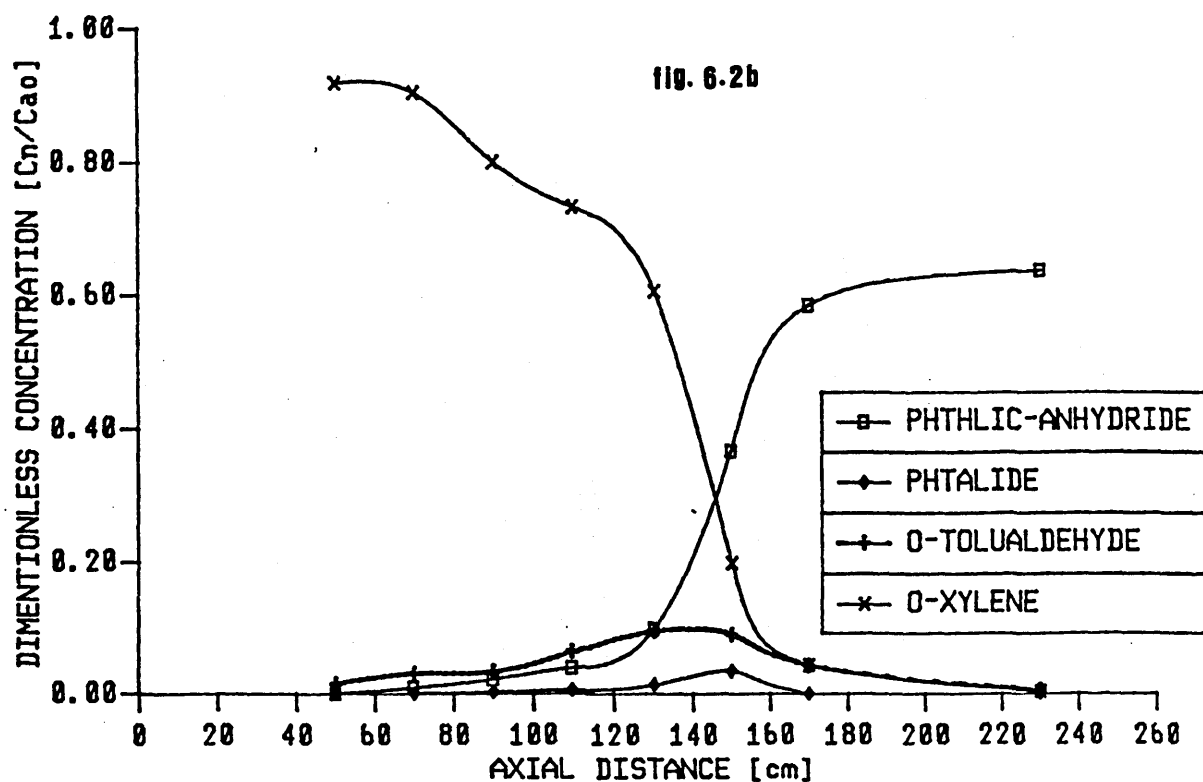
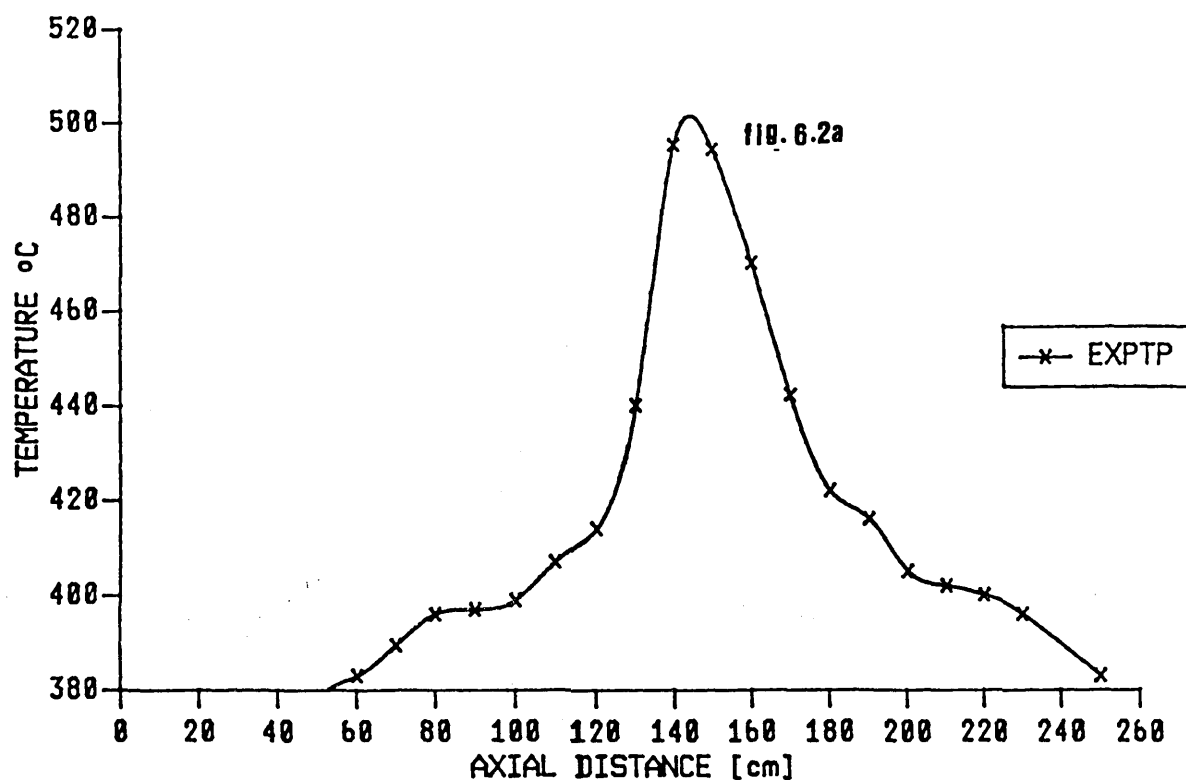


Fig. 6.2 Experimental steady state axial temperature and concentration profiles at normal catalyst activity; salt bath temperature 375°C and o-xylene flowrate 168gm/hr(see table 6.1).

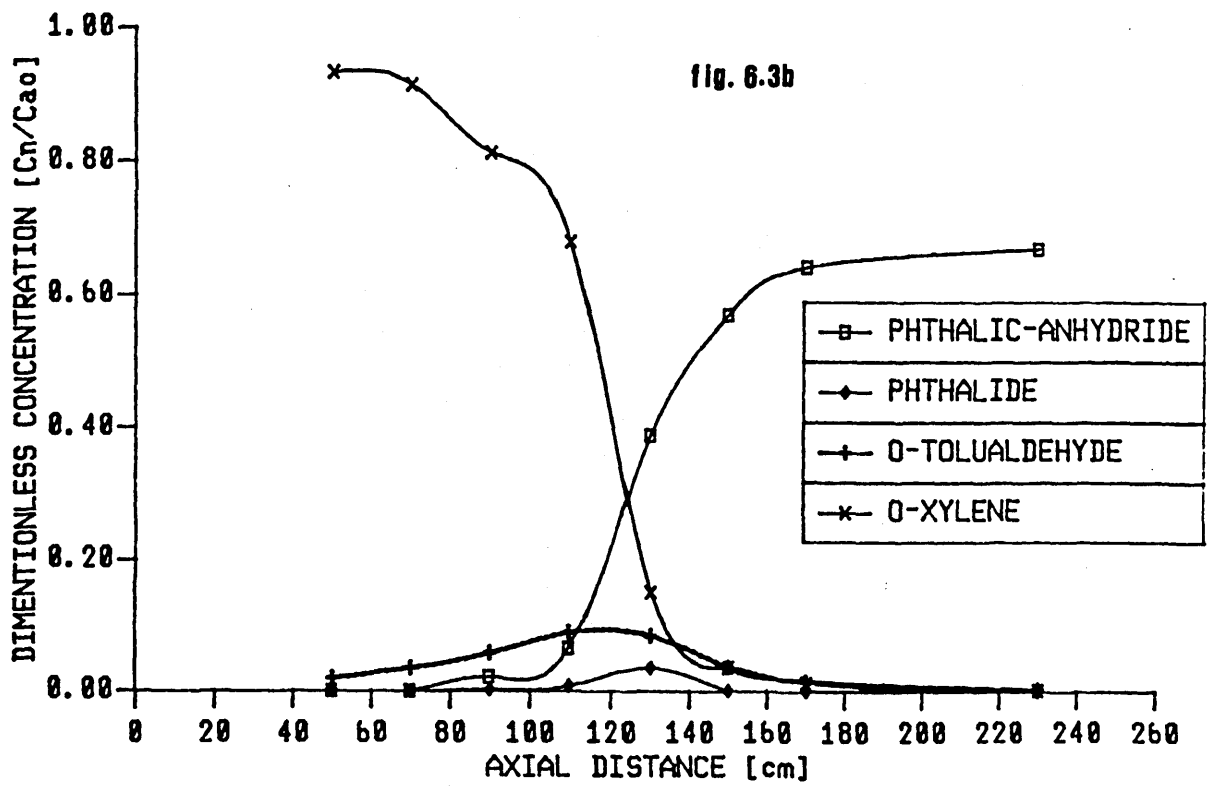
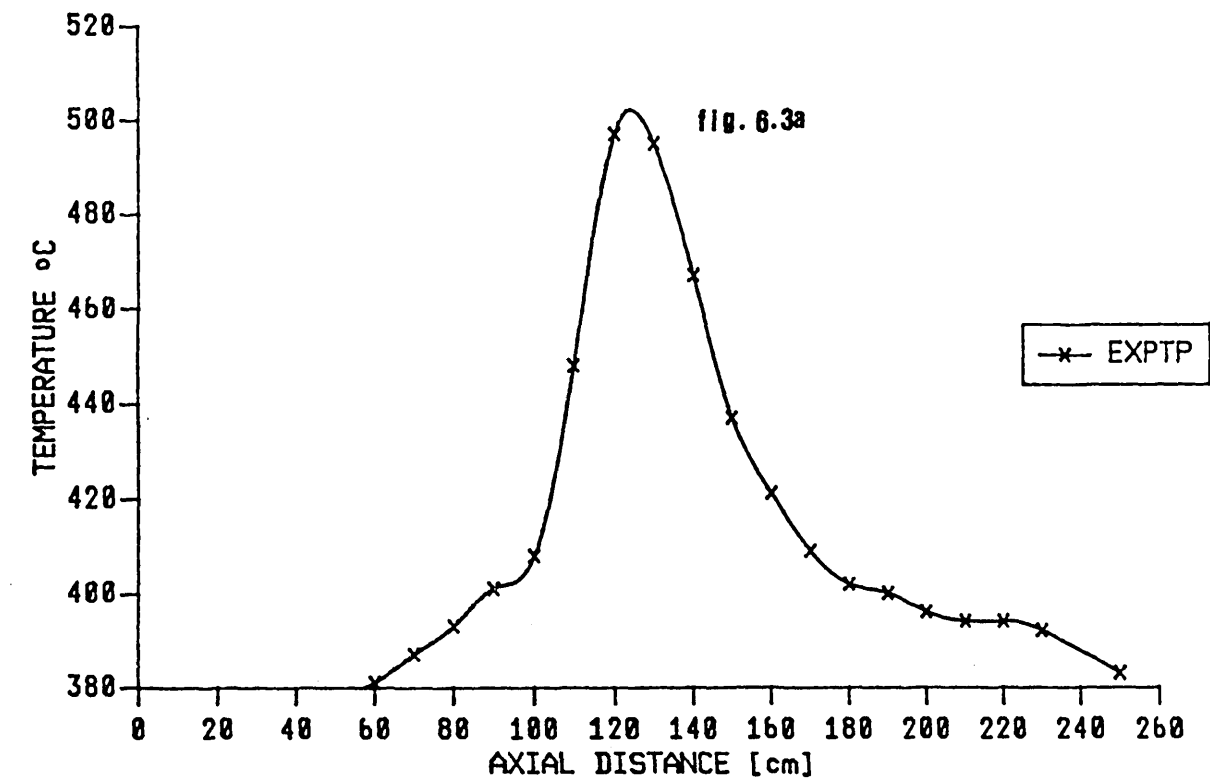


Fig. 6.3 Experimental steady state axial temperature and concentration profiles at normal catalyst activity; salt bath temperature 380°C and o-xylene flowrate 168gm/hr(see table 6.1).

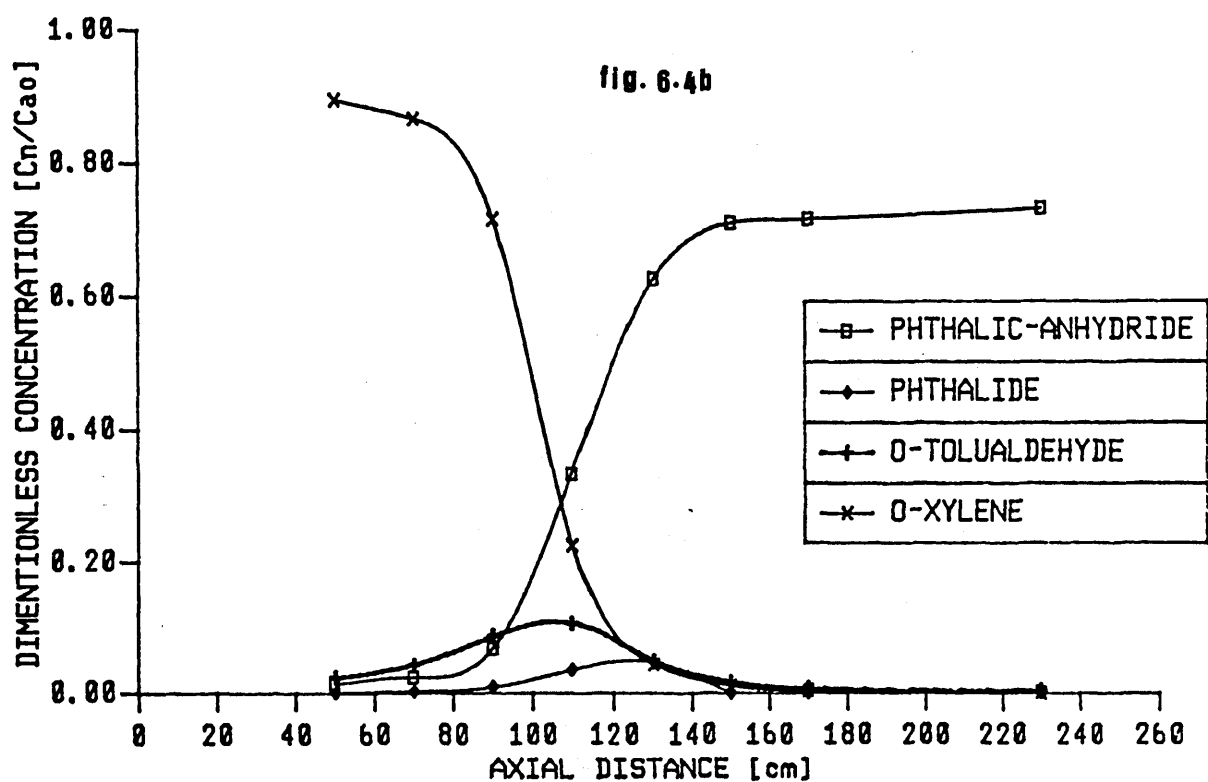
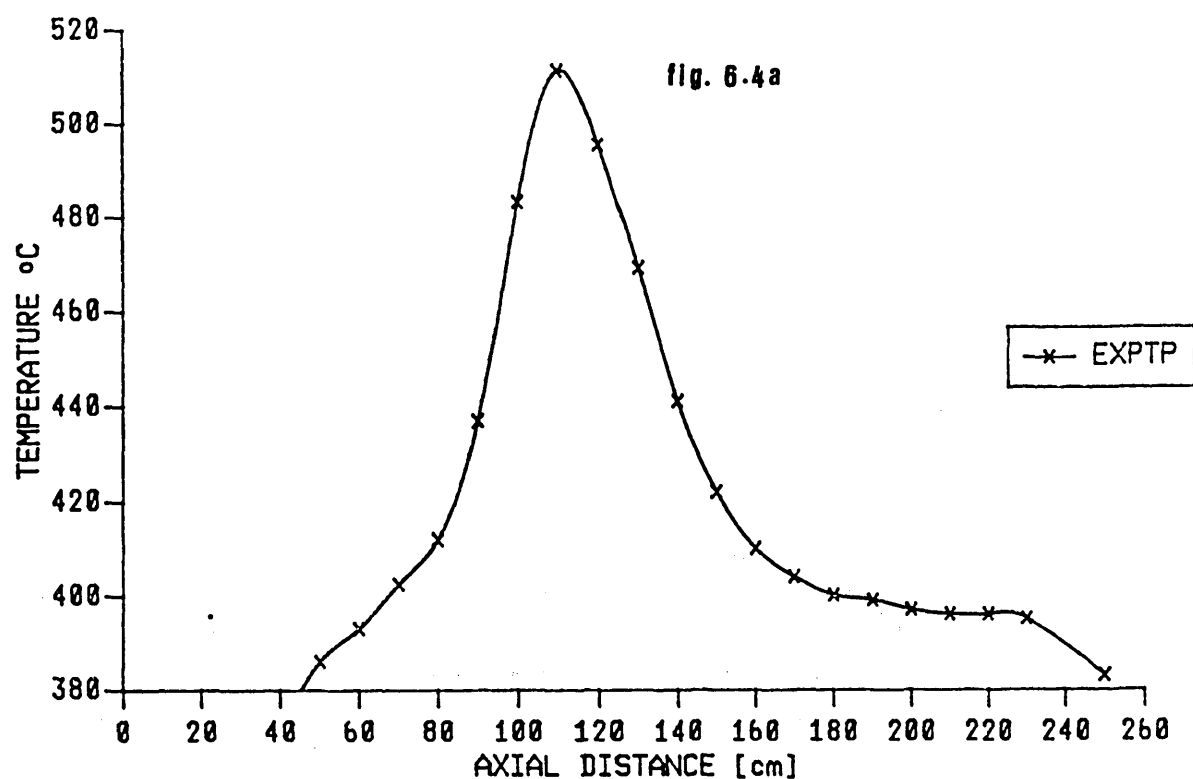


Fig. 6.4 Experimental steady state axial temperature and concentration profiles at normal catalyst activity; salt bath temperature 384°C and o-xylene flowrate 168gm/hr(see table 6.1)

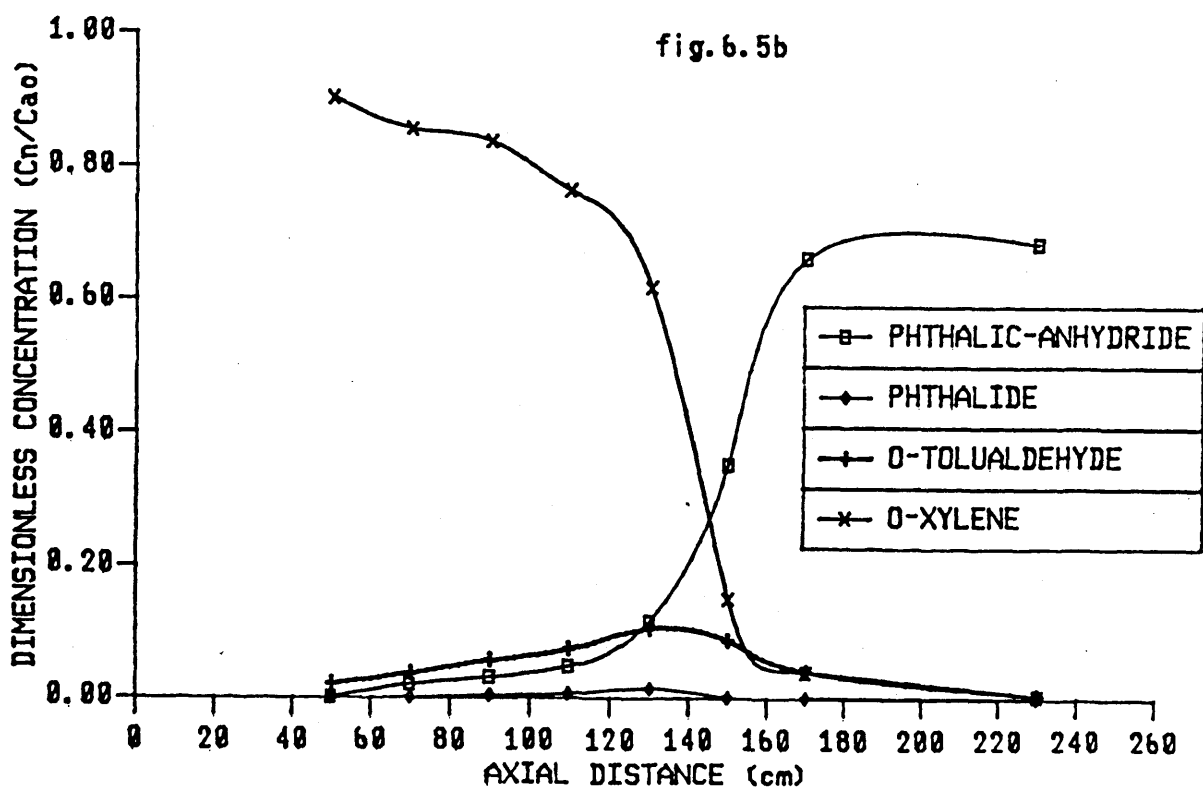
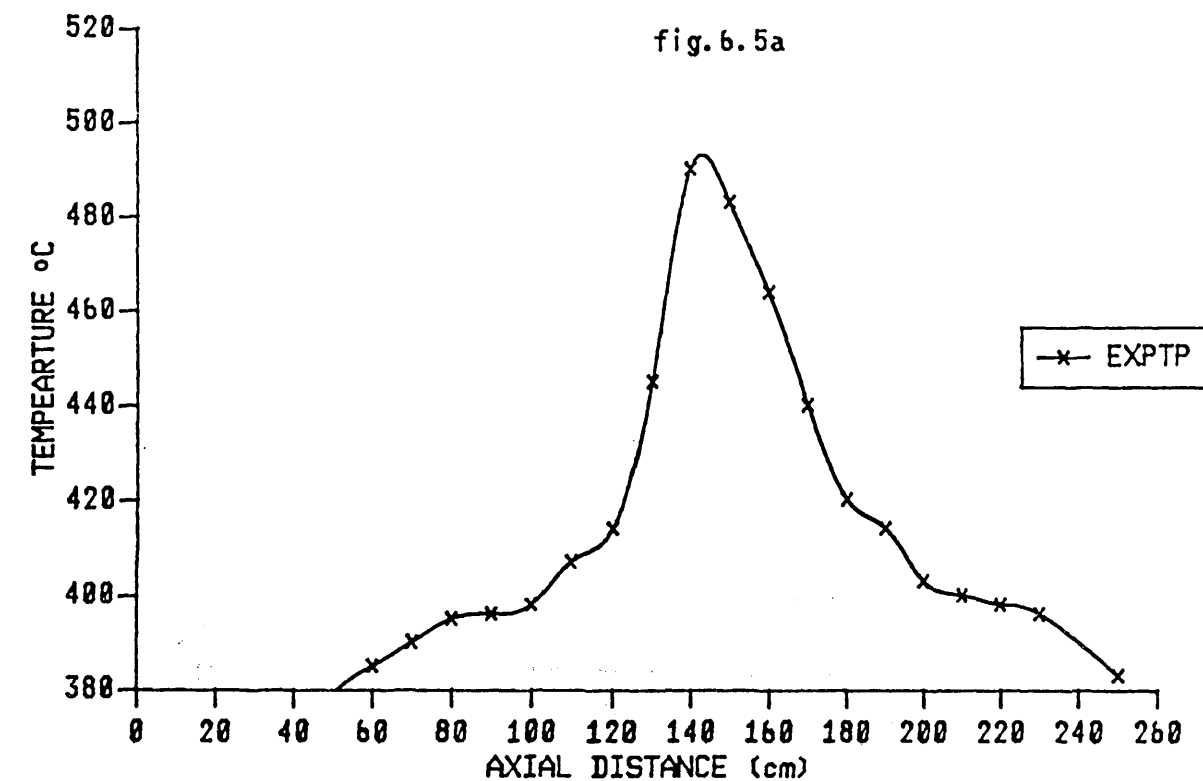


Fig. 6.5 Experimental steady state axial temperature and concentration profiles at normal catalyst activity; salt bath temperature 375°C and o-xylene flowrate 176gm/hr(see table 6.1).

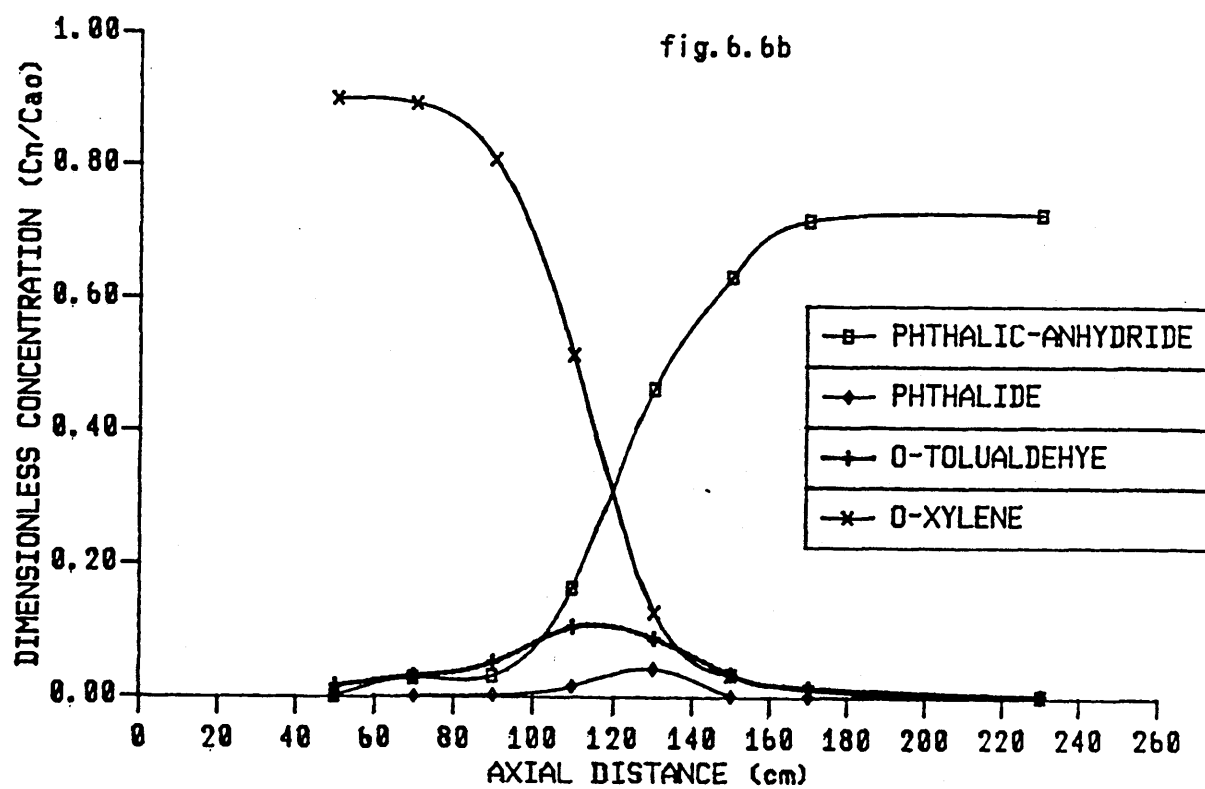
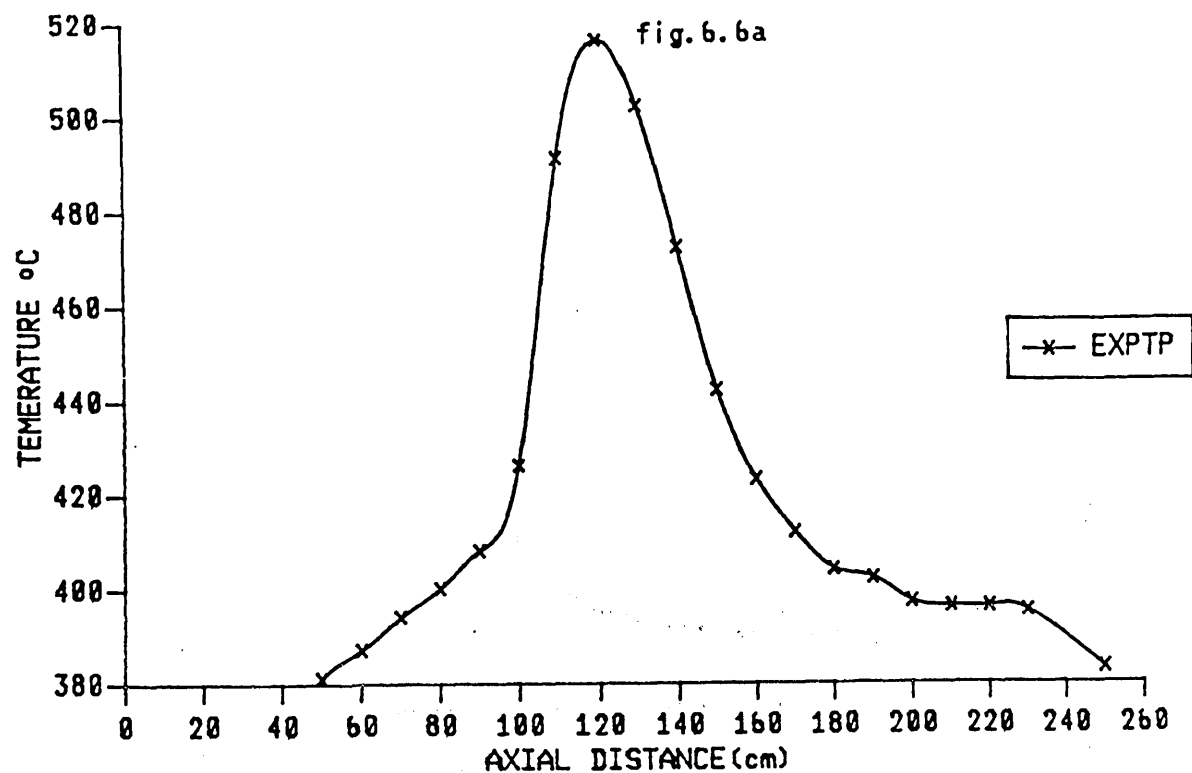


Fig. 6.6 Experimental steady state axial temperature and concentration profiles at normal catalyst activity; salt bath temperature 380°C and o-xylene flowrate 176gm/hr(see table 6.1).

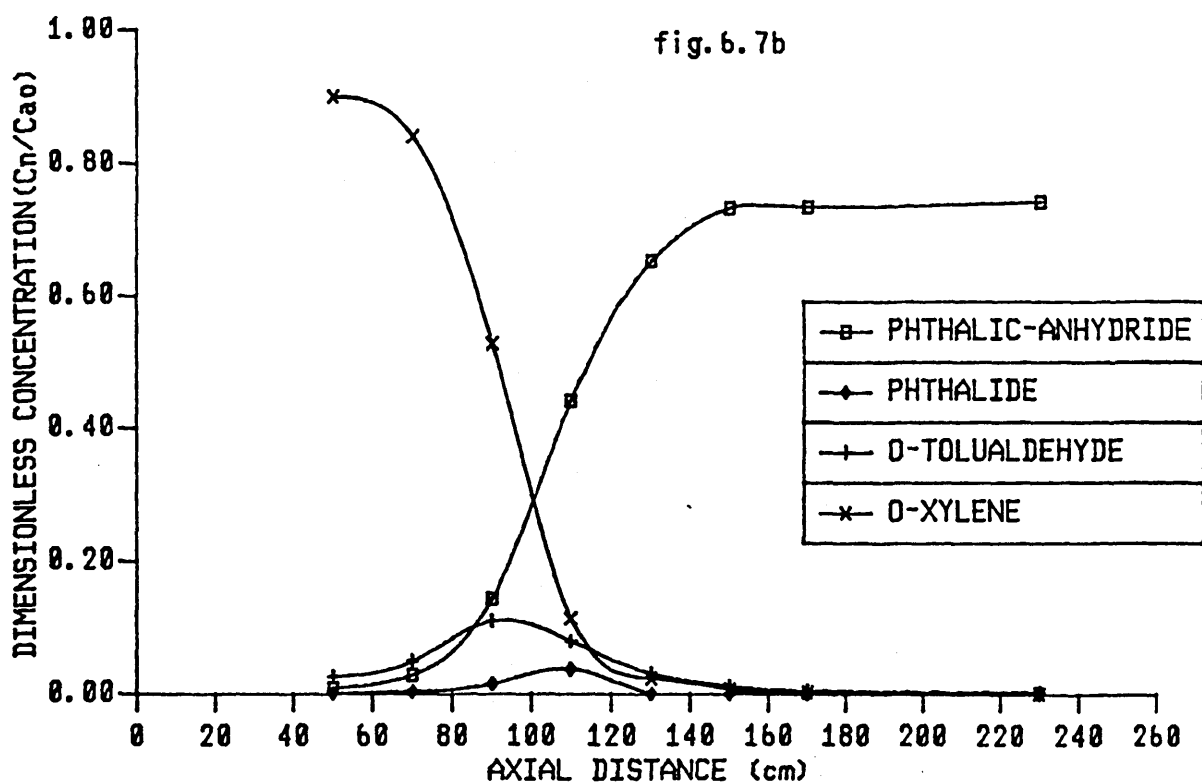
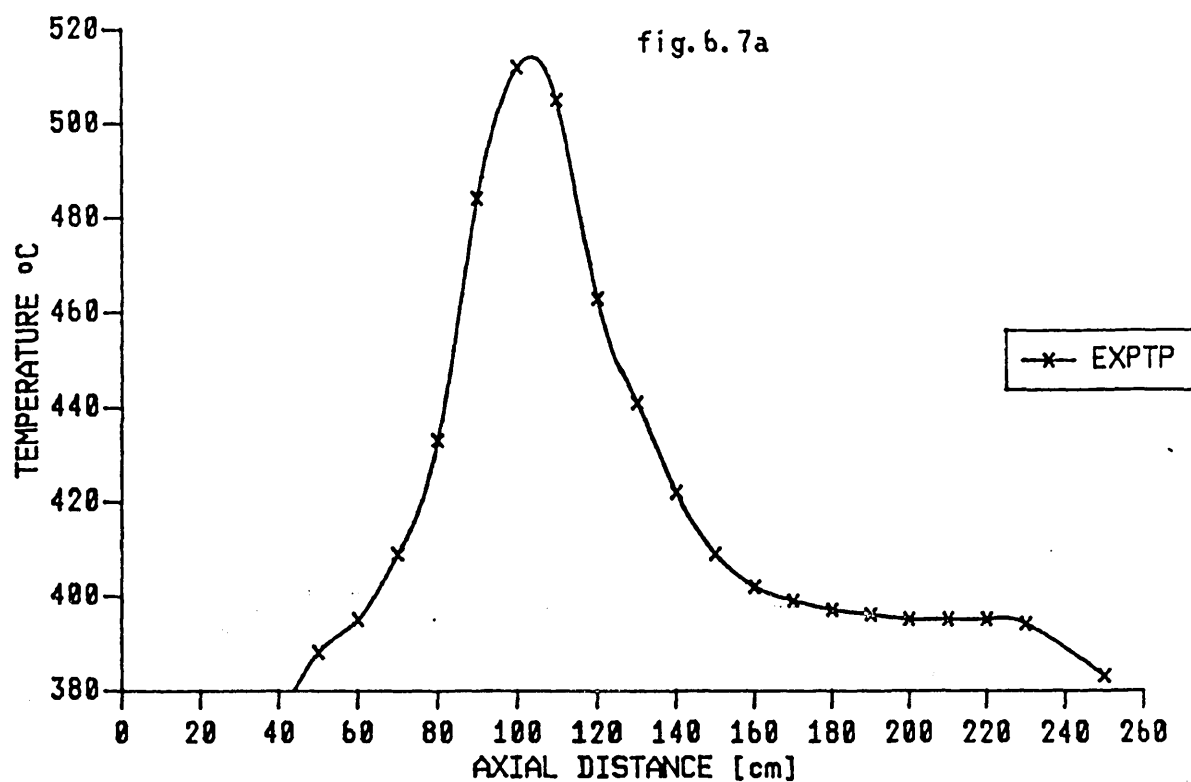


Fig. 6.7 Experimental steady state axial temperature and concentration profiles at normal catalyst activity; salt bath temperature 384°C and o-xylene flowrate 176gm/hr(see table 6.1).

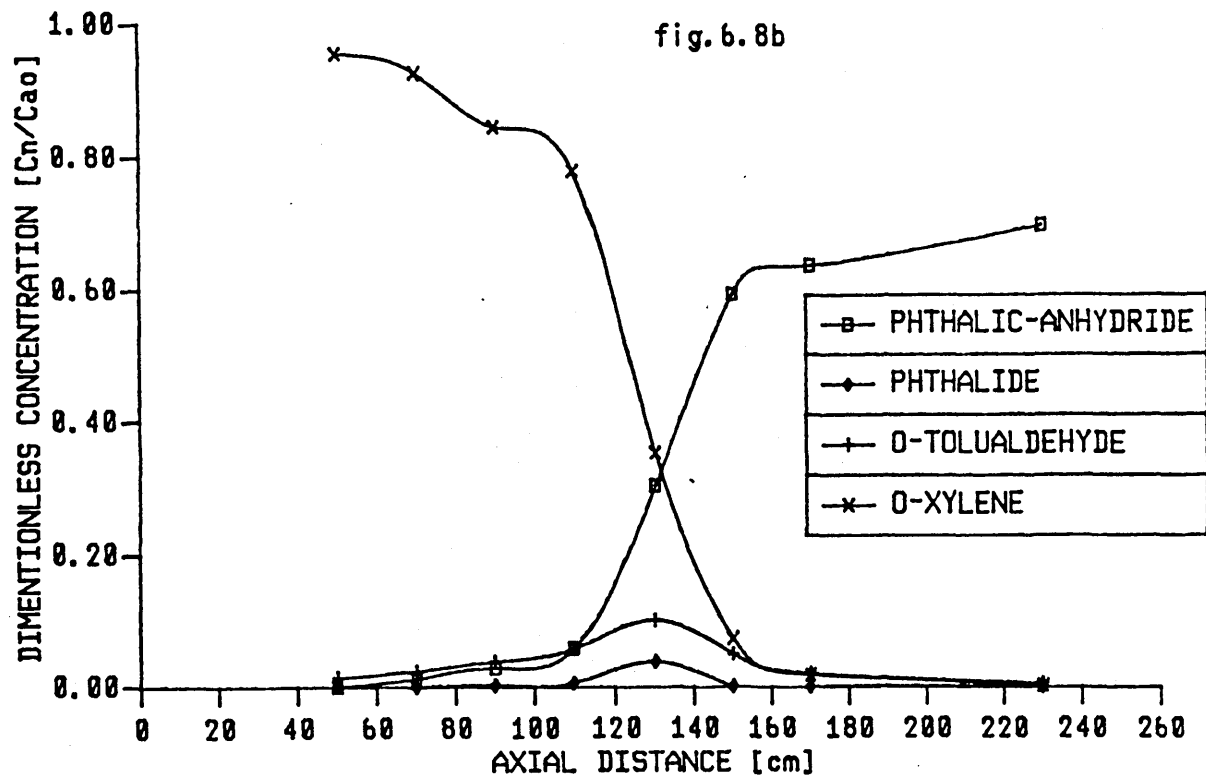
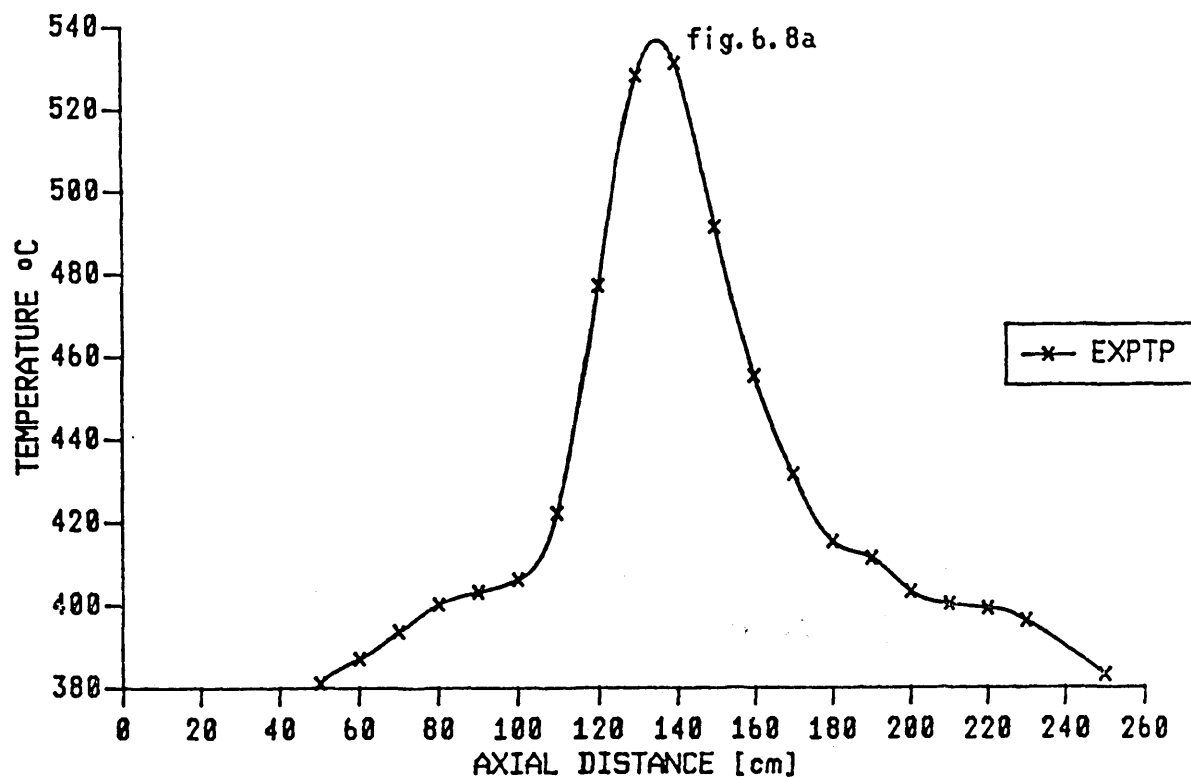


Fig. 6.8 Experimental steady state axial temperature and concentration profiles at normal catalyst activity; salt bath temperature 375°C and o-xylene flowrate 205gm/hr(see table 6.1)

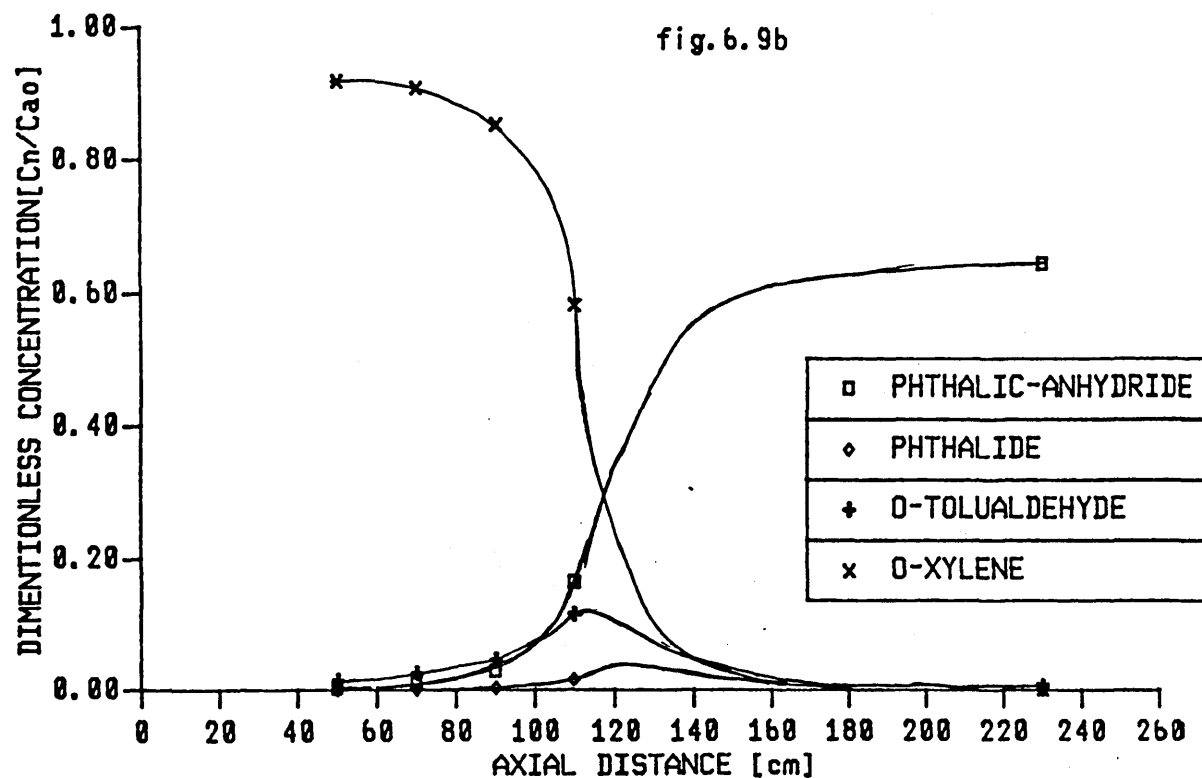
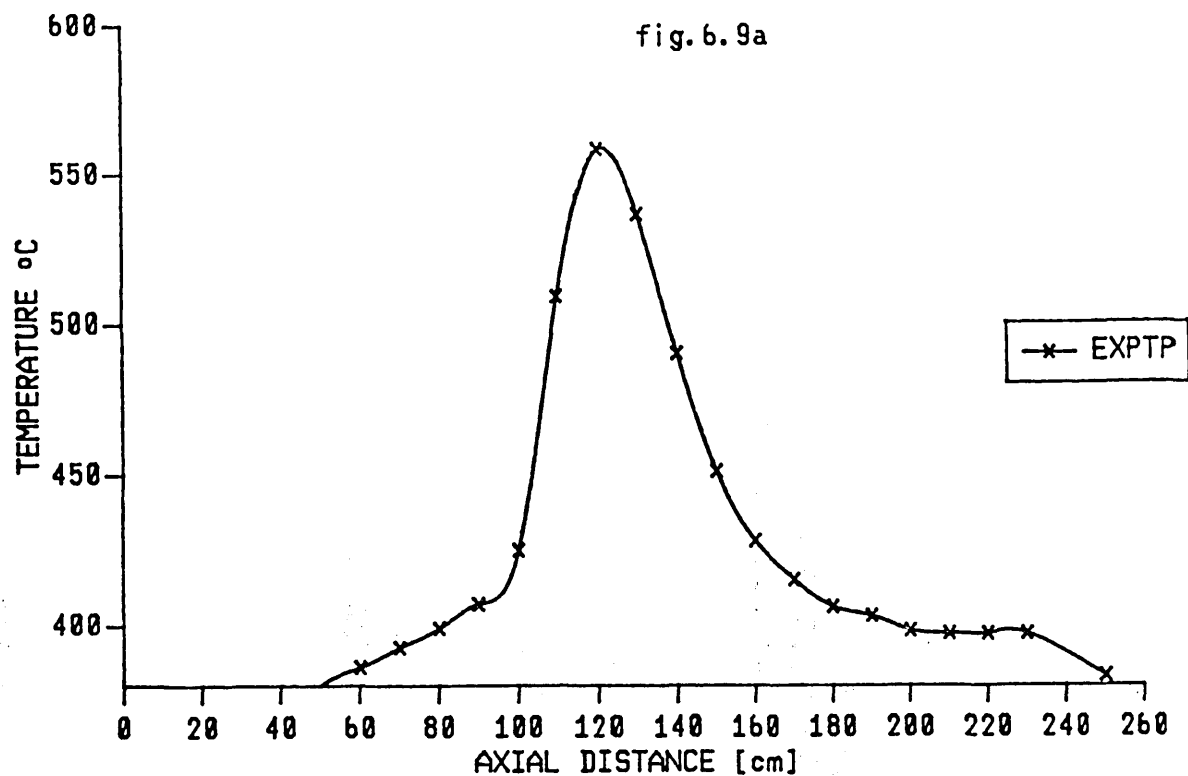


Fig. 6.9 Experimental steady state axial temperature and concentration profiles at normal catalyst activity; salt bath temperature 380°C and o-xylene flowrate 205gm/hr(see table 6.1).

6.2 EVALUATION OF HEAT TRANSFER PARAMETERS

The heat transfer parameters used in this study were evaluated from correlations by Dixon & Cresswell (1978, 1979), Spechia et al. (1980) and Wellauer et al. (1982). They are presented in Appendix 2. As mentioned earlier in Chapter 3, these correlations which are based on the two-phase continuum model, incorporating combined conduction, convection and radiation, have been tested for packed reactor tubes of diameters suitable for selective oxidation and found to give very good results of the overall heat transfer coefficient (to within $\pm 10\%$) [Wellauer et al. (1982)].

In order to further verify the suitability of these correlations for this reactor system, a very simple approach was taken to evaluate the heat transfer parameter group $\left(\frac{6 \text{ Biw/Ph}}{3 + \text{Biw}}\right)$ which appears in the reduced dimensionless heat balance Eq. 3.15.

During the fourth experimental stage (Chapter 4), a few steady state heat transfer experiments without chemical reaction were performed and axial temperature profiles taken at the radial position 0.72 cm corresponding to the one interior collocation point approximation of the model. Fig. 6.10 shows a typical plot of the axial temperature profile for a salt bath temperature of 390°C and air flowrate 4 Nm³/hr.

This figure 6.10 shows that the asymptotic region starts after about axial position 5 (i.e. 40 cm from the reactor inlet). Only temperature measurements located prior to this region were used to estimate the heat transfer parameter group as described below.

For steady state without reaction, Eq. 3.15 becomes,

$$\frac{dY}{dz} = \frac{6 \text{ Biw/P}_h}{3 + \text{Biw}} (Y_w - Y) \quad (6.1)$$

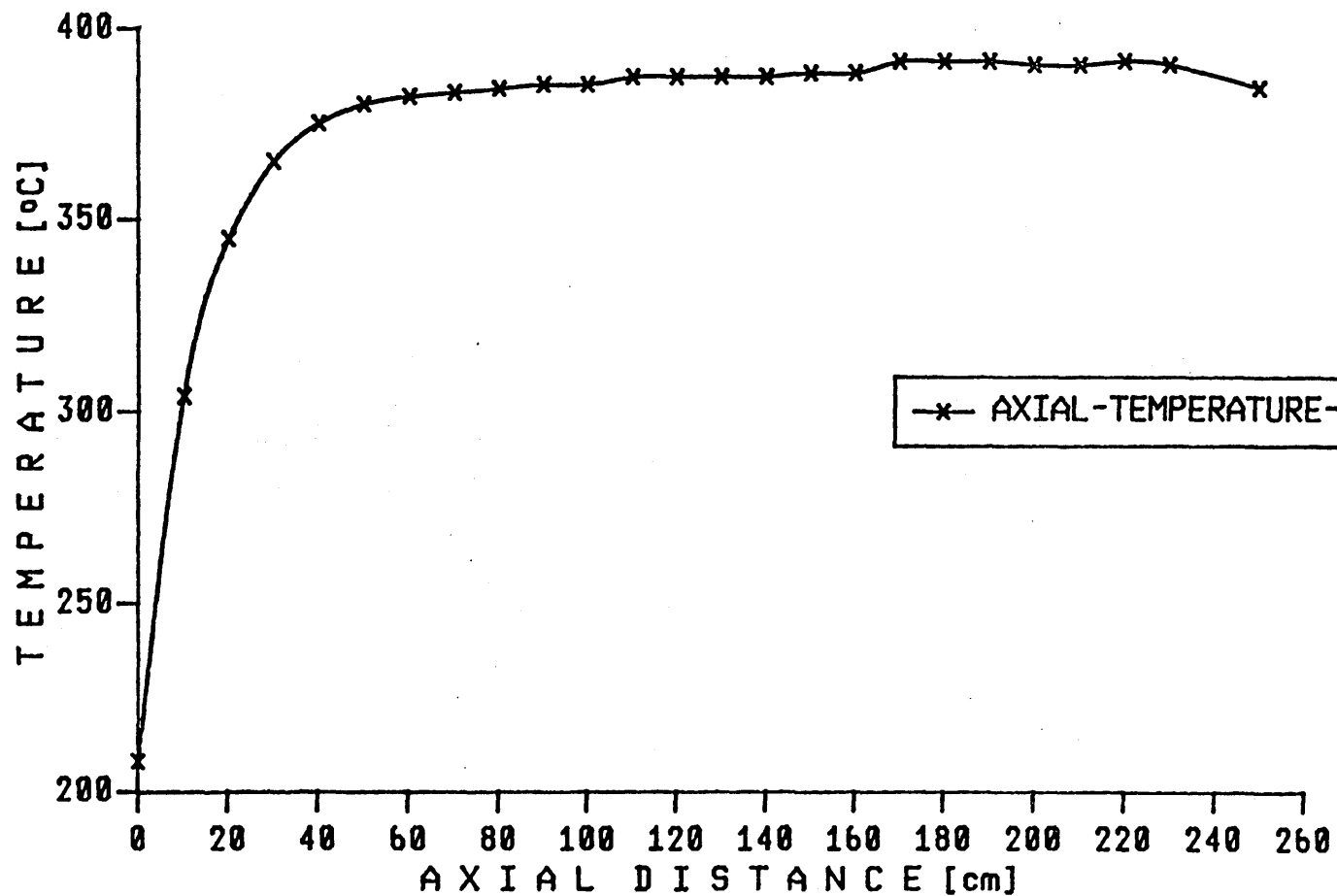


Fig. 6.10 Experimental steady state axial temperature profile for heat transfer without reaction; salt bath temperature 390°C and air flowrate 4Nm³/hr.

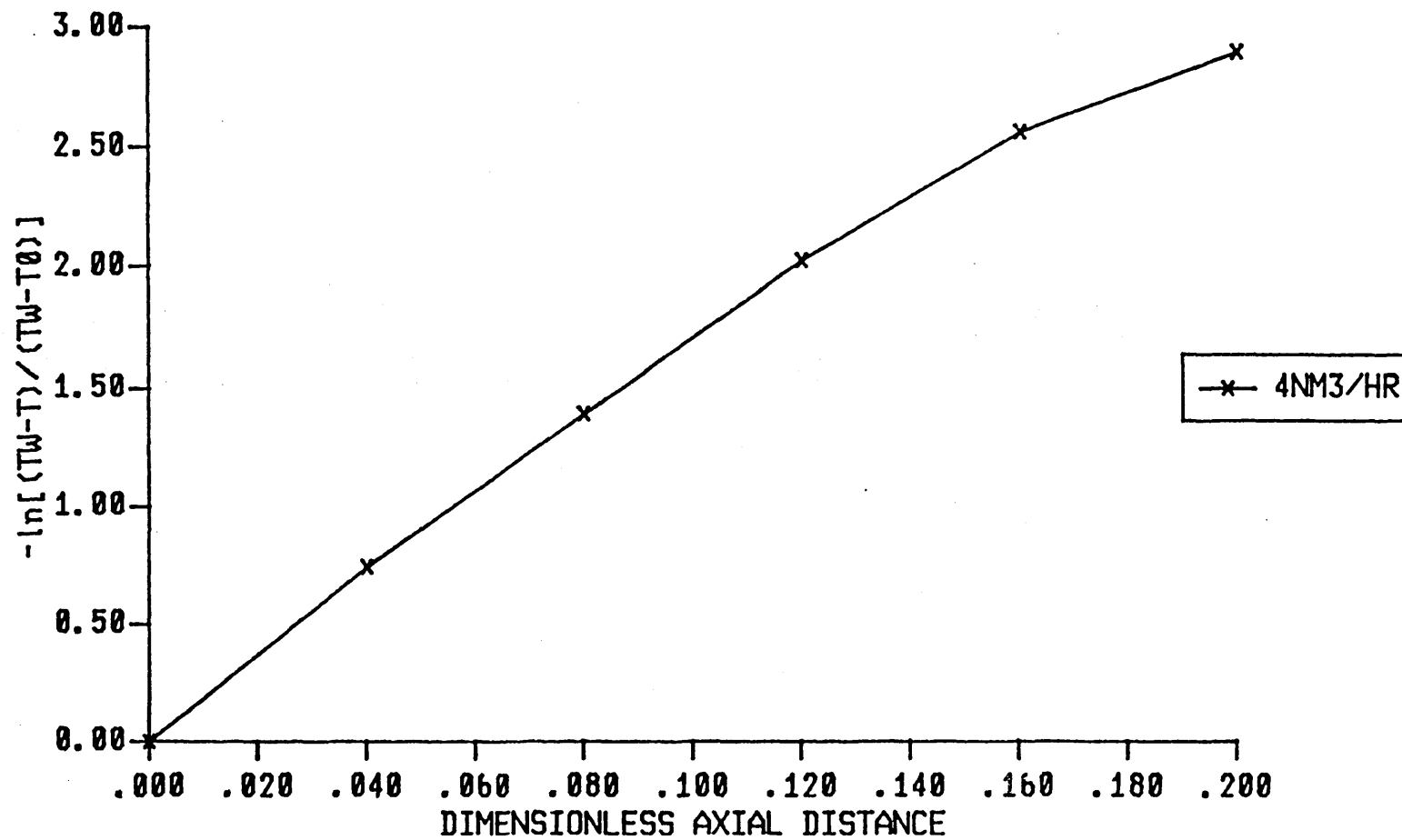


Fig. 6.11 A plot of $\ln[(T_w - T)/(T_w - T_o)]$ versus dimensionless axial distance z for the heat transfer experiments without reaction at 4 Nm³/hr air flowrate.

Integrating we have

$$\ln\left(\frac{Y_w - Y}{Y_w - Y_o}\right) = - \frac{6 \text{ Biw}/P_h}{3 + \text{Biw}} z \quad (6.2)$$

Estimates of this parameter group were obtained by plotting $\ln\left(\frac{\Delta T}{\Delta T_o}\right)$ versus the dimensionless bed depth z , where $\Delta T = T_w - T(z)$ is the difference between bath and bed temperature at the interior collocation point. ΔT_o is the corresponding difference at the reactor inlet.

From the plot shown in Fig. 6.11 it can be seen that a straight line can be approximated up to the dimensionless axial position 0.16.

The heat transfer parameter group was then obtained from the slope of this curve. Table 6.2 compares the value estimated from axial temperature measurements using Eq. 6.1 with those estimated from radial temperature measurements [Lopez-Isunza (1983)] and heat transfer parameter correlations given in Appendix A.2 [Wellauer et al. (1982)] for air flowrate $4\text{Nm}^3/\text{hr}$.

TABLE 6.2
Heat transfer parameters

Method	Biw	$P_h = Pe_{hr} \frac{R_o^2}{L_o dp}$	$\frac{6 \text{ Biw}/P_h}{3 + \text{Biw}}$	Obtained from
1	0.83	.09336	13.926	Radial temperature measurements ([Lopez-Isunza (1983)])
2	1.7639	.1562	14.218	Heat transfer parameter correlations Appendix A.2 [Wellauer <u>et al.</u> (1982)]
3	--	--	15.59	Axial temperature measurements [this work]

Table 6.2 shows that despite the fact that the values of the wall biot number (Bi_w) and the radial heat peclect number (Pe_{hr}) are widely dependent on the method employed for their evaluation, the value of the heat transfer parameter group ($\frac{6 Bi_w/P_h}{3 + Bi_w}$) is fairly constant.

It can also be seen from this Table 6.2 that the correlations (method 2) predict the heat transfer parameter group to within +2% or -8% depending upon whether the value determined from either method 1 or 3 is accurate. The predictions by both methods 1 and 3 were prone to experimental errors.

6.3 PREDICTION OF THE STEADY STATE BEHAVIOUR OF THE REACTOR FROM ACTIVITY PROFILES ESTIMATION

In Chapter 3, it was established that the activity of the catalyst plays a very important role in both the steady state and dynamic simulation of this reactor-reaction system. Consequently, methods of approximation of the catalyst activity profile were developed in Chapter 5 and will now be used to predict the steady state behaviour of the reactor by estimating activity profiles from experimental data. For this exercise, measurements obtained during experimental runs 1, 4, 6 and 7 (Table 6.1) were used.

The amount of data (temperature and concentration measurements) collected during each of these experimental runs was rather large - 9 concentration and 25 temperature measurements. Usually, industrial reactors are not as over instrumented as the one considered in this work. In most industrial reactors only very few measurements may be available and they are usually one or two thermocouples for temperature measurements plus exit composition measurement.

Since the ultimate objective of this work is to be able to obtain real time predictions of temperature and composition profiles from parameter estimation of catalyst activity profiles using on-line measurements, it was appropriate to look for a more efficient and accurate procedure to do the estimation of the activity.

This necessitated the search for an approach that would entail less storage requirements and less computation times and at the same time give reasonable predictions of the reactor behaviour. In this light, the question of whether to estimate all the activity parameters of an activity profile sequentially or simultaneously was considered.

Since the model used in this work is not very accurate, it is possible that even if reasonable predictions of the reactor behaviour are obtained the estimated activity profile might not offer any physically meaningful explanation of the "state" of the catalyst. Hence it was appropriate to impose some constraints on the activity parameters so as to ensure that the estimated activity profile was monotonic or S-shaped.

The idea of using a few selected temperature and concentration measurements as well as using only temperature measurements to estimate the catalyst activity in order to predict the reactor behaviour was also considered. This would correspond more nearly to a typical industrial situation.

The estimation of catalyst activity profiles was therefore considered under the following cases:

- a. Activity parameters in all the finite elements estimated sequentially using both temperature and concentration measurements.

- b. Activity parameters in some of the finite elements estimated simultaneously with the rest estimated sequentially using both temperature and concentration measurements.
- c. Same as case (a) but requiring that the estimated activity profile increases monotonically so that the activity in a given finite element is greater or equal to that in the previous one. This implies that for the second method of parameterization of the activity profile the parameters are constrained so that $\bar{\alpha}_1 < \bar{\alpha}_2 < \bar{\alpha}_3 < \dots < \bar{\alpha}_n$, when n is the total number of finite elements.
- d. Same as case (a) but requiring that the activity also increases monotonically as in case (c). But in this case a spatially uniform catalyst activity was assumed over a large section at the downstream end of the reactor and the value estimated using all the temperature and concentration measurements located in that region.
- e. Same as case (a) but only temperature measurements used.
- f. Same as case (c) but only temperature measurements used.
- g. Same as case (d) but only temperature measurements used.

Cases (a) and (b) are considered in Sections 6.3.1 and 6.3.2 respectively. Cases (c) and (d) are treated in Section 6.3.3 while Section 6.3.4 deals with cases (e), (f) and (g).

6.3.1 Sequential estimation of catalyst activity profiles using both the temperature and concentration measurements

I Case (a)

As already mentioned in Chapter 5, it can be seen from Figs. 6.1 to 6.9 that very little reaction took place between axial positions 1 and 6, irrespective of the operating conditions considered. As a

result the temperature and concentration measurements at axial position 6 (50 cm downstream) were taken as the inlet conditions of the reactor and catalyst activity profile estimation was started from that point considered to have a zero activity. Henceforth, axial position 6 will be referred to as the reactor inlet. Twenty temperature and eight concentration measurement points were available, from the reactor inlet to the exit, and were all used for the estimation of catalyst activity profiles in this particular case.

In order to ensure the best possible approximation of the activity profile, special attention was given to the region preceding the hot-spot where the activity of the catalyst is considered to play a very prominent role in the simulation of the reactor following the prevalence of reversible partial deactivation within that region. The reactor was subdivided into finite elements (subreactors) using the shape of the temperature profile as described in Chapter 5. The sizes and number of the finite elements were determined by both the shape of the temperature profile and the number of concentration sampling points. It must be emphasized that the greater the number of finite elements, especially within the inlet region, the better the approximation of the activity profile. Since it was decided to include at least one concentration measurement point in each finite element, the maximum number of finite elements was limited to 7.

The optimum number of finite elements required for improved predictions from the reactor inlet to the hotspot region was determined exclusively by the number of concentration sampling points available within that area. For example, in Fig. 6.1a the hotspot is located very close to axial position 14 (130 cm) and since there were four concentration sampling points (excluding the inlet) located within the

region from the reactor inlet to this point, the maximum number of finite elements possible in that region was 4, each having a length of 20 cm. The rest of the finite elements were obtained in the same manner and also with the help of the temperature profile. In Fig. 6.6, the hotspot is located very close to axial position 13 (120 cm). The axial distance between the reactor inlet (axial position 6) and this point is 70 cm and for 3 concentration sampling points within this region, 3 finite elements were used, their sizes determined by the shape of the temperature profile to be 30 cm for the first one and 20 cm apiece for the remaining two. In Fig. 6.7, the hotspot is located very close to axial position 11 (100 cm) and with only 2 concentration sampling points (axial positions 8 and 10) available the estimated values of the activity in the two finite elements within this region were too low resulting in predictions far from approaching the experimental profiles. The next concentration measurement point after the hotspot (axial position 12) was then considered together with the two previous ones so as to obtain three finite elements, each 20 cm long, within this region.

Figs. 6.12 to 6.15 show the activity profiles and the predicted temperature and concentration profiles compared with the experimental profiles obtained during the experimental runs 1, 4, 6 and 7 respectively. In this case the activity profiles were approximated by the second method of parameterization of an activity profile described in Chapter 5.

Despite the fact that the predicted temperature and concentration profiles of o-xylene and phthalic anhydride are in close agreement with the corresponding experimental profiles, for all the steady state opera-

ting conditions considered, the behaviour of the activity profile after the hotspot is very much questionable.

The falling and rising again of the estimated activity after hotspot does not offer any physically meaningful explanation to the state of the catalyst. However, a possible explanation of this behaviour may be attributed to model limitations. Since it is assumed that the model is accurate, the estimated activity parameter must be corrupted by the model errors especially towards the downstream end of the reactor where the activity of the catalyst is not an important factor in determining the behaviour of the reactor.

Evidence to support this explanation may be obtained from Chapter 5 where simulated temperature and concentration measurements were used to estimate catalyst activity profiles. In this case, the model was very accurate and it was found that the behaviour of the estimated activity profile closely approximated that which was arbitrarily imposed.

Since reversible partial deactivation of the catalyst is thought to be caused by a combination of high o-xylene concentrations and low temperatures [Calderbank et al. (1977), Lopez-Isunza (1983), Kershenbaum et al. (1984)], one would expect the influence of the catalyst activity on the behaviour of the reactor after the hotspot to be much reduced considering the fact that about 70 to 80% of the o-xylene has already disappeared. On the other hand, the heat transport mechanism should become the limiting factor in determining the reactor behaviour and this might not have been well accounted for in the model. Efforts directed towards tuning the overall heat transfer coefficient by adjusting the value of the "heat transfer parameter group" to obtain improved results were futile. At this juncture, one may suggest that the

possibility of introducing additional heat transfer parameters particularly through the incorporation of axial heat dispersion into the model should be explored in order to see whether any further improvement in the estimation results after the hotspot can be obtained.

Figs. 6.12 to 6.15 show that although the positions of the hotspot temperatures are well predicted, the magnitudes are slightly less than the experimental values in some cases. This is not entirely unexpected considering the fact that the activity profiles are only approximations of the true situation. In all the cases, the final yield of phthalic anhydride was well predicted.

One major limitation of this method of approximation of the catalyst activity is due to the existence of discontinuities in the rate of reaction engendered by the fact that the activity profile is discontinuous from one finite element to the next. The implication of this is that there is bound to be discontinuity in the predicted temperature and concentration profiles. This effect is greatly felt at the upstream end of the reactor, where the rate of reaction is a limiting factor in determining the behaviour of the reactor, as manifested by the ripples in the predicted temperature profile around that region.

In general, all the predictions, except those of o-tolualdehyde and phthalide concentration profiles, were very satisfactory. The reason for the poor predictions of o-tolualdehyde and phthalide concentration profiles was partly due to the fact that the measurements themselves were not reliable following the poor resolutions between the peaks of o-tolualdehyde and maleic anhydride on the one hand and those of phthalide and phthalic anhydride on the other hand. However, from preliminary simulations it was found that the model predictions were

not very sensitive to measurements of these components in the optimization scheme and their weightings were therefore set to zero.

As stated earlier in Chapter 5, the original concentration measurement weightings of 0.333, 1.0, 0.2 and 0.167 for o-xylene, o-tolualdehyde, phthalide and phthalic anhydride respectively, were only associated with errors involved in fitting straight line graphs to the experimental data points obtained for the calibration of the species. Since the other errors present, particularly those associated with poor resolution of some of the peaks by the chromatographic column, could not be quantified, it was therefore appropriate to perform a sensitivity analysis of the model predictions with respect to those components whose measurements were widely corrupted by these types of error. Hence, using the reactor data obtained during experimental run 1 (Table 6.1) for the estimation of catalyst activity profile, the measurement weightings of o-tolualdehyde and phthalide were adjusted to lower values and it was found that even when they were set to zero the model predictions were only marginally affected.

Fig. 6.16 shows the activity profile and model predictions when the original measurement weightings of 0.333, 1.0, 0.2, 0.167 and 1.7 for o-xylene, o-tolualdehyde, phthalide, phthalic anhydride and temperature were used in the optimization scheme. It can be seen that these results are very close to those depicted by Fig. 6.12 where both o-tolualdehyde and phthalide weightings were set to zero.

Hence, in all the estimations presented, except those shown by Fig. 6.16, the weightings of o-tolualdehyde and phthalide were set to zero.

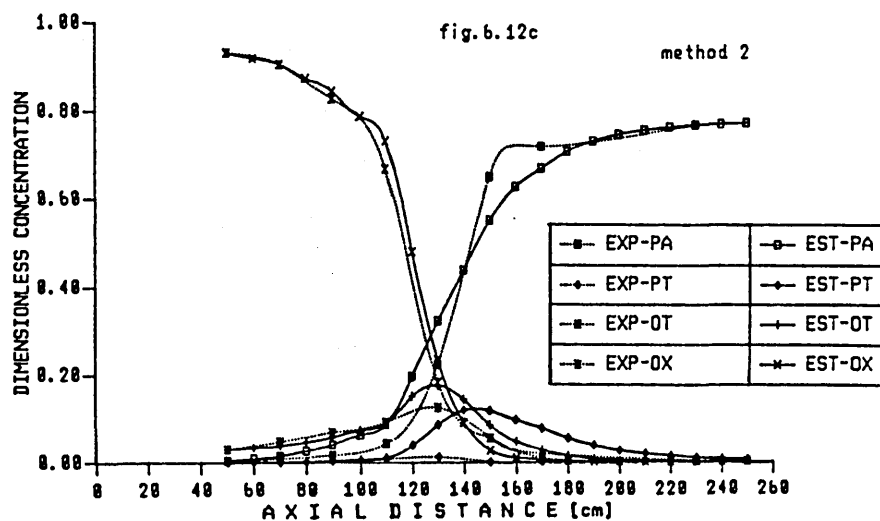
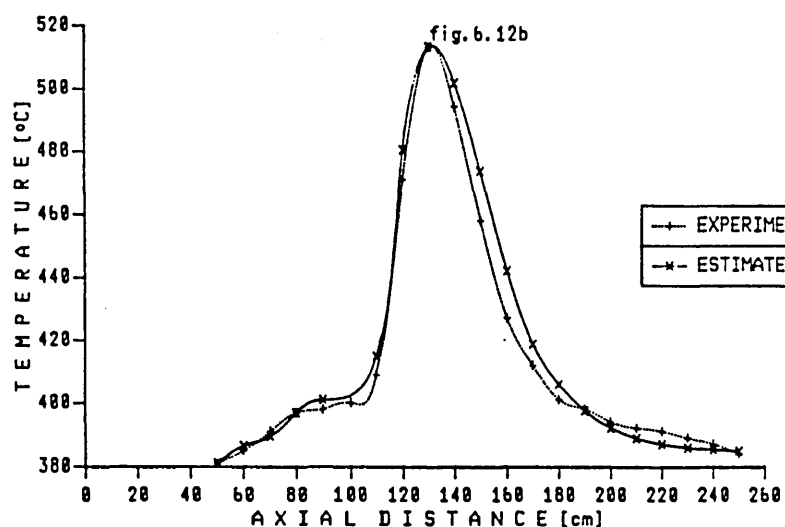
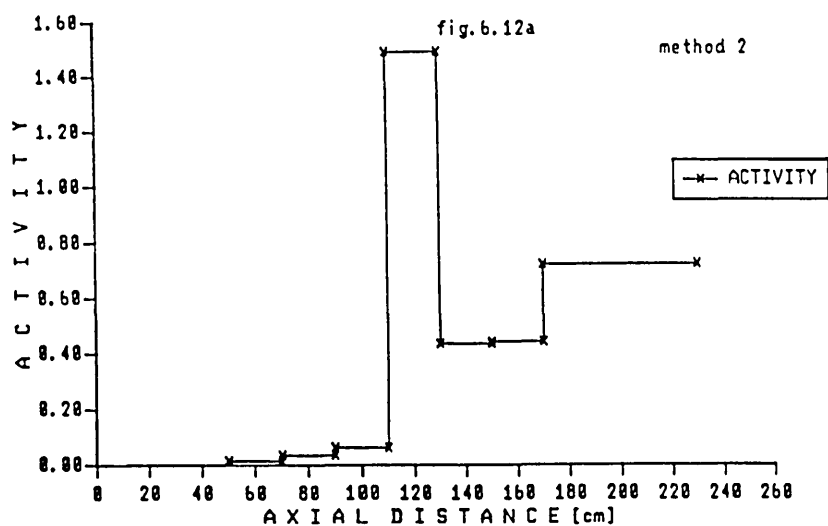


Fig. 6.12 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using all the temperature and concentration measurements obtained during experimental run 1(see table 6.1)

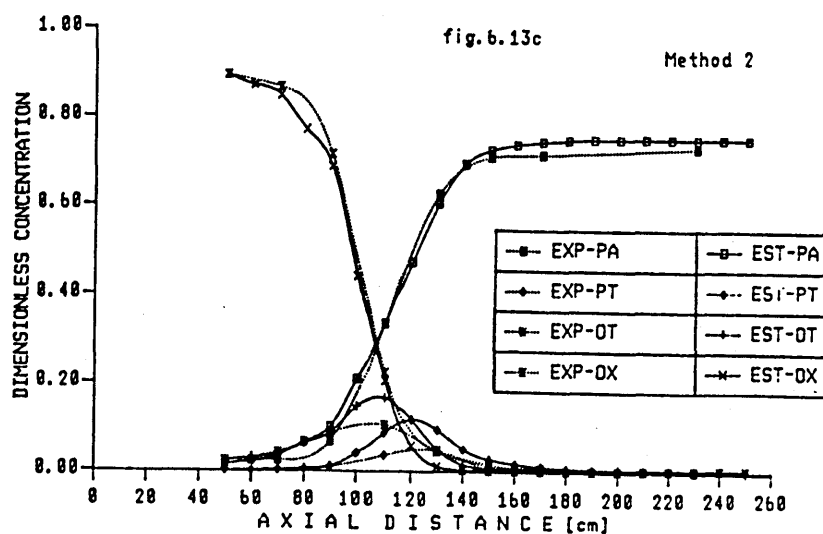
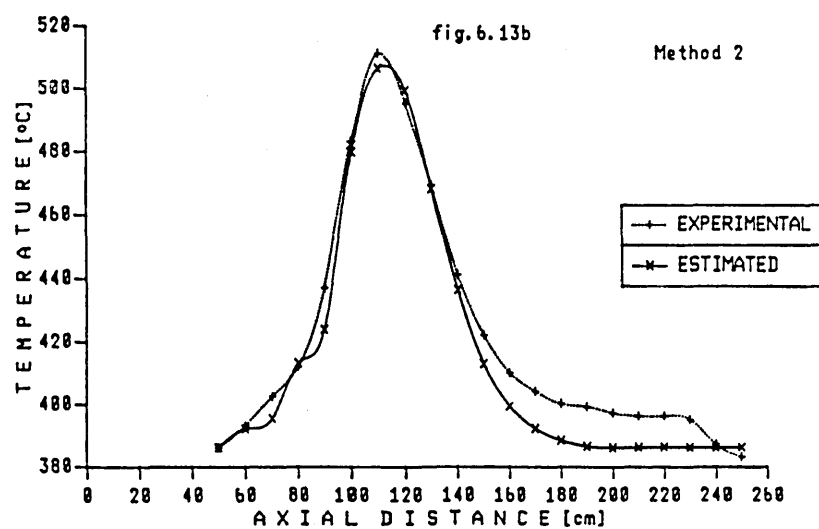
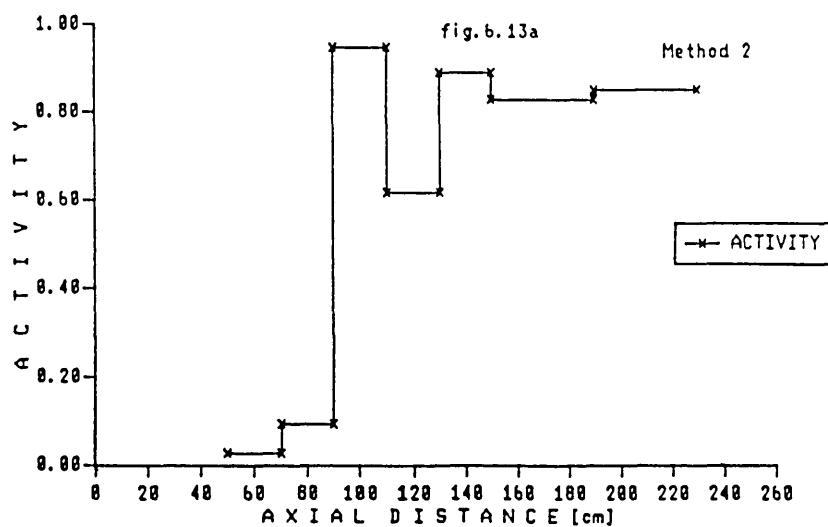


Fig. 6.13 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using all the temperature and concentration measurements obtained during experimental run 4(see table 6.1).

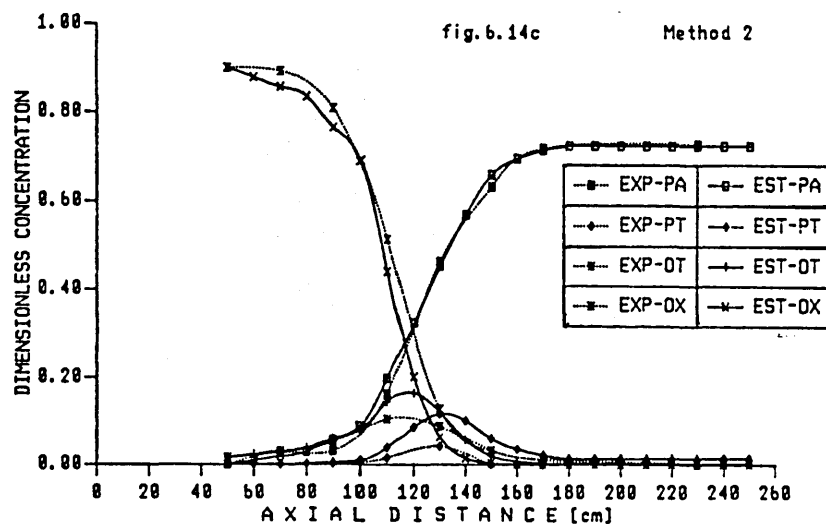
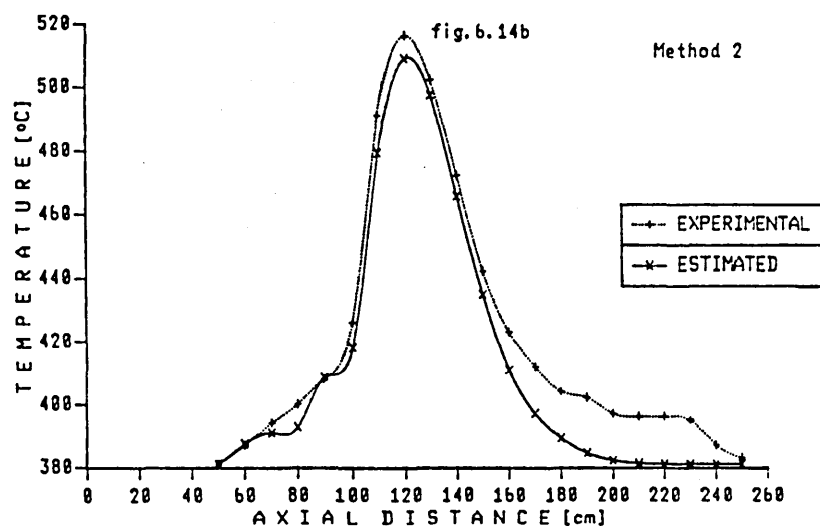
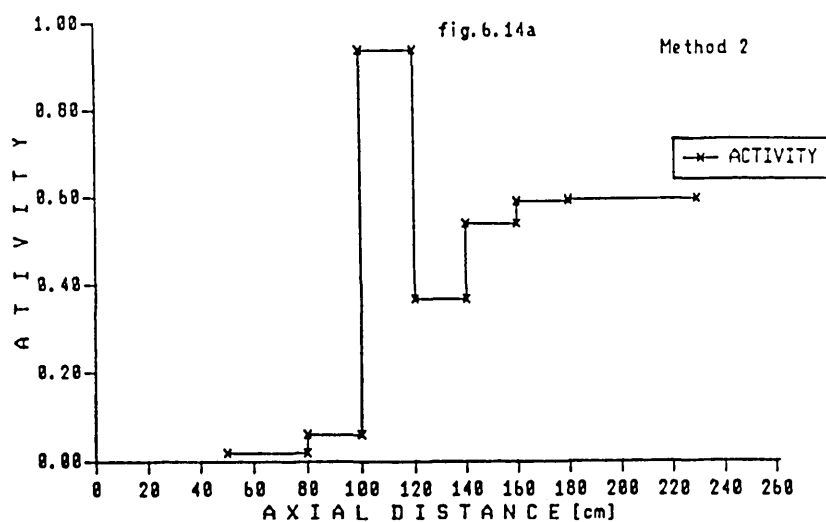


Fig. 6.14 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using all the temperature and concentration measurements obtained during experimental run 6(see table 6.1).

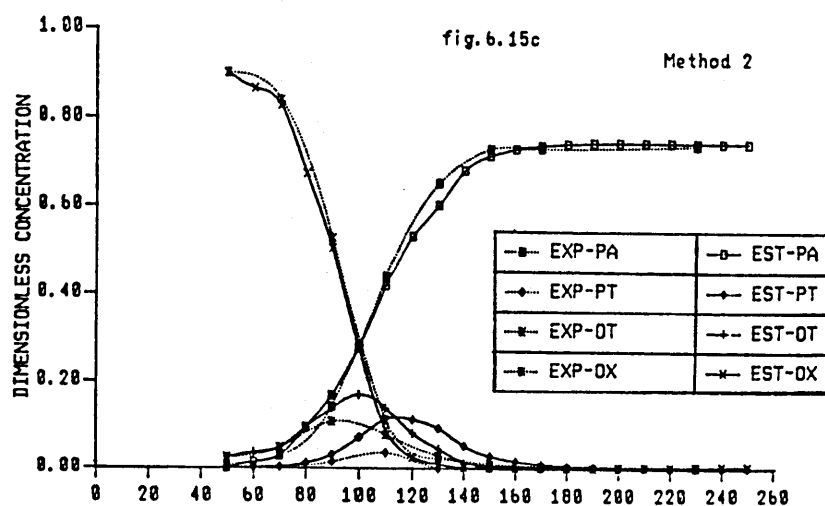
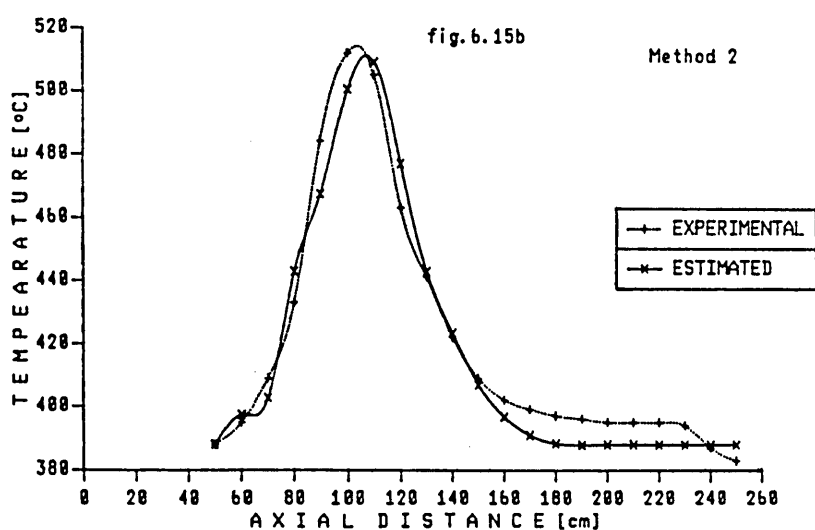
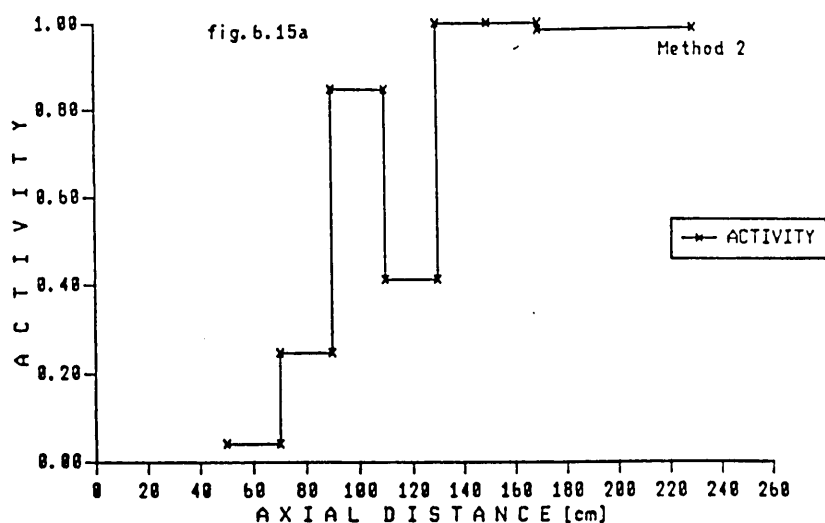


Fig. 6.15 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using all the temperature and concentration measurements obtained during experimental run 7 (see table 6.1).

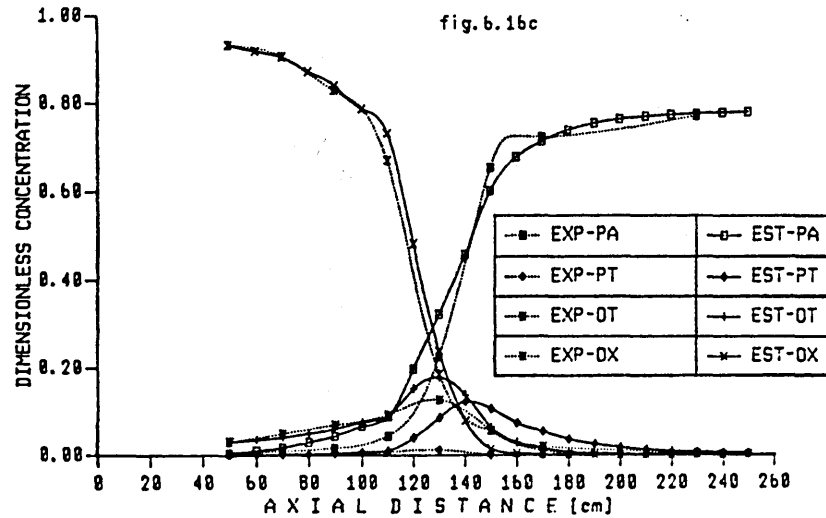
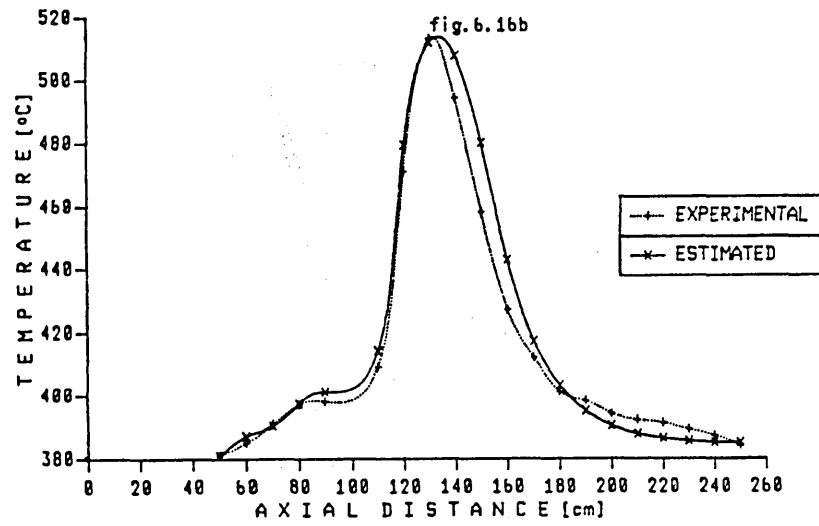
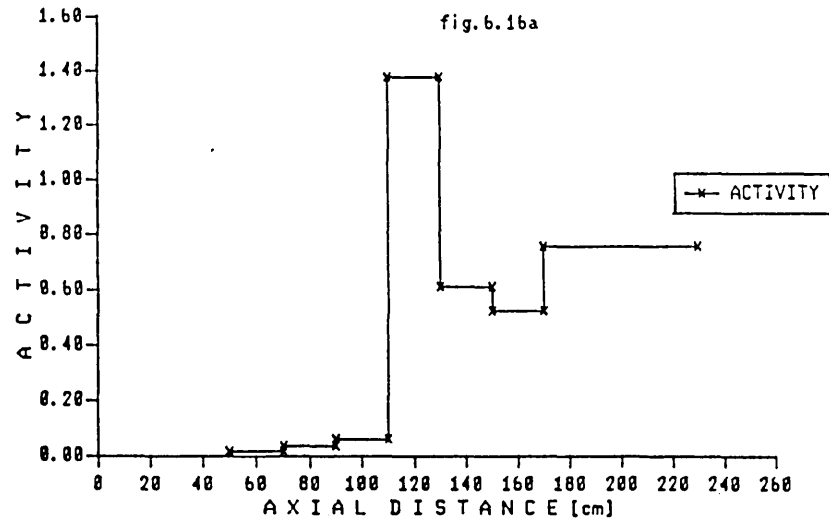


Fig. 6.16 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using all temperature and concentration measurements obtained during experimental run 1 with measurement weightings of OX,OT,PT,PA and temp. equal to .333,1.000,.200,.1667 and 1.7 respectively.

6.3.2 Simultaneous estimation of catalyst activity parameters

II Case (b)

In order to justify the computationally simple method of sequential estimation of the parameters of the activity profile it was appropriate to estimate them simultaneously so as to determine whether the results were significantly different from those obtained in the previous case (a). It must be emphasized that this is a very costly approach since the computation time required to estimate two to three to the parameters simultaneously was many times greater than when they were estimated sequentially.

The reactor data obtained during experimental run 1 (Table 6.1) was again used for this exercise and the results obtained by estimating the activity parameters in the first three finite elements simultaneously with the rest sequentially determined are shown in Fig. 6.17. When these results are compared with those depicted by Fig. 6.12 where all the parameters were estimated sequentially, for the same operating conditions, it can be found that there are virtually no differences either in the predicted temperature and concentration profiles or the behaviour of the estimated activity profiles except for the fact that a slightly higher value of the activity parameter is estimated in the fourth finite element in the latter case. Moreover, the computation time taken to estimate the parameters in this manner was about 9 times greater than when they were all estimated sequentially (i.e. ~181 versus ~20 C.P.U. seconds for the two cases from C.D.C. Cyber 855 computer system).

It is therefore clear that any marginal improvement in the simulation results by estimating the activity parameters simultaneously cannot be justified and that meaningful estimates of the activity

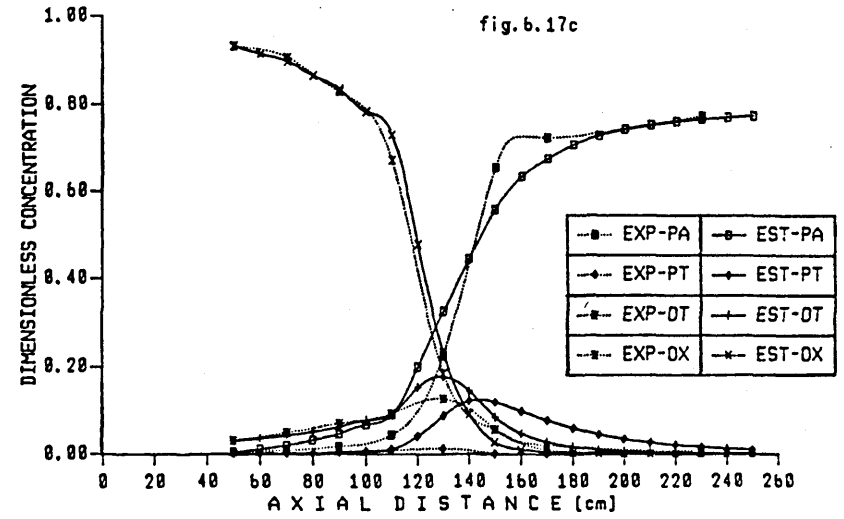
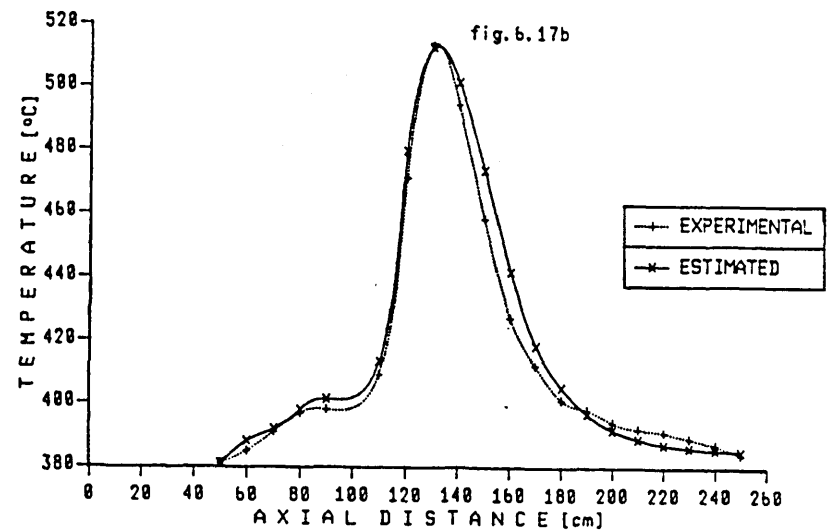
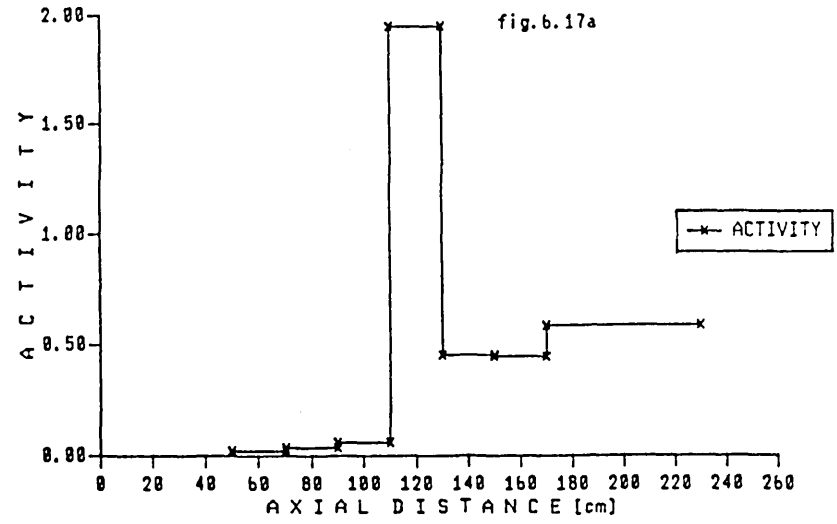


Fig. 6.17 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile parameters in the first three finite elements estimated simultaneously using all the temperature and concentration measurements obtained during experimental run 1 (see table 6.1)

profile particularly after the hotspot cannot be achieved in this way except if some constraint is imposed on the activity parameters.

6.3.3 Estimation of catalyst activity profiles with constraints using both temperature and concentration measurements

In order to obtain physically meaningful estimates of the catalyst activity profiles particularly at the downstream end of the reactor some constraints were imposed on the activity parameters. Two types of constraints were used as stated previously in cases (c) and (d).

III Case (c)

In this case the value of the activity parameter in each finite element was required to be greater or equal to that in the previous finite element from the reactor inlet to the exit, for the second method of parameterization of the activity profile. For the first method, the activity profile was required to increase smoothly from one finite element to the next. The aim here was to approximate an activity profile which is S-shaped.

From Figs. 6.12 to 6.16, it can be seen that, in general, the maximum activity parameter was estimated at the finite element around the hotspot region. This implies that imposing this constraint necessarily reduces the estimation to using effectively only the temperature and concentration measurements located between the reactor inlet and the hotspot or a few centimeters after the hotspot. The estimation of catalyst activity profile in this case was therefore treated as such.

Starting from the first finite element, the activity parameters at the upstream end of the reactor, from the inlet to the hotspot or a few centimeters after the hotspot, were estimated sequentially so that the

rest of the catalytic bed had a uniform activity whose value was that obtained in the finite element where the activity was lastly estimated.

Fig. 6.18 shows the activity profile and the predicted temperature and concentration profiles compared with experimental data obtained during experimental run 1 (Table 6.1) when the algorithm for the estimation of the catalyst activity was terminated at the hotspot (i.e. at the fourth finite element) as compared to Fig. 6.12. From Fig. 6.18b it can be seen that the hotspot temperature is overestimated by about 10°C and is shifted about 7 cm downstream of the reactor. The reason for the predicted high hotspot may be due to the fact that a very high value of the catalyst activity was estimated in the finite element around the hotspot region which then forced the remaining reaction to take place at a much faster rate resulting in a further release of heat of reaction within a very short axial distance after the hotspot. This evidence is apparent from Fig. 6.12 where a very low value of the activity parameter is shown to have been estimated in the fifth finite element (the finite element coming immediately after the hotspot) in order to slow down the rate of reaction. In this case about 57 mole% of phthalic anhydride ($\sim 72\%$ of the total PA produced) was produced after the hotspot (at the hotspot about 80% of o-xylene has disappeared and only 20 mole% of PA produced, see Fig. 6.1). The faster rate of production of phthalic anhydride after the hotspot is manifested by the steeper profiles (especially the phthalic anhydride concentration profile, Fig. 6.18c) as compared to either the experimental profiles or the predictions shown by Fig. 6.12 where all the measurements were used to estimate catalyst activity profiles (case (a)).

Figs. 6.19 and 6.20 show the catalyst activity profile and the predicted temperature and concentration profiles compared with experi-

mental data obtained during experimental runs 4 and 6 respectively, when the estimation was also terminated at the hotspot. In both cases it can be found that the temperature and concentration profiles of o-xylene and phthalic anhydride are very well predicted. Figs. 6.19b and 6.20b show that the predicted hotspot temperatures are even much better than in the previous case (a), Figs. 6.13b and 6.14b, where all the temperature and concentration measurements, from the reactor inlet to exit, were used to estimate catalyst activity profiles although they are shifted slightly downstream. The reason for this may again be explained by the fact that the very high value of the catalyst activity estimated in the finite element around the hotspot region forced the rest of the reaction to occur very rapidly releasing much heat of reaction within a very short axial distance after the hotspot. In these two sample cases only about 43 mole% of phthalic anhydride was produced after the hotspot (at the hotspot about 70% of the o-xylene has disappeared and about 30 mole% of phthalic anhydride produced, see Figs. 6.4 and 6.6). The resulting rise in temperature was therefore just enough to compensate for the inadequacies of the method of approximation of the catalyst activity profile.

Fig. 6.21 shows the corresponding results for experimental run 7 when the estimation routine was terminated about 7 cm after the hotspot (at axial position 12). In this sample case very little reaction occurred after this point (at axial position 12 about 90% of the o-xylene has disappeared and about 45 mole% phthalic anhydride produced which is equivalent to more than 60% of the total PA obtained at the exit, see Fig. 6.7). As a result, there is hardly any change in the predicted hotspot temperature despite the high value of the catalyst activity estimated around the hotspot region. On the whole, the temp-

erature profile was still very well predicted as shown in Fig. 6.21b. Fig. 6.21c shows that the predicted concentration profiles of o-xylene and phthalic anhydride are still in very good agreement with the experimental profiles, although they are steeper after the hotspot as compared to Fig. 6.15c.

In general, Figs. 6.18 to 6.21 show that the predicted temperature profiles at the downstream end of the reactor, particularly towards the exit, are much lower than the experimental profiles. The reason is partly due to the neglecting of axial heat dispersion in the model but mostly because the salt bath temperature measured at that end of the reactor was always 5 to 10°C greater than in the rest of the reactor upstream where nearly a uniform salt bath temperature was measured. This observation also applies to all the other estimation results that have been presented including Figs. 6.12 to 6.17.

In order to ascertain that the ripples observed on the predicted temperature profiles, Figs. 6.18 to 6.21, at the upstream end of the reactor were caused by discontinuities in the rate of reaction, the activity profile in each finite element was approximated by straight lines according to the first method of parameterization of an activity profile (cf Chapter 5). Applying this method, the algorithm for the estimation of catalyst activity parameter was again terminated at exactly the same axial position as before so that subsequent finite elements were given a uniform activity whose value was that obtained at the end of the finite element where the catalyst activity was lastly estimated.

Figs. 6.22 to 6.25 show the activity profiles and the predicted temperature and concentration profiles compared with experimental data obtained under the various operating conditions considered.

It can be seen from these figures that the temperature predictions within the region prior to the hotspot temperature have greatly improved. However, a further shift downstream of the hotspot position is observed. Again, the predicted concentration profiles of o-xylene and phthalic anhydride are still in very good agreement with the experimental data.

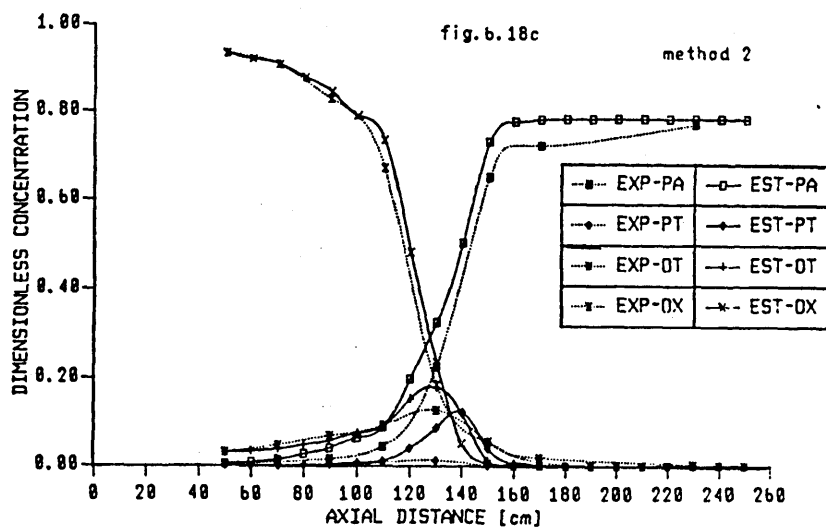
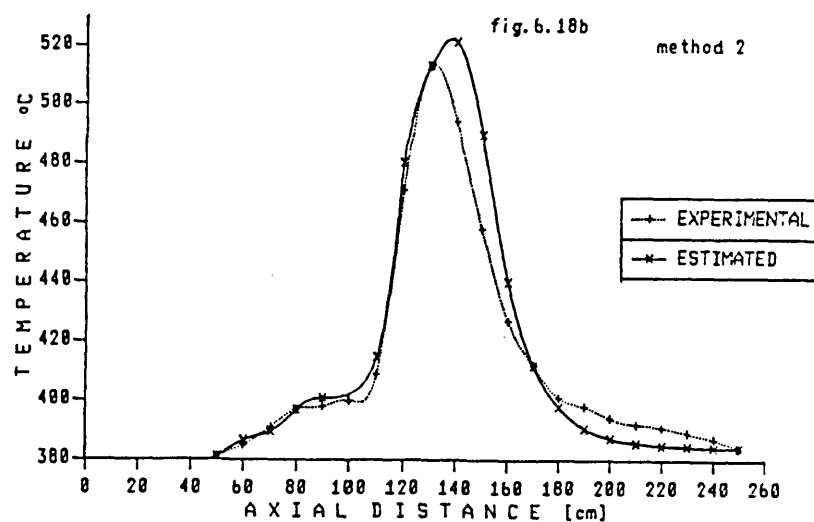
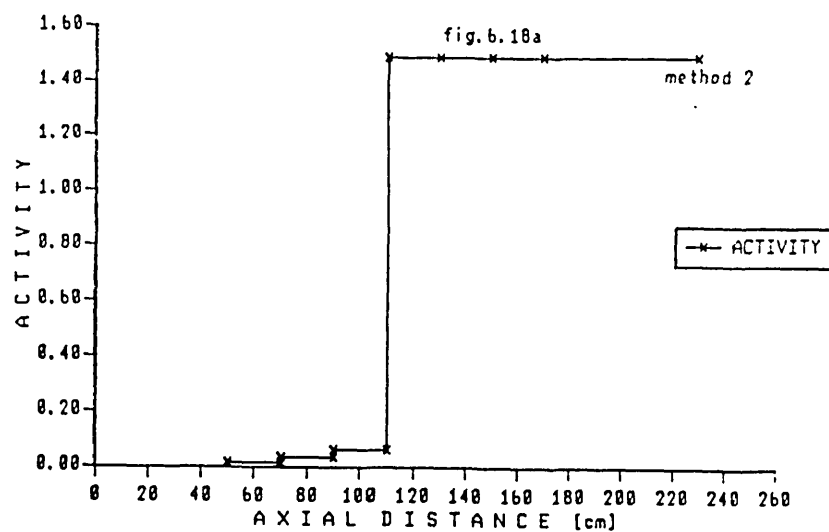


Fig. 6.18 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using only temperature and concentration measurements located between the reactor's inlet and the hotspot for operating conditions corresponding to experimental run 1 (see table 6.1).

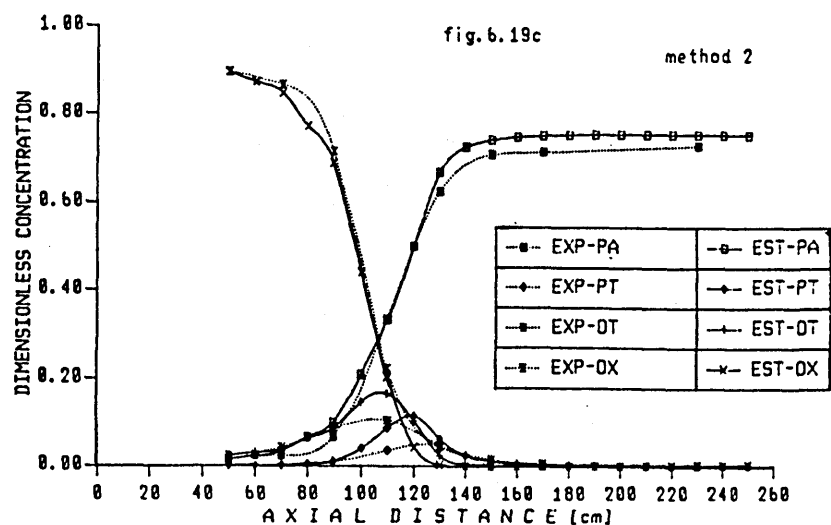
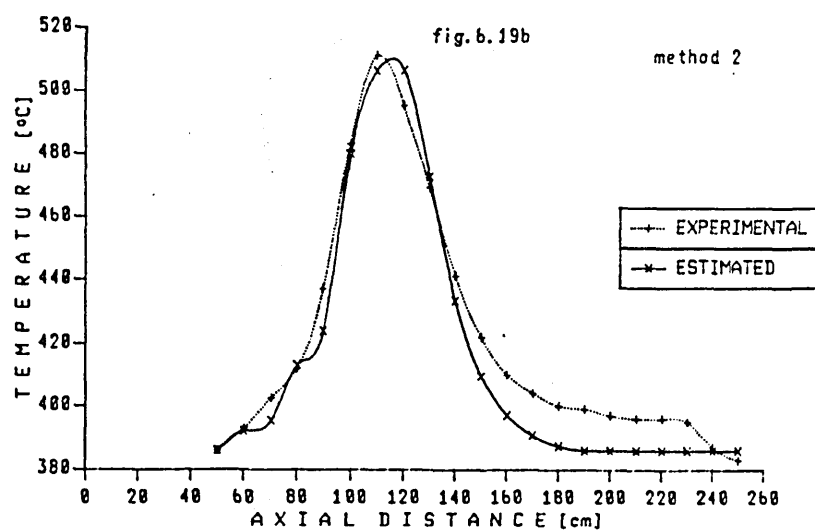
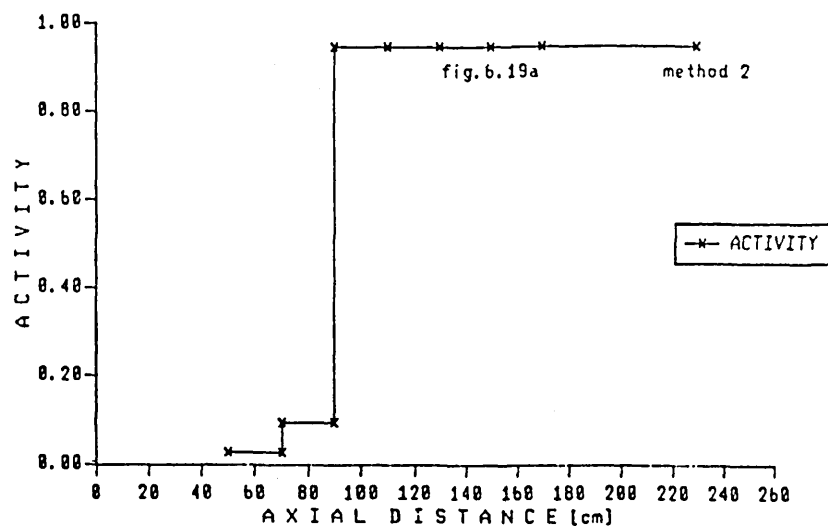


Fig. 6.19 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using only temperature and concentration measurements located between the reactor's inlet and the hotspot for operating conditions corresponding to experimental run 4 (see table 6.1)

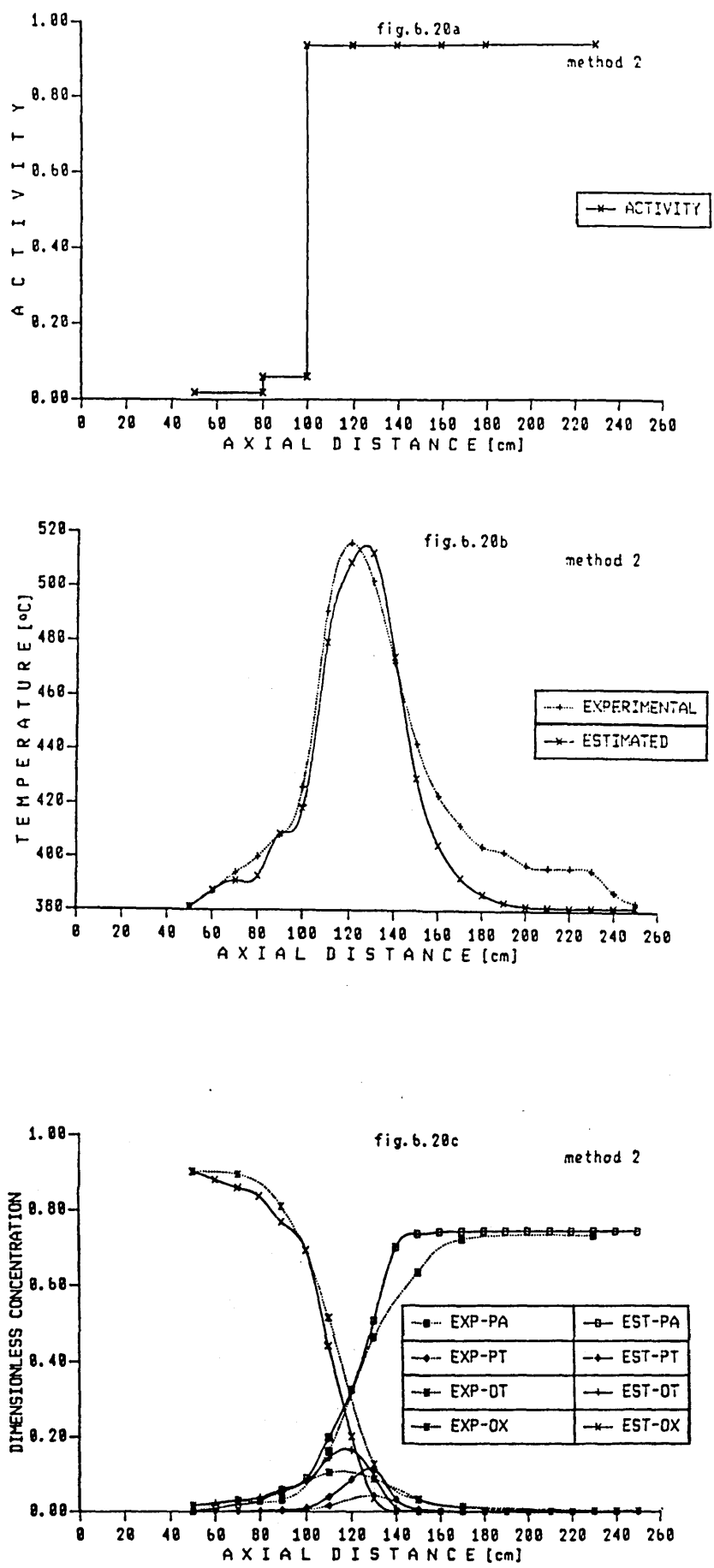


Fig. 6.20 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using only temperature and concentration measurements located between the reactor's inlet and the hotspot for operating conditions corresponding to experimental run 6 (see table 6.1).

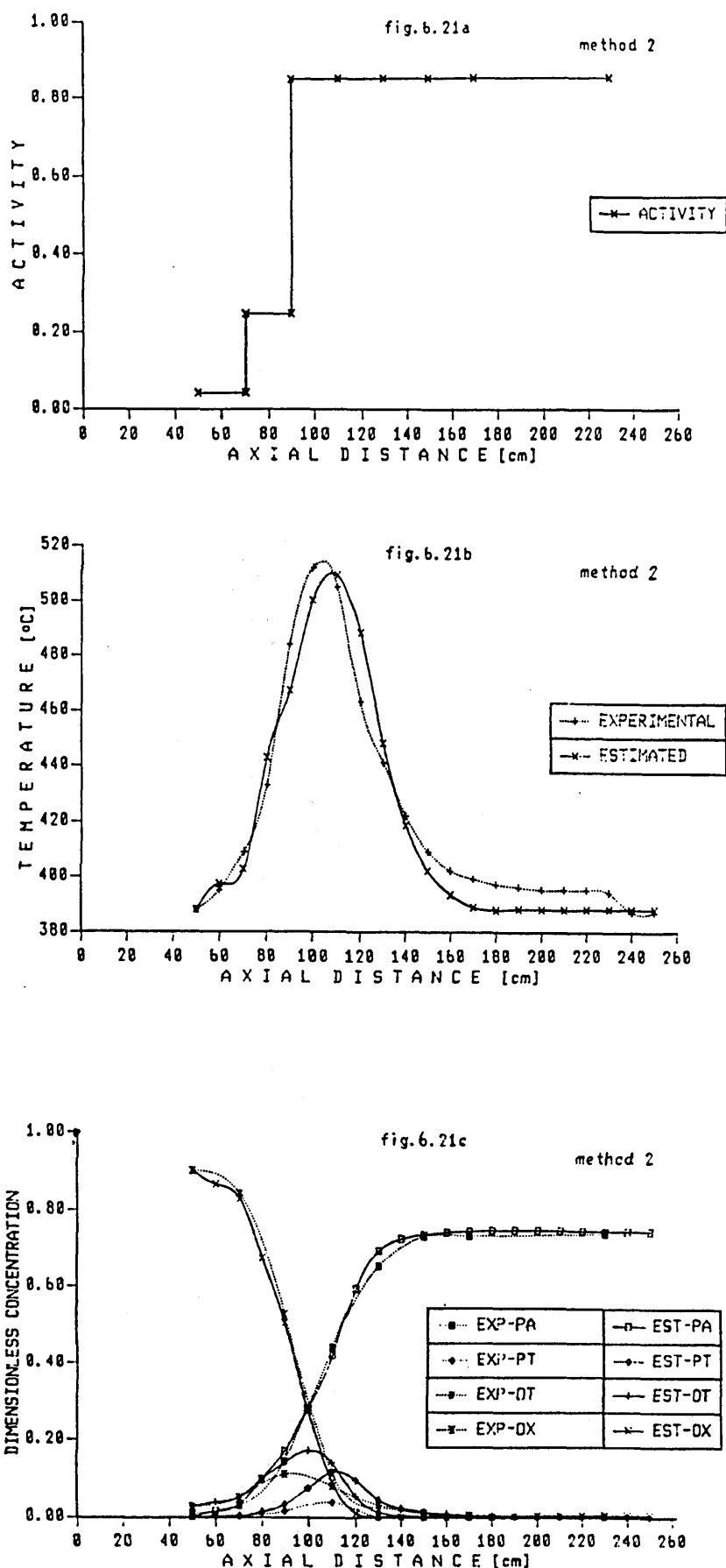


Fig. 6.21 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using only temperature and concentration measurements located between the reactor's inlet and axial position 12 (7cm after the hotspot) for operating conditions corresponding to experimental run 7 (see table 6.1).

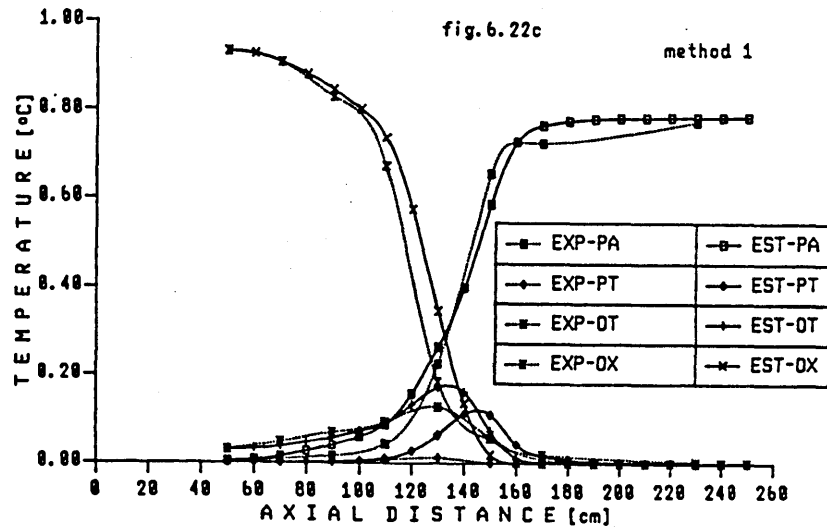
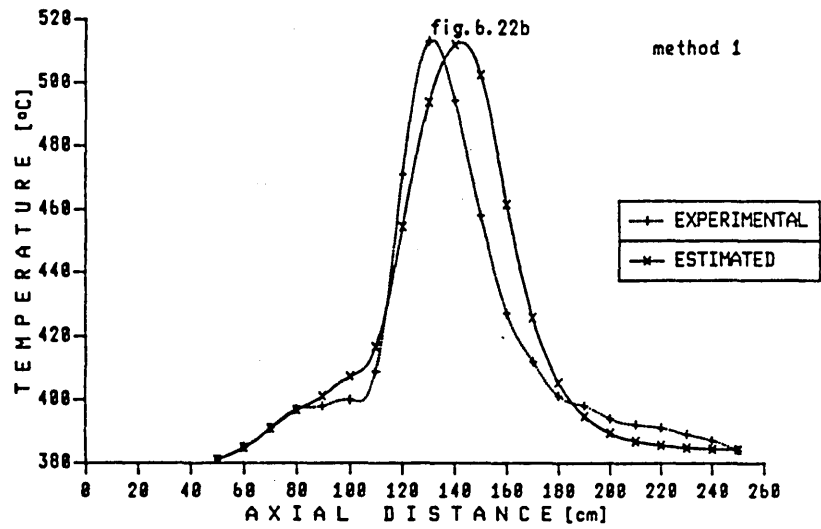
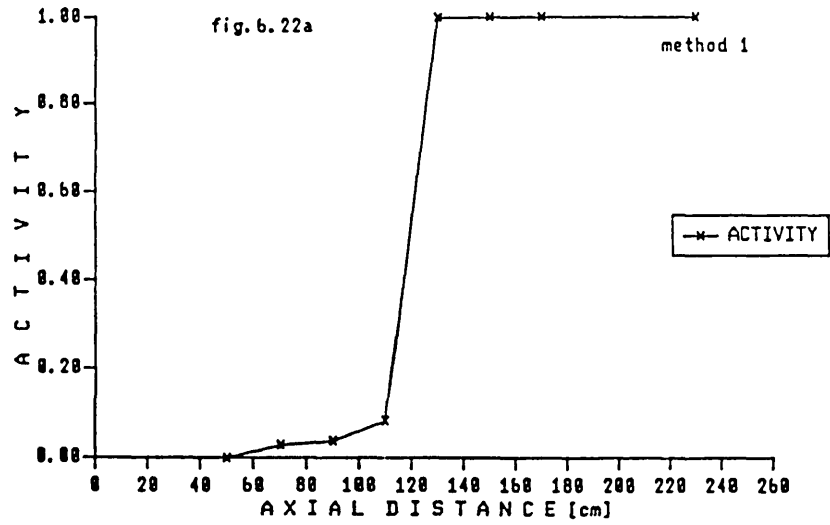


Fig. 6.22 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile approximated by method 1(cf chapter 5) and estimated using only temperature and concentration measurements located between the reactor's inlet and the hotspot for operating conditions corresponding to experimental run 1 (see table 6.1).

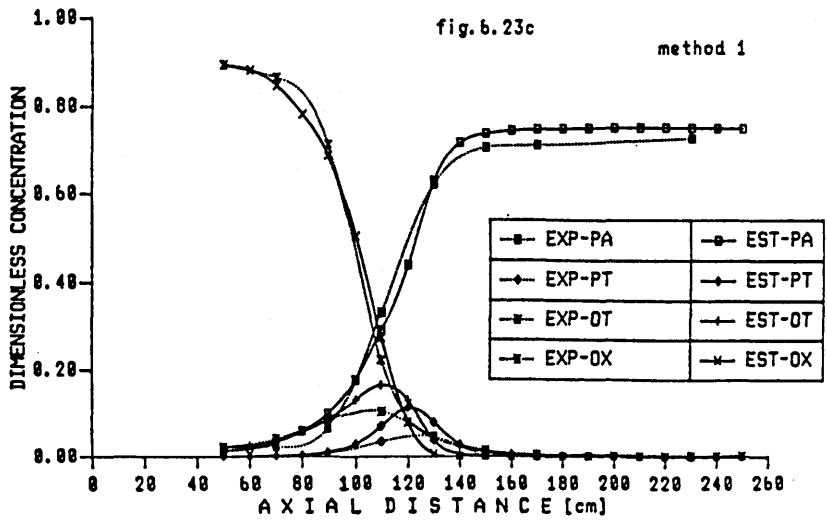
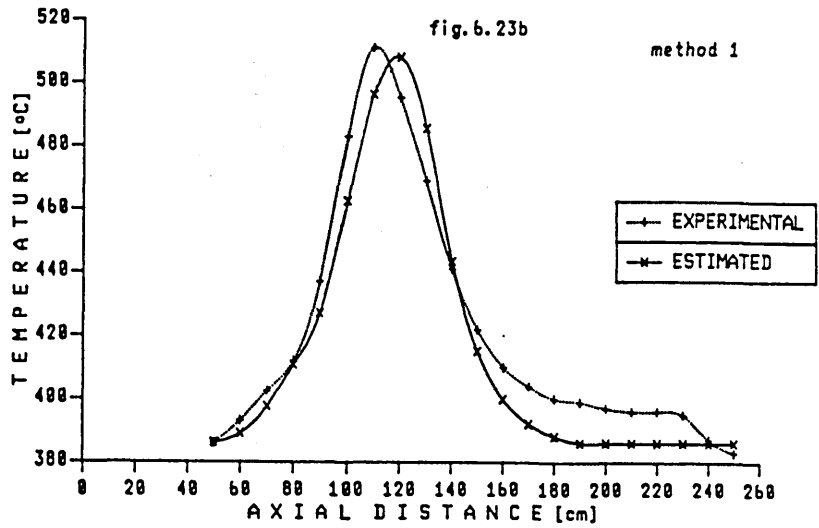
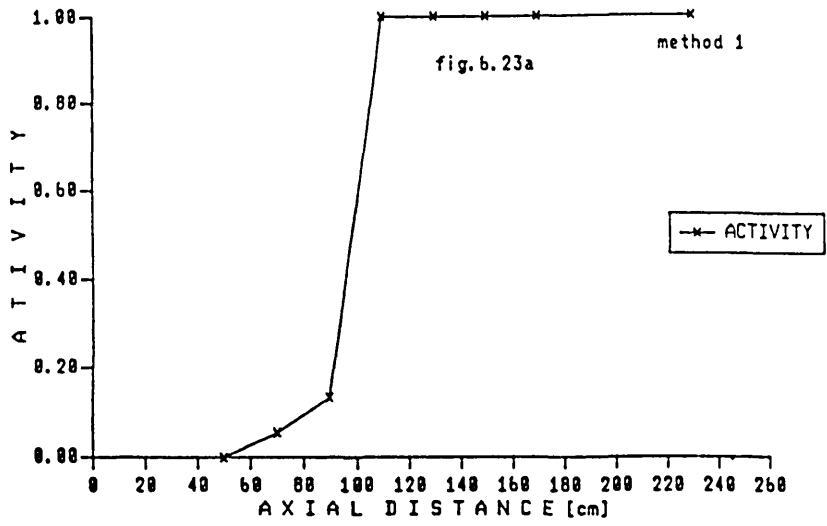


Fig. 6.23 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile approximated by method 1 (cf chapter 5) and estimated using only temperature and concentration measurements located between the reactor's inlet and the hotspot for operating conditions corresponding to experimental run 4 (see table 6.1).

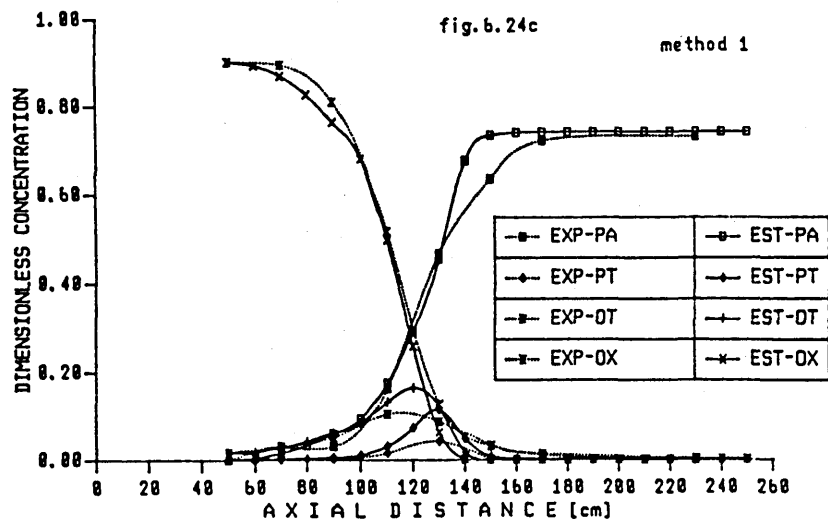
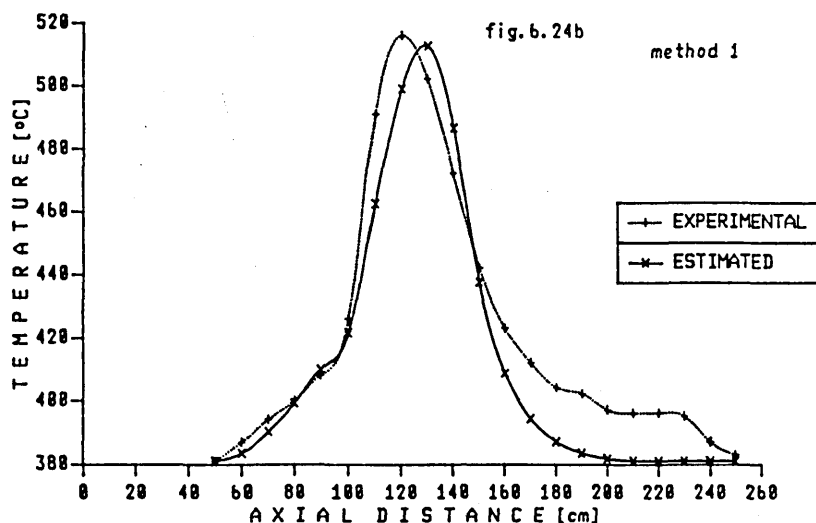
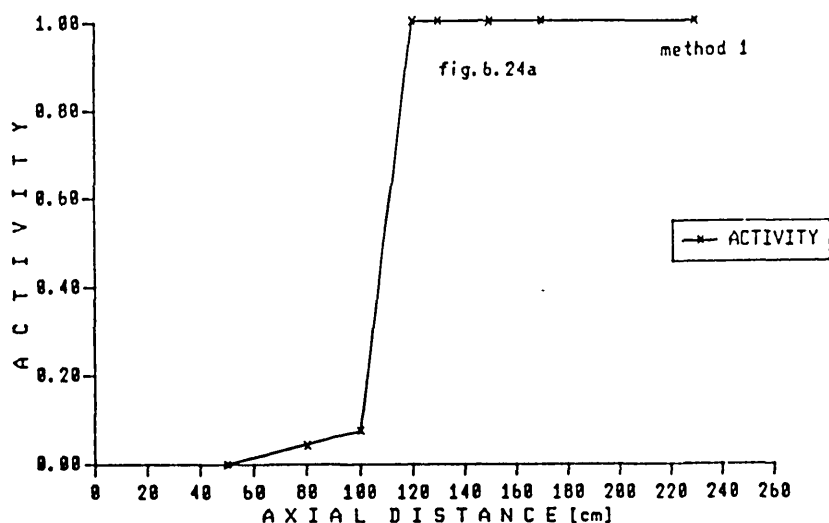


Fig. 6.24 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile approximated by method 1 (cf chapter 5) and estimated using only temperature and concentration measurements located between the reactor's inlet and the hotspot for operating conditions corresponding to experimental run 6 (see table 6.1).

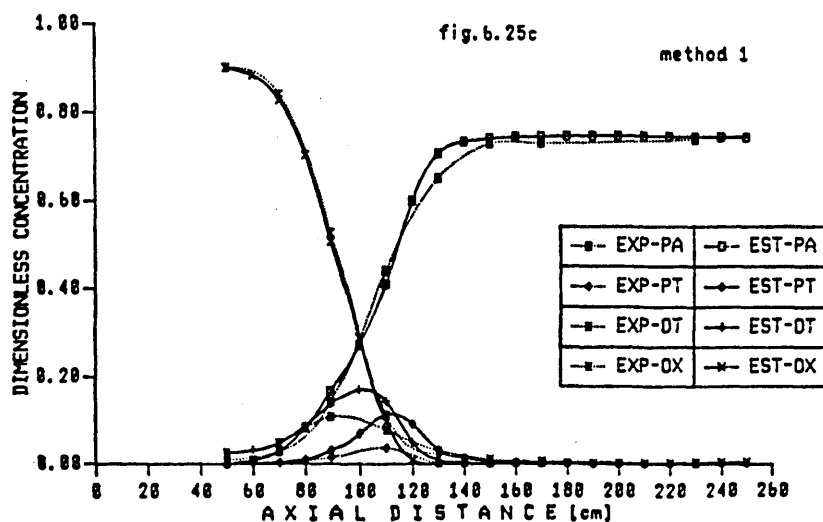
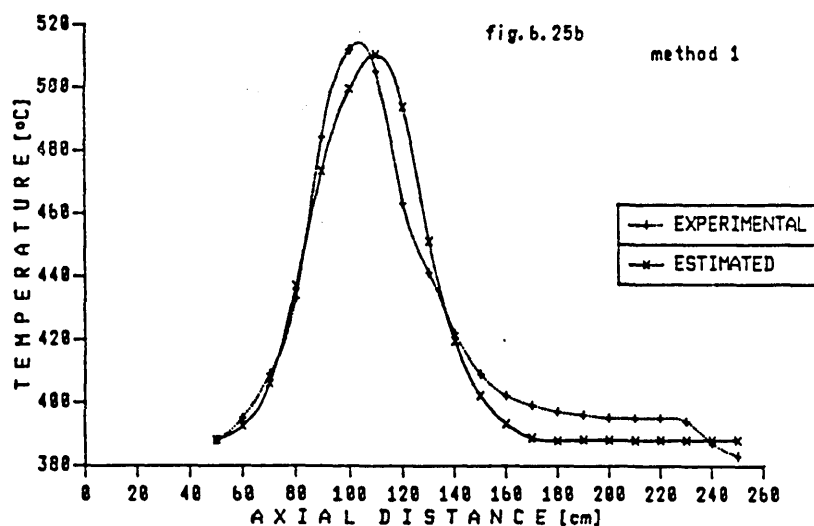
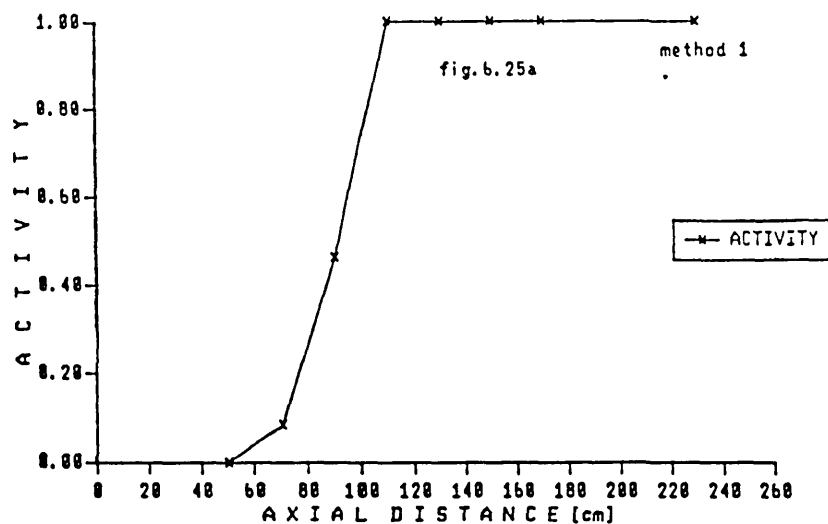


Fig. 6.25 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile approximated by method 1 (cf chapter 5) and estimated using only temperature and concentration measurements located between the reactor's inlet and axial position 12 (7cm after the hotspot for operating conditions corresponding to experimental run 7.

IV Case (d)

In this case, the activity profile parameters in the first two to three finite elements was estimated sequentially and the rest of the reactor was considered to have a uniform average activity ($\bar{\alpha}$) whose value was estimated using all the temperature and concentration measurements located within the region, and requiring that $\bar{\alpha}_1 \leq \dots \leq \bar{\alpha}_K = \bar{\alpha}_{K+1} = \dots = \bar{\alpha}_n = \bar{\alpha}$; where K is either 2 or 3 as the case might be. In this case, all the measurements from the hotspot region to the reactor exit were used to estimate the activity parameter in the region of uniform activity, as opposed to case (c) where only measurements around the hotspot region were used.

Fig. 6.26 shows the activity profile and the predicted temperature and concentration profiles compared with experimental data obtained during experimental run 1 (Table 6.1) when the activity parameters in the first three finite elements together with uniform average activity for the rest of the finite elements combined were estimated sequentially. From this figure, it can be seen that the value of the uniform average activity is very close to 1 as compared to a maximum activity parameter of ~ 1.5 shown by Figs. 6.12a and 6.18a. This value is still high enough to cause the observed rise in the predicted hotspot temperature of about 3°C which is, of course, less than that shown by Fig. 6.18b. Also the temperature and concentration profiles depicted by Fig. 6.26 are less steep after the hotspot as compared to those shown by Fig. 6.18.

Figs. 6.27 to 6.29 show the corresponding results when the reactor data obtained during experimental runs 4, 6 and 7 respectively (Table 6.1) was used and the activity parameters in the first two finite elements together with uniform average activity for the rest of the finite elements combined were estimated sequentially.

From these figures, 6.27 to 6.29, it can be observed that the concentration profiles of o-xylene and phthalic anhydride are well predicted despite the fact that the predicted hotspot temperatures are generally low.

The reason for low hotspot predictions is due to the fact that the values of the uniform average activity estimated after the first two finite elements are much lower than the maximum activity parameter values estimated at the finite element around the hotspot in the previous case (a) as shown in Figs. 6.13 to 6.15.

Perhaps the only way to improve upon the results in this particular case is to allow the weightings, especially those for the temperature measurements, to vary axially so as to give more influence in the objective function to those measurements located at the hotspot region.

6.3.4 Activity profiles estimation using temperature measurements only

The possibility of using only temperature measurements to estimate catalyst activity profiles in order to predict the reactor behaviour was also investigated. This is particularly useful if it is required to estimate the activity of the catalyst during the transient state since the time constant associated with concentration measurements is very low. Also, in industrial reactors only temperature measurements may be available. There are usually one or two thermocouples for temperature measurement plus exit composition measurement. Three cases (e), (f) and (g) for the estimation of catalyst activity profiles were considered in this section.

To ease comparison of results the same finite elements determined for each operating condition when both temperature and concentration measurements were used to estimate catalyst activity profiles were also used for the cases considered in this section.

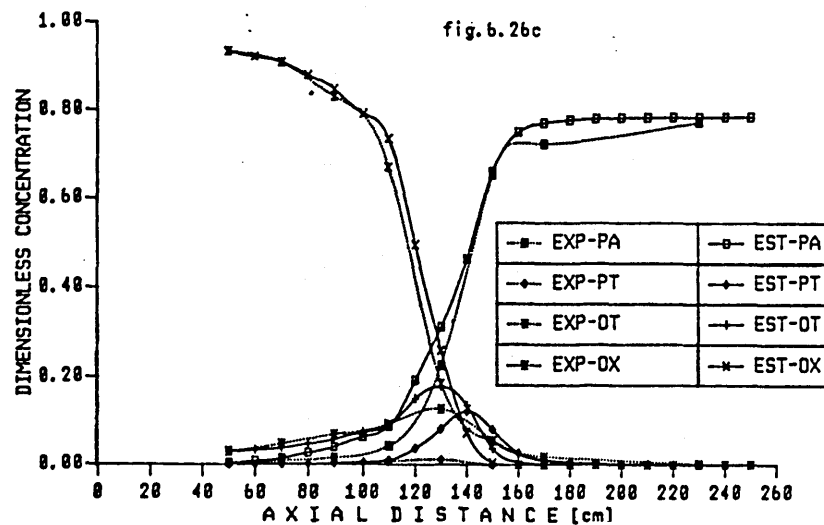
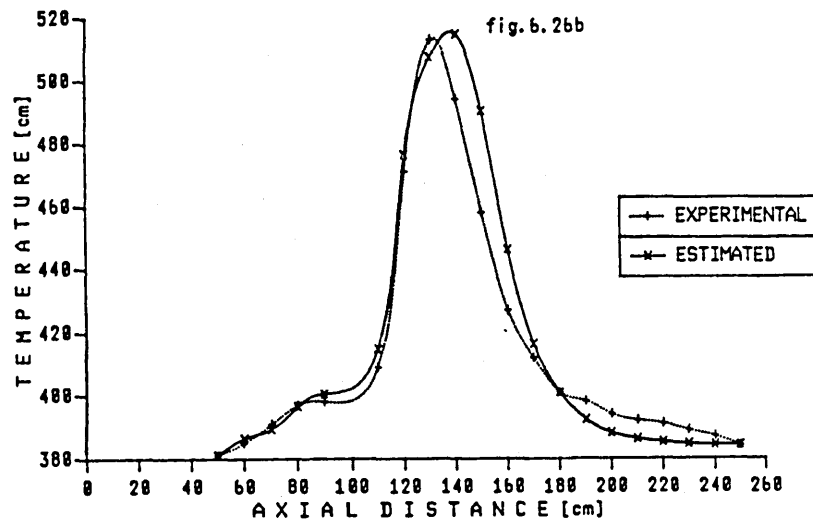
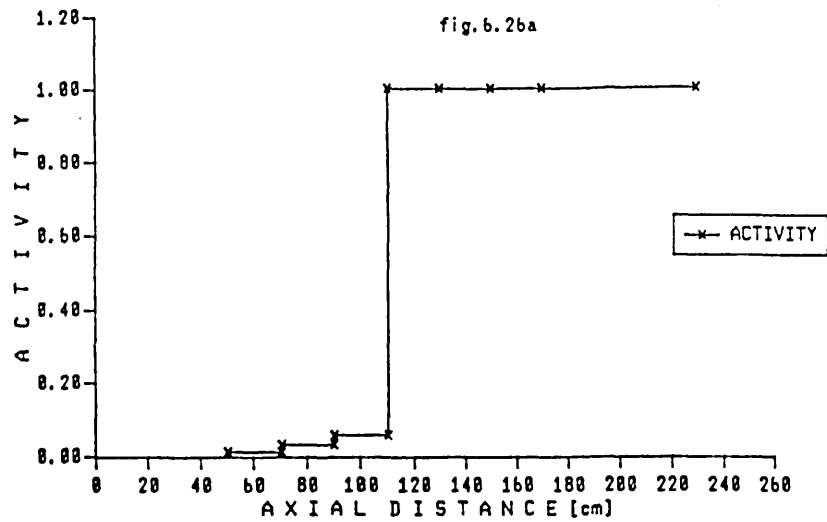


Fig. 6.26 Predicted or estimated temperature and concentration profiles compared with experimental data; spatially uniform catalyst activity profile at the downstream end of the reactor, including the hotspot, estimated using all the temperature and concentration measurements located in that region for operating conditions corresponding to experimental run 1 (see table 6.1).

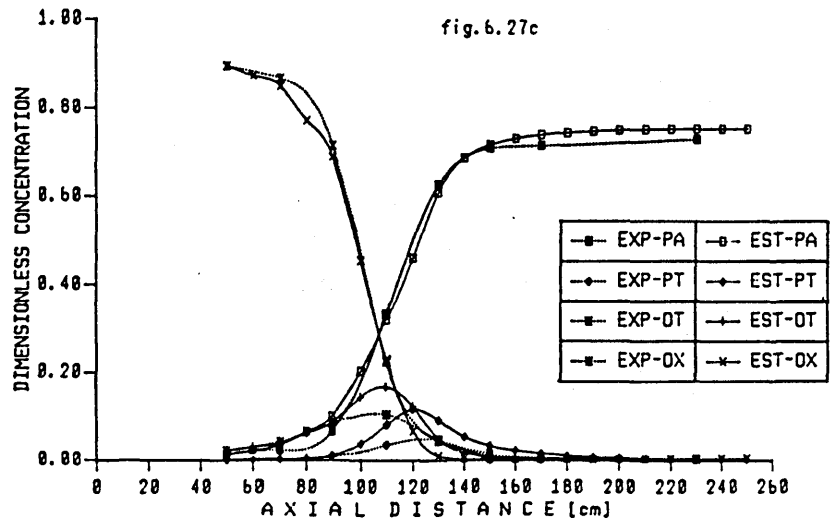
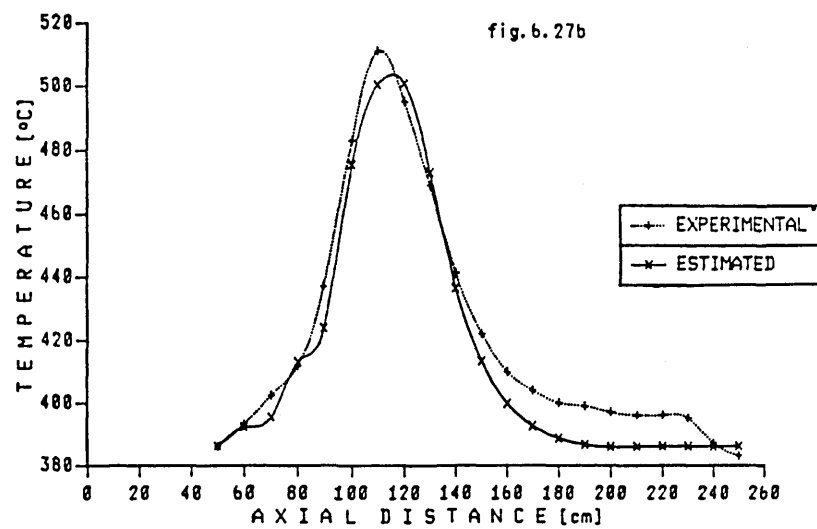
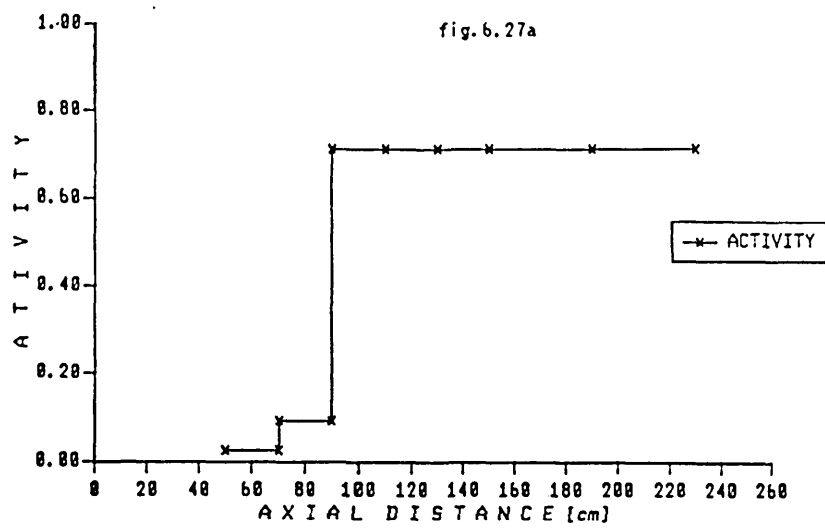


Fig. 6.27 Predicted or estimated temperature and concentration profiles compared with experimental data; spatially uniform activity profile at the downstream end of the reactor, including the hotspot, estimated using all the temperature and concentration measurements located in that region for operating conditions corresponding to experimental run 4 (see table 6.1).

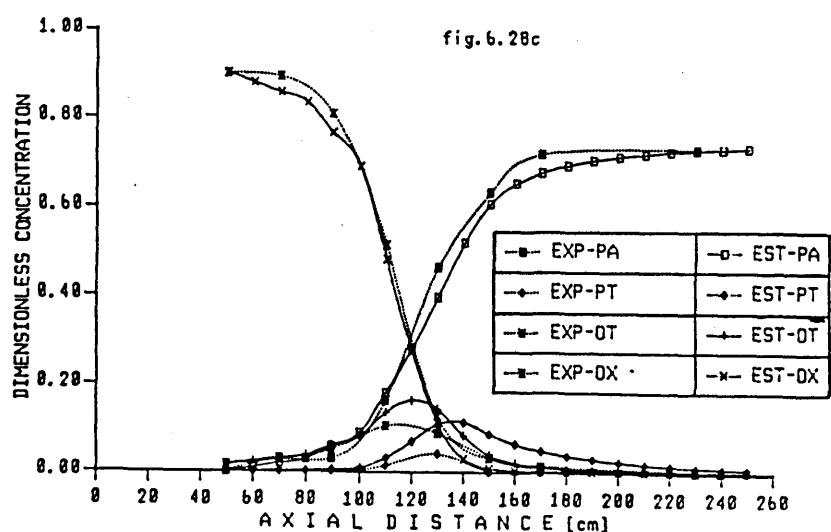
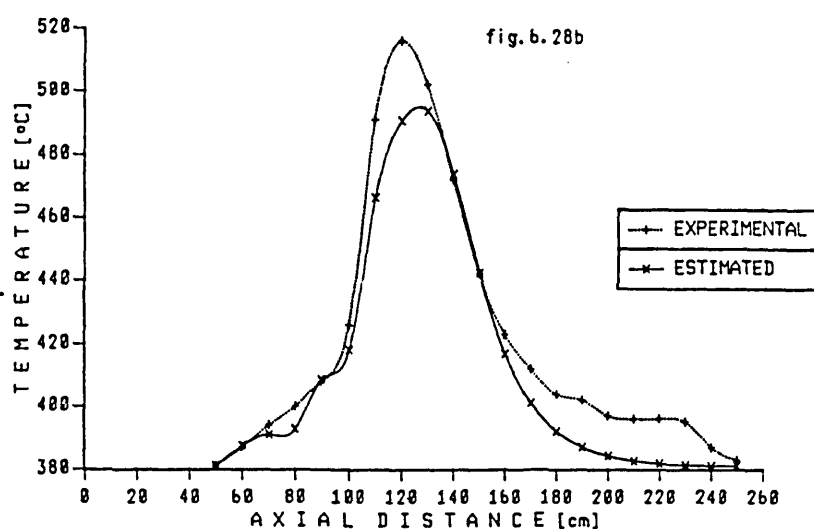
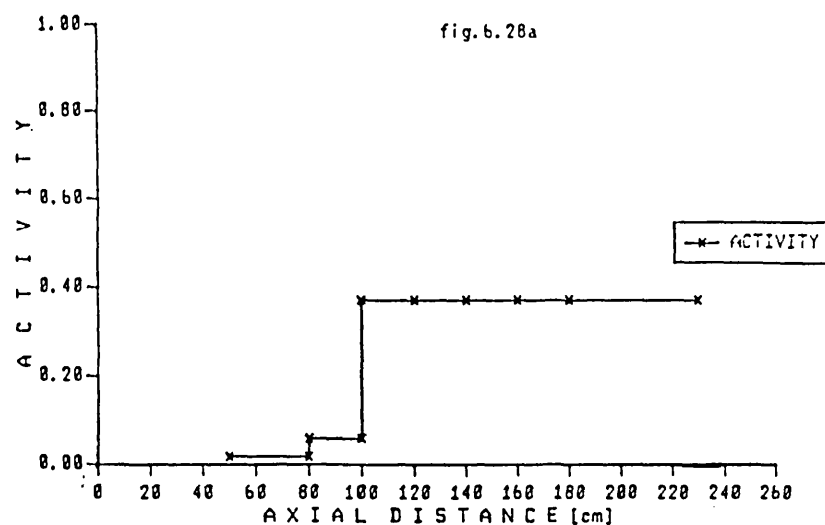


Fig. 6.28 Predicted or estimated temperature and concentration profiles compared with experimental data; spatially uniform activity profile at the downstream end of the reactor, including the hotspot, estimated using all the temperature and concentration measurements located in that region for operating conditions corresponding to experimental run 6 (see table 6.1).

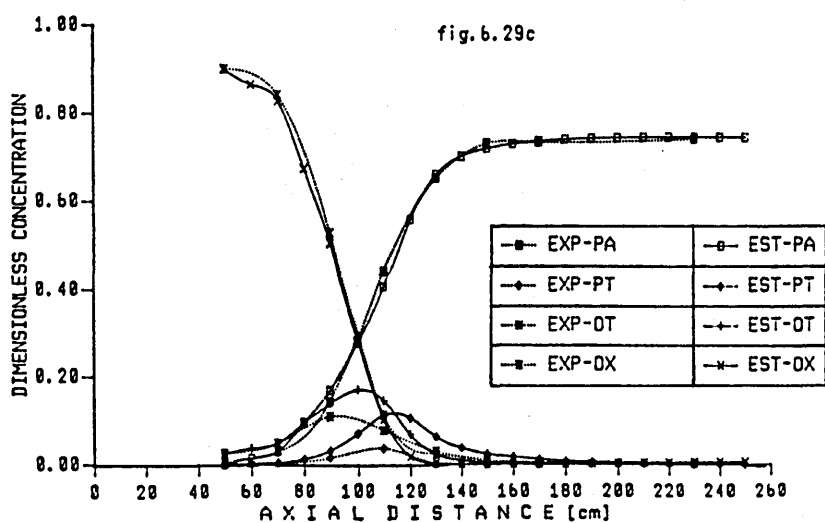
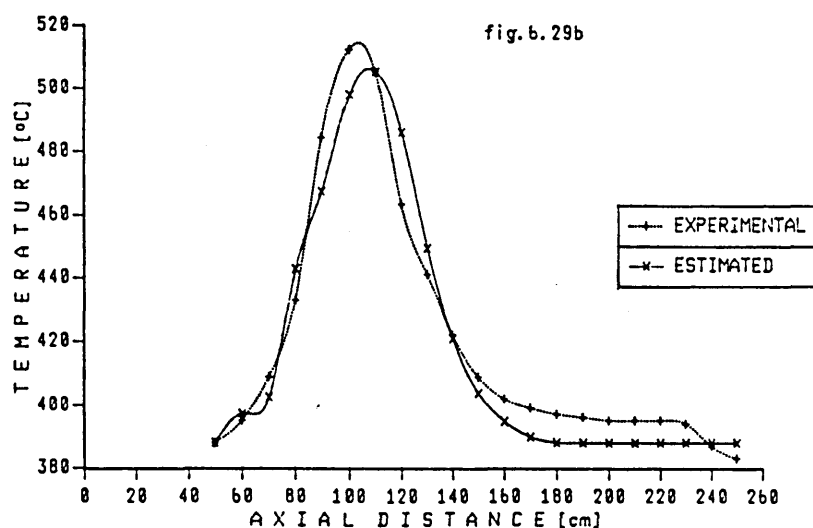
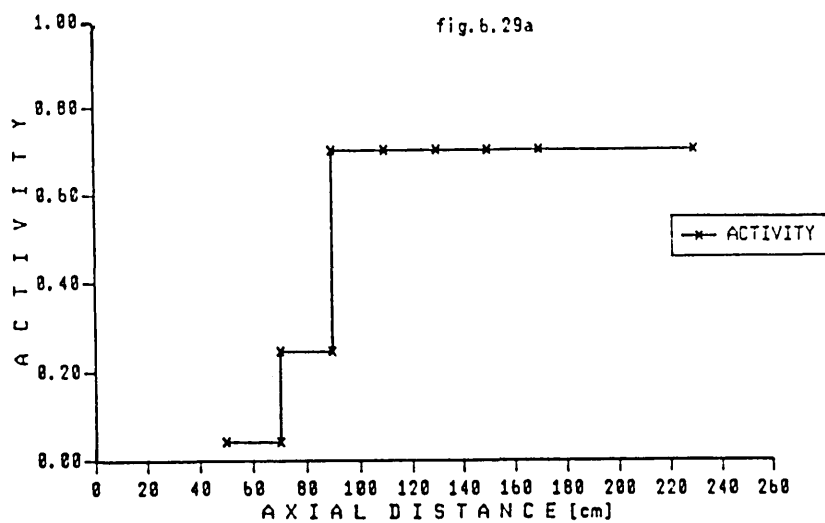


Fig. 6.29 Predicted or estimated temperature and concentration profiles compared with experimental data; spatially uniform activity profile at the downstream end of the reactor, including the hotspot, estimated using all the temperature and concentration measurements located in that region for operating conditions corresponding to experimental run 7 (see table 6.1).

V Case (e)

In this case the activity parameters in all the finite elements were estimated sequentially without imposing any constraints on their values, using only temperature measurements.

As an example, the temperature measurements obtained during experimental run 6 (Table 6.1) were used to estimate the catalyst activity profile in order to predict the steady state behaviour of the reactor.

Fig. 6.30 shows the estimated activity profile and the model predictions of temperature and concentration profiles compared with experimental data. It can be seen that the value of the activity parameters at the hotspot region (the third finite element) is about three times greater than that shown in Fig. 6.14a where both temperature and concentration measurements were used to estimate catalyst activity profiles. The result of this is a faster rate of production of phthalic anhydride within a very narrow region around the hotspot. This is manifested by the steeper temperature and concentration profiles as compared with those in Fig. 6.14. In order to reduce this rate of reaction, and hence reduce the amount of heat of reaction released which might result in higher hotspot predictions, the estimated activity (~ 0.6) in the finite element coming immediately after the hotspot is about 76% lower than the maximum value of 2.5 estimated in the previous finite element.

There is no doubt that this behaviour of the estimated activity profile, with the parameters rising and falling, does not offer any meaningful explanation to the state of the catalyst.

VI Case (f)

In order to obtain physically meaningful estimates of the activity profile using only temperature measurements, some constraint was impos-

ed on the activity parameters as demonstrated in case (c).

Again, the temperature measurements obtained during experimental run 6 were used and the activity profile was estimated up to the third finite element (the hotspot region) so that the rest of the finite elements had a uniform activity whose value was that estimated at the third finite element. This implies that, effectively, only the temperature measurements located between the reactor inlet (axial position 6) and the hotspot were used to estimate catalyst activity profiles, in this case.

Fig. 6.31 shows the activity profile and the predicted temperature and concentration profiles compared with experimental data. Fig. 6.31b shows that the temperature profile at the region prior to the hotspot is very well predicted but there is an intolerable rise in the predicted hotspot temperature.

As explained earlier, the very high activity estimated around the hotspot region forces the rest of the reaction to take place at a very fast rate resulting in the release of a large amount of heat within a very narrow axial distance. In this case, the amount of heat of reaction released is large enough to cause the observed high temperature rise after the experimental hotspot. It can be seen from Fig. 6.31b that the temperature drops very fast after this region since little or no more heat of reaction is being released. Again, the final yield of phthalic anhydride is well predicted.

VII Case (g)

The results obtained by applying the constraints on the activity parameters as shown in case (d) with only temperature measurements used to estimate the parameters are shown in Figs. 6.32 and 6.33 for reactor data obtained during experimental runs 6 and 7 respectively.

Figs. 6.32 and 6.33 show that both the temperature and concentration profiles are very poorly predicted. The reason for the poor predictions is due to the fact that very low values of the uniform average activity were estimated at the downstream end of the reactor. The low activity estimated was as a result of equal weighting given to all temperature measurements and since the experimental temperature profiles are narrow, most of the measurements were very low compared to the hotspot temperature. For example, in Fig. 6.32, the region of uniform average activity starts from axial position 11 (100 cm) and ends at axial position 24 (230 cm) with only five temperature measurements between 440 and 515°C; the remaining eight having lower values between 380 and 420°C. The predicted temperature profile in this region is just the average value of all these measurements.

At this point, one may conclude that in order to obtain reasonable predictions particularly around the hotspot the temperature measurements weighting must be made to vary axially, in this particular case (g).

In general when spatially uniform activity is estimated over a large section of the reactor comprising a wide range of measurements the need to vary the weightings axially so as to give the greatest influence to measurements located at the critical regions of the reac-

tor, in the optimization scheme, becomes very apparent. Otherwise, the effect of the critical measurements in the objective function will be diluted by measurements which are relatively unimportant and therefore lead to poor overall predictions of the experimental profiles.

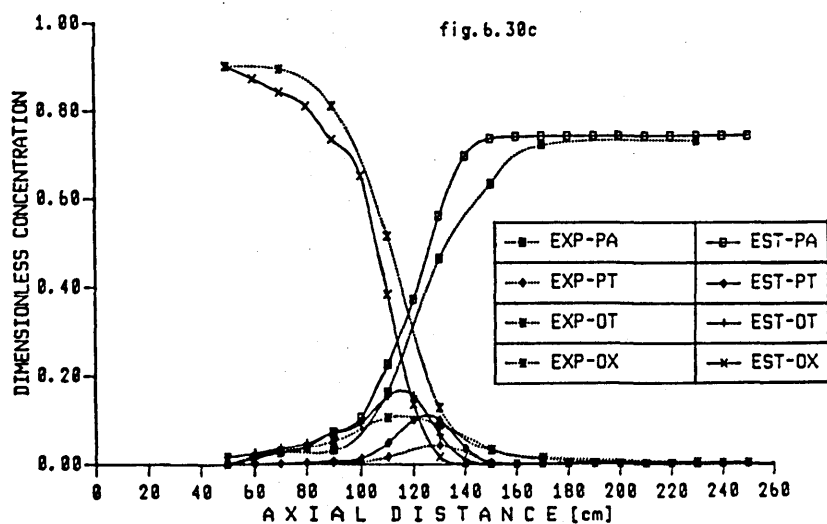
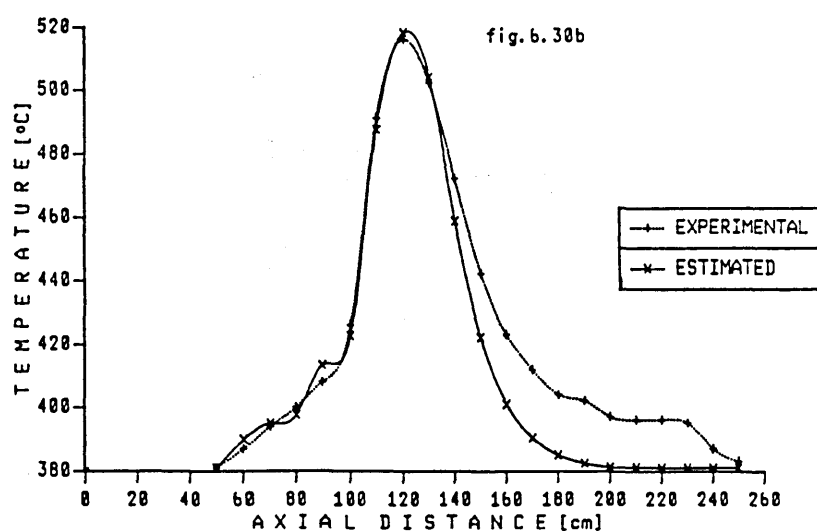
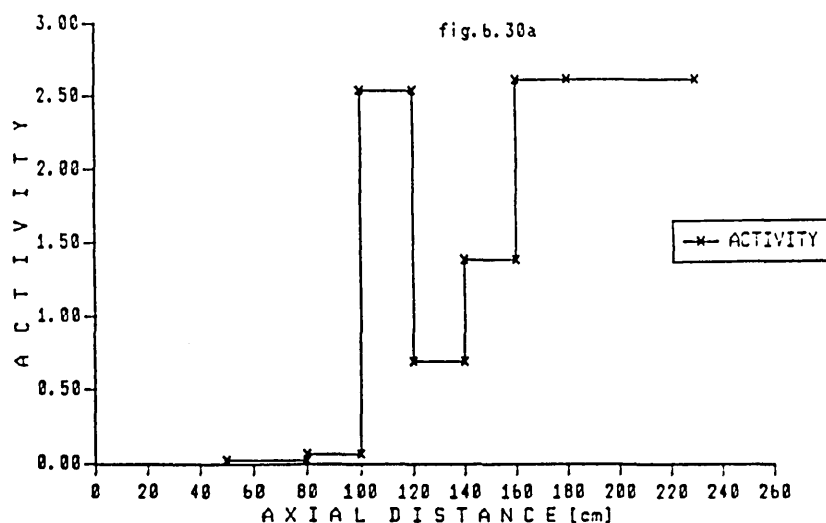


Fig. 6.30 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using only temperature measurements from the reactor's inlet to the exit for operating conditions corresponding to experimental run 6 (see table 6.1).

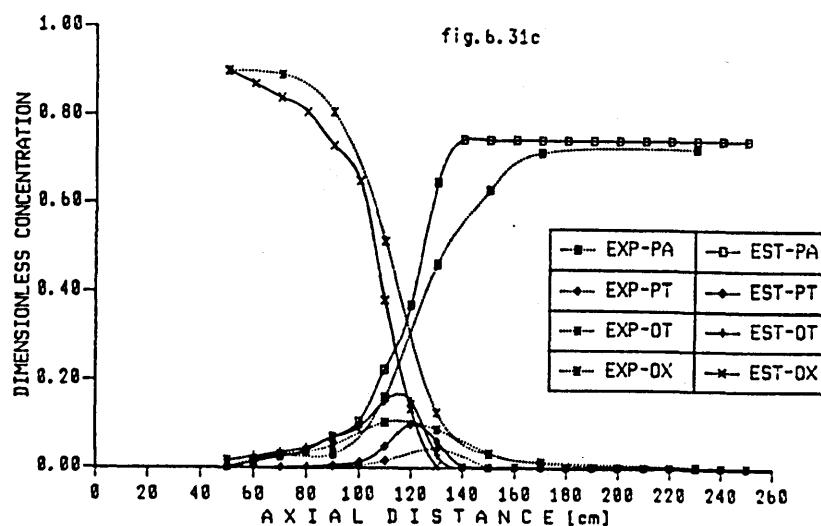
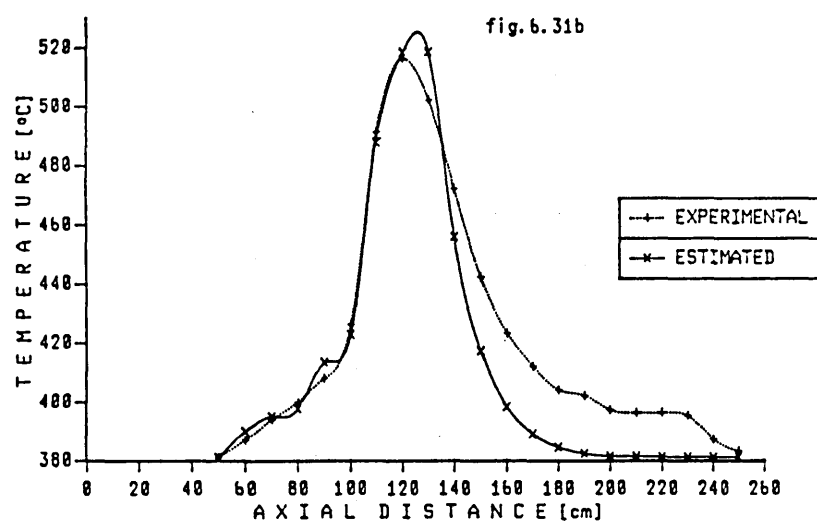
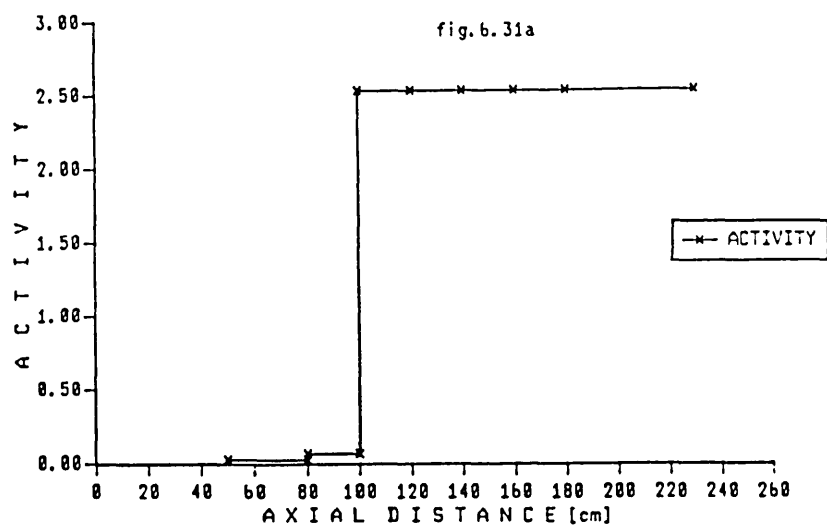


Fig. 6.31 Predicted or estimated temperature and concentration profiles compared with experimental data; catalyst activity profile estimated using only temperature measurements located between the reactor's inlet and the hotspot for operating conditions corresponding to experimental run 6 (see table 6.1)

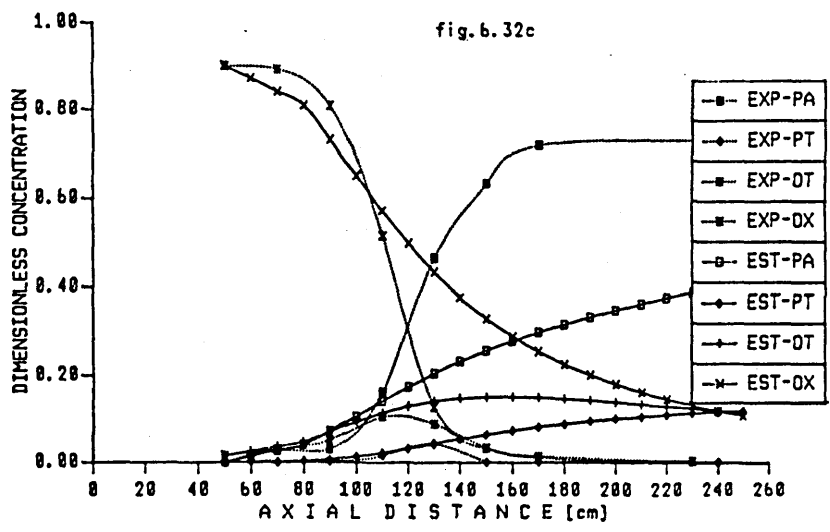
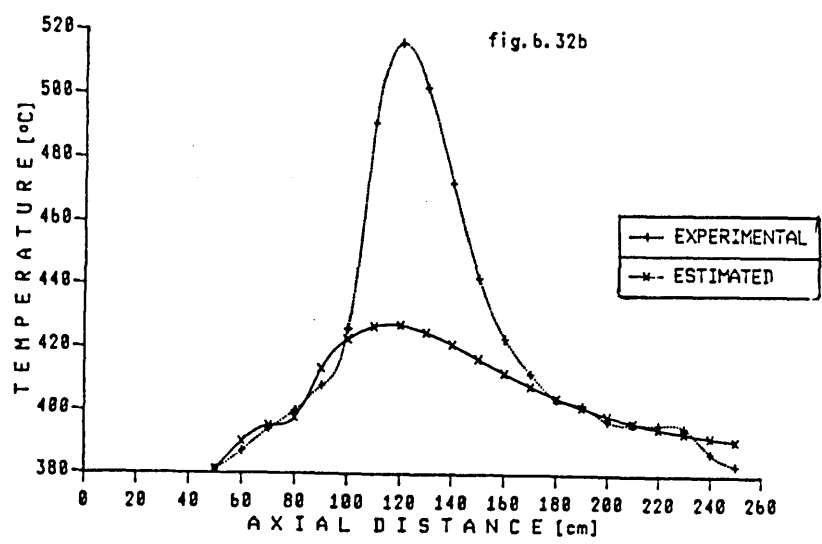
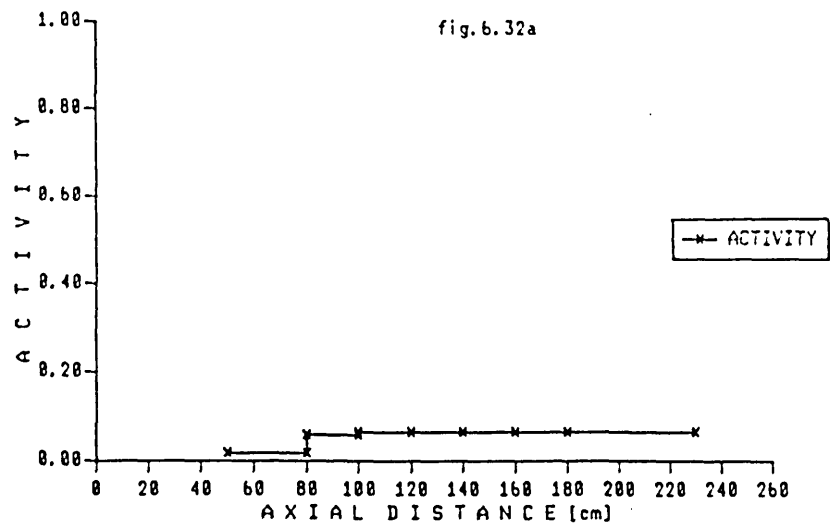


Fig. 6.32 Predicted or estimated temperature and concentration profiles compared with experimental data; spatially uniform activity profile at the downstream end of the reactor, including the hotspot, estimated using only temperature measurements (all) located in that region for operating conditions corresponding to experimental run 6 (see table 6.1).

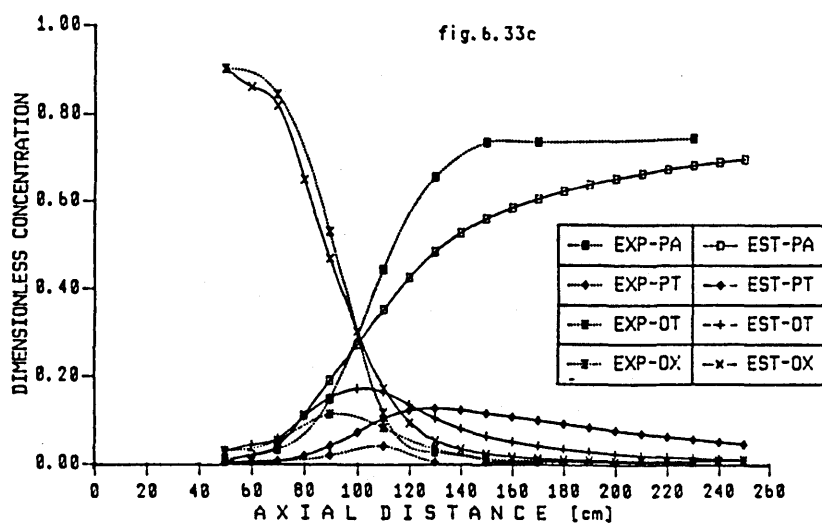
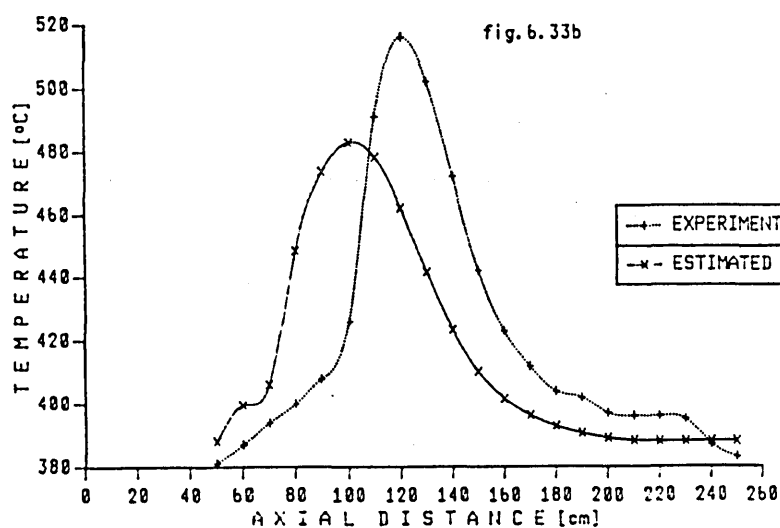
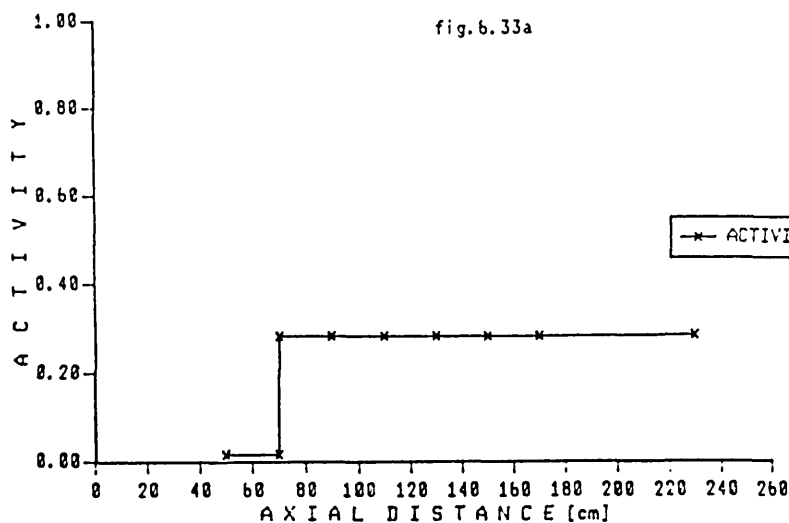


Fig. 6.33 Predicted or estimated temperature and concentration profiles compared with experimental data; spatially uniform activity profile at the downstream end of the reactor, including the hotspot, estimated using only temperature measurements (all) located in that region for the operating conditions corresponding to experimental run 7 (see table 6.1).

6.3.5 Summary

The predictions of the steady state behaviour of this reactor-reaction system have been found to be in reasonably good agreement with the experimental data if both temperature and concentration measurements are used to estimate catalyst activity profiles. The predictions were found to be insensitive to the measurement weightings of o-tolualdehyde and phthalide used.

Only marginal improvement in the simulation results were obtained by estimating the activity parameters of an activity profile simultaneously and this could not justify the amount of computation time taken. For example, the computation time taken to estimate three activity parameters simultaneously was about nine times greater than when they were estimated sequentially. Hence, in almost all the simulations, the parameters were estimated sequentially.

Since a greater part of the reversible partial deactivation of the catalyst occurred within the inlet region, where temperatures are low and o-xylene concentrations high, the quality of the predictions was determined by how well the activity profile was approximated in that region (from the reactor inlet to the hotspot).

The predicted temperature values at the downstream end of the reactor, particularly towards the exit, were generally very low compared to the experimental data. This was attributed partly to neglecting axial dispersion of heat but mostly to the fact that the measured salt bath temperature towards the exit end of the reactor was always about 5° to 10°C higher than in the rest of the reactor upstream where the temperature was almost uniform.

By imposing some constraints on the estimated activity parameters in order to obtain monotonic estimates of the activity profiles using

both temperature and concentration measurements, the concentration profiles of o-xylene and phthalic anhydride were, on the whole, reasonably well predicted although the temperature profile predictions especially around the hotspot region were generally not very good.

When only temperature measurements were used to estimate catalyst activity profiles without imposing any restrictions on the values of the activity parameters, the behaviour of the estimated activity profile after the hotspot was still unreasonable despite the fact that the final yield of phthalic anhydride was still well predicted. Although the hotspot temperature was predicted to within a few degrees, the overall temperature profile together with the concentration profiles were poorly predicted.

The predicted temperature and concentration profiles were even poorer when some constraints were imposed on the values of the activity parameters in order to obtain physically meaningful estimates of the activity profiles using only temperature measurements. The problem of introducing axially varying temperature measurement weightings became very apparent especially for the case where uniform average activity parameter was estimated over a very large region comprising measurements of a wide range of magnitudes.

In the light of the above results, one may conclude that the best way to predict the steady state behaviour of the reactor reasonably well is to estimate catalyst activity profiles using both temperature and concentration measurements as outlined in case (a). One major limitation of this procedure is that the estimated activity profile at the downstream end of the reactor does not offer any physically meaningful explanation of the state of the catalyst. Another shortcoming is that all the temperature and concentration measurements are required

to be used to estimate the activity profile. This is not a very attractive procedure for industrial reactors where only a few measurements may be available.

Although some of these shortcomings may be eliminated if the procedure outlined in case (c) is adopted (where the activity profile is estimated using only temperature and concentration measurements located at the upstream end of the reactor) there is still the problem of determining exactly where to stop the estimation procedure. Moreover, all the temperature and concentration measurements located within this region of the reactor (from the reactor inlet to the hotspot or a few centimeters after the hotspot) are still required to be used in order to obtain reasonable predictions of the reactor behaviour. The number of measurements that entails is still more than is possible in industrial reactors.

Perhaps the closest we can get to estimating catalyst activity profiles from industrial reactors is by adopting the procedure outlined in case (f) where only temperature measurements located at the upstream end of the reactor (from the reactor inlet to around the hotspot region) were used in the estimation. In this case, provided the hotspot is not too far away from the reactor inlet (axial position 6), only very few temperature measurements may be used to estimate catalyst activity profiles in order to predict reasonably well the final yield of phthalic anhydride. As was shown in Fig. 6.31c, this procedure led to poor overall predictions of both the temperature and concentration profiles but predicted the final yield of phthalic anhydride very closely.

Since industrial reactors are normally operated at salt bath temperatures close to 390°C , the hotspot would normally be located

between axial positions 6 and 12 for a freshly regenerated catalyst and, therefore, three or four thermocouples located in this region may be sufficient to estimate catalyst activity profiles in order to predict the total yield of phthalic anhydride.

However, it is known that the hotspot moves gradually towards the downstream end of the reactor with time of operation as the catalyst deactivates reversibly (see Section 6.4). It is therefore suggested that periodic regeneration of the catalyst should be done in order to relocate the hotspot within the region where a few temperature measurements can be used to predict the yield of phthalic anhydride by estimating catalyst activity profiles.

In this way, there is no need to use the outlet composition measurement in industrial reactors in the optimization scheme in order to predict the total yield of phthalic anhydride.

6.4 LONG-RUN STEADY STATE EXPERIMENTS

These experiments were conducted during the fourth experimental stage. After regeneration of the catalyst for a period of about 40 hrs, the reactor was started up and run continuously for a period of thirteen days from 14th to 26th July 1985. The operation conditions were 380°C salt bath temperature, 4 Nm³/hr air flowrate and 176 gm/hr o-xylene flowrate.

The purpose of the experiments was to investigate the long-term steady state behaviour of the reactor when operated continuously in the light of gradual partial deactivation of the catalyst.

The relevance of these type of experiments can be fully appreciated if it is considered that in industry the reactors are normally run continuously, with only one or two brief short downs, usually for maintenance, throughout the year*.

One would expect that in the face of reversible catalyst deactivation, the reaction front should move gradually towards the reactor exit so that eventually the reaction would die out. Of course, it is already known that such is not the case else it would be impossible to operate industrial reactors continuously for such a long period of time without catalyst regeneration.

It was also expected that changes in the activity and selectivity of the catalyst should result in lower yields of phthalic anhydride with time since no sulphur compounds were included in the feed, as these changes are sometimes associated with loss of SO₃ [Wainwright & Foster (1979)].

* The practice at B.P. Chemicals Ltd. Hull Works is to run the reactors continuously with only a two-week short down period for maintenance throughout the year; the catalyst is discarded after four years [Allen (1986)].

The reason for the reaction persisting throughout the period of continuous operation may be apparent from Fig. 6.34 which shows the axial temperature profiles (Fig. 6.34a) and the concentration profiles of o-xylene (Fig. 6.34b) and phthalic anhydride (Fig. 6.34c) for measurements taken after every 24 hrs at 1700 hrs throughout the period.

Fig. 6.34a shows that the typical steady state axial temperature profile with a pronounced inflection in the region preceding the hotspot was obtained on the first day. The hotspot was very sharp and located between axial positions 12 and 13. By the second day, more of the reactant (o-xylene) was consumed at the upstream end of the reactor following the re-oxidation of the catalyst within that region. This re-oxidation of the catalyst may be attributed to axial dispersion of heat. The resultant effect was a broadening of the temperature profile which led to the reduction of the magnitude of the hotspot by 11°C from 507 to 496°C . This trend continued and by the 5th day the hotspot temperature was 482°C , a reduction of 25°C . The position of the hotspot hardly changed within the first five days of operation.

By the 6th day, the partially oxidized catalyst had started to undergo further reduction causing the hotspot to shift downstream to between axial positions 13 and 14 and since the catalyst was no longer as active as before the temperature profile remained very broad and the magnitude of the hotspot was further reduced to 481°C . This process of re-oxidation and re-reduction of the catalyst continued and by the end of the 9th day an equilibrium state was attained which resulted in a steady state hotspot temperature of 472°C located between axial positions 14 and 15, observed throughout the rest of the period. However,

a very gradual shift of the temperature profile towards the reactor exit, after the 9th day, could still be observed as depicted in Fig. 6.34a.

Despite the internal disturbances created by catalyst deactivation-reactivation process, it is interesting to observe that the yield of phthalic anhydride was not adversely affected. As a matter of fact, Fig. 6.34c shows that the yield slightly increased with time of operation. This probably may explain the reason why the idea of shutting down industrial plants for catalyst regeneration is not very popular. However, the trade-off engendered by getting improved yields of phthalic anhydride in this manner is an inevitable increase in the quantity of phthalide in the product with a resultant increase in the cost of separation of the components.

A fresh start-up of the reactor after shutting down to re-oxidize the catalyst by passing only air at 2 Nm³/hr and maintaining the salt bath temperature constant between 400 and 410°C for a period of about 40 hrs can lead to repetition of the initial temperature and concentration profiles.

Concentration measurements of CO and CO₂ taken on several days during this long term operation of the reactor led to the conclusion that the improvement in the yield of phthalic anhydride was probably due to the fact that the rate of over-oxidation of phthalic anhydride to CO and CO₂ gradually decreased with time of operation. See Appendix A for the concentration profiles of CO and CO₂, the ratio of CO₂/CO concentration profiles and the combined selectivity profiles of o-xylene to CO and CO₂.

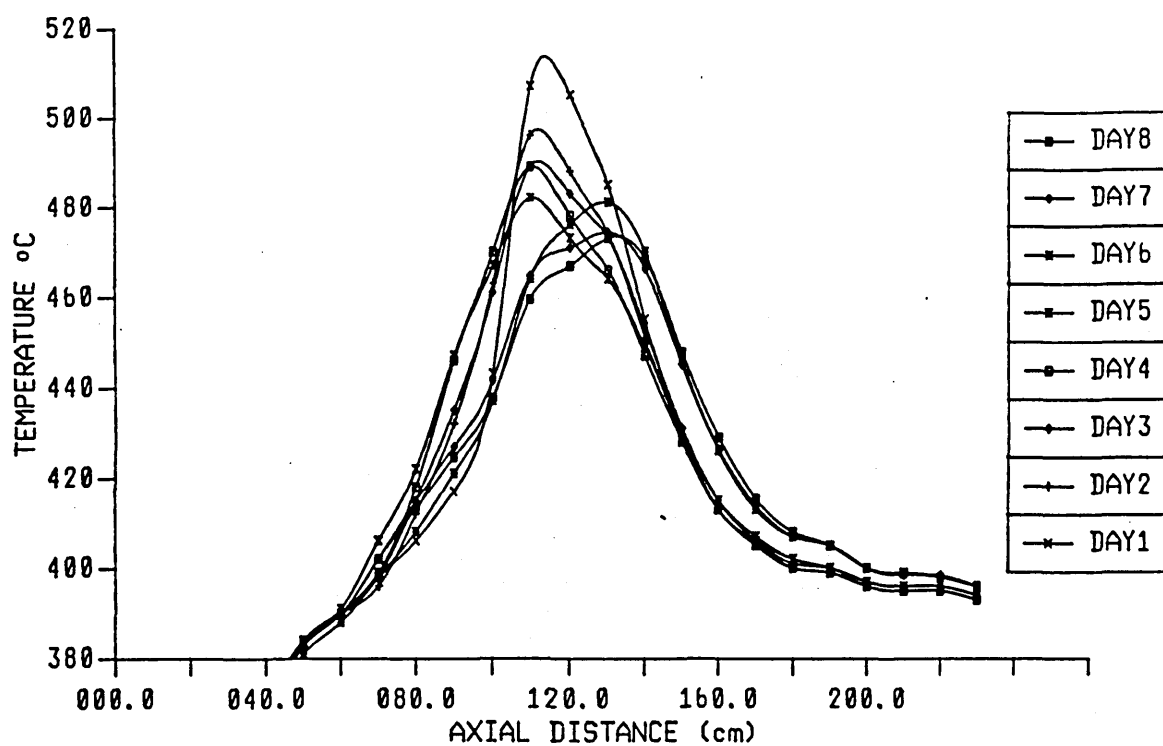
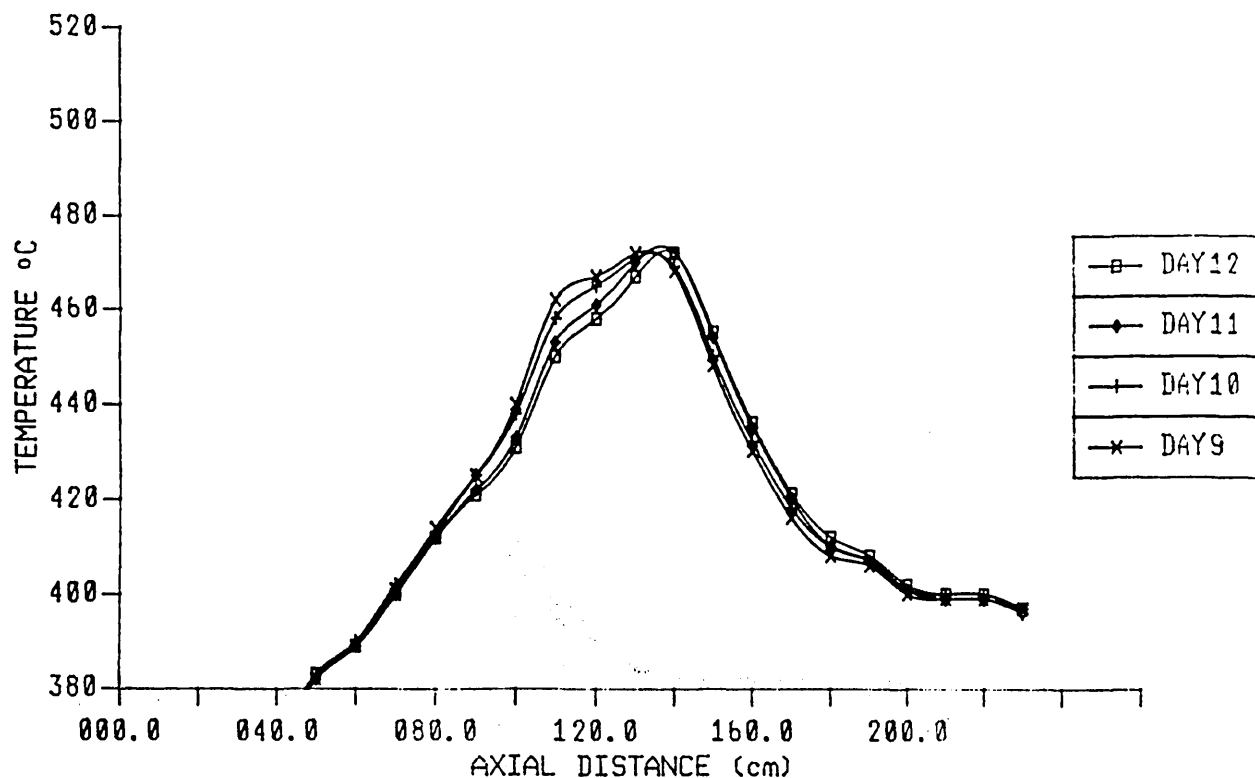


Fig. 6.34a Long term steady state axial temperature profiles; salt bath temperature 380°C, o-xylene flowrate 176gm/hr.

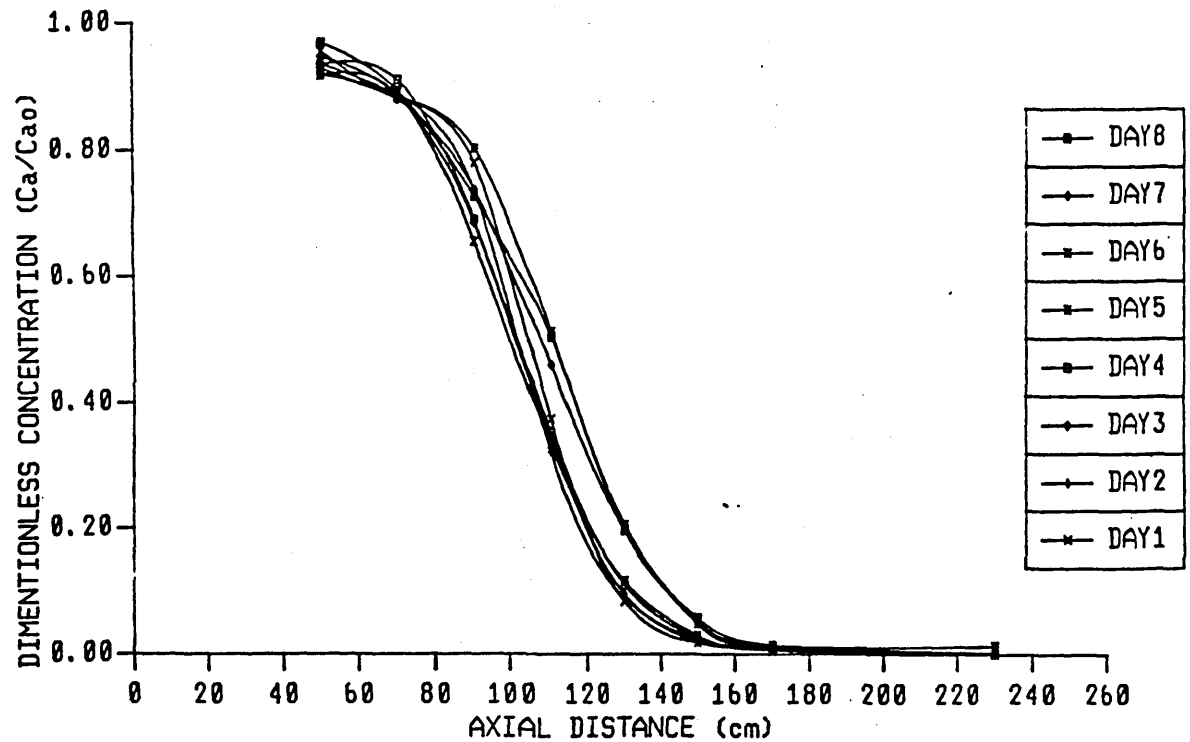
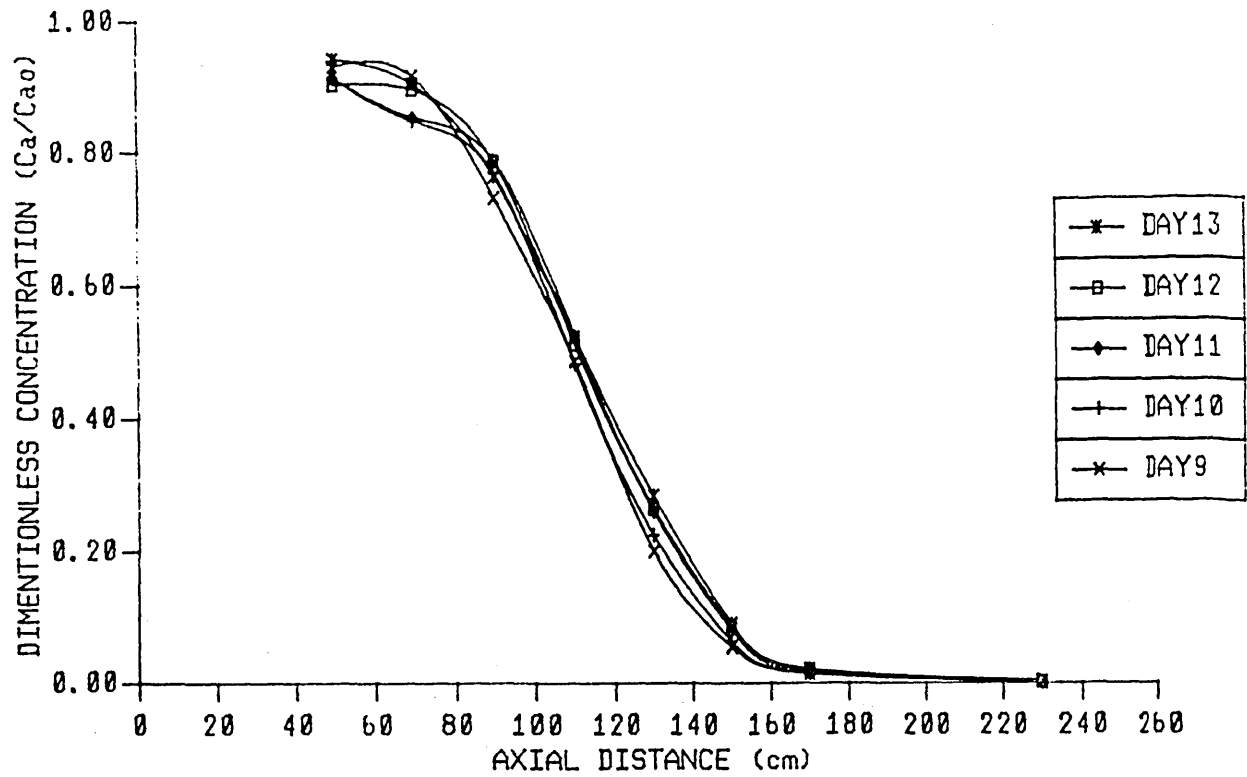


Fig. 6.34b Long term steady state axial o-xylene concentration profiles; salt bath temperature 380°C, o-xylene flowrate 176gm/hr. (see fig. 6.34a).

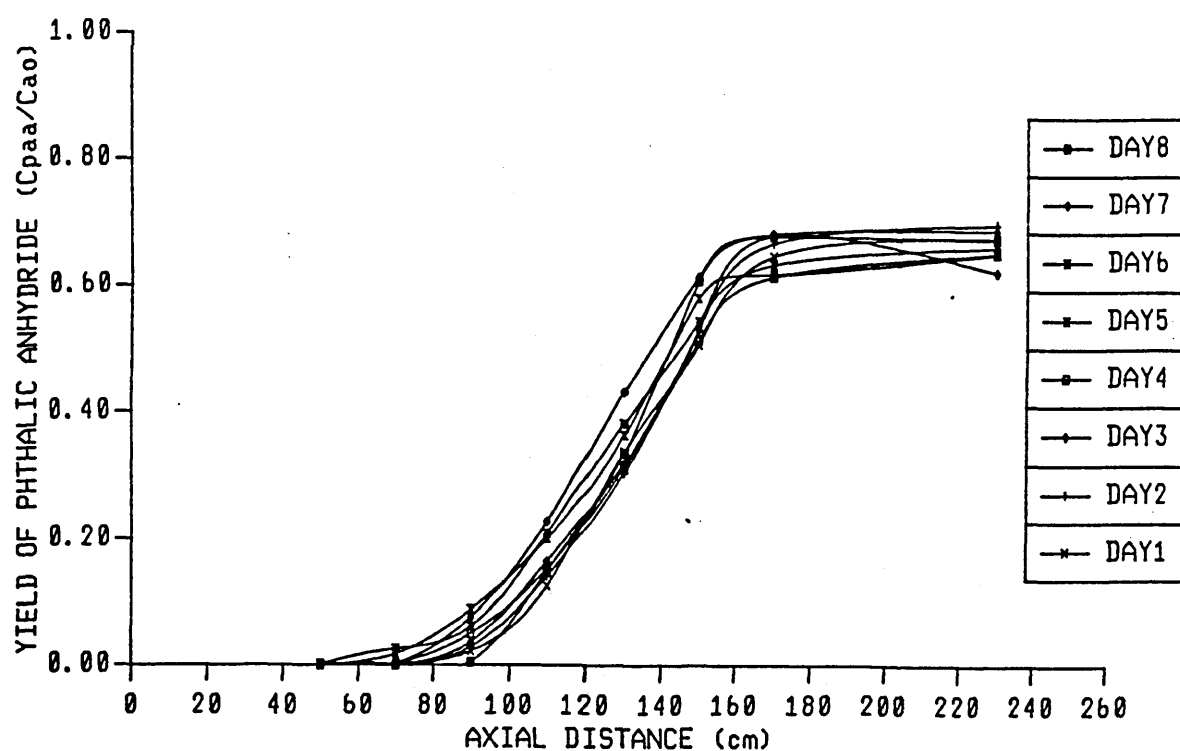
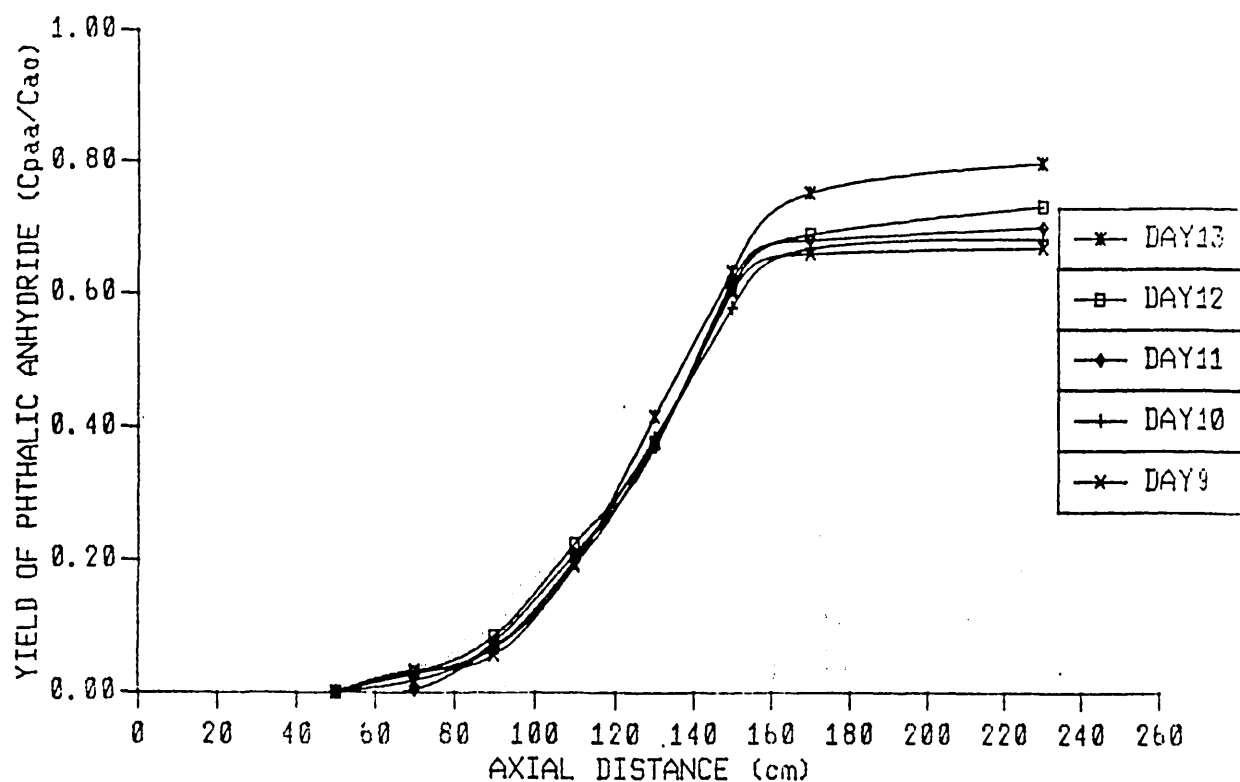


Fig. 6.34c Long term steady state axial phthalic anhydride concentration profiles; salt bath temperature 380°C, o-xylene flowrate 176gm/hr (see fig.6.34a).

6.5 DYNAMIC EXPERIMENTS

The dynamic experiments carried out in this work were very few and consisted mainly of step changes of o-xylene feed concentration and ramp changes of the salt bath temperature with the air flowrate maintained at 4 Nm³/hr. Detailed dynamic experiments on this reactor-reaction system involving the various air flowrates, salt bath temperatures and o-xylene flowrates have been reported elsewhere [Lopez-Isunza (1983)].

The aim of these experiments was to study the dynamic behaviour of the reactor subject to the perturbations listed in Table 6.3 and to explore the feasibility of predicting the behaviour by considering the activity of the catalyst, and also to examine variation of activity profiles during dynamic changes.

TABLE 6.3

Operation conditions corresponding to Fig. 6.35 to 6.39

Conditions at the initial steady state				Conditions during the transient behaviour	
Figure	O-xylene	Salt bath	Inlet pressure	Perturbation: C_{Ao} = O-xylene feed concentration T_{SB} = salt bath temperature	Magnitude of the perturbation
6.35	168	375	1.33	Step increase in C_{Ao}	4.5%(169-176gm/hr)
6.36	168	380	1.33	" " " C_{Ao}	4.5%(168-176gm/hr)
6.37	176	376	1.33	" decrease " C_{Ao}	9.0%(176-160gm/hr)
6.38	176	380	1.33	" " " C_{Ao}	16.5%(176-205gm/hr)
6.39	176	380	1.33	" " " T_{SB}	1°C (380-381°C)

6.5.1 Step changes in o-xylene feed concentration

Dynamic experiments consisting of step changes to o-xylene feed concentration, of different magnitudes, were performed to study the parametric sensitivity of the reactor.

Figs. 6.35 to 6.38 show the dynamic temperature responses to the various magnitudes of perturbations of the o-xylene feed concentration with the air flowrate maintained at 4 Nm³/hr. It can be observed from the figures that there is no apparent change in the location of the hotspot with time irrespective of the magnitude of the perturbation, within the range considered. On the other hand, the magnitude of the hotspot is seen to change proportionally with the magnitude of the perturbation.

For example, a typical dynamic response to a 4.5% step increase for conditions at 4 Nm³/hr air, 168 gm/hr o-xylene and 380°C salt bath temperature, shown in Fig. 6.37, produced a 7°C increase in the magnitude of the hotspot, while for a step increase of 16.5% at the same salt bath temperature and air flowrate but with an initial o-xylene flowrate of 176 gm/hr, shown in Fig. 6.38, the magnitude of the hotspot was increased by 28°C.

Similar observations were made by Lopez-Isunza (1983) who concluded that at high air flowrates (4 Nm³/hr) there was no partial deactivation of the catalyst occurring during the transient state of the reactor, for small and large perturbation of the o-xylene feed concentration. For low air flowrates (2 and 3 Nm³/hr), similar perturbations particularly larger ones resulted in significant displacements of the hotspot location with time and this effect was attributed to partial deactivation of the catalyst.

From Figs. 6.35 to 6.38, one can therefore conclude that, given the initial activity profile of the catalyst, the dynamic response of the system to small and large perturbations of o-xylene feed concentration should be predicted without further re-estimation of catalyst activity profiles. However, for low air flowrates, where partial deactivation occurs during the transient state, it may be necessary to re-estimate the activity profile of the catalyst at every time interval in order to predict the reactor behaviour.

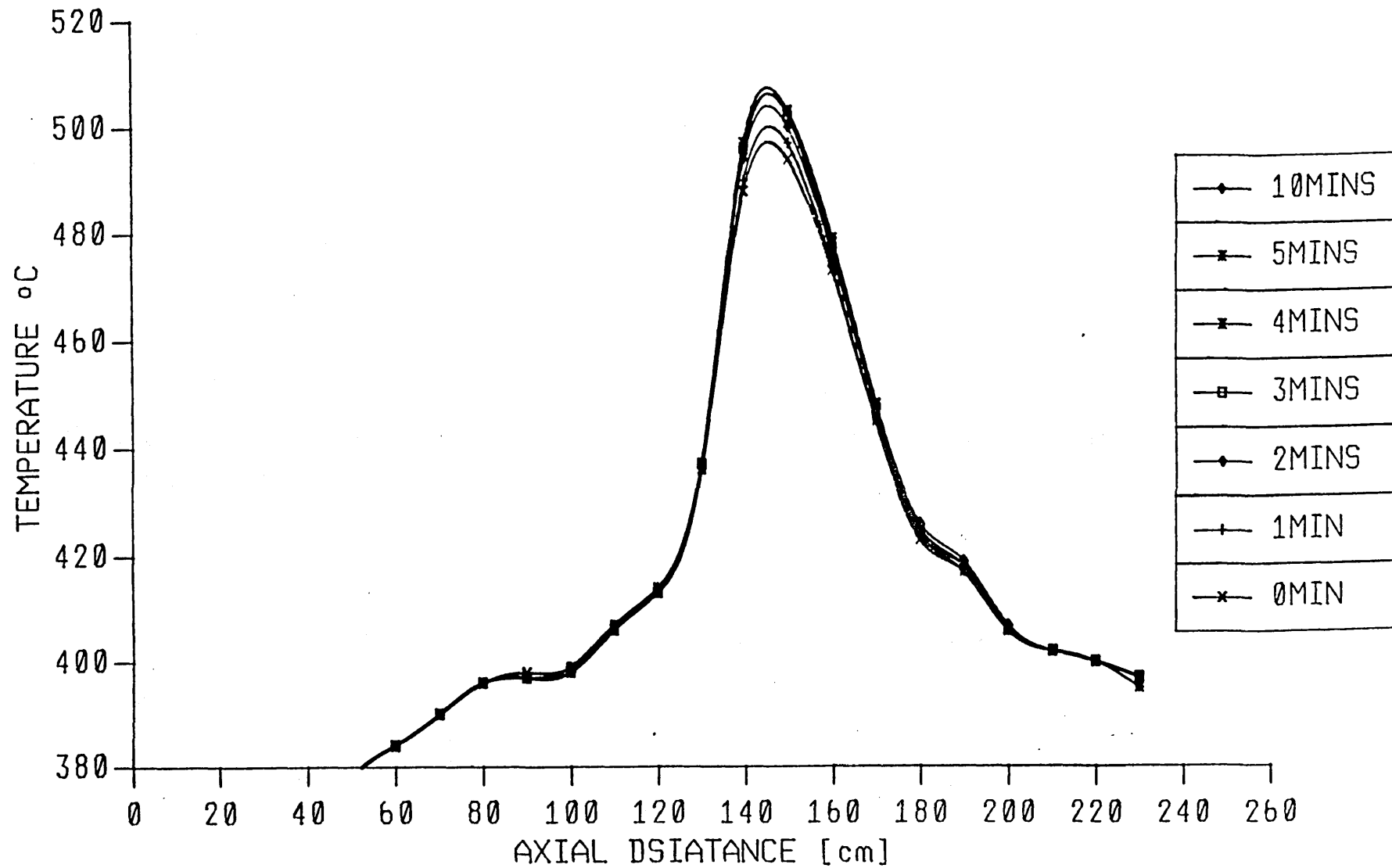


Fig. 6.35 Transient state axial temperature profiles for a step increase in o-xylene feed concentration from 168 to 176gm/hr, $T_{sb}=375^{\circ}\text{C}$ (see table 6.3).

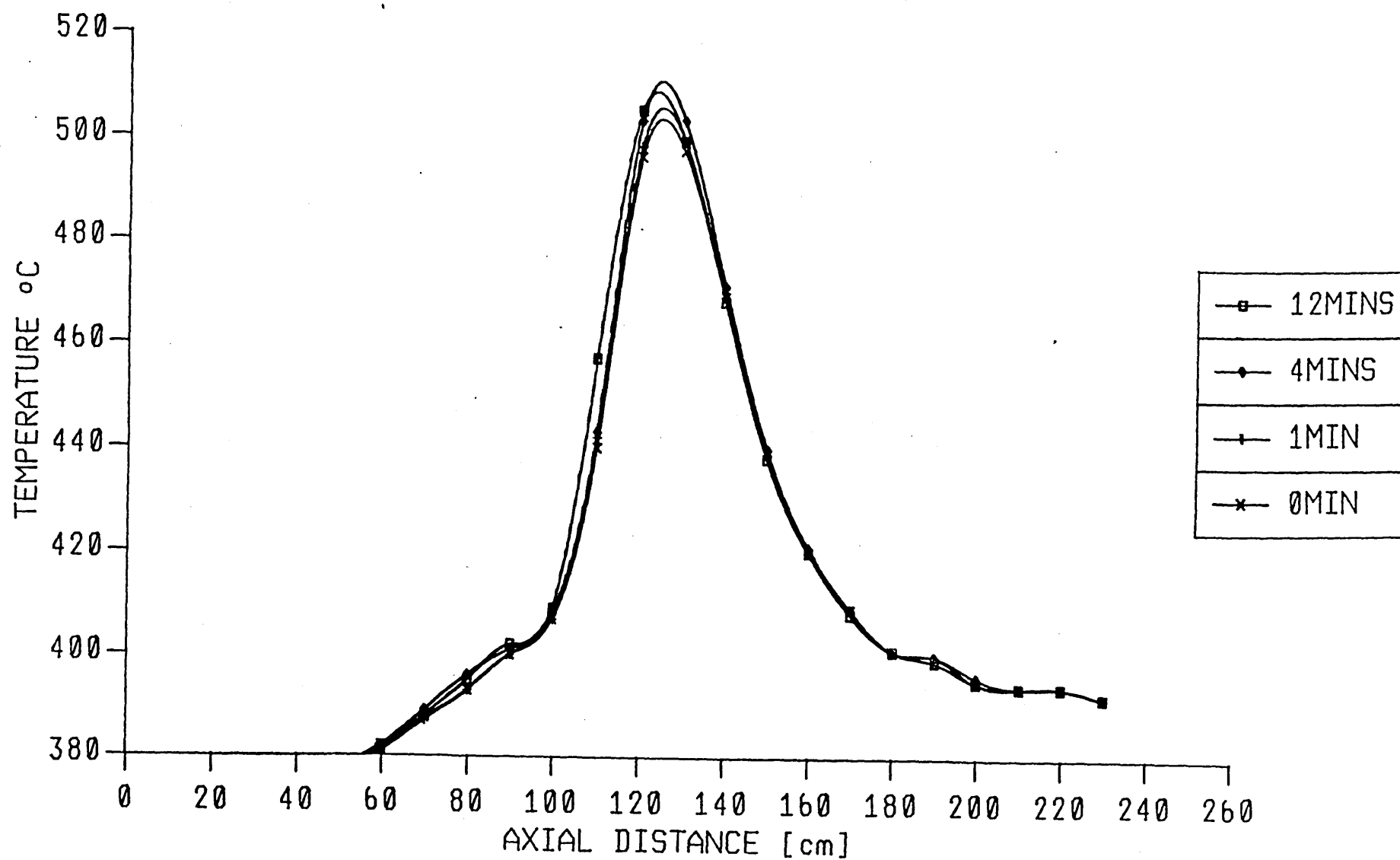


Fig. 6.36 Transient state axial temperature profiles for a step increase in o-xylene feed concentration from 168 to 176gm/hr, $T_{sb}=380^{\circ}\text{C}$ (see table 6.3)

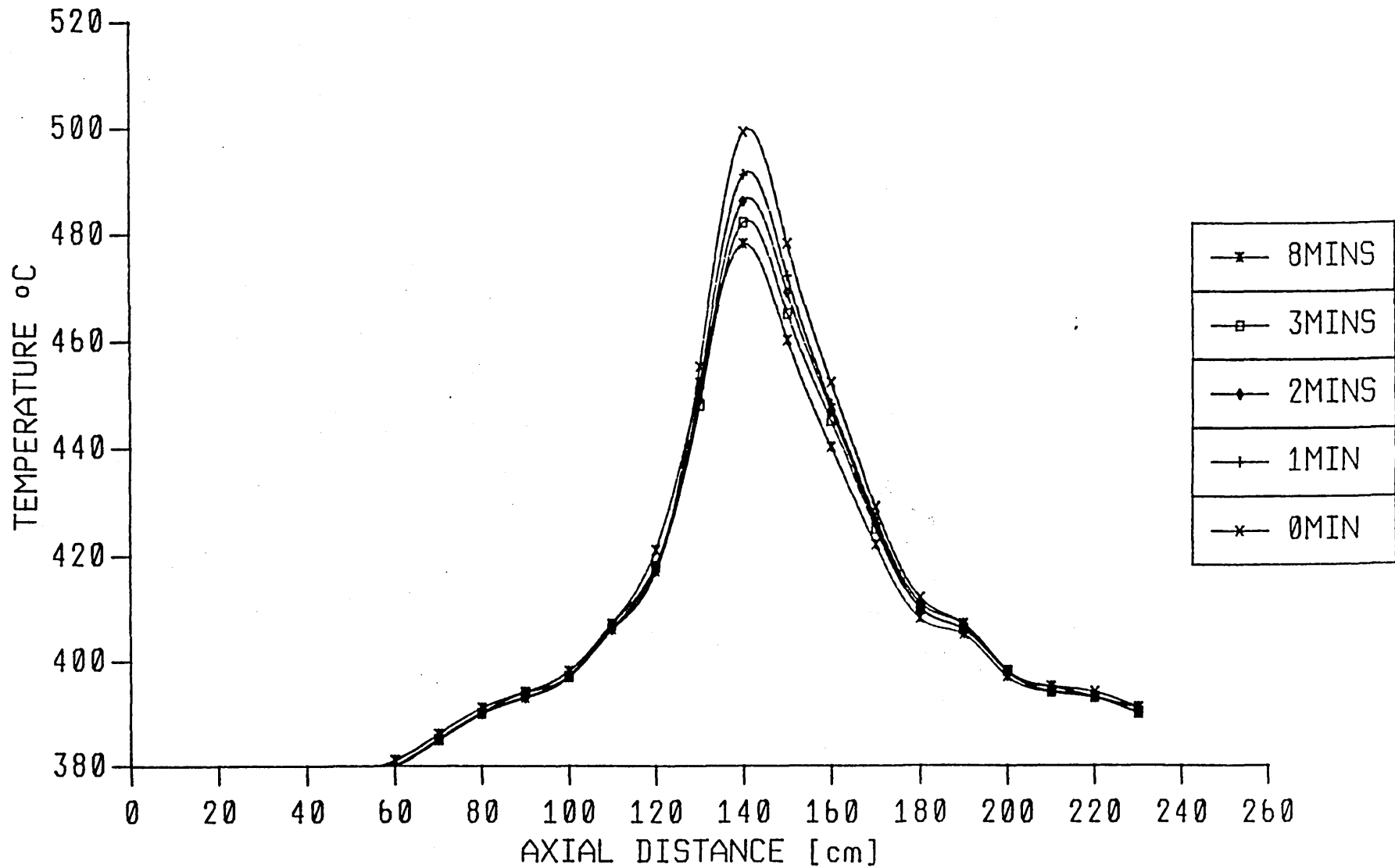


Fig. 6.37 Transient state axial temperature profiles for a step decrease in o-xylene feed concentration from 176 to 160gm/hr, $T_{sb}=376^{\circ}\text{C}$ (see table 6.3)

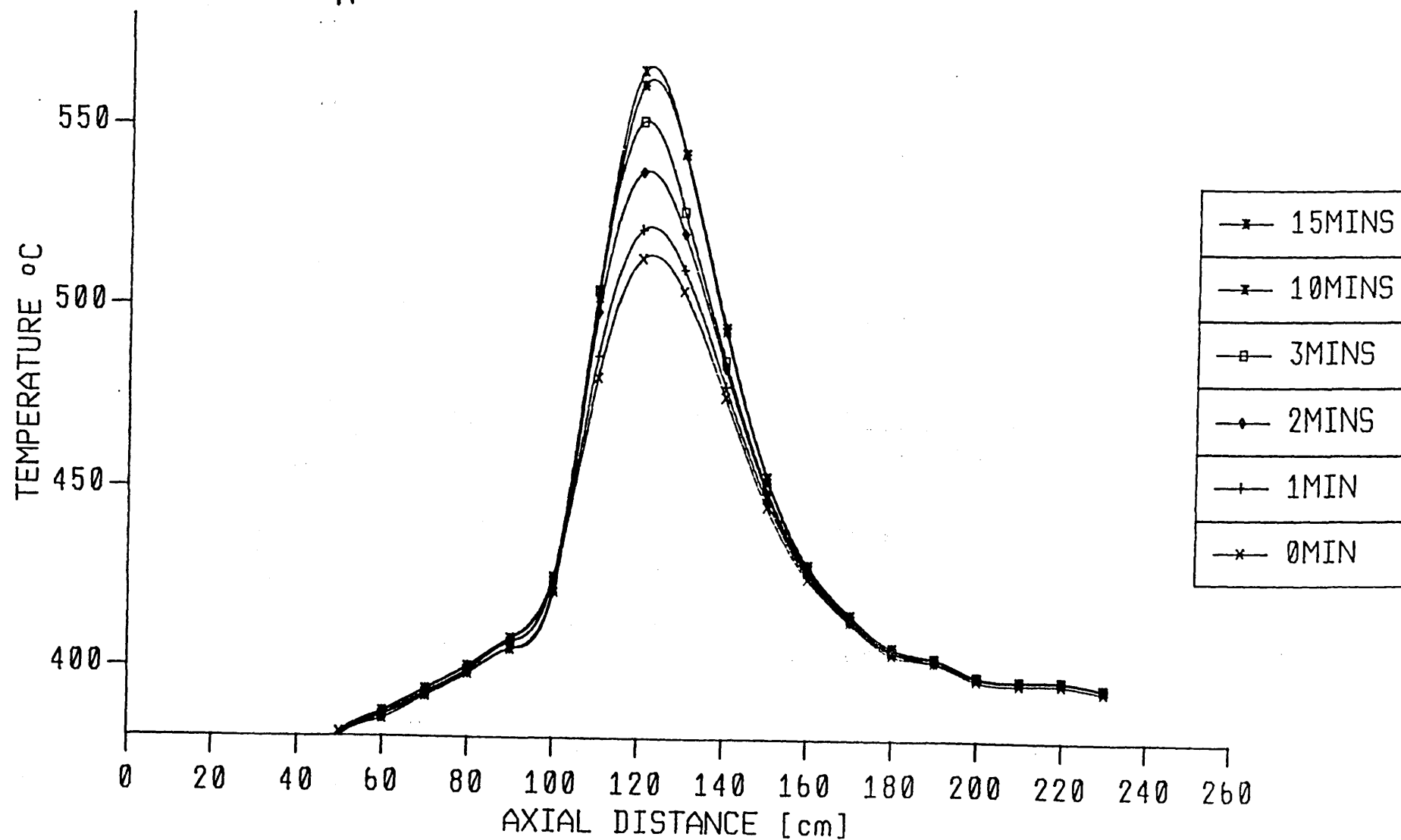


Fig. 6.38 Transient state axial temperature profiles for a step increase in o-xylene feed concentration from 176 to 205gm/hr, $T_{sb}=380^{\circ}\text{C}$ (see table 6.3).

6.5.2 Ramp increase in salt bath temperature

Dynamic experiments consisting of ramp changes in the salt bath temperature were performed by changing the set point to the salt bath temperature controller. The ramp changes were of the order of 1°C and the rate of change was $\sim 0.2^{\circ}\text{C}/\text{min}$.

The experiments demonstrated the existence of a strong parametric sensitivity of the reactor with respect to changes in the salt bath temperature.

Fig. 6.39 shows the dynamic response of the system when a 1°C ramp increase in the salt bath temperature, for conditions of $4 \text{ Nm}^3/\text{hr}$ air, 176 gm/hr o-xylene and 380°C initial salt bath temperature, was made.

Fig. 6.39a shows that, at first the magnitude of the hotspot decreases by about 13°C , 10 mins after the perturbation, then moves upstream, passes through a minimum, and begins to increase until it reaches a peak $\sim 20 \text{ cm}$ upstream of the initial steady state where a new steady state is attained after about 120 mins; the new steady state hotspot temperature located around axial position 12 being 17°C higher than the previous one found around axial position 14.

This behaviour is due to the effect of more reactant being consumed in the region before the hotspot, in which the perturbation propagates upstream fast enough to cause a dramatic drop in the o-xylene concentration and therefore in the magnitude of the hotspot. In this region, which is between axial locations 10 to 12, the catalyst becomes more active because of an increase in the rate of re-oxidation which causes an increase in the rate of reaction.

Fig. 6.39c shows the concentration-time plots of o-xylene, o-tolualdehyde and phthalic anhydride for measurements taken at axial position 12 at 5 mins intervals during the transient state. It can be

seen that the rate of disappearance of o-xylene is approximately equal to the rate of production of phthalic anhydride. On the other hand, there is little or no change in the concentration of the intermediate product o-tolualdehyde.

Fig. 6.39d shows sketches of the axial concentration profiles of o-xylene and phthalic anhydride at 0 mins, 40 mins, 60 mins and 120 mins. These sketches were made under the following assumptions.

- (a) At any given time, the concentration profiles of o-xylene and phthalic anhydride intersect each other at the hotspot position.
- (b) At the point of intersection almost 70% of the o-xylene has disappeared and about 30 mole% of phthalic anhydride produced.
- (c) The rest of the phthalic anhydride after the hotspot is produced within an axial distance of 40 cm after the hotspot.
- (d) The concentrations at axial position 12 are well-known (obtained from interpolation of measurements taken during the transient period, Fig. 3.9c).
- (e) The total selectivity of phthalic anhydride is constant at about 74 mole%

It is clear from the above observations (Figs. 6.39a to d) that the activity of the catalyst changes very significantly during the transient state caused by a perturbation to the salt bath temperature. This implies the need to incorporate a catalyst deactivation-regeneration model into the reactor model in order to be able to predict the dynamic behaviour of this reactor-reaction system.

Alternatively, this calls for the re-estimation of the activity profile of the catalyst at every time step in order to predict the dynamic behaviour.

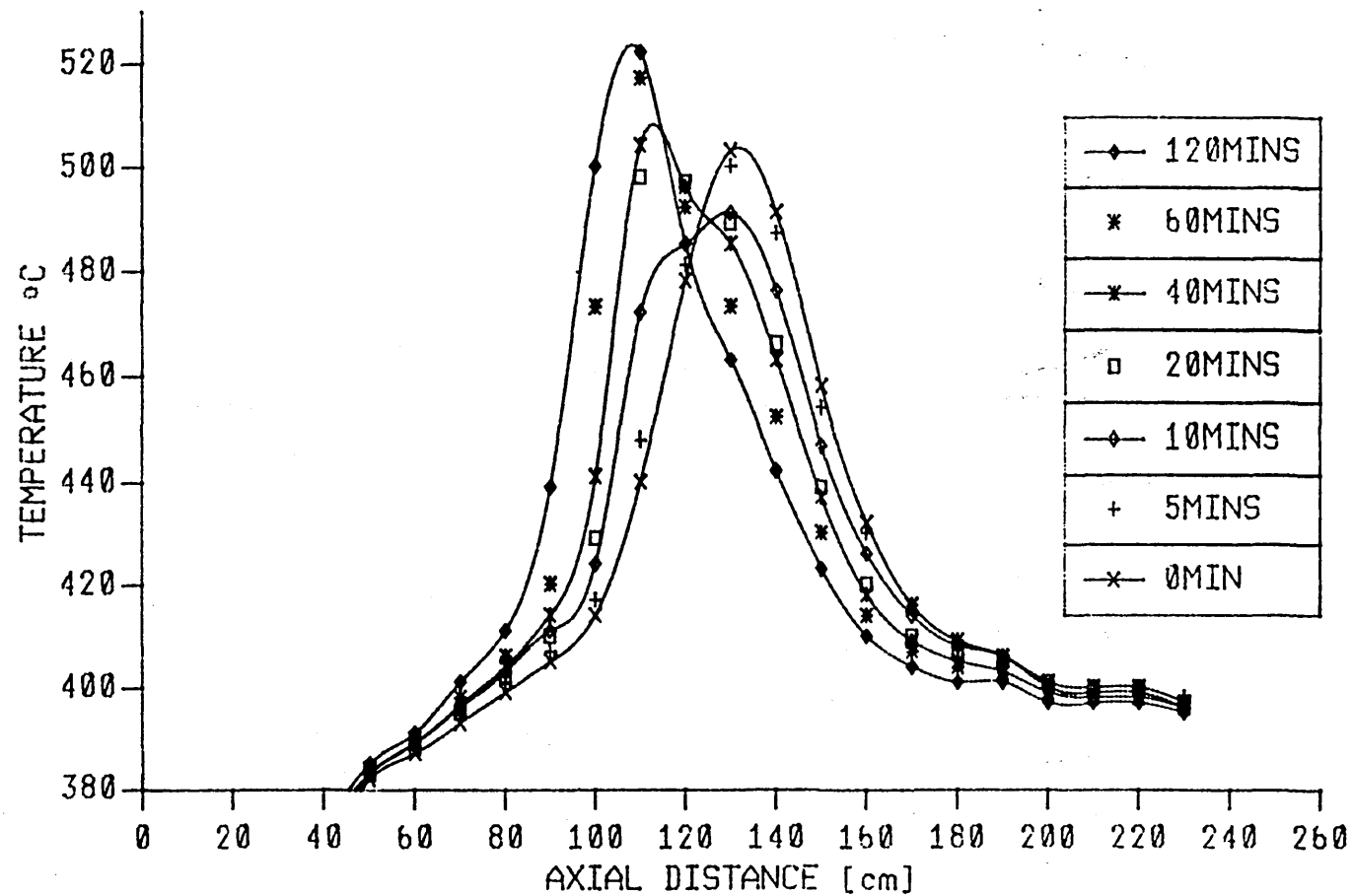


Fig. 6.39a Transient state axial temperature profiles for a ramp increase in the salt bath temperature from 380 to 381°C; o-xylene flowrate 176gm/hr (see table 6.3)

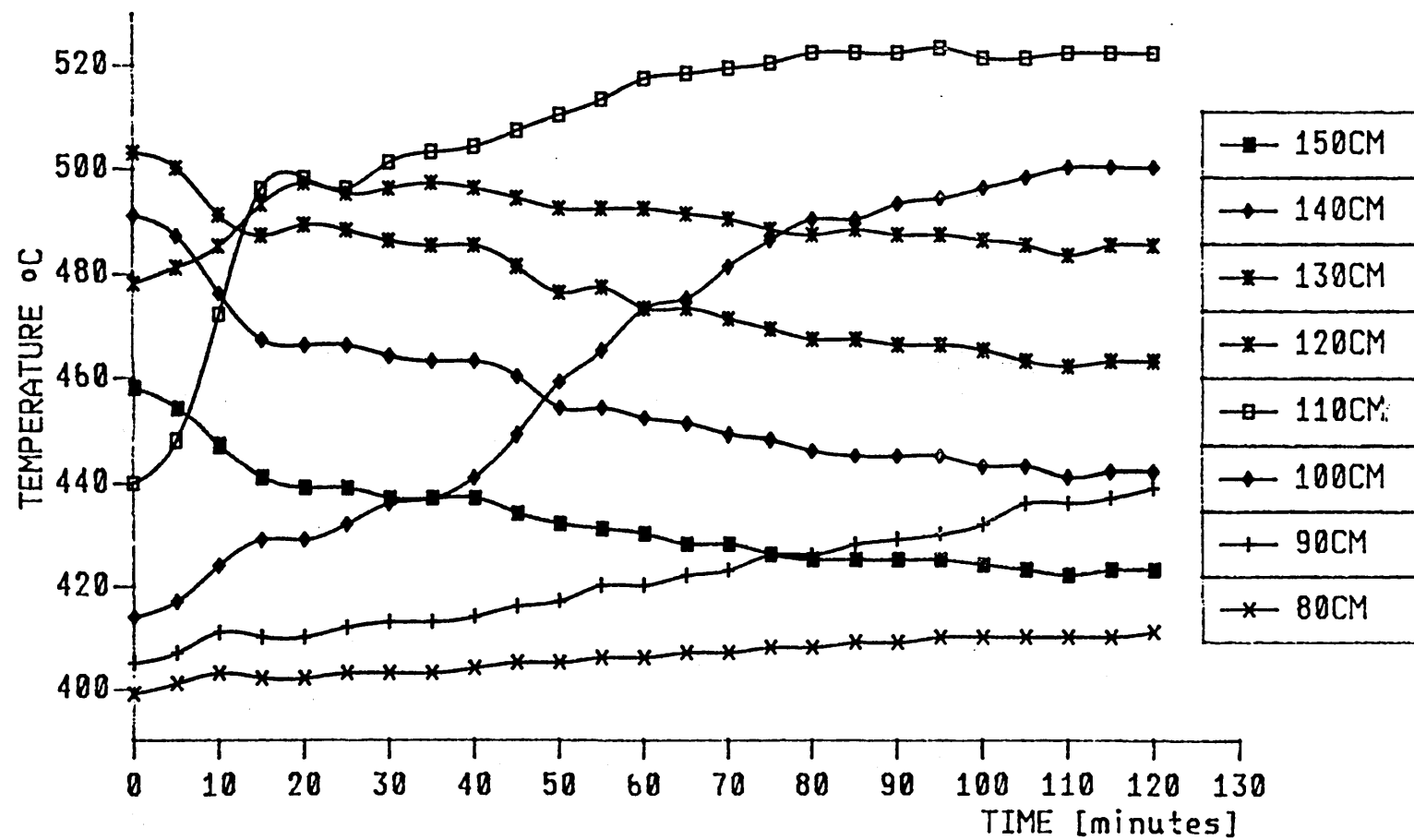


Fig. 6.39b Transient state temperature-time profiles at the various axial positions for a ramp increase in the salt bath temperature from 380 to 381°C;o-xylene flowrate 176gm/hr(see table 6.3).

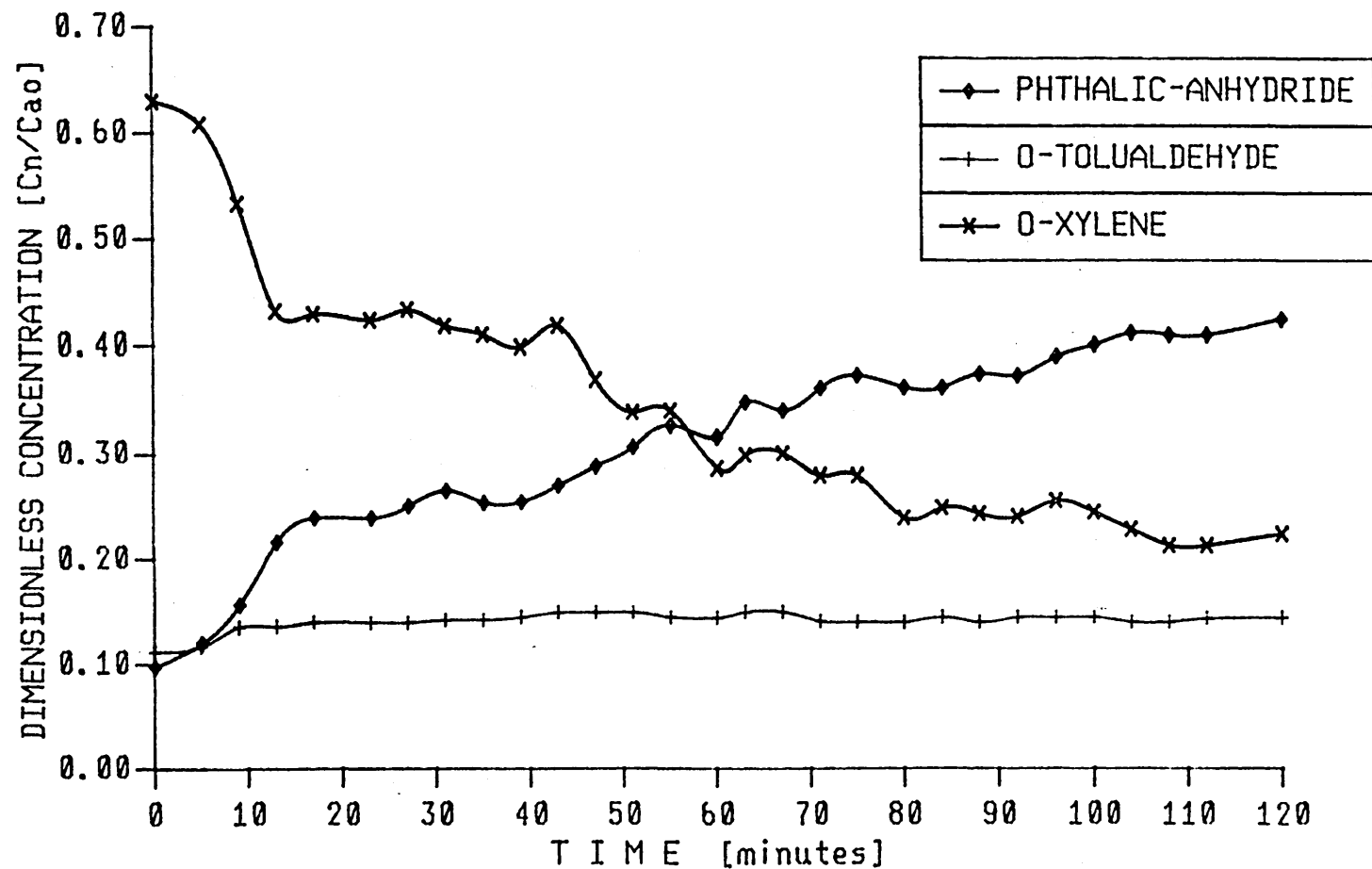


Fig. 6.39c Transient state concentration -time profiles at axial position 12. (110cm) for a ramp increase in the salt bath temperature from 380 to 381°C; o-xylene flowrate 170gm/hr (see table 6.3).

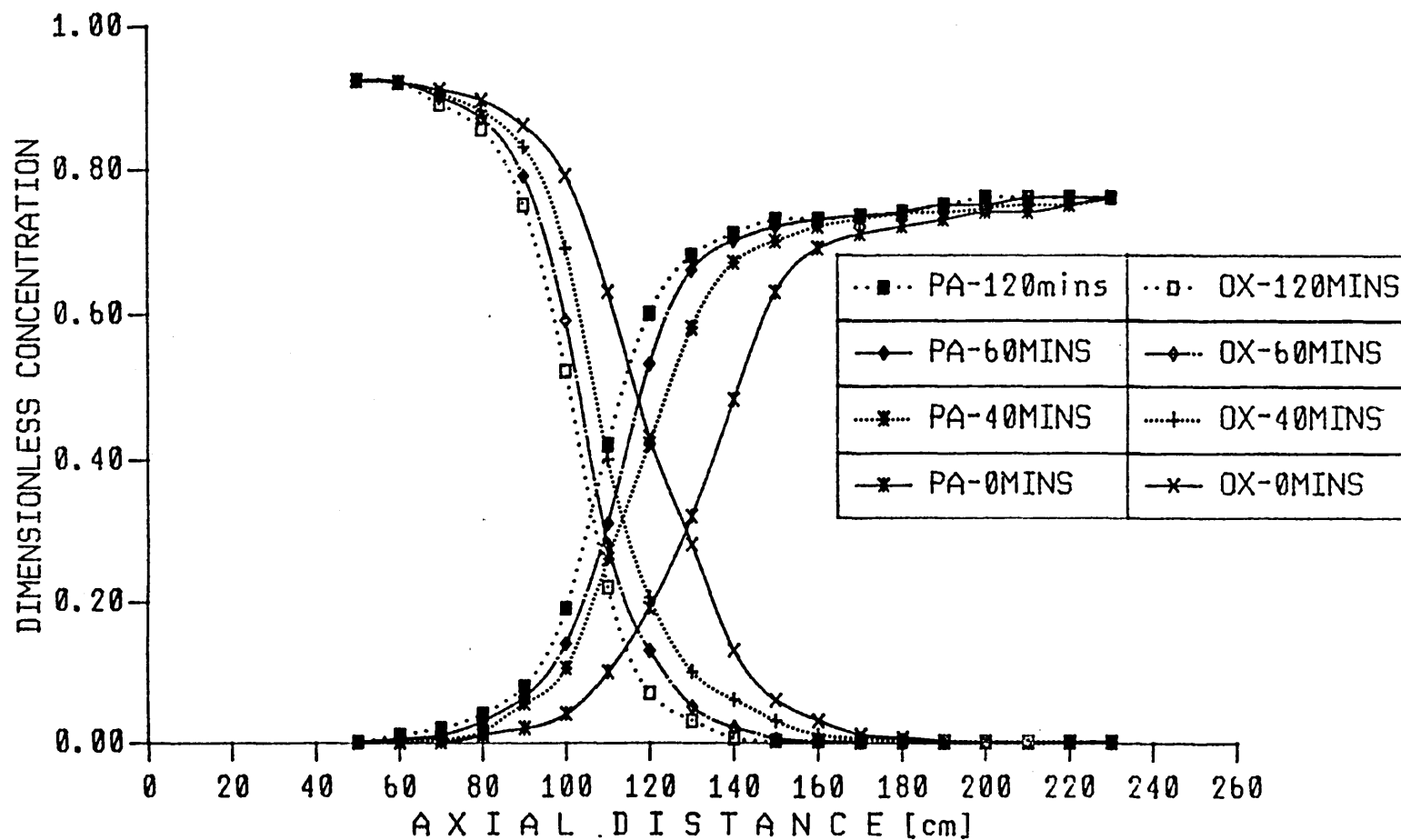


Fig. 6.39d Sketched axial concentration profiles of o-xylene and phthalic anhydride during the transient state for a ramp increase in the salt bath temperature from 380 to 381°C (see fig. 6.39a for corresponding axial temperature profiles).

6.5.3 Prediction of the dynamic behaviour of the reactor from catalyst activity profile estimation

In this section, the experimental data obtained during the transient state engendered by a 1°C ramp increase in the salt bath temperature was used to estimate catalyst activity profiles in order to predict the dynamic behaviour of the reactor.

Fig. 6.40b shows the predicted and experimental temperature profiles compared at the initial steady state, at 40 mins and at 60 mins after the perturbation. Only temperature measurements from the reactor inlet to exit were used to estimate catalyst activity profiles. From the figure, it can be seen that the predictions are in qualitative agreement with the experimental data although the magnitude of the hotspot temperature is, in general, underestimated. At the initial steady state the predicted hotspot temperature is about 3°C lower than the experimental value while at 40 and 60 mins the difference is about 5°C . No significant improvement on the predictions was obtained when the one concentration measurement at axial position 12 was used together with the temperature measurements to estimate catalyst activity profiles.

Fig. 6.40a shows that, in general, the estimated activity in the finite elements within the inlet region of the reactor increases with time. This is expected since it has already been suggested that the observed transient behaviour of the reactor for a ramp increase in salt bath temperature was due to catalyst re-oxidation (reactivation).

Since axial dispersion of heat contributes to increasing the rate of catalyst re-oxidation [Lopez-Isunza (1983)], one may suggest that improved predictions could be obtained if this phenomenon is accounted for in the model.

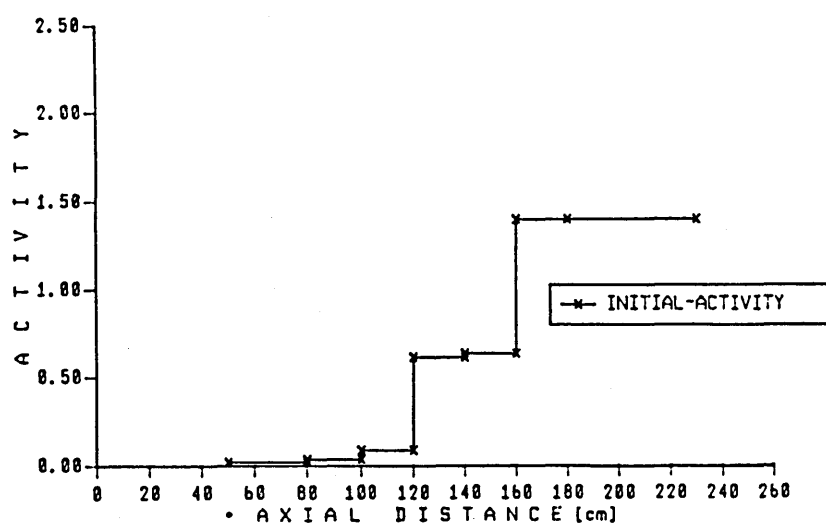
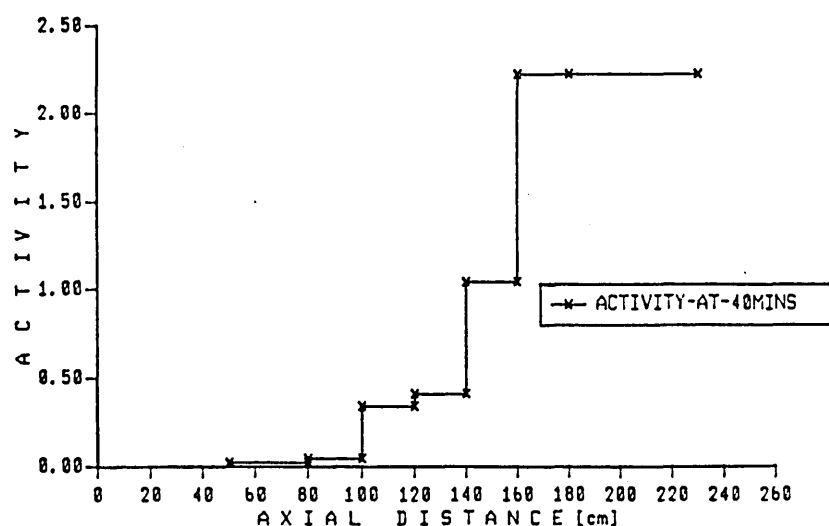
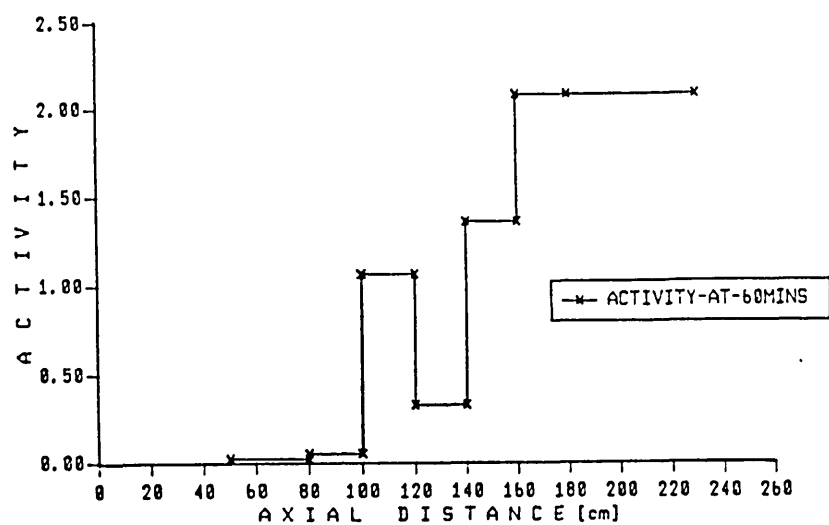


Fig. 6.40a Catalyst activity profile at a given time step estimated using only current temperature measurements (from the reactor's inlet to the exit); measurements taken during transient state for a ramp increase in the salt bath temperature from 380 to 381°C (see fig. 6.39a).

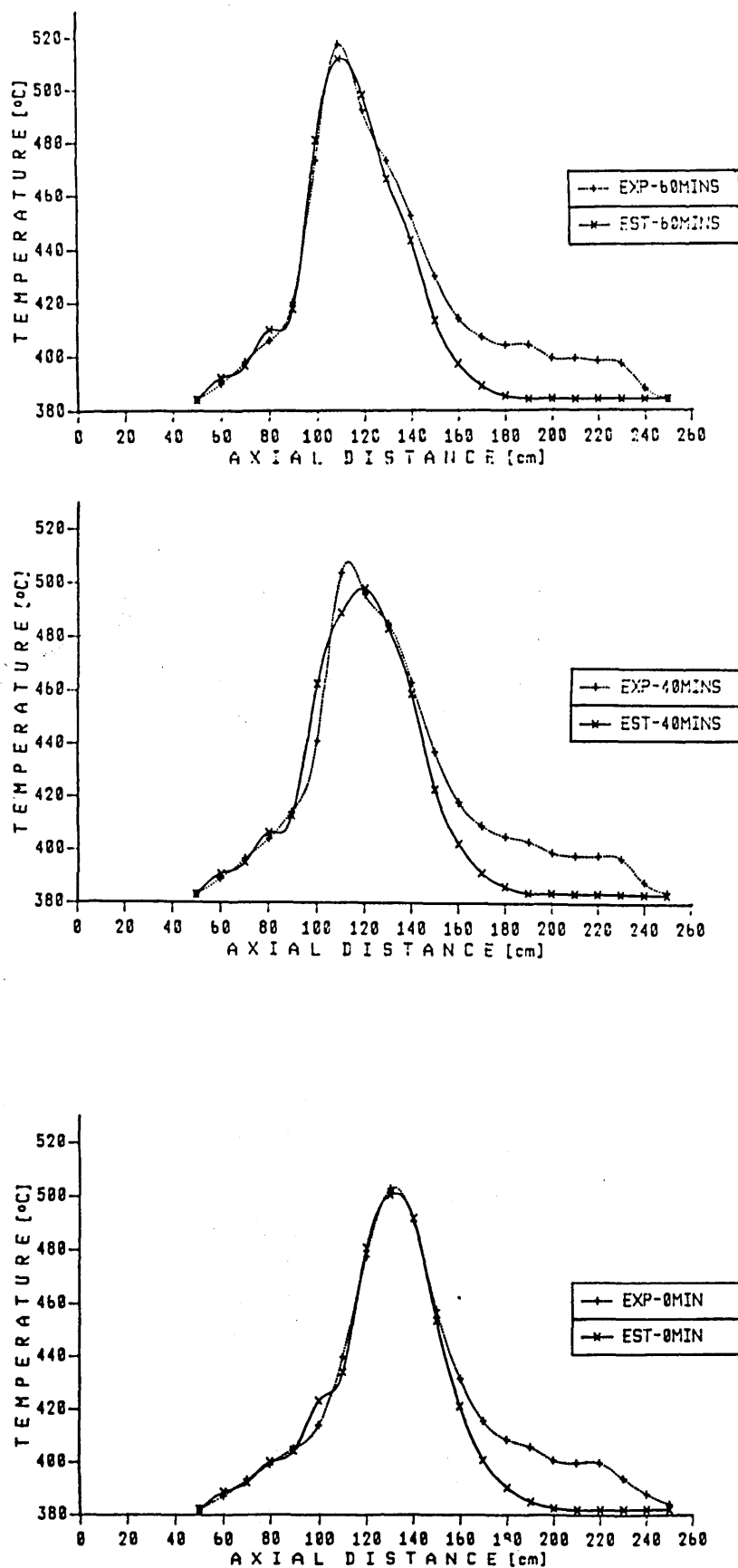


Fig. 6.40b Experimental temperature profiles compared with predicted or estimated profiles corresponding to the activity profiles shown in fig. 6.40a

CHAPTER SEVEN

CONCLUSIONS

In this study, an attempt has been made to simulate both the steady state and dynamic behaviour of a reactor hosting a series of highly exothermic reactions. The main reaction is the partial oxidation of o-xylene to phthalic anhydride on a V_2O_5/TiO_2 catalyst.

Since the main objective of this work was to develop a dynamic model suitable for on-line estimation and control, a relatively simple model was selected for the exercise. The model chosen was a pseudo-homogeneous two dimensional model without axial dispersion.

Due to the presence of steep axial temperature and concentration gradients, the method of orthogonal collocation on finite elements, hitherto used for solving boundary value problems with steep solution profiles [Carey & Finlayson (1975)], Pedersen & Tanoff (1982)] was modified and extended to tackle the initial-value problem. The main features of the new algorithm are:

- a. Automatic selection of the sizes and number of finite elements.
- b. Automatic selection of the number of interior collocation points in each finite element.

Since the smaller the size of the finite element the lower the order of the polynomial required to approximate the solution in that particular finite element, the total computation time was found to reduce, passing through a minimum, with increase in the number of finite elements specified.

By allowing for sequential and automatic increase in the order of the approximating polynomial in each finite element, the same finite

elements could be used to simulate both the steady state and dynamic behaviour of the reactor when the perturbations are small and the profiles do not experience any large displacements with time.

However, for large perturbations or large displacements of the solution profiles it may be necessary to re-partition the whole axial domain in order to keep low both the order of the approximating polynomial and the total computation time.

Steady state and dynamic experiments have shown that the catalyst undergoes both reversible and irreversible deactivation; the former caused mainly by a combination of low temperatures and high o-xylene concentrations [Calderbank et al. (1977), Lopez-Isunza (1983) and this work (Chapter 6)]. The consequence of partial catalyst deactivation being the presence of spatially varying catalyst activity profiles.

Due to time limitations, it was not possible to develop a deactivation model for this type of complex deactivation system. Instead two methods of approximation of an activity profile were developed and used to estimate catalyst activity profiles directly and exclusively from current reactor data at any given time. The first method approximated the activity profile in each finite element by a straight line whose slope and intercept were estimated by least squares estimation techniques. In the second method, the activity profile was approximated by a piece-wise constant function so that the activity in each finite element was uniform.

The second method was found to be superior to the first, if the reactor was properly subdivided into suitable finite elements, in that it gave better overall predictions of the temperature and concentration profiles although ripples on the profiles, caused by discontinuities in

the rate of reaction as a result of the activity profile being discontinuous from one finite element to the next, were observed at the upstream end of the reactor. This method was then used extensively to simulate the reactor behaviour.

The important aspects that emerged from an analysis of the experimental data of this study are summarized as follows:

I STEADY STATE EXPERIMENTS

1. Axial temperature profiles have shown the existence of severe temperature gradients. Typical temperature differences - around the hotspot - were in the order of 80° to 120°C in about 20 cm axial distance.
2. Continuous shutdowns of the plant for long periods of time can deactivate the catalyst irreversibly reducing the selectivity to phthalic anhydride.
3. For a freshly regenerated (re-oxidized) catalyst at normal activity the following findings were observed.
 - a) Partial (reversible) deactivation of the catalyst took place at the reactor inlet region where temperatures are low and o-xylene concentrations high.
 - b) Little or no reaction occurred at temperatures lower than 415°C.
 - c) At low salt bath temperatures the hotspot was located at the downstream end of the reactor. For a salt bath temperature of 375°C it was located between axial positions 14 and 16. At high salt bath temperatures (380 to 384°C) it was located upstream between axial positions 11 and 14.

- d) The dependence of the final yield of phthalic anhydride on the salt bath temperature within the range 375 to 384°C was not very significant.
4. For a reversibly deactivated catalyst which has not yet undergone irreversible catalyst deactivation due to prolonged shutdown, a phthalic anhydride selectivity of above 80% was obtained, for a salt bath temperature of 384°C, o-xylene flowrate of 176 gm/hr and air flowrate 4 Nm³/hr. Under these conditions, about 80% of the o-xylene reacted and about 20 mole% of phthalic anhydride was produced before the hotspot.
 5. For a catalyst whose activity has previously undergone irreversible catalyst deactivation following a continuous shutdown period of about 3 months a constant phthalic anhydride selectivity of about 65 to 74 mole% was obtained. Experiments conducted at this activity showed that about 70% of the o-xylene reacted and about 30 mole% of phthalic anhydride was produced before the hotspot.
 6. Catalyst re-activation using air at 2 Nm³/hr and salt bath temperature maintained at 400 to 410°C for a period of 30 to 40 hrs was successful, allowing reproducibility of experiments.

These experiments highlight the importance of locating as many measurements as possible between the reactor inlet and the hotspot if it is intended to obtain good estimates of the catalyst activity profiles, a consequence of reversible catalyst deactivation.

II LONG-RUN STEADY STATE EXPERIMENTS

1. Prolonged steady state experiments carried out with the reactor run continuously at 380°C salt bath temperature, 176 gm/hr o-

xylene flowrate and 4 Nm³/hr air flowrate, for a period of 13 days have shown that catalyst reduction and re-oxidation are dynamic processes occurring throughout the period of operation of the catalyst, with axial heat dispersion helping the latter towards an equilibrium state.

2. Equilibrium between the two processes was attained after about 9 days of continuous operation although a very gradual shift of the profiles towards the reactor exit was observed. The equilibration of these two processes is the key behind the catalyst having a very long operating life.
3. The yield of phthalic anhydride gradually improved with time throughout the period of continuous operation.

The relevance of these results can be fully appreciated if it is considered that in the industry the reactors are operated continuously, without any shutdowns for catalyst regeneration, throughout the year. Shutdowns are brief and are only for maintenance.

III DYNAMIC EXPERIMENTS

1. Experiments consisting of step changes in the o-xylene feed concentration at 4 Nm³/hr air have shown that for perturbations up to 16.5%, no apparent catalyst deactivation seems to take place. There was no apparent change in the position of the hotspot although a proportional change in its magnitude with respect to the magnitude of the perturbation was observed. However, for low air flowrates (2 to 3 Nm³/hr), Lopez-Isunza (1983) observed a very strong parametric sensitivity to o-xylene feed concentrations particularly for large perturbations (>10%).

2. Experiments consisting of ramp changes in salt bath temperature at $4 \text{ Nm}^3/\text{hr}$ of air have shown that the system's dynamic response is affected by the relative contributions of the rate of catalyst re-oxidation and axial dispersion of heat. There is a strong correlation between partial deactivation of the catalyst (changes in the activity profile) and parametric sensitivity during the dynamic behaviour of the system.

The experiments highlighted the need to incorporate a catalyst deactivation-reativation model into the kinetic model if it is intended to predict the dynamic behaviour of the reactor caused by perturbations to salt bath temperature.

IV MODEL PREDICTIONS

The following conclusions were reached when experimental data was used to estimate catalyst activity profiles in order to predict the reactor behaviour.

A. Steady State Predictions

1. When both temperature and concentration measurements were used to estimate catalyst activity profiles, the predicted temperature and concentration profiles of o-xylene and phthalic anhydride were found to be in reasonable agreement with the experimental data.
2. The hotspot temperature and final yield of phthalic anhydride were still well predicted when only temperature and concentration measurements located upstream of the reactor, from the reactor inlet to the hotspot or a few centimeters after the hotspot, were used to estimate catalyst activity profiles. This is expected since the partial (reversible) deactivation of the catalyst occurred at

the reactor inlet region where temperatures are low and o-xylene concentrations high. Hence the influence of the catalyst activity in determining the reactor behaviour should be greatly reduced after the hotspot as little or no reactant was left.

3. When the catalyst activity was assumed to be uniform over a large region starting from about 20 cm before the hotspot to the reactor exit, and both temperature and concentration measurements used to estimate the resulting monotonic activity profile, the predicted temperature profile was generally very poor. However, the predicted concentration profiles of o-xylene and phthalic anhydride were still in very good agreement with the experimental data.

The prediction of both the temperature and concentration profiles was very poor if only temperature measurements were used to estimate the activity profile in this case.

4. When only temperature measurements (from the reaction inlet to the exit) were used to estimate catalyst activity profiles the predictions were reasonable but not too reliable. The predicted concentration profiles were far from approaching those obtained from the experimental data especially around the hotspot.
5. The concentration profiles of o-xylene and phthalic anhydride as well as the temperature profile were poorly predicted but the final yield of phthalic anhydride was closely predicted when only temperature measurements located at the upstream end of the reactor, from the reactor's inlet to the hotspot or a few centimeters after the hotspot, were used to estimate catalyst activity profiles.
6. The predicted temperature values at the downstream end of the reactor particularly towards the exit were generally very low

compared to the experimental data. This was attributed partly to neglecting of axial dispersion but mostly to the fact that the measured salt bath temperature towards the exit end of the reactor was always about 5 to 10°C higher than in the rest of the reactor upstream where the temperature was almost uniform.

7. The one or two temperature measurements plus exit composition measurements normally available in industrial reactors are not sufficient for the estimation of catalyst activity profiles.

However, since they are normally operated at salt bath temperatures close to 390°C, the hotspot would normally be located between axial positions 6 and 12 for a freshly re-oxidized (regenerated) catalyst and, therefore, three or four thermocouples located in this region for temperature measurements may be adequate to estimate an approximate activity profile in order to predict the total yield of phthalic anhydride. It is therefore suggested that periodic regeneration of the catalyst should be carried out in order to make sure that the hotspot is always within the region where a few temperature measurements can be used to predict the final yield of phthalic anhydride by estimating catalyst activity profiles.

B. Transient State Predictions

1. When only temperature measurements were used to estimate catalyst activity profiles in order to predict the dynamic behaviour of the reactor during the transient period caused by a 1°C ramp increase in the salt bath temperature it was found that the predicted hotspot temperature was generally lower by about 3 to 5°C.

2. The estimated activity in the finite elements located at the upstream end of the reactor increased with time. This is expected since it has already been established that the observed transient behaviour of the reactor for a ramp increase in the salt bath temperature is due to catalyst re-oxidation (reactivation).

RECOMMENDATIONS

From the above conclusions, the following recommendations can be made for future investigations.

Since the time scale associated with changes in the catalyst activity profile during steady state operation is in the order of several hours (>12 hours), the algorithm can be implemented to perform on-line estimation of catalyst activity profiles using both temperature and concentration measurements. For this purpose it is recommended that a simpler optimization routine capable of handling just a single parameter at a time may be written to replace the more robust quasi-Newton algorithm developed for several parameters which is used in this work.

Since the predictions obtained by estimating catalyst activity profiles from temperature measurements are not very reliable, an alternative approach of simulating the dynamic behaviour of the reactor may be sought.

Perhaps the best alternative to estimating catalyst activity profiles directly from experimental data may be to develop a catalyst deactivation-reactivation model in order to incorporate it into the kinetic model. This requires extensive temperature and concentration measurements during steady state and dynamic experiments in order to evaluate (possibly by off-line estimation) the parameters of the model.

APPENDIX A

A.1 THE HEATS OF REACTION AND CO/CO₂ EXPERIMENTAL RESULTS

For the Kinetic scheme considered in this study, the heats of reaction for each reaction step, are given in Table A.1:

TABLE A.1

Heats of reaction

Step _j	M _j	(-ΔH _j (KJ/mole))
1	1	456.361
2	2	414.493
3	9.5	4001.534
4	3	1239.293
5	1	368.438
6	6.5	2762.241

The heat of reaction in steps 3 and 6 depend on the molar ratio of CO₂ to CO. From experimental evidence [Von Heyden (1974), Jordan (1977), Wainwright & Hoffman (1977), Flower & Craven (1985)] the ratio was approximately 3.

The values of M₃, M₆, (-ΔH₃) and (-ΔH₆) correspond to a molar ratio of CO₂/CO = 3. Jordan (1977) measured a value of 2.75 while Flower & Craven (1985) obtained an average value of 2.84.

The measurements of CO and CO₂ concentrations at the various axial locations were carried out during the long-run steady state experiments. Gas samples were collected via the vent of the sampling valve and analysed using a T.c chromatograph.

Figs. A.1a and b show the concentration profiles of CO and CO₂ respectively, taken over the days indicated. Plots of the ratio of CO₂ to CO versus axial distance are shown in Fig. A.1c while the combined axial selectivities of o-xylene to CO and CO₂ are shown in Fig. A.1d.

Figs. A.1a and A.1b show very steep axial concentration profiles of CO and CO₂ between axial positions 8 and 14 (i.e. 70 cm and 150 cm from the reactor inlet). This region corresponds to where most of the o-xylene reacted, suggesting that most of the CO and CO₂ was produced directly from the total oxidation of o-xylene (see Chapter 6, Section 6.4 for the corresponding temperature and concentration profiles of o-xylene and the partial oxidation products).

The fact that the ratio of CO₂ to CO remained almost constant at about 2.84 after axial position 12 (110 cm) implies that little or no CO oxidation to CO₂ took place during the reaction (see Fig. A.1c).

The combined axial selectivity profiles of o-xylene to CO and CO₂ (Fig. A.1d) confirm the observation that most of the CO and CO₂ was produced directly from o-xylene, since they are very steep within the region where most of the o-xylene reacted. Fig. A.1d shows that some over-oxidation of phthalic anhydride to CO and CO₂ occurred and reduced with time of operation as manifested by the shallow gradient of the selectivity profiles after an axial distance of 140 cm. The reduction of the over-oxidation of phthalic anhydride to CO and CO₂ led to improved yields of phthalic anhydride as observed in Chapter 6, Section 6.4.

The sensitivity of the mathematical model with respect to the ratio of CO₂ to CO ($R_{\text{CO}_2/\text{CO}}$) was found to be very small within the experimental range $2.5 < R_{\text{CO}_2/\text{CO}} < 3.5$. Hence the value 3 was used throughout in this work.

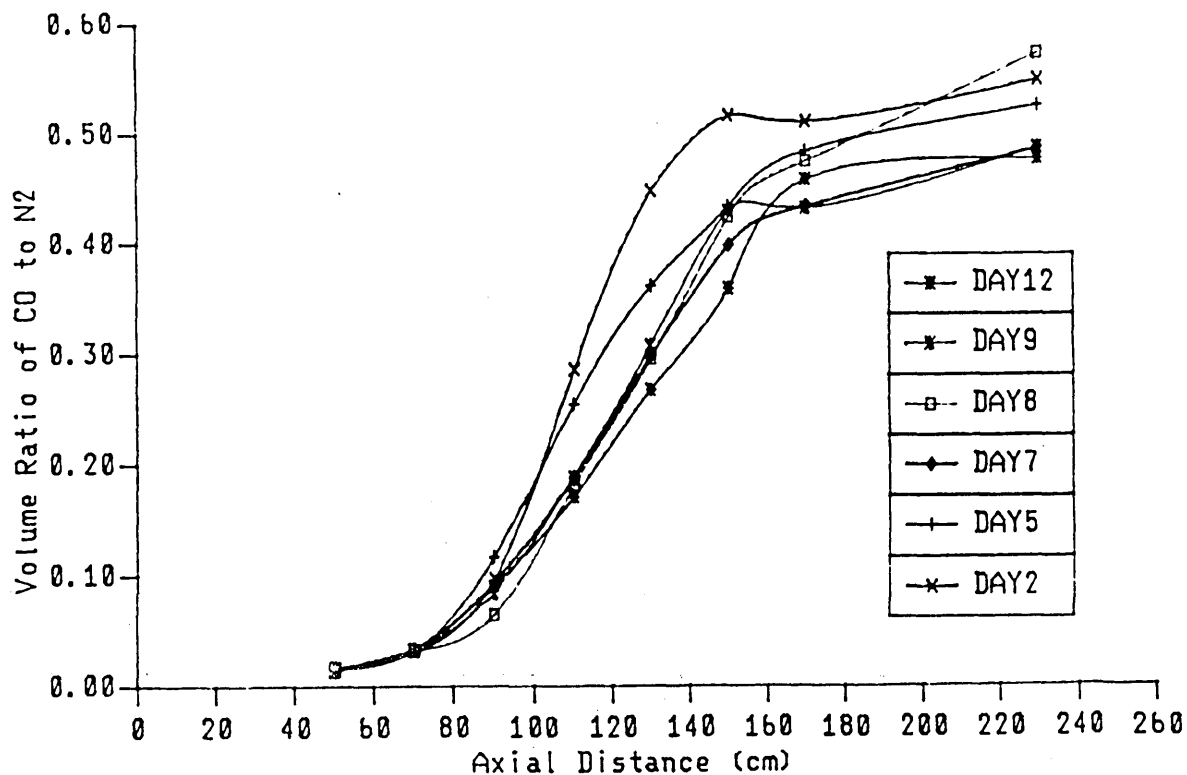


Fig. A.1a Axial concentration profiles of carbon monoxide obtained during the long-run steady state operation of the reactor.

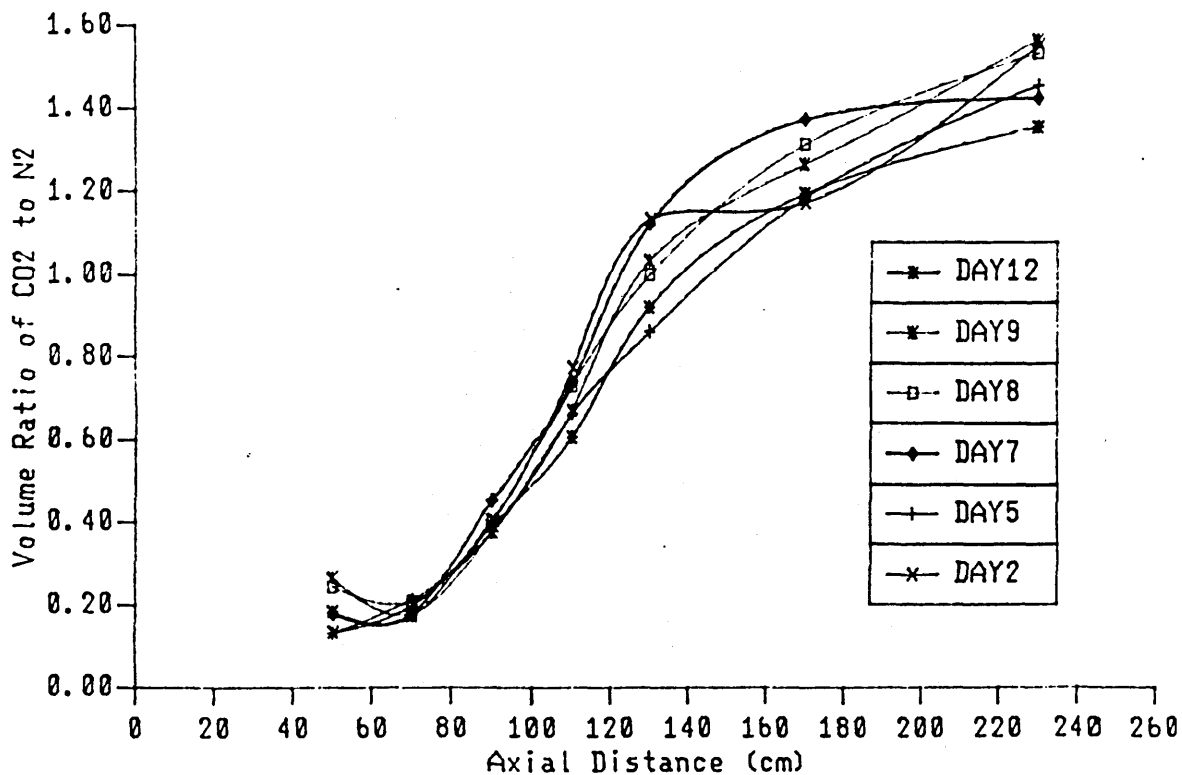


Fig. A.1b Axial concentration profiles of carbon dioxide obtained during the long-run steady state operation of the reactor.

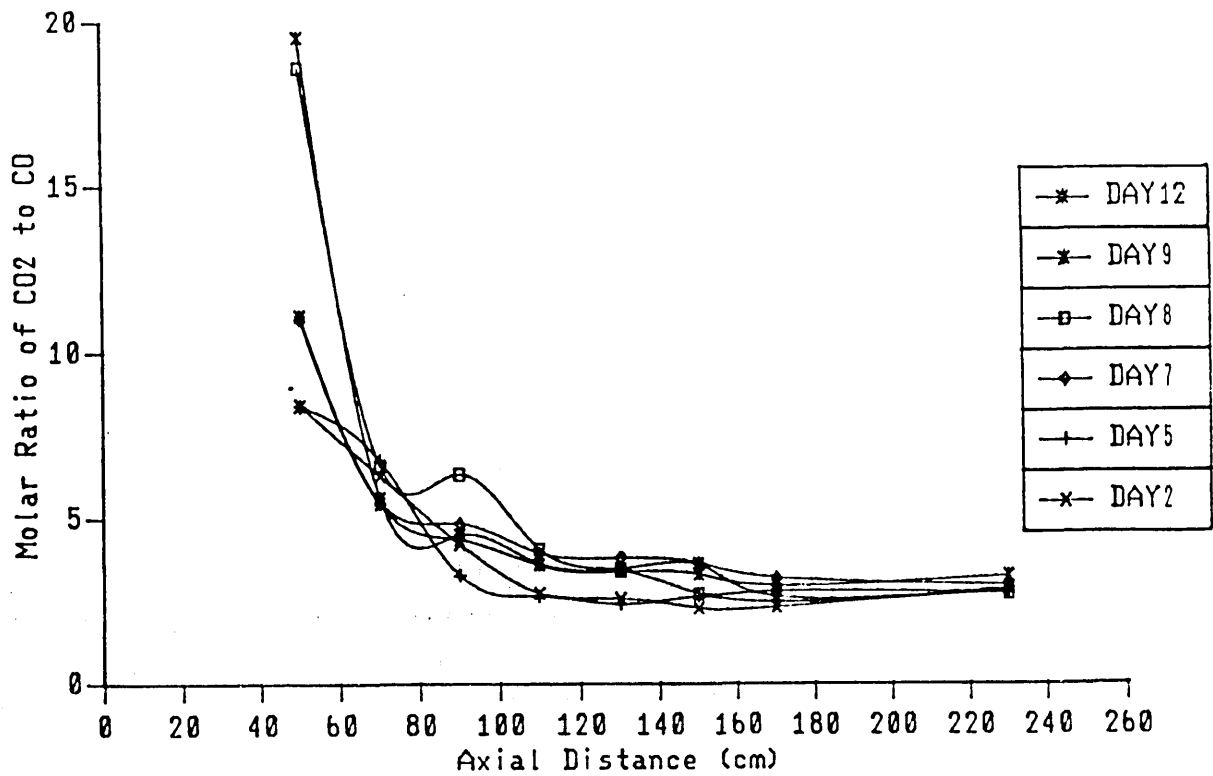


Fig. A.1c Axial molar ratios of carbon dioxide to carbon monoxide for measurements taken over the days indicated.

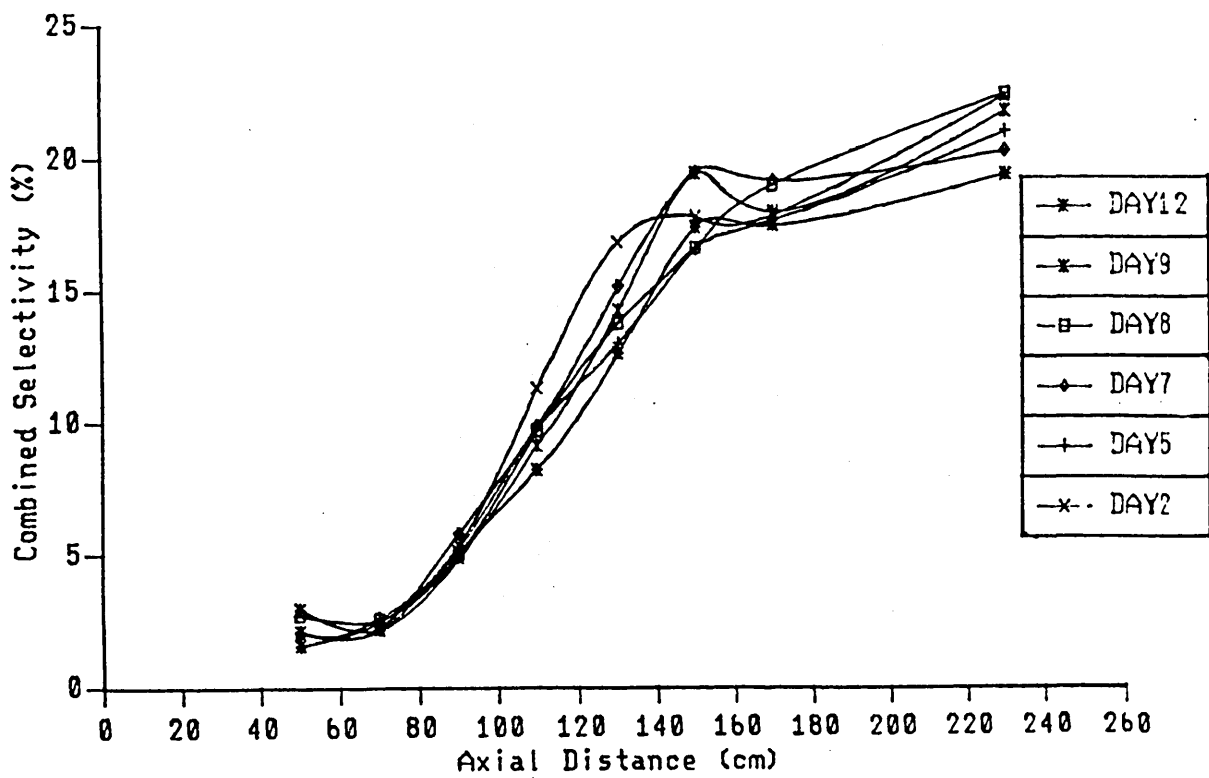


Fig. A.1d Axial 'combined selectivity' of o-xylene to carbon monoxide and carbon dioxide

A.2 HEAT AND MASS TRANSFER CORRELATIONS USED IN THIS STUDY

A.2.1 Gas/solid mass transfer coefficient

The following expressions, due to Petrovic & Thodos (1968) was used in this study:

$$\epsilon J_d = \frac{Kg\epsilon}{u} Sc^{2/3} = \frac{0.357}{Re_p^{0.359}}$$

This correlation accounts for correction to axial dispersion of mass, and is valid for $0.6 < Sc < 5.4$ and $3 < Re_p < 10^3$.

A.2.2 Gas/solid heat transfer coefficient

The following correlation, due to Aerov & Todes (1968) [Hlavacek & Votruba (1977)] was used, which is valid for $30 < Re_p < 10^5$.

$$\epsilon J_h = \frac{h\epsilon}{u\rho C_p} Pr^{2/3} = \frac{0.395}{Re_p^{0.36}}$$

A.2.3 Effective radial thermal conductivity ($K_{r,eff}$).

The correlation used was by Dixon & Cresswell (1979) and is given by:

$$K_{r,eff} = K_{r,f} + \frac{K_{r,s}(1 + 4/Bi_f)}{(1 + \frac{8}{Ns})}$$

$$Bi_f = \frac{hw_{,f}.d_t}{2K_{r,f}} ; \quad Ns = \frac{1.5 (1 - \epsilon) h d_t^2}{K_{r,s}.d_p.(V/A)}$$

A.2.4 Apparent wall heat transfer coefficient ($h_{w,eff}$)

The correlation used was by Dixon & Cresswell (1978, 1979) and is given by:

$$Bi = \frac{h_{w,eff} \cdot d_t}{2 K_{r,eff}} = 5.73 \left(\frac{d_t}{d_{p,(v)}} \right)^{\frac{1}{2}} Re_v^{-0.26}$$

Components of $K_{r,eff}$

A.2.5 Apparent fluid conductivity ($K_{r,f}$)

The following correlation due to Specchia et al. (1980) was used:

$$K_{r,f} = \frac{G C_p d_{p,(v)}}{B \left[1 + 19.4 \left(\frac{d_{p,(v)}}{d_t} \right)^2 \right]}$$

$$B = 8.6 \text{ (spheres)}$$

$$= 6.5 \text{ (other shapes)}$$

A.2.6 Apparent solid conductivity ($K_{r,s}$)

The following correlation, due to Wellauer et al. (1982) was used:

$$K_{r,s} = \hat{K}_{r,s} \left\{ 1 + 2.66 \left(\frac{d_{p,(v)}}{d_t} \right)^{\frac{1}{2}} \right\}$$

with

$$\frac{\hat{K}_{r,s}}{K_g} = \frac{(1-\epsilon)}{\left[\frac{2}{3A} + \frac{1}{\left(\frac{1}{\phi} + \frac{h_R d_{p,(v)}}{K_g} \right)} \right]}$$

$$h_R = 2.72 \times 10^{-7} \left(\frac{e}{2-e} \right) T^3 \quad \frac{W}{m \cdot K}$$

$$\epsilon < 0.26 \quad \phi = \phi_2 = \frac{0.072 (1-1/A)^2}{[\ln\{A-0.577(A-1)\}-0.423(1-1/A)]} - \frac{2}{3A}$$

$$0.26 \leq \epsilon \leq 0.476; \quad \phi = \phi_2 + \frac{(\phi_1 - \phi_2) (\epsilon - 0.26)}{0.216};$$

$$A = K_p / K_g$$

APPENDIX B

B.1 THE ORTHOGONAL COLLOCATION METHOD

The theory and techniques of the orthogonal collocation method are presented by Villadsen & Stewart (1967), Villadsen (1970), Finlayson (1972, 1974) and Villadsen & Michelsen (1978), and only a brief description of the method, and the relevant derivations to the particular problem considered in this work, are given here.

Orthogonal Collocation, promoted by Villadsen & Stewart (1967) is a special case of the collocation method, itself a class of the methods of weighted residuals. In these methods (which includes Galerkin) the unknown solution is expanded in terms of known trial functions of the form:

$$y(u) \sim y_N(u) = y_0(u) + \sum_{i=1}^N a_i y_i(u) \quad (B.1.1)$$

where $y_i(u)$ are known functions of position, often chosen to satisfy the boundary conditions, and the unknown coefficients $\{a_i\}$ are to be determined in a way that the differential equation is satisfied.

In the collocation method the differential equation is required to be zero at a set of grid points, called collocation points. The trial function is substituted into the differential equation, and the result is called the residual. The residual will be zero in all $0 \leq u \leq 1$ for the exact solution $y(u)$. For the approximate solution $y_N(u)$, the residual is required to be zero at the collocation points, and this determines $\{a_i\}$ in the trial function.

Two different kinds of problems are normally encountered. In the first kind are those in which the solution in the domain $0 \leq u \leq 1$ is symmetrical about $u=0$ (e.g. temperature and concentration profiles in

the radial direction) for which the trial function has the form:

$$y(r^2) \sim y_N(r^2) = b + (1-r^2) \sum_{i=1}^N a_i P_{i-1}(r^2) \quad (\text{B.1.2})$$

The second kind, are the problems with no special symmetry (e.g. temperature and concentration profiles in the axial direction) for which trial function has the form:

$$y(z) \sim y_N(z) = b+cz + z(1-z) \sum_{i=1}^N a_i P_{i-1}(z) \quad (\text{B.1.3})$$

In both cases, N is the number of interior collocation points which are chosen as the zeros of an orthogonal polynomial $P_N(u)$. When the collocation points are the zeros of any Jacobi polynomial, the collocation method is called orthogonal collocation. Then $P_N(r^2)$ and $P_N(z)$ are any Jacobi polynomials satisfying the orthogonality condition:

$$\int_0^1 W(u) P_j(u) P_N(u) du = 0 \quad (\text{B.1.4})$$

$$j = 0, 1, \dots, N-1$$

where $W(u)$, the weighting function is given by

$$W(u) = u^\beta (1-u)^\alpha \quad (\text{B.1.5})$$

which is the specific weight function of the shifted Jacobi polynomials.

The parameters α and β characterise the shifted Jacobi polynomials, $P_N(u) = P_N^{\alpha, \beta}(u)$ which can be expressed by the recurrence formula [Villadsen (1970)]:

$$P_N(u) = P_N^{\alpha, \beta}(u) = \gamma_N u^N - \gamma_{N-1} u^{N-1} + \gamma_{N-2} u^{N-2} - \dots + (-1)^N \gamma_0 \quad (\text{B.1.6})$$

with:

$$\begin{aligned}\gamma_0 &= 1 \\ \gamma_{K+1} &= \frac{(N-K)(N+\alpha+\beta+K+1)}{(K+1)(\beta+K+1)} \gamma_K\end{aligned}\quad (\text{B.1.7})$$

when $K = 0, 1, 2, \dots, N-1$ and $\alpha, \beta > -1$; $0 < u < 1$

Villadsen & Michelsen (1978) stated that equation B.1.7 is not suited for machine computation of $P_N(u)$ of a specific u -value since $\gamma_{N,i}$ are rapidly increasing with N and since the terms in B.1.7 occur with alternating sign, a significant loss of digits is unavoidable. They recommended the following recurrence relation:

$$P_N(u) = (F_N u - G_N) P_{N-1} - H_N P_{N-2} \quad (\text{B.1.8})$$

where F_N , G_N and H_N are functions of N , α and β .

The rescaled polynomials $p_N = P_N/\gamma_{N,N}$ are given by:

$$p_N(u) = [u - g_N(N, \alpha, \beta)] p_{N-1}(u) - h_N(N, \alpha, \beta) p_{N-2} \quad (\text{B.1.9})$$

$$g_1 = \frac{\beta+1}{\alpha+\beta+2} \quad g_N = \frac{1}{2} \left[1 - \frac{\alpha^2 - \beta^2}{(2N+\alpha+\beta-1)^2 - 1} \right] \quad (\text{B.1.10})$$

for $N > 1$

$$h_1 = 0, \quad h_2 = \frac{(\alpha+1)(\beta+1)}{(\alpha+\beta+2)^2(\alpha+\beta+3)} \quad (\text{B.1.11})$$

$$h_N = \frac{(N-1)(N+\alpha-1)(N+\beta-1)(N+\alpha+\beta-1)}{(2N+\alpha+\beta-1)(2N+\alpha+\beta-2)^2(2N+\alpha+\beta-3)}$$

The recursive evaluation of $p_N(u)$ is started with $N=1$, $p_{-1}(u)$ arbitrary, and $p_0(u_1) = 1$.

The sub-routine JCOBI available in Villadsen & Michelsen (1978) uses equations B.1.9 to B.1.11 to calculate the zeros of the orthogonal polynomials by Newton Method with root suppression. The sub-routine calculates the zeros of $p_N^{\alpha, \beta}(u)$ and also three first derivatives of the node polynomial

$$p_{NT}(u) = u^{NO} p_N(u) (u-1)^{N1} \quad (B.1.12)$$

at the interpolation points. Each of the parameters NO and $N1$ may be given the value 0 and 1. $NT = N + NO + N1$.

Although by choosing N , α and β ($\alpha, \beta > -1$) we may have some flexibility to place collocation points where needed (e.g. to cluster the points around some specific location in $0 < u < 1$), it has recently been shown [Michelsen & Villadsen (1980), Villadsen (1980)] that the choice of $\alpha = 0$, $\beta = \frac{s-1}{2}$ (when $s = 0, 1, 2$ for slabs, cylinders and spheres respectively) is optimum in terms of accuracy, as for this case orthogonal collocation is equivalent to Galerkin's method - which has proved to be superior to other methods of weighted residuals [Villadsen & Michelsen (1978)]. This is also important "as for Galerkin's method considerable knowledge concerning approximation error, rate of convergence, etc. is readily available" [Michelsen & Villadsen (1980)], and therefore can be extended to orthogonal collocation.

Finally, following Villadsen & Stewart (1967), it can be shown [Finlayson (1972)] that the gradient and Laplacian operators for the function $y_n(u)$ are given by:

$$\left. \frac{dy_N}{du} \right|_{u=u_i} = \sum_{j=1}^{N+1} A_{ij} y_n(u_j) \quad (B.1.13)$$

$$\left. \nabla^2 y_N \right|_{u=u_i} = \sum_{j=1}^{N+1} B_{ij} y_n(u_j)$$

for $i = 1, N+1$

The matrices A and B and $\{u_i\}$, $i=1, \dots, N$ with $u_{N+1} = 1.0$ are easily calculated with the method given by Villadsen & Michelsen (1978). In this work the matrices were calculated using a sub-routine PLANAR which is available in Finlayson (1980). The parameters that have to be specified are:

NT = N + NO + N1 total number of collocation points

NA = Array Dimensions of matrices

u_i $i = 1, NT$ zeros of the polynomials from JCBI.

The model, pseudo-homogeneous two-dimensional model described in Chapter 3, was solved numerically using orthogonal collocation.

In all situations where there was no symmetry, the recommended values of $\alpha = \beta = 0$ were used, for which $w(u) = 1$ and $p_N^{(0,0)}(u)$ is a shifted Legendre polynomial. When symmetry was considered, as was the case with the radial direction, orthogonal collocation was applied, using $\alpha = 1, \beta = 0$, for which $w(r^2) = (1-r^2)$ and $p_N^{(1,0)}(r^2)$ is a Jacobi polynomial. Finlayson (1971) has shown that this is a proper choice when only one interior collocation point is used since the reaction rate expression is evaluated at a temperature above the average [as obtained with $p_N^{(0,0)}$], and this approximates more closely the average rate of reaction.

Radial collocation

For this case, using one interior collocation point, the zero of $P_n^{(1,0)}(r^2)$, in the radial direction, it is easy to show, using (B.1.13) that the following terms of Eqs. 3.8 and 3.9 reduce to

$$\frac{1}{P_m} \left(\frac{\partial^2 X_n}{\partial r^2} + \frac{1}{r} \frac{\partial X_n}{\partial r} \right) = \frac{1}{P_m} \sum_{k=1}^{N+1} B_{ik} X_{n_K} = 0 \quad (\text{B.1.14})$$

$$\frac{1}{Ph} \left(\frac{\partial^2 Y}{\partial r^2} + \frac{1}{r} \frac{\partial Y}{\partial r} \right) = \frac{1}{Ph} \sum_{k=1}^{N+1} B_{ik} Y_k = \frac{6 Biw/Ph}{3 + Biw} (Y_w - Y_1) \quad (\text{B.1.15})$$

using boundary conditions at $r_2 = 1.0$ given by

$$\frac{\partial X_n}{\partial r} = \sum_{K=1}^{N+1} A_{N+1,k} X_{n_K} = 0$$

$$-\frac{\partial Y}{\partial r} = - \sum_{K=1}^{N+1} A_{N+1,K} Y_K = Biw (Y_{N+1} - Y_w)$$

and the following values for the matrices A and B [Finlayson (1972), p.103]:

$$\underline{A} = \begin{bmatrix} -1.732 & 1.732 \\ -3 & 3 \end{bmatrix}; \quad \underline{B} = \begin{bmatrix} -6 & 6 \\ -6 & 6 \end{bmatrix}$$

with $N = 1$, and the collocation points

$$r_0 = 0.0; \quad r_1 = 0.57735, \quad r_2 = 1.0.$$

The solution is given at the interior collocation point, r_1 . As we are also interested in knowing the temperature at $r_0 = 0$ and $r_2 = 1.0$ (the centre line and the wall of the reactor respectively), following Finlayson [(1972), p.101] we obtain

$$Y [r=0] = Y_0 = 1.5 Y_1 - 0.5 Y_2 \quad \text{B.1.16}$$

and from the boundary conditions at $r_2 = 1.0$:

$$Y_2 = \frac{3Y_1 + Bi_w Y_w}{3 + Bi_w} \quad \text{B.1.17}$$

Using the above expressions for the Laplacian terms in Eqs. 3.8 and 3.9 in Chapter 3, we obtain the reduced set of partial differential equations, at the collocation point $i = 1$, given by:

$$\frac{\partial X_n}{\partial t} = - \frac{\partial X_n}{\partial z} + \sum_{j=1}^R \delta m_j f_j(X, Y) \quad \text{B.1.18}$$

$$\frac{\partial Y}{\partial t} = - \frac{\partial Y}{\partial z} + \frac{6Bi_w/Ph}{3 + Bi_w} (Y_w - Y) + \sum_{j=1}^R \beta_j \delta h_j f_j(\underline{X}, Y) \quad \text{B.1.19}$$

with initial conditions

$$\begin{aligned} \text{at } t = 0 \quad X_n(z, 0) &= X_n(z)_{ss} \\ Y(z, 0) &= Y(z)_{ss} \end{aligned} \quad \text{B.1.20}$$

$$\begin{aligned} \text{at } z = 0 \quad X_n(0, t) &= X_{n_0}(t) \\ Y(0, t) &= Y_0(t) \end{aligned} \quad \text{B.1.21}$$

B.2 ORTHOGONAL COLLOCATION ON FINITE ELEMENTS [CAREY & FINLAYSON (1975)] OR GLOBAL SPLINE COLLOCATION [VILLADSEN & MICHELSEN(1978)]

This method was developed to combine the small truncation error associated with orthogonal collocation and the ability of the finite difference method to locate grid points where needed. In this method the whole domain $0 \leq z \leq 1$ is divided into NE sub-intervals of finite elements $\Delta z_1, \dots, \Delta z_K, \dots, \Delta z_{NE}$ where orthogonal collocation is applied at N_K interior points, requiring continuity of functions and its first derivatives at the boundaries between elements.

Let us divide the domain $0 \leq z \leq 1$ into NE elements by placing the dividing points at z_K , $K = 1, \dots, NE + 1$, with $z_1 = 0.0$ and $z_{NE+1} = 1.0$, we define a new variable within each element:

$$u^K = \frac{z - z_K}{z_{K+1} - z_K} = \frac{z - z_K}{\Delta z_K}$$

placing interior collocation points at the zeros of $P_N^{0,0}(u)$ defined on

$0 \leq u \leq 1$. For the i^{th} interior collocation point on the K^{th} element

we have $z = z_K + u \Delta z_K$

$K = 1, \dots, NE$ and $i = 2, \dots, N+1$

B.2.1 Axial direction

The method of orthogonal collocation on finite elements which was developed and used in solving boundary value problems [Carey & Finlayson (1975), Villadsen & Michelsen (1978), Pedersen & Tanoff (1982)] was extended to, and used in, solving an initial value-problem with steep temperature and concentration profiles.

Applying the method in the axial direction to Eq. B.1.18 and B.1.19 we have

$$\frac{dX_{n_i}^K}{dt} = - \frac{1}{\Delta z_K} \sum_{j=1}^{N_K+2} A_{ij} X_{n_j}^K + \sum_{\ell=1}^R \delta m_{\ell} f_{\ell}^K(\underline{X}, Y_i) \quad (\text{B.2.1})$$

$$\frac{dY}{dt} = - \frac{1}{\Delta z_K} \sum_{j=1}^{N_K+2} A_{ij} Y_j^K + \frac{6Bi_w/Ph}{3 + Bi_w} (Y_w - Y_i^K) + \sum_{\ell=1}^R \beta_{\ell} \delta m_{\ell} f_{\ell}^K(X, Y_i) \quad (\text{B.2.2})$$

$$i = 1, \dots, N_K+2$$

requiring continuity of the functions at the boundaries of the finite elements.

$$X_{n_{N_K+2}}^K = X_{n_1}^{K+1} \quad (\text{B.2.3})$$

$$Y_{N_K+2}^K = Y_1^{K+1}$$

Since Eqs. B.2.1 and B.2.3 represent an initial-value problem, the elements can be considered as independent small reactors as shown in Fig. B.2.1. The inlet conditions to an element being the output values of the previous one and in the case of the first element the reactor inlet conditions.

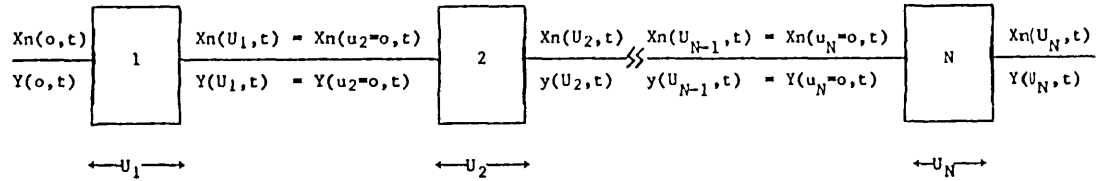


Fig. B.2.1 Schematic diagram of finite elements.

In theory the reactor can be broken into as many independent reactors as possible but in order to minimize computation times and storage requirements, it is important to get the right number and sizes of the elements. This calls for suitable criteria to be developed in order to partition the domain properly. The number of interior points required in each element depends upon the size of the element and the gradient of the solution profiles.

B.3 NUMERICAL SOLUTION OF NON-LINEAR ALGEBRAIC EQUATIONS

In this section, a brief description of Newton's method to solve non-linear algebraic equations, together with certain modifications to this method, due to Broyden (1965) are presented [Lopez-Isunza (1983)].

B.3.1 Newton's method

Consider the set of n non-linear algebraic equations:

$$\begin{aligned} f_1(x_1, x_2, \dots, x_n) &= 0 \\ f_2(x_1, x_2, \dots, x_n) &= 0 \\ &\cdot \\ &\cdot \\ &\cdot \\ f_n(x_1, x_2, \dots, x_n) &= 0 \end{aligned} \tag{B.3.1}$$

Then, in matrix notation, Eq. B.3.1 may be represented as:

$$\underline{f}(\underline{x}) = 0 \tag{B.3.2}$$

Where $\underline{x}$ is the column vector of independent variables and $\underline{f}$ the column vector of functions f_j , $j=1, 2, \dots, n$. If $\underline{x}_i$ is the i^{th} approximation of the solution of Eq. B.3.2 and $\underline{f}_i$ is written $\underline{f}(\underline{x}_i)$, then Newton's method is defined by:

$$\underline{x}_{i+1} = \underline{x}_i - \underline{J}_i^{-1} \underline{f}_i \tag{B.3.3}$$

where $\underline{J}_i$ is the Jacobian matrix

$$\underline{J}_i = \{ \partial f_j / \partial x_k \} \tag{B.3.4}$$

evaluated at $\underline{x}_i$.

B.3.2 The Broyden modification to the Newton Method [Broyden (1965)]

Newton's method, as expressed in Eq. B.3.3 suffers from two serious disadvantages from the point of view of practical calculation. The first of these is the difficulty of computing $\underline{J}$, and therefore the

time required to evaluate the Jacobian matrix $\underline{J}$. The second disadvantage of Newton's method is that it may not converge unless the initial estimate of the solution is sufficiently good, a requirement that is often impossible to realise in practice.

In order to overcome some of the disadvantages of Newton's method, Broyden (1965) proposed a class of methods (quasi-Newton methods), in which the elements of the Jacobian matrix $\delta f_i / \delta x_k$, are not estimated or evaluated directly, but corrections to the approximate inverse of the Jacobian matrix are computed from values of the vector function $\underline{f}$.

A correction of this type is carried out at each iteration and is much simpler to perform than the evaluation of the complete Jacobian.

Let $\underline{x}_i$ be the i^{th} approximation to the solution of Eq. B.3.2 and define $\underline{P}_i$ by:

$$\underline{P}_i = - \underline{B}_i^{-1} \underline{f}_i \quad (\text{B.3.5})$$

where $\underline{B}_i$ is some approximation to $\underline{J}_i$, evaluated at $\underline{x}_i$.

Then a simple modification to Newton's algorithm gives $\underline{x}_{i+1}$ as:

$$\underline{x}_{i+1} = \underline{x}_i + t_i \underline{P}_i \quad (\text{B.3.6})$$

where t_i is a scalar multiplier chosen to prevent the process diverging. The value of t_i or t that is finally used to determining $\underline{x}_{i+1}$, may be chosen in various ways, and two of these are: t_i is chosen to minimize the norm of $\underline{f}_{i+1}$, or choosing a value of t_i which merely reduces the norm.

To sequentially update the approximate Jacobian at each iteration step, Broyden proposed that $\underline{B}_{i+1}$ be calculated as follows:

$$\underline{B}_{i+1} = \underline{B}_i + \frac{\underline{y}_i - s_i \underline{B}_i \underline{P}_i}{s_i \underline{P}_i^T \underline{P}_i} \quad (\text{B.3.7})$$

where $\underline{y}_i$ is defined by:

$$\underline{y}_i = \underline{f}_{i+1} - \underline{f}(t_i - s_i) \quad (\text{B.3.8})$$

and s_i is a particular value of s^* .

Now, in the class of methods proposed by Broyden, $\underline{B}_{i+1}$ is chosen in such a way as to satisfy the equation

$$\underline{f}_{i+1} - \underline{f}_i(t_i - s_i) = s_i \underline{B}_{i+1} \underline{P}_i \quad (\text{B.3.9})$$

If we define:

$$\underline{H}_j = -\underline{B}_j^{-1} \quad (\text{B.3.10})$$

then Eqs. B.3.5 and B.3.9 become

$$\underline{P}_i = \underline{H}_i \underline{f}_i \quad (\text{B.3.11})$$

and

$$\underline{H}_{i+1} \underline{y}_i = -s_i \underline{P}_i \quad (\text{B.3.12})$$

However, instead of using Eq. B.3.7, it is recommended to store in the computer $\underline{H}_i$ as opposed to $\underline{B}_i$. Therefore the equation that defines the first of the quasi-Newton methods - which is the most effective - is:

$$\underline{H}_{i+1} = \underline{H}_i - \frac{(s_i \underline{P}_i + \underline{H}_i \underline{P}_i)^T \underline{P}_i \underline{H}_i}{\underline{P}_i^T \underline{H}_i \underline{P}_i} \quad (\text{B.3.13})$$

* Assume that the norm $N(t)$ has been evaluated successively at $t = t^{(K)}$, $K = 1, 2, \dots, m$, where:

$$t^{(1)} = 1 \text{ and } t^{(m)} = t_i$$

and where t_i is either the value of t that minimizes $N(t)$ or the first $t^{(K)}$ for which $N(t^{(K)}) < N(0)$. If $s^{(K)}$ is defined by

$$s^{(K)} = t^{(m)} - t^{(K)} \quad K = 1, 2, \dots, m-1$$

then s_i is best chosen to be the $s^{(K)}$ having the smallest modulus, i.e.

$$s_i = t^{(m)} - t^{(m-1)}.$$

B.4 TABLES OF SIMULATION RESULTS

Tables B.4.1 to B.4.5 present the properties of the finite elements used in simulating both the steady state and dynamic behaviour of the reactor as described in Chapter 3.

TABLE B.4.1a
Steady state simulation without activity profiles:-
properties of the finite elements when 4 interior points
were initially specified in each finite element

Number of finite elements	Number	Size	Number of interior points	Computational time CPU (secs)
4	1	.13779	4	No convergeance
	2	.07672	4	
	3	.08842	4	
	4	.69708	14	
6	1	.13779	4	3.3710
	2	.07672	4	
	3	.08841	4	
	4	.29767	6	
	5	.36804	4	
	6	.03136	4	
8	1	.13779	4	1.5290
	2	.07672	4	
	3	.08841	4	
	4	.09648	4	
	5	.10060	4	
	6	.10060	4	
	7	.36804	4	
	8	.03136	4	
10	1	.13779	4	1.8690
	2	.07672	4	
	3	.08841	4	
	4	.09648	4	
	5	.10060	4	
	6	.10060	4	
	7	.18489	4	
	8	.13862	4	
	9	.04453	4	
	10	.03136	4	

TABLE B.4.1b

Steady state simulation without activity profile:-
 Properties of the finite elements when 2 interior points
 were initially specified in each finite element

Number of finite elements	Number	Size	Number of interior points	Computational time CPU (secs)
4	1	.13779	2	No convergence
	2	.07672	2	
	3	.08841	2	
	4	.69708	14	
6	1	.13779	2	4.2070
	2	.07672	2	
	3	.08841	2	
	4	.29767	6	
	5	.36804	3	
	6	.03136	2	
8	1	.13779	2	1.0510
	2	.07672	2	
	3	.08841	2	
	4	.09648	2	
	5	.10060	2	
	6	.10060	2	
	7	.36804	3	
	8	.03136	2	
10	1	.13779	2	.9050
	2	.07672	2	
	3	.08841	2	
	4	.09648	2	
	5	.10060	2	
	6	.10060	2	
	7	.18489	2	
	8	.13862	2	
	9	.04453	2	
	10	.03136	2	

TABLE B.4.2

Steady state simulation with activity profile:-
 Properties of the finite elements when 4 interior points
 were initially specified in each finite element

Number of finite elements	Number	Size	Number of interior points	Computational time CPU (secs)
4	1	.30292	14	No convergence
	2	.09698		
	3	.10060		
	4	.5000		
6	1	.21451	5	20.796
	2	.08891	4	
	3	.09698	4	
	4	.10060	4	
	5	.42410	12	
	6	.07590	4	
8	1	.07590	4	8.2410
	2	.13862	4	
	3	.08841	4	
	4	.09648	4	
	5	.10060	4	
	6	.28549	8	
	7	.13862	4	
	8	.07590	4	
10	1	.07590	4	1.7350
	2	.13862	4	
	3	.08841	4	
	4	.09648	4	
	5	.10060	4	
	6	.10060	4	
	7	.09648	4	
	8	.08841	4	
	9	.13862	4	
	10	.07590	4	

TABLE B.4.3a

Steady state simulation with activity profile:-
 Properties of the finite elements with one boundary point inserted
 at the point of discontinuity of the activity profile

Number of finite elements	Number	Size	Number of interior points	Computational time CPU (secs)
6	1	.21451	5	No convergence
	2	.03549	4	
	3	.05292	4	
	4	.09698	4	
	5	.10060	4	
	6	.5000	14	
8	1	.21451	5	5.9840
	2	.03544	4	
	3	.05292	4	
	4	.09648	4	
	5	.10060	4	
	6	.28549	7	
	7	.13862	4	
	8	.07590	4	
9	1	.07590	4	5.3300
	2	.13862	4	
	3	.03547	4	
	4	.05292	4	
	5	.09648	4	
	6	.10060	4	
	7	.28547	4	
	8	.13862	4	
	9	.07590	4	
10	1	.07590	4	1.7190
	2	.13862	4	
	3	.03549	4	
	4	.05292	4	
	5	.09648	4	
	6	.10060	4	
	7	.10060	4	
	8	.18489	4	
	9	.13862	4	
	10	.07590	4	
11	1	.07590	4	1.8730
	2	.13862	4	
	3	.03549	4	
	4	.05292	4	
	5	.09648	4	
	6	.14060	4	
	7	.10060	4	
	8	.09648	4	
	9	.08841	4	
	10	.13862	4	
	11	.07590	4	

TABLE B.4.3b

Steady state simulation with activity profile:-
 Properties of the finite elements when two interior
 points were initially specified in each element

Number of finite elements	Number	Size	Number of interior points	Computational time CPU (secs)
8	1	.21451	2	5.4480
	2	.03549	2	
	3	.05292	2	
	4	.09648	2	
	5	.10060	2	
	6	.26549	7	
	7	.13862	2	
	8	.07590	2	
9	1	.07590	2	5.5065
	2	.13862	2	
	3	.03547	2	
	4	.05292	2	
	5	.09648	2	
	6	.10060	2	
	7	.28547	7	
	8	.13862	2	
	9	.07590	2	
10	1	.07590	2	0.6770
	2	.13862	2	
	3	.03549	2	
	4	.05292	2	
	5	.09648	2	
	6	.10060	2	
	7	.10060	2	
	8	.18489	2	
	9	.13862	2	
	10	.07590	2	
11	1	.07590	2	.7280
	2	.13862	2	
	3	.03549	2	
	4	.05292	2	
	5	.09648	2	
	6	.10060	2	
	7	.10060	2	
	8	.09648	2	
	9	.08841	2	
	10	.13862	2	
	11	.07590	2	

TABLE B.4.4

Dynamic simulation with constant activity profile:
comparison of the number of interior points used
at various time intervals

Number of finite elements	Position	Number of interior points at						
		0 min	1 min	2 min	3 min	4 min	5 min	10 min
8	1	2	2	2	2	2	2	2
	2	2	2	2	2	2	2	2
	3	2	2	2	2	2	2	2
	4	2	2	2	2	2	2	2
	5	2	2	3	3	3	3	3
	6	7	8	9	9	9	9	9
	7	2	2	2	2	2	2	2
	8	2	2	2	2	2	2	2
9	1	2	2	2	2	2	2	2
	2	2	2	2	2	2	2	2
	3	2	2	2	2	2	2	2
	4	2	2	2	2	2	2	2
	5	2	2	2	2	2	2	2
	6	2	2	2	3	3	3	3
	7	7	8	9	9	9	9	9
	8	2	2	2	2	2	2	2
	9	2	2	2	2	2	2	2
10	1	2	2	2	2	2	2	2
	2	2	2	2	2	2	2	2
	3	2	2	2	2	2	2	2
	4	2	2	2	2	2	2	2
	5	2	2	2	2	2	2	2
	6	2	2	2	3	3	3	3
	7	2	3	3	3	3	3	3
	8	2	2	3	3	3	3	3
	9	2	2	2	2	2	2	2
	10	2	2	2	2	2	2	2

TABLE B.4.5

Dynamic simulation with time-varying activity profile:
comparison of the number of interior points used
at various time intervals

Number of finite elements	Position	Number of interior collocation points at:						
		0 min	1 min	2 min	3 min	4 min	5 min	10 min
8	1	2	3	3	3	3	3	3
	2	2	2	2	2	2	2	2
	3	2	2	2	2	2	2	2
	4	2	2	2	2	2	2	2
	5	2	5	5	5	5	5	5
	6	7	8	8	8	8	8	8
	7	2	2	2	2	2	2	2
	8	2	2	2	2	2	2	2
9	1	2	2	2	2	2	2	2
	2	2	2	2	2	2	2	2
	3	2	2	2	2	2	2	2
	4	2	2	2	2	2	2	2
	5	2	2	2	2	2	2	2
	6	2	5	5	5	5	5	5
	7	7	8	8	8	8	8	8
	8	2	2	2	2	2	2	2
	9	2	2	2	2	2	2	2
10	1	2	2	2	2	2	2	2
	2	2	2	2	2	2	2	2
	3	2	2	2	2	2	2	2
	4	2	2	2	2	2	2	2
	5	2	2	2	2	2	2	2
	6	2	5	5	5	5	5	5
	7	2	3	3	3	3	3	3
	8	2	2	2	2	2	2	2
	9	2	2	2	2	2	2	2
	10	2	2	2	2	2	2	2

APPENDIX C

TYPICAL CHROMATOGRAMS AND CALIBRATION CURVES

Typical chromatograms at the various axial positions and column temperatures are shown in Figs. C.1a to C.1d. Calibration curves are presented in Figs. C.2a to C.2c. Table C.1 presents the compositions of the various components shown in Figs. C.1a to C.1d.

TABLE C.1

Composition of the various components shown in the sample chromatograms C.1a to C.1d.

Figure	Column temperature	Axial position	Composition			
			OX	OT	PA	PT
D.1a	190°C	24	2.4549×10^{-3}	3.7650×10^{-3}	7.3860×10^{-1}	1.0645×10^{-2}
D.1b*	190°C	12	7.2072×10^{-1}	8.4788×10^{-1}	7.5304×10^{-2}	
D.1c	230°C	14	1.2000×10^{-1}	8.6927×10^{-2}	3.5106×10^{-1}	
D.1d*	230°C	12	3.1916×10^{-1}	1.3735×10^{-1}	1.6720×10^{-1}	

*Readings taken at different salt bath temperatures.

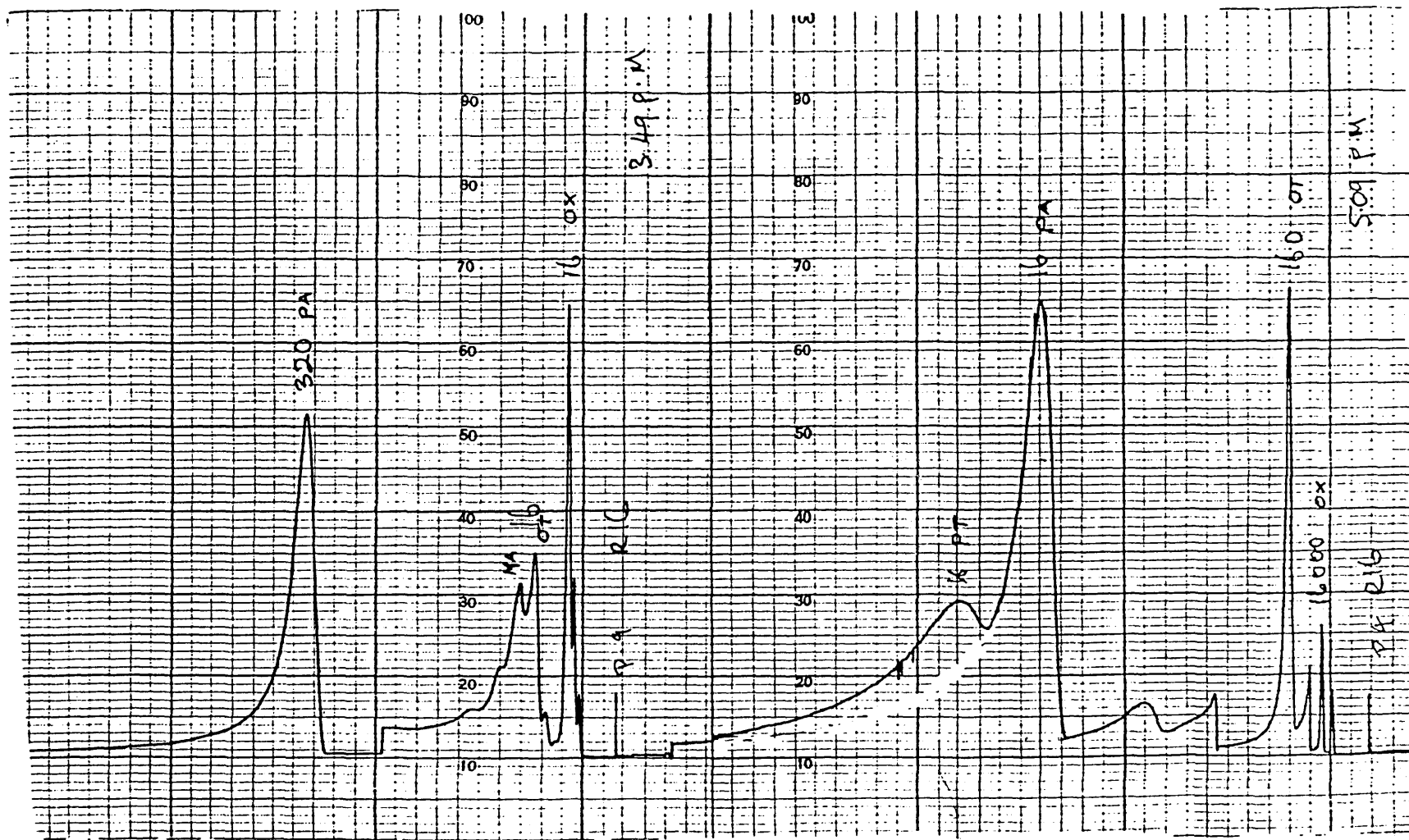


Fig. C.1a Typical chromatogram of the oxidation products at axial position 24; column temperature 190°C.

Fig. C.1b Typical chromatogram of the oxidation products at axial position 14; column temperature 190°C

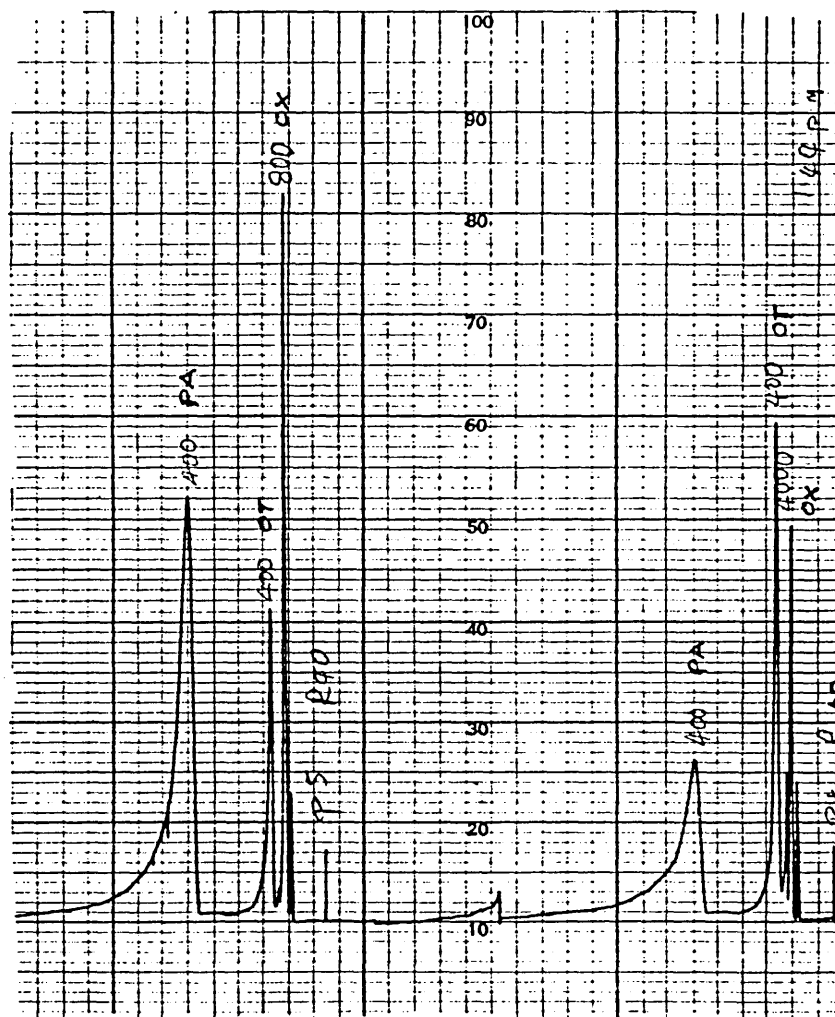


Fig. C.1c Typical chromatogram of
the oxidation products
at axial position 14;
column temperature 230°C

Fig. C.1d Typical chromatogram of
the oxidation products
at axial position 12;
column temperature 230°C

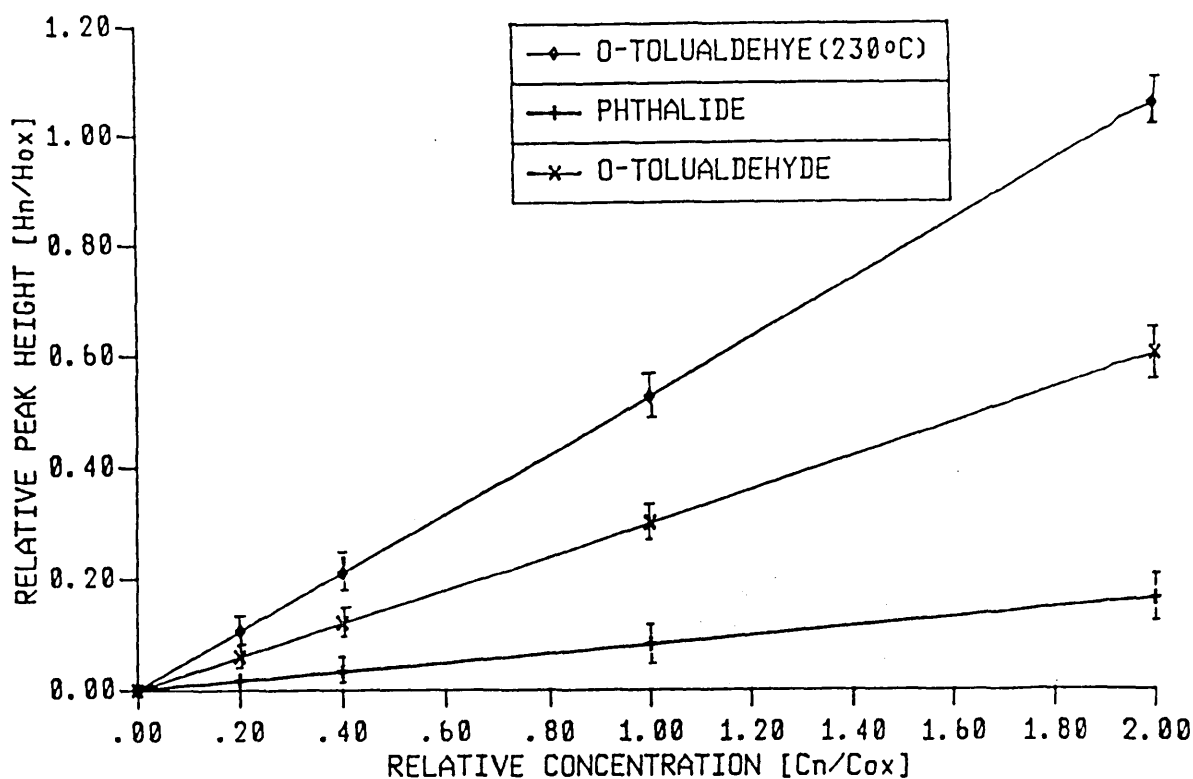


Fig. C.2a Liquid-phase calibration curves of the components indicated; column temperature 190°C except specified otherwise.

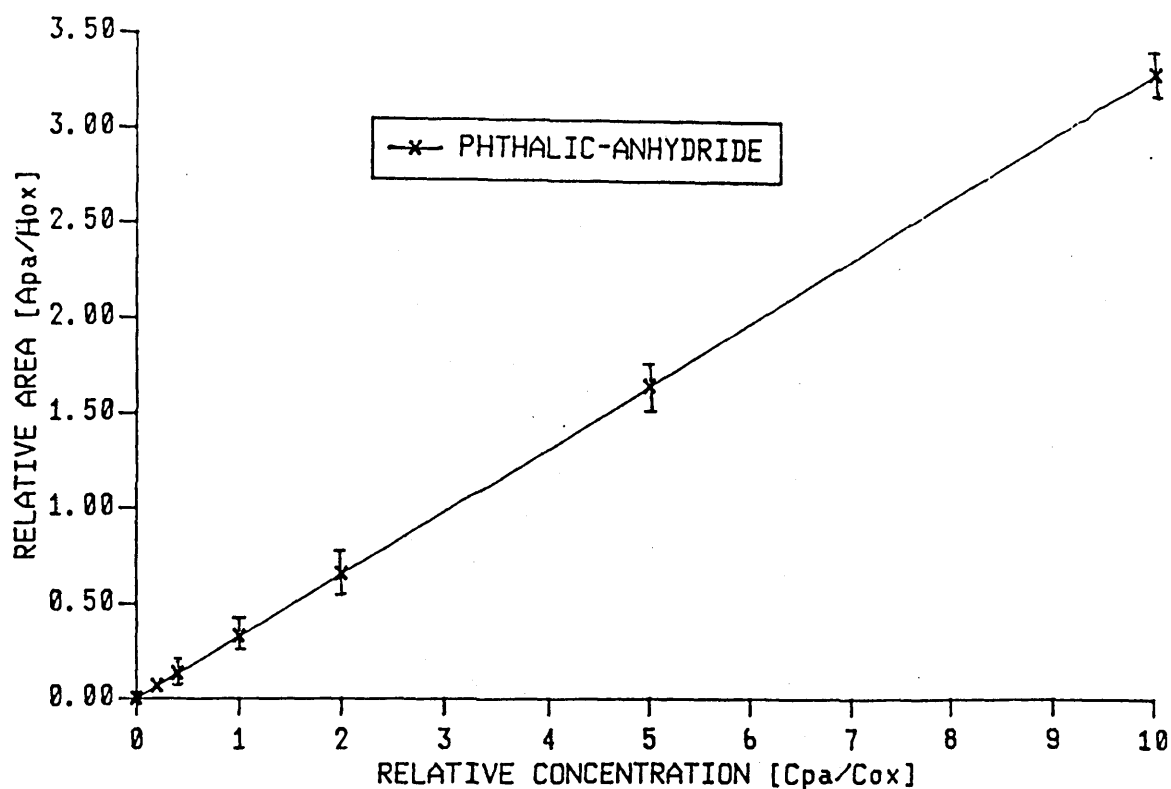


Fig. C.2b Liquid-phase calibration curve for phthalic anhydride; column temperature 190°C.

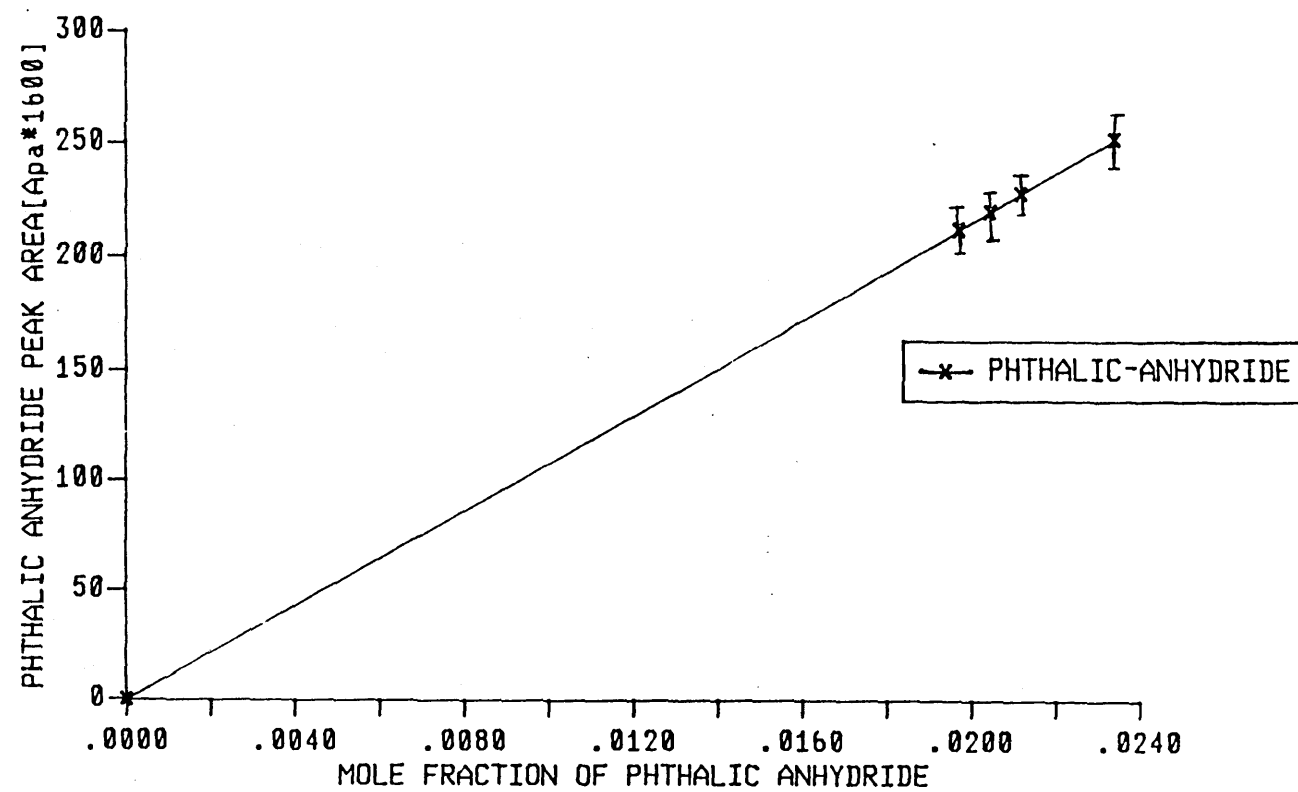


Fig. C.2c Vapour-phase calibration curve of phthalic anhydride;
column temperature 230°C.

APPENDIX D

ESTIMATION OF THE BEST RADIAL POSITION FOR AXIAL TEMPERATURE

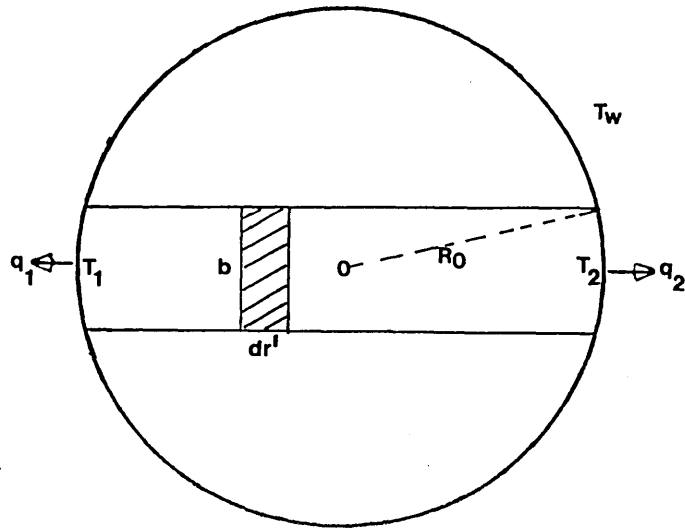
MEASUREMENTS

In order to estimate the best possible radial location of the thermocouples for axial temperature measurements, in the face of distortions of the radial temperature profiles due to conductive heat losses along the sampling tubes welded to one side of the reactor, a very simple approach was followed which considers the solution of the one-dimensional heat balance equation for a slab with the assumptions that the distortions do not extend right to the opposite side of the reactor so that the inside wall temperature and the rate of heat loss at the side, with or without the sampling tubes, is unchanged. With the two boundary conditions, the 2nd order ordinary differential equation was solved and symmetrical radial temperature profiles were constructed and compared with those estimated from measurements at the various axial locations. The two sets of profiles were found to be fairly close up to and including the normalised radial position of 0.423 from the free side of the reactor (see Fig. D.1). This position corresponds to the single radial interior collocation point approximation of the model. All axial temperature measurements were carried out at this point.

D.1 Detail calculations.

D.1.1 Solution of the one-dimensional heat balance equation for a slab.

A rectangular slab of width b , thickness b and length d_T is cut and considered as shown in the figure below.



For an element of thickness dr' , width b and length dr' , the energy balance equation is

$$b \cdot b \left(q_{r'} \Big|_{r'} - q_{r'} \Big|_{r'+dr'} \right) + b \cdot b \, dr' \, Q = 0$$

$$- \frac{dq_{r'}}{dr'} + Q = 0$$

(D.1)

$$Ke \frac{d^2 T'}{dr'^2} + Q = 0$$

Where Q is the net heat generated per unit volume of slab.

With $T = T'/T_w$ and $r = r'/R_0$ Eq. D.1 is expressed in dimensionless form as

$$\frac{d^2T}{dr^2} = \frac{Ro^2 Q}{Ke Tw}$$

$$\frac{d^2T}{dr^2} = E \quad \text{where } E = \frac{Ro^2 Q}{Ke Tw} \quad (D.2)$$

Boundary conditions when sampling tubes are present.

$$@ \text{ at } r = -1 \quad Ke \left. \frac{dT}{dr} \right|_{r=-1} = q_1 = h_1 Ro (T - Tw) \quad (D.3)$$

$$@ \text{ at } r = 1 \quad -Ke \left. \frac{dT}{dr} \right|_{r=1} = q_2 = h_2 Ro (T - Tw) \quad (D.4)$$

Integrating Eq. D.2

$$\frac{dT}{dr} = Er + C_1 \quad (D.5)$$

$$T(r) = \frac{E}{2} r^2 + C_1 r + C_2 \quad (D.6)$$

The values of E , C_1 and C_2 were estimated using radial temperature measurements [Lopez-Isunza (1983)].

From Eq. D.3, D.4, D.5, and D.6 we have

$$\frac{Ke}{h_1 Ro} = \left(\frac{E}{2} - C_1 + C_2 - Tw \right) / (C_1 - E) \quad (D.7)$$

$$\frac{Ke}{h_2 Ro} = - \left(\frac{E}{2} + C_1 + C_2 - Tw \right) / (C_1 + E) \quad (D.8)$$

$$C_1 = \left(\frac{\left(\frac{Ke}{h_1 Ro} - \frac{Ke}{h_2 Ro} \right) E}{2 + \frac{Ke}{h_1 Ro} + \frac{Ke}{h_2 Ro}} \right) \quad (D.9)$$

$$C_2 = \left(1 + \frac{Ke}{h_1 Ro} \right) C_1 - \frac{E}{2} - \frac{Ke}{h_1 Ro} E + Tw \quad (D.10)$$

$$T(-1) = T_1 = \frac{E}{2} - C_1 + C_2 \quad (D.11)$$

$$T(+1) = T_2 = \frac{E}{2} + C_1 + C_2 \quad (D.12)$$

Boundary conditions when sampling tubes are absent.

$$\text{at } r = \pm 1 \quad \mp Ke \frac{dT}{dr} \bigg|_{r=\pm 1} = q_1 = h_1 Ro (T - Tw) \quad (D.13)$$

$$T(-1) = T(+1) = T_1 \quad (D.13b)$$

Using the boundary condition D.13b we have

$C_1 = 0$ when Eq. D.11 is equated to Eq. D.12.

From Eq. D.10

$$C_2 = -\frac{E}{2} - \frac{Ke}{h_1 Ro} E + Tw \quad (D.14)$$

$$\therefore T(r) = \frac{E}{2} r^2 - \frac{E}{2} - \frac{Ke}{h_1 Ro} E + Tw$$

$$\text{or } T(r) = \frac{E}{2} \left(r^2 - \frac{2Ke}{h_1 Ro} - 1 \right) + Tw$$

Expressing E in terms of T_1 and $\frac{Ke}{h_1 Ro}$ we have

$$\frac{E}{2} = - (T_1 - T_w) / \frac{2Ke}{h_1 Ro}$$

$$\text{and } T(r) - T_1 = \Delta T \frac{h_1 Ro}{2Ke} (1 - r^2) \quad (D.15)$$

where $\Delta T = T_1 - T_w$.

Eqs. D.6 and D.15 were then used to construct radial temperature profiles.

In Fig. D.1 the symmetrical radial temperature profiles of Eq. D.15 are compared with those estimated from temperature measurements at the various axial distances.

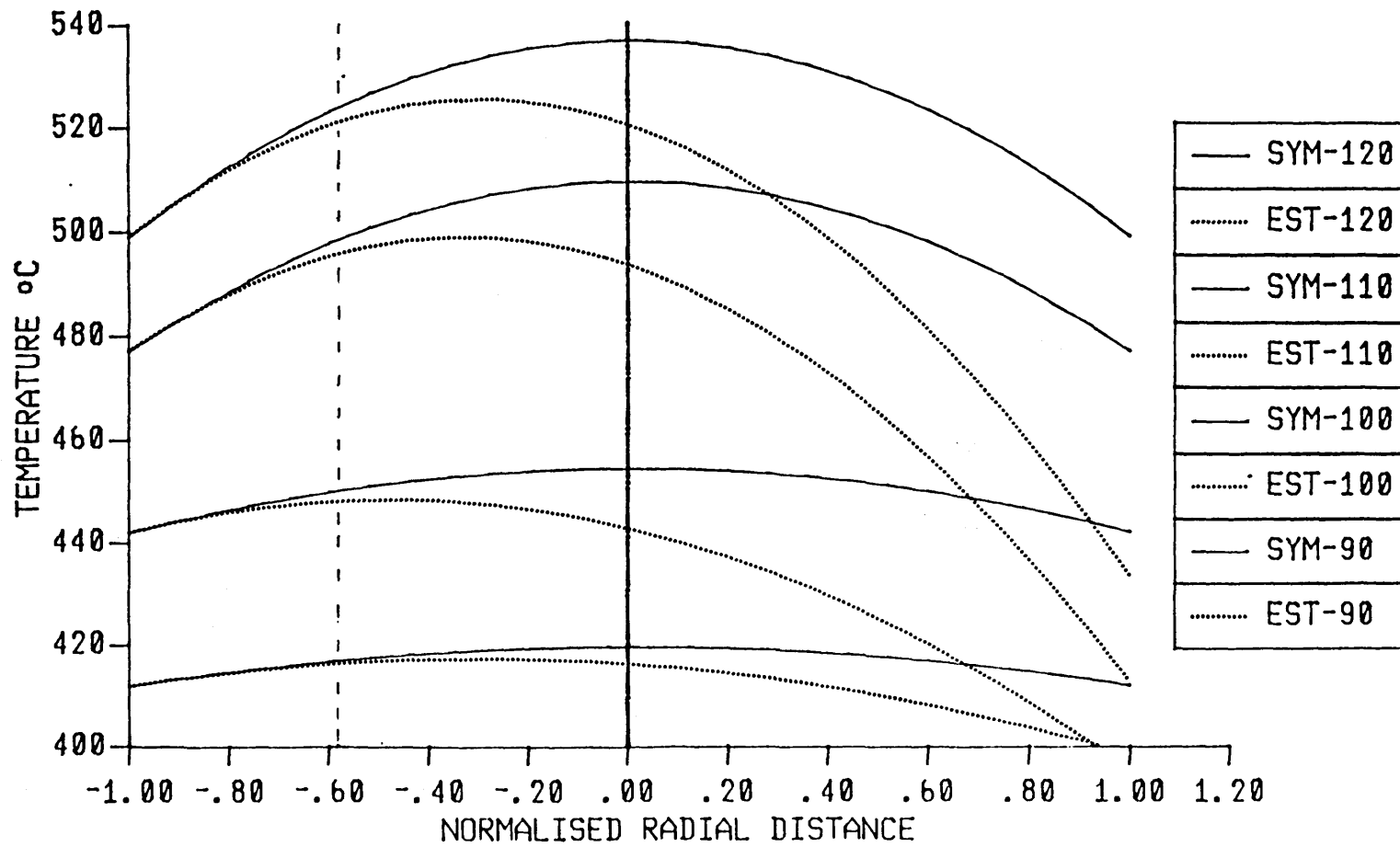


Fig. D.1 Estimated radial temperature profiles compared with symmetrical profiles obtained from the solution of the one-dimensional heat balance equation for a slab.

APPENDIX E

DESIGN AND OPERATION OF THE AUXILLARY COMBUSTION REACTOR

E.1 Design and construction

A sketch diagram of the combustion reactor is given in Fig. E.1. The tubes were made from standard steel pipes of nominal diameter, 4" and 6" respectively. One end of the inner tube and both ends of the outer tube were welded to flanges and assembled to facilitate periodic inspection, cleaning and changing of catalyst. The thermowells were made of stainless steel. All construction work was carried out by the technical staff in the Departmental Workshop. The reactor was properly lagged to avoid excessive heat loss to the surroundings and also for safety reasons (outside wall temperature could be as high as 700°C).

The preheater consisted of two pyrobar heaters, each 60" long and rated at 1250 watts, connected in parallel to mains electricity supply through a variac and tracing the inlet pipe. The whole assembly was also properly lagged.

E.2 Choice of catalyst

The catalyst selected was Cobalt III oxide Co_3O_4 . This catalyst was chosen because of its very high activity with respect to oxidation of hydrocarbons [Krylov (1970), Anderson et al. (1963)]. Other active catalysts in the list were Cr_2O_3 , MnO_2 , CuO and NiO .

The catalyst was supplied in pellets of dimensions $\frac{1}{4}$ " x $\frac{1}{4}$ " and was mixed with inert solids (α -alumina) before charging into the reactor. The total amount of active catalyst was 703 gm while the total weight of inert catalyst was 3342 gm.

E.3 Operational procedure

Before starting the o-xylene pump, power to the combustion reactor preheater was adjusted to about 600 watts (about 115 volts or 50% of mains voltage and total current of 5 amps). Due to the large heat capacity of the combustion tube, a period of about 30 minutes was allowed for the inlet temperature to rise above 300°C.

It is important to note that the reaction could not start when inlet temperatures were below 300°C. With fresh catalyst, the reaction was very rapid and because of the very high inverse response of the reactor, much care was needed in bringing down hotspot temperatures below 800°C by introducing diluent air. However, the catalyst gradually deactivated with time and it was possible to operate the burner stably with peak temperature below 800°C without introducing any diluent air. The inlet temperature required for the reaction to start also increased gradually between 300 to 380°C.

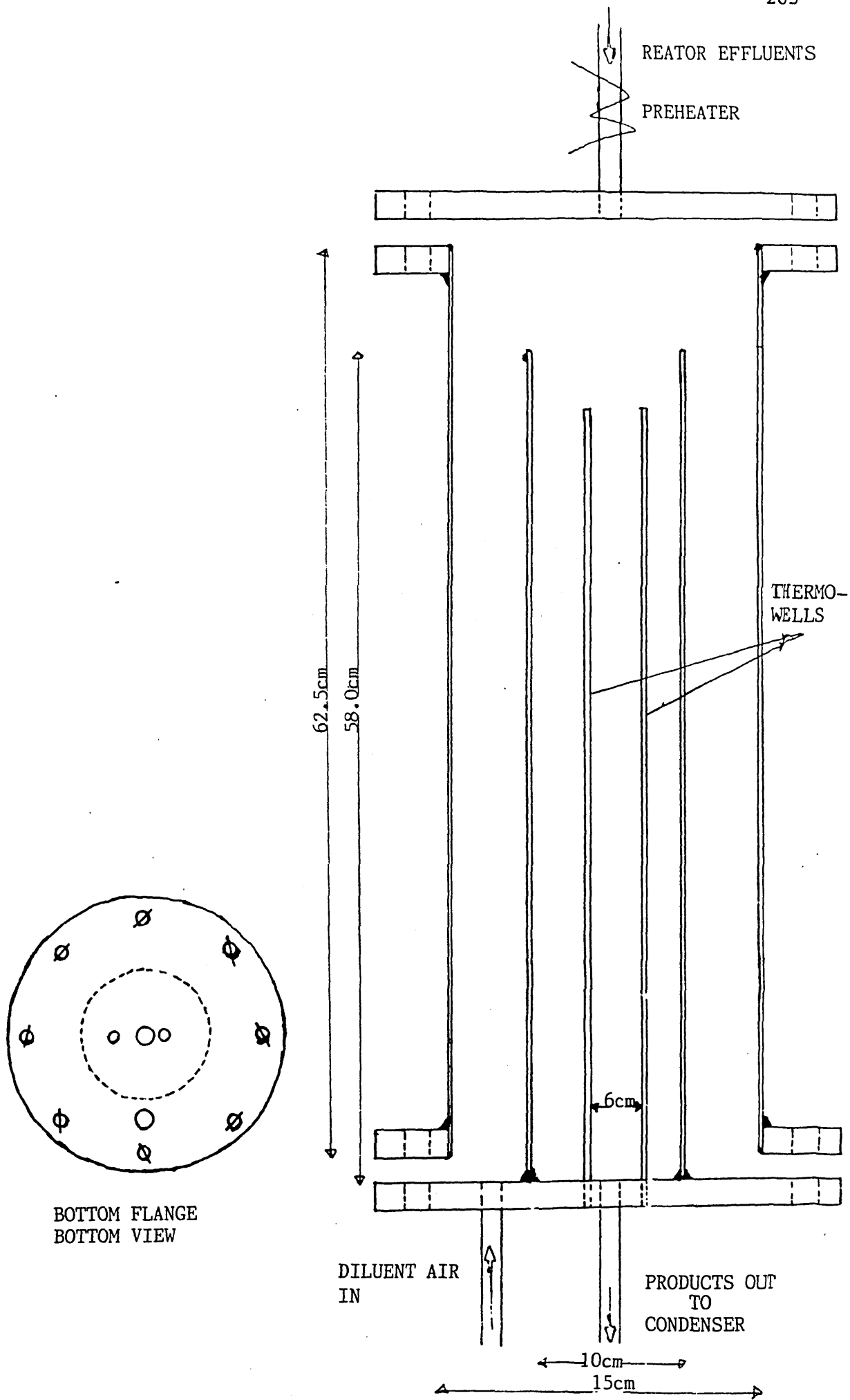


Fig. E.1 Schematic diagram of the combustion tube

E.4 Detail design calculations

E.4.1 Design equations

The following assumptions were considered in deriving the design equations.

- a) Plug flow of reacting mixture.
- b) No radial gradients.
- c) Pseudo-homogeneous reacting system.
- d) Steady state operation.
- e) First order kinetics.

Thus: the mass balance equation is given by

$$\frac{dX}{dz} = KC_{A0} (1-X) \rho_B A / F_{A0} \quad (E.1)$$

The energy balance equations are:

$$\frac{dT}{dz} = - \frac{UA_e}{FC_p} (T - T_c) + \frac{KC_{A0}}{FC_p} (1-X) \rho_B A (-\Delta H) \quad (E.2)$$

(inside the reactor)

$$\frac{dT_c}{dz} = - \frac{UA_e(T - T_c)}{F^* C_p^*} \quad (E.3)$$

(outside the reactor)

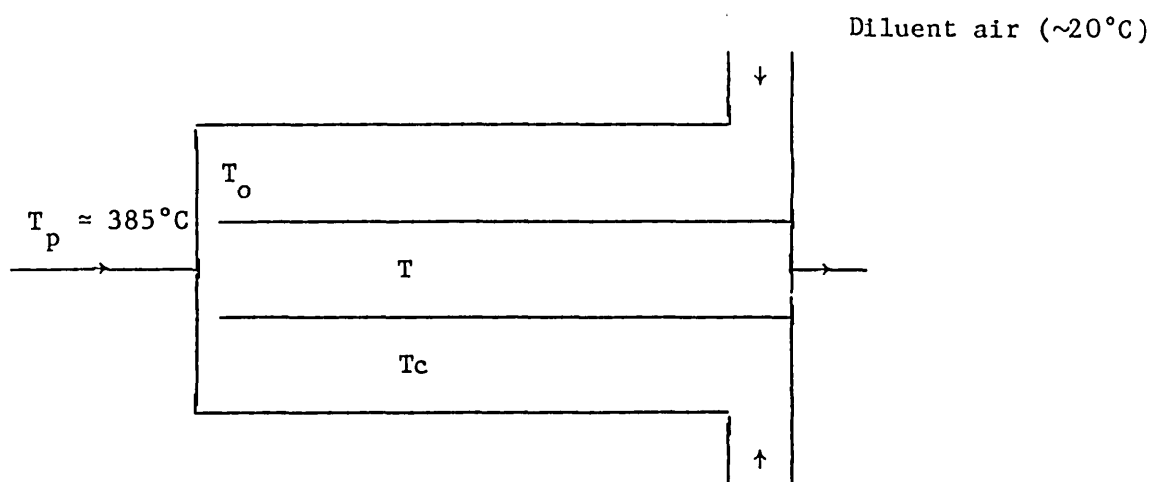
With boundary conditions.

$$\text{at } z = 0 \quad X(0) = X_{in} = 0$$

$$T(0) = T_p$$

$$T_c(0) = T_o$$

$$\text{at } z = L \quad T_c(L) = 20^\circ\text{C}$$



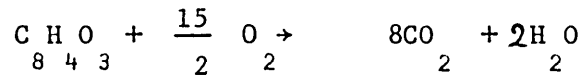
$$\text{where } C_p = \sum Y_i C_{p_i}$$

$$C_p = A_i + b_i T - C_i / T^2$$

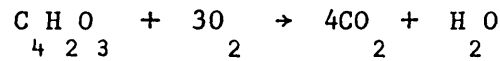
*
 C_p, F^* properties of pure air.

E.4.2 Reaction and kinetics

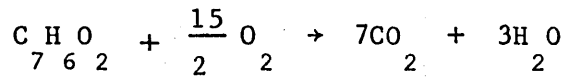
The reactions considered were



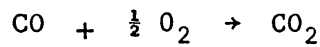
(PA)



(MA)



(BA)



For the purpose of design, the four equations were considered as a single first order reaction with respect to the total concentration of the combustible reacting species.

$$\text{i.e. } r = KC_A$$

$$\text{where } C_A = C_{PA} + C_{BA} + C_{MA} + C_{CO}$$

$$K = K_0 e^{-E/RT}$$

The value of K was assumed to be close to that of methane obtained by Anderson et al. (1963) for methane oxidation.

$$K = \begin{cases} 32.4 \times 10^{-2} \text{ m}^3/\text{Kg hr at } 300^\circ\text{C} \\ 648 \times 10^{-2} \text{ " " " } 450^\circ\text{C} \end{cases}$$

$$\therefore K(T) = 604658 \text{ EXP}(-8273.8/T)$$

E.4.3 Mass/mole balance of the components

Basis: 4 Nm³/hr of air and 176 gm/hr of o-xylene

Specie	Moles in (Kmol/hr)	Moles converted (Kmol/hr)	Moles out for X Conversion Kmol/hr
P A	$F_{O_1} = 1.2299 \times 10^{-3}$	$- X F_{O_1}$	$1.2299 \times 10^{-3} (1-X)$
M A	$F_{O_2} = 1.0771 \times 10^{-4}$	$- X F_{O_2}$	$1.0771 \times 10^{-4} (1-X)$
B A	$F_{O_3} = 1.4432 \times 10^{-5}$	$- X F_{O_3}$	$9.17312 \times 10^{-5} (1-X)$
C O	$F_{O_4} = 9.17312 \times 10^{-4}$	$- X F_{O_4}$	$9.17312 \times 10^{-4} (1-X)$
C O ₂	$F_{O_5} = 1.9719 \times 10^{-3}$	$+ 8X F_{O_1} + X F_{O_2} + 7X F_{O_3} + F_{O_4}$	$1.9719 \times 10^{-3} (1+5.7246X)$
H ₂ O	$F_{O_6} = 8.1928 \times 10^{-3}$	$+ 2X F_{O_1} + X F_{O_2} + 3X F_{O_3}$	$8.1928 \times 10^{-3} (1+1.144X)$
O ₂	$F_{O_7} = 1.4212 \times 10^{-2} + .21 \text{ Fair}$	$-\frac{15}{2} F_{O_1} - 3X F_{O_2} - \frac{15}{2} X F_{O_3} - \frac{1}{2} X F_{O_4}$	$0.21 \text{ Fair} + 2.992 \times 10^{-2} (1-.338X)$
N ₂	$F_{O_8} = 1.4212 \times 10^{-1} + .79 \text{ Fair}$	- - -	$0.79 \text{ Fair} + 1.4212 \times 10^{-1}$
Total	$F_O = \text{Fair} + 1.8447 \times 10^{-1}$		$F = \text{Fair} + 1.8447 \times 10^{-1} (1+0.0447X)$

$$F_O = \text{Fair} + 1.84475 \times 10^{-1} \text{ (Kmol/hr)}$$

$$F(X) = \text{Fair} + 1.84475 \times 10^{-1} (1+0.0447X) \text{ (Kmol/hr)}$$

$$F_{Ao} = F_O - F_{O_7} - F_{O_8} = 2.269354 \times 10^{-3} \text{ Kmole/hr}$$

$$C_{Ao} = F_{Ao} / (4 + F_v)$$

$$\text{where } F_v = \frac{\text{Fair} \times 28.84}{\rho_{\text{air}}}$$

E.4.4 Calculation of heat of reaction

E.4.4.1 Thermodynamics

Heat of combustion of start products at 25°C

0.18568 Kg PA x 22133.36 KJ/Kg	=	4109.7222 KJ
0.01056 Kg MA x 14016.40 KJ/Kg	=	148.0132 KJ
0.02569 Kg CO x 10167.12 KJ/Kg	=	261.1933 KJ
0.00176 Kg BA x 26359.20 KJ/Kg	=	46.3922 KJ
0.001056 Kg TA x 21756.80 KJ/Kg	=	22.9752 KJ
<u>Total</u>		<u>4588.2961 KJ</u>

Average molecular weight of combustible start products

$$M_{av} = \frac{\frac{148.11}{.18568} + \frac{98.06}{.01056} + \frac{122.12}{.00176} + \frac{28.01}{.025696}}{\frac{1}{.18568} + \frac{1}{.01056} + \frac{1}{.00176} + \frac{1}{.025696}} = 97.0219$$

Heat of combustion of the end products = 0.0

From energy balance,

Heat of reaction at 25°C is given by

$$\begin{aligned} \Delta H_{25^\circ\text{C}} &= \text{Heat of combustion of the start products} - \text{heat of} \\ &\quad \text{combustion of the end products.} \\ &= -4588.2961 - 0 \text{ (KJ/.176 Kg o-xylene)} \\ &= -2021851.2 \text{ KJ/Kmol combustible start products.} \end{aligned}$$

T

$$\Delta H_{\text{rxn}}(T) = \Delta H_{25} + \int \Delta n C_{pd} T$$

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E.4.4.2 Heat capacities of components

CO	=	27.6145	+	0.00502T	KJ/Kmol deg.
CO ₂	=	43.2625	+	0.01146T - 667348	" "
H ₂ O(g)	=	34.3925	+	0.00628T	" "
N ₂	=	27.1960	+	0.004184	" "
PA	=	162.791	at	27°C	" "
MA	=	109.45344	at	27°C	" "
BA	=	243.3163	at	121.7°C	" "

E.4.5 Calculation of overall heat transfer coefficient

E.4.5.1 Correlations used

The correlations used for heat transfer parameters were obtained from H.F. Rase (1977).

The wall heat-transfer coefficient (h_w) is given by

$$h_w = h_w^o + 0.0482 \frac{D}{D_p} \left(\frac{D G}{P \mu} \right) \quad (\text{KJ/m}^2 \text{ hr}^\circ\text{C}) \quad (\text{E.5})$$

Effective thermal conductivity, λ_r (for air) is given by

$$\lambda_r = \lambda_r^o + \frac{.01046}{1 + 46 \left(\frac{D}{D_p} \right)^2} \left(\frac{D G}{P \mu} \right) \quad (\text{E.6})$$

$$\text{where } h_w^o = \frac{8.4 \lambda_r^o}{D^{1.33}} \quad (\text{E.7})$$

The overall heat transfer coefficient (U) is given by

$$\frac{1}{U} = \frac{1}{h_w} + \frac{D}{8\lambda_r} \quad (\text{E.8})$$

Values for λ_r^o and h_w^o are reported by H.F. Rase (1977) for various tube diameters and catalytic oxidation reactions. Values of λ_r^o are found to be not so dependent on tube diameter and it is suggested that a value of λ_r^o could be selected and h_w^o obtained from Eq. 7 above in dealing with problems for diameters other than those specified.

E.4.5.2 Sample calculations

The value of $\lambda_r^o = 0.9372$ was selected for the phthalic anhydride catalyst and tube diameter 0.099 m. Considering for example a tube diameter 0.08m,

$$A_e = \Pi D = \Pi(8 \times 10^{-2}) = 2.5133 \times 10^{-1} \text{ m}$$

$$A = \frac{\Pi D^2}{4} = 5.0265 \times 10^{-3} \text{ m}^2$$

$$\text{For diluent air flowrate } (F_v) = 8 \text{ m}^3/\text{hr}$$

$$\begin{aligned} G &= 13.6044 / 5.265 \times 10^{-3} \\ &= 2706.5353 \text{ Kg/m}^2\text{hr} \end{aligned}$$

$$\begin{aligned} \frac{D_p G}{\mu} &= \frac{2706.5353 \times 6.35 \times 10^{-3}}{3.1 \times 10^{-5} \times 3600} \\ &= 154 \end{aligned}$$

$$\begin{aligned} h_w^o &= \frac{8.4 (.9372)}{(0.8)^{1.33}} \\ &= 226.4537 \end{aligned}$$

$$\begin{aligned} h_w &= 226.46537 + 0.0482 \left(\frac{.08}{6.35 \times 10^{-3}} \right)^{154} \\ &= 319.981 \text{ KJ/m}^2\text{hr } ^\circ\text{C} \end{aligned}$$

$$\begin{aligned}\lambda_r &= 0.9372 + \frac{.01046}{1+46 \left(\frac{6.35 \times 10^{-3}}{0.08} \right)} 154 \\ &= 1.2835 \text{ KJ/m hr } ^\circ\text{C}\end{aligned}$$

$$\begin{aligned}\frac{1}{U} &= \frac{1}{319.981} + \frac{.08}{8(1.2835)} \\ &= 91.605 \text{ KJ/m}^2\text{r } ^\circ\text{C}\end{aligned}$$

E.4.6 Solution of design equations

The design Eqs. E.1 to E.4 were solved simultaneously by fourth order Runge-Kutta method. The integration step chosen was 0.001 and convergence was achieved for all the initial conditions chosen.

The parameters which had to be fixed before integration proceeded were the tube diameter, the temperature of diluent air at the inlet end of the feed (T_0) and the diluent air flowrate (F_v). The integration was terminated when the calculated inlet temperature of diluent air from the exit end of the reactor was less than or equal to 27°C .

E.4.7 Results and Discussion

Sample simulation results are presented in Table E.1. Of the tube diameters considered 0.1m was chosen because, as the results show, very high conversions were possible with relatively low hotspot temperatures and moderate reactor lengths. For the 0.05 m tube diameter the conversions were very low and even for small flow rates of diluent air very high values of T_0 were required to get an appreciable conversion. In the case of the 0.15 m tube diameter, the hotspot temperatures were very high and large quantities of catalyst were needed, although there was greater probability of obtaining complete combustion of the reacting mixture.

TABLE E.1

Sample simulation results

Flow rate of air = $8\text{Nm}^3/\text{hr}$ (Diluent air)

T_o (°K)	D = 0.05m				D = 0.1 m				D = .15 m			
	X	L (m)	T_{peak} (°K)	CAT (Kg)	X	L (m)	T_{peak} (°K)	CAT (Kg)	X	L (m)	T_{peak} (°K)	CAT (Kg)
600	.0563	.4830	658	.7587	.6161	.4390	714	2.7583	1.000	.3380	903	4.7784
620	.0745	.5970	658	.9378	.8102	.4580	759	2.8777	1.000	.3710	911	5.2449
640	.1108	.744	659	1.1687	.9427	.4740	809	2.9782	1.000	.4060	917	5.7397
660	.1929	.9040	674	1.420	.9870	.4960	849	3.1165	1.000	.4450	923	6.2911
680	.3941	.9730	722	1.5284	.9973	.5270	878	3.3112	1.000	.4890	929	6.9131
700	.7393	.9150	812	1.4373	.9995	.5640	900	3.5437	1.000	.5370	934	7.5914
Flow rate = $6\text{Nm}^3/\text{hr}$												
600	.0583	.3650	658	.5733	.5614	.2980	817	1.8724	1.000	.234	967	3.3081
620	.0777	.444	658	.6974	.9707	.3090	868	1.9415	1.000	.255	972	3.600
640	.1137	.5430	661	.8529	.9951	.323	902	2.0295	1.000	.278	976	3.9301
660	.1932	.6490	678	1.0194	.9992	.3410	926	2.1426				
680	.3943	.699	730	1.098	.9999	.3630	946	2.2808				
700	.7760	.659	937	1.0352	1.000	.384	960	2.4127				
Flow rate of diluent air = $4\text{Nm}^3/\text{hr}$												
600					.9931	.181	972	1.373	1.000	.144	1048	2.0358
620					.9993	.1900	992	1.1938				
640	.1149	.3550	644	.5576	.9999	.199	1008	1.2504				
660					1.00	.210	1022	1.3195				
680	.4087	.4560	746	.7163								
700	.8692	.433	908	.6802	1.000	.236	1043	1.4828				

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