SELECTIVE OXIDATION OF C₄ HYDROCARBONS
IN A FLUIDIZED-BED REACTOR

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by

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Catalytic reactions between gases and solids are of the utmost industrial importance. Gas-solid catalytic reactors can be divided into two main classes, those in which solids remain stationary such as fixed-bed reactors, and those in which the solids are in motion, such as fluidized-bed reactors.

Fluidized-bed reactors have been used on an industrial scale for over 60 years and during that time a large number of mathematical models have been devised to predict reactor performance. Many of these models apply to gas-solid catalytic processes in which the fluidized-bed operates in the bubbling mode and there have been many reports of laboratory scale tests of the models, in most cases simple first-order kinetic schemes being applied.

The object of the work described here was to apply the models to a more complex form of kinetics in which both consecutive and parallel processes were occurring. The reactions chosen were the catalytic oxidation of C4 hydrocarbons, butane and butenes, in which maleic anhydride was an important product.

Two series of experiments were performed: (i) the determination of the chemical kinetics of the reactions using a small fixed-bed micro reactor, (ii) measurements of conversion and selectivity using a fluidized-bed reactor.
A laboratory pilot-scale fluidized-bed reactor was built to obtain experimental data for comparison with the prediction of the models. The main variables studied were temperature, fluidizing gas flowrate and quantity of catalyst in the reactor, each being varied over as wide a range as possible. An industrial catalyst was used for the investigation.

A number of previously published fluid-bed reactor models were programmed in Fortran and their predictions of conversion and selectivity were compared with the experimental results. In some cases good agreement was found but in others the predictions differed considerably from the measurements. The reasons for this are discussed and suggestions made of ways in which model applications can be improved.
Dedicated to my parents for their endless encouragement and support
Those who embraced (every) excellence and civility, and in cultivating perfection became candles to disciples, did not find their way out of this dark night—they told a legend and went to sleep.

THE RUBĀ‘IYĀT OF UMAR KHAYYĀM
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ABSTRACT

DEDICATION

ACKNOWLEDGEMENT

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3 FIXED-BED AND FLUIDIZED-BED EXPERIMENTAL RESULTS AND DISCUSSION.

Fixed-bed results and analysis. Determination of rate constants. A description of the fluidized-bed experimental results. The presentation of the theoretical results and a comparison with the experimental results. Discussion of the experimental and theoretical results.

4 CONCLUSIONS

Conclusions and suggestions for further work.

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1 INTRODUCTION AND LITERATURE SURVEY

1.1 INTRODUCTION

1.1.1 Gas solid catalytic reactors

Catalytic reactions between gases and solids are of the utmost industrial importance. Gas-solid catalytic reactors can be divided into two main classes, those in which solids remain stationary such as fixed-bed reactors and those in which the solids are in motion. The latter include moving beds, rotary kilns, spouted beds and fluidized beds. Fluidized beds have certain advantages over the alternative designs: (i) high wall-to-bed heat transfer coefficients enable heat to be extracted from, or absorbed by, the reactor with considerable efficiency. (ii) A mechanical advantage is also gained by the relative ease with which solids may be conveyed to and from the bed and, because of the good solids mixing the reactor operates essentially isothermally. Extremely valuable is the large external surface area exposed by the solid to the gas, and this gives a good conversion in fluidized-bed reactors.

For catalytic reactions, the fixed-bed reactor is normally operated continuously. The problem of frequent catalyst regeneration is usually over-come by using a multiplicity of reactors in parallel, or by periodically alternating the feed and regeneration stages.
1.1.2 OBJECTIVE AND METHOD OF APPROACH

1.1.2.1 Objectives

A large number of models have been devised describing fluidized-bed catalytic reactors in the bubbling regime. Testing of these models has generally been carried out by experiment using laboratory-scale equipment with simple first order reactions, limiting the range of conditions under which the model has been investigated and leaving open the question of how well the models work as tools for scale-up.

In this work we compared data for the catalytic oxidation of n-butane and 1-butene to maleic anhydride over a commercial metal oxide catalyst and a vanadium phosphorus oxide (VPO) catalyst with predictions from three representative models, those of Davidson and Harrison (1963), Kunii and Levenspiel (1969), and Kato and Wen (1969).

1.1.2.2 Method of approach

The experiments were performed in two parts: (i) the determination of chemical kinetics for the reactions using a small fixed-bed micro reactor, (ii) the measurements of conversion and selectivity for the catalysts in the fluidized-bed.

The effect of the number of parameters such as the total flow rate, concentration of reactants and
products, the temperature of the fluidized-bed, and the kinetics of the reaction on the applicability of the models were be evaluated.

The rest of this chapter will consist of a literature survey on fluidization and fluidized-bed and fixed-bed reactor models, followed by a critical discussion of n-butane and 1-butene oxidation. Chapter Two describes all the experimental equipment used as well as the experimental procedures. The fixed-bed and fluidized-bed results and discussion are presented in Chapter Three and finally conclusions and suggestions for further work are given in Chapter Four.

1.2 LITERATURE SURVEY
1.2.1 FLUIDIZED-BED REACTORS
1.2.1.1 Introduction

The fluidized-bed is only one of the many types of reactor employed in industry for carrying out gas-solid reactions. It has a number of advantages over its competitors (which have been mentioned before) which are worth noting at the outset.

The use of gas-solid fluidization as an industrial process was started in the early 1930's with the Winkler process for the gasification of coal. The first large scale application of the fluidized-bed technique was in the USA
in the 1940's by a group of oil companies, which included Standard Oil New Jersey, M. W. Kellogg, Shell and Universal Oil Products, and was the Fluid Catalytic Cracking (FCC) process for the manufacture of gasoline. Since then the technique and applications of fluidized-beds have become widespread.

Fluidized-bed reactors are widely used by industry. Zenz (1978) listed over 100 examples of fluid-bed applications up to 1978 and commented that 'fluidization as a unit operation has touched almost every process industry'.

Table 1.1 lists many of the process which have been developed commercially.
<table>
<thead>
<tr>
<th>Classification</th>
<th>Process</th>
</tr>
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<tbody>
<tr>
<td><strong>Catalytic</strong></td>
<td><strong>Non-catalytic</strong></td>
</tr>
<tr>
<td>Petroleum cracking</td>
<td>Fluid coking</td>
</tr>
<tr>
<td>Hydroforming</td>
<td>Ethylene from crude oil</td>
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<tr>
<td>Acrylonitrile production</td>
<td></td>
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<tr>
<td>Chlorinated hydrocarbon production</td>
<td></td>
</tr>
<tr>
<td>Phthalic anhydride production</td>
<td></td>
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<tr>
<td>Melamine production</td>
<td></td>
</tr>
<tr>
<td>Hydrogen cyanide production</td>
<td></td>
</tr>
<tr>
<td><strong>Inorganic chemicals</strong></td>
<td></td>
</tr>
<tr>
<td>Pyrites roasting for sulphuric acid</td>
<td>Miscellaneous sulphide roasters</td>
</tr>
<tr>
<td>Reduction roasting of iron oxide</td>
<td>Calcination of limestone and other quarry products</td>
</tr>
<tr>
<td>Uranium processing</td>
<td></td>
</tr>
</tbody>
</table>
1.2.1.2 General description of fluidization

Fluidization is the operation by which fine solid particles are transformed into a fluid-like state through contact with a gas or liquid. If a fluid is passed upward through a bed of fine particles at a low flow rate, the fluid merely percolates through the void space between the stationary particles. With an increase in flow rate, particles move apart and a few are seen to vibrate and move about in restricted regions. At a still higher velocity, a point is reached when the particles are all just suspended in the upward flowing gas or liquid. The bed is then considered to be just fluidized and is referred to as an incipiently fluidized bed or bed at the point of minimum fluidization. Fig. 1.1 shows the definition of minimum fluidization velocity \( U_{mf} \). In many practical cases the point of minimum fluidization is not clearly observed as in Fig. 1.1(a) and it is then defined by extrapolation as indicated in Fig. 1.1(b). The fluid bed behavior depends on the nature of the fluidizing medium. If it is a liquid, increasing fluid velocity above minimum fluidization produces uniform bed expansion which is known as "particulate fluidization". If the fluidization medium is a gas, further increase in the gas velocity above the minimum fluidization value results in the formation of bubbles which rise through the bed, and burst at the surface of the bed. This is known as "aggregative fluidization".
Figure 1-1 Diagrammatic representation of the minimum fluidization velocity ($U_{mf}$).
1.2.1.3 Two-phase theory of fluidization

This theory was proposed originally by Toomey and Johnstone (1952) and states that "all gas in excess of that necessary to just fluidize the bed passes through in the form of bubbles". Thus, if $Q_T$ is the total volumetric flow rate into the bed, $Q_{mf}$ the minimum fluidization flow rate and $Q_b$ the bubble flow rate,

$$Q_T = Q_{mf} + Q_b$$  \hspace{1cm} (1.1)

or alternatively:

$$U = U_{mf} + Q_b/A_t$$  \hspace{1cm} (1.2)

By this assumption the bed is divided into two phases, a lean or bubble phase and a dense or particulate or emulsion phase which is similar to the bed at incipient fluidization.

In recent years, however, a large number of experimental studies have been reported in which the flow of bubble gas in freely bubbling beds has been measured and the general conclusion drawn has been that in the majority of systems the two phase theory overestimates the visible bubble flow, in some cases by a considerable amount. In other words, in these systems a larger quantity of gas flows through the emulsion phase than is predicted by the theory and this has given rise to a modified two-phase theory. Deviations from the simple theory may be expressed
in the form:

$$\frac{Q_B}{A_t} = U - KU_{mf}$$  \hspace{1cm} (1.3)

where, generally $K > 1$ and can be expanded to:

$$K = 1 + n\delta$$  \hspace{1cm} (1.4)

where $\delta$ is the fractional volume of the bed occupied by the bubbles.

1.2.1.4 BUBBLES IN FLUIDIZED-BEDS

Bubbles which are formed in excess of the minimum bubbling velocity ($U_{mb}$), are one of the most intriguing features of gas fluidized beds.

They have been the subject of many theoretical and experimental studies but largely because of the interaction between bubbles, their behavior in the bed, their instantaneous position, size and shape are difficult to predict with certainty.

Owing to the solids mixing which they induce bubbles are the cause of the observed uniform bed temperature and high heat transfer coefficients between the bed and the wall of the container or immersed objects. They grow by a process of coalescence as they rise toward the surface and their rise velocity is clearly proportional to their size.
A wake of particles is carried at the bottom of the bubble which grows as fresh particles are entrained, thus the wake volume for a particular bubble varies with time, and as they erupt from the bed and the gas they contain escapes into the free board, the wake solids are dumped on to the bed surface. This motion is a major cause of solids mixing in the fluidized bed.

Figure 1.2 Bubble with particle stream lines flowing around it.
1.2.1.4.1 Bubble diameter

The bubbles are considered to grow continuously while passing through the bed until they reach the maximum stable size or reach the diameter of the bed column. Harrison et al. (1961) showed that the maximum stable bubble diameter is attained when the upward velocity of the flowing particles becomes equal their terminal velocity, \( U_T \). The maximum stable bubble diameter, \( D_T \) can be found from:

\[
D_T = \frac{(U_T/0.71)^2}{g} \tag{1.5}
\]

The studies on bubble growth are numerous, noteworthy among the early studies are the work of Yasui and Johnson (1958), Toei et al. (1965), Hiraki, et al. (1965), Kobayashi, et al. (1965), and Baumgarten and Pigford (1960). The bubble diameter and the distance from the distributor can be approximately related by the correlation equation of Kobayashi et al. (1965) as:

\[
d_b = 1.4\rho_p d_p (U/U_{mf})h \tag{1.6}
\]

The above correlation is based on the data obtained using a porous plate as the distributor. For perforated plates the sizes of the bubbles at the surface of the distributor are substantial and therefore must be taken into consideration. According to Cooke et al. (1968) the bubble size at the surface of a perforated plate, \( D_o \), having a number of holes, \( n_o \), can be calculated from:
\[ D_0 = \frac{(6G/\pi)^{0.4}}{g^{0.2}} \]  

(1.7)

based on the work of Davidson and Harrison (1963) where

\[ G = \frac{(U - U_{mf})}{n_0} \]  

(1.8)

Therefore, in general the diameter of bubbles in a fluidized bed can be approximated by:

\[ d_b = 1.4p_d \left( \frac{U}{U_{mf}} \right) h + D_0 \]  

(1.9)

The above correlation is based on the work of Kato and Wen (1969).

There are a number of other published correlations for estimating bubble size in fluidized beds: Rowe (1976) based on X-ray work and examination of the literature:

\[ d_b = (U - U_{mf})^{1/2} (h + H_{mf})^{3/4} g^{-1/4} \]  

(1.10)

Darton et al. (1979):

\[ d_b = 0.54(U - U_{mf})^{2/5} (h + 4A_0^{1/2})^{4/5} g^{-1/5} \]  

(1.11)

where \( A_0 \) is the "catchment area" and is the area of distributor per orifice.
1.2.1.4.2 Bubble rise velocity

By analogy with single bubbles of gas rising in beds of liquid of low viscosity Davis and Taylor (1950) established the following relation for their rise velocity,

\[ U_{br} = 0.35 (gD_r)^{0.5} \]  \hspace{1cm} (1.12)

when the bubble diameter equals the column diameter \((D_r)\), and

\[ U_{br} = 0.711 (g d_b)^{0.5} \]  \hspace{1cm} (1.13)

where \(d_b\) is the diameter of the sphere with the same volume as the bubble.

Davidson et al. (1959) and Harrison and Leung (1968) suggested that this equation may also be applied to single bubbles of gas rising in fluidized beds. They measured the rise velocity for single bubbles in a fluidized bed and proposed the relation:

\[ U_{br} = 0.64 (g d_b)^{0.5} \]  \hspace{1cm} (1.14)

Following Davidson and Harrison (1963), the velocity of rise of a crowd of bubbles through a fluidized bed can be calculated by:

\[ U_b = U - U_{mf} + 0.711 (g d_b)^{1/2} \]  \hspace{1cm} (1.15)

Some authors (eg. Yasui and Johnson, 1958) have reported the bubble rise velocity to be independent of
particle properties but later measurement using X-ray photography (Rowe and Partridge, 1965) showed that, bubble velocity increased by a small but significant amount with decreasing particle size.

A large number of experimental investigations of bubble rise velocities have been reported (Harrison et al., 1967; Kobayashi et al. 1972) but there seems to be little general agreement among them.

1.2.1.5 THE DENSE PHASE
1.2.1.5.1 Voidage

According to the two-phase theory, the dense phase voidage is equal to the voidage at minimum fluidization and is given by:

\[ \varepsilon = \varepsilon_{mf} = \frac{M}{\rho_p H_m A} = 1 - \frac{\rho_{bulk}}{\rho_p} \]  

where \( M \) is the mass of the particles.

Once the bed expansion ratio is known, the voidage from the distributor up to a height corresponding to \( H_{mf} \) and that from \( H_{mf} \) to the top of the bed can be computed as (Kato and Wen 1969):

\[ 1 - \varepsilon = \frac{H_{mf}}{H(1 - \varepsilon_{mf})} \]  

up to \( H_{mf} \), and
from \( H \) to the top of the bed.

However the height of bed \( H \), and consequently the voidage \( c \), can only be considered to be a time average value because the upper surface of the bed is usually uneven and more or less oscillating.

1.2.1.5.2 Solids mixing

One of the most important properties of gas-solid fluidized beds of particles of uniform density is the degree of solids mixing that they can achieve. Bubbles are directly responsible for this particle mixing. Solids mixing through a fluid bed has been extensively studied by a number of workers (Rowe et al., 1962, 1965; Toei et al., 1965; and Rowe, 1971).

Early theories of the mechanism of solids mixing in fluidized beds assumed it to be the result of particle diffusion, but it has been shown (Rowe and Partridge, 1965) that the particle mixing is due to two processes. Firstly a displacement by a spherical solid body moving through a fluid bed, and secondly by the transportation of solid particles to the bed surface in the bubble wakes, the space vacated by the wake particles being filled by particles from positions higher up in the bed.

\[
1-c = \frac{H_{mf}}{H(1-c_{mf})} - \frac{H_{mf}(1-c_{mf})(H-H_{mf})}{2H(H-H_{mf})}
\]
From X-ray observations of single bubbles rising through a bed, the wake fraction of the bubbles has been reported to range between 0.25 and 0.61 (Rowe and Partridge, 1964). Therefore each bubble displaces upwards approximately 0.6 of volume of the bubble.

From continuity and applying the two-phase theory, Rowe (1965) estimated the degree of mixing from the particle circulation time \( t_p \).

\[
t_p = \frac{H_{mf}}{0.6(U - U_{mf})(1 - \frac{U - U_{mf}}{U_b})}
\]  

(1.19)

1.2.1.6 FLUIDIZED-BED REACTOR MODELS

1.2.1.6.1 Introduction

Fluidized beds are notoriously difficult to model because of their complex hydrodynamic behavior and because of complications which arise whenever solid particles of various sizes and shapes are contacted with a fluid phase. The chemical reactions (solid catalysed, heterogeneous and homogeneous) which are carried out in fluidized-bed reactors cover a broad range of conditions, controlling kinetic mechanisms and reaction schemes. In view of these complexities and the wide range of reactions and operating conditions encountered, it is not surprising to find a broad spectrum of reactor models. Some of these models,
especially those for heterogeneous gas-solid reactions are specific to a certain chemical process application. Others are designed as general purpose models, intended to represent a broad range of cases, although they are usually written in terms of simple first order irreversible reaction kinetics.

1.2.1.6.2 Models studied in this work

The three models presented in this work are derived from those introduced by Davidson and Harrison (1963), Kunii and Levenspiel (1969), and Kato and Wen (1969). The details of each are given below.

1.2.1.6.3 The Davidson-Harrison model

The Davidson-Harrison model is one of the fluidized-bed reactor models which are based on bubble dynamics. The model has been developed on the basis of the following assumptions:

(i) emulsion phase gas flows with a superficial velocity of $U_{mf}$ and is either completely mixed or in plug flow,
(ii) bubbles are of uniform size throughout the bed (and hence all have equal velocities),
(iii) reaction takes place only in the emulsion, 
(iv) interphase gas transfer occurs by a combined process of molecular diffusion and through flow (convection):

$$Q = K_c + q$$  (1.20)
The velocity of the fluid which flows as bubbles through the emulsion phase is represented by \( U - U_{mf} \), and from continuity:

\[
NV_{b} U_{b} = U - U_{mf}
\]  
(1.21)

where, 
- \( N \) = number of bubbles per unit volume,
- \( V_{b} \) = bubble volume,
- \( U_{b} \) = bubble rising velocity.

Since the bubbles cause the bed expansion from height \( H_{mf} \) to height \( H \), so:

\[
NV_{b} H = H - H_{mf}
\]  
(1.22)

The absolute bubble velocity is assumed to be:

\[
U_{b} = U - U_{mf} + 0.711(gd_{b})^{0.5}
\]  
(1.15)

where \( d_{b} \) = bubble diameter,
- \( g \) = acceleration due to gravity.

The molecular diffusion can be calculated from the gas diffusivity and the bubble size as:

\[
K_{g} = 0.975D_{g}^{0.5}(g/d_{b})^{0.25}
\]  
(1.23)

where \( D_{g} \) = gas diffusivity.

The convection is also found from the bubble size and the minimum fluidization velocity:
The interphase gas transfer for a rising bubble becomes:

\[ Q = q + K_c S_b \]  \hspace{1cm} (1.25)

where \( S_b \) = surface area of the rising bubble

1.2.1.6.3.1 The model equations

a) Perfectly mixed

(i) Bubble phase

A material balance on a single rising bubble gives the equation:

Flow into the bubble = Flow out of the bubble + Transfer

\[ NV_{b} U_{b} C_{b} = NV_{b} U_{b} (C_{b} + dC_{b}) + NV_{b} Q(C_{b} - C_{e}) dh \]  \hspace{1cm} (1.26)

and,

\[ V_{b} U_{b} \frac{dC_{b}}{dh} + Q(C_{b} - C_{e}) = 0 \]  \hspace{1cm} (1.27)

or:

\[ V_{b} \frac{dC_{b}}{dt} + Q(C_{b} - C_{e}) = 0 \]  \hspace{1cm} (1.28)
Equation 1.27 can be integrated with respect to \( h \), with the boundary condition of \( C_b = C_0 \) at \( h = 0 \), and giving

\[
C_b = C_e + (C_0 + C_e) \exp\left(-\frac{Qh}{V_b U_b}\right) \tag{1.29}
\]

(ii) Emulsion phase

From the material balance on the emulsion phase:

Flow into the emulsion + Transfer =

Flow out of the emulsion + Disappearance by reaction

\[
U_m C_0 + NQ \int_0^H (C_b - C_e) \, dh = U_m C_e + (1-NV_b) \int_0^H r_e \, dh \tag{1.30}
\]

where \( r_e \) is the rate of reaction in the emulsion phase.

Equation 1.30 may be integrated for first order reaction by substitution \( C_b \) from Eq. 1.29 giving:

\[
NV_b U_b (C_0 - C_e) \left(1 - \exp\left(-\frac{QH}{U_b V_b}\right)\right) + U_m f (C_0 - C_e) = KHC_e (1-NV_b) \tag{1.31}
\]

The overall concentration which results from mixing the streams leaving the bubble and emulsion phases at the top of the bed can be calculated as:

\[
U C_h = (U - U_m f) C_b + U_m f C_e \tag{1.32}
\]

\( C_b \) and \( C_e \) are obtained from the Eqs. 1.29 and 1.31 and are substituted in Eq. 1.32. This equation can be rearranged using the Eqs 1.21 and 1.22 to eliminate \( NV_b U_b \) and \( NV_b \),
giving the following expression for the reactant concentration which leaves the reactor:

\[
C_H = C_0 \left( \beta e^{-x} + \frac{(1 - \beta e^{-x})^2}{K' + 1 - \beta e^{-x}} \right) \quad (1.33)
\]

where

\[
\beta = 1 - \frac{U_{mf}}{U}
\]

\[
K' = \frac{K H_{mf}}{U}
\]

\[
X = \frac{Q H}{U_b V_b}
\]

b) Piston flow

With the assumption of piston flow the equation for bed bubble phase in perfectly mixed still applies within each bubble, but the equation for the emulsion phase (1.31) is replaced by a material balance on the emulsion phase.

Flow into the emulsion + Transfer =
Flow out of the emulsion + Disappearance by reaction

\[
U_{mf} C_0 + N Q (C_b - C_e) dh = U_{mf} (C_0 + dC_e) + (1-NV) r_e dh \quad (1.35)
\]
\[
\frac{dC_e}{dh} - NQ(C_b - C_e) + (1-NV)r_e = 0 
\] (1.36)

Over the whole bed within \( dh \) and for a first order reaction, the latter procedure gives a simple result:

\[
U_{mf} \frac{dC_e}{dh} + (U-U_{mf}) \frac{dC_b}{dh} + KC_e(1-NV_b) = 0 
\] (1.37)

The above equation is the result of a material balance on the whole bed. The first two terms are the incremental terms for the bubble and emulsion phases, and the last term represents the disappearance of reactant with the reaction in the emulsion phase. Equation 1.37 can be written in dimensionless form as:

\[
(1 - \beta) \frac{dC_e}{dh} + \beta \frac{dC_b}{dh} + \frac{K'}{H} C_e = 0 
\] (1.38)

Equation 1.27 can be also written in dimensionless form as:

\[
\frac{dC_b}{dh} + \frac{X}{H} (C_b - C_e) = 0 
\] (1.39)

where \( \beta, K', \) and \( X \) have been already defined in Eq. 1.34.

\( C_e \) can be eliminated from between Eqs 1.38 and 1.39, giving a linear second-order differential equation as:
The differential equation 1.40 can be solved with the boundary conditions of \( C_b = C_e = 0 \) and \( \frac{dC_b}{dh} = 0 \) at \( h = 0 \) gives:

\[
C_b = C_0 \left( \frac{m_1 - m_2}{m_1 e^{-m_2 h} - m_2 e^{-m_2 h}} \right) e^{-(m_1 + m_2)h} \quad (1.41)
\]

where \( m_1 \) and \( m_2 \) are the roots of the quadratic obtained from Eq. 1.40, so that:

\[
2H(1-\beta)m = (X + K') \pm \left( (X + K') - 4K'X(1-\beta) \right)^{0.5} \quad (1.42)
\]

where \( m = m_1 \) with the positive sign and \( m = m_2 \) with the negative sign.

Substitution of \( C_b \) from Eq. 1.41 as a function of the bed height \( h \) into the Eq. 1.39 to give \( C_e \) as a function of bed \( h \). The concentration of the reactant at the top the bed can be calculated from these expressions of \( C_b \) and \( C_e \) by substitution \( h = H \) for each phases. The overal concentration can be calculated from the Eq. 1.32 to give the following expression:

\[
C_h = \frac{C_0}{m_1 - m_2} \left( m_1 e^{-m_1 H} \left( 1 - \frac{m_1 HU_{mf}}{XU} \right) - m_2 e^{-m_2 H} \left( 1 - \frac{m_2 HU_{mf}}{XU} \right) \right).
\quad (1.43)
\]
and the conversion can be calculated as:

\[ x = \frac{C_0 - C_H}{C_0} \]  

(1.44)

1.2.1.6.4 The Kunii-Levenspiel model

In developing this model which is also called "the bubbling bed model" a number of simplifying assumption are made:

a) The gas flows as spherical bubbles surrounded by a spherical cloud. Bubbles are of a uniform size and shape
and the velocity of rise a single bubble of diameter \(d_b\) is:

\[ U_{br} = 0.711(gd_b)^{0.5} \]  

(1.13)

The velocity of rise of a crowd of bubbles is related to the velocity of a single bubble by:

\[ U_b = U - U_{mf} + U_{br} \]  

(1.45)

and the size of the cloud is given by:

\[ \left( \frac{d_c}{d_b} \right)^3 = \left( \frac{R_c}{R_b} \right)^3 = \frac{U_b + 2U_f}{U_b - U_f} \]  

(1.46)

where

\[ U_f = \frac{U_{mf}}{\epsilon_{mf}} \]  

(1.47)
b) Bubbles are considered to be empty of solids and so the bubble voidage, \( \varepsilon_b \), is considered to be unity. If \( \delta \) is the volume fraction of bubbles in the bed, the average bed voidage \( \varepsilon_f \) is related to the voidage in bubbles and emulsion by:

\[
\varepsilon_f = \delta \varepsilon_b + (1 - \delta) \varepsilon_e = \delta + (1 - \delta) \varepsilon_e \tag{1.48}
\]

The voidage and bed height are related by:

\[
1 - \delta = \frac{H_{mf}}{H} = \frac{1 - \varepsilon_f}{1 - \varepsilon_m} \tag{1.49}
\]

c) Every rising bubble has an associated wake of material rising behind it. The ratio of wake to bubble volume, \( V_w/V_b \), is found by experiment. This solid is carried up the bed at velocity \( U_b \) and is continually exchange with fresh emulsion solid. At the top of the bed solids rejoin the emulsion to move down the bed at velocity \( U_s \), so:

\[
U_e = U_f - U_s = \frac{U_{mf}}{\varepsilon_{mf}} - U_s \tag{1.50}
\]

Relationship among variables \( d_b, U_b, \delta, U_e, \) and \( U_s \) is given by \( U \) and \( U_{mf} \).
A material balance for the solids crossing any horizontal plane gives:

\[
\begin{align*}
\frac{\text{fraction of cross section where solids are moving downward, hence everywhere but bubble and wake}}{A_t} &= U_s = A_t \left\{ \frac{\text{fraction of cross section where solids are moving upward, hence wake only}}{U_b} \right\} \\
\end{align*}
\]

In symbols this becomes:

\[(1-\delta-\alpha\delta)U_s = \alpha\delta U_s \quad (1.51)\]
where \( \alpha \) is defined as:

\[
\alpha = \frac{\text{volume of emulsion transported upward behind a bubble}}{\text{volume of a bubble}} = \frac{V_w}{V_b} \tag{1.52}
\]

and the downward velocity of solids in the emulsion is:

\[
U_s = \frac{\alpha \delta U_b}{1 - \delta - \alpha \delta} \tag{1.53}
\]

the total flow of gas and the flow in the emulsion phase and bubble phase with its wake is:

\[
U = \left( \frac{\text{void volume of emulsion}}{\text{bed volume}} \right) U_e + \left( \frac{\text{void volume of bubbles and wake}}{\text{bed volume}} \right) U_b
\]

or:

\[
U = (1 - \delta - \alpha \delta) \varepsilon_{mf} U_e + (\delta + \alpha \delta \varepsilon_{mf}) U_b \tag{1.54}
\]

Combining the three equations for \( U_e \), \( U_s \), and \( U \) to eliminate \( U_s \) and \( U_e \) gives an expression relating bubble velocity with \( U \) and \( U_{mf} \), thus:

\[
U_b = \frac{1}{\delta} \left( U - (1 - \delta - \alpha \delta) U_{mf} \right) \tag{1.55}
\]

or:
The upward velocity of gas in the emulsion is found directly by combination of Eqs. 50, 53, 55, and 56 as:

\[ U_e = \frac{U_{mf}}{\bar{c}_{mf}} \left( \frac{\alpha U}{1 - \delta - \alpha \delta} - \alpha U_{mf} \right) \]  

\[ (1.57) \]

d) There are three phases (the bubble, cloud plus wake and the dense or emulsion phase) and the gas interchange between them is calculated on the basis of the Davidson-Harrison model (1963).

Based on unit volume of bubble the interchange coefficient between bubble and cloud, \( k_{bc} \), cloud and emulsion, \( k_{ce} \), and the overall coefficient between bubble and emulsion, \( k_{be} \), can be defined as:

\[ - \frac{1}{V_b} \frac{dN_b}{dt} = - U_b \frac{dc_b}{dt} = k_{bc}(C_b - C_c) \]  

\[ = k_{ce}(C_c - C_e) \]  

\[ = k_{be}(C_b - C_e) \]  

\[ (1.58) \]

\[ (1.59) \]

\[ (1.60) \]

so:

\[ \frac{1}{k_{be}} = \frac{1}{k_{bc}} + \frac{1}{k_{ce}} \]  

\[ (1.61) \]
\[ k_{be} = \frac{\text{volume of gas moving from bubble to emulsion or emulsion to bubble}}{(\text{volume of bubbles in the bed})(\text{time})} \]

e) Evaluation of the interchange coefficients:

Figure 1-4 The gas interchange between the bubble and emulsion phases (Kunii and Levespiel, 1969).

The interchange between bubble and cloud involves both bulk flow across the boundary and mass transfer between gas in the bubble and gas in the cloud, so referring to Fig. 1-4 for a single bubble:
\[ - \frac{dN_b}{dt} = (q + k_{bc}S_{bc})(C_b - C_c) \]  \hspace{1cm} (1.62)

where \( q \) is the volumetric gas flow into or out of a single bubble and \( k_{bc} \) is the mass transfer coefficient between bubble and cloud. From the Davidson model (1963), the value of \( q \) is given by:

\[ q = \frac{3\pi}{4} U_{mf} d_b^2 \]  \hspace{1cm} (1.24)

Davidson and Harrison (1963) derived the following expression for the mass transfer coefficient between bubble and cloud:

\[ k_{bc} = 0.975D_g^{0.5} \left( \frac{g}{d_b} \right)^{0.25} \]  \hspace{1cm} (1.23)

by substituting these two expressions in Eq. (1.62) and matching with Eq. (1.58) interchange coefficient between bubble and cloud-wake region may be found:

\[ K_{bc} = 4.5 \left( \frac{U_{mf}}{d_b} \right) + 5.85 \left( \frac{D_g^{1/2} g^{1/4}}{d_b^{5/4}} \right) \]  \hspace{1cm} (1.63)

Next the model estimates a transfer coefficient between cloud and emulsion. Because there is no flow of gas between these regions, diffusion will be the only mechanism of transfer operating, so:
\[
\frac{-dN^c}{dt} = S k_{ce} (C^c - C^e)
\]  
(1.64)

where \( k_{ce} \) is the mass transfer coefficient between cloud and emulsion.

Analogous to the contact of a bubble with a liquid, the characteristics of this system are equivalent to the contact of a vertical cylinder with the same diameter and height as the spherical cloud (Higbie, 1935), thus:

\[
k_{ce} = \left( \frac{4D_{e mf}}{\pi t} \right)^{1/2} = \left( \frac{4D_{e mf} (U_{br} - U_{fr})}{\pi d_c} \right)^{1/2}
\]  
(1.65)

and in terms of bubble diameter:

\[
k_{ce} = 1.13 \left( \frac{D_{e mf} (U_{br} - U_{fr})}{d_b} \right)^{1/2} \left( \frac{1 - U_f/U_b}{1 + U_f/U_b} \right)_r^{1/6}
\]  
(1.66)

where \( r \) refers to velocities with respect to the emulsion and \( D_e \) is the effective diffusivity of gas in the emulsion phase. Inserting Eq. (1.66) in Eq. (1.64) and matching with Eq. (1.62) gives the coefficient of gas interchange between cloud-wake region and emulsion phase:

\[
K_{ce} = \frac{k_{ce} S_{bc} (d_c/d_b)^2}{V_b} = 6.78 \left( \frac{D_{e mf} (U_{br} - U_{fr})}{d_b^3} \right)^{1/2} \left( \frac{1 + 2U_f/U_b}{1 - U_f/U_b} \right)_r^{1/6}
\]  
(1.67)

or:
In the absence of experimental data, it is assumed the numerical value of $D_e$ is comparable to $D_g$ as follows:

$$D_e \approx \frac{\epsilon}{\epsilon_m} D_g \approx D_g$$  \hspace{1cm} (1.69)$$

Based on the model developed, the mass balance for the flow pattern in a fluidized-bed for flow of gas gives:

$$\{\text{overall}\} = \{\text{reaction}\} + \{\text{transfer to}\}$$

$$\text{disappearance} = \text{in the bubble} + \text{the cloud and wake}$$

$$\{\text{transfer to}\} = \{\text{reaction in the}\} + \{\text{transfer to}\}$$

$$\text{cloud and wake} = \text{cloud and wake} + \text{the emulsion}$$

$$\{\text{transfer to}\} = \{\text{reaction in}\}$$

$$\text{the emulsion} = \text{the emulsion}$$

Restating the above in symbol for an irreversible first-order reaction, and for a single bubble as it ascends through the fluidized bed.

$$- \frac{dC_b}{dt} = - U_b \frac{dC_b}{dh} = K_f C_b = \gamma_b K_{bc} + K_{bc}(C_b - C_c)$$  \hspace{1cm} (1.70)$$

$$K_{bc}(C_b - C_c) = \gamma_c K_{cc} + K_{cc}(C_c - C_e)$$  \hspace{1cm} (1.71)$$

$$K_{ce}(C_c - C_e) = \gamma_e K_{ce}$$  \hspace{1cm} (1.72)$$

where $K_f$ is the effective overall reaction rate coefficient.
which accounts for reaction transport in the bed, and the
γ's are the fraction of solids in each phase defined by:

\[
\gamma_b = \frac{\text{volume of the solids within the bubble phase}}{\text{volume of bubbles}}
\]

\[
\gamma_c = \frac{\text{volume of solids within the cloud & wake phase}}{\text{volume of bubbles}}
\]

\[
\gamma_e = \frac{\text{volume of solids within the emulsion phase}}{\text{volume of bubbles}}
\]

By a material balance these quantities can be related by:

\[
\delta (\gamma_b + \gamma_c + \gamma_e) = (1 - \varepsilon_{mf})(1 - \delta)
\] (1.73)

Since it is assumed that the bubbles are free of solids,
the values for \( \gamma_b \) can be:

\[
\gamma_b \approx 0.001 - 0.01
\]

Values of \( \gamma_c \) can be estimated by considering a spherical
bubble and accounting for solids in both cloud and wake.
This gives:

\[
\gamma_c = (1 - \varepsilon_{mf}) \left\{ \frac{V_c}{V_b} + \frac{V_w}{V_b} \right\}
\] (1.74)

\[
= (1 - \varepsilon_{mf}) \left\{ \frac{3U_{mf}}{\varepsilon_{mf}} \right\} \left\{ \frac{0.711(gd_b)^{0.5} - (U_{mf}/\varepsilon_{mf})}{0.711(gd_b)^{0.5} - (U_{mf}/\varepsilon_{mf})} \right\}
\] (1.75)

The overall reaction rate \( (K_f) \) can be calculated by
combining the Eqs. 1.70, 1.71, and 1.72 and eliminating
concentrations as:

\[
K_f = K \left( \gamma_b + \frac{1}{K_{bc}} + \frac{1}{\gamma_c} \right) + \left( \frac{1}{K_{ce}} + \frac{1}{\gamma_e} \right)
\] (1.76)

and the conversion, \( x \), is given by:

\[
x = 1 - \exp\left(-K_f \tau_b\right)
\] (1.77)

where \( \tau_b \) is the bubble contact time,

\[
\tau_b = \frac{H}{U_{br}}
\] (1.78)

1.2.1.6.5 The Kato-Wen model

This model which is also called the 'Bubble Assemblage Model' is based on multiple bubbles of varying sizes with interchange of gas taking place between the bubble phase and emulsion phase.

The model is based on the following assumptions:

(a) A fluidized bed may be represented by a numbers of compartments in series, \( n_r \). The height of each compartment is equal to the average size of a bubble at the corresponding bed height.

(b) Two phases, the bubble phase and the emulsion phase,
exist in each compartment and the gas flowing through the phases is considered to be completely mixed.

(c) The void fraction within the emulsion phase is considered to be equal to that of the bed at the incipient fluidization condition.

(d) Every bubble has an associated spherical cloud. The diameter of bubbles and that of cloud are given by Davidson (1961) as:

\[ \left( \frac{R_c}{R_b} \right)^3 = \left( \frac{U_b + 2U_{mf}/c_{mf}}{U_b - U_{mf}/c_{mf}} \right) \]  \hspace{1cm} (1.46)

(e) Gas interchange takes place between the two phases. The overall interchange coefficient per unit volume of gas bubbles is given by:

\[ F_d = F_0 + K'M' \]  \hspace{1cm} (1.79)

where,

\( F_d \), is the overall gas interchange coefficient per unit volume of gas bubbles \((1/s)\).

\( F_0 \), the gas interchange coefficient per unit volume of gas bubbles \((1/s)\).

\( K' \), absorption equilibrium constant.

\( M' \), solid interchange coefficient between the bubble phase and emulsion.

Since no experimental data are available for the
particle interchange rate, $M'$, and the absorption equilibrium constant, $K'$, for the reacting gas on the particle surface, the analysis presented in this model will neglect gas interchange due to adsorbed gas on interchanging particle. So the overall gas interchange coefficient equation is reduced to $F_d = F_0$. Therefore, the following equation based on the experimental work of Kobayashi et al. (1967) will be used:

$$F_0 = \frac{11}{d_b} \quad (1.80)$$

The bubble diameter and the distance from distributor can be approximately related by the correlation equation of Kobayashi et al. (1965) as:

$$d_b = 1.4\rho_p d_p \left( \frac{U}{U_{mf}} \right) h + D_0 \quad (1.6)$$

It is assumed that the bubbles grow continually while passing through the bed till they reach the maximum stable size, $D_r$, (or reach the diameter of the bed column) given by:

$$D_r = \left( \frac{U_r}{0.711} \right)^2 \frac{1}{g} \quad (1.5)$$

where $U_r$ is the terminal velocity of the particles.

The bed expansion ratio can be expressed as:
\[
\frac{H - H_{mf}}{H_{mf}} = \frac{U - U_{mf}}{0.711(gd_b)^{0.5}} \tag{1.81}
\]

where \(d_b\) is an average bubble diameter of the bed given by:

\[
d_b = 1.4\rho_p d_p \left( \frac{U}{U_{mf}} \right) \left( \frac{H_{mf}}{2} \right) + D_0 \tag{1.82}
\]

F) The model calculation:

If the height of \(n\)-th compartment is \(\Delta h_n\) where \(n=1,2,3,...\) the height of initial compartment immediately above the distributor becomes:

\[
\Delta h_1 = \frac{D_0 + (m\Delta h_1 + D_0)}{2} \quad \text{or} \quad \Delta h_1 = \frac{D_0}{(1-m/2)} \tag{1.83}
\]

where \(m = 1.4\rho_p d_p (U/U_{mf})\)

and the height of second compartment:

\[
\Delta h_2 = 2D_0 \frac{(2+m)}{(2-m)^2} \tag{1.84}
\]

and that of \(n\)-th compartment becomes:

\[
\Delta h_n = 2D_0 \frac{(2+m)^{n-1}}{(2-m)^n} \tag{1.85}
\]

The number of bubbles in the \(n\)-th compartment is:
The volumes of cloud, bubble phase, and emulsion phase in the n-th compartment can be simultaneously computed as:

\[
V_{cn} = \frac{\pi(\Delta h_n)^3}{6} \left[ \frac{3U_{mf}/\epsilon_{mf}}{U_b - U_{mf}/\epsilon_{mf}} \right] \tag{1.87}
\]

\[
V_{bn} = \frac{N\pi(\Delta h_n)^3}{6} \left[ \frac{U_b + 2U_{mf}/\epsilon_{mf}}{U_b - U_{mf}/\epsilon_{mf}} \right] \tag{1.88}
\]

\[
V_{en} = SA_n - V_{bn} \tag{1.89}
\]

where, \( U_b = 0.711(g\Delta h_n)^{0.5} \)

The gas interchange coefficient based on unit volume of bubbles from the equation, \( F_0 = 11/d_b \), can be shown as:

\[
F_{0n} = \frac{(U_b - U_{mf}/\epsilon_{mf})}{(U_b + 2U_{mf}/\epsilon_{mf})} \tag{1.90}
\]

The material balance for the gaseous reactant around the n-th compartment becomes:

\[
\begin{align*}
\text{(Inlet)}_{\text{from } n-1 \text{ compartment}} & = \text{(Outlet)}_{\text{from } n \text{ compartment}} + \text{interchange} + \text{disappearance} \\
& \text{by reaction}
\end{align*}
\]

for the bubble phase:
\[(SUC_b)_{n-1} = (SUC_b)_n + (F'_0n V_{bn} (C_b - C_e))_n + (r_b V_{cn})_n \quad (1.91)\]

and for the emulsion phase:

\[\left( F'_0n V_{bn} (C_b - C_e) \right)_n = \left( r_e V_{en} \right)_n \quad (1.92)\]

By solving the above equations simultaneously, the concentration of the gaseous reactants in the \(n\)-th compartment becomes:

\[C_{en} = \frac{C_{bn}}{F'_0n} - \alpha_n - \beta_n - (r_{bn}) - \alpha_n C_{bn-1} \quad (1.93)\]

for the bubble phase, and for the emulsion phase:

\[C_{en} = \frac{C_{bn}}{F'_0n} - \gamma_n \bar{C}_{en} \quad (1.94)\]

where,

\[
\begin{align*}
\alpha_n &= \frac{SU}{V_{bn} F'_0n} \\
\beta_n &= \frac{V_{cn}}{V_{bn} F'_0n} \\
\gamma_n &= \frac{V_{en}'}{V_{bn} F'_0n}
\end{align*}
\quad (1.95)
\]

The overall concentration of the reactant which leaves the reactor, from the last compartment, is an average concentration found from the bubble and emulsion phases as:

\[C_n = \frac{H - H_{mf}}{H_{mf}} C_{bn} + \frac{H_{mf}}{H} C_{en} \quad (1.96)\]
1.2.2 THE FIXED-BED REACTOR

The tubular flow reactor is used when it is desired to operate the reactor continuously but without back mixing of reactant and products. In the case of an ideal tubular reactor, the reactant mixture passes through in plug flow, and it is assumed that not only the local mass flow rate but also the fluid properties, temperature, pressure, and composition are uniform across any section normal to the fluid motion. There are in general three types of fixed-bed reactor: differential, mixed, and integral.

A differential flow reactor is one in which the reaction rate is to be constant at all points within the reactor. Since rates are concentration-dependent this assumption is usually reasonable only for small conversions or for shallow reactors. It is not necessarily so in the case of slow reactions where the reactor can be large, or for zero-order kinetics where the composition change can be large.

In a mixed reactor, the composition is constant, and this is usually achieved in a basket-type mixed reactor. As for the differential reactor, the rates are obtained directly from the data, thus making the analysis very quick.

When the variation in reaction rate within the reactor is so large that we choose to account for these variation in the method of analysis, then we have an integral reactor. Since the rates are concentration-dependent, such
a large variation in rate may be expected to occur when the composition of reactant fluid changes significantly in passing through the reactor.

1.2.2.1 Choice of reactor

The following requirements must be taken into account when choosing a reactor:

(i) The reactor must be isothermal.

(ii) The reactor should operate at an appreciable velocity to ensure good heat and mass transfer from gas to particle.

As it requires accurate analysis, the differential reactor was not considered in this work. For technical reasons an integral reactor was employed to obtain the kinetic data. The design of the reactor had to take account of the following:

(a) Reactor length-to-diameter ratio should be large to avoid appreciable axial diffusion effects.

(b) Reactor-to-catalyst diameter ratio should be large to avoid short-circuiting effects.

(c) Catalyst dilution should be avoided as diluted effects may becomes important.

(d) The operating conditions relative to mass of catalyst to flow rate of reactant should be similar to those in the fluidized-bed reactor.

1.2.2.2 Fixed-bed reactor model

In a plug flow reactor the composition of the fluid varies from point to point along a flow path consequently,
the material balance for a reaction component must be made for a differential element of volume. Thus for reactant \( A \), the material balance becomes:

\[
\begin{align*}
F + dF + dL & = X + dX + dF + dX + dX \\
\end{align*}
\]

\[\text{Input} = \text{Output + Disappearance by reaction + Accumulation}\]

It can be seen for volume \( dV \) that:

- input of \( A \), moles/time = \( F_A \)
- output of \( A \), moles/time = \( F_A + dF_A \)
- disappearance of \( A \) by reaction, mole/time:
  \[
  \text{moles } A \text{ reacting} = \frac{\text{moles } A \text{ reacting}}{\text{(volume of differential element)}}
  \]
  \[
  \text{(volume of differential element)} \]
  
  \[
  \text{(time)(volume of fluid)}
  \]

Introducing these three terms in material balance equation we obtain

\[
F_A = (F_A + dF_A) + (-r_A) dV
\quad (1.97)
\]

Nothing that

\[
dF_A = d(F_A X_A) = F_A dX_A
\quad (1.98)
\]

\[
F_A dX_A = (-r_A) dV
\quad (1.99)
This, then, is the equation accounting for A in the differential section of reactor of volume dV. For the reactor as a whole the expression must be integrated. Now $F_{A0}$, the feed, is constant, but $r_A$ is certainly dependent on the concentration of materials or conversion. Grouping the terms accordingly, we obtain:

$$\int_0^V \frac{dV}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

(1.100)

The space-time or contact time, $\tau$, is defined as: time required to process on reactor volume of feed measured at specific condition. Thus:

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

(1.101)

or:

$$\tau = \frac{V}{U_0} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

(1.102)

As a more general expression for plug flow reactors, if the feed on which conversion is based, subscript $o$, enter the reactor partially converted, subscript $i$, and leaves at a conversion designated by subscript $f$, we have:
\[
\frac{V}{F_{A0}} = \frac{V}{C_{A0}u_0} = \int_0^{x_A} \frac{dX_A}{-r_A} \tag{1.103}
\]

or:

\[
\tau = \frac{V}{u_0} = C_{A0} \int_{x_{A1}}^{x_{Af}} \frac{dX_A}{-r_A} \tag{1.104}
\]

For the special case of constant-density system:

\[
X_A = 1 - \frac{C_A}{C_{A0}} \quad \text{and} \quad dX_A = -\frac{dC_A}{C_{A0}} \tag{1.105}
\]

In which case the performance equation can be expressed in terms of concentration.

\[
\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{x_{Af}} \frac{dX_A}{-r_A} = \frac{1}{C_{A0}} \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} \tag{1.106}
\]

\[
\tau = \frac{V}{u_0} = C_{A0} \int_0^{x_{Af}} \frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} \tag{1.107}
\]
1.2.3 OXIDATION OF C4 HYDROCARBONS TO MALEIC ANHYDRIDE

1.2.3.1 Oxidation of butenes to maleic anhydride

Various kinetic studies to investigate the mechanisms for the selective oxidation of C4 hydrocarbons to maleic anhydride have appeared in the literature as reviewed by Varma and Saraf (1979). The increasing application of maleic anhydride in production of alkyd resins, polyesters, fumaric acid, and other food additives is well known. Many investigators have emphasized a two-stage redox mechanism as first proposed by Mars and Van Krevelen (1954) or have used the classical approach of Langmuir and Hinshelwood (Sunderland, 1976) or a combination of these two mechanisms (Brkic and Trifiro 1979).

The oxidation of butene to maleic anhydride is generally believed to proceed with 1,3-butadiene as the primary intermediate (Varma and Saraf, 1978; Ostroushko et al., 1972). Some authors have also included crotonaldehyde (Ai et al., 1970; Seeboth et al., 1976) or furan (Ostroushko et al., 1972) as reaction intermediate together with CO, CO2, acetic acid and other aldehydes as side products.

Brkic and Trifiro (1979) investigated the selective oxidation of 1-butene to maleic anhydride in a continuous flow integral micro reactor over a catalyst consisting of vanadium phosphorus oxide (VPO) alone and various quantities of bismuth molybdate. The probable reaction pattern which they suggested is:
They also investigated the use of bismuth molybdate (Bi/Mo = 2) as a promoter for VPO catalyst. The maleic anhydride yield increased as a result of an increased rate of dehydrogenation of 1-butene to 1,3-butadiene. Sunderland (1976) investigated the kinetics of 2-butene to maleic anhydride in a laboratory scale recycle reactor over $\text{V}_2\text{O}_5$-$\text{P}_2\text{O}_5$ catalyst under isothermal conditions in the temperature range 300-350 °C. 2-butene was found to be oxidized by two competing routes, one leading initially to maleic anhydride and water and the other to a mixture of carbon monoxide, carbon dioxide and water. The carbon monoxide was then further oxidized to carbon dioxide and the maleic anhydride to carbon dioxide and water.

$$8\text{O}_2 + 2\text{C}_2\text{H}_8 \rightarrow 4\text{H}_2\text{O} + 2\text{CO}_2 + 2\text{CO} \xrightarrow{\text{O}_2} 2\text{CO}_2$$

$$\rightarrow \text{H}_2\text{O} + 4\text{CH}_2\text{O}_3 \xrightarrow{2\text{O}_2} \text{H}_2\text{O} + 2\text{CO}_2 + 2\text{CO} \xrightarrow{\text{O}_2} 2\text{CO}_2$$

Recent development in C4 processes for making maleic anhydride have been critically investigated by Varma and Saraf (1979) over a vandyle-Phosphate catalyst (P/V =1.6) supported on silica gel. The yield of maleic anhydride which they found, depended significantly on the valence of
the vanadium ions in the catalyst and the addition of phosphorus was found to decrease the activity of the catalyst. For the purpose of kinetic analysis, the following reaction scheme was used by Varma and Saraf.

\[
\begin{align*}
\text{butene} & \quad \xrightarrow{k_1} \quad \text{butadiene} \quad \xrightarrow{k_3} \quad \text{maleic anhydride (MA)} \\
& \quad \xrightarrow{k_4} \quad \text{side products} \\
& \quad \text{(mainly carbon oxide)} \quad \xrightarrow{k_2}
\end{align*}
\]

The reaction of butene to maleic anhydride has been widely studied by Ai et al. (1970) and Ostroushko et al. (1972). They found the butene transformation proceeds by consecutive steps:

\[
1\text{-butene} \quad \longrightarrow \quad \text{butadiene} \quad \longrightarrow \quad \text{furan} \quad \longrightarrow \quad \text{MA} \quad \longrightarrow \quad \text{CO, CO}_2
\]

1.2.3.2 Oxidation of n-butane to maleic anhydride

Kinetic studies on the selective oxidation of n-butane to maleic anhydride are far fewer in number than those reported for butene. An early paper by Breton et al. (1952) described the oxidation of C\textsubscript{4} hydrocarbons over silver, silver oxide and vanadium pentoxide catalyst. They found n-butane to be quite resistant to oxidation over silver and silver oxide catalyst, while V\textsubscript{2}O\textsubscript{5} catalyst proved to be non-selective, resulting in complete combustion. Hartig (1954) has reported an appreciable yield of maleic
anhydride from butane. He employed an unsupported cobalt or nickel molybdate in a fluidized solid reactor. Carbon dioxide or carbon monoxide were the only by products in greater than trace quantities. Bissot and Benson (1963) studied the kinetics of n-butane oxidation to maleic anhydride over a cobalt molybdate catalyst in a fluidized-bed reactor in a temperature range between 425 and 475°C. The air-butane ratio in the feed was 20. The reaction was modeled with two consecutive first order reactions: dehydrogenation of n-butane and decomposition of maleic anhydride.

\[
\text{butane} \rightarrow \text{butene} \rightarrow \text{maleic anhydride} \\
\text{CO}_2, \text{CO}, \text{and water}
\]

The dehydrogenation of n-butane was rate controlling with the intermediate oxidation of butene to maleic anhydride being very rapid, and having no influence on the kinetics of the overall reaction. A number of n-butane investigations were carried out by Agasiev et al. (1969) on Co-Mo-O and V-Mo-O catalyst. The V-Mo-O catalyst was more active, although the yield of maleic anhydride was quite low (18% based on moles of n-butane reacted). The reaction was first order in n-butane with activation energy of 19.5 kcal. per mole. They later developed a complex catalyst consisting of cerium chloride and Co-Mo oxides supported on silica. A higher yield of maleic anhydride resulted (29.8% based on moles of n-butane reacted at 490 °C) and the
concentration of n-butane in the feed was relatively high at 4.7%.

Escardino et al. (1973) have studied the mechanism of kinetics of this reaction over a 55.5% V_2O_5—44.5% P_2O_5 catalyst at reaction temperature of 400 to 480°C. They found that the oxidation rate was controlled by both the oxygen chemisorption and the surface oxygen reaction with the butane gas. At large butane pressure (20 torr at 400°C), the rate determining step was the oxygen chemisorption, whereas at low butane pressure (below 7 torr) the reaction step was rate controlling. At partial pressures of butane less than 7.5 mmHg, the behavior of the butane oxidation reaction may be predicted with three single pseudo-first-order reactions:

\[
\begin{align*}
n\text{-butane} & \quad \xrightarrow{k_1} \quad \text{maleic anhydride} \\
\downarrow k_2 & \quad \text{CO, CO}_2, \text{H}_2\text{O} & \quad \downarrow k_3 & \quad \text{CO, CO}_2, \text{H}_2\text{O}
\end{align*}
\]

Varma and Saraf (1979) estimated reaction velocity constants (g/mol/(kg of cat. h. atm)):

\[
k_1 = (1.44 \times 10^5) \exp(-7180/T)
k_2 = (7.20 \times 10^5) \exp(-9301/T)
k_3 = (2.53 \times 10^4) \exp(-5558/T)
\]

where T is reaction temperature in °K.
The entire literature on n-butane oxidation to maleic anhydride over V-P-O catalyst makes no mention of detectable amount of butenes or 1,3-butadiene. However, Agasiev et al. (1969) reported detectable quantities of 1 and 2-butene in their studies with Co-Mo-O and V-Mo-O catalysts at 420 to 500 °C with four mole percent n-butane in feed. In the oxidation of n-butane, lattice oxygen can play a role similar to that which it plays in other selective oxidations. The reaction can take place in the absence of O₂(g). The fact that oxidations, total and partial, continued in the absence of gas-phase oxygen until very low average oxidation state of vanadium (AV) values are reached indicates that bulk lattice oxygen must have been capable of diffusion through the lattice at the substantial rate to react at the surface (Hodnet, 1984). When n-butane, in an oxygen free atmosphere, is passed over some V-P-O catalysts a considerable amount of maleic anhydride was formed and continued to be formed until the catalyst reached an AV value between 4⁺ and 3⁺, indicating that some bulk and not only surface lattice oxygen must have been incorporated into the reaction products. The increased activity with unchanged selectivity were observed (Hodnet and Delmon, 1984) for reduced catalyst with high P:V ratios indicates that an increased absolute amount of lattice oxygen capable of selective oxidation become available. The oxidation of n-butane at low and high hydrocarbon concentrations on vanadium(iv)-phosphorus mixed oxide has been extensively studied by some workers.
It has been shown the formation of olefins from n-butane oxidation at high n-butane concentration with total consumption of the inlet oxygen, the formation of olefins from n-butane was not observed when there was not total consumption of the oxygen at low n-butane concentration (Centi et al.; 1985). A greater number of studies involving catalytic materials with various P/V ratios have been reported, although these systems probably do not have single phase compositions (Hodnet, 1984;Morselli et al., 1978; Martini, 1982; Nakamura, 1974). Many of these studies have also involved 1-butene oxidation beside n-butane oxidation.

1.2.3.3 Oxidation catalyst

A number of catalysts which allow the formation of oxygenated products from hydrocarbons have been discovered. The principal catalysts used in selective oxidation of C4 hydrocarbons, both saturated and unsaturated, are mixed oxides of vanadium and phosphorus, they so-called VPO materials. In these systems the oxidation state of vanadium appears to be the crucial factor in their performance, a high concentration of the V\(^{4+}\) state favoring selective oxidation and the V\(^{5+}\) state promoting complete conversion to carbon oxides and water. The structures of VPO catalyst were first studied in detail by Bordes and Courtine (1979). They showed that the oxidation state of vanadium depends on three factors: (i) the nature of the precursors, (ii) the gaseous atmosphere during calcination, (iii) the phosphorus
content. However, notwithstanding the academic and scientific effort in recent years on the characterization of this catalytic system, some questions are still open. In particular, a survey of patent literature (Wohlfahart, et al., 1980; Hodnett, 1985) indicates a large number of preparation procedures which differ in respect of (i) the solvent utilized (water or an organic solvent), (ii) the starting vanadium compound (such as $V_2O_5$, $NH_4VO_3$, or $VOPO_4$), (iii) the reducing agent ($HCl$, oxalic acid or other organic acid, the organic solvent itself, other reducing agent), and (iv) the P:V ratio and activation procedure. In spite of the great number of parameters varied in the preparation procedure, a general aspect is that the preparations which utilize an organic solvent and reducing agent, lead to catalysts which are more active as compared to those prepared with water as the solvent (Cavani, et al. 1983; Cavani, et al. 1985; Bordes, and Courtine 1985; Schneider, 1977).

Recently Guido et al (1986) reported difference in line intensities in the X-ray diffraction patterns of $(VO)_{2}P_{2}O_{7}$ prepared utilizing water or an alcohol as the solvent. Also Bordes et al. (1979, 1984, 1985), studying the preparation of $(VO)_{2}P_{2}O_{7}$ with different procedures, found different forms of $(VO)_{2}P_{2}O_{7}$ ($\beta$ and $\gamma$). It has been reported that the best catalysts have a P:V ratio of 1 or somewhat higher than 1 (Van Gleem, and Nobel, 1986). Activity decreases with increasing P:V ratio but selectivity increases (Cavani et al 1985). It is also
suggested (Sleight, 1987) that the best VPO catalysts are made through a \( (VP)_2H_2O(PO_3OH) \) precursor which contains some \( VO(H_2PO_4)_2 \) if the P:V ratio exceeds 1. Optimum catalytic properties are obtained if the precursor is prepared under nearly anhydrous conditions.

Although most investigations of butane and butene conversion have used vanadium-phosphorus-oxygen catalysts, molybdenum based catalysts have been the subject of far fewer investigations. Pasquon et al. (1973) have studied the oxidation of butene to maleic anhydride on iron molybdate catalysts and have attributed the formation of maleic anhydride to the presence of adsorbed oxygen on tetrahedrally coordinated molybdenum (V) ions. The same argument was forwarded by Trifiro et al. (1973, 1974) for the oxidation of butenes to maleic anhydride on manganese, iron, cobalt, and cadmium molybdate. In their study of oxidation of butene over \( \text{CdMoO}_4 \), Trifiro et al. (1973) reported the formation of only butadiene and carbon oxides. Investigations of the selective oxidation of butenes over bismuth molybdate catalyst have been restricted to the oxidative dehydrogenation step (Adams, et al., 1964).

1.2.3.4 Kinetics and mechanism

In several of the studies already referred to attempts were made to fit kinetic schemes to rate data. Thus Varma and Saraf using an integral reactor applied the two-stage redox model of Mars and Van Krevelen to their data and
found good agreement. For a reaction stoichiometry of:

\[ \text{RH} + \alpha_0 \text{O}_2 \rightarrow \text{products} \]

the rate expression is:

\[ R = \frac{k_h k_0 p_h p_o}{k_0 p_0 + \alpha_0 k_h p_h} \quad (1.108) \]

which may be linearised to:

\[ \frac{1}{R_h} = \frac{1}{\alpha_0 k_h p_h} + \frac{1}{k_0 p_0} \quad (1.109) \]

where

- \( k_h \) = rate constant for hydrocarbon.
- \( k_0 \) = rate constant for oxygen adsorption.
- \( p_h \) = partial pressure of hydrocarbon.
- \( p_o \) = partial pressure of oxygen.
- \( \alpha_0 \) = average number of moles of oxygen required per mole of hydrocarbon (stoichiometric number).

The validity of the redox model implies that the reaction takes place between the hydrocarbon in the gas phase and the oxygen ions of the oxide lattice. Sunderland (1976) has studied the kinetics of 2-butene oxidation in a laboratory scale reactor over a \( \text{V}_2\text{O}_5-\text{P}_2\text{O}_5 \) catalyst. It is interesting to note that two-stage redox model proposed by Mars and Van Krevelen (1954) is not very different from the
findings of Sunderland that the reaction between gaseous butene and adsorbed oxygen was controlling. Varma and Saraf (1976) reported that below 1 mole percent concentration of butene in the feed, its disappearance can be represented by first order kinetics. Similar results have been reported by Ai et al. (1970) and Ostroushko et al. (1972). Cavani et al. (1983) studied butene oxidation in both differential and integral reactors and found the differential data to be in agreement with the Langmuir-Hinshelwood (1940) mechanism where the rate determining step for maleic anhydride formation is the surface reaction between adsorbed oxygen on a single site and the inter-mediate butadiene and adsorbed oxygen on two adjacent sites.
CHAPTER 2

EXPERIMENTAL TECHNIQUES
2 EXPERIMENTAL TECHNIQUES

2.1 Experimental requirements

In section 1.2 it was shown how kinetic data may be obtained from the reactant gas breakthrough from a fixed bed reactor under certain conditions, for the reaction mechanism:

\[
\text{butene} \xrightarrow{k_1} \text{butadiene} \xrightarrow{k_2} \text{furan} \xrightarrow{k_3} \text{MA} \xrightarrow{k_4} \text{CO}_2
\]

It was also indicated that below 1 mole percentage concentration of reactant in feed, the rate equation can be represented by first order kinetics. The kinetic data can be obtained by measurement of inlet and outlet reactant and product concentrations of catalyst mass, feed flow rate and temperature. By using the kinetic data obtained from the fixed-bed reactor, the efficiency of a fluidized-bed reactor was determined. Thus the reaction was followed in the same way in each case the same analysis equipment was used. These requirements were:

(i) A fixed-bed reactor system, which could be operated isothermally at temperatures 250-500 °C with suitable means of monitoring of inlet and outlet gas compositions, the flow rate and bed temperatures and pressure.

(ii) A three dimensional fluidized-bed reactor system with properties similar to those of the fixed bed system.

An overall view of the apparatus is shown in Plate 1-1.
2.2 THE FIXED-BED REACTOR SYSTEM

The apparatus shown on the Plate 2.2 was used to study the catalytic oxidation of C_4 hydrocarbons. The schematic diagrams of the main and sample flow system are given in Fig. 2.1 and 2.2. The specification of the major items of equipment are given in Table 2.1. The experiments carried out in this apparatus are described in section 2.6.

2.2.1 Materials of construction

The chemically contrasting characteristics of the reactant gaseous and products and the temperatures at which the reactions were to be carried out made the choice of constructional materials somewhat difficult.

Stainless steel was found to be satisfactorily corrosion resistant and the most suitable material that could be used for the reactor and all the sampling lines, where the temperature had to be kept above 200 °C to prevent condensation of some products.

All valves between the fixed-bed reactor and the analyzing system were stainless steel. All connections and pipe works from the mixing tee, MT, to the analyzing system were in 3.18mm thin walled stainless steel tubing. The air line connections were in 6.35mm and 3.18mm outside diameter copper tubing. The hydrocarbon/nitrogen and oxygen feed line were in 3.18mm o.d. copper tubing. Silica gel and molecular sieve containers were made from brass.
Figure 2-1  Fixed bed flow system
Figure 2-2 Flow diagram of the analytical system
<table>
<thead>
<tr>
<th>Item</th>
<th>Size</th>
<th>Material</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valve V1</td>
<td>1.27cm(1/2&quot;)</td>
<td>Steel</td>
<td>Diaphragm</td>
</tr>
<tr>
<td>Valves V2,V3</td>
<td>6.35mm(1/4&quot;)</td>
<td>Glass/metal</td>
<td>Pressure regulators with filter and water trap</td>
</tr>
<tr>
<td>Valves V4,V5</td>
<td>3.18mm(1/8&quot;)</td>
<td>Stainless steel</td>
<td>needle valve</td>
</tr>
<tr>
<td>Valves V6,V7</td>
<td>6.35mm(1/4&quot;)</td>
<td>Brass</td>
<td>ON/OFF toggle valve</td>
</tr>
<tr>
<td>Valve V9</td>
<td>6.35mm(1/4&quot;)</td>
<td>Stainless steel</td>
<td>ON/OFF valve</td>
</tr>
<tr>
<td>Valves V10,V11, V12,V13</td>
<td>6.35(1/4&quot;)</td>
<td>Stainless steel</td>
<td>3 way valve</td>
</tr>
</tbody>
</table>

**Mass Flow meters**

<table>
<thead>
<tr>
<th>Item</th>
<th>Range</th>
<th>Type</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-50</td>
<td>0-50 cc/min. air f.s.d</td>
<td>Hasting (manufacture)</td>
<td></td>
</tr>
<tr>
<td>F-300</td>
<td>0-300 cc/min. air f.s.d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-500</td>
<td>0-500 cc/min. air f.s.d</td>
<td>Digital type</td>
<td></td>
</tr>
</tbody>
</table>

**Pressure devices**

<table>
<thead>
<tr>
<th>Item</th>
<th>Range</th>
<th>Material</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regulators</td>
<td>6.35mm-6.35mm</td>
<td>Glass/Metal</td>
<td>Norgren (manuf) with water trap</td>
</tr>
<tr>
<td>Pressure gauge</td>
<td>3.18 i.d. inlet</td>
<td>metal Bourden-type</td>
<td>diaphragm</td>
</tr>
<tr>
<td>Mercury manometers</td>
<td>3.18mm arms</td>
<td>Glass/Hg</td>
<td>Home made</td>
</tr>
<tr>
<td>Thermocouples</td>
<td>1mm dia. sheathing</td>
<td>stainless steel</td>
<td>Chromol/alumel</td>
</tr>
<tr>
<td>T1,T2,T3</td>
<td>0-1000 C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2.2 Gas supply, metering and control

Air for the reaction system was supplied from the 6 bars laboratory main via a molecular sieve drier and a pressure reducing valve. All other gases were supplied from cylinders: 1.25% vol%vol n-butane or 1-butene in nitrogen, and oxygen for the reactor and hydrogen and helium for the analysis system.

The mainstream gas (nitrogen or oxygen) was selected by setting the three position (nitrogen-off-oxygen) valve, and the on/off valve (V6) and the needle valve (V4). The reactant gas (n-butane or 1-butene/nitrogen) was set by the on/off valve (V7) and the needle valve (V5). This rather complicated selection valve system was provided in order to minimize the risk of accidentally selecting the hazardous mixture, air and hydrocarbon. Mass flow meters F300 and F500 were calibrated to read volumetric flow (ml/min.) for all four gases. A reactor bypass was provided by means of a 3-way valve V10, so that the inlet feed to the reactor could be diverted to the analytical system for analysis.

The reactor stream was heated to the reactor temperature in a 15 cm long by 2 cm diameter coil of 2.5 m of 3.18 mm o.d. stainless steel tubing maintained within the fluidized bath, FB.
2.2.3 The fixed-bed reactor

The fixed-bed reactor consisted of a stainless steel tube 151 mm long, 4.45 mm internal diameter. The temperature of the mixture entering and leaving the reactor was controlled by two chromel/alumel thermocouples, T1, T2, connected to a digitron 275 potentiometer. The reactor was heated to the required temperature by being kept in a fluidized bath, FB, by connection into an 3.18 mm steel plate which had had two 3.18mm Swagelock couples welded in the top. Different amounts of catalyst up to 2g could be put into the reactor, and were kept in it by two silica wool plugs. Schematic diagram for the fixed-bed reactor is shown in Fig. 2.3.

2.2.4 Fluidized bath construction

The preheater and the reactor were placed in a fluidized-bed heater as shown in Fig. 2.3. It was constructed of a steel tube 15cm diameter, 48cm high, filled with sand, fluidized by compressed air. The fluidized bath was heated by three 1KW 4A Klippon electrical band heaters situated around the outside of the tube. The heating was controlled by two 10A(maximum) output Test Temp temperature controllers with chromel/alumel thermocouples(TT1, TT2), situated inside the bath.

The distributor consisted of two stainless steel plate perforated with a series of holes, with a disk of gauze in between to prevent any loss of particles. The top of the
Figure 2-3  Fixed-bed reactor (sectional)

Legend
1. inlet tube  2. windbox with 6.35mm dia. glass balls
3. heating tape  4. distributor plate  5. flanges secured
   with 6x7.94mm steel bolts  6. inlet thermocouple-reactants
7. fixed-bed reactor  8. glass wool  9. catalyst charge
10. preheater coil  11. band heaters  12. outlet
    thermocouple  13. asbestos box  14. fluidized bath
15. glass fibre lagging  16. two control thermocouples
17. inlet tube  18. fluidized bath thermocouple
19. reactor outlet  20. top cover plate (see Fig. 2-4).
fluidized bath was also covered with gauze to prevent any elutriation of particles. The reactor and the preheater were hung from a strip of steel situated on top of the fluidized bath, as well as a thermocouples measuring the temperature of the bed itself. The bath was insulated with glass fiber lagging and placed in an asbestos box.

Figure 2-4  Top securing plate

Legend
1  45-micron mesh  
2  upper securing plate  
3  Swagelock connector (inlet & outlet)  
4  thermocouple well  
5  base plate
2.3 THE FLUIDIZED-BED REACTOR APPARATUS

The fluidized-bed reactor apparatus which was used for the study of the selective oxidation of \( \text{C}_4 \) hydrocarbons is shown in diagram Fig.2.5 and Plate 2-3. The alphanumeric codes in the text refer to the corresponding codes in this schematic diagram. The specification of the major items of the equipment are given in Table 2.2.

2.3.1 General description

The flow rate of air was controlled by a pressure regulator and a needle valve, and was measured by a range of two rotameters covering a range from 2-300 l/min. The air was then preheated before being mixed with the flow of the reactant. The gas mixture then entered the windbox of the reactor where a sample point allowed an analysis of the reactants just before the reactor. The gas stream then passed through the catalyst in the reactor at a controlled temperature.

The sample of the oxidized products could be taken either from the top of the fluidized-bed reactor, just above the catalyst level, or from the top of the disengaging section, just before the reacted gases enter to the external cyclone, where the possible elutriated catalyst could separated from the main stream which was directed to the waste.

The temperature of the gas mixture was measured in many points of the system by chromel/alumel thermocouples.
Figure 2-5 Schematic diagram of fluidized-bed flow system
<table>
<thead>
<tr>
<th>Item</th>
<th>Size/Capacity</th>
<th>Material</th>
<th>type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valve V20</td>
<td>inlet max.150psi</td>
<td>steel</td>
<td>pressure reducing</td>
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<tr>
<td></td>
<td>outlet 0-60psi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Valve V35</td>
<td>6.35 mm</td>
<td>stainless steel</td>
<td>3-way valve</td>
</tr>
<tr>
<td>Valve V45</td>
<td>3.18 mm</td>
<td>glass/PTFE</td>
<td>3-way capillary</td>
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<td>Valves V21,</td>
<td>2.54 cm</td>
<td>steel/rubber</td>
<td>diaphragm ON/OFF</td>
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<tr>
<td>V23, V30,</td>
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<td></td>
<td></td>
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<td>V31</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Valves V22,</td>
<td>1.905cm</td>
<td>steel/rubber</td>
<td>diaphragm ON/OFF</td>
</tr>
<tr>
<td>V24, V27-V29, V32, V36-V40</td>
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<tr>
<td>Valves V25,</td>
<td>1.905cm</td>
<td>brass</td>
<td>Globe valve</td>
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<tr>
<td>V33, V41</td>
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<td>Valves V26,</td>
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<td>fine needle valve</td>
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<td>V34, V42</td>
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<tr>
<td>Valves V43,</td>
<td>6.35mm</td>
<td>steel/PTFE</td>
<td>needle/regulating</td>
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<tr>
<td>V44</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Valves V46-</td>
<td>3.18mm</td>
<td>glass/PTFE</td>
<td>vacuum tap</td>
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<tr>
<td>V48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Valves SV1,</td>
<td>240v, 50Hz</td>
<td>steel</td>
<td>solenoid valves</td>
</tr>
<tr>
<td>SV2</td>
<td>max. pressure 10bar</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Pressure devices
Pressure gauge, P1-P4
- 6.35mm brass Fischer (manufacturer)
- 0-30psi
Pressure gauge, P5,P6
- 6.35mm steel Norgren (manufacturer)
- 0-100psi
Manometer, M1, M2
- 0-1atm Hg/glass Home-made
Air filter, F1 Course glass/metal/plastic Norgren (manufacturer) Type F13-A3
Air filter, F2 Fine as above Type F50-308A
Flow Devices
Rotameter, R1 32-280L/min. glass tube/SS float Metric 18xP
Rotameter, R2 10-66L/min. glass tube/SS float Metric 10xP
Rotameter, R3 6-22L/min. glass tube/dural float Metric 7xP
<table>
<thead>
<tr>
<th>Item</th>
<th>Range</th>
<th>Material/Specifications</th>
</tr>
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<tbody>
<tr>
<td>Rotameter, R4</td>
<td>2-21L/min.</td>
<td>Glass tube/ ceramic float Metric 7xE</td>
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<tr>
<td>Rotameter, R5</td>
<td>1-10L/min</td>
<td>Glass tube/ ceramic float Metric 7xP</td>
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<tr>
<td>Rotameter, R6</td>
<td>0.5-4L/min.</td>
<td>Glass tube/ dural float Unknown origin</td>
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<td>Mass Flow Meter, F-300</td>
<td>0-200ml/min.</td>
<td>Metal Hasting(manuf)</td>
</tr>
<tr>
<td>Mass Flow Meter, K5000</td>
<td>0-1700ml/min.</td>
<td>Metal Teledyne-Hasting Raydist(manuf) (based 1-butene)</td>
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<tr>
<td>Thermocouples</td>
<td>12 OFF</td>
<td>Chromel/alumel</td>
</tr>
<tr>
<td>Band Heaters</td>
<td>20 OFF</td>
<td>1mm dia. sheathing with stainless steel 0-1000 °C</td>
</tr>
<tr>
<td>Safety Devices</td>
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<td>10.2cm x 11.5cm dia. metal/ceramic 400W, 1.7A</td>
</tr>
<tr>
<td>Bursting disc</td>
<td></td>
<td>Ruptures at 22psi at 22°C stainless steel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18psi at 350°C</td>
</tr>
<tr>
<td>Flow Sensors</td>
<td>2 OFF</td>
<td>Light sensing FLOS CAN</td>
</tr>
<tr>
<td>Saffire Flashback</td>
<td>0-16psi for 1-butene</td>
<td>B.O.C England (manuf)</td>
</tr>
<tr>
<td>Arrestor</td>
<td></td>
<td>Operating pressure</td>
</tr>
<tr>
<td>Differential Temp. Sensor</td>
<td></td>
<td>0-80 °C range Home-made</td>
</tr>
<tr>
<td>Also:</td>
<td></td>
<td>1 24-point input thermocouple switching device, Digitron(manu)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 10-point electronic thermometer, type 1601 Comark (manuf)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 0-999 °C Newtronic temperature controllers (15A max. output).</td>
</tr>
</tbody>
</table>
connected to a Digitron 275 potentiometer.

PLATE 2 shows a photograph of the fluidized-bed reactor system.

2.3.2 Material of construction

Because of the highly exothermic reaction of oxidation of the hydrocarbons, it was necessary that all equipment in contact with the hot gas stream to be made from stainless steel, i.e. preheater, reactor, internal cyclone and sample probes. All the sample probes were made from 3.18mm o.d. wide bore stainless steel tubing and all pipe work from the rotameter board to the reactor system were in 1.27cm o.d. stainless steel tubing. Glass was used for the rotameters and were connected to the metal system by neoprene.

2.3.3 Preheaters construction

Diagrams of hydrocarbon preheater and air preheater are given in Fig.2.6 and Fig.2.7 respectively. They were constructed from a 0.686m. long, 11.3cm. i.d. tube with 9.5mm. thick 14.9cm. o.d. stainless steel flanges at the ends.

The bottom of the air preheater was connected to a windbox by a 9.53mm. thick, 15cm. diameter flange. A 1.59mm. thick, 15cm. diameter stainless steel grid plate with 9.53mm. holes was secured between the windbox and the air preheater section. The top of the air preheater was connected to a mixing chamber section by a 9.53mm. thick
Figure 2-6  Air preheater and mixing chamber construction

Legend
Figure 2-7  1-butene preheater construction (sectional)

Legend
1. ss inlet pipe  2. preheater tube  3. band heaters
4. packed with 6.35mm rasing rings  5. securing nut & niple  6. control thermocouple  7. asbestos gasket
8. 3.18mm screws 12 off  9. heating tape  10. outlet pipe
11. porous ss distributor plate  12. cover plate
13. thermocouple (measuring)  14 upper preheater flange
15. Grylock couple
and 15cm. diameter flange. Two 11.43cm. diameter stainless steel porous plate were fitted, one between the bottom of mixing chamber and preheater section, and the other between the upper mixing chamber flange and the reactor system.

Each of preheaters was heated by five 400W 11.43cm. diameter band heaters. Power was supplied by two 15A (maximum) proportional controller. The temperature of the stream gas was monitored by a thermocouple which was inserted through Darllium connector ports located in the mixing chamber.

2.3.4 Fluidized-bed reactor

The fluidized bed consisted of two main sections: the reactor tube and disengaging section, connected together by 9.53mm. thick 15cm. diameter flanges secured by eight 4mm. high-tensile strength steel bolts. They were made gas-tight by a 1.59mm. thick 15cm diameter asbestos gasket ring.

The 0.838m. long 11.43cm. i.d. reactor was constructed from stainless steel tube fitted with 9.53mm. thick 15cm. diameter flanges at both end. It was furnished with eight chromel/alumel thermocouples, one just above the distributor plate and others placed throughout the reactor.

The disengaging section consisted of a cone 0.457m. high, 11.43cm. diameter at base (equal to the reactor tube diameter) and 30.5cm. at the top. The top the cone was
Figure 2-8  Fluidized-bed reactor construction (sectional)
Legend
1. sample gas outlet  2. bursting disc  3. vertical sampling probe  4. lower disengaging flange  
20. external cyclone  21. fibreglass lagging  22. rubber connector  23. dip-leg (external)  24. securing nut & nipple  25. thermocouple or sampling point
sealed by a 2mm. thick stainless steel plate, which was provided with three ports for a rupture disk, a sample prob, and gas outlet.

The whole reactor unit was thermally insulated by glass fiber lagging 5cm, in thickness.

All the reactor characteristics are shown in Fig 2.8.

2.3.5 Heat supply, temperature measurement and control

The heat for the reactor was provided by seven 10.2cm. by 11.43cm. o.d. 400W ceramic band heaters, supplied by two 15A(maximum) output "Newtronic" proportional temperature controllers. Temperature control was by three 1mm. diameter chromel/alumel thermocouples TT3, TT4, TT5, as indicated in Fig. 2.5.

To prevent any condensation of the products, the disengaging section and all the sample lines were surrounded by "Electrothermal" heating tape controlled by two Variac transformers to keep the temperature above 200°C in any part of the reactor system.

The temperatures were measured by Philips "Thermocoax" 1mm. diameter stainless steel chromel/alumel thermocouples, connected to a 24-point Digitron device and digital temperature indicator.
2.3.6 Safety devices

Because of highly explosive hydrocarbon/air mixture, it was necessary to have an emergency shut-down device in order to shut off all the gas flows in emergency cases.

The main layout of the emergency shut-down devices are indicated in Fig.2.5. A complete wiring diagram is given in Appendix 1. The emergency shut-down unit consisted of two solenoid valves; two flow sensors; and a differential temperature sensor. The solenoid valves, SV1 and SV2, were situated in the air and the hydrocarbon feed lines. Flow sensors were attached to the air and hydrocarbon rotameters, and were arranged so that if the rotameters bob moved out of the bob beam, either by gas failure or regulator malfunction, this triggered the immediate closure of the solenoid valves, SV1 and SV2.

The differential temperature sensor consisted of 0-80°C Test Temp temperature controller and two thermocouples linked to the master safety control box. One thermocouple sensed the fluidized bed temperature and the other the reactor wall temperature. The "allowed" difference, between 0-80°C, was preset by the Test-Temp unit and if the bed temperature increased above the reactor wall temperature by this amount, the solenoid valves were automatically closed, halting the feed stream. In addition a stainless steel rupture disk (22psi at 20°C or 18psi at 350°C) was situated on the top of the reactor.
2.4 GAS ANALYSIS

The gas stream leaving the reactor consisted of wide ranges of organic and inorganic components, thus making its analysis impossible to achieve in a single step. It was necessary to decide whether to carry out a detailed but time consuming analysis to account for all the intermediates in each sample, or whether to analyze the major products and lump the remained together as oxygenated intermediate. Since a part of the project was to derive a workable kinetic expression, such an expression in term of major reactants and products was thought to be sufficiently complex and therefore acceptable. For this reason, in the majority of the experiments, analysis for only the major reacting species was the norm. However, in the early experiments a detailed analysis was carried out in an attempt to isolate all the intermediates. These experiments show that some oxygenated intermediates were present in only very small quantities. This was regarded as sufficient justification for ignoring them in subsequent experiments.

The ideal solution would have been one in which a complete analysis was provided accurately, rapidly, and automatically using a single step. Analysis for the feed was possible using a single step by means of gas chromatography. Analysis of the products, as it was mentioned, was not possible using a single sample because of the complexity of the mixture and so a compromise solution by using two individual samples was sought.
2.4.1 Analysis requirements

Gas chromatography was chosen as the most suitable analytical technique in this work, using a hot wire detector for the permanent gases, i.e. air, CO₂, water etc., and a flame ionization detector for butenes. It was necessary to use multiple columns and detectors and ovens together to achieve a good separation.

A flow diagram and a photograph of the analytical system is given in Fig. 2.2 and Plate 2.4 respectively. The system consisted of a Perkin Elmer Sigma2 Gas Chromatograph (GC1) equipped with two thermal conductivity detectors (TCD), and a Perkins Elmer F17 Gas Chromatograph (GC2) equipped with a flame ionization detector (FID). An automatic integration was possible with a Perkin Elmer Sigma10 computing recorder and integrator.

Two four-port sampling valves, SV1 and SV2, were fixed to the chromatographs. The sampling loops provided accurate 0.9ml injection of both feed or products streams. The GC1 sample loop and valves were placed in an oven with a temperature above 200°C in order to prevent condensation of water or crystallization of maleic anhydride. The SV1 fed to a Porapak QS (80-100 mesh, 2m long, 3.18mm o.d.) column in the GC1 oven. The flow through this column emptied into the thermal conductivity detector. All the inorganic products and most of the organic products were completely separated in this column. The SV2 fed to a 4m
long and 3.18mm o.d. Durapack/n-octane chemically bonded column which were placed in GC2 oven. The flow through this column ended to the flame ionization detector. Butenes and 1.3 butadiene were separated in this column.

2.4.2 Sampling and chromatographs operation

The analytical system was brought to operation conditions approximately 24 hours before the first sampling. This ensured that the detectors and the injector blocks temperatures were stable. The flame ionization detector (FID) did not require continuous operation unless the chromatograph oven was set at a temperature near that or higher than that used for conditioning the column. Typically, the FID was operated only during the time required to sample the feed or products. The chromatograph’s operation conditions are summarized in table 2.3. The sampling procedures of both chromatographs are given below:

(i) GC1 (HWD) procedure
All the sample lines and the valve oven’s temperature were brought to 200-250°C. The chromatograph oven was set at 90°C. The required vacuum for the system was adjusted by the vacuum control valve, V17, and manometers M2. 3-way valve, V16, was positioned to sample from the fixed-bed or fluidized-bed reactor. In the case of taking a sample from the fixed-bed reactor, the 3-way valve V15 was switched over from the waste to the sample and desired sample either
from the inlet or outlet of the reactor was selected by valve V13. In case of taking sample from the fluidized-bed reactor, the stream from the fixed-bed reactor was directed to the waste by valve V15, and desired sample from the inlet or outlet of the reactor was selected by 4-port valve V14.

The chosen stream was allowed to flush the sampling loop for 1-2 minutes, and then the sample valve SV2 was turned to injection position, and the programmed integrator was started to record and integrate the peaks. After 7-minutes the oven temperature was brought to 220°C with a rate of 20°C/min. to let all the high boiling component to come out of the column. Typical chromatograms from inlet and outlet of the fluidized-bed reactor are shown in Appendix 3 and Appendix 4.

(ii) GC2 (FID) procedure:

The chromatograph oven temperature was set to 30-40°C. The sample from inlet or outlet of the reactors was selected by valve V12. The feed or products sample flushed to the sample loop which was fitted on the sample valve SV2. The filled sample loop was then injected to the column by positioning the sample valve SV2 to the injection position, and the integrator was started simultaneously.

Since this chromatograph was just used for the low boiling point C₄ hydrocarbons, it was not necessary to keep
the sample lines or the sample valve hot or to have temperature programing for the chromatograph oven.

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>SETTING</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GC1:</strong></td>
<td></td>
</tr>
<tr>
<td>Carrier gas</td>
<td>helium</td>
</tr>
<tr>
<td>Supply pressure</td>
<td>120 psi</td>
</tr>
<tr>
<td>Carrier gas flowrate</td>
<td>30cc/min</td>
</tr>
<tr>
<td>Column pressure</td>
<td>30-80 psi</td>
</tr>
<tr>
<td>Detector blocks temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Injector blocks temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Initial oven temperature</td>
<td>90°C</td>
</tr>
<tr>
<td>Rate of temperature prog.</td>
<td>20°C/min</td>
</tr>
<tr>
<td>Final oven temperature</td>
<td>220°C</td>
</tr>
<tr>
<td><strong>GC2:</strong></td>
<td></td>
</tr>
<tr>
<td>Carrier gas</td>
<td>helium</td>
</tr>
<tr>
<td>Supply pressure</td>
<td>120 psi</td>
</tr>
<tr>
<td>Columns pressure</td>
<td>30-40 psi</td>
</tr>
<tr>
<td>Flame gas</td>
<td>hydrogen</td>
</tr>
<tr>
<td>Hydrogen pressure</td>
<td>30 psi</td>
</tr>
<tr>
<td>Oven temperature</td>
<td>30-40°C</td>
</tr>
<tr>
<td><strong>INTEGRATOR:</strong></td>
<td></td>
</tr>
<tr>
<td>Area sensitivity</td>
<td>250</td>
</tr>
<tr>
<td>Base sensitivity</td>
<td>50</td>
</tr>
<tr>
<td>Skim sensitivity</td>
<td>0</td>
</tr>
<tr>
<td>Attenuation</td>
<td>0</td>
</tr>
<tr>
<td>Chart speed</td>
<td>10 mm/min.</td>
</tr>
<tr>
<td>Delay time</td>
<td>0.01 min.</td>
</tr>
</tbody>
</table>
2.5 CATALYST

Vanadium phosphate based catalysts are considered as the principal catalysts in selection oxidation of C$_4$ hydrocarbons. Although most experiments in this work were carried out by using a commercial catalyst (UCL41), a number of experiments were performed to prepare and characterize of the vanadium phosphorus catalysts.

A variety of methods has been proposed for the preparation of vanadium-phosphorus oxidation (VPO) catalysts. Generally, a V$^{+5}$ compound is reduced to V$^{+4}$, followed by addition phosphate compound. As a vanadium compound, V$_2$O$_5$ has often been used (Bordes et al, 1979; Morselli et al, 1978; Centi et al, 1983) but also NH$_4$VO$_3$ has been applied (Nakamura et al, 1974; Bordes et al, 1979; Martini et al, 1978; Poli et al, 1980). Reduction to V$^{+4}$ is carried out using HCL (Morselli et al, 1978; Centi et al, 1983; Centi et al, 1984), isopropyl alcohol (Centi et al, 1984; Katsumoto et al, 1979), lactic (Hodnet et al, 1983; Hodnet et al, 1984), oxalic (Nakamura et al, 1974; Bordes et al, 1979; Poli et al, 1981; Martini et al, 1978), maleic, citric and tartaric acid (Nakamura et al, 1974), or gaseous SO$_2$ at 1073 °K (Brutowsky et al, 1982). An NH$_4$H$_2$PO$_4$ solution (Bordes et al, 1979), or, more usually, concentrated H$_3$PO$_4$ is added to the V$^{+4}$-containing solution. Precipitates or solids obtained after evaporation to dryness are finally activated by calcination.
In this work, the VPO catalyst precursor derived from the use of V$_2$O$_5$ as a reducing agent was investigated. Since the optimum catalytic activity is being claimed for atomic P/V ratio near 1.1 (Mount et al., 1975; Schneider R. A., 1977), most of the studies were carried out considering a P/V range centered about this ratio.

2.5.1 Catalyst Preparation

One standard VPO catalyst was synthesized in an organic medium following procedure reported by Katsumoto and Marquis (1979) by reduction of V$_2$O$_5$ with alcohol followed by the addition of H$_3$PO$_4$ (98%) as:

vanadium pentoxide (100 g) was stirred into a mixture of isobutyle alcohol (1 lit.) and benzyle alcohol (0.1 lit.). The solution was refluxed at 110 °C for 10 hours. The alcohol slurry containing V$^{4+}$ was cooled to 25 °C and 98% phosphoric acid (150 g) was slowly added, followed by refluxing for an additional 10 hours. After cooling, the products was filtered and dried at 110°C for 12 hours. The dried sample was calcined in nitrogen at 450 °C for four hours.

The prepared VPO catalyst was extremely fine, and it was entirely unsuitable for both the fixed-bed or fluidized-bed reactor. So in order to avoid having a large pressure drop through the fixed-bed reactor and to have an appreciable bubbling mode in the fluidized-bed reactor, it was necessary to make bigger particles. The catalyst powder
was compacted by introducing a 20 tonnes force. Although the crushed and ground catalyst was in an appropriate shape for using in the fixed-bed reactor, it was far from ideal and also with very poor attrition resistance for using in the fluidized-bed reactor. The classical approach to this problem is to add 30-50% by weight of colloidal silica or some binders like bentonite or avicel before the drying process. Adding silica or the binders usually causes selectivity losses for selective oxidation reactions. In the case of the selective oxidation of \( \text{C}_4 \) hydrocarbons to maleic anhydride, we regarded the selectivity losses caused by additional materials to be unacceptable. Thus, use of a commercial catalyst (UCL41) for the fluidized-bed reactor was decided upon.

2.5.2 Characteristics

2.5.2.1 Particle diameter

The particle size distribution for the UCL41 catalyst was determined by sieve analysis (3" brass Endecoates Analytical Sieve) for particle diameter in the range 38-250 microns. The analysis was made before the fluidized-bed reactor experiments and after. No significant differences were found, which indicated that over the period of experiments, no appreciable elutriation and no appreciable attrition took place. The results of the sieve analysis are shown in Table 2.4.
Table 2.4 The results of the sieve analysis

<table>
<thead>
<tr>
<th>dp (microns)</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>212+</td>
<td>0.45</td>
</tr>
<tr>
<td>212</td>
<td>0.45</td>
</tr>
<tr>
<td>180</td>
<td>0.9</td>
</tr>
<tr>
<td>150</td>
<td>5.8</td>
</tr>
<tr>
<td>125</td>
<td>8.2</td>
</tr>
<tr>
<td>106</td>
<td>19.0</td>
</tr>
<tr>
<td>90</td>
<td>26.0</td>
</tr>
<tr>
<td>75</td>
<td>16.5</td>
</tr>
<tr>
<td>63</td>
<td>12.5</td>
</tr>
<tr>
<td>63-</td>
<td>10.5</td>
</tr>
</tbody>
</table>

The mean diameter is then = 85 \mu m.

2.5.2.2 Solid bulk density measurements

The volume of catalyst in a measuring cylinder was recorded as a function of its weight. The bulk density of the catalyst sample was measured by tap packing a 5 ml tube with powder and weighing. This procedure was repeated several times.

Bulk density measurement for the fluidized bed
experiments were made in a 40 cm. high by 12 cm. diameter prespex bed with a porous stainless steel distributor. Two kilograms of sample were fluidized slightly above $U_{mf}$, and then the gas flow was slowly turned off. Bulk density was calculated from the settled bed height. The experiments were repeated three times.

2.5.2.3 Measurement of $U_{mf}$

The minimum fluidization velocity, $U_{mf}$, was measured at ambient temperature and pressure in a 40 cm high and 12 cm diameter perspex bed, fitted with a porous stainless steel distributor plate. A manometer was attached to the bed: one arm was open to the atmosphere, the other was connected to the bottom of the bed particles, just above the distributor plate. Various gas flow rates were set and the corresponding pressure drops were measured. A range of flow rates from no flow to well fluidized was covered. The experiments were repeated from the well fluidized state to no flow. Results from these determinations are given in Chapter 3.
2.6 EXPERIMENTAL PROCEDURES FOR THE FIXED BED

2.6.1 Start-up

The reactor was charged with the required quantity of catalyst which could be up to 1g for UCL41, and up to 2g for VPO catalyst.

The reactor was connected to the stream, valves V10 and V11 were fully opened, valve V12 was closed. Valve V13 was set to the reactor outlet and valve V15 was switched to the waste. The fluidizing air to the bath, the temperature controllers and rheostats were turned on. Heating of the fluidized bath was slowly increased while the fluidizing air was consequently reduced in order to keep a normal state of fluidization. Air was passed through the reactor at about 100 ml/min (STP).

After approximately four hours, steady temperature was reached, and then the second step the reaction process was started.

The required reactant gas was connected in line and opened to pressurize the reactant stream to 15-25 psi. The oxidizing gas stream was pressurized by means of valves V2 and V3. Valves V6 and V7 were opened and the volumetric flow rates of the oxidizing and reactant gas streams were set by the valves V4 and V5 respectively.

2.6.2 Reaction procedure

The desired feed rate and concentration of the reactants were set by valves V4 and V5 and the reaction
procedure was started by turning on valves V6 and V7. The system was allowed to reach to its chemical steady state. Temperatures and flow rates were regularly checked. A maximum difference of 2 °C could be observed between the temperature of the bath and the inlet of the reactor, on one hand, and between inlet and outlet of the reactor in steady state condition, on the other hand, showing that the reactor is small enough to avoid any important temperature gradient, and that the heat exchange is sufficient to remove the heat of reaction. At that stage, analysis could be performed.

2.6.3 Sampling procedure

2.6.3.1 GC1 procedure

Valve V12 was closed and Valves V10 and V11 were fully opened. Valve V15 was switched over from the waste to sample position. Selective valve V16 was set to the stream of the fixed-bed reactor. The inlet and the outlet pressure to and from the sample loop were measured and the vacuum could be adjusted by the 3-way manometer tap, V17, in order to have a sufficient suction to evacuate the product stream through the main stream pipe work via the sampling system to the waste. By turning the sample valve SV1 to the filling position, the gas sample could be passed through the sample loop. After 1-2 min the gas sample was injected from the sample loop to the GC1 system by turning the sample valve SV1 to injection position.
2.6.3.2 GC2 procedure

Valves V11 and V13 were completely closed and valve V10 was fully opened. The sample from inlet or outlet of the reactor could be selected by valve V12. The same procedure for adjusting the vacuum system and filling the sample loop and injecting the sample to the GC2 system were carried out as explained for GC1.

2.6.4 Catalyst regeneration procedure

In order to ensure that the catalyst was of constant activity, the reactor was heated overnight so that the catalyst could be regenerated by a stream of air (100 ml/min) which was about 50°C hotter than the reaction temperature.

Since the reaction took place at high temperatures, above 280 °C, and the feed contained a maximum of 1% of hydrocarbon, most of the time the catalyst activity remained constant.

2.7 EXPERIMENTAL PROCEDURE FOR THE FLUIDIZED-BED REACTOR

2.7.1 Start-up

The reactor was charged with the required amount of catalyst (1-3 kg). Air was passed through the bed at a velocity slightly above the $U_{mf}$. The preheaters and the bed heaters were switched on and adjusted to the desired temperature (in the range 280-420 °C). After approximately two hours, when the temperatures were steady, the air flow was increased to the required amount. The air-line flow
sensor was adjusted by placing the floater of the rotameter between the light beam. The Variac transformers providing the heat to the sampling lines and the valve oven were turned on and adjusted at temperature above 200 °C. Mass flow meters (MFM) K5000 and F300 were switched on. The analyzer system was set as described in section 2.4.2.

The temperature profile over the reactor was recorded, and the differential thermocouple controller was set to +30.

2.7.2 Reaction procedure

The run was started by opening valve V43 and adjusting the reactant flow rate in order to have 1 mole% of the hydrocarbon in the feed. Since low molar feed was used for the most of the experiments, mass flow meter K5000 and valve V43 were employed to control the hydrocarbon flow. Temperatures and flow rates were checked regularly and a record was kept of all temperatures, flow rates, and instrument settings and of any external conditions which could have influenced the results. An analysis of the mixture in the wind box was carried out, in order to check the theoretical expected value.

Samples were taken from the reactor outlets, from the top or the middle part of the reactor, each being checked from time to time to give a complete picture of the response of the system.
When all the required analysis had been performed, the flow of the hydrocarbon was turned off by valve V43 and the cylinder head.

2.7.3 Gas-sampling procedure.

The gas sampling procedure was essentially the same as for the fixed-bed reactor. The desired sample was selected by valves V14 and V16 for GC1 and valve V12 for GC2.

The vacuum pump was switched on and the sample valves, SV1 or SV2, were set to the filling position so that sample stream could be sucked through the sample loop. The gas sample was injected into the GC systems by turning the sample valve to the injection position.

2.7.4 Catalyst regeneration procedure

Normally after 5-6 runs which took one day, the reactor and the air preheater temperatures were set to 450 °C with air passing through. The reactor was run at this temperature overnight. All the sample stream valves were closed. After catalyst reactivation the reactor temperature was reset to the desired amount the next morning.

2.8 CALIBRATION

2.8.1 Mass flow meters and rotameters calibration

All mass flow meters (P500, F300, and F50) handling air, oxygen, nitrogen, butane, butane in nitrogen, 1-butene, 1-butene in nitrogen were individually calibrated with a bubble flow meter. All rotameters handling air,
nitrogen, and hydrocarbon were individually calibrated against a standard water-type gas meter. All the calibration graphs were corrected to standard temperature and pressure (20 °C, and 1 atm). The K5000 mass flow meter carrying hydrocarbon was calibrated for air against a standard water-type gas meter and correction made for the hydrocarbon.

2.8.2 Calibration of the response factors

In a standard analysis, the area of the peak corresponding to a component of interest was corrected by a response factor to yield the absolute amount of that component present in the sample. This relationship is expressed by the following equation:

\[ C_i = f_i A_i \]  

(2.1)

where:

- \( C_i \) = amount of component \( i \) (to be calculated)
- \( f_i \) = absolute response factor
- \( A_i \) = area of peak corresponding to component \( i \).

Through calibration, the response factors were obtained for all the components present in the reactor feed and products individually. The calibrations were carried out by using the sample loop for the gaseous components, and syringes for the liquid components. A known amount of each species was injected onto the column and the corresponding peak area was measured by the integrator. The absolute
response factors were easily calculated from Eq.(2.1) for each species.

2.8.3 Calibration of sample loop

Samples loops were cleaned prior to calibration in a 10% vol/vol nitric acid solution, followed by washing in distilled water and isopropanol and dried in an oven at 80 °C for two hours. Loops were filled with clean mercury and weighed. The procedure was repeated three times in order to obtain accurate volumes of the sample loops.
CHAPTER 3

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3.1 FIXED BED RESULTS AND DISCUSSION

3.1.1 Range of parameters investigated

The measurements of conversion of n-butane and 1-butene together with the product distributions in the fixed-bed reactor were made under the conditions which are shown in Table 3-1.

<table>
<thead>
<tr>
<th></th>
<th>Catalyst</th>
<th>VPO</th>
<th>UCL41</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reaction temperature, °C</strong></td>
<td>320-520</td>
<td>280-420</td>
<td></td>
</tr>
<tr>
<td><strong>Quantity of catalyst, g</strong></td>
<td>1-2</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td><strong>Partial pressure of hydrocarbon, atm</strong></td>
<td>0.01-0.015</td>
<td>0.01-0.015</td>
<td></td>
</tr>
<tr>
<td><strong>Volumetric flowrate, L/min</strong></td>
<td>0.015-0.27</td>
<td>0.03-0.27</td>
<td></td>
</tr>
<tr>
<td><strong>Contact time, s</strong></td>
<td>0.3-2.0</td>
<td>0.1-1.5</td>
<td></td>
</tr>
<tr>
<td><strong>Ratio W/F (g-cat)mole hr</strong></td>
<td>5.1-92.6</td>
<td>3.4-30.8</td>
<td></td>
</tr>
</tbody>
</table>

The characteristic of the catalysts have been described in Chapter 2 section 2.5.2 and can be found in Appendix 2.
3.1.2 Experimental measurements

3.1.2.1 Temperature

As has already been noted in paragraph 2.2.4, the temperature control on the fixed bed was performed by means of a fluidized bath and the bed temperature could be kept relatively constant. The inlet and outlet gas temperatures were measured by two thermocouples inserted at the inlet and outlet of the reactor showed a difference of 1 or 2 °C which corresponds to the fluctuation of the bath temperature and shows that there was no significant gradient of temperature in the reactor. The characteristic temperature of the bed was taken to be the mean of the steady state temperature at the inlet and outlet of the reactor. Reaction runs were performed for characteristic temperatures ranging 280-520 °C as indicated in Table 3-1.

3.1.2.2 Gas flow rate

The volumetric flow rate of the oxidant gas (air or oxygen), at the laboratory temperature, was obtained for each run from the mass flow meter reading and calibration curves. These flow rates were corrected to the bed temperature by assuming that air behaves as an ideal gas. It was particularly important to keep the oxidant gas flow rates steady through a run, since the molar feed rate of hydrocarbon was calculated from this and the inlet hydrocarbon concentration.

A contact time in the reactor, which has been defined
by Eq. (3-1) could be estimated.

\[
\tau = \frac{\text{Volume of the catalyst bed}}{\text{Volumetric feed rate of reactants}} \tag{3-1}
\]

all volumes being at reaction temperature and pressure.

3.1.2.3 Reactant and product concentrations

The hydrocarbon concentration in the bed inlet stream could be predicted for the hydrocarbon/nitrogen-oxygen mixtures to within \( \pm 5\% \) from the setting of the mass flow meters. In order to have a more accurate measurement of the hydrocarbon concentration, a sample of inlet gas was taken every time a sample was analysed from the outlet of the reactor.

The ultimate accuracy of the determination of the reactant and product concentrations lies in the calibration of the analytical system. After allowing for the impurities in the calibration gases the gas-chromatographic analysis was capable of measuring gas concentration to within \( \pm 2.5\% \). From time to time the calibrations were checked against the analytical standard obtained from the British Oxygen Company (BOC).

3.1.3 External mass transfer study

Before evaluation of the rate constants, it was necessary to verify that the reaction rates are not
controlled by external mass transfer in order to use these kinetic constants in the case of the fluidized bed.

External mass transfer can control the rate at sufficiently high temperatures or with very active catalyst particles. All authors mentioned in Chapter 1 section 1.2.3 agreed that up to a certain temperature, varying with each author, mass transfer was very fast and therefore the rate equation in the temperature range 200-500 °C is not limited by external mass transfer effects and could be used safely.

Therefore, in this study, no experimental check was performed, but a simple estimate of the effect of mass transfer was made. Wheeler (1955) has shown that when a reaction is completely controlled by external mass transfer, it has an apparent first order rate constant of:

\[ K_m = 10 \left( \frac{U}{M \frac{d^3}{d_p} P} \right)^{1/2} \]  

(3-2)

where:

- \( K_m \) = diffusion controlled first order rate constant / unit volume of reactor (s⁻¹)
- \( U_l \) = linear gas velocity through empty reactor (cm/s)
- \( d_p \) = mean particle size (cm)
- \( P \) = absolute pressure (atm)
- \( M \) = average molar mass of the gas.

Thus in order to be sure that external mass transfer is negligible, \( K_m \) should be larger by at least an order of
magnitude than the experimentally determined rate constant. In this work:

\[ U_L = 0.32-5.7 \text{ cm/s} , \quad M = 29 \text{ g-mole} \]
\[ d_p = 80 \times 10^{-4} \text{ cm} , \quad \text{and} \quad p = 1 \text{ atm} \]

Using these values, \( K_m \) is estimated to be in range 1.3-2.45 \( \times 10^{15} \) s\(^{-1}\). The measured rate constants are much lower and so the effects of external mass transfer can be considered to be negligible.

### 3.1.4 Catalyst activity

In order to have a reliable set of data on a catalyst, experimental runs should be carried out on a catalyst of constant activity. While the catalyst was on-stream, however, its activity decreased and it became necessary to reactivate it. Catalyst activation was achieved by passing air or oxygen through the bed at 400-450 °C for 5-7 hours as previously described in Chapter 2 section 2.6.4.

In this work, some checks were performed in order to monitor the catalyst activity. For first order oxidation reactions of n-butane over VPO catalyst and 1-butene oxidation on UCL41 catalyst with reaction temperatures above 300 °C constant conversions of n-butane and 1-butane were observed for over 5 hours, indicating that the catalyst activity remained constant for that period of time. A typical plot of n-butane and 1-butene conversion with time are shown in Fig.3-1 and Fig.3-2.
Figure 3-1  The influence of VPO catalyst activity on n-butane conversion

- 1 0 6 -

![Graph showing conversion as a function of temperature and time.](image)

Figure 3-2  The UCL41 catalyst activity on 1-butene conversion as a function of time

![Graph showing conversion as a function of temperature and time.](image)
3.1.5 Selective oxidation of n-butane over VPO catalyst

The major products from the oxidation of n-butane over VPO catalyst were maleic anhydride and carbon dioxide. A series of experiments were carried out with varying quantities of catalyst, reaction temperature and contact time. The conversion of n-butane was defined as:

\[
\text{Conversion} = \frac{\text{Moles of n-butane consumed}}{\text{Moles of n-butane in feed}} \times 100 \quad (3-3)
\]

and the selectivity to products as:

\[
\text{Selectivity} = \frac{\text{Moles of product produced}}{\text{Moles of n-butane in feed}} \times 100 \quad (3-4)
\]

The reactivity and selectivity of n-butane oxidation over VPO as a function of temperature are shown in Fig.3-3 and Fig.3-4. The maximum selectivity for maleic anhydride formation (27% at a 0.5 second contact time and 34% at a 1 second contact time) was observed between 445-475 °C. A minimum carbon dioxide selectivity was observed simultaneously with a maximum in maleic anhydride selectivity. Only trace amounts of 1,3-butadiene were detected above 475 °C.

The effect of contact time on n-butane oxidation is shown in Fig.3-5. The selectivity to maleic anhydride went through both a maximum (45% at 1.2 seconds contact time)
Figure 3-3 Variation of n-butane conversion and maleic anhydride selectivity with temperature (0.5 s contact time)
and a minimum (2% at 2 seconds contact time). The selectivity to carbon dioxide showed both a minimum and a maximum being coincident with the maximum and minimum selectivity to maleic anhydride respectively. The conversion of n-butane monotonically increased with increasing contact time.

3.1.5.1 Analysis of reaction network

The reaction scheme was derived on the basis that under more severe conditions only maleic anhydride, carbon dioxide and water were formed. The result is the following:

\[
\text{n-butane} \rightarrow \text{maleic anhydride}
\]

\[
\text{CO}_2 + \text{H}_2\text{O}
\]

Therefore the following reactions were chosen for the investigations in this work.

\[
\text{C}_4\text{H}_{10} + 3.5 \text{O}_2 \rightarrow \text{C}_4\text{H}_3\text{O}_3 + \text{H}_2\text{O} \quad -\Delta H = 1.2606 \times 10^6 \text{kJ/kmole}
\]

\[
\text{C}_4\text{H}_{10} + 6.5 \text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O} \quad -\Delta H = 2.6586 \times 10^6 \text{kJ/kmole}
\]

The redox mechanism with the influence of lattice oxygen from the catalyst for reaction 1 is well established (Haber, 1973). Such redox reactions can be formally described by the kinetic scheme of Mars and Van Krevelen
Figure 3-4 Variation of n-butane conversion and maleic anhydride selectivity with temperature (1 s contact time)

Figure 3-5 Variation of n-butane conversion and maleic anhydride selectivity with contact time (at 450°C)
(1954) or Eley and Rideal (1943). The essential difference between the two models is the mechanism of the formation of maleic anhydride. In the Mars-Van Krevelen model, after an adsorption step of butane, the adsorbed butane and lattice oxygen react to form maleic anhydride, whereas with the Eley-Rideal model, butane from the gas phase (without a proceeding adsorption step) reacts directly with the oxygen from the metal oxide lattice, forming a surface compound. Since temperature-programmed desorption, TPD, (Schneider, 1985) revealed that n-butane is not adsorbed noticeably on the investigated VPO catalyst the formal kinetics could be derived following the Eley-Rideal model.

3.1.6 Selective oxidation of 1-butene over UCL41 catalyst

The catalytic oxidation of 1-butene would be first order in the hydrocarbon disappearance if the oxygen concentration was kept in excess, as has already been mentioned in Chapter 1 section 1.2.3.4. Since the 1-butene concentration in the experiments was kept very low in relation to the oxygen concentration (1% vol/vol in air), it was reasonable to assume that the reaction can only be described by a first order scheme.

3.1.6.1 Analysis of reaction network

Based on a reaction mechanism proposed by previous workers (Cavani et al., 1983; Bordes et al., 1979; Varma and Saraf, 1979) the general network for 1-butene oxidation to maleic anhydride may be written as shown in reaction
The chemical components of the above network are listed in Table 3-2.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butene</td>
<td>$C_2H_5-CH=CH_2$</td>
<td>A1</td>
</tr>
<tr>
<td>1,3 butadiene</td>
<td>$CH_2=CHCH=CH_2$</td>
<td>A2</td>
</tr>
<tr>
<td>furan</td>
<td>$C_4H_4O$</td>
<td>A3</td>
</tr>
<tr>
<td>maleic anhydride</td>
<td>$C_4H_2O_3$</td>
<td>A4</td>
</tr>
<tr>
<td>carbon oxides</td>
<td>$CO_2$</td>
<td>A5</td>
</tr>
<tr>
<td>acetic acid</td>
<td>$CH_3COOH$</td>
<td></td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>$CH_3CHO$</td>
<td></td>
</tr>
<tr>
<td>acrolein</td>
<td>$CH_2=CHCHO$</td>
<td>A6</td>
</tr>
<tr>
<td>butyraldehyde</td>
<td>$CH_3CH_2CH_2CHO$</td>
<td></td>
</tr>
</tbody>
</table>

In order to simplify the reaction network for the
kinetic analysis some assumptions were made based on observations from the experimental study. Since carbon monoxide was detected in only trace amounts, it was ignored from the reaction products. The organic side products were of the order of 1% of the reaction products, so they too could be simply ignored. It may be noted from the Fig. 3-6 to Fig. 3-13 that the yield curve for furan and maleic anhydride is not affected by the increasing yield of carbon dioxide, so it can be concluded that most of the carbon dioxide was produced from either 1-butene or 1,3-butadiene. Since the experiments were conducted at high residence time, when 1-butene conversion was essentially completed, no significant decrease in the yields of carbon dioxide and maleic anhydride were observed.

Based on the above discussion, the following network seems justified.

\[
\begin{align*}
1\text{-butene} & \xrightarrow{k_1} 1,3\text{-butadiene} & \xrightarrow{k_2} \text{furan} & \xrightarrow{k_3} \text{MA} \\
\text{CO}_2 & \xrightarrow{k_4} & & \\
\end{align*}
\]

3.1.6.2 Kinetic model

It has been previously mentioned in Chapter 1 section 1.2.3.4 that models based on theories propounded by Mars and Van Krevelen (1954), have been widely employed to interpret vapor-phase oxidation reactions. Mars and Van Krevelen proposed a two-step model (redox mechanism) for
Figure 3-6  Variation of concentration with contact time (1gr catalyst, 320°C)

Figure 3-7  Variation of furan & maleic anhydride concentration with time (320°C)
Figure 3-8  Variation of concentration with contact time (1gr catalyst, 340°C)

Figure 3-9  Variation of furan & maleic anhydride concentration with contact time (340°C)
Figure 3-10 Variation of concentration with contact time (Igr catalyst, 355°C)

Figure 3-11 Variation of furan & maleic anhydride concentration with contact time (355°C)
Figure 3-12 Variation of concentration with contact time (1gr catalyst, 375°C)

Figure 3-13 Variation of furan & maleic anhydride concentration with contact time (375°C)
hydrocarbon oxidation. The rate expression according to this model is:

$$R_h = \frac{k_h k p p_o}{k_o p_o + \alpha_k p_h} \quad (1-104)$$

Although the redox model has been found to be valid over a wide range of butene concentrations studied (Varma and Saraf, 1979), butene concentration in the feed above the critical limit (1.3% vol/vol in air and 3.0% vol/vol in oxygen) was found to give a markedly low yield of maleic anhydride. In addition, high butene concentration in the feed cause an explosive risk. Due to these considerations, the concentration of butene should not usually exceed about 1% vol/vol in air. This condition was maintained in most of runs carried out in this investigation. This region of practical interest allowed a major simplification in the rate expression to be made. At low butene concentration, oxygen is in large excess and so does not effect the rate equations. It has been shown that 1-butene disappearance follows first order kinetics remarkably well (Newton, 1984)

3.1.6.3 Evaluation of rate constant

Since the oxygen in the reactant mixture was maintained in large excess, first-order kinetics were assumed in formulating the rate expression. Thus for the reaction scheme II, rate equations for the five components areas:
\[
\frac{dC_A}{dt} = -k_1 C_A \quad (3-5)
\]

\[
\frac{dC_A}{dt} = k_1 C_A - (k_2 + k_4) C_A \quad (3-6)
\]

\[
\frac{dC_A}{dt} = k_2 C_A - k_3 C_A \quad (3-7)
\]

\[
\frac{dC_A}{dt} = k_3 C_A \quad (3-8)
\]

\[
\frac{dC_A}{dt} = k_4 C_A \quad (3-9)
\]

Equations 3-5 to 3-9 can be integrated with the initial condition, \( C_{A_1} = 1, C_{A_2} = 0, C_{A_3} = 0, C_{A_4} = 0, \) and \( C_{A_5} = 0 \) at \( t=0 \), to give:

\[
C_{A_1} = e^{-k_1t} \quad (3-10)
\]

\[
C_{A_2} = \frac{k_1}{k_2 + k_1} \left( e^{-k_1t} - e^{-k_2t} \right) \quad (3-11)
\]

\[
C_{A_3} = X e^{-k_3t} + Ye^{-k_1t} - Ze^{-k_4t} \quad (3-12)
\]

\[
C_{A_4} = -X e^{-k_3t} - \frac{Y k_3}{k_1} e^{-k_1t} + \frac{Z k_3}{k_2} e^{-k_4t} + W \quad (3-13)
\]
\[
C_{AS} = \frac{k_4 k_1}{k_{24} - k_1} \left( \frac{e^{-k_{24} t}}{k_{24}} \right) + \frac{k_4 k_1}{k_{24} - k_1} \left( \frac{1}{k_2} - \frac{1}{k_{24}} \right)
\]  

(3-14)

where: \( k_{24} = k_2 + k_4 \)  

(3-15)

\[
Y = \frac{k_1 k_2}{(k_{24} - k_1)(k_3 - k_1)} 
\]  

(3-16)

\[
Z = \frac{k_1 k_2}{(k_{24} - k_1)(k_{24} - k_3)} 
\]  

(3-17)

\[
X = Z - Y 
\]  

(3-18)

\[
W = X + \frac{Y k_3}{k_1} - \frac{Z k_3}{k_{24}} 
\]  

(3-19)

Equations 3-11 to 3-14 are too complicated to be solved analytically, so preliminary estimation of rate constants were carried out by the following procedure. (a) Because of the high residence times employed in this work, 1-butene conversion was complete and no significant amount of 1-butene was observed in the reactor outlet gases, Eq. 3-5 was therefore practically useless and could be omitted from the calculation. Since all 1-butene was converted to 1,3-butadiene as has been shown in the reaction scheme II, it was reasonable to assume that the initial concentration of 1,3-butadiene before reaction 2 and 4 was the same as the initial concentration of 1-butene. Eq. 3-6 can be
written as:

\[
\frac{dC_{A2}}{dt} = -(k_2 + k_4)C_{A2}
\]  \hspace{1cm} (3-20)

Eq. 3-20 can be integrated with the initial condition \( C_{A2} = 1 \) at \( t \approx 0 \) to give

\[
C_{A2} = e^{-(k_2 + k_4)t}
\]  \hspace{1cm} (3-21)

Eq. 3-21 can be plotted as log \( C_{A2} \) vs \( t \), as shown in Fig.3-14 to Fig.3-17. The slope of the straight line gives the value of \( (k_2 + k_4) \).

(b) Eq. 3-7 can be rearranged to give:

\[
\frac{1}{C_{A3}} \frac{dC_{A3}}{dt} = k_2 \frac{C_{A2}}{C_{A3}} - k_3
\]  \hspace{1cm} (3-22)

Thus a plot of \( \left( \frac{1}{C_{A3}} \frac{dC_{A3}}{dt} \right) \) vs \( \left( \frac{C_{A2}}{C_{A3}} \right) \) gives a straight line as is shown in Fig.3-18 to Fig.3-21. The slope and intercept give the values \( k_2 \) and \( k_3 \) respectively. The value for \( k_4 \) could be simply calculated by knowing the values for \( k_2 \) and \( (k_2 + k_4) \).

(c) Newton (1984) studied the oxidation of 1-butene to 1,3-butadiene over the same catalyst as was employed in this work. The value for \( k_1 \) was found directly from his
Figure 3-14 Regression of lnBTD on contact time for the determination of k2+k4 at 320°C

Figure 3-15 Regression of lnBTD on contact time for the determination of k2+k4 at 340°C
Figure 3-16  Regression of lnBTD on contact time for the determination of $k_2+k_4$ at 355$^\circ$C

Figure 3-17  Regression of lnBTD on contact time for the determination of $k_2+k_4$ at 375$^\circ$C
Figure 3-18  Regression of $1/[\text{furan}] \times \frac{d[\text{furan}]}{dt}$ vs $[\text{furan}]/[\text{butadiene}]$ at 320°C

Figure 3-19  Regression of $1/[\text{furan}] \times \frac{d[\text{furan}]}{dt}$ vs $[\text{butadiene}]/[\text{furan}]$ at 340°C
Figure 3-20 Regression of $\frac{1}{[\text{furan}]} \times \frac{d[\text{furan}]}{dt}$ vs $\frac{[\text{butadiene}]}{[\text{furan}]}$ at 355°C

Figure 3-21 Regression of $\frac{1}{[\text{furan}]} \times \frac{d[\text{furan}]}{dt}$ vs $\frac{[\text{butadiene}]}{[\text{furan}]}$ at 375°C
work.

The values of rate constants at each reaction temperature are given in Table 3-3.

<table>
<thead>
<tr>
<th>Reaction rate constant, s⁻¹</th>
<th>593 K</th>
<th>613 K</th>
<th>628 K</th>
<th>648 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁</td>
<td>28</td>
<td>30.7</td>
<td>32.75</td>
<td>35.8</td>
</tr>
<tr>
<td>k₂</td>
<td>0.027</td>
<td>0.032</td>
<td>0.082</td>
<td>0.11</td>
</tr>
<tr>
<td>k₃</td>
<td>0.183</td>
<td>0.24</td>
<td>0.63</td>
<td>2.7</td>
</tr>
<tr>
<td>k₄</td>
<td>0.493</td>
<td>1.15</td>
<td>2.2</td>
<td>3.55</td>
</tr>
</tbody>
</table>

3.1.6.4 Variation of the reaction rate constants with temperature

The variation of reaction rate constant with temperature is usually correlated with the Arrhenius equation.

\[ k = A \exp(-E/RT) \]  \hspace{1cm} (3-23)

or in its logarithmic form,
Figure 3-22 Determination of the Arrhenius parameters (E, A) from the reaction rate constant, $k_1$ s$^{-1}$

Figure 3-23 Determination of the Arrhenius parameters (E, A) from the reaction rate constant, $k_2$ s$^{-1}$
Figure 3-24 Determination of the Arrhenius parameters \((E, A)\) from the reaction rate constant, \(k_3 \text{ s}^{-1}\)

![Graph showing the Arrhenius plot for \(k_3\) with data points and a line of best fit.]

Figure 3-25 Determination of the Arrhenius parameters \((E, A)\) from the reaction rate constant, \(k_4 \text{ s}^{-1}\)

![Graph showing the Arrhenius plot for \(k_4\) with data points and a line of best fit.]

\[
\ln k \quad \text{vs} \quad \frac{1}{T} \quad (\text{K})
\]
\ln k = \ln A - \frac{E}{RT} \quad (3-24)

which indicates that \ln k varies linearly with the reciprocal of the absolute temperature.

The calculated rate constants are plotted against reciprocal of the absolute temperature in Fig.3-22 to Fig.3-25 for the consecutive reaction mechanism. It is apparent that the calculated rate constants obey this linear relationship and consequently, the "best" straight line through each set values was computed by the least squares methods. The resulting values of A and E are given in Table 3-4.

<table>
<thead>
<tr>
<th>reaction rate constants</th>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( k_3 )</th>
<th>( k_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>slop (-E/R)</td>
<td>-1817.52</td>
<td>-10944</td>
<td>-20099.8</td>
<td>-14348</td>
</tr>
<tr>
<td>intercept(lnA)</td>
<td>6.4</td>
<td>14.7</td>
<td>31.76</td>
<td>23.51</td>
</tr>
<tr>
<td>E / kj mole(^{-1})</td>
<td>15.1</td>
<td>90.8</td>
<td>166.83</td>
<td>119.1</td>
</tr>
<tr>
<td>A/ s(^{-1})</td>
<td>602</td>
<td>2.4\times10^6</td>
<td>6.2\times10^{13}</td>
<td>1.6\times10^{10}</td>
</tr>
</tbody>
</table>

These values were used in the fluidized-bed reactor models to be discussed in section 3.3 below.
3.2 FLUIDIZED BED EXPERIMENTAL AND THEORETICAL RESULTS AND DISCUSSION

3.2.1 Range of parameters investigated

The range of parameters employed for the measurements of 1-butene conversions and product concentrations in the fluidized-bed reactor are summarized in Table 3-5.

<table>
<thead>
<tr>
<th>Table 3-5 Range of parameters employed in the fluidized-bed experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor temperature, °C</td>
</tr>
<tr>
<td>Quantity of catalyst, kg</td>
</tr>
<tr>
<td>Volumetric feed flow rate, L/min (STP)</td>
</tr>
<tr>
<td>Concentration of 1-butene in feed, mole%</td>
</tr>
<tr>
<td>Ratio W/F , (g-cat)mole(^{-1})hr(^{-1})</td>
</tr>
</tbody>
</table>

3.2.2 Experimental measurements

3.2.2.1 Temperature

Due to the good heat transfer properties of a fluidized bed, the observed temperature gradients in the experimental fluidized-bed reactor were negligible. As with the fixed bed experiments, the start of a run was followed by an increase in the bed temperature of up to 20 °C due to exothermic reaction. The temperature rise in this case, however, took up to 20 minutes to reach a maximum and then decayed to the initial preset bed temperature. During this period of temperature rise, the temperature controllers
switched off power to the heaters and the reactor temperature was maintained by the enthalpy of the reaction. The sharpest temperature rise (about two-thirds of the maximum rise) occurred in the first five minutes. After this initial period, temperature rose more gradually to its maximum and then gradually fell back to its initial value. This temperature rise and decay is shown diagrammatically in Fig 3-26.

3.2.2.2 Gas flow rates

The volumetric flow rates were measured for the fluidized bed using rotameters $R_1$ and $R_2$ for the air flow rates and mass flow meter K5000 for 1-butene feed rates. It was possible to obtain a constant input concentration by correcting the air flow rate when it was necessary. The
constancy of 1-butene feed rate was known to be reliable because of the accuracy of the calibration curves and the precision of the flow controller used.

Air flow rates were varied from 5-30 L/min (STP), which depending on the bed temperature, gave a range of superficial gas velocity of 5-30 times $U_{mf}$. 1-butene flow rates were set to give input concentrations of about 1% vol/vol. The reactor input gas stream was sampled either before or after a reaction run to determine the exact concentration of the 1-butene feed.

3.2.2.3 Reactant and product concentrations

Although the 1-butene concentration in the bed input stream could be predicted from the rotameters and/or mass flow meter reading, the exact concentration was measured and recorded by gas chromatography as previously described in Chapter 2, section 2.7.3. The 1-butene and product concentrations in the bed outlet stream were measured and recorded on a continuous basis from the start of reaction, with occasional interruptions for checking the input concentrations. All reaction runs were performed in air, with a 1-butene concentration 1% vol/vol, in order to avoid the explosion hazards and also to keep the reaction first order with respect to the 1-butene.

The accuracy of the concentration measurements was only dependent upon the accuracy of calibration of the analytical system. It has been already assessed in section 3.1.2.3 that this accuracy is about ±2.5%.
3.2.3 Measurement of catalyst characteristics

Many of the physical properties of the particles have previously been described in Chapter 2 section 2.5.2. Those described in this section are those affecting, or concerned with, the fluidization of a bed of the solid.

3.2.3.1 Particle size distribution

The particle size distribution of the UCL41 catalyst was found by test sieving as has previously been described in detail in Chapter 2 section 2.5.2.1. The results are given as the weight percent retained by each sieve in the series in Table 2.4. These results are shown graphically in Appendix 2. The mean particle size based on surface, \( dp \) (the size of the particle with the same specific surface as the mixture (Coulson and Richardson, 1963) was calculated from:

\[
\frac{1}{dp} = \frac{1}{\sum \frac{x_i}{d_i}} \quad (3-25)
\]

where \( x_i \) is the weight fraction with a size \( d_i \). This mean particle size was found to be 85 \( \mu \)m.

The particle size distribution was also measured by a Malvern 2200/3300 Particle Sizer V2.1 analyzer. The results of the Malvern analysis are given in Appendix 2.
3.2.3.2 Minimum fluidization velocity

The experimental procedure for this measurement was described in Chapter 2 section 2.5.2.3. The measured volume flow rates were corrected to the bed temperature by assuming ideality of the air. The results are plotted as the pressure drop against the superficial gas velocity in Fig 3-27. The minimum fluidization velocity was taken as the point of the intersection of the best straight line through the points describing the unfluidized bed and that through the points describing the well fluidized bed. The minimum fluidization velocity was thus found to be 0.0045 m/s at room temperature.

The measured minimum fluidization velocity is compared with predictions from some correlations in the literature. Table 3-6 shows the results of these comparisons.

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Calculated $U_{mf}$ (m/s)</th>
<th>Measured $U_{mf}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thonglimp et al, (1984)</td>
<td>0.0032</td>
<td>0.0045</td>
</tr>
<tr>
<td>(Eq. 3.26)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wen and Yu, (1966)</td>
<td>0.0029</td>
<td>0.0045</td>
</tr>
<tr>
<td>(Eq. 3.27)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Babu et al, (1978)</td>
<td>0.006</td>
<td>0.0045</td>
</tr>
<tr>
<td>(Eq. 3.28)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3-27  Measurement of minimum fluidization velocity (room temperature)

Pressure drop (mm water)

increasing velocity

decreasing velocity

Gas velocity (m/s)  \( \times 10^{-3} \)
It can be seen that the correlation of Thonglimp et al predicts satisfactorily (maximum deviation of 0.28) for \( U_{mf} \). This correlation was chosen for calculation \( U_{mf} \) at higher temperature.

3.2.3.3 Fluid-bed expansion and voidage

The height of the bed is one of the simplest parameters to measure, although one has to be careful of the periodic fluctuation of the surface due to bursting of the bubbles.

The variation in the bed height with gas velocity was determined in a 40 cm high and 12 cm diameter perspex bed, fitted with a porous stainless steel distributor. The results are shown in Fig 3-28 for the catalyst used for fluid bed experiments (UCL41). As can be seen from Fig 3-28, for the gas velocities slightly in excess of minimum bubbling velocity (\( U_{mb} \)) the bed heights were found to remain constant. The experimental bed height was taken to be the value at which no further pressure drop was observed.

Bed voidages were calculated for the catalyst powder from the expanded fluid-bed height, \( h \), using equation 1.16. The static reactor bed heights were calculated from \( \rho_{bulk} \) values which were measured in a small laboratory perspex bed.
It can be seen from Fig. 3-28 that the particles behave like group A particle in Geldart's classification (1972). The minimum bubbling occurs at a velocity much in excess of the minimum fluidization velocity.
3.3 EXPERIMENTAL AND THEORETICAL RESULTS

3.3.1 PRODUCT DISTRIBUTION

The graphs giving the product distributions of 1,3-butadiene, furan, maleic anhydride (MA), and CO$_2$ have been plotted on Fig. 3-29 to Fig. 3-35 as a function of the gas velocity, in different reaction temperatures and initial bed heights.

1-butene was oxidized to maleic anhydride via 1,3-butadiene and furan. Major products from the oxidation reaction were found to be 1,3-butadiene, furan, maleic anhydride, and carbon dioxide. The other oxygenated products (acrolein, butylaldehyde, etc) amounted to less than 4% of total conversion. Preliminary experiments were carried out to check the reproducibility of the experimental results, and to estimate the range of variables best suited for a good selective oxidation to maleic anhydride. No significant decline in activity and selectivity of the catalyst was found up to about 20 hours of use. However, the catalyst was kept fresh by passing hot air after each run. Experiments conducted at high butene conversion to study the effect of operating conditions, indicated that butene concentration in the feed and the gas velocity were the operating variables which should be controlled within rather narrow limits to obtain a substantial yield of maleic anhydride. On the other hand, reactor temperature could be varied within a relatively wide range. Mass balances have equally been performed in all cases. They were better than those for the fixed bed, which
Figure 3-29  Product distribution vs gas velocity
Figure 3-30 Product distribution vs gas velocity
could be expected as less tar was obtained, nevertheless, a range of 85-105% mass balance between the inlet and outlet of the reactor was observed. This can be explained by experimental error together with the presence of tar and by the fact that some products, acrolein and butylaldehyde, were neglected.

A series of experiments were carried out at varying values of gas velocity, reaction temperature and initial bed height (mass of the catalyst). The range of operating variables are given in Table 3-5. The effect of these variables on the yield of products have been shown on Fig. 3-29 to Fig. 3-35. The yield of each species was defined and calculated as follows:

\[
\text{Yield of species A} = \frac{\text{moles of species A}}{\Sigma \text{moles of all species}} \times 100
\]

Fig. 3-29 to Fig. 3-35 shows that as 1,3-butadiene concentration decreases with decreasing the gas velocity or increasing the residence time, yields of maleic anhydride and carbon dioxide increase. This shows the yield of 1,3-butadiene behavior is akin to that of an intermediate product. An increase in reaction temperature favoured the formation of maleic anhydride within the limits. Higher temperature (>400 °C) caused a sharp decrease in the yield of 1,3-butadiene and a sharp increase in the yield of CO₂.
Figure 3-31  Product distribution vs gas velocity
Figure 3-32  Product distribution vs gas velocity
as shown in Fig. 3-35. This shows that at high temperature most of the products convert to \( \text{CO}_2 \) and water by the combustion process. In order to avoid such combustion in the reactor, the reaction temperature was kept below 400 \( ^\circ \text{C} \).

The yield of maleic anhydride was relatively insensitive to changes of the initial bed height, indicating that the most if not all of the fluid-bed conversion had taken place within the first few centimeters of the bed. High yields of maleic anhydride (30-35\%) were obtained in the temperature range of 360-380 \( ^\circ \text{C} \) with the gas velocity of 5-10 times of minimum fluidization velocity. 1-butene conversion at these conditions were 100\% and no significant concentration of 1-butane was detected in the outlet of the reactor. The lower temperature runs at 280 \( ^\circ \text{C} \) still showed high conversions of 1-butene for all gas velocities employed in this work. A decrease in the maleic anhydride yield was found with increasing gas velocity for all temperatures studied. It can be shown from Fig. 3-30 that the gas velocity was crucial in determining the overall reactor product distribution and selectivity. It was observed that in the fixed bed, the selectivity of maleic anhydride decrease with increase in gas velocity or decrease in contact time, while in the fluidized bed, the variation of selectivity with contact time passed through a maximum giving an optimum contact time for the operation.
Figure 3-33  Product distribution vs gas velocity
Figure 3-34  Product distribution vs gas velocity
It can be seen from the graphs of product distributions, the oxidation reaction of 1-butene over the catalyst UCL41 is very selective to 1,3-butadiene. Under certain conditions, however, as has been previously mentioned that 30-35% yields of maleic anhydride were observed. The normal yield of maleic anhydride obtained from 1-butene oxidation over VPO catalyst (which is supposed to be the best catalyst for this reaction) is 40-45% (Varma and Saraf, 1979).

3.3.2 Study of different parameters

Since the main object of this work was to determine a non-arbitrary mathematical model for a catalytic gas-solid chemical reaction in a fluidized-bed reactor, the arbitrary variation of the model parameters in order to fit the experimental results was avoided. However, it was important when deciding on the choice to know how sensitive the models are to these parameters.

Most chemical reactor models for fluidized beds are based on the presence of bubbles in the bed. The number, size and velocity of these bubbles figure prominently in many of the models, and accordingly the reactor models are invariably tested with these hydrodynamic features. There are two problems about the diameter of the bubbles. First, in some it is taken as constant through the whole bed which is obviously an over simplification, and secondly, this diameter is considered as being independent of the gas velocity. This introduces another source of error and
Figure 3-35  Product distribution vs gas velocity
explains why the data can not be fitted on a particular curve of constant bubble diameter because bubble diameter varies also with gas velocity.

Fluidized bed reactor models are evaluated by predicting the concentration of different species in the outlet of the reactor. This concentration is the overall concentration of the bubble phase and the dense phase. It is apparent that a given model may predict the correct overall concentration for a given set of conditions by predicting too high a concentration in one phase coupled with too low a concentration for the other phase. Thus even if a given model gives a good prediction of overall conversion, its failure to represent observed concentration profiles raises serious doubts about the general validity of the model. Although it was outside the scope of this work to measure the bubble phase and dense phase concentration profiles, the concentration could be calculated separately for the individual phases from the computer programs used to apply these models.

There are many models available for predicting the performance of bubbling fluidized-bed reactors (Yates, 1983). It was beyond the scope of this work to compare the performance of a fluidized bed as a chemical reactor with all available models. In this work the experimental data for the catalytic oxidation of 1-butene to maleic anhydride were compared with predictions from three of the more popular fluidized-bed reactor models, those of Davidson and
Harrison, perfectly mixed and piston flow (1963); Kunii and Levenspiel (1969); and Kato and Wen (1969). These models represent a broad range of basic assumptions which have been described in detail in Chapter 1 section 1.2.1.6. For example, clouds and/or wakes are assumed in some models (Kunii-Levenspiel and Kato-Wen) and not in others (Davidson-Harrison, both versions); a single average bubble diameter is assumed in some models (Davidson-Harrison, Kunii-Levenspiel) while the other allows for changes in bubble size with height (Kato-Wen). The fundamental assumptions of these models are summarized in table 3-7.

In order to apply the models to the experimental data, measured bed properties and published correlations were used to calculate bubble diameter, interphase mass transfer rates, and other hydrodynamic parameters. No parameters were fitted. However a series of calculations were performed to test the sensitivity of the models to possible variations in some the parameters. These parameters which were varied and their range of values are listed in Table 3-6 for each model.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Davidson-Harrison</td>
<td>bubble diameter</td>
<td>0.007-0.063 m</td>
</tr>
<tr>
<td>Kunii-Levenspiel</td>
<td>bubble diameter</td>
<td>0.013-0.1 m</td>
</tr>
<tr>
<td></td>
<td>wake fraction, $f_w$</td>
<td>0.2-0.5</td>
</tr>
<tr>
<td>Kato-Wen</td>
<td>wake fraction, $f_w$</td>
<td>0.2-0.5</td>
</tr>
</tbody>
</table>
Table 3-7 Assumptions of three fluidized-bed reactor models

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>phases</td>
<td>1- bubble</td>
<td>1- bubble</td>
<td>1- bubble + cloud (or cloud + wake)</td>
<td>1- bubble + cloud (or cloud + wake)</td>
</tr>
<tr>
<td></td>
<td>2- dense</td>
<td>2- dense</td>
<td>2- emulsion</td>
<td>2- emulsion</td>
</tr>
<tr>
<td>particles associated with bubble</td>
<td>bubbles empty of particles</td>
<td>bubbles empty of particles</td>
<td>bubble empty of particles</td>
<td>bubbles empty of particles</td>
</tr>
<tr>
<td>gas flow in bubble-phase</td>
<td>$U - U_{mf}$</td>
<td>$U - U_{mf}$</td>
<td>$U$, plug-flow</td>
<td>$U$, perfectly mixed in each compartment</td>
</tr>
<tr>
<td>gas flow in dense or emulsion-phase</td>
<td>completely mixed</td>
<td>plug flow</td>
<td>negligible</td>
<td>negligible</td>
</tr>
<tr>
<td>interphase transfer</td>
<td>B-E diffusion + through-flow</td>
<td>B-E diffusion + through-flow</td>
<td>B-E diffusion + through-flow</td>
<td>C-E diffusion</td>
</tr>
<tr>
<td>bubble size</td>
<td>constant</td>
<td>constant</td>
<td>constant</td>
<td>varies with height</td>
</tr>
<tr>
<td>reaction takes place</td>
<td>emulsion-phase</td>
<td>emulsion-phase</td>
<td>cloud+wake and emulsion</td>
<td>emulsion + cloud phase or cloud+wake</td>
</tr>
</tbody>
</table>
a) Influence of wake fraction

Kunii and Levenspiel (1968) recommended a range of 0.25-0.4 for wake fraction and Rowe et al. (1961) determined an experimental value of 0.3 which is the value chosen in this study. As can be seen from Fig. 3-36 and Fig. 3-37, however, this parameter is not very sensitive for both the Kunii-Levenspiel and Kato-Wen models. A maximum difference of 5% was observed on the calculation of conversion for these two models as the wake fraction was varied from 0.2 to 0.5. Chavarie and Grace (1975) in their work testing the Kunii-Levenspiel model adopted wake fraction of 0.5 quietly arbitrarily.

b) Influence of bubble diameter

The influence of bubble diameter is shown in Fig. 3-37 to Fig. 3-33 for the Davidson-Harrison and Kunii-Levenspiel models.

The influence of bubble size is much greater than that of wake fraction for the Kunii-Levenspiel model. As expected, the assumption of smaller bubbles results in the prediction of higher conversion. The similar results were observed in the case of the Davidson-Harrison model (perfectly mixed). It is noticeable from Fig. 3-39, the Davidson-Harrison model, piston flow is not very sensitive to bubble diameter and it can be due to the assumption of uniform concentration across a horizontal plane, and no mixing in a vertical direction which the bubbles are directly responsible for in the other models.
Figure 3-36 Theoretical conversion of 1-3 butadiene from the K-W model for different wake fractions
Figure 3-37

Prediction of K-L model for 1-butene conversion for different wake fractions

- FW=0.2  \( U = 0.06 \) m/s
- FW=0.25 kg catalyst
- FW=0.3
- FW=0.35
- FW=0.4
- FW=0.45
- FW=0.5

1-butene conversion

Reaction temperature (°C)

280 300 320 340 360 380 400
The influence of the gas velocity on the conversion is more when the bubbles are assumed to be small. On the other hand, the conversion decreases much faster with increasing gas velocity in the case of small bubbles.

c) Effect of the exchange coefficient

The exchange rate coefficient can be expressed by Eq.1-25 for the Davidson-Harrison model, Eq.1-63 and Eq.1-68 for the Kunii-Levenspiel model (bubble-cloud and cloud-emulsion), and Eq.1-90 for the Kato-Wen model. These equations have been plotted as a function of gas velocity on Fig.3-41.

Since there is no flow passing through the emulsion phase in the Kunii-Levenspiel and Kato-Wen models, the gas exchange coefficients are much larger for these models than that for the Davidson-Harrison model. The values for the exchange coefficients for the Kunii-Levenspiel and Kato-Wen models are very close, although the relations are based on different assumptions. The exchange rate coefficient was calculated for the Kato-Wen model as an average exchange coefficient in all the compartments.

The gas exchange coefficient decreases with increasing gas velocity in the cases of Kunii-Levenspiel and Kato-Wen models, whereas it is fairly constant in the case of the Davidson-Harrison model.
Figure 3-38

Theoretical conversion of 1-butene from the D-H model (perfectly mixed), \( U = 0.03 \) m/s
Figure 3-39

Theoretical conversion of 1-3 butadiene from the D-H model (piston flow), U=0.03 m/s

Conversion

Temperture (°C)

1 kg catalyst
Figure 3-40

Theoretical conversion of 1-butene from the K-L model, \( U = 0.06 \) m/s, \( F_W = 0.3 \)

Conversion

\( db = 0.13 \) m
\( db = 0.26 \) m
\( db = 0.4 \) m
\( db = 0.52 \) m
\( db = 0.65 \) m
\( db = 0.8 \) m
\( db = 1 \) m

Temperature (c)
Figure 3-41
Gas exchange coefficient as a function of gas velocity

- D-H model
- K-L model, bubble-cloud
- K-L model, cloud-emulsion
- K-W model

Gas exchange coefficient vs. Gas velocity (m/s)
3.3.2 Solution of the model equations

The model equations developed in Chapter 1, section 1.2.1.6.2 were solved numerically for the consecutive reactions by a computer program written in Fortran 77 for each model individually.

In the models the minimum fluidization velocity was calculated using three different correlations each based on particle Reynolds number at onset of fluidization. These correlation were:

(i) Thonglimp et al. (1984);

\[ (N_{Re})_{mf} = (31.6 + 0.0425 N_{Ga})^{0.5} - 31.6 \]  \hspace{1cm} (3.26)

(ii) Wen and Yu (1966);

\[ (N_{Re})_{mf} = (33.7 + 0.0408 N_{Ga})^{0.5} - 33.7 \]  \hspace{1cm} (3.27)

(iii) Babu et al. (1978);

\[ (N_{Re})_{mf} = (25.25 + 0.0651 N_{Ga})^{0.5} - 25.25 \]  \hspace{1cm} (3.28)

where \( N_{Ga} \) is the Galileo number, which is:

\[ N_{Ga} = \frac{\rho_g (\rho_p - \rho_g) g d_p^3}{\mu^2} \]  \hspace{1cm} (3.29)

and the minimum fluidization velocity is calculated from the particle Reynolds number at onset of fluidization
The models were solved for the bubble size by employing five bubble size correlations, those of: (i) Kato-Wen (1969);

\[
d_b = 1.4 \rho_p \frac{d_p}{\rho_g} (U - U_{mf}) h + D_o
\]

(ii) Geldart (1971);

\[
d_b = 0.027 (U - U_{mf})^{0.94} h + D_o
\]

(iii) Rowe (1976);

\[
d_b = 0.54 (U - U_{mf})^{2/5} (h + h_{mf})^{3/4} g^{-1/4}
\]

(iv) Mori-Wen (1975);

\[
d_b = d_{bm} - (d_{bm} - D_o) \exp(-0.3h/D_r)
\]

where \(d_{bm}\) is the bubble diameter would exist in a fluidized bed if the fluidizing gas above that required for minimum fluidization went to form a single train of bubbles rising along the center line of the bed. Mori and Wen calculated \(d_{bm}\) from:

\[
(N_{Re})_{mf} = \frac{d_p \rho_g U_{mf}}{\mu}
\]
\[ d_{bm} = 0.652 \left( A_t (U - U_{mf}) \right)^{2/5} \]  

(3.33)

(v) Davidson-Harrison (1963):

\[ d_b = \frac{0.031 \left( 4 \left( \frac{\rho_d - \rho_g}{\rho_p} \right)^2 \right)^{1/5}}{(U/U_{mf} - 1)^{2/5}} \frac{d^2}{\mu} h^{4/5} \]  

(3.34)

where \( d_b \) is the diameter of the sphere with the same volume as the bubble. \( D_o \) is the bubble size at the surface of a perforated plate which is calculated from Eq (1.7).

Two different types of average bubble size definition were used.

(a) \( d_b \), the diameter of the bubble in the middle of the bed. This is the definition which is commonly used.

(b) \( d_{bav} \), the integral average diameter which is given by:

\[ d_{bav} = \frac{\int_0^H d_b(h)dh}{h} \]  

(3.35)

where \( d_b(h) \) is the bubble diameter as a function of height which can be any of the bubble diameter-height correlations given in this section.

Two types of numerical algorithms were used according to type of flow in the emulsion phase. For models whose
flow in the emulsion is assumed to be perfectly mixed, the application of the respective model equation to each chemical species involved in the reaction results in a system of simultaneous non-linear equations. The outlet concentrations of the species in each phase are the unknown in these equations. They were solved by an iterative numerical algorithm based on Newton-Raphson Method. In the case of plug flow in the emulsion phase, one obtains a system of ordinary differential equations. They were solved numerically by a forth order Runge-Kutta method with automatic variation of steps.

A flowchart and listing of the computer program written in Fortran 77 to solve the models is given in the Appendix 5.

3.4 Comparison of predictions with experiments

Yield profile of the reactor products are plotted as a function of reaction temperature at different gas velocities (U) and initial bed height (h) on Fig 3-42 to Fig 3-54. On each graph, four different theoretical curves have been plotted, corresponding to the Davidson-Harrison perfectly mixed model (D-H, pm), Davidson- Harrison piston flow model (D-H, pf), Kato-Wen model (K-W), and Kunii-Levenspiel model (K-L). The interpretation of the prediction of each model are presented below.

a) The Davidson-Harrison model

The concentrations calculated using D-H,pm model are
Figure 3-42  Comparison of the experimental and predicted 1,3 butadiene yields

Comparison of the experimental and predicted maleic anhydride yields

Comparison of the experimental and predicted CO2 yields
Figure 3-43  Comparison of the experimental and predicted 1,3 butadiene yields

Butadiene yield (mole%)

Reaction temperature (°C)

Comparison of the experimental and predicted maleic anhydride yields

Maleic anhydride yield (mole%)

Reaction temperature (°C)

Comparison of the experimental and predicted CO2 yields

CO2 yield (mole%)

Reaction temperature (°C)
in reasonable agreement with the experimental results. In most cases, the maximum difference between experiment and theory occurred in the prediction of CO$_2$ concentrations at high temperature. The theoretical 1,3-butadiene concentration was found to be in very good agreement with the experimental results in all cases.

While the Davidson-Harrison perfectly mixed model offers a fair estimate of the 1,3-butadiene concentration profiles, predicted concentrations by the Davidson-Harrison piston flow, were far too high. Consequently the high prediction of 1,3-butadiene caused the low prediction of CO$_2$ and maleic anhydride as may be seen from the comparison graph of Fig 3-42. Given this lack of agreement, one immediately suspects that the model is deficient in assuming a piston flow in the dense phase.

b) The Kunii-Levenspiel model

The bubbling bed model of Kunii and Levenspiel may be considered as a back-mixing or dense phase flow-reversal model. Since the bubbles are assumed to carry considerable quantities of solid particles in their clouds and wakes, solids must be moving downward in the rest of the bed to compensate for net upward solid motion.

A comparison between experimental results and theoretical concentrations calculated using this model showed that the model can provide a good representation of experimental data for U/U$_{mf}$ values greater than 20. This is
Figure 3-44  Comparison of the experimental and predicted 1,3 butadiene yields

Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model

U= 0.05 m/s
h= 0.2 m

Figure 3-44  Comparison of the experimental and predicted maleic anhydride yields

Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model

U= 0.05 m/s
h= 0.2 m

Figure 3-44  Comparison of the experimental and predicted CO2 yields

Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model

U= 0.05 m/s
h= 0.2 m
Figure 3-45
Comparison of the experimental and predicted 1,3 butadiene yields

Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model
U = 0.06 m/s
h = 0.2 m

Comparison of the experimental and predicted maleic anhydride yields

Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model
U = 0.06 m/s
h = 0.2 m

Comparison of the experimental and predicted CO2 yields

Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model
U = 0.06 m/s
h = 0.2 m
understandable because it was expected that the model with the assumption of a reversed flow of gas in the emulsion phase would not be applicable at low gas velocities. Such a reversal of flow must be assumed to occur for $U/U_{mf}$ more than 20. The poor agreement of the Kunii-Levenspiel model with the observed results at low gas velocities had been demonstrated in the figures 3-43, 3-44, and 3-47 for different operating conditions. It may be seen from the figures 3-48 and 3-49, at the relatively high initial bed height and high gas flow rate, the predicted concentrations become closer to the experimental values.

c) The Kato-Wen model

It was expected that the best predictions would be given by a model with complex hydrodynamics. The Kato-Wen model due to its allowance for variable bubble properties is probably the closest representation of reality.

A comparison between experimental results and theoretical concentrations calculated using this model showed that the model provides the best agreement with the experimental data for the highest values for the mass of the catalyst, figures 3-46 and 3-47. The predicted conversions for the lower values of mass of the catalyst and high gas velocities are seriously underestimated by the Kato-Wen model. Since it is assumed that the gas can only flow in the bubble phase and there is no flow of gas in the emulsion phase, the only contact between gas and solid occurs through the gas exchange between the bubble and
dense phases. Therefore the knowledge of gas interchange between the two phases is a very important factor particularly for a fast reaction such as the reaction investigated in this work. As can be seen from Fig 3-41, as the gas velocity increases, the exchange rate coefficient decreases due to the bigger bubble size. Consequently the conversion, which is directly depended on the gas exchange, drops significantly. As the bed height increases the number of the compartments increases as well. Since there are more stages for the gas exchange, higher conversion will be predicted by the model.

3.5 Model comparison and discussion

A comparison of three classical types of fluidized-bed reactor models, Davidson-Harrison, Kunii-Levenspiel and Kato-Wen, for the prediction of conversion and yield of product during the catalytic oxidation of 1-butene to maleic anhydride revealed that these models were generally in good agreement with the experimental results under certain conditions. However, certain systematic deviations were shown to occur. It is clear from Fig. 3-42 to Fig. 3-54 that the model of Davidson-Harrison, perfectly mixed (pm), gave the best predictions of 1,3-butadiene which was the major intermediate product and with overestimation of CO₂ and underestimation of maleic anhydride gave the perfect agreement with the overall conversion of 1-butene. The model interphase transfer rate was shown to be modest (Fig. 3-41) and the model in general was found to be
Figure 3-46  Comparison of the experimental and predicted 1,3 butadiene yields

![Graph showing the comparison of experimental and predicted 1,3 butadiene yields.](image)

Comparison of the experimental and predicted maleic anhydride yields

![Graph showing the comparison of experimental and predicted maleic anhydride yields.](image)

Comparison of the experimental and predicted CO2 yields

![Graph showing the comparison of experimental and predicted CO2 yields.](image)
Comparison of the experimental and predicted 1,3 butadiene yields

Comparison of the experimental and predicted maleic anhydride yields

Comparison of the experimental and predicted CO2 yields
appropriate over the range of experimental conditions investigated.

The model of Davidson-Harrison strongly overestimates the conversion when the gas is assumed to percolate the emulsion phase in plug flow. Clearly the assumption of plug flow is an over-simplification, and the truth must be that there is some mixing in the dense phase, due to the agitation caused by the rising bubbles. It is clear from Fig. 3-42 to Fig. 3-54 and from other similar comparisons (Chavarie and Grace, 1975) that the agreement between measured and predicted concentration is rather poor. One of the most important factors of applicability of this model rests on the type of reaction occurring in the reactor. It is assumed that the bubble size is constant in this model. It is now well known that the bubble size increases with height above the distributor plate. This means that the bubbles form in very small sizes just above the distribution plate and consequently near the distributor the gas-solid contact is very good, and this excellent contact leads to high conversion right above the distributor plate. This effect is more significant for reactions with a very high reaction rate constant in which a high conversion takes place just above the distributor plate. As can be seen from the Table 3-3, the reaction rate constant for the first reaction of consecutive reaction of 1-butene to maleic anhydride ($K_1$) is very high. It means that the first reaction is much faster than the rest of this chain reaction. That is why the model gives a very
Figure 3-48  Comparison of the experimental and predicted 1,3 butadiene yields

Butadiene yield (mole%)

Reaction temperature (°C)

Exp. points  
D-H model, pm  
D-H model, pf  
K-W model  
K-L model

U = 0.06 m/s
h = 0.265 m

Figure 3-48  Comparison of the experimental and predicted maleic anhydride yields

Maleic anhydride yield (mole%)

Reaction temperature (°C)

Exp. points  
D-H model, pm  
D-H model, pf  
K-W model  
K-L model

U = 0.06 m/s
h = 0.265 m

Figure 3-48  Comparison of the experimental and predicted CO2 yields

CO2 yields (mole%)

Reaction temperature (°C)

Exp. points  
D-H model, pm  
D-H model, pf  
K-W model  
K-L model

U = 0.06 m/s
h = 0.265 m
Figure 3-49  Comparison of the experimental and predicted 1,3 butadiene yields

- Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model

Reaction temperature (c)

Comparison of the experimental and predicted maleic anhydride yields

- Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model

Reaction temperature (c)

Comparison of the experimental and predicted CO2 yields

- Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model

Reaction temperature (c)
good prediction of 1-butene conversions but not completely satisfactory of the concentration predictions. Therefore more emphasis should be given to the reaction with lower rate constants. This would lead to larger bubble diameter, as recommended by the authors (Davidson and Harrison, 1963), which would in turn lead to more satisfactory agreement between the model, particularly in the case of plug flow, and the experimental observations.

The Kunii-Levenspiel model demonstrated a very good agreement with the prediction of the overall conversion of 1-butene, it showed, however, a poor agreement with the product concentration for the operating conditions studied in this work.

The Kunii-Levenspiel model has been found to give good predictions for the overall conversions and product distribution by some investigators (Chavarie and Grace, 1975; Gregoire, 1980; Newton, 1984; Grace, 1987). The range of gas velocities which were experimentally employed by these investigators to test this model were such that $U > U_{mf}$ in order to achieve a vigorously bubbling bed, because the assumptions presented in this model make it particularly applicable to a vigorously bubbling bed.

In order to have a good selective oxidation of 1-butene to maleic anhydride over this particular catalyst (UCL41), it was necessary to have a relatively high contact time between the particles and gas. So most of the experiments were carried out at low gas velocities.
Figure 3-50: Comparison of the experimental and predicted 1,3 butadiene yields

- Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
U = 0.02 m/s
h = 0.33 m

Comparison of the experimental and predicted maleic anhydride yields

- Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
U = 0.02 m/s
h = 0.33 m

Comparison of the experimental and predicted CO2 yields

- Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
U = 0.02 m/s
h = 0.33 m
Figure 3.51: Comparison of the experimental and predicted 1,3 butadiene yields

Butadiene yield (mole%) vs. Reaction temperature (°C)

- Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model

U = 0.05 m/s  h = 0.33 m

Comparison of the experimental and predicted maleic anhydride yields

Maleic anhydride yield (mole%) vs. Reaction temperature (°C)

- Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model

U = 0.05 m/s  h = 0.33 m

Comparison of the experimental and predicted CO2 yields

CO2 yield (mole%) vs. Reaction temperature (°C)

- Exp. points
- D-H model, pm
- D-H model, pf
- K-W model
- K-L model

U = 0.05 m/s  h = 0.33 m
Consequently such a vigorously bubbling bed could not be achieved in most of the cases in this work.

The most noticeable difference between the Kunii-Levenspiel model and the Davidson-Harrison model is the shape of the lower part of the bubbles. As can be seen from Fig. 1-2, each bubble is associated with a wake of particles. The reason for this is that the pressure in the lower part of the bubble is less than in the nearby emulsion phase. Therefore the particles are drawn up behind the rising bubble and form a wake. A range of 0.25-0.4 was recommended by the authors (Kunii and Levenspiel, 1968) for the fraction of wake to bubble. A value of 0.3 was adopted for this work. However, as has already been mentioned in section 3.3.1 and as can be seen from Fig. 3-37 this parameter is not very sensitive as a difference of only 5% in the conversion was observed when wake fraction (fw) was changed from 0.2-0.5.

Another very important parameter of the Kunii-Levenspiel model is the bubble size, since it determines the size of the mass transfer coefficients as predicted by equations 1.63 and 1.66. It can be seen from Fig. 3-40 that the model predicts larger conversions for smaller bubble sizes. Since it is assumed that the bubbles are of a uniform size in the entire bed, the model was solved by using the average bubble diameters calculated from the correlations based on gas velocity (U) and minimum fluidization velocity (U_{mf}).
Figure 3-52  Comparison of the experimental and predicted 1,3 butadiene yields

Comparison of the experimental and predicted maleic anhydride yields

Comparison of the experimental and predicted CO2 yields
Figure 3-53  Comparison of the experimental and predicted 1,3 butadiene yields

Comparison of the experimental and predicted maleic anhydride yields

Comparison of the experimental and predicted CO2 yields
Fig. 3-54 shows better agreement between experimental and theoretical values of concentrations given by the model of Kunii-Levenspiel for the highest values for the gas flow rate and the initial bed height employed in this work, but the model is not feasible for lower flow rates. This is not surprising since it mainly rests on the assumption of reversed flow of gas in the emulsion phase due to upward movement of particles as a wake behind the bubbles. As can be seen from Fig. 3-41 the model presents relatively high gas exchange rates. That is why the model even in at high gas velocity still overestimates the products concentrations. It can be thought that the model strongly overestimates the interphase mass transfer. In some cases the values of the mass transfer coefficient per unit bubble volume have been found to be three times higher than those calculated for the other models under the same conditions.

The Davidson-Harrison and Kunii-Levenspiel models use single average bubble properties for an entire fluidized bed. Kato and Wen (1969) allowed for the variation of bubble size using the correlation of Kobayashi et al. (1965) and Cooke et al. (1968) to represent bubble diameter as a function of bed height. Although the Kato-Wen model presents complex hydrodynamics with assumption of variable bubble properties, its outstanding weakness lies in its assumption of spherical bubbles in the series compartment. It is now well-known that gas bubbles in large fluidized beds are far from spherical, and carry considerable quantities of solid particles in their wake. Therefore,
Comparison of the experimental and predicted 1,3 butadiene yields

Comparison of the experimental and predicted maleic anhydride yields

Comparison of the experimental and predicted CO2 yields
the model was modified by including a wake with the cloud, but as may be seen from Fig. 3.36, the overall performance of the model is completely insensitive to this parameter.

A comparison of the experimental results with the predicted concentrations by the Kato-Wen model indicated that the model provides satisfactory agreement for the highest value of the mass of catalyst or the lowest values of the gas flow rates for the experimental conditions tested in this work. The model gives reasonable predictions for CO₂ and maleic anhydride but over predicts 1,3-butadiene in most of the cases. The results of this work indicate that the bed height or the residence time is more effective for the Kato-Wen model with the assumption of no flow of gas through the dense phase than the Davidson-Harrison model which assumed flow of gas in the dense phase. It can be shown that, for the conditions of this work, the decay of the major intermediate product, 1,3-butadiene, with the bed height for the Kato-Wen model is more than for the Davidson-Harrison model. In the Kato-Wen model, the product is extracted from the dense phase only by mass transfer to the bubble phase and is conducted out of the reactor by the rising bubbles. As the bed height increases or the gas velocity decreases due to increase of residence time, a good transfer occurs between the bubble phase and the dense phase and leads to better conversion of the intermediate reactant. Hence, the Davidson-Harrison model predicts a smaller decay of the intermediate reactant due to the percolation of product
through the dense phase.

Since the Kato-Wen model contains no adjustable parameter, it appears to be the most valuable tool for scale-up purposes and computer simulation of the fluidized-bed reactors. A list of the computer program which has been written in Fortran 77 to solve this model is given in Appendix 5.

3.7 CONCLUSION

Fluidized-bed reactors have been widely investigated and a large number of models have been devised. Although most of these models are based on the results of studies on bubbling, they often differ in many important aspects due to degree of sophistication they involve. The objective of this work was to evaluate and discriminate between three among the most important and popular bubbling bed reactor models, those of Davidson-Harrison (1963), Kunii-Levenspiel (1969), and Kato-Wen (1969). Each one of these models can be considered as a representation of a group of models with similar basic assumptions. For instance, Davidson-Harrison model for its assumptions of uniform bubble size and gas flow pattern in the emulsion phase which can be either perfectly mixed or plug flow, the Kunii-Levenspiel model for its assumption of three phases: bubble, cloud and wake, and emulsion, and also back-mixing or dense phase flow-reversal, and the Kato-Wen model for its assumption of variable bubble properties. The discrimination of these models was based on a comparison between the theoretical
and experimental conversions and selectivities for the catalytic oxidation of 1-butene to maleic anhydride. It is a rather complex and highly exothermic reaction, leading to several by-products.

The theories of catalytic gas-solid reaction in a fluidized bed developed in Chapter 1 section 1.2.1.6 were applied to a 11 cm diameter experimental fluidized-bed reactor using the kinetic data obtained from the fixed-bed reactor.

Three parameters have been investigated in this study: gas flow rate, initial bed height and temperature. An increase in gas flow rate was found to cause a decrease in the overall efficiency of the reactor. The yields and selectivities of the main product (maleic anhydride) were shown to be insensitive to the bed height. The study of the effect of temperature indicated that there was an optimum temperature for each gas flow rate and the initial bed height to get a maximum yield of maleic anhydride.

The suitability of the different models varied widely depending on these parameters. Although the predictions of the Davidson-Harrison, perfectly mixed, and the Kato-Wen models were closer to the experimental results than those of the Davidson-Harrison, piston flow, and the Kunii-Levenspiel models, they are far from being completely satisfactory. Both the theoretical and experimental results indicated that a good contact between gas and solid allowed a very high conversion to occur. As the height of the
catalyst bed was increased in the reactor or the flow rate of the gas was decreased, the theoretical curves approached the experimental values. It seems likely that this applies generally to the kind of reaction studied here and is thus a useful fact to be considered in fluidized-bed reactor design.

The main overall conclusions of predictions of three groups of models studied in this present work may be stated as follows:

(1) The model of Davidson-Harrison which assumes piston flow in the dense phase overestimates seriously the overall conversion for the reaction studied. While the counter part model which assumes perfect mixing in the dense phase gives much better predictions of overall conversion and the predicted concentration for each species was found to be in good agreement with the experimental results. The success of the model appears to be to the moderate interphase mass transfer and the assumption of flow of gas through the emulsion phase with rate of $(U - U_{mf})$.

(2) The assumption of back-mixing or dense phase flow-reversal in the bubbling bed model of Kunii and Levenspiel produced a serious problem in the applicability of the model in this case. Since the range of gas flow rates employed in this work were not high enough, such a back-mixing had not occurred in most of the cases in this study. This model due the assumption of occurrence of reaction within clouds and wakes can give good agreement
with measured yields for a complex reaction scheme in a commercial reactor (Johnsson et al, 1987).

(3) The Kato and Wen bubble assemblage model can provide the best representation experimental data for the highest value of the bed initial height or lowest value for the gas velocity. This shows that the model requires an excellent retention time to complete its gas exchange between the bubble and emulsion phases. While this model was found to give the best prediction of CO₂, the concentration of the intermediate product was seriously overpredicted. The certain advantage of this model to the other models studied in this work rests on its complex hydrodynamics due to allowance bubble properties.
CHAPTER 4

CONCLUSIONS AND SUGGESTIONS
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4 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

4.1 Conclusions from this study

Early in Chapter 1, the objective of this work was set of applying a series of suitable mathematical models to describe a fluidized-bed reactor for a complex form of gas-solid catalytic reactions in which both consecutive and parallel reactions are occurring in the reactor. Four models of fluidized-bed reactors were taken as representation of a broad range of basic assumptions concerning the physical and the hydrodynamic processes in a bubbling fluidized bed.

The suitability of these models was tested experimentally with a reaction of topical interest: oxidation of 1-butene to maleic anhydride, a reaction of actual and potential use of C_4 hydrocarbon rather than benzene to produce maleic anhydride.

In order to study the reaction kinetics, a small fixed-bed reactor was built. A literature survey concerning this reaction kinetic models showed that, in spite of the redox model propounded by Mars and Van Krevelen (1954) which has been found to be valid over a wide range of hydrocarbon oxidations, it was generally unsuitable for the determination of the kinetic parameters for the experimental conditions employed in this study. A kinetic model was developed with some practical facts which allowed major simplifications in the rate expression. The rate constants obtained were found to obey the Arrehenius
correlation with temperature.

The rate constants found from the fixed-bed reactor experiments were used in the evaluation of the fluidized bed models for the conditions of each of the fluidized-bed experiment runs. The minimum fluidization velocity was determined experimentally and all other factors were found from published physical chemical data and theoretical and empirical correlations.

The fluidized-bed experiments were carried out at a variety of flow rates, initial bed heights and different temperatures. In nearly all cases a generally good agreement was found between the Davidson-Harrison, perfectly mixed, and the Kato-Wen models. The best fit was obtained at the low gas flow rate and relatively high initial bed height when there was excellent contact between gas and the catalyst as can be seen from Fig 3-46 and Fig 3-50.

The bubble size is one of the most important parameter in application of the models. Since no description of the bubble size distribution is presented in most of the models, the theory had to compromise by using a mean bubble size, and hence a mean bubble velocity at any given height in the bed.

An alternative is to select a bubble size variation, using reliable published correlations. A reasonably good agreement obtained from the Davidson-Harrison bubble
correlation when employing the mean bubble bubble diameter. The Davidson-Harrison bubble correlation is the only correlation in which the bubble size varies with temperature through the viscosity term (Eq. 3.34).

One of the most significant findings of this work was the effect of bubble size in the performance of these models. It is seen that, the Kunii-Levenspiel model is very sensitive to bubble size, whereas the Davidson-Harrison is less sensitive and would result in the most optimistic predictions. The mass transfer coefficients of the Kunii-Levenspiel and Kato-Wen models are direct and strong functions of bubble size, while mass transfer rates are mostly dependent on the superficial gas velocity in the Davidson-Harrison model. This rests on the basic assumptions of these models. It is noteworthy that, the flow of gas through the emulsion phase has been taken into consideration only by the Davidson-Harrison model among these three models which were investigated. The type of the gas distributor or use of internal baffles are very important for controlling the bubble size in the bed. A stainless steel porous plate was employed as the gas distributor and the fluidized-bed reactor contained an internal in the form a cooling coil. These made the fluid-bed reactor close to those which are used in industry, because most commercial catalytic fluid-bed reactors contain extensive baffle plate arrangement or immersed tubes as the heat exchanger.
The models and experimental gas breakthrough results were compared at 100% 1-butene conversion with the excess gas velocity and with the bed temperature. Since 1-butene conversion was essentially completed close to the distributor plate, in the case of the piston flow models (Davidson-Harrison, piston flow and Kato-Wen) it was necessary to assume that 1,3-butadiene was the main reactant in the system.

In conclusion, the catalytic oxidation of n-butane and 1-butene were studied in a fixed-bed reactor, followed by the study of 1-butene oxidation in fluidized-bed reactor. 1-butene oxidation has been shown to be complex and influenced by several parameters e.g. reaction temperature, contact time, concentration of 1-butene and oxygen and the gas velocity.

The reaction only obeys first order kinetics in air if the 1-butene concentration is kept below 1.3% vol/vol.

Three fluidized-bed reactor models containing no arbitrary parameters have been applied and shown that the applicability of these models is strongly dependent on the range of conditions under which the models have been investigated and leaving open the question of how well the models work as tools for scale-up, for complex kinetics, and for simulation of industrial-scale units. Nevertheless, it is of interest to point out that two of these models compare very favorably with the experimental data under the conditions which were employed in this study.
4.2 Suggestions for further work

One of the achievement of this work was to apply fluidized-bed reactor models to a complex form of gas-solid catalytic reaction. Most previous investigators have chosen a simple first-order kinetic scheme for this purpose.

Engineering calculations of fluidized bed systems rely on empirical correlations available in the literature and on theoretical models. The first approach is limited by the fact that many of the correlations were obtained under conditions which are often different from those envisaged for a given project and experience has shown that design by extrapolating such empirical correlations can be risky. It would therefore be useful to develop a procedure which assembles the different empirical correlations in the literature and provides guidelines on their use and domain of validity.

Regarding the second approach, there are a number of theoretical models available in the literature, but their applications have in general been limited to very simple reaction systems. It would be useful to provide an interface to enable engineers to introduce different kinetic schemes to a particular model.

Use of the fluidized-bed reactor models involves invariably some simplifying assumptions. These assumptions could be further improved for a particular reaction through a better understanding of the processes, physically and chemically, taking place in the reactor. For example, for
gaseous reactions involving a change of volume. The volume change can affect the fluidized state of the bed and consequently the chemical conversion. This aspect is not covered in any of the available models.

It would be extremely useful to develop a computer software package for some well known models, like those which have been used in this work with some modifications on their assumptions based on the aspects discussed in this work particularly in this Chapter.

Another achievement of this work was to demonstrate the performance of two classical types of reactor, fixed-bed and fluidized-bed reactors,. The great majority of reactors used industrially for the selective oxidation for C\textsubscript{4} hydrocarbons are of the fixed bed type although the development of hot spot in these units can be a severe problem. In principle fluidized beds are to be preferred for such highly exothermic reactions but to date there are relatively few processes that use them. Although fluidized-bed reactors offer considerable advantages over fixed beds, they do require an attrition resistant catalyst. The UCL41 catalyst which was employed in this work was quite attrition resistant and of the desired particle size, but the catalyst in its present form is not selective enough to maleic anhydride to be commercially attractive.

Alternative catalysts which are commonly used in the selective oxidation of C\textsubscript{4} hydrocarbons, both the saturated and unsaturated, are mixed oxides of vanadium and
phosphorus; they are also called VPO materials. These catalysts which are normally prepared by reduction of $\text{V}_2\text{O}_5$ with a reducing agent such as an acid or an alcohol and stabilized with phosphoric acid, are of poor attrition resistance and are entirely unsuitable for a fluid-bed reactor. A number of methods were employed in this work to solve this problem by adding 30-50% by weight of colloidal silica or some binders. Adding silica usually causes selectivity losses for selective oxidation reactions. Although the exact nature of the cause of selectivity losses of the catalyst by adding silica is uncertain, it is most probable that the surface of the catalyst is covered by the silica. Further investigation to find some other additive materials to make the VPO catalyst attrition resistant and also keep its selectivity would be desirable. Contractor (1988) suggested that instead of adding large quantities of colloidal silica, use of small quantities of polysilicic acid would lead to an attrition resistant catalyst without loss of the selectivity. This has yet to be demonstrated in a detailed academic investigation which could constitute a future project.
LIST OF SYMBOLS
A pre-exponential factor in Arrhenius equation \( \text{s}^{-1} \)

\( A_o \) catchment area (area of distributor per orifice)

\( A_t \) cross section area \( \text{cm}^2 \)

\( C_o \) reactant concentration in the entering gas stream \( \text{g-mole cm}^{-3} \)

\( C_{Ao} \) reactant gas concentration at the inlet of the fixed-bed reactor \( \text{g-mole cm}^{-3} \)

\( C_{Af} \) reactant gas concentration at the outlet of the fixed-bed reactor \( \text{g-mole cm}^{-3} \)

\( C_{A1} \) 1-butene concentration \( \text{g-mole cm}^{-3} \)

\( C_{A2} \) 1,3-butadiene concentration \( \text{g-mole cm}^{-3} \)

\( C_{A3} \) furan concentration \( \text{g-mole cm}^{-3} \)

\( C_{A4} \) maleic anhydride concentration \( \text{g-mole cm}^{-3} \)

\( C_{A5} \) CO\(_2\) concentration \( \text{g-mole cm}^{-3} \)

\( C_b \) reactant concentration in the bubble phase \( \text{g-mole cm}^{-3} \)

\( C_{bn} \) reactant concentration in the bubble phase at n-th compartment \( \text{g-mole cm}^{-3} \)

\( C_e \) reactant concentration in the emulsion phase \( \text{g-mole cm}^{-3} \)

\( C_{en} \) reactant concentration in the emulsion phase at n-th compartment \( \text{g-mole cm}^{-3} \)

\( C_H \) overall reactant concentration in the top of the fluid-bed reactor \( \text{g-mole cm}^{-3} \)

\( C_n \) overall reactant concentration leaving the n-th compartment \( \text{g-mole cm}^{-3} \)

\( D_o \) bubble size at the surface of perforated plate \( \text{cm} \)

\( d_b \) bubble diameter \( \text{cm} \)

\( d_{bm} \) maximum bubble diameter due to total coalescences of bubbles \( \text{cm} \)

\( d_{be} \) average bubble diameter by integral \( \text{cm} \)
\( d_c \) diameter of cloud \( \text{cm} \)

\( D_e \) effective diffusion coefficient of gas into emulsion \( \text{cm}^2 \text{s}^{-1} \)

\( D_G \) molecular diffusion coefficient of gas \( \text{cm}^2 \text{s}^{-1} \)

\( d_p \) particle diameter \( \mu \text{m} \)

\( \bar{d}_p \) mean particle size \( \mu \text{m} \)

\( D_r \) column diameter or bubble diameter equal to column diameter \( \text{cm} \)

\( D_T \) maximum stable bubble diameter \( \text{cm} \)

\( E \) activation energy \( \text{Kj mole}^{-1} \)

\( F_{ao} \) volumetric flow rate of reactant at the inlet of the fixed-bed reactor \( \text{g-mole s}^{-1} \)

\( F_{ao} \) volumetric flow rate of reactant at the outlet of the fixed-bed reactor \( \text{g-mole s}^{-1} \)

\( F_o \) gas interchange coefficient per unit volume of gas bubble \( \text{s}^{-1} \)

\( F_d \) overall gas interchange coefficient per unit volume of gas bubble \( \text{s}^{-1} \)

\( F_w \) wake fraction

\( G \) gas volume flow rate \( \text{cm}^3 \text{s}^{-1} \)

\( g \) acceleration due to gravity \( \text{cm s}^{-2} \)

\( H \) fluidized-bed reactor height \( \text{cm} \)

\( H_{mf} \) fluidized-bed reactor height at minimum fluidization velocity \( \text{cm} \)

\( h \) distance from the distributor \( \text{cm} \)

\( h_n \) distance between the distributor and \( \text{n-th compartment} \) \( \text{cm} \)

\( K \) rate constant for first order chemical reaction \( \text{s}^{-1} \)

\( K' \) absorption equilibrium constant

\( k \) coefficient in modified two phase theory, Eq. 1.4
\( k_1 \) reaction rate constant for 1-butene oxidation \( s^{-1} \)
\( k_2 \) reaction rate constant for 1,3-butadiene oxidation to furan \( s^{-1} \)
\( k_3 \) reaction rate constant for furan oxidation to maleic anhydride \( s^{-1} \)
\( k_4 \) reaction rate constant for 1,3-butadiene oxidation to \( CO_2 \) \( s^{-1} \)
\( k_{bc} \) mass transfer coefficient between bubble and cloud-wake region \( cm \ s^{-1} \)
\( k_{ce} \) mass transfer coefficient between cloud-wake region and emulsion phase \( cm \ s^{-1} \)
\( k_{be} \) mass transfer coefficient between bubble and emulsion phases \( cm \ s^{-1} \)
\( K_{bc} \) coefficient of gas interchange between bubble and cloud-wake region \( s^{-1} \)
\( K_{ce} \) coefficient of gas interchange between cloud-wake region and emulsion phase \( s^{-1} \)
\( K_{be} \) coefficient of gas interchange between bubble and emulsion phases \( s^{-1} \)
\( K_f \) effective overall reaction rate coefficient \( s^{-1} \)
\( K_G \) mass transfer coefficient between a bubble and its surface \( cm \ s^{-1} \)
\( M \) mass of particle \( g \)
\( M' \) solid interchange coefficient between the bubble and emulsion phases \( s^{-1} \)
\( m_1, m_2 \) roots of quadratic equation
\( N \) number of bubbles per unit volume
\( n_o \) number of holes per unit surface area of distributor
\( N_c \) number of moles of reactant in cloud-wake region
\( (N_{Re})_{mf} \) particle Reynolds number at onset of fluidization
\( N_G \) Galileo number

\( Q \) interphase gas exchange rate \( \text{cm}^{-3}\text{s}^{-1} \)

\( q \) rate of gas interchange between a bubble and the dense phase \( \text{cm}^{-3}\text{s}^{-1} \)

\( Q_b \) volumetric flow rate of bubbles \( \text{cm}^{-3}\text{s}^{-1} \)

\( Q_{mf} \) volumetric flow rate at minimum fluidization velocity \( \text{cm}^{-3}\text{s}^{-1} \)

\( Q_t \) total volumetric flow rate \( \text{cm}^{-3}\text{s}^{-1} \)

\( R \) universal gas constant \( \text{JK}^{-1}\text{mole}^{-1} \)

\( r_1 \) rate of 1-butene oxidation reaction to 1,3-butadiene \( \text{g-mole s}^{-1} \)

\( r_2 \) rate of 1,3-butadiene oxidation reaction to furan \( \text{g-mole s}^{-1} \)

\( r_3 \) rate of furan oxidation reaction to maleic anhydride \( \text{g-mole s}^{-1} \)

\( r_4 \) rate of 1,3-butadiene oxidation reaction to \( \text{CO}_2 \) \( \text{g-mole s}^{-1} \)

\( r_A \) disappearance of reactant A by reaction \( \text{g-mole s}^{-1} \)

\( R_c \) radius of cloud surrounding a bubble \( \text{cm} \)

\( r_e \) rate of reaction in the emulsion phase \( \text{mole s}^{-1} \)

\( S_b \) surface area of the rising bubble \( \text{cm}^2 \)

\( S_{ce} \) outer boundary area of cloud of single bubble \( \text{cm}^2 \)

\( T \) temperature \( ^\circ\text{K} \)

\( U \) superficial gas velocity \( \text{cm s}^{-1} \)

\( U_b \) bubble rise velocity \( \text{cm s}^{-1} \)

\( U_{br} \) rise velocity of a single undisturbed bubble \( \text{cm s}^{-1} \)

\( U_e \) upward velocity of gas through the emulsion phase \( \text{cm s}^{-1} \)
**Greek symbols**

- $\alpha$  ratio of wake volume to the volume of bubbles
- $\delta$  fraction volume of bed occupied by the bubbles
- $\Delta h$  length of n-th compartment
- $\varepsilon$  bed voidage
- $\varepsilon_{mf}$  bed voidage at minimum fluidization velocity
\( \varepsilon_e, \varepsilon_b, \varepsilon_f, \varepsilon_m \) void fraction in the emulsion phase, in the bubble phase, in a bubbling phase as whole, and in a packed bed, respectively.

\( \gamma_b \) ratio of solid dispersed in bubbles to the volume of bubbles.

\( \gamma_c \) ratio of solid dispersed in cloud-wake region to the volume of bubbles.

\( \gamma_e \) ratio of solid dispersed in the emulsion to the volume of bubbles.

\( \mu \) gas viscosity \( \text{g cm}^{-1} \text{s}^{-1} \)

\( \nu_i, \nu_f \) volumetric flow rate of reactant at the inlet and outlet of the fixed bed.

\( \rho_{\text{bulk}} \) particle bulk density \( \text{g cm}^{-3} \)

\( \rho_p \) particle density \( \text{g cm}^{-3} \)

\( \tau \) fixed bed space time or contact time \( \text{s} \)

\( \tau_b \) bubble contact time \( \text{s} \)


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Kunii D. and Levespiel O.


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Martini G., et al.


Mori S. and Wen C. Y.

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Reference</th>
</tr>
</thead>
</table>


APPENDIX
APPENDIX 1

Wiring diagram of the gas shut off safety unit

Any variation in the gas flow rate or excessive heat generation in the fluidized bed caused both the 1-butene and air solenoid valves to close.
APPENDIX 2

Particle size distribution

The particle size distribution of the catalyst used in the fluidized-bed reactor, UCL41, was measured by sieve analysis and the Malvern Particle Sizer as describe in Chapter 2 section 2.5.2.1. The results of each determination are shown graphically here.
MALVERN INSTRUMENTS LTD, SPRING LANE, MALVERN, ENGLAND.

PRINTING RESULTS FROM DATA BLOCK 1

TIME 06-08-40  RUN NO. 2  LOG ERROR = 4.12

SAMPLE CONCENTRATION = 0.0148 % BY VOLUME
OBSCURATION = 0.20

<table>
<thead>
<tr>
<th>SIZE BAND</th>
<th>CUMULATIVE WEIGHT</th>
<th>CUMULATIVE LIGHT ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>UPPER</td>
<td>LOWER</td>
<td>WT BELOW IN BAND</td>
</tr>
<tr>
<td>188.0</td>
<td>87.2</td>
<td>100.0</td>
</tr>
<tr>
<td>87.2</td>
<td>53.5</td>
<td>89.0</td>
</tr>
<tr>
<td>53.5</td>
<td>37.6</td>
<td>68.8</td>
</tr>
<tr>
<td>37.6</td>
<td>28.1</td>
<td>37.8</td>
</tr>
<tr>
<td>28.1</td>
<td>21.5</td>
<td>17.7</td>
</tr>
<tr>
<td>21.5</td>
<td>16.7</td>
<td>6.7</td>
</tr>
<tr>
<td>16.7</td>
<td>13.0</td>
<td>2.2</td>
</tr>
<tr>
<td>13.0</td>
<td>10.1</td>
<td>0.8</td>
</tr>
<tr>
<td>10.1</td>
<td>7.9</td>
<td>0.4</td>
</tr>
<tr>
<td>7.9</td>
<td>6.4</td>
<td>0.3</td>
</tr>
<tr>
<td>6.4</td>
<td>4.8</td>
<td>0.2</td>
</tr>
<tr>
<td>4.8</td>
<td>3.8</td>
<td>0.2</td>
</tr>
<tr>
<td>3.8</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>3.0</td>
<td>2.4</td>
<td>0.2</td>
</tr>
<tr>
<td>2.4</td>
<td>1.5</td>
<td>0.2</td>
</tr>
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</table>

WEIGHT ON DIODE SIZES
Appendix 3  Typical chromatogram from inlet stream of the fluidized-bed reactor.

RUN 1 REACTOR INLET

SENSITIVITIES 200 10

<table>
<thead>
<tr>
<th>TIME</th>
<th>AREA</th>
<th>BC</th>
<th>RRT</th>
<th>RF</th>
<th>G. NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>0.0244</td>
<td>T</td>
<td>0.089</td>
<td>1.000</td>
<td>0.0142 :</td>
</tr>
<tr>
<td>0.35</td>
<td>0.3366</td>
<td>T</td>
<td>0.038</td>
<td>0.938</td>
<td>98.6338 AIR:</td>
</tr>
<tr>
<td>0.66</td>
<td>0.0934</td>
<td>T</td>
<td>0.072</td>
<td>1.040</td>
<td>0.0567 CO2:</td>
</tr>
<tr>
<td>2.30</td>
<td>0.2000</td>
<td>0.251</td>
<td>2.210</td>
<td>0.2578 WATER:</td>
<td></td>
</tr>
<tr>
<td>5.96</td>
<td>0.0157</td>
<td>V</td>
<td>0.651</td>
<td>1.000</td>
<td>0.0092 !</td>
</tr>
<tr>
<td>6.72</td>
<td>0.0101</td>
<td>V</td>
<td>0.734</td>
<td>1.000</td>
<td>0.0059 !</td>
</tr>
<tr>
<td>9.15</td>
<td>2.6811</td>
<td>V</td>
<td>1.000</td>
<td>0.654</td>
<td>1.0224 1-BUTENE:</td>
</tr>
</tbody>
</table>
Appendix 4  Typical chromatogram from outlet stream of the fluidized-bed reactor.

**RUN 1  OUTLET AT 355, FLOW SUMF, 1KG CAR**

**SENSITIVITIES  200  50**

<table>
<thead>
<tr>
<th>TIME</th>
<th>AREA</th>
<th>BC</th>
<th>RRT</th>
<th>RF</th>
<th>C</th>
<th>NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>0.0162</td>
<td>0.009</td>
<td>1.000</td>
<td>0.0108</td>
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<td></td>
</tr>
<tr>
<td>0.36</td>
<td>152.1480</td>
<td>0.038</td>
<td>0.938</td>
<td>0.51825</td>
<td>AIR</td>
<td></td>
</tr>
<tr>
<td>0.68</td>
<td>1.5768</td>
<td>0.072</td>
<td>1.040</td>
<td>1.0938</td>
<td>CO2</td>
<td></td>
</tr>
<tr>
<td>2.09</td>
<td>1.6598</td>
<td>0.222</td>
<td>2.210</td>
<td>2.4466</td>
<td>WATER</td>
<td></td>
</tr>
<tr>
<td>3.84</td>
<td>0.0141</td>
<td>0.939</td>
<td>1.000</td>
<td>0.0094</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.41</td>
<td>1.3572</td>
<td>1.000</td>
<td>0.680</td>
<td>0.6156</td>
<td>1.3 BUTADIENE</td>
<td></td>
</tr>
<tr>
<td>11.28</td>
<td>0.2916</td>
<td>1.198</td>
<td>1.200</td>
<td>0.2334</td>
<td>FURAN</td>
<td></td>
</tr>
<tr>
<td>14.45</td>
<td>0.0394</td>
<td>1.533</td>
<td>0.700</td>
<td>0.0184</td>
<td>PROTONALDEHYDE</td>
<td></td>
</tr>
<tr>
<td>14.74</td>
<td>0.1015</td>
<td>1.566</td>
<td>1.000</td>
<td>0.0677</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.42</td>
<td>0.3860</td>
<td>1.957</td>
<td>1.250</td>
<td>0.3219</td>
<td>MALEIC ANHYDRIDE</td>
<td></td>
</tr>
</tbody>
</table>

**INST 1 METH 2 FILE 122**

**RUN 1  OUTLET AT 355, FLOW SUMF, 1KG CAR II : 3.4  1 / 26 / 90**

**SENSITIVITIES 200 50**
Appendix 5 Logic diagram for computer simulation of the Kato and Wen fluidized-bed reactor model.

Start

Read all the data, e.g.
name and % of each species
physical data of the catalyst
dimension of the reactor
type of the distributor

Select correlations for
minimum fluidization velocity
bubble diameter
bed expansion, etc

Calculate physical properties
at the desired temperature
e.g. density, viscosity,
diffusivity

Calculation of fluidization
properties e.g.
\( U_{mf}, H_{mf}, d_b' \) etc

Solve the model equations for
the bubble and dense phases
numerically

print out all the calculated
fluidization properties,
concentration of each species
at the inlet and outlet of
the reactor, conversion and
selectivity.

End Stop
MODIFIED KATO & WEN MODEL FOR FLUIDIZED-BED REACTORS

BUTENE OXIDATION TO MALEIC ANHYDRIDE

CHARACTER*20 FICHI,CORPU(20)
COMMON /VARI/ PARAM(50)
COMMON /KINET/ DMOL
  /FEED/FO(20),CO(20),PO(20)
  /CONCEP/CB(20,100),CE(20,100),CBP(20)
  /EXIT/SELEC(50),XCON(50),FMX(20,50),FMM(20)
COMMON /SOLID/DP,RHOP
  /RACTOR/DR,IDIST,ANTRU
  /CONDOP/FRAT,AMC,UF,P,T
COMMON /COMPTE/N,NEX
COMMON /NEST/NESP

OPEN(UNIT=7,FILE='gdat1',STATUS='OLD')
WRITE(6,*)'ENTER THE NAME OF THE RESULTS FILE'
READ(7,*),FICHI
OPEN(UNIT=8,FILE=FICHI,STATUS='OLD',FILEOPT='EOF')
NEX=0

C...........definition of the system
C NESP=number of component

WRITE(6,*)'REACTION SYSTEM'
WRITE(6,*)'ENTER THE NUMBER OF COMPONENT'
READ(7,*),NESP
WRITE(6,*)'---'
WRITE(6,*)'ENTER THE NAME OF THE COMPONENTS'
DO 10 I=1,NESP
  WRITE(6,*)'COMPONENT NO. ':'',I
  10 READ(7,*),CORPU(I)

C.......composition of the inlet gas
DO 11 I=1,NESP
  WRITE(6,*)'PERCENTAGE OF ','CORPU(I)
  11 READ(7,*),FO(I)

C.......specification of components for definition of conversion
C and selectivity
C KR=component which is defined for conversion
C KP=component which is defined for selectivity

WRITE(6,*)'ENTER THE DEFINED COMPONENT FOR CONVERSION'
READ(7,*),KR
WRITE(6,*)'ENTER THE DEFINED COMPONENT FOR SELECTIVITY'
READ(7,*),KP

WRITE(6,*)'ENTER THE STOICHIOMETRIC CHANGE IN VOLUME'
READ(7,*),DMOL
C                      REACTOR                      

   WRITE(6,*)' ENTER THE REACTOR DIAMETER ' 
   READ(7,*')DR 
   WRITE(6,*)' ENTER THE TYPE OF DISTRIBUTION PLATE' 
   WRITE(6,*)' POROUS PLATE ----------------------- > 0' 
   WRITE(6,*)' PERFORATED PLATE ------------------ -> 1' 
   READ(7,*')IDIST 
   WRITE(6,*)' ENTER THE NUMBER OF THE DISTRIBUTOR HOLES' 
   WRITE(6,*)' FOR POROUS PLATE JUST ENTER -----> 0.' 
   READ(7,*') ANTRU 

C...minimum fluidization voidage 

   WRITE(6,*)' ENTER THE DEGREE OF VOID AT MINIMUM FLUIDIZATION' 
   READ(7,*') EPSM 

C                      CATALYST                      

   WRITE(6,*)' ENTER THE CATALYST PARTICLE SIZE(IN MICRON)' 
   READ(7,*') DP 
   DP=DP*1. E-6 
   WRITE(6,*)' ENTER THE CATALYST DENSITY' 
   READ(7,*') RHO 

C                      CHOISE OF CORRELATIONS ............ 

   WRITE(6,*)' CHOOSE THE CORRELATION FOR UMF' 
   WRITE(6,*)' THONGLIMP et al. ------- > 1' 
   WRITE(6,*)' WENT & YU ------- > 2' 
   WRITE(6,*)' BABU et al. ------- > 3' 
   READ(7,*') NUMF 

   WRITE(6,*)' CHOOSE THE CORRELATION FOR BUBBLE SIZE' 
   WRITE(6,*)' KATO & WEN ------- > 1' 
   WRITE(6,*)' GELDART ------- > 2' 
   WRITE(6,*)' ROWE ------- > 3' 
   WRITE(6,*)' MORI & WEN ------- > 4' 
   WRITE(6,*)' DAVIDSON-HARRISON -----> 5' 
   READ(7,*') NSIZ 

   WRITE(6,*)' CHOOSE THE TYPE OF BUBBLE DIAMETER' 
   WRITE(6,*)' IN THE MIDDLE OF THE BED ------ > 1' 
   WRITE(6,*)' AVERAGE BUBBLE DIAMETER BY INTEGRAL ------ > 2' 
   READ(7,*') NTYP 

   WRITE(6,*)' *** EXPANSION OF THE BED' 
   WRITE(6,*)' CHOOSE THE CORRELATION FOR BED EXPANSION ' 
   WRITE(6,*)' BABU et al. ------- > 1' 
   WRITE(6,*)' DAVIDSON & HARRISON ------- > 2' 
   READ(7,*') NEXP 

C                      CHOISE OF PARAMETER VARIABLES ............. 

   WRITE(6,*)' WHICH PARAMETER WOULD YOU LIKE TO BE VARIABLE ?' 
   WRITE(6,*)' MASS OF THE CATALYST(AMC) --> 1'
WRITE(6,*)' GAS VELOCITY(UF) --> 2'
WRITE(6,*)' PRESSURE OF REACTOR(P) --> 3'
WRITE(6,*)' TEMPERATURE OF REACTOR(T) --> 4'

READ(7,*)IPARA
GO TO(1,2,3,4),IPARA

1 WRITE(6,*)' ENTER PARAMETER VARIABLE : VMIN, VMAX, NUMBER OF INTERVALS'
READ(7,*)VMIN, VMAX, ANVA
AINC=(VMAX-VMIN)/ANVA
WRITE(6,*)' PARAMETERS FIXED : UF, P, T'
READ(7,*)UF, P, T
T=T+273
DO 101 I=1,ANVA+1
  AMC=VMIN+(I-1)*AINC
  PARAM(I)=AMC
  NEX=NEX+1
  CALL KATWEN(DR,IDIST,ANTRU,EPSM,DP,RHOP,AMC,UF,P,T,DMOL,#
  NUMF,NEXP,NSIZ,NTYP,NESP,CORPU,CR,KP,FICHI,IPARA)
101 CONTINUE
GO TO 109

2 WRITE(6,*)' PARAMETER VARIABLE : VMIN, VMAX, NUMBER OF INTERVALS'
READ(7,*)VMIN, VMAX, ANVA
AINC=(VMAX-VMIN)/ANVA
WRITE(6,*)' PARAMETERS FIXED : AMC, P, T'
READ(7,*)AMC, P, T
T=T+273
DO 102 I=1,ANVA+1
  UF=VMIN+(I-1)*AINC
  PARAM(I)=UF
  NEX=NEX+1
  CALL KATWEN(DR,IDIST,ANTRU,EPSM,DP,RHOP,AMC,UF,P,T,DMOL,#
  NUMF,NEXP,NSIZ,NTYP,NESP,CORPU,CR,KP,FICHI,IPARA)
102 CONTINUE
GO TO 109

3 WRITE(6,*)' PARAMETER VARIABLE : VMIN, VMAX, NUMBER OF INTERVALS'
READ(7,*)VMIN, VMAX, ANVA
AINC=(VMAX-VMIN)/ANVA
WRITE(6,*)' ENTRER PARAMETERS FIXED: AMC, UF, T'
READ(7,*)AMC, UF, T
T=T+273
DO 103 I=1,ANVA+1
  P=VMIN+(I-1)*AINC
  PARAM(I)=P
  NEX=NEX+1
  CALL KATWEN(DR,IDIST,ANTRU,EPSM,DP,RHOP,AMC,UF,P,T,DMOL,#
  NUMF,NEXP,NSIZ,NTYP,NESP,CORPU,CR,KP,FICHI,IPARA)
103 CONTINUE
GO TO 109

4 WRITE(6,*)' PARAMETER VARIABLE : VMIN, VMAX, NUMBER OF INTERVALS'
READ(7,*)VMIN, VMAX, ANVA
AINC=(VMAX-VMIN)/ANVA
WRITE(6,*)' PARAMETERS FIXED : AMC, UF, P, DMOL'
READ(7,*)AMC, UF, P
VMIN=VMIN+273
DO 104 I=1,ANVA+1
  T=VMIN+(I-1)*AINC
  CALL KATWEN(DR,IDIST,ANTRU,EPSM,DP,RHOP,AMC,UF,P,T,DMOL,#
  NUMF,NEXP,NSIZ,NTYP,NESP,CORPU,CR,KP,FICHI,IPARA)
104 CONTINUE
GO TO 109
PARAM(I) = T
NEX = NEX + 1
CALL KATWEN (DR, IDIST, ANTRU, EPSM, DP, RHOP, AMC, UF, P, T, DMOL,
# NUMF, NEXP, NSIZ, NTYP, NESP, CORPU, KR, KP, FICHI, IPARA)

CONTINUE
GO TO 109

CONTINUE
CLOSE(7)
CLOSE(8)

STOP
END

C ........... END OF THE MAIN PROGRAM .......................

C

C ++++++++++++++++++++++++++++++ SIMULATION ++++++++++++++++++++++++++++++++

SUBROUTINE KATWEN (DR, IDIST, ANTRU, EPSM, DP, RHOP, AMC, UF, P, T, DMOL,
# NUMF, NEXP, NSIZ, NTYP, NESP, CORPU, KR, KP, FICHI, IPARA)

C

PARAMETER (RG = 8.314E-2, PI = 3.14159, ACC = 9.81, ERRMAX = 1. E-5, OMEGA =
PARAMETER (NC = 100, NMAX = 20)
PARAMETER (CRIT = 1. E-10, EPS = 1. E-5, NORM = 0, NAP = 100, KIMP = 0, OM = .5,
# IMAX = 0, IDERIV = 0)
CHARACTER*20 CORPU(20)
DIMENSION UFS(NC), UB(NC), UBR(NC), HN(NC), ANB(NC), DHN(NC),
# DB(NC), DC(NC)
DIMENSION XI(NMAX), FI(NMAX), HESS(NMAX, NMAX), VP(NMAX, NMAX),
# FX(NMAX, NMAX), BMII(NMAX), BMII(NMAX)
COMMON /VARI/PARAM(50)
COMMON /COEFT/FOV(100), FOC(100), QBE(100),
# /FEED/FO(20), CO(20), PO(20)
# /PHASE/VBT(100), VET(100), VCT(100), VW(100), VB(100)
# /CONCEP/CB(20, 100), CE(20, 100), CBP(20)
# /EXIT/SELEC(50), XCON(50), FMX(20, 50), FMM(20)
COMMON /PROMEL/VISM, RHOM, DIFF
COMMON /EXPAN/EXPA, HF
COMMON /VITMIN/UMF, EXVO
COMMON /DVIDE/EPSMF, EPSL
COMMON /COMPTE/N, NEX
EXTERNAL BUBEXP
DATA RG, PI, ACC, ERRMAX, OMEGA/8.314E-2, 3.14159, 9.81, 1.E-5, .5/
DATA CRIT, EPS, NORM, NAP, KIMP, OM/1.E-10, 1.E-5, 0, 100, 0, .5/
DATA IMAX, IDERIV/0, 0 /
WRITE(6, *) 'RESULTS OF SIMULATION '
GO TO (1, 2, 3, 4), IPARA

1 WRITE(6, *)' VARIABLE: MASS OF THE CATALYST(kg) = ', PARAM(NEX)
GO TO 5
2 WRITE(6, *)' VARIABLE: GAS VELOCITY(m/s) = ', PARAM(NEX)
GO TO 5
3 WRITE(6, *)' VARIABLE: REACTOR PRESSURE(bar) = ', PARAM(NEX)
GO TO 5
4 WRITE(6, *)' VARIABLE: REACTOR TEMPERATURE(K) = ', PARAM(NEX)
GO TO 5
C ................................ reactor/distributor/flowrates.............

5  SR=PI*(DR*DR)/4.
QGAZ=SR*UF
QNTP=QGAZ*(P/1.013)*(273./T)

C ............................................ initial concentrations ..............

DO 6 I=1,NESP
   PO(I)=P*FO(I)/100.
   CO(I)=PO(I)/(RG*T)
6

C ...calculation the inlet gas properties:
   density(RHOM), viscosity(VISM), diffusivity(DIFF)
FRAT=FO(2)/FO(1)
Y1=1./(FRAT+1.)
Y2=1.-Y1
RHOM=RHOMEL(T)
VISM=VISCOM(T)
DIFF=DIFUS(T,P)

C ...calculation the minimum fluidization velocity
   and minimum fluidization height.
EPSMF=EPSM
HMF=AMC/(RHOP*SR*(1.-EPSMF))
UMF= CALUMF(DP,RHOP,RHOM,VISM,NUMF)

C ...calculation the bubble diameter

IF(NTYP .EQ. 1) GO TO 27
IF(NTYP .EQ. 2) GO TO 28
IF(NTYP .EQ. 3) GO TO 29

27  EXPA=EXPAND(UF,UMF,DP,RHOP,RHOM,DR,DBMOY,NEXP)
   HF=(1.+EXPA)*HMF
   REXP=1.+EXPA
   DBMOY=BUBEXP(NTYP,NSIZ,UF,HF/2.)
   GO TO 30
28
28  EXPA=EXPAND(UF,UMF,DP,RHOP,RHOM,DR,DBMOY,NEXP)
   HF=(1.+EXPA)*HMF
   REXP=1.+EXPA
   HMIN=0.
   HMAX=HF
   NPAS=200
   DBMOY=SIMPS(HMIN,HMAX,NPAS,NTYP,NSIZ,UF,BUBEXP)/HF
   GO TO 30
29
29  HF=2.0*HMF
24  HMIN=0.
24  HMAX=HF
24  NPAS=200
   SUM=SIMPS(HMIN,HMAX,NPAS,NTYP,NSIZ,UF,BUBEXP)
   HNX=HMF/(1.-SUM/HF)
   ERR=ABS((HNX-HF)/HF)
C   WRITE(6,*)HNX,UF,ERR
   IF(ERR.LE.01) GO TO 23
HF = HNX * OMEGA + (1 - OMEGA) * HF
GO TO 24

23 HF = (HF + HNX) / 2.
DBMOY = (HMF / (HF - HMF)) * (UF - UMF) / (.71 * ACC**.5) / 10.) ** 2
EXPA = HF / HMF - 1.
REXP = 1. + EXPA
CONTINUE

C
C PREMIER COMPARTMENT
N = 1
UFS(N) = UF
DBO = (((6. * (UF - UMF) * 1.6 / (PI * ANTRU / SR)) ** .4
# *(ACC*100.0)**(-.2)) / 100.0
DB(N) = DBO
UBR(N) = .711 * SQRT(ACC * DB(N))
UB(N) = UFS(N) - UMF + UBR(N)
UE = UMF / EPSMF
RDCDB = ((UBR(N) + 2. * UE) / (UBR(N) - UE)) ** (1. / 3.)
DC(N) = DB(N) * RDCDB
DH(N) = DC(N)
HN(N) = .5 * DC(N)
VB(N) = (PI * DB(N) ** 3) / 6.
UE = UMF / EPSMF
GO TO 15

THE NEXT COMPARTMENTS
N = N + 1
DVR = QBE(N-1) * VBT(N-1)
UFS(N) = UFS(N-1) - DVR / SR
ITER = 0
HI = HN(N-1) + DC(N-1) * 1.5
ITER = ITER + 1

C BUBBLE VELOCITY
D1 = BUBEXP(1, NSIZ, UFS(N), HI)
UBR(N) = .711 * SQRT(ACC * D1)
UB(N) = UFS(N) - UMF + UBR(N)

C DEGREE OF VOIDAGE
IF(HN(N-1) + .5 * DC(N-1) .LE. HMF) THEN
EPSL = EPSMF
UE = UMF / EPSL
GO TO 10
ELSE
RREXP = (1. / REXP) - (HN(N) - HMF) / (2. * REXP * (HF - HMF))
EPSL = 1. - RREXP * (1. - EPSMF)
UE = UMF / EPSL
GO TO 10
ENDIF

END OF THE DEGREE OF VOIDAGE
RDCDB = ((UBR(N) + 2. * UE) / (UBR(N) - UE)) ** (1. / 3.)
D2 = RDCDB * D1
HIN = HN(N-1) + .5 * DC(N-1) + .5 * D2
ERR = ABS(HI - HIN)
IF(ERR .LE. ERRMAX) THEN
HN(N)=(HIN+HI)/2.

WRITE(6,*)
WRITE(6,*) 'COMPARTIMENT No ',N
WRITE(6,*) 'CONVERGENCE : ITERATION NUMBER=',ITER
WRITE(6,*) 'HIN=',HIN,'HI=',HI,'HN=',HN(N)

C ........... MAXIMUM HEIGHT .........................

IF((HN(N)+.5*D2)-(HMF+2.*(HF-HMF)).LE.0.) THEN
    GO TO 55
ELSE
    GO TO 100
ENDIF

C ........... END OF MAXIMUM HEIGHT .................

ELSE
    IF(ITER.LE.1000) THEN
        HI=HIN*OMEGA+(1.-OMEGA)*HI
        GO TO 17
    ELSE
        WRITE(6,*)'Input OMEGA'
    ENDIF
ENDIF

C ................ BUBBLE DIAMETER AND VELOCITY

55 DB(N)=BUBEXP(1,NSIZ,UFS(N),HN(N))
UBR(N)=.711*SQRT(ACC*DB(N))
UB(N)=UFS(N)-UMF+UBR(N)
RDCDB=(((UBR(N)+2.*UE)/(UBR(N)-UE))**1.3)
DC(N)=RDCDB*DB(N)
DHN(N)=DC(N)

C ............... VOLUME OCCUPIED IN EACH PHASE ..............

15 ANB(N)=6.*SR*(HF-HMF)*DHN(N)/(PI*HF*DB(N)**3)
VB(N)=(PI*DB(N)**3)/6.
VBT(N)=VB(N)*ANB(N)
VCT(N)=VBT(N)*3.*UE/(UBR(N)-UE)
VET(N)=SR*DHN(N)-(VBT(N)+VCT(N))
FW=0.30
VW(N)=FW*VB(N)*ANB(N)

C ...... COEFFICIENT OF BUBBLE-EMULSION GAS EXCHANGE ......

FOC(N)=.11/DHN(N)
FOV(N)=FOC(N)**(UBR(N)-UE)/(UBR(N)+2.*UE)

IF (N.EQ.1)THEN
    DO 70 IK=1,NESP
        BMIN(IK)=0.
    70 CONTINUE
ELSE
    DO 71 IK=1,NESP
        BMIN(IK)=0.
        BMAX(IK)=CB(1,N-1)
    71 CONTINUE
IF(N.EQ.1) THEN
  DO 46 K=1,NESP
    CBP(K)=CO(K)
    I=(K-1)*2+1
    IF(CO(K).GT.0) THEN
      XI(I)=CO(K)*.8
      XI(I+1)=CO(K)*.7
    ELSE
      XI(I)=1.E-3
      XI(I+1)=1.E-4
    ENDIF
  CONTINUE
ELSE
  DO 32 K=1,NESP
    I=(K-1)*2+1
    XI(I)=CB(K,N-1)*.8
    XI(I+1)=CE(K,N-1)*.8
  ENDIF
NEP=2*NEP
CALL NEWTON(NEP,NEP,XI,OM,KIMP,IDERIV,NORM,ESP,CRIT,
# NAP,KAR,FI,HESS,VP,FX,IMAX,MIN,MAX)
DO 33 K=1,NESP
  I=(K-1)*2+1
  CB(K,N)=XI(I)
  CE(K,N)=XI(I+1)
GO TO 21
C .......... calculation of the outlet mole flowrates..........
100 NLAST=N-1
DO 35 JJ=1,NESP
  FMM(JJ)=CB(JJ,NLAST)*(UFS(NLAST)-UMF)+CE(JJ,NLAST)*UMF
35
C ................. the total outlet moles..............
FTOT=0.
DO 76 K=1,NESP
  FTOT=FTOT+FMM(K)
76 CONTINUE
C ......... composition of outlet gas mixture................
DO 77 K=1,NESP
  FMX(K,NEX)=FMM(K)/FTOT*100.
77 CONTINUE
C ..... calculation the conversion and selectivity...........
SELEC(NEX)=FMM(KP)/(UF*CO(KR)-FMM(KR))*100.
FOVTOT=0.0
DO 113 J=1,N
  FOVTOT=FOVTOT+FOV(N)
113 FOVAV=FOVTOT/N
C ********** PRINTING THE RESULTS OF SIMULATION **********
WRITE(8,*), SIMULATION OF FLUIDIZED-BED CATALYTIC REACTOR
WRITE(8,*), KATO AND WEN MODEL
WRITE(8,*), -------------------------------------
WRITE(8,*), DIMENSIONS OF REACTOR AND DISTRIBUTER
WRITE(8,*), -------------------------------
WRITE(8,*), Diameter of reactor = ',DR ,'m'
WRITE(8,*), Number of distributor holes = ',',ANTRU
WRITE(8,*), -------
WRITE(8,*), OPERATION CONDITIONS
WRITE(8,*), -------------------------------
WRITE(8,*), Gas velocity (m/s) = ',UF
WRITE(8,*), Reactor temperature (K) = ',T
WRITE(8,*), Reactor pressure (bar) = ',P
WRITE(8,*), Amount of catalyst (kg) = ',AMC
WRITE(8,*), CATALYST PROPERTIES
WRITE(8,*), -------------------------------
WRITE(8,*), Particle size = ',DP*1.E6,'microns'
WRITE(8,*), Particle density = ',RHOP,'kg/m3'
WRITE(8,*), CHARACTERISTIC OF FLUIDIZED BED REACTOR
WRITE(8,*), -------------------------------
WRITE(8,*), Minimum fluidization velocity = ',UMF,'m/s'
WRITE(8,*), Bubble diameter = ',DB(NLAST),'m'
WRITE(8,*), Minimum fluidization height = ',HMF','m'
WRITE(8,*), Bed height = ',HF','m'
WRITE(8,*), Superficial gas velocity = ',UFS(NLAST),'m/:
WRITE(8,*), COMPOSITION OF GAS, CONVERSIONS AND SELECTIVITIES
WRITE(8,*), -------------------------------
WRITE(8,*), Outlet Inlet
WRITE(8,*), -------------------------------
DO 84 J=1,NESP
CO(J)=CO(J)*UF
WRITE(8,*), CORPU(J), FMM(J), CO(J)
CONTINUE
WRITE(8,*), Percentage of concentrations in the outlet'
DO 85 J=1,NESP
WRITE(8,*), CORPU(J), FMX(J,NEX),FO(J)
CONTINUE
WRITE(8,*), Conversion of',CORPU(KR),'= ',XCON(NEX),' %'
WRITE(8,*), Selectivity of',CORPU(KP),' = ',SELEC(NEX),' %'
WRITE(8,*), '
WRITE(8,*), END OF THE SUBROUTINE -------
SUBROUTINE FONCT(XI,FI,NV)

C***************************************************************************

PARAMETER (RG=8.314E-2,PI=3.14159,ACC=9.81)
DIMENSION XI(NV),FI(NV)
COMMON /COEFT/FOV(100),FOC(100),QBE(100),
#  /KINET/DMOL
#  /CONCEP/CB(20,100),CE(20,100),CBP(20)
#  /PHASE/VBT(100),VET(100),VCT(100),VW(100),VB(100),
#  /CONDOP/FRAT,AMC,UF,P,T
#  /SOLID/DP,RHOP
#  /RACTOR/DR,IDIST,ANTRU
COMMON /COMPTE/N,NEX
COMMON /NEST/NESP

CX=RHOP*(1.-EPSL)
CY=RHOP*(1.-EPSL)
SR=PI*DR*DR/4.
DVOL=DMOL
QBE(N)=RATE(9,XI,EPSL,RHOP,T,P)*VET(N)*DVOL/VBT(N)
AF=QBE(N)/FOV(N)
BF=SR*UF/(VBT(N)*FOV(N))
CF=((VCT(N)+VW(N))/VBT(N))/FOV(N)
DF=(VET(N)/VBT(N))/FOV(N)
DO 1 K=1,NESP
     I=(K-1)*2+1
     FI(I)=BF*CBP(K)-(XI(I)-XI(I+1))-AF*XI(I)-BF*XI(I)
#     +CF*RATE(I,XI,EPSL,RHOP,T,P)
     IF(I+1)=(XI(I)-XI(I+1))+AF*XI(I)+
#     DF*RATE(I+1,XI,EPSL,RHOP,T,P)
1  CONTINUE

RETURN
END

SUBROUTINE NEWTON(NF,NV,XI,OM,KIMP,IDERIV,NORM,EPS,CRT,NAP,KAR,
&FI,HESS,VP,FX,IMAX,BMIN,BMAX)

C***************************************************************************

DIMENSION XI(NV),FI(NV),FX(NV,NV),HESS(NV,NV)
DIMENSION VP(NV,NV)
DIMENSION XAI(100),FAI(100),W(100),GRAD(100)
DIMENSION BMIN(NV),BMAX(NV)

C     INITIALISATION

IMP=6
KMP=KIMP/10
KIMP=KIMP-(KIMP/10)*10
NAPMAX=NAP
NAP=0
ITER=0
KAR=1
NP=NV+1

CALCULATION OF THE CRITERIA

10 CALL FONCT(XI,FI,NV)
NAP=NAP+1
G=0.0
DO 20 I=1,NV
20 G=G+FI(I)*FI(I)

IMPRESSIONS

IF(KIMP.NE.1.AND.ITER.NE.0) GO TO 22
WRITE(IMP,4) ITER,NAP,G,OMEGA
4 FORMAT(/,5X,I4,' ITERATION(S)',6X,'CALCUL(S) OF THE FONCTIONS
&5X, ' CRITERE=',1PG13.6,' FACT. RELAX.=',1PG13.6,//)
WRITE(IMP,1) XI
WRITE(IMP,2) FI
1 FORMAT(IX,' XI',3X,8(1PG13.6))
2 FORMAT(IX,' FI',3X,8(1PG13.6))
CONTINUE

TESTS

IF(NAP.EQ.1) GO TO 30
TEST 1
IF(G.LE.CRIT) KAR=12
TEST 2
IF(G.GT.GA) GO TO 50
EC=ABS(GA-G)/GA
IF(EC.LT.EPS) KAR=11
TEST 3
IF(NAP.GE.NAPMAX) KAR=13
IF(KAR.GT.2) GO TO 220
REMEMORIZING OF THE LAST POINT
30 KDIV=0
GA=G
DO 40 I=1,NV
40 XAI(I)=XI(I)
FAI(I)=FI(I)
GO TO 70
DIVERGENCE. ONE POINT BACKWARD
50 KAR=2
DO 60 I=1,NV
60 XI(I)=XAI(I)
G=GA
KDIV=KDIV+1
GO TO 180
CONTINUE

STUDY OF THE SENSIBILITY

IF(I DERIV.EQ.1) GO TO 104

CALCULATION OF THE JACOBIAN

DO 80 I=1,NV
FX(I,NV)=FI(I)
DO 100 J=1,NV
DX=0.05*XI(J)
IF(DX.EQ.0.) DX=0.001
XST=XI(J)
XI(J)=XI(J)+DX
CALL FONCT(XI,FI,NV)
NAP=NAP+1
DO 90 I=1,NV
DERI=(FI(I)-FX(I,NV))/DX
FI(I)=FX(I,NV)
90 FX(I,J)=DERI
XI(J)=XST
GO TO 105
104 CONTINUE
105 CONTINUE
IF(NORM.NE.1) GO TO 108

NORMALIZATION OF THE JACOBIAN

DO 107 I=1,NV
W(I)=ABS(FX(I,1))
DO 106 J=2,NV
IF(ABS(FX(I,J)).GT.W(I)) W(I)=ABS(FX(I,J))
106 CONTINUE
IF(W(I).EQ.0.) W(I)=1.
107 FX(I,J)=FX(I,J)/W(I)
108 CONTINUE
IF(KMP.NE.1) GO TO 118
IF(ITER.NE.0) GOTO 118
WRITE (IMP,114)
DO 110 1=1,NV,8
DO 110 J=1,NV,8
12=1+7
IF(12.GT.NV) I2=NV
110 WRITE (IMP,116) (FX(I1,J1), J1=J,J2)
114 FORMAT (//,IX,'MATRICE JACOBIAN'/)
115 FORMAT (/5X,'I  J ',2I5/)
EPSM=1.E-20
EPSM=1.E-30
ITER=ITER+1
C CALCUL DE J*(J-1)
IF (KMP.NE.1) GOTO 140
IF (ITER.NE.1) GOTO 140
C
DO 120 I=1,NV
DO 120 J=1,NV
TOT=0.
DO 120 K=1,NV
TOT=TOT+FX(I,K)*VP(K,J)
120 HESS(I,J)=TOT
C
WRITE (IMP,121)
121 FORMAT (/,'MATRICE J*(J-1) '/)
DO 130 I=1,NV,8
DO 130 J=1,NV,8
I2=I+7
IF(I2.GT.NV) I2=NV
WRITE(IMP,115) I,J
J2=J+7
IF (J2.GT.NV) J2=NV
DO 130 II=1,12
130 WRITE (IMP,116) ( HESS(II,J1),J1=J, J2)
140 CONTINUE
C
C CALCULATION OF THE INITIAL SLOPE
IF(ITER.EQ.1) OMEG=( OM-1.0)/G
OMEGA=1.0+OMEG*G
IF(KAR.EQ.1) GO TO 190
180 CONTINUE
C
OMEGA=OMEGA/(2.**KDIV)
OMEG=( OMEGA-1.0)/G
KAR=1
190 CONTINUE
C
C CALCULATION OF THE NEW POINT IN THE INITIAL SPACE
DO 210 I=1,NV
XI(I)=0.
IF(NORM.EQ.O) W(I)=1.
DO 200 J=1,NV
200 XI(I)=XI(I )-OMEGA*VP(I ,J)*FAI( J )/W( I )
210 XI(I )=XI(I )+XAI(I )
C
C LIMITS OF VARIABLES
IF(IMAX.EQ.O) GO TO 10
L=0
DO 215 I=1,NV
CONTINUE
IF(L.NE.0) GO TO 50
GO TO 10
C
CRIT=G
KAR=KAR-10
WRITE(IMP,3) KAR
FORMAT(/,'  ',12,/)  
WRITE(IMP,6) CRIT
FORMAT('  'MINIMUM VALUE OF CRITERIAN=',1PG13.6,//, 
&10X,'PARAMETRES',15X,'FUNCTIONS')
DO 230 I=1,NV
WRITE(IMP,7) I,XI(I),I,FI(I)
FORMAT(1OX,' XI=',1PG13.6,5X,' FI=',1PG13.6)
KIMP=ITER
OM=OMEGA
WRITE(IMP,8) NAP,ITER,OM
FORMAT}//NUMBER OF THE CALLED FUNCTION=',16,/, 
&NUMBER OF ITERATIONS=',15,/, 
&FINAL RELAXATION FACTOR=',1PG13.6,//)
RETURN
END
C **************************************************************
FUNCTION CALUMF(DP,RHOP,RHOG,VIS,NUMF)
COMMON /VITMIN/UMF,EXVO
AR=9.81*DP**3*RHOG*(RHOP-RHOG)/VIS * 2
GO TO (1,2,3), NUMF
C THONGLIMP et al
1 REYMF=SQRT(31.6**2+.0425*AR)-31.6
GO TO 10
C WEN AND YU
2 REYMF=SQRT(33.7**2+.0408*AR)-33.7
GO TO 10
C BABU et al
3 REYMF=SQRT(25.25**2+.0651*AR)-25.25
GO TO 10
10 CALUMF=REYMF*VIS/(RHOG*DP).
RETURN
END
C **************************************************************
CALCULATION THE BED EXPANSION

FUNCTION EXPAND(UF, UMF, DP, RHOP, RHOG, DR, DB, NEXP)
PARAMETER(EPSMF=.39)
COMMON /EXPAN/EXPA,HF

GO TO (1,2), NEXP
BABU et al.

1 EXPAND=.762*(UF-UMF)*.57*RHOG*.083/
   # (RHOP*.166*UMF*.063*DR*.445)
   GO TO 10

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2 EXPAND=(UF-UMF)/(.711*SQRT(9.81*DB))
GO TO 10

10 RETURN
END

ESTIMATION THE GAS VISCOSITY

FUNCTION VISCOM(T)
PARAMETER(AMI=29, SIGMA1=3.617, FC1=97)

OMEGA(X)=1.09*X**(-.1662)
AKTEPS=T/FC1
VISCOM=(2.6693E-6*SQRT(AMI*T)/((SIGMA1**2)*OMEGA(AKTEPS)))
RETURN
END

ESTIMATION THE GAS DENSITY

FUNCTION RHOMEL(T)
RHOML1=1.2928
RHOMEL=(273*RHOML1)/T
RETURN
END

DIFFUSIVITY
FUNCTION DIFUS(T,P)
  PARAMETER (AM1=29,AM2=64,FC1=97,FC2=410,
             SIGMA1=3.617,SIGMA2=4.997)
  COMMON /PROMEL/VISM,RHOM,DIF
  OMEGA(X)=1.09*X**(-.1662)
  EPSKM=SQR(F1*FC2)
  SIGMAM=(SIGMA1+SIGMA2)/2.
  AKTEPS=T/EPSKM
  DIFUS=.00185*T**1.5*SQR((AM1+AM2)/(AM1*AM2))/
  # (.9869*P*SIGMAM**2*OMEGA(AKTEPS))*1.E-4
  RETURN
END

FUNCTION BUBEXP(NTYP,NSIZ,UF,H)
  PARAMETER(ACC=9.81,PI=3.14159)
  COMMON /RACTOR/DR,IDIST,ANTRU
  COMMON /SOLID/DP,RHOP
  COMMON /SIZE/DB, DBO, DBM, HO
  COMMON /VITMIN/UMF,EXVO
  C Definition of the functions
  --
  C Integration function for the determination the average
  C bubble size corresponding to the expansion of the fluid bed.
  --
  FUN(BUB)=1./(1.+(.71/(UF-UMF))*SQR(9.81*BUB))
  C Initial bubble size
  --
  DBI(UF, UMF, DTRU)=((6.*(UF-UMF)*1.E6/( PI*DTRU))**.4
  #*(ACC*100.0)**(-.2))/100.0
  C Calculation of the initial bubble size
  IF(IDIST.EQ.0) THEN
    DBO=0.
  ELSE
    SR=PI*DR*DR/4
    DTRU=ANTRU/SR
    DBO=DBI(UF, UMF, DTRU)
  ENDIF
  C ................
  C beginning of the calculation of bubble size at a given height
  GO TO (1,2,3,4),NSIZ
  C KATO AND WEN
  C
  1 DBH=14.*1.E-2*RHOP*DP*(UF/UMF)*H+DBO
  GO TO 100
C  ------------------------
2 DBH=2.048159*(UF-UMF)**.94*H+DBO
GO TO 100

C  ------------------------
3 HO=DBO**((4./3.)*9.81**(1./3.)*(UF-UMF)**(-2./3.))/100.
DBH=(UF-UMF)**0.5*(H+HO)**.75*9.81**(-.25)
GO TO 100

C  ------------------------
4 DBM=1.6377*(.25*PI*DR*DR*(UF-UMF))**.4
DBH=DBM-(DBM-DBO)*EXP(-.3*H/DR)
GO TO 100

C  ------------------------
5 DBH=(0.031*(ACC*DP**4*(RHOP-RHOM)**2)**(1/5))/(VISM**2/5)
#*(UF/UMF-1)**2/2/5*H**4/5
GO TO 100

100 NTY=NTYP*10
GO TO (10,20,30),NTY

10 BUBEXP=DBH
GO TO 11

20 BUBEXP=DBH
GO TO 11

30 BUBEXP=FUN(DBH)
GO TO 11

11 CONTINUE

RETURN
END

FUNCTION SIMPS(A,B,N,NTY,NSI,UH,BUBEXP)
EXTERNAL BUBEXP

TWOH=(B-A)/N
H=TWOH/2.
SUMEV=0.
SUMOD=0.
DO 1 K=1,N
   X=A+FLOAT(K-1)*TWOH
   SUMEV=SUMEV+BUBEXP(NTY, NSI, UH, X)
   SUMOD=SUMOD+BUBEXP(NTY, NSI, UH, X+H)
1 CONTINUE
SIMPS=(2.*SUMEV+4.*SUMOD-BUBEXP(NTY, NSI, UH, A)
# +BUBEXP(NTY, NSI, UH, B))*H/3.

RETURN
END

FUNCTION RATE(N,CI,EPSL,RHOP,T,P)
PARAMETER(NMAX=20)
DIMENSION CI(6)
\[ R_1(T, C_1) = (602 \times \exp(-1817.52/T)) \times C_1 \]
\[ R_2(T, C_2) = (2.4 \times 10^6 \times \exp(-10944/T)) \times C_2 \]
\[ R_3(T, C_2) = (1.6 \times 10^{10} \times \exp(-14348/T)) \times C_2 \]
\[ R_4(T, C_4) = (6.2 \times 10^{13} \times \exp(-20099.8/T)) \times C_4 \]

\[
\begin{align*}
RR1C &= R_1(T, Cl(1)) \\
RR1E &= R_1(T, Cl(2)) \\
RR2C &= R_2(T, Cl(3)) \\
RR2E &= R_2(T, Cl(4)) \\
RR3C &= R_3(T, Cl(3)) \\
RR3E &= R_3(T, Cl(4)) \\
RR4C &= R_4(T, Cl(5)) \\
RR4E &= R_4(T, Cl(6)) \\
\end{align*}
\]

GO TO (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16), N

1 \ RATE = -RR1C \\
2 \ RATE = -RR1E \\
3 \ RATE = RR1C - (RR2C + RR3C) \\
4 \ RATE = RR1E - (RR2E + RR3E) \\
5 \ RATE = 4 \times RR3C \\
6 \ RATE = 4 \times RR3E \\
7 \ RATE = RR2C - RR4C \\
8 \ RATE = RR2E - RR4E \\
9 \ RATE = RR4C \\
10 \ RATE = RR4E \\
11 \ RATE = -(0.5 \times RR1C + RR2C + 5.5 \times RR3C + 2 \times RR4C) \\
12 \ RATE = -(0.5 \times RR1E + RR2E + 5.5 \times RR3E + 2 \times RR4E) \\
13 \ RATE = 0.0 \\
14 \ RATE = 0.0 \\
15 \ RATE = RR1C + RR2C + 3 \times RR3C + RR4C \\
16 \ RATE = RR1E + RR2E + 3 \times RR3E + RR4E \\
END