THE CATALYTIC OXIDATION OF BENZENE

TO MALEIC ANHYDRIDE

BY

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THESIS PRESENTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
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1974
TO MY PARENTS

MA. LUISA y FAUSTINO

TO MY BROTHERS

VICTOR MANUEL y JOSE LUIS
ACKNOWLEDGMENTS

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PREFACE

The work described in this thesis is the original work of the author except where specific reference is made to other sources. It has not been submitted, in whole or in part, for any degree at any other University.
Summary

A study of the catalytic oxidation reaction of benzene to maleic anhydride in the vapour phase is presented from literature survey and catalyst preparation followed by determination of the kinetics at isothermal conditions to the mathematical modelling of one and two inch diameter large scale non-isothermal reactors from experimental measurements of their temperature profiles.

Experiments at isothermal conditions in small diameter tubular reactors were performed to assess the effect of catalyst dilution, free space after the catalyst bed, packing after the catalyst bed, reactor materials of construction and change in reactor diameter. It was found that maleic anhydride readily combusted on almost any surface with the catalyst among the most inert of all materials. No evidence was found of the possible existence of linked and concurrent heterogeneous-homogeneous steps in the formation of maleic anhydride and its further oxidation. Dilution of the catalyst bed proved detrimental to the selectivity of the reaction which otherwise maintained constant high selectivity levels (± 60%).

Use of different reactor materials of construction (aluminium, titanium and stainless steel) yielded the same selectivities when packed with equal amounts of the same catalyst.

Increase in reactor diameter from \( \frac{3}{4} \) to 1 and 1\( \frac{1}{2} \) inch diameter resulted in catalyst deactivation ascribed as due to overheating.

The kinetics of the reaction were determined using aluminium tubular reactors and a spinning catalyst basket reactor (SCBR) over the temperature range 400 to 500\(^\circ\)C. The results show that the reaction can be adequately represented, for the purposes of modelling the reactor, by a triangular scheme of pseudo first order heterogeneous reactions.
To extend the work to the modelling of large scale non-isothermal reactors, kinetic measurements were performed on a sample of a large batch of prepared catalyst. Part of this catalyst was used in a one inch diameter reactor and temperature profiles and outlet concentration were measured. The catalyst from this reactor was later mixed with fresh catalyst to provide a bed for a two inch diameter reactor.

Initial attempts to fit the experimental temperature profiles using the kinetics obtained beforehand, extrapolated where necessary, allowing the heat transfer coefficients to be decided proved unsuccessful. The kinetic parameters were shown to be the cause of the discrepancies.

Re-determination of the kinetics for pellets of different colour taken from the two inch diameter reactor revealed differing catalyst deactivation. A change in the rate controlling mechanism of the reaction at about 425-450 °C also became apparent from the extension to higher temperatures of the kinetics. Proper incorporation of the re-determined kinetics into the model allowed a good fit of the experimental temperature profiles and the outlet concentrations with acceptable values of 'best-fit' heat transfer coefficients.

A comparison between the 'best-fit' heat transfer coefficients and those yielded by literature correlations is made to show that the internal bed resistance rather than that at the wall apparently controls the transfer of heat. Probable catalyst activity profiles are also made evident from this analysis.

Analysis of the catalyst behaviour shows its 'self-adjusting' activity which constrains the reactor to operate in a stable region even at high jacket temperatures.
It was found that a one-dimensional model adequately describes the non-isothermal reactors probably due to the tendency of the bed to operate in a one-dimensional mode due to this 'self-adjusting' mechanism, which reduces the catalyst activity most in those regions where high temperatures would otherwise be experienced.
Introduction

In a large number of industrially important reactions, especially in the partial oxidation of aromatic hydrocarbons in the gas phase, vanadium pentoxide based catalysts play a very important role.

Among some of the important reactions are the oxidation of naphthalene and o-xylene to phthalic anhydride, benzene to maleic anhydride, toluene to benzaldehyde and benzoic acid and anthracene to anthraquinone.

In order to point out the difficulties in carrying out these reactions, let us consider the partial oxidation of benzene to maleic anhydride. This reaction is particularly useful to consider as it is typical of aromatic hydrocarbon oxidations in the gas phase over $V_2O_5$ based catalysts. In this case the catalyst used consists of a mixture of $V_2O_5 - MoO_3$, with a molar ratio of about 1/3 in MoO$_3$ to V$_2$O$_5$. Small amounts of P$_2$O$_5$ and some cations of the group VIII of the transitionals are sometimes added to the catalyst.

Industrial practice has given rise to yields of around 60-70% based on benzene. To understand why these yields do not approach 100% and to define the key factors in trying to improve the selectivity of the process, we must look at the kinetic scheme.

In general, the reactant A (benzene), reacting with an agent X (oxygen from the air), is converted into a product B
(maleic anhydride), which may further react to form a final product C (carbon oxides), with A going directly at the same time to C according to:

\[
A \xrightleftharpoons[k_3]{k_1} B \xrightarrow{k_2} C
\]

The differential equations describing the variation of the concentration with time of the elements of the above scheme have been integrated by De Doer and Van der Borg (1) assuming first order kinetics to yield:

\[C_A = (C_A)_0 \exp \left[ -(k_1 + k_3) t \right] \]  

(1)

\[C_B = (C_A)_0 \left( -\frac{k_1}{k_1 + k_3 - k_2} \exp\left[ -(k_1 + k_3) t \right] - \exp\left[ -k_2 t \right] \right) \]  

(2)

\[C_C = (C_A)_0 \left\{ \frac{k_2 - k_3}{(k_1 + k_3 - k_2)} \exp\left[ -(k_1 + k_3) t \right] - \frac{k_1}{(k_1 + k_3 - k_2)} \exp\left[ -k_2 t \right] \right\} \]  

(3)

with:

\[C_B \text{max} = (C_A)_0 \left( \frac{k_1}{k_1 + k_3} \right) \left[ \frac{k_2}{k_1 + k_3} \right] \frac{k_2}{(k_1 + k_3 - k_2)} \]  

(4)

If it is considered, in an heterogeneous catalysed reaction, that the reactant A is adsorbed on the surface of the catalyst and reacts in this adsorbed state to yield the intermediate product B, there are two possibilities. The first is that the intermediate product B is desorbed into the fluid phase, either remaining there or being readsorbed and then reacting further to give the final product C. The second is that B does not desorb and it reacts at the same site to give C, in which case B does not contribute towards the concentration \(C_B\) in the fluid phase.
It can be said, therefore, that the path $A \rightarrow C$ accounts for those molecules of $A$ which, after having been converted to $B$, react further to give $C$ without being desorbed during this process.

Since this direct route will always be followed by at least some molecules, in practice, $k_3$ cannot become zero. From equations (1)-(4) and from the above discussion it can be seen that if a high yield of $B$ is desired one should try to exercise influence on the two selectivity coefficients, viz. $\frac{k_1}{k_3}$ and $\frac{k_1}{k_2}$, and obtain their highest possible value. In order to do so, knowledge of the physical and chemical elementary steps involving reactants, products and catalyst is desirable.

Each elementary step may be studied and then an attempt made to integrate them into an overall process - a difficult and inaccurate procedure - or the overall process may be analysed to obtain information on the elementary steps. In most cases, for practical purposes, the latter approach is used.

Clearly, the study of the catalytic oxidation of aromatic hydrocarbons represents an industrial as well as an academic challenge owing to the complexity of the reaction schemes and often high exothermicity* which makes separation of transport and kinetic effects difficult.

The main type of reactor used in catalytic aromatic oxidation is of the fixed bed tubular type. This reactor has an arrangement similar to a heat exchanger with the catalyst pellets packed inside the tubes and the cooling medium flowing on the shell side.

Large control problems occur when working in industrial scale reactors due to the high exothermicity* of the reactions.

* 10500 - 13500 BTU per pound benzene converted (2).
The liberation of large amounts of heat due to chemical reaction raises the temperature of the system in such a way that isothermality is rarely achieved at high conversions. A high bed temperature may be desirable in as much as it reduces the size of the reactor; on the other hand, it may lead to the promotion of undesirable side reactions and possible deactivation of the catalyst.

The maximum temperature reached inside the catalytic bed is known as the "hot spot". Control over the temperature profile in the bed and indeed over the "hot spot" is a primary concern in the design of chemical reactors.

In practice, several approaches can be followed to achieve control over the hot spot temperature. A jacket design of several sections each one having a different rate of cooling was proposed by Paris and Stevens (3). Calderbank, Caldwell and Ross (4) studied the effect of diluting the catalyst bed with inert packing as a policy to optimise the temperature profile in the bed.

Another way of gaining control over the temperature profile in the bed is the addition of cold reactants as the reaction proceeds; the so-called "cold shooting". However, this policy is more suitable for a batch reactor or a sequence of reactors.

Despite the above design conditions, it is well recognised that reactors do go out of control with the temperature, at some point or in the whole bed, rising rapidly or oscillating strongly after a perturbation in the inlet conditions. This leads, sometimes, to irreversible damage to the catalyst. In order to overcome these difficulties, a theoretical mathematical model of the performance of the reactor must be developed to allow for the prediction of the effects of the variations of inlet conditions.
on the performance of the reactor. However, a "good" mathematical model can only be achieved if an experimental kinetic study of the reaction is at hand.

The most reliable procedure is then, the study of the kinetics of the reaction on the laboratory scale. These kinetic data are then incorporated in a mathematical model of the larger scale reactor. The predictions of the model should then be compared with the results obtained from experiments in a pilot plant scale. The mathematical model can be further modified until reasonable agreement is reached with the pilot plant experiences.

Under these conditions, the model will provide the "safe region" within which the commercial reactor is to be built and operated.

The development of a mathematical model for packed bed chemical reactors is guided by two conflicting considerations, accuracy and practicability. One is tempted to include mathematical relationships for every part of the reactor system. This may lead to an almost impossible system to solve which, additionally, may give very little extra useful information. It is the task of the engineer then to neglect, at first, the processes which seem to be of minor importance in order to achieve a balance. It is normal practice to start with the simplest possible model, which is further extended into a more complex one depending on the difference between the predictions of the model and the results obtained in the pilot plant experiments.

Clearly, there is a need to examine both the experimental and reactor model aspects of oxidation reactions concurrently as
part of one project. It is this frame of reference which defines the work encompassed by this thesis.
Chapter 1

Literature Survey

Vapour Phase Catalytic Oxidation
of
Benzene to Maleic Anhydride

1.1) General
1.2) Reaction Models and Mechanism
1.3) Homogeneous-Heterogeneous Interactions
1.4) Object of the study
1.1) General

Maleic anhydride, maleic acid and fumaric acid constitute a group of related, industrially important chemicals. They were prepared and characterised for the first time by Pelouze \((S)\) who in 1834 obtained these compounds by heating malic acid. Maleic anhydride assumed industrial importance much later after Weiss and Downs \((6, 7)\) prepared it by the catalytic oxidation of benzene. Maleic acid became commercially available in 1928 and the anhydride in 1933.

![Chemical structures of Maleic Anhydride, Maleic Acid, and Fumaric Acid](https://via.placeholder.com/150)

Maleic Anhydride  Maleic Acid  Fumaric Acid

Most of the maleic anhydride produced commercially is made by the catalytic oxidation of benzene in the vapour phase \((6, 8)\). Many other raw materials have been used, one manufacturer uses butene \((9)\). Nearly any four or five carbon (except a paraffin) affords maleic anhydride in some yield, particularly furfural, crotonaldehyde and olefins \((8, 10)\).

Economics in the United States favours the use of benzene. A cost calculation \((11)\) for production from benzene at 3.75 c./lb shows a cost of 11.3 c./lb at a rate of 10 million
pounds per year. Maleic anhydride is obtained as a byproduct in the manufacture of phthalic anhydride.

Maleic anhydride is mainly produced by the fixed bed process (12, 13) although patents have been taken out for a fluid bed operation (14). The multitubular converter is equipped for cooling the tubes by means of circulating mercury or molten salts (15). The need for efficient heat removal is dictated by the highly exothermic reaction which liberates 10500 - 13500 BTU per pound of benzene reacted.

In general, a vapour mixture of 1.2 - 1.5 mole percent benzene in air (127) is fed through the catalyst bed which is maintained at 300 - 400°C (16, 17). Usually, the bed is of cylindrical form with random packing of $V_2O_5$ based catalyst particles. The contact times vary between 0.1 sec to 5.0 sec (15, 16) at atmospheric pressure and can be changed according to the conversion and temperature. The effluent gases contain: maleic anhydride, maleic acid, carbon dioxide, carbon monoxide and water as well as some benzene unreacted. The reaction mixture is passed through a cooler, if maleic acid is required the cooled gases are absorbed in water to yield a 40% solution which is purified with carbon, concentrated and crystallised (18-20). If maleic anhydride is wanted the cooled gases are partially condensed (21) at 60°C which is slightly above the melting point of the maleic anhydride. The remaining gases are absorbed in solvents from which the anhydride is recovered by dehydration and distillation. The condensed maleic anhydride and maleic acid are dehydrated by vacuum or azeotropic distillation. Purification is effected by vacuum distillation.
or sublimation (18-20). Overall yield of the purified anhydride is 50 - 60% based on benzene.

The breakdown, in the U.S.A., of maleic anhydride usage is presented in Table I (2).

<table>
<thead>
<tr>
<th>Product</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyesters</td>
<td>40</td>
</tr>
<tr>
<td>Alkyd resins and drying oils</td>
<td>16</td>
</tr>
<tr>
<td>Agricultural Chemicals</td>
<td>10</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>16</td>
</tr>
<tr>
<td>Plastics, Lubricants, Copolymers</td>
<td>14</td>
</tr>
<tr>
<td>Miscellaneous and Export</td>
<td>4</td>
</tr>
</tbody>
</table>

The major application of maleic anhydride is in the formation of resins. The primary reaction in the preparation of maleic resins is esterification. Additional polymerization can take place which leads to three dimensional molecules and consequently to extremely hard resins.

A wide variation in the final properties of a resin and product can be governed by the types of polyhydric alcohols used for esterification, by mixtures of maleic anhydride with other polybasic acids, the use of polimerizable compounds such as olefins and of course by the manner of processing the resin. Polyester resins are made from glycol maleates or fumarates copolymerized with styrene monomer. The resin cures rapidly at low temperature and pressure to yield a rigid insoluble solid with good dielectric properties and high
structural strength mainly used with glass fibre and other reinforcing materials to produce large rigid mouldings. Among the products for which these laminating resins and glass fibres are used are: automobile bodies, structural building panels, moulded boats, chemical storage tanks, lightweight pipes, machinery housings, furniture, radar domes, luggage and bath tubs. Maleic anhydride when substituted for a part of the phthalic anhydride in alkyd formulations, shortens the processing time and develops a harder resin used in baking enamels, plasticising resins, marine paints, and varnishes.

Among the agricultural chemicals derived from maleic anhydride are maleic hydrazide, a growth retardant, and Malathion (Reg. Trade Mark, American Cyanamid Co.), an exceptionally effective insecticide. Alkyd maleates are not only insecticides and repellents but are intermediates for the manufacture of fungicides and more specifically acting insecticides (22). Many commercially important chemicals are easily made from maleic anhydride. These include fumaric acid, aspartic acid, and tartaric acid. When reacted with sodium bisulfite, sulfosuccinic acid is formed which is the basic raw material for the production of some wetting agents. Many derivatives of maleic anhydride have important uses in pharmaceuticals (22), textile finishes, photographic chemicals, surface active agents, dyestuffs, tanning agents, petroleum additives, rubber chemicals and synthetic lubricants.
1.2) Reaction Models and Mechanisms

Following the work of Weiss and Downs (7), several research publications and patents have appeared on the vapour phase catalytic oxidation of benzene to maleic anhydride or related subjects, giving an insight into the mechanism of reaction, the structure of the $V_2O_5 - MoO_3$ based catalysts, the role of the oxygen on the reaction or simply empirical relationships.

The literature on hydrocarbon oxidation has been thoroughly reviewed by Marek and Hann (23), Dixon and Longfield (8) and more recently by Germain (24) and Margolis (25, 26). In addition, a number of reviews have appeared on the various scientific aspects of catalysis: on the principles of catalysis by Seitz (27) and Schwab (28), on chemisorption by Taylor (29), Kwan (30), de Boer (31) and Trapnell (32), on physical structure and texture by de Boer (33) and Emmett (34), on the defect structure by Gray and Darby (35), on electronic factors in catalysis by Garner (36) and Baker and Jenkins (37), on magnetic susceptibility of metal catalysts by Marted (38) and on active centres and reaction models by Baladin (39).

Up to now no overall picture of all the above mentioned aspects of catalysis has emerged to unlock the mysteries of catalysis.

It is not the intention of this literature survey to give a full and comprehensive account of all the work on the above mentioned subjects but rather to summarise and discuss the particular features of the benzene partial oxidation reaction.

Several authors (40 - 44) have suggested that the reaction proceeds through a number of intermediates including phenol,
quinone, and hydroquinone and the presence of formaldehyde, diphenyl and acrylic acid has also been reported (7, 45) among the products. However, maleic anhydride is the only product economically attractive and, in general, it has been found by a number of researchers (8, 24, 48, 52) that the principal overall reactions involved can be described by the triangular scheme:

\[ \text{C}_6\text{H}_6 \xrightarrow{1} \text{Maleic Anhydride} \]
\[ \xrightarrow{2} \text{Carbon Oxides} \]
\[ \xrightarrow{3} \]

in which both reactions 1 and 3 may proceed through a number of short lived intermediates. Nevertheless, the prediction of reaction schemes for hydrocarbon catalytic oxidation on metal oxides is a difficult task due to the complexity of the reactions involved, the diversity of products formed and the lack of information on the nature of the elementary acts.

Charlot (46), investigated the activity of a great number of various metal oxides in the reaction of toluene with oxygen and stated that the total and partial oxidation processes in a consecutive scheme of reactions are independent of each other. On the other hand, Marek (23) believes that a catalyst accelerating the first step will accelerate all the subsequent steps as well, since it is difficult to conceive a catalyst that would accelerate the oxidation of hydrocarbons and have no effect on the oxidation of formaldehyde to water and carbon dioxide. In general, the ratio of consecutive to parallel reactions is a function of the hydrocarbon structure, the type of catalyst and the reaction temperatures.
Hammar (47) studied the oxidation of benzene over a series of catalysts consisting of $V_2O_5$ and $MoO_3$ on aluminium and came to the conclusion that benzene oxidizes by two different independent routes and interpreted his data according to the scheme:

$$C_6H_6 + O_2 \rightarrow X_1 \rightarrow C_4H_2O_3 + CO_2 + H_2O$$  
1.

$$C_4H_2O_3 + O_2 \rightarrow X_2 \rightarrow CO + CO_2 + H_2O$$  
2.

$$C_6H_6 + O_2 \rightarrow X_3 \rightarrow CO + CO_2 + H_2O$$  
3.

where $X_1$, $X_2$, $X_3$ are hypothetical intermediates.

The effect of contact time at constant feed concentration and mass velocity on the conversions to maleic anhydride, CO and $CO_2$ could be described by assuming that reactions 1, 2 and 3 were all first order with respect to the organic reagent. However, it was not possible to establish positively that all of the reactions are exactly first order since similar results might be obtained by other kinetic combinations. In a single experiment in which benzene inlet concentration was reduced by 50%, the first order reaction constants for reactions 1 and 3 remained essentially unchanged whereas that of reaction 2 decreased by about 40%, indicating that reactions 1 and 3 are first order with respect to benzene, whilst reaction 2 is more nearly second order with respect to maleic anhydride.

Hammar (47) found as well that the rate constants $k_1$ and $k_3$ vary directly with the mass transfer coefficient, $k_g$, concluding that the rates of reactions 1 and 3 are equal to the mass transfer rates. Against this argument is the fact that the activation energy of 28 kcal/mole appears too high to be consistent with
The idea of mass transfer controlling. The activation energy of maleic anhydride combustion was found to be the same as for benzene, 28 kcal/mole.

Vaidyanathan and Doraismwamy (48) studied the reaction over a catalyst containing $V_2O_5$ and $MoO_3$ supported on silica gel and interpreted their results by the same triangular scheme outlined before. Simple first order rate equations were fitted to each one of the three steps.

The experimental results show that there is a shift in the controlling mechanism at about 350°C as evidenced by the change in activation energy from about 20 kcal/mole in the lower temperature range to about 2 kcal/mole in the higher temperature range. The possibility of pore diffusion and/or mass transfer being the controlling step at the higher temperatures was examined. The results showed that neither of these was operative and therefore the reaction is essentially chemically controlled over the entire temperature range, the fall in the activation energy being probably due to a change in the structure and orientation of the catalyst at higher temperatures.

Pinchbeck (49) in a study of naphthalene oxidation pointed out that this reaction is also characterised by a shift in reaction mechanism at higher temperatures even though the controlling mechanism was not delineated.

Steger (50) studied the oxidation of benzene using a catalyst consisting of $Ag_2O$, $V_2O_5$, $MoO_3$ and $Al_2O_3$ on silicon carbide in a fixed bed. He concluded that the rate of benzene oxidation in reactions 1 and 3 combined was approximately first order with respect to the benzene concentration. Reaction 3
was found to account for the 30% of the benzene oxidized over a considerable range of conditions.

Contrary to the findings of Hammar (47), the first order rate constants for benzene oxidation were found to be approximately constant over a range of inlet concentrations from 1.2 to 2.4 mole % and a range of superficial gas velocities from 4 to 11 ft./sec., indicating no dependence of the reaction rate on the mass transfer rate. Activation energy of about 15 kcal/mole was also observed over a range of temperatures from 450 to 530°C.

Steger (50) also studied the oxidation of MAA over the same catalyst as was used in the study of benzene oxidation. The order of reaction as determined from the effect of the initial MAA concentration (in the range of 1.5 to 3.0 mole % in air), on initial rate was approximately one half. However, at a given initial concentration, the observed changes in concentration with increasing contact time indicated zero order kinetics. Contact times were varied by changing the space velocity at a fixed bed length. The addition of products to the feed had no effect on the reaction rate. No apparent reason for the discrepancy between the kinetics determined by the two different methods was found.

The rate of MAA oxidation was found to be essentially independent of the oxygen partial pressure even down to partial pressure values of about 0.03 atm. However, at very low O₂ partial pressures there was a fall off in the reaction rate. The observed activation energy over the temperature range 400 to 500°C was 16 ± 1 kcal./mole.

The oxidation of benzene, phenol, quinone and maleic
anhydride over a fixed bed catalyst of $V_2O_5$ precipitated on 1/8 inch alumina pellets has been the subject of a dissertation by Holsen (51). It was observed that at temperatures above $450^\circ C$, the selectivity of the catalyst was permanently changed leading to somewhat higher maleic anhydride yields but this effect was not studied in enough detail. The oxidation of benzene yielded mainly maleic anhydride, carbon monoxide and carbon dioxide although small amounts of phenol and quinone were also detected.

Both the total benzene conversion and the conversion to maleic anhydride were found to be approximately first order with respect to benzene inlet concentration in the range 0.9 to 1.9 mole %. Contact times were varied by changing the space velocity from 1.19 to 0.16 sec$^{-1}$ at constant catalyst volume. First order rate constants, although approximately constant, did show a slight decrease with decreasing mass transfer rate.

The maleic anhydride oxidation to CO and CO$_2$ was also studied in the temperature range from 325 to $450^\circ C$. Assuming first order kinetics, the activation energy changes from 8-9 kcal./mole below $350^\circ C$ to 13-14 kcal./mole at about $375-450^\circ C$. The increase in activation energy being probably due to the onset of a pyrolysis of MAA. The fact that the ratio CO:CO$_2$ increased with temperature adds support to this theory.

The conversions of MAA observed in the benzene oxidation study are in good agreement with those calculated using the equation:

$$\frac{MAA}{B_1} = \frac{k_1}{k_3 - (k_1 + k_2)} \left[ \exp \left[ -(k_1 + k_2)t \right] - \exp[-k_3t] \right]$$
were:

- $k_1$ = first order rate constant for benzene oxidation to MAA.
- $k_2$ = first order rate constant for direct oxidation of benzene to CO and CO$_2$.
- $k_3$ = first order rate constant for MAA oxidation.
- $B_1$ = Initial benzene concentration.

The factor $\frac{k_1}{k_1 + k_2}$ was found to be 0.7 and essentially independent of temperature and, within the range investigated, of benzene inlet concentration.

Dmuchovsky, Marshall et al (52) studied the reaction using a catalyst containing V$_2$O$_5$, MoO$_3$, P$_2$O$_5$ and NiNO$_3$ supported on carborundum pellets over the range 319 to 377°C. A first order law was found to be obeyed over the first 75% of the reaction.

Dmuchovsky and co-workers arrived at the conclusion that benzene is oxidized by two different paths and put forward a mechanism suggested by the absolute rate theory in which the difference between these paths resides in the manner in which the oxygen attack occurs. A singlet oxygen molecular species with two modes of attack was postulated. One a 1,2 the other a 1,4 addition of oxygen to the benzene ring, resulting in the two structures pictured below.

![Structure A](image1)
![Structure B](image2)
This is the same kind of attack proposed by Boocock and Cvetanovic (53) for the reactions of oxygen atoms with benzene in which the subscript \( x \) is 1 or 2, depending on the number of atoms involved. Structure A should be of a lower energy because of the resonance energy of the conjugated system which is 3 - 3.5 kcal/mole (54). Thus, identifying Structure B resulting from the 1,4 addition, with the higher energy path leading to maleic anhydride and structure A with the path resulting in complete combustion.

The mode of oxygen attack is ascribed to excited singlet oxygen molecules which form on the surface of the catalyst by thermal activation of the normal triplet state molecules. The transition from the triplet ground state to the higher singlet state requiring 23 kcal/mole. On the catalyst surface, the triplet-singlet transition of oxygen is thought to be induced by the unpaired electrons present and the required energy is provided by the activation energy which is in the 30 kcal/mole neighbourhood.

In studying the kinetics of benzene oxidation to maleic anhydride over a vanadium molybdenum catalyst and in order to eliminate diffusion hindrance, Ioffe and Lyubarskii (55) used the flow circulating method. Their results show the presence of a retarding effect on the benzene oxidation rate by maleic anhydride.

Benzene oxidation rates show a somewhat higher order of reaction, i.e. second order with respect to oxygen at concentrations of oxygen below 10%. At higher oxygen concentrations the benzene oxidation rate is independent of oxygen concentration in the gas phase. Care was taken to show that this effect was not due to a change in reaction order with respect to benzene or maleic
anhydride at low oxygen concentrations.

On the basis of experimental data the following empirical kinetic equations were proposed:

I) For oxygen concentrations below 4 x 10^{-3} mole/litre

\[ W_1 = k_1 [O_2]^2 [B]^{0.78} \frac{[MAA]^{0.74}}{[MAA]^{0.71}} \]  
\[ W_2 = k_2 [MAA] \]  \hspace{1cm} (1.1)  
\[ W_3 = k_3 [O_2]^2 [B]^{0.71} \frac{[MAA]^{0.74}}{[MAA]^{0.71}} \]  \hspace{1cm} (1.2)

II) For oxygen concentrations above 4 x 10^{-3} mole/litre

\[ W_1 = k_1 [B]^{0.78} \frac{[MAA]^{0.74}}{[MAA]^{0.71}} \]  \hspace{1cm} (1.3)  
\[ W_2 = k_2 [MAA] \]  \hspace{1cm} (1.4)  
\[ W_3 = k_3 [B]^{0.71} \frac{[MAA]^{0.74}}{[MAA]^{0.71}} \]  \hspace{1cm} (1.5)

where

- \( W_1 \) = Rate of reaction of benzene to maleic anhydride
- \( W_2 \) = Rate of reaction of maleic anhydride combustion
- \( W_3 \) = Rate of reaction for direct benzene combustion to CO, CO_2

\( \Delta H_1 = 22.6 \text{ kcal/mole} \)
\( \Delta H_2 = 12.6 \text{ kcal/mole} \)
\( \Delta H_3 = 37.0 \text{ kcal/mole} \)

In order to explain their results Ioffe and Lyubarskii assumed that the catalysis of their scheme was as follows:

1) The major portion of the benzene is oxidised by oxygen adsorbed on the surface of the \( V_2O_5 \).
2) A minor portion of the benzene is oxidised on account of the oxygen of the $\text{V}_2\text{O}_5$ lattice.

3) Maleic anhydride is well adsorbed on the surface of $\text{V}_2\text{O}_5$, the absorption coefficient of MAA being greater than those of oxygen and benzene.

4) The oxidation rate of benzene by adsorbed oxygen is considerably greater than the rate of its oxidation by oxygen of the $\text{V}_2\text{O}_5$ lattice.

A derivation for the benzene oxidation rate, allowing for phase transitions in the $\text{V}_2\text{O}_5$ lattice, was presented. The benzene oxidation rate having the form:

$$W_B = k \frac{3}{2} (1 - Q_m) C_B \quad (1.7)$$

where,

$$\frac{3}{2} = \frac{[\text{V}_2\text{O}_5]}{[\text{V}_2\text{O}_5] + [\text{V}_0]} \quad (1.8)$$

$Q_m$ = fraction of surface covered by MAA

assuming that $S_{\text{V}_2\text{O}_5} :: [\text{V}_2\text{O}_5] \quad (1.9)

$S_{\text{V}_0} :: [\text{V}_0]_{xy} \quad (1.10)$

Where $S_i$ is the surface of the corresponding phase, then

$$\frac{3}{2} = x \frac{S_{\text{V}_2\text{O}_5}}{S_{\text{V}_2\text{O}_5} + S_{\text{V}_0} \frac{x}{y}} \quad (1.11)$$

Where $x$ is a proportionality coefficient and $1 - Q_m = \theta_0$ is the fraction of $\text{V}_2\text{O}_5$ surface covered with $O_2$.

let

$$\theta_m = \frac{b_m C_m}{1 + b_m C_m + b_B C_B + b_{O_2} C_{O_2}} \quad (1.12)$$

since $b_m > b_B$ or $b_{O_2}$ then
By examining the processes connected with phase transitions in the lattice of the catalyst:

\[ \text{VO}_2 + \text{C}_6\text{H}_6 \longrightarrow \text{VO}_x\text{C}_y \] (First process) (1.15)

According to X-ray data (56) the phase \( \text{VO}_x\text{C}_y \) corresponds to \( \text{VO}_4\text{C}_3 \) (or \( \text{VO}_{12}\text{C}_{26} \))

\[ \text{VO}_4\text{C}_3 + 2\text{O}_2 \longrightarrow 6 \text{VO}_2 \] (Second process) (1.16)

Assuming that the rates of the first and second process are, respectively,

\[ v_1 = \frac{S_{\text{VO}_2}}{V_1 \text{sp}} \] (1.17)

\[ v_2 = \frac{S_{\text{C}_6\text{H}_6}}{V_2 \text{sp}} \] (1.18)

at the steady state,

\[ \delta \left[ \frac{[\text{VO}_2]}{6t} \right] = \frac{S_{\text{VO}_2}}{V_1 \text{sp}} \cdot V_1 \text{sp} - \frac{S_{\text{C}_6\text{H}_6}}{V_2 \text{sp}} \cdot V_2 \text{sp} = 0 \] (1.19)

when

\[ \frac{S_{\text{C}_6\text{H}_6}}{S_{\text{VO}_2}} = \frac{V_1 \text{sp}}{V_2 \text{sp}} \text{ or } \frac{S_{\text{C}_6\text{H}_6}}{S_{\text{VO}_2}} + \frac{S_{\text{VO}_2}}{S_{\text{C}_6\text{H}_6}} = \]

\[ \frac{V_2 \text{sp}}{V_1 \text{sp} + \frac{V_2 \text{sp}}{6}} \]

\[ \frac{V_1 \text{sp}}{V_2 \text{sp}} = \frac{S_{\text{C}_6\text{H}_6}}{S_{\text{VO}_2}} \]

\[ \frac{S_{\text{C}_6\text{H}_6}}{S_{\text{VO}_2}} = \frac{V_1 \text{sp}}{V_2 \text{sp}} = \frac{S_{\text{C}_6\text{H}_6}}{S_{\text{VO}_2}} \]

\[ V_1 \text{sp} = \beta_1 \cdot C_B (1 - C') \] (1.21)

\[ V_2 \text{sp} = \beta_2 \cdot C_O^2 \cdot C' \] (1.22)
Where \( C' = \frac{N_T}{N_H} \) \( \quad \text{(1.23)} \)

- \( N_H \) is the quantity of oxygen sites per unit surface.
- \( N_T \) is the quantity of unfilled oxygen sites per unit surface.
- \( C' \) is the concentration of oxygen vacancies per unit surface.
- \( (1-C') \) is the concentration of oxygen ions per unit surface.

At the stationary state:

\[
D_1 C' = \beta_1 \cdot C_B (1-C') \quad \text{(1.24)}
\]

\[
D_2 (1-C') = \beta_2 \cdot c_{O_2}^2 \cdot C' \quad \text{(1.25)}
\]

Where \( D_1 \) is the coefficient of diffusion of the oxygen vacancies into the bulk of the crystal.

\( D_2 \) is the coefficient of diffusion of the oxygen vacancies to the surface of the crystal.

From (1.24) we have:

\[
C' = \frac{\beta_1 C_B}{D_1 + \beta_1 C_B} \quad \text{or} \quad D_1 C' = \beta_1 C_B (1-C')
\]

\[
D_1 C' = \frac{D_1 \beta_1 C_B}{D_1 + \beta_1 C_B} = V_{1sp} \quad \text{(1.26)}
\]

Similarly from (1.25)

\[
V_{2sp} = \frac{D_2 \beta_2 c_{O_2}^2}{D_2 + \beta_2 c_{O_2}^2} \quad \text{(1.27)}
\]
Then the expression for \( \frac{2}{J} \) assumes the form:

\[
\frac{D_2^2 \beta_2 \text{C}_0^2 \text{O}_2}{D_2 + \beta_2 \text{C}_0^2} = \frac{D_1 \beta_1 \text{C}_B}{D_1 + \beta_1 \text{C}_B} + \frac{D_2 \beta_2 \text{C}_0^2 \text{O}_2}{D_2 + \beta_2 \text{C}_0^2}
\]

\( \frac{\gamma}{J} = X \).

And the benzene oxidation rate will be:

\[
W_B = k \cdot X \cdot \left( \frac{D_2^2 \beta_2 \text{C}_0^2 \text{O}_2}{D_2 + \beta_2 \text{C}_0^2} \right) \left( \frac{1}{1 + \text{bm} \cdot C_M} \right) \cdot \text{C}_B
\]

\( \text{(1.29)} \)

And for the extreme cases:

1) With \( \text{C}_0^2 \) small and if \( D_1 \ll \beta_1 \text{C}_B \)

\[
W_{B_1} = k' \frac{\text{C}_0^2 \text{C}_B}{\text{C}_M} \frac{\text{C}_P}{\text{C}_Q}
\]

\( \text{(1.30)} \)

where \( p, q \) 1

2) With \( \text{C}_0^2 \) large:

\[
W_{B_2} = k'' \frac{\text{C}_P}{\text{C}_M}
\]

\( \text{(1.31)} \)

The work by Simmard (57) on \( \text{o-xylene} \) oxidation, Lyubarskii (56) and Popova (58) provide support to the above scheme of Ioffe and Lyubarskii.
Earlier experiments by Sensimian (59), Schreiber (60) and Weiss (61) pointed out the existence of a reduced state of the vanadium pentoxide catalyst for different oxidation reactions. Experiments made by Maxted (62) in which markedly differing oxidations, i.e., naphthalene to phthalic anhydride, benzaldehyde to benzoic acid and toluene to benzoic acid showed a good yield at about the same temperature, suggested that the operating temperature of a catalyst seemed to be independent of the substance to be oxidised. The above experimental findings encouraged Mars and Van Krevelen (63) to interpret their results on the oxidation of benzene, toluene, naphthalene and anthracene on the basis of the reduction-oxidation scheme. The hydrocarbon being first oxidized at an active site,

\[
RH + S^* \xrightarrow{k_A} \text{Prod} + S^0 \quad (1.32)
\]

(\( \theta \))

(1-\( \theta \))

Where \( \theta = \text{fraction of the total surface containing active sites } S^* \).

The active sites reoxidation rate was assumed to be proportional to some power 'n' of the oxygen partial pressure, and to the fraction of surface not containing active sites (1-\( \theta \)).

\[
S^0 + O_2 \xrightarrow{k_B} S^* \quad (1-\theta) \quad (\theta) \quad (1.33)
\]

The rate of reaction of the hydrocarbon being

\[
- \frac{d}{dt} P_{RH} = kA \cdot P_{RH} \cdot \theta \quad (1.34)
\]

Where \( P_{RH} = \text{partial pressure of hydrocarbon} \)

\( t = \text{time} \)
The rate of oxidation of the surface is

$$k_B \cdot P_{O_2}^n \cdot (1-\theta)$$  \hspace{1cm} (1.35)

If $\beta$ molecules of oxygen are required for the oxidation of one molecule of hydrocarbon, then, in the steady state,

$$\beta k_A \cdot P_{RH} \cdot \theta = k_B P_{O_2}^n \cdot (1-\theta)$$  \hspace{1cm} (1.36)

$$\frac{k_B \cdot P_{O_2}^n}{\theta} = \beta k_A \cdot P_{RH} + k_B P_{O_2}^n$$  \hspace{1cm} (1.37)

$$\theta = \frac{k_B \cdot P_{O_2}^n}{\beta k_A \cdot P_{RH} + k_B P_{O_2}^n}$$  \hspace{1cm} (1.38)

therefore the rate of hydrocarbon oxidation takes the form:

$$- \frac{dP_{RH}}{dt} = \frac{k_A \cdot P_{RH} \cdot k_B P_{O_2}^n}{k_B P_{O_2}^n + \beta k_A P_{RH}}$$  \hspace{1cm} (1.39)

or

$$- \frac{dP_{RH}}{dt} = \frac{1}{\frac{1}{k_A \cdot P_{RH}} + \frac{\beta}{k_B P_{O_2}^n}}$$  \hspace{1cm} (1.40)

As excess of oxygen is used then $P_{O_2}^n$ remains practically constant.

Equation (1.40) shows that for small values of $P_{RH}$ the rate is first order with respect to the hydrocarbon whereas for large values of $P_{RH}$ the rate is zero order.
A model proposed by Shelstad, Downie and Graydon (64) known as the steady state adsorption model (SSAM), suggests a surface reaction between adsorbed hydrocarbon and adsorbed (gas phase) oxygen. The form of this model is identical to the Mars and Van Krevelen (63) model with the reoxidation constant being replaced by the oxygen adsorption rate constant. This model has been successfully applied to several hydrocarbon oxidations (66-71) predicting similar adsorption constants for different hydrocarbons including benzene.

Since the two models are identical in mathematical form, kinetic data cannot discriminate between the two. However, they are a powerful way of correlating kinetic data since apparent reaction orders from zero to one can be fitted.

The several mechanisms proposed by the different workers give rise to various questions such as whether lattice oxygen or gas phase oxygen accounts for the surface reaction and whether one or various forms of oxygen are present and responsible for the attack. From the several possible phases of the catalyst which are the most active and what sort of advantages can be brought about by the use of promoters or mixed catalysts. In addition to all these, the possibility of homogeneous components has not been taken into consideration in most of the previous treatments of the reaction scheme. Before going into some detail on the above mentioned topics brief mention will be made of the publications which do not deal with the mechanism of the benzene oxidation reaction but are nevertheless technologically valuable.

Darby (72) claims that maleic anhydride yields may be improved by treating steel catalyst containment equipment with
SIRM ammonia or ammonium carbonate at 400 to 600°C. The pretreatment is reported to reduce the overoxidation of maleic anhydride formed in the catalytic reaction.

Kiprianov and Shostak (73) studied the effect of varying the MoO₃/V₂O₅ ratio in the catalyst and found the optimum about 70-85% V₂O₅ and 15-30% MoO₃. Oxides of cobalt added to the catalyst resulted in an increase of MAA yield.

Fukuda (74) studied the effect of inlet benzene concentration on reaction rate as well as the effect of the ratio molybdenum-vanadium on the catalyst activity.

The initial selectivity of the reaction, about 70% for a molar ratio MoO₃/V₂O₅ of 1/3, varies very little with partial pressures or temperatures indicating similar kinetics for benzene partial and total combustion in good agreement with Ioffe's (55) results. This selectivity, however, changes very sharply with the MoO₃/V₂O₅ molar ratio going through a maximum through the above mentioned composition (56); the overall activity follows the same trend. This maximum coincides with a maximum in magnetic susceptibility (75), and therefore of V⁺⁴ cation concentration and with the limit of solubility of MoO₃ in V₂O₅. The same remarks are made for butene oxidation (76).

A large selectivity improvement is observed when P₂O₅ in small amounts is incorporated to the above catalyst. Yields of MAA of 80% are obtained and decrease only slowly with conversion, showing that the ratios ν₁/ν₂ and ν₁/ν₃ in the triangular scheme mentioned earlier are thus increased (77).

Matsumoto et al (78) studying the effect of varying the
catalyst particle size in fixed and fluidised beds found that, for the fixed bed reactor, with a change in carrier size from 4-6 mesh to 8-10 mesh productivity of MAA can be increased from 60% to 80%.

In the fluid bed reactor the best size of the carrier was 20-40 mesh with a productivity of 70% concluding that the fixed bed reactor gives better results than the fluid bed. In analysing the effect of reactor diameter Matsumoto et al (78) found that a 22 mm diameter tube gave better yields than those using a 27 mm diameter tube, assuming that it was due to a higher temperature in the reactor.

The patent literature emphasises the role of the catalyst support, most commonly as $\alpha-Al_2O_3$ of low surface area; microporosity is to be avoided. Activity improvement in the catalyst is also brought about by small additions of group VIII (Ni, Co) oxides (79-84).

A theory of heterogeneous catalytic oxidation of hydrocarbons would be impossible without knowledge of the elementary mechanism of oxidation, its laws and the rate determining steps.

In addition to the general steps involved in the overall process of a catalytic reaction i.e., diffusion of reacting molecules to the surface, adsorption of the reactants on the surface, chemical reaction on the surface, desorption of the products and diffusion of the products into the fluid, the catalytic process comprises a number of consecutive elementary acts such as the breaking and formation of bonds in reactant molecules, and electron transfers between the latter and the
solid catalyst. Consequently, the electronic, structural and geometric characteristics of the catalytic surfaces are of great importance in the understanding of the oxidation mechanism.

Metals, metal oxides (semiconductors i.e. vanadium pentoxide, molybdenum trioxide, tungsten and copper oxides etc.) and complex semiconductors are the most widely used catalysts for hydrocarbon oxidations. Metals and semiconductors would be expected to differ in behaviour due to their different electronic properties. However, under reaction conditions many metals become coated with a film of the oxide therefore behaving in a very similar manner to that of the respective oxide.

Temkin and Kulkova (85) found that the amount of oxygen adsorbed by a silver layer adjacent to the surface was many times that required for a monolayer. Hiroto and Kobajashi (86) reported that even with prolonged reduction of silver in hydrogen at 275°C oxygen atoms are not removed from the metal, suggesting chemical reaction between oxygen and metal.

Simmard et al (57) made an X-ray study of the structure of the vanadium oxide compositions which were active in oxidizing o-xylene to phthalic anhydride. Compositions between the stable lattice structures V₂O₅ and V₂O₄.₃₄ were found to be active, and the transitions between them were found to occur readily. The active surface was pictured as oscillating through a variety of defects between these two compositions. However, Volfsen (87)
found \( V_2O_4 \) and \( V_6O_{13} \) to a lesser extent to be the active components for naphthalene oxidation with vanadium pentoxide just being a starting material. Schaefer (88) found \( VO_{1.99} \) the most selective and most active oxide for benzene oxidation but for maleic anhydride oxidation no marked maximum in activity was found with catalyst compositions between \( VO_{2.5} - VO_{1.99} \).

In studying the effect of adding \( MoO_3 \) and \( GeO_2 \) to vanadium pentoxide catalysts for benzene oxidation, Butler and Weston (89) found that by increasing the quasi-free electron concentration of the lattice using \( MoO_3 \) and reducing it with the use of \( GeO_2 \), the activation energy for the benzene disappearance rate increased with the latter's addition being insensitive to the addition of \( MoO_3 \). Thus the loss of quasi-free electrons, equivalent to a higher oxidation state, gave further support for the lower oxide structures \( (V_2O_4)^{3+}, V_2O_4 \) being the more active. Selectivity was found to be independent of the ratio of the phases.

Studies made by Ioffe et al (56), as well as by Popova (58), show that under the conditions in which hydrocarbons are oxidized both vanadium and copper catalysts are polyphase systems. Later, Ioffe (150) developed a mechanism for oxidation reactions based only on kinetic parameters and neglecting the thermodynamic parameters on the assumption that in irreversible reactions the phase composition is not dictated by thermodynamics. Ioffe (150) concluded that oxidation and reduction of the catalyst are not direct and reverse reactions. Hence, additives which accelerate one of these reactions may not accelerate the other one resulting in a change in the ratio of amount of active phase to total amount of catalyst and, accordingly, in the activity and
selectivity of the catalyst. Concluding therefore, that there is a new way of modifying catalysts which they called phase modification, different from the electronic modification, depending on the type of additive used.

Studies of the isotopic exchange of oxygen over oxide catalysts (111) including vanadium pentoxide (90) show that heterolytic exchange as shown below does occur at temperatures above 440°C.

\[
\text{lattice} \quad 0^{16} + 2 \quad 0^{18} \quad \text{Ads} \quad \text{lattice} \quad 0^{18} \quad + \quad 0^{16} \quad 0^{18} \quad \text{Ads}
\]

The activation energy of this process, approximately 4.5 kcal/mole over V₂O₅, suggests either oxygen dissociation or V-O bond loosening. Since the exchange was independent of oxygen (90), the latter was favoured. At lower temperatures homolytic exchange occurs.

Keulks (91) and Wregg (92), in a recent study, found that 0₁₈ labelled oxygen was converted to oxygen compounds in the absence of heterogeneous oxygen exchange, indicating the intervention of the lattice oxygen in the oxidation.

Although the interaction of the lattice oxygen in vanadium oxide with the hydrocarbon and a subsequent reoxidation of the catalyst seem to be reasonable steps, Odrin (93), in recent work, found that the catalytic oxidation of naphthalene on vanadia catalysts proceeds much faster than the reduction or oxidation of the catalyst.

Earlier, Roiter (94) found that in the presence of hydrocarbon, a vanadium catalyst doped with O₁₈ failed to exchange with gaseous oxygen below 450°C. For a naphthalene/
air feed at 320-390°C, the $^{18}O$ content of the catalyst was not reduced to a significant extent after 30 hours. To counter arguments that under those conditions the lattice oxygen was not mobile (94), Roiter first reduced the catalyst with naphthalene alone (products containing $^{18}O$) then reoxidized the catalyst with $^{16}O$ and repeated the experiments. The $^{18}O$ content of the products was the same concluding therefore that the reaction mechanism in the presence of gaseous oxygen does not involve the lattice oxygen to any appreciable extent.

As one can see from the above results, the conclusion of whether, in general, hydrocarbon oxidation takes place via reduction-oxidation mechanism is not yet at hand since evidence has been found to support (57, 37, 88, 89) as well as to reject (93, 94, 25) the validity of this scheme.

Clark and Berets (95), under the assumption that defect structures and electrical properties are closely related, followed the changes occurring in a $V_2O_5$ catalyst during the oxidation of o-xylene to phthalic anhydride by means of thermoelectric power and a.c. and d.c. electrical resistance measurements. The lowering of the resistance by xylene even well below 350°C, where no reaction is to be expected, appears to indicate that adsorbed xylene forms positive ions on the surface by donation of electrons to the surface regions of the solid becoming a positive chemisorbed ion while introducing defects into the solid by the consumption of oxygen in their catalytic oxidation reactions as evidenced by the thermoelectric power measurements. The problem becomes more complicated when mixed catalysts are studied since these
are complex polyphase systems, the electronic properties of which may vary at the interphase boundaries or due to formation of solid solutions by substitution or incorporation. A factor which introduces an extra complication, revealed in recent work (56, 96), is that the change in specific surfaces with increasing content of one metal oxide in the other is not additive. The concentration of defects may increase at the interphase boundary during the preparation of mixed catalysts yielding different activities depending on the method of catalyst preparation.

A good example on the effect of the ratio of oxides, used to prepare the catalyst, on variations on selectivity and activity is presented by Ioffe et al (56) in their study of benzene oxidation to maleic anhydride over vanadium-molybdenum catalysts.

Modification of V$_2$O$_5$ was investigated (25) for propene oxidation to saturated aldehydes, acrolein, etc. Impurities of two groups were added to the V$_2$O$_5$: acid (metalloid) anions of SO$_4^-$, P$_2$O$_5$ and other alkali cations such as Na, K. The additions of SO$_4^-$ resulted in a sharp rise in the activation energy for the formation of products while the addition of Na and K produced a fall in the activation energy. Sodium was found to decrease and acids to increase the electron work function.

Margolis (25, 97) postulated that the surface charge of a solid varies as a function of electronic donor or acceptor properties of additives, with consequent variations in surface coverage and consequently in the rates of partial or total oxidation. The effect of additives in mixed oxide systems requires a more cautious treatment.
It was found experimentally (25) that additives had a very small effect on the electronic properties of a surface (the electron work function remained virtually unchanged), but altered the process selectivity. Further analysis showed that it could favour topochemical processes in the solid affecting the solid structure. Because of these investigations much attention has been given to the modification of catalysts as an extremely good method for controlling hydrocarbon oxidation and a number of patents have been taken out in the past years concerning the selective oxidation of hydrocarbons over modified oxide catalysts.

In recent publications (98 - 113) another factor that has been put forward concerning the rates of individual reactions and the selectivity of organic compounds is the effect of the metal-oxygen bond energy. Low energies being required for total oxidation (98, 100) and higher energies characterizing partial oxidation (101).

Some of the information on the metal-oxygen bond energy has been deduced from studies on the isotopic exchange of oxygen (103, 100, 110, 113).

Many studies have been made on the simple oxides and the results are well presented in reviews by Winter (114, 115), Boreskov (111, 112, 113) and Novakova (116). On the contrary only few experiments have been carried out with mixed oxides systems, Boreskov (117), Muzykantov (118) and Adamia (119), although these are widely used as catalysts in the selective oxidation of hydrocarbons.

Blanchard and Boreskov et al (120) studied the isotopic
exchange of oxygen in the $\text{MoO}_3-\text{V}_2\text{O}_5$ systems in order to establish a relationship between the metal-oxygen bond energy and the selectivity of the reaction. The catalytic properties of these systems had been studied previously by Ioffe et al. (56) and Germain et al. (121) for the benzene oxidation reaction and for Delgrange and Blanchard (122) in the oxidation of butenes.

Studies on the properties of pure $\text{V}_2\text{O}_5$ (115, 90, 123) and pure $\text{MoO}_3$ (115, 116, 117, 118, 119, 124) had also been made previously.

Blanchard and Boreskov (120) results show agreement between the experiments on a static system and those conducted in a flow system. Their results show that the exchange occurs between two atoms from the oxygen molecule in the gas phase and two oxygen atoms from the oxide surface and on the other hand that the activation energy of the isotopic exchange and the selectivities of the reaction vary in a similar fashion. Fig. (I-1) shows Blanchard and Boreskov's results. It can be said then that the metal-oxygen bond energy seems to be an important factor in assessing the selective properties of an oxidation catalyst, above all when one has to judge between mixed catalysts of the same series.

Much attention has been given in the past to the various forms of oxygen on the catalyst surface. Evidence (125-134) indicates the existence of at least the molecular ion $\text{O}_2^-$, the atomic $\text{O}^-$ and of the regular ions in the lattice $\text{O}^{2-}$. Kazanskii et al. (135, 136), in studying the reoxidation step of oxides, suggests a sequence of steps in which the various forms of oxygen take part.
FIGURE 1.1 - Activation Energy of the Isotopic Exchange of Oxygen and Selectivity in the Oxidation of Benzene and Butene to Maleic Acid.

- -- Apparent activation energy of oxygen exchange as a function of composition

Selectivity to maleic acid in the oxidation of benzene at 420°C (121)

Selectivity to maleic acid in the oxidation of butene at 405°C (122)

rather than a single step.

\[ \text{O}_2 + e \rightarrow \text{O}_2^- \]
\[ \text{O}_2 + e \rightarrow 2\text{O}^- \]
\[ \text{O}^- + e \rightarrow \text{O}^{2-} \]

This was confirmed by the results on reoxidation of reduced zinc and titanium oxides.
Sachtler (137) believes that the contribution of the regular lattice ions to hydrocarbon oxidation is probable for transition metal oxides as well as for complex oxide systems such as bismuth molybdate and discusses several arguments supporting the participation of various oxygen forms in organic oxidation.

1.3) Homogeneous - Heterogeneous Interactions

The oxidation of hydrocarbons as discussed in the previous sections was analysed on the basis that it takes place only at the catalyst surface, with the exception of the work by Dmuchovsky et al (52). However, the present concepts accept the possibility of homogeneous-heterogeneous interactions taking place on the solid surface as well as in the fluid phase. These ideas were originated mainly by the pioneering work of Semenov and his collaborators on the study of reaction chains (138).

Since the early stages of the development of the reaction chain theory by Semenov, a hypothesis admitting the possibility of a heterogeneous initiation of the chains was postulated. For instance as a result of a heterogeneous reaction on a surface, the formation of active centres i.e. atoms or radicals, may proceed. These new formed centres reacting later in the gaseous phase leading to further reaction without participation of the solid surface. In the case of branching chains the effect of the volume available will not be too difficult to assess but if unbranched reactions are present, this will be overshadowed by the heterogeneous processes.

Gorokhovatskii (139) examined the possibilities of a method proposed by Sysa and Korneichuk (140) which works under
the assumption that homogeneous steps may take place in the
unoccupied volume between catalyst granules, this volume changing
when granule size is varied.

According to Gorokhovatskii (139) during catalysis by the
homogeneous-heterogeneous mechanism with chains nucleated at the
external surfaces of the granules, the reaction rate is,

\[ W = S n_o \frac{a d}{1 - 6 a d} \]

where \( S \) = external surface area of the catalyst

\( n_o \) = number of primary centres nucleated per unit
surface area

\( \delta \) = Probability for branching chain on a given granule

\( d \) = diameter of granule

for two different sizes of granule \( n \), and \( N \),

\[ W_n = S_n n_o \frac{a d}{1 - 6 a d} \,, \quad W_N = S_N n_o \frac{a D}{1 - 6 a D} \]

if \( \frac{S_n}{S_N} = 1 \) then \( \frac{d}{D} = \frac{1}{1} \)

\[ \frac{W_n}{W_N} = \frac{1 - 6 a D}{1 - 6 a d} < 1 \]

Thus, with a decrease in granule size, the rate of a
heterogeneous-homogeneous reaction per unit external surface area
of catalyst should decrease. With small branchings, the decrease
is slight and the quantity \( \frac{W_n}{W_N} \) approaches to one. In this case
the method is not sensitive, the only alternative is to discuss the
rate in terms of unit total surface area, \( S_{\text{Tot}} \) (or per unit mass
of catalyst in the case of porous catalysts), rather than per unit external surface area in order to make the change more obvious, in this case we have,

$$\frac{W_n}{W_N} = \frac{d}{D} \frac{1 - \frac{aD}{a}}{1 - \frac{a}{a}} = \frac{1}{1 - \frac{aD}{a}}$$

since $S_{\text{Tot}}^n \approx S_{\text{Tot}}^n$

Data in the literature on the oxidation of ethylene on silver, propylene on cuprous oxide, acetylene on manganese dioxide and naphtalene on vanadium pentoxide were examined for possible existence of homogeneous-heterogeneous processes using this method. It is interesting to note that the analysis showed no homogeneous steps during complete or partial oxidation of these hydrocarbons but in view of the available evidence (20-23) showing the important role of volume steps in the cases of apparently typical heterogeneous reactions and being aware of the limitations of the method, which is not very sensitive in the case of small branching of the chains, due to the small change in volume brought about by a change in granule size, the possibility of occurrence of homogeneous steps or parallel heterogeneous and homogeneous-heterogeneous steps was left open.

McCain and Godin (141) working with a bismuth molybdate catalyst found that homogeneous steps are present in the propene oxidation reaction.

Satterfield and Loftus (142) and Irshad and Trimm (143), observed gas phase oxidation reactions concurrent to the catalytic oxidation for alkyl-aromatics being oxidized on vanadium catalyst.

Kovalski (144) observed while studying the reduction of sulphurous gas by carbon oxide that the rate of reaction depended
on the volume of the reaction vessel turning out that for larger vessels the reaction was quicker although the catalyst was the same in both cases. Without catalyst the reaction did not take place in the empty vessels. As this experiment showed enough evidence of the existence of bulk reactions with heterogeneous origin, Kovalskii developed a calorimetric method to evaluate quantitatively the observed effect. This method assumes that a thin layer of catalyst deposited on the walls of a reactor will be at the wall temperature. Thus in the case of a purely heterogeneous reaction when all the heat is emitted on the catalyst, the temperature of the gas in a stationary state will be equal to the wall temperature. If the homogeneous reaction also takes place, then the heat produced in the bulk of the gas phase will warm it and its temperature will exceed that of the walls of the vessel. In this way Kovalskii determines to what extent the reaction occurs in the volume and on the surface by comparing temperatures measured within the reaction vessel with those calculated from the rate and heat yield of the reaction assuming some mode of heat liberation.

In the case of a homogeneous-heterogeneous process the heating of the gas at the centre of the vessel, whilst the catalyst is supported on the walls, will clearly be between $\Delta T_H$ and 0. If the catalyst is supported on a capillary on the centre of the vessel then the heating should be between $\Delta T_H$ and $\Delta T_k$ in the first case according to equations (1.41) and (1.43) second case according to equations (1.42) and (1.43);
where, $Q_H$ is the heat emitted per second in the bulk of the vessel per centimetre of its length due to the homogeneous reaction, $Q_k$ is the equivalent of $Q_H$ but for the catalytic reaction, $W$ is the rate of reaction; $\lambda$ is the coefficient of thermal conductivity of the gas.
The above method proved successful in Kovalski's experiments on reduction of S\textsubscript{2}O by CO on glass coated with alumina, the experimental arrangement being as depicted below:

In a recent paper by Brown and Trimm (145) evidence was obtained for the existence of homogeneous-heterogeneous interaction in the benzene oxidation reaction over a vanadia/molibdena/phosphorous catalyst. Their experiments were conducted in catalytic tubular reactors with different free volumes after the catalytic bed and introducing different amounts of inert surface in the post-catalytic volume, keeping constant the amount of catalyst.

Brown and Trimm (145) explain their experimental results, which show a variation on the benzene consumption by altering the conditions in the postcatalytic volume, in terms of an intermediate being formed on the catalyst by the reaction of benzene with oxygen either from the gas phase or from the catalyst, this intermediate reacting further on in the gas phase. The intermediate is proposed to be a benzene-oxygen adduct of the type suggested earlier by Cvetanovic and Boocock (53) and Dmuchovsky et al (52). A more complex mechanism than any one suggested previously is postulated for the benzene oxidation reaction.
Heterogeneous-homogeneous interaction of this type has been observed for the oxidation of propene over bismuth molybdate by Daniel and Keneka (146), the products of total oxidation were found to depend on the postcatalytic volume particularly in the presence of acrolein or acetaldehyde. Moreover, it can be seen from the presence of propene oxide in combustion products that its formation is strictly homogeneous. The following mechanism is proposed:

\[
\begin{align*}
C_3 = CH &= CH_2 \\
\text{gas} &\rightarrow (CH_2 \quad CH \quad CH_2) \quad \text{ads} \quad CH_2 = CH - CH_2 \quad \text{gas} \\
\text{o}_2_{\text{latt}} &\rightarrow CH_2 = CH - CHO \\
\text{ads} &\rightarrow CH_2 = CH - CH_2 \quad \text{OO} \\
C_3H_6 \quad \text{gas} &\rightarrow CH_3 - CH - CH_2 \\
\text{o}_2 &\rightarrow \text{ads} \\
\end{align*}
\]

This process resembles very much the oxidation in liquid phase, which is very rarely a strictly heterogeneous process.
1.4) Object of the Present Study

Brown and Trimm's paper (145) on benzene oxidation injected new interest in catalytic aromatic oxidation. Obviously, one would like to know if the effect they detected was commercially significant.

In complex reactions of the nature of the benzene partial oxidation, there always exists the possibility of the intermediate product being overoxidized. Thus, attempts of providing free space for any possible adduct to react in the gas phase may jeopardise the selectivity of the reaction due to overoxidation of the maleic anhydride in the free space after the bed or on the walls of the reactor.

Therefore, to obtain more information which could be used for the modelling of a large scale non-isothermal reactor, the following objectives were set:

1) Preparation of a catalyst with a selectivity close to that reported commercially, i.e. 70%.

2) Design of a system which will allow the acquisition of isothermal data, preferably with the use of a reactor with metallic walls, i.e. aluminium, stainless steel or titanium.

3) Study of Brown and Trimm's effect in the system designed.

4) Determination of the kinetics of the benzene partial oxidation reaction.

5) Evaluation of the effect of reactor materials of construction and reactor diameter on the selectivity of the reaction.

6) Modelling of 1 and 2 inch diameter reactors in a pilot plant scale using the kinetic parameters obtained in the laboratory study.
This scheme was subject to review, dependent on the nature of the findings during the course of the work.
Chapter 2

Experimental Apparatus and Procedures (I)

2.1) Catalyst Preparation
2.2) General Description of the Experimental Apparatus
2.2.1) Delivery of Reactants
2.2.2) The Reactors
   A) Tubular Reactors
   B) The Spinning Catalyst Basket (SCB) Reactor.
2.2.3) Analytical Equipment
2.3) Catalyst Life and Stability
2.4) Typical Experimental Schedule
2.5) Calibration
2.1 Catalyst Preparation

From the various methods of catalyst preparation known, wet impregnation was chosen because by using it the few pores available in the low porosity-low surface area support could be filled. In this way a non-porous catalyst, convenient from the point of view of avoiding overoxidation of the intermediate product, could be anticipated.

The formulation of the catalyst was chosen after inspection of the literature on the subject. The number of theories involved is vast and no straightforward method of catalyst design has yet emerged. In our particular case it has been established by several workers (56, 121) that the best ratio MoO₃ to V₂O₅ is about 3/1.

Phosphorous was added to the formulation since it is believed to increase the work function of the catalyst and therefore reduce the oxidising power of the catalyst. This was with the purpose of avoiding overoxidation of the intermediate product (maleic anhydride). The rest of the components of the formulation were mainly added to produce discontinuities on the structure of the catalyst and thus probably create more active centres. Another factor taken into consideration was the differences in valency between the elements added and the three main components, i.e. vanadium, molybdenum and phosphorous.

Method of Preparation

Alundum spheres 3/16 inch in diameter with the specifications given in Appendix A were washed with concentrated hydrochloric acid diluted with a volume of water by refluxing them for 24 hrs. The pellets were later impregnated with a hydrochloric acid
solution containing the catalyst components, i.e. vanadium pentoxide, molybdenum trioxide and phosphorous pentoxide dissolved therein. This solution was then slowly concentrated to almost dryness, allowing enough time for the pellets to be well impregnated.

At time intervals, a pellet was taken out of the solution and broken in half to see if impregnation of the pellets was taking place at the speed used to concentrate the solution.

The coated pellets were further dried in an oven for two hours. The batch to be used in the reactor was activated in a glass tube by passing a stream of air over it and slowly increasing the temperature up to 500°C, this process taking 3 hrs. approximately.

Various catalysts were prepared but throughout this work only three formulations were used. The composition of the solutions used for these three catalysts is given below.

**Catalyst 4**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Weight (gms.)</th>
<th>Molar ratio to $V_2O_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_2O_5$</td>
<td>19.9155</td>
<td>1:1</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>5.2575</td>
<td>1:3</td>
</tr>
<tr>
<td>$P_2O_5$</td>
<td>0.5010</td>
<td>1:21.7</td>
</tr>
<tr>
<td>CH$_3$COOLi</td>
<td>0.7180</td>
<td></td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>0.3830</td>
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### Catalyst 6 *

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* to be used in pilot plant experiments.
2.2) General Description of the Experimental Apparatus

Several factors have to be kept well in mind when designing experimental equipment to study the rates of rapid and complex gas reactions such as benzene oxidation to maleic anhydride (MAA).

Among them, accurate monitoring of reactants delivery and reaction products analysis are essential. In addition, for highly exothermic reactions to obtain isothermal kinetic data represents a major problem.

A general description of the experimental apparatus used in this work, which meets the above requirements, is given below. Individual items are discussed in more detail in the following sections. Fig. (2.1) shows a flow diagram of the apparatus which operated in the following way: a stream of air supplied by an Edwards centrifugal blower (P) was sent to a copper tank (CT) to diminish the pulses generated by the blower. This stream, after passing through a pressure regulator (PR), was divided in three parts. Stream (1) was saturated by bubbling it through benzene. Stream (2) was used to dilute stream (1) to the required reactor inlet concentration. Stream (3) was saturated with o-xylene. This last stream bypassed the reactor and was used as an internal standard to detect variations in the sensitivity of the analytical equipment.

Streams (1) and (2) were fed into the reactor, which was placed in an oven (RO). A sample from the exit gas stream of the reactor was fed by means of a hot sampling valve (HSV) to a chromatographic column (CC) coupled to a flame ionization detector (FID). The amplified signal from the FID was then recorded and integrated. The remaining tail gas was continuously fed to
FIGURE 2.1 - Flow Diagram of Experimental Apparatus
infrared CO and CO$_2$ analysers. For simplicity, the analytical unit composed of chromatographic column, FID, amplifier, recorder and integrator will be referred to as the chromatograph in the following sections.

All the lines were heated with thermocord and insulated with asbestos tape to avoid condensation.

The whole system comprising rotameters, bubblers, ovens, reactor and chromatograph was mounted on a mobile three level Handy-angle frame.

2.2.1) **Delivery of Reactants**

Several methods have been proposed in the past for the delivery of highly diluted streams of hydrocarbons in air. In our particular case, the saturation of a small stream of air bubbling through the liquid hydrocarbon (benzene) which was later diluted to the required concentration, proved successful. This system has the advantage, over systems such as the use of infusion pumps, that it does not depend on the operating properties of any mechanical device therefore reducing the number of variables to control. All that is needed then to control the concentration of the hydrocarbon is an accurate control over the temperature of the reactant. The flow of gases was monitored by rotameters and accurately controlled by needle valves. The characteristics of the rotameters which were supplied by the Rotameter Manufacturing Company are given in Appendix A.

Tests were conducted to ensure that the bubblers were working at saturation levels by testing the response of the chromatograph at different flowrates, including several higher than the maximum experimental used. It was found that the modified Dreschnel bottles with an integral sintered disc
at the bottom were the best choice of bubbler.

With the high vapour pressure of benzene, a very accurate method of controlling the temperature at which the bubbler is kept is necessary. At the beginning of the work, the bubblers were submerged in a water bath but this had a cold point in the zone between the water surface and the heating cords.

A system of liquid injection of the benzene into the reactants stream was also tested. This system consisted of a glass syringe with a stainless steel capillary tube in the tip driven by a variable speed motor. The accuracy of this system measured in terms of reproducibility of the chromatograph response oscillated between 2 and 10 per cent error. Improvements to this system were attempted by placing a wick at the tip of the capillary tube and incorporating a mixing chamber before the entrance of the reactor but the fluctuations persisted.

The stainless steel piston of the syringe which had an 'O' rubber ring to prevent leakage was then replaced by 'Teflon' but not even with these improvements did the infusion system prove better than the bubblers.

The solution to the problem of avoiding a cold point at the bubbler outlet was provided by the use of an air bath controlled by a contact thermometer and relay system. In this case all the connections to the bubblers were made inside the oven. The thermocord on the outlet lines was brought almost inside the oven, avoiding in this manner any possible condensation. The contact thermometer gave an accuracy of \( \pm 0.2 \, ^\circ\text{C} \). A mercury thermometer was used to monitor the air bath temperature and a thermocouple was used to measure the temperature of the benzene in the bubbler.
2.2.2) **The Reactors**

Since the modelling of a large scale non-isothermal tubular reactor was the final objective of the present work, reactors of the tubular type were mainly employed for the kinetic studies. Use was also made of a spinning catalyst basket (SCB) reactor to obtain a more complete picture of the reaction.

A) **Tubular Reactors**

The most important factor to obtain reliable kinetic data for highly exothermic reactions is to achieve isothermal behaviour of the reactor. To this end, several types of reactors were tested under reaction conditions.

Preliminary work was carried out in a glass reactor 13 mm. diameter and a wall thickness of 1.5 mm, bent in a U shape. It was found that the catalyst gave a good performance in this reactor but it was very difficult to maintain isothermality.

It was decided then to use a metallic tube of a smaller diameter in order to facilitate the transfer of heat. A 3/8 inch diameter metallic tube (aluminium) was found to maintain isothermal conditions; this tube which had a 5/16 inch internal diameter and closely contained a string of catalyst pellets, shown in Fig. (2.2), was found to operate satisfactorily and was the main type of reactor used throughout this work.

The tests for the isothermality of the reactors were conducted by inserting a thermocouple at the end of the catalytic bed and measuring the difference in temperature between this point and the wall temperature, which was assumed equal to the oven temperature, with and without reaction taking place.

Several flowrates were used in this experiment in order
FIGURE 2.2 - Aluminium Tubular Reactor Used in the Experiments at Isothermal Conditions.
to move the possible hot spot in case this was undetected. It was found that the 13 mm. diameter glass reactor gave a rise in temperature of about 10°C whereas the 3/8 inch diameter metallic reactor gave only 1 °C. No dilution of bed was attempted to give a better performance since earlier experiments had shown this to be detrimental to the selectivity of the reaction by promoting maleic anhydride combustion.

Four types of reactor materials of construction were used during the course of this work, i.e. glass, aluminium, titanium and stainless steel. The type of reactor used for each experiment will be stated where appropriate.

To provide a quick and reliable method of connection between the reactors and the rest of the system, 'Simplefix' brass compression fittings were used with good results. In addition, by replacing the copper barrel of these fittings by a rubber 'O' ring, connections between the glass reactors and the metal pipes were also possible.

B) The Spinning Catalyst Basket Reactor (SCBR)

The spinning catalyst basket reactor which in this section will be referred to as 'the reactor', shown in Fig. (2.3A), and which is similar to the circular spinning basket designed by Brisk (152), was built in aluminium of 99.9% purity supplied by British Aluminium and consisted of an aluminium circular basket rotating concentrically in a 60 cm³ unbaffled circular pot. The basket was bolted to the bottom of a shaft which was completely enclosed and ran on enclosed bearings. The shaft was driven by rotating an outer casing which contained permanent magnets locked on magnets located in the top section of the shaft. The lower section of the inner magnet provided a signal for a
FIGURE 2.3A - SCB Reactor and Drive Unit.

FIGURE 2.3B - Detail of the Catalyst Basket.

KEY:
1. Belt drive groove
2. Outer magnet bearings
3. Upper bearing
4. O ring seals
5. Outer magnet
6. Inner magnet
7. Relay
8. Lower bearing
9. Inlet port
10. Catalyst basket
11. Thermocouple entry
12. Outlet port
13. Reactor pot
tachometer through a Reed relay.

An air bleed inlet pipe in the shaft casing provided a small air flow, about 5 percent of the total feed to the reactor, which prevented diffusion of the organic compounds up the shaft where they might solidify on the bearings.

The outer magnet casing was driven by a 1/2 HP A.C. motor through a V belt and two pulleys with a 1:2 diameter ratio.

The power supply to the motor came from a 'Variac' speed controller and a maximum speed of 3000 R.P.M. was obtainable.

Inlet and outlet reactor ports were respectively placed at the top and bottom of the reactor pot. A thermocouple port at the bottom of the pot allowed the reactor temperature to be known. The reactor pressure was considered essentially atmospheric as part of the exit stream was almost immediately vented to atmospheres.

The catalyst basket, Fig. (2.3B), which contained approximately 10 grams of our catalyst, had perforated discs at top and bottom and aluminium wire sides. An asbestos gasket was used to seal the reactor pot to the top plate. Gas lines entering and leaving the reactor were all of 3/8 inch diameter aluminium tubing.

When an SCB reactor is used in catalytic research, one has to be well aware of the premises on which this type of reactor relies. The main assumptions Brisk (152) considered in obtaining kinetic data with a reactor of this type were:

A) The rotation of the basket at high enough speeds would cause the gas phase to be perfectly mixed in such a way that the concentrations of the gas in every part of the free space and catalyst surface will be identical; in other words, the inflowing gas to the reactor will mix instantaneously with the gases
circulating in the basket and the reaction will only depend on
the bulk reacting gas concentrations i.e. the outlet concentration.

B) Interfacial resistances are diminished due to the high gas
circulating rates therefore giving high rates of heat and mass
transfer allowing the reactor to operate near isothermal conditions.

The flowrate and rotating speed of the basket are two
conditions that have to be properly selected if the reactor is to
operate close to ideal mixing.

Tajbl (151) and Brisk (152) studied the effect of flowrate
and rotating speed on the mixing conditions, each one arriving
at different conclusions. Tajbl, using the reactor designed by
Carberry (153), produces a plot, Fig. (2.4A), in which at the
higher flowrates one would be able to reduce the rotating speed
and still get perfect mixing whereas Brisk finds that the higher
the flowrate, the higher the rotating speed required to achieve
perfect mixing; see Fig. (2.4B). However, this discrepancy
could be due to the differences in the shape and size of the
reactors. The main difference being the ratio of 16.8:1 free
volume to catalyst volume in Carberry's reactor, used by Tajbl,
as compared with 1.2:1 in Brisk's reactor.

Brisk (152) and Choudary (154) reported that mass transfer
rates were little affected by the position of the pellet in the
basket. However, Pereira and Calderbank (155) found significant
differences in the mass transfer coefficient with the position of
the pellet in the basket as well as with rotating speed.

Very recently, a model to evaluate the relative velocity
between the gas and the pellets in the SCB reactor has been
formulated by Pereira and Calderbank (155) allowing the prediction
of the mass transfer coefficients and hence, the heat transfer
FIGURE 2.4A - SCBR, Mixing Characteristics of Carberry's Reactor.

FIGURE 2.4B - SCBR, Mixing Characteristics of Brisk's Reactor.
coefficients from the well known correlations for packed beds.

Brisk (152), with experimentally determined mass transfer coefficients, calculated the heat transfer coefficients and predicted gradients of temperature of about 25°C, for his particular kinetics, between the bulk gas and the pellet surface at different rotating speeds. This is an important factor which has to be taken into account for each experiment carried out in a SCB reactor.

2.2.3) Analytical Equipment

Based on previous experiences in this laboratory (149,156) it was decided to take gas samples of the exit reactor stream, using a heated sampling valve, and to feed them directly to the chromatograph. After several tests with chromatographic columns and loop sizes a satisfactory resolution of the peaks of reactant and products was achieved. The final system consisted of a model F-11 Perkin Elmer single column chromatograph unit consisting of precision oven, flame ionization detector (FID) and flame ionization amplifier. The chromatographic column used finally was a Hewlet Packard (1.83 metres, 10% U.C.C.W. 982 chrom. WAWDMOS, 80-100 No. 19020A) consisting of 10% silicone gum rubber on 'Chromosorb W' packing. The pressure of the nitrogen carrier gas was kept at 12 psig. A 0.1 ml. loop was fitted to the Perkin Elmer sampling valve. This size of sampling loop avoided overlapping of the peaks of benzene and maleic anhydride at a temperature of 85°C. A schematic diagram of the sampling valve is shown in Fig. (2.5).

In order to allow for detection of variations in the sensitivity of the flame ionization detector as well as for leaks in the system, an internal standard was incorporated in the reactor
FIGURE 2.5 – Schematic Diagram of the Hot Sampling Valve
outlet stream before it was fed to the sampling valve. Two different standards were tried, i.e. napthalene and o-xylene, both having the required vapour pressure and residence time in the column to avoid interferences with the rest of the products being analysed. It was decided to use o-xylene as this had the advantage of being in the liquid state and could be placed in a bubbler in the same oven as the benzene bubbler. The o-xylene peak came approximately one minute after the maleic anhydride peak. Fig. (2.6) shows a typical chromatogram.

The amplified signal from the FID was fed in parallel to a Kent Chromalog Mk III digital integrator and a Leeds Northrup speedomax type W recorder. In this way the integrator operating conditions could be adjusted allowing for any drift in base line or peak tailing. Fortunately, the base line was very steady and no peak tailing occurred.

The SCB reactor arrangement permitted sampling from the inlet and outlet of the reactor by means of a two-way valve cased in an asbestos box heated with 'Thermocord'.

The supply gases to the FID i.e. air, nitrogen and hydrogen were controlled by standard pressure reducing valves on the supply cylinders as well as by a Perkin Elmer pressure control unit. The setting was as follows:

- Air pressure - 30 psi (500 ml/min)
- N\textsubscript{2} pressure - 12 psi
- \textsubscript{2}H\textsubscript{2} pressure - 17 psi

These values gave a satisfactory performance of the chromatograph.

The CO and CO\textsubscript{2} analysis was carried out with the use of Grubb Parsons infrared analysers with a range of 0.1 to 1.0 vol. percent CO or CO\textsubscript{2} in air. For the high conversion runs,
FIGURE 2.6 - Typical Chromatogram
where the above range was not adequate for CO₂ measurements, a third infrared with a range 0.0 to 5.0 vol. percent CO₂ in air was connected in series to the other two.

2.3) **Catalyst Life and Stability**

After a fresh charge of catalyst was introduced in any of the reactors, the equipment was adjusted to a fixed set of conditions and monitoring of the products was carried out until constant results were obtained. After an initial time of deactivation which usually lasted between 5 and 10 hrs. of operation, the catalyst settled to a stable level of activity which was maintained from then on. Periodical checks of the catalyst activity were made during the course of the work by reverting to the conditions at which the activity was originally determined. No catalyst deactivation effects were observed during the course of the work, therefore no correction was necessary to compare the results of the different runs.

However, when runs to assess the effect of reactor diameter on the reaction were performed, the catalyst deactivated when larger reactor diameters were used. This deactivation was thought to be due to the large departure from isothermality produced as the reactor diameter increased (vide infra).

2.4) **Typical Experimental Schedule**

The FID amplifier and oven, the reactor oven, the infrared analysers and the integrator were left switched on in order to avoid any fluctuations in sensitivity due to changes in electrical conductivity with temperature as well as to maintain the chromatograph column at the same state during the course of the work. The reactor oven was also left on to keep the catalyst at constant temperature overnight. All other parts of the
equipment were switched off until needed.

The bubbler air bath, thermo cords, gas sampling valve and dilution air were switched on approximately four hours before the run was to begin. The bubbler air bath took approximately two hours to reach the required temperature, at the end of which time the rest of the equipment was already at the desired level.

Two hours before the run was due to begin the hydrocarbon rotameters were opened at a lower level than required in order to allow the catalyst to reach the steady state. The required hydrocarbon concentration was set approximately 1 hr. before samples were taken. Gas flows to the FID and chromatographic column were turned on one hour before samples were taken. In the case of the SCBR the speed was set to the normal value (3000 RPM) at the same time as the bubbler bath was switched on.

Once all systems were equilibrated, samples were taken for analysis. Sampling was repeated until constant values were obtained.

At the end of the run, the hydrocarbons were switched off first as well as the bubbler oven, leaving the dilution air on to flush the system until no trace of reactants or products was detected in the chromatograph. The rest of the equipment was then switched off.

As the rig used for the runs with tubular reactors had no facilities for sampling the concentration at the inlet side of the reactor, at the end of a run a check was made on the value of the benzene inlet concentrations used during the run. This 'everyday standard' was used for the calculations of that particular run.
2.5) **Calibration**

Calibration of the FID response was made in situ by setting the reactor temperature at 200°C and running the equipment with no reaction taking place. In this way, knowing the flowrate of air and the temperature and pressure of the system, the detector response could be plotted against the vapour pressure or mole percent hydrocarbon in the air. Fig. (2.7) shows typical calibration curves obtained in this way for benzene and maleic anhydride.

In addition, since the benzene concentration was highly sensitive to small changes in the bubbler's bath temperature, the inlet benzene concentration was checked, using the above procedure, at the end of the experimental day.

The SCB reactor arrangement had facilities to sample at the inlet and outlet of the reactor, therefore for every sample of the outlet stream, an inlet concentration sample was taken. This provided a continuous check on the calibration curve used.

The infrared analysers were calibrated periodically with gas samples of CO and CO₂ in N₂ prepared for this purpose in the laboratory. All rotameters were calibrated using the soap bubble method for the low flowrates and a gas meter for the air of dilution which operated at rates of up to 3 litres per minute.
FIGURE 2-7. Benzene and Maleic Anhydride (FID) Calibration Curves

INTEGRATOR AREA

BENZENE

MAA

MOLE
Chapter 3

Experimental Results

3.1) Measurements

3.2) Preliminary Experiments

3.3) Detection of Heterogeneous-Homogeneous Interactions in the Overall Reaction. Discussion.

3.4) Detection of Heterogeneous-Homogeneous Interactions in the MAA Combustion.

3.5) Effect of Reactor Materials of Construction on the Selectivity of the Overall Reaction.

3.6) Kinetics of Benzene Disappearance and Selectivities to MAA.

3.6.1) Introduction

3.6.2) Experiments in a 100 catalyst-pellet catalytic bed.

3.6.3) Experiments in a 250 catalyst-pellet catalytic bed.

3.6.4) Effect of Reactor Diameter on Selectivity.

3.6.5) The SCB Reactor, kinetics of benzene disappearance.

3.7) Kinetics of MAA combustion.

3.7.1) Introduction.

3.7.2) The Tubular reactor, kinetics of MAA combustion.

3.7.3) The SCB Reactor, kinetics of MAA combustion:

A) Oxidation of MAA in the presence of catalyst.
B) Oxidation of MAA in the absence of catalyst.

3.8) Discussion of Results:

A) The Catalyst.
B) Incorporation of the experimental data in the overall scheme of reaction.
3) Experimental Results

3.1) Measurements

During the experimental runs, conducted in the apparatus described earlier (Fig. 2.1.), the following quantities were measured directly: temperature of the benzene in the bubbler \( T_B \), temperature of the bubbler's bath \( T_{BB} \), flowrate of air, temperature of the reactor \( T_R \), room temperature, pressure in the inlet of the reactor (at the outlet of the bubbler), volume \% of CO and CO\(_2\) in the tail gas coming from the reactor, temperature of the sampling valve, temperature of the chromatographic column, and the peak responses of the flame ionization detector for benzene, maleic anhydride and the o-xylene used as internal standard. The weight of the catalyst charge to the reactor was known as well.

From the above information the reactant and product concentrations were calculated and used for the analysis of the reaction.

Full tables of results are given in Appendix B, the results in this chapter are shown in the form of plots.

3.2) Preliminary Experiments

Some preliminary experiments were necessary to obtain an idea of the reaction behaviour. It was important to know to what extent the reactants underwent reaction when there was no catalyst present. Tests were conducted for this purpose by feeding benzene through the reactor without catalyst in it. No significant oxidation took place even at temperatures of 500\(^\circ\)C. No combustion of benzene was detected either when the reactor was packed with \( \text{Al}_2\text{O}_3 \) support pellets at 500\(^\circ\)C.
Tests were conducted on the oxidation of maleic anhydride (MAA) to find out what materials were inert to this reaction, so that they could be used as diluents in the catalytic bed to study the existence of homogeneous components in the reaction and to achieve isothermality in the reactor behaviour.

The materials tested were: support $\text{Al}_2\text{O}_3$ pellets, glass pellets, aluminium and quartz. It was found that MAA combusted on all of them, being therefore unsuitable as bed diluents.

To obtain reliable kinetic data requires an isothermal performance of the reactor. As explained before, initially a glass reactor 13 mm. diameter was used but temperature gradients between the catalyst bed and the reactor wall of up to $10^\circ\text{C}$ were experienced and judged to be unacceptable.

Since the dilution of the bed was not possible due to the promotion of MAA overoxidation by all the materials tested, a smaller diameter reactor had to be used.

Finally, after some trials, it was decided to use 3/8 inch dia. aluminium tubes which closely contained a string of pellets. This arrangement proved satisfactory. Temperature gradients of only one or two degrees centigrade, between the bed temperature and the oven temperature, occurred.

3.3. Detection of Heterogeneous-Homogeneous Interaction in the Overall Reaction

A review of the methods to detect homogeneous components occurring concurrently and linked to the heterogeneous reaction in catalysis has been given in a previous section.

In our particular case, the detection of the effect reported by Brown and Trimm (145), which was discussed in Chapter One of this thesis, in the catalytic oxidation of benzene
to MAA was our primary concern. It was decided, therefore, to use a similar method of detection to the one used by them.

Essentially, the method consists of an analysis of the inconsistencies produced in the product yields and reactant consumption when the volume after the catalyst bed is varied under a variety of reaction conditions. This method had already been used by Godin (141). It is expected that any homogeneous reaction that could occur will be favoured by the presence of free volume. Since homogeneous reaction rates are more temperature sensitive than catalytic rates (147) any increase in temperature should enhance the contribution of the homogeneous component.

The various possibilities of homogeneous steps being present in the reaction scheme are: overoxidation of products, homogeneous reactions concurrent but independent of the catalytic reaction and a homogeneous reaction concurrent and linked with the catalytic reaction.

Since overoxidation effects will confuse the analysis of results, it is more reliable to base the study on inconsistencies produced on reactant consumption when conditions in the catalytic bed are varied. Thus, heterogeneous-homogeneous interaction in the formation of MAA will be detected through the analysis of benzene converted when the volume after the catalyst bed is varied and inert packing is placed after and inside the catalyst bed.

The experiments were performed using constant flowrate and fixed amount of catalyst over the temperature range 400 to 500°C. The free space after the bed was varied between "0" and 21.5 inches of tube length. The dilution of the catalyst, when it
took place, was done with the same type of pellets used as support for the catalyst in a ratio of 1:1. Any other special condition in the experiments will be stated where appropriate.

In order to assess the extent and nature of the effects it was decided, first, to examine extreme cases, i.e. zero and 21.5 inches reactor length free space after the catalyst bed. In each case two tests were carried out; one with fixed amount of catalyst diluted and the other using the same amount of undiluted catalyst. The runs with the diluted catalyst used 2 and 10½ in. reactor length of free space after the catalyst bed. Figs (3.31, 3.32) show the details of reactor arrangement and results. Catalyst No. 4 was used in these tests.

The results show a drastic fall in the amount of MAA in the products when free space is incorporated after the catalyst bed. Dilution of the catalyst with Al₂O₃ pellets also produces a drop in the amount of MAA at the outlet. These results show that over-oxidation of MAA takes place in the postcatalytic volume and that the presence of the diluent produces MAA combustion as evidenced as well by traces of other products similar to the ones obtained when MAA is combusted in a bed packed only with Al₂O₃ pellets.

The most important result is that the amounts of benzene converted are not significantly different in the four cases studied. This indicates that the 'inert' packing has no influence on the conversion of benzene.

Further tests were conducted to see to what extent the postcatalytic volume was influencing the selectivity of the reaction and if the use of inert packing after the catalyst bed would induce a different behaviour.
FIGURE 3.3.1 - Effect of Dilution and Free Space After the Bed, Reactor Arrangements. © CATALYST, © Al₂O₃ PELLETS.
Different amounts of free space after the catalyst bed were obtained by moving the catalyst along the axis of the reactor tube. The packing placed after the catalyst bed consisted of 25 3/16 in. dia. \( \text{Al}_2\text{O}_3 \) pellets.

Again, the selectivity of the reaction consistently dropped with the extent of free space provided after the catalyst bed. Poor selectivity was found as well when alundum (\( \text{Al}_2\text{O}_3 \)) pellets were placed after the catalyst bed.

Once more, no significant difference, other than the random scatter of data, was found in the amounts of benzene converted in each case. Fig. (3.3.3) shows the amount of benzene converted as a function of free space after the bed at five temperatures.

A last test was conducted by packing the reactor with catalyst pellets, from the same batch, of two different sizes in an attempt to change the surface to volume ratio inside of the catalytic bed. This method proposed by Gorokhovatskii (139) and discussed previously relies on the fact that with a decrease in granule size, the rate of a heterogeneous-homogeneous reaction per unit external surface area of catalyst should decrease.

Since measurement of the extent of catalytic surfaces could lead to errors, it was decided to use a bed with two different sizes of catalyst pellets. The ratio surface to volume in the bed being changed by using different arrangements of the catalyst pellets.

The reactor was packed, first, with two sections of bed, each one having one size of pellets. Runs were conducted at some operating conditions, and then the different sizes of pellets were mixed and measurements taken again at the same operating
FIGURE 3.3.3 - Effect of Packing and Free Space After the Bed on Benzene Converted.

- □ - 100 Catalyst pellets
- ○ - 100 Catalyst pellets + 25 Al₂O₃ pellets placed after the bed.
conditions used before. No significant difference was found between the two modes of operation.

A method like the above is only sensitive when there is a strong contribution from the homogeneous components. For highly exothermic reactions, an increase in reactant consumption due to higher bed temperatures, originated by a decrease in catalyst size, could be easily mistaken for a contribution of a homogeneous step if the temperature in the catalytic bed is not accurately measured.

The results of these tests, since they do not show a large difference, will not be considered as a strong argument in the discussion of the results.

Discussion on the Heterogeneous-Homogeneous interaction on the formation of MAA

Clearly, the most relevant tests in the search for a homogeneous component occurring concurrently and linked to the heterogeneous step, in the formation of MAA, are those using alundum pellets inside and after the catalyst bed.

According to the mechanism proposed by Brown and Trimm (145),

\[ \begin{align*}
&C_6H_6 + \text{Cat} \rightarrow (C_6H_6)_{\text{ads}} \quad \text{(4)} \\
&\text{heterogeneous} \\
&(C_6H_6)_{\text{ads}} + O_x \rightarrow (C_6H_6 - O_x) \quad \text{(5)} \\
&(C_6H_6 - O_x) + \text{Cat} \rightarrow \text{Products} \quad \text{(6)} \\
&(C_6H_6)_{\text{ads}} + \text{Cat} \rightarrow \text{Products} \quad \text{(7)} \\
&\text{homogeneous} \\
&(C_6H_6 - O_x) + O_2 \rightarrow \text{MAA} + \text{free radicals} + CO_2 \quad \text{(8)} \\
&(C_6H_6 - O_x) + \text{Inert} \rightarrow C_6H_6 + O_x + \text{Inert} \quad \text{(9)}
\end{align*} \]

Inert packing would be expected to favour reaction (9) at the expense of reaction (8), leading to the isolation of more benzene and
less MAA in the final products.

Since the same amount of adduct is produced catalytically, differences in benzene conversion should give a measure of the amount of adduct that would have gone to MAA had the packing not been there.

However, our results show no significant difference, other than that due to the random scatter of data, in the amounts of benzene converted when alumina pellets are placed inside and after the catalyst bed. Clearly, our results offer no evidence to support the above mechanism. Nevertheless, the tests carried out here cannot reject it in absolute terms.

Since the above mechanism gives room for many possible variations, we can only say that reaction (9) only takes place to an insignificant extent or does not take place at all. As regards reaction (8), again, it could take place in the immediate neighbourhood of the catalyst, therefore making its detection very difficult. If this is the case, the reaction will, in practice, be proportional to the amount of adduct formed and therefore to the amount of catalyst. This, under the conditions studied here, would make it practically impossible to distinguish between a purely heterogeneous and a heterogeneous-homogeneous scheme. It is interesting to know that Downie* did not detect any heterogeneous-homogeneous interaction in the o-xylene oxidation reaction.

Clearly, for the purposes of modelling a reactor, the reaction can be safely considered as being strictly heterogeneous in nature at the reaction conditions covered here with no advantage gained by incorporating free space after the catalytic bed since, thereby,

(* Personal communication)
the selectivity of the reaction to MAA drops considerably due to overoxidation.

Since the tests carried out in this section were concerned with the production of MAA, the next section deals with experiments exploring the several possible ways of MAA oxidation.

3.4) Detection of Heterogeneous-Homogeneous Interaction in MAA Oxidation

Earlier results showed that MAA combusts on almost all surfaces and some combustion takes place in empty glass reactors to a lesser extent. As MAA oxidation seemed to be highly unselective, the possibility of a homogeneous reaction initiated on the reactor walls had to be analysed.

Maleic anhydride combustion could be initiated on a surface and then continue as a gas phase chain reaction to produce carbon oxides. If the assumed chains were of a branched nature, then the results would depend largely on the volume provided and be practically independent of the surface used to initiate the reaction.

On the other hand, if the reaction is non-branched or strictly heterogeneous then the extent of reaction will depend on the amount or nature of the surface.

It was decided that a method providing the requirements for these tests was the use of empty reactors of the same dimensions but of different materials of construction.

The materials of construction used for the reactors were: aluminium, titanium, stainless steel and glass. These reactors, which were bent in a U form had 3/8 inch dia. The runs were performed using a total flowrate of 1.0 l/min and 0.66 mole % MAA.
inlet conc. Reactor temperatures of 400, 425, 450, 475 and 500°C were covered in these experiments.

The results, see Fig. (3.4.1), show that MAA combusts to a different extent depending on the material of the reactor walls. Since almost no combustion was found when the glass reactor was used, it was assumed that purely homogeneous combustion only took place to a very small extent. It is clear from the results that, at the conditions studied, MAA combustion is not solely initiated at a metallic surface and then propagated in the gas phase. On the contrary, it appears to be mainly of a heterogeneous nature.

3.5) Effect of Reactor Materials of Construction on the Selectivity of the Overall Reaction

Since MAA appeared to combust at different rates on different materials, a change in the nature of the reactor metal could influence the selectivity of the overall reaction if the combustion of MAA depended largely on the nature of the metal present.

A study was necessary to provide information on the above possibility. This would also enable us to conduct the kinetic study of the reaction using the type of reactor yielding the best selectivity.

The experiments were conducted using catalyst No. 4 over the temperature range 400 to 500°C at a fixed flowrate of 1.0 l/min.

Plots of the effect of temperature on product distribution are shown in Figs. (3.5.1), (3.5.2), and (3.5.3). The effect of the reactor material of construction is shown in Fig. (3.5.4) where selectivity to MAA is plotted as a function of benzene converted. From this figure it is clearly shown that the nature of the reactor
(1) Titanium Reactor (empty)
(2) Aluminium Reactor (empty)
(3) Stainless Steel Reactor (empty)
(4) Glass Reactor (empty)

FIGURE 3.4.1 - MAA Combustion in Empty Reactors (Aluminium, Titanium, Stainless Steel and Glass).
FIGURE 3.5.1: Aluminium Reactor, Product Distribution with Temperature.
FIGURE 3.5.2 Titanium Reactor, Product Distribution with Temperature
FIGURE 3.5.3 - Stainless Steel Reactor, Product Distribution with Temperature.
FIGURE 3.5.4 - Effect of Reactor Materials of Construction on Selectivity to MAA.
FIGURE 3.5.5 - Benzene Disappearance, Arrhenius Plots Using Different Reactors but Same Catalyst.
wall has very little influence on the selectivity of the reaction and therefore on the combustion of maleic anhydride, when the overall reaction is taking place, even at levels of benzene conversion of up to 80%.

The above findings suggest that under the conditions at which the overall reaction takes place, the oxidation of MAA is not significantly affected by the nature of the reactor walls. This could be due to a possible inhibition by some species present in the overall reaction which when not present allows the combustion of MAA to take place at a larger extent and shows dependence on the nature of metal present, as was the case when only MAA was fed into the reactor.

A comparison of the Arrhenius plots for the benzene disappearance step, shown in Fig. (3.5.5) for the three reactor materials of construction, shows a smaller activity for the runs performed in the aluminium reactor but, since there is no apparent reason for this difference, this was assumed to be due to slight changes in the catalyst steady state from day to day.

Although the selectivity of the reaction is little affected for the materials tested here by the nature of the reactor wall, nevertheless, aluminium was chosen as a suitable reactor material since it was the least active of the metals tested when only MAA was fed into empty reactors.

3.6) Kinetics of Benzene Disappearance and Selectivity to MAA

3.6.1) Introduction

Based on the results of the previous sections, the study of the kinetics of benzene disappearance will be carried out assuming that the reaction is purely heterogeneous. However, care will be
taken to see if the results show any evidence of the existence of a heterogeneous-homogeneous interaction.

The kinetics of benzene disappearance will be studied, initially in aluminium tubular reactors with no free space provided, at reaction conditions in the postcatalytic volume to avoid as much as possible the overoxidation of MA at the reactor outlet. The reactor, as before, consisted of a 3/8 in. bore aluminium tube packed with a string of catalyst pellets.

It has been established conclusively by different investigators (67, 55) that variations in the partial pressure of oxygen in the range used here is without influence on the reaction rate. No study is made, then, of the influence of oxygen partial pressure on the reaction rate. The initial concentration of benzene, in the experiments with tubular reactors, was kept in the neighbourhood of 1.0 mole % hydrocarbon in air.

In order to ensure behaviour of the reactors close to plug flow, the minimum amount of pellets used in the catalytic bed was 100.

It was decided to study the effect of temperature on the reaction rate. Experiments were conducted over a 100°C temperature range and, in general, measurements were taken at 400°C, 425°C, 450°C, 475°C and 500°C, where the study of heterogeneous-homogeneous interactions had been conducted. Flowrates were varied between 0.5 l/min. to 3.0 l/min.

Further experiments were conducted in a spinning catalyst basket reactor (SCB reactor), described before, in order to obtain point selectivities of the reaction since the use of tubular reactors yielded only integral data.

The experiments to obtain the kinetic behaviour of benzene disappearance were conducted then in three phases: studies in a
short catalytic bed (100 catalyst pellets), studies using a long
catalyst bed (250 catalyst pellets) and studies in a SCB reactor.

3.6.2) Experiments in a 100 Catalyst-Pellet Catalytic Bed

A full list of results for these experiments is given in Appendix B. Catalyst No. 5 was used for these experiments.

Several experiments were conducted using this short bed but it was found that the levels of conversion, which only reached a maximum of 50% in benzene at the higher temperatures, were not enough to perform an accurate analysis of the characteristics of the reaction.

Fig. (3.6.1) shows a plot of benzene converted versus space velocity, W/F. It can be observed that analysis of the results, which plot almost as straight lines, will result in high inaccuracies. Apparently, according to Fig. (3.6.1) the reaction is nearly zero order since the rate of reaction appears to be constant over the entire range of space velocities, only at the higher temperatures a slight change is noted.

Figs. (3.6.2) and (3.6.3) show product distribution curves of the experiments at 475°C and 500°C and Fig. (3.6.4) shows the selectivities found at 500°C as a function of benzene converted. Due to the small size of bed used, high conversions were difficult to achieve without the use of very low flowrates, which in turn gave error due to the unstable behaviour of the rotameters at these conditions. Thus, a larger catalytic bed was needed if more meaningful results were to be obtained.

3.6.3) Experiments in a 250 Catalyst-Pellet Catalytic Bed

A new batch of catalyst (catalyst No. 5) was prepared to conduct these experiments. With this size of bed conversions of up to 100% in benzene were reached at the higher temperatures and a better assessment of the influence of temperature was achieved.
FIGURE 3.6.1 - Short Bed Reactor (100 Catalyst Pellet Bed),
$X_B$ vs ($W/F$)
FIGURE 3.6.2 - Short Bed Reactor (100 Catalyst Pellet Bed) Product Distribution at 475 °C
FIGURE 3.6.4 - Short Bed Reactor (100 Catalyst Pellet Bed)
Selectivity vs Benzene Converted at 500 °C.

FIGURE 3.6.3 - Short Bed Reactor (100 Catalyst Pellet Bed)
Product Distribution at 500 °C.
The reaction was studied over the range of temperatures 400°C to 500°C. As before, benzene inlet concentration was kept approximately at 1.0 mole % and the total throughput was varied between 0.5 l/min to 3.0 l/min. This meant space velocities between 16 and 91 g cat-min·l⁻¹. A full list of results for the experiments performed under the above conditions appears in Appendix B.

Product conversion at the various temperatures is shown in Figs. (3.6.5), (3.6.6) as a function of space velocity. Figs. (3.6.7) to (3.6.11) show the product distribution curves at the different temperatures.

The reasonably good fit of the rate of benzene disappearance to a simple first order expression at the studied temperatures is shown in Fig. (3.6.12). This result is corroborated by the graphical differentiation of the integral data at 440°C plotted in a typical logarithmic plot of reaction rate (slope of the integral curve) versus benzene concentration, as shown in Fig. (3.6.13).

Arrhenius plots of the pseudo first order rate constant for benzene disappearance, shown in plot I, Fig. (3.6.15), show some scatter when runs performed at different flowrates are compared. However, the results of runs at fixed flowrate show very little scatter. The greater scatter appears in the low temperature range, consequently at low conversions, where the analysis of products becomes more inaccurate. Since the runs were usually performed from the lower to the higher temperature and although the catalyst was left overnight in a stream of air at the initial temperature of the next day, slight changes in the oxidation state of the catalyst would produce certain scatter between the runs of two different days, especially at the low temperatures where the catalyst was just becoming active.
FIGURE 3.6.5 - Benzene Conversion vs Space Velocity (W/F). (250 Catalyst Pellet Bed).
FIGURE 3.6.6 - MAA Production vs Space Velocity (250 Catalyst Pellet Bed).
FIGURE 3.6.7: Overall Reaction (250 Catalyst Pellet Bed), Product Distribution at 400 °C.
FIGURE 3.6.8 - Overall Reaction (250 Catalyst Pellet Bed), Product Distribution at 420 °C.
FIGURE 3.6.9 - Overall Reaction (250 Catalyst Pellet Bed),
Product Distribution at 440 °C.
FIGURE 3.6.10. Overall Reaction (250 Catalyst Pellet Bed), Product Distribution at 460 °C.
FIGURE 3.6.11 - Overall Reaction (250 Catalyst Pellet Bed), Product Distribution at 480 and 500 °C.
TUBULAR REACTOR

BENZENE DISAPPEARANCE

FIGURE 3.6,12: Benzene Disappearance, First Order Plot
FIGURE 3.6.13 - Benzene Disappearance Order Plot from $X_B$ vs $(W/F)$ Curve at 440 °C (Figure 3.6.5).
FIGURE 3.6.14 - 3/8 Inch Diameter Reactor, Experimental Selectivities as a Function of Benzene Converted.

KEY:
- 380 °C
- 400 °C
- 420 °C
- 440 °C
- 460 °C
- 480 °C
- 500 °C
A statistical analysis of all the data collected during several days shows that the activation energy of benzene disappearance oscillates between 22.18 and 23.91 kcal/mole, with the best value at 23.01 kcal/mole. At this value the pre-exponential factor is $1.03509 \times 10^6 \text{ mol}^{-1}\text{cat}^{-1}\text{hr}^{-1}\text{atm}^{-1}$.

As with catalyst No. 4, the selectivity of the reaction to maleic anhydride production is best correlated as a function of benzene converted. Fig. (3.6.14) shows the experimental values of the selectivity found over the range of temperatures 400 to 500°C as function of benzene converted. In this plot it can be seen that the initial selectivity of the reaction is approximately 75%. Since a first order behaviour was found for the disappearance of benzene, the selectivity factor $\frac{k_1}{k_1 + k_3}$ for a triangular scheme of reaction of the form:

$$\begin{align*}
\text{A} & \xrightarrow{k_3} \text{B} \\
\text{B} & \xrightarrow{k_2} \text{C}
\end{align*}$$

for this particular catalyst has a value of 0.75.

3.6.4) Effect of Reactor Diameter on the Selectivity to MAA

Since selectivity to MAA appeared to be practically independent of temperature this implied that a change in reactor diameter would produce the same selectivities as observed in the smaller diameter reactor.

An increase on reactor diameter increases the ratio catalyst surface to reactor wall surface; therefore, a slight improvement in the selectivity of the reaction is expected if MAA combustion is promoted on the reactor walls. On the other hand departures from isothermality are also expected as a result of the larger
amount of heat liberated by the reaction per unit tube length.

To conduct the experiments, the catalyst from the 3/8 inch diameter aluminium reactor used in the previous tests was transferred into a 3/4 inch diameter aluminium reactor. Experiments were conducted over the temperature range 400 to 500°C with the flowrates varying from 0.5 to 2.8 litres per minute.

It was found that under these conditions the catalyst showed a progressive decrease in activity, presumably caused by the high temperatures reached in the core of the catalytic bed. This result was evidenced when the Arrhenius plots for the two different reactors were compared at the same conditions when the large reactor had been run for some time.

Although the activation energy for benzene disappearance was maintained at about the same level, the rate velocity constants were lower for the larger diameter reactor as shown in Fig. (3.6.15). Nevertheless, as shown in Fig. (3.6.16), when the selectivity of the reaction to MAA is plotted as a function of benzene converted the results are little different.

Further increase of the reactor diameter to 1 1/4 inches produced an almost total deactivation of the catalyst after some time, evidenced by the very low levels of conversion achieved even at the higher temperatures. In addition, the deactivated catalyst appeared completely black in contrast with its normal greenish colour.

Although the deactivated catalyst was not then tested in the 3/8 inch diameter reactor to confirm its deactivation, nevertheless, the efforts made in the larger diameter reactor to restore its activity, by passing air only at reaction conditions through the bed, proved unrewarding.
FIGURE 3.6.15 - Benzene Disappearance, Arrhenius Plots (3/8, 3/4, and 1 1/4 inch Dia. Reactors)
FIGURE 3.6.16 - 3/4 inch Diameter Reactor, Experimental Selectivities as a Function of Benzene Converted.

KEY:
- X 380 °C
- △ 400 °C
- ○ 420 °C
- ○ 440 °C
- □ 460 °C
- □ 480 °C
- △ 500 °C
Behaviour like this could explain the fact that the predicted hot spot temperatures in large diameter non-isothermal reactors is in many cases higher than the experimentally found values (vide infra). In other words, the prediction of 'run away' fails because of catalyst deactivation at the hot spot.

Finally, the above results suggest that, as regards the selectivity of the reaction, there is no penalty in working at high temperatures, the only limiting factor being the temperature at which the catalyst suffers irreversible damage.

3.6.5) The SOB Reactor, Kinetics of Benzene Disappearance

Since the values of the selectivities to MAA plotted in the previous figures were the result of integral analysis it was interesting to try to obtain point selectivities by using a SOB reactor in which the concentration of reactants and products is kept constant at each measurement. In this way the catalyst will not be subjected to changing concentrations as in the tubular reactor. It was considered important to obtain selectivities of the reaction at the extremes; that is at the low and high benzene conversions, to obtain a better understanding of the kinetics.

The SOB reactor used was described earlier in Chapter Two of this thesis.

Measurements were carried out over the temperature range 400 to 500°C and benzene initial concentrations were varied between 0.15 to 1.0 mole %. A flowrate of 1.113 l/min. was used throughout the experiments.

Unfortunately, almost no MAA was detected at the outlet of the reactor. This extremely poor selectivity of the reaction was thought to be due to MAA combustion on the metallic walls of the reactor. As described earlier, the reactor has a very high metal to catalyst
Dr. Crosswell has expressed some doubt about the possible existence of product inhibition needed to explain the differences in rates of reaction between the tubular and SCB reactor (Fig 3.6.10). He suggests the following possibility may explain the discrepancy.

1. Non-Isothermality - Presumably, the tubular reactor would become increasingly non-isothermal the higher the temperature. Bearing in mind that reaction rate tends to roughly double every 10°C rise in temperature, the higher rates in the tubular reactor at high temperatures could be explained in terms of an average bed temperature 5°C more 10°C higher than the wall. This would seem a real possibility for very exothermic reactions.

This possibility would also explain why the rate curves for tubular and spinning basket come together at lower temperatures than the tubular reactor is more nearly isothermal.

In answer to Dr. Crosswell's suggestion I would like to say that the obtaining of isothermality in the tubular reactor used for the laboratory experiments was a thoroughly studied matter before any kinetic determination was launched.

In pages 55, 57 and 72 of this thesis it is clearly described how it was arrived at the final reactor arrangement to achieve isothermality, the final choice of reactor arrangement registering only a difference between the bath temperature and cooling medium of about 1°C.

On the other hand, the temperature difference needed to double the rate of reaction in more nearly 30°C and not 10°C as Dr. Crosswell suggests (see Fig 3.6.10). A temperature increase of this magnitude would have been clearly detected when the tests for the isothermality of the reactor, described in pages 55 and 57 were performed.

I therefore do not believe Dr. Crosswell's suggestion is a likely possibility in this case.
surface ratio and this promotes the combustion of MAA in the
internals of the reactor as well as in the outlet pipe, a good
part of which was necessarily kept at reaction conditions. This
being the case, the only significant data obtained from the SCB
reactor were those of the rate of benzene disappearance.

A typical plot of rate of benzene disappearance versus
benzene outlet concentration, shown in Fig. (3.6.17), reveals a
close to first order benzene disappearance, in good agreement with
the data from the tubular reactor.

A comparison between the values of the rate constants
obtained in the tubular reactor with those from the SCB reactor is
shown in Fig. (3.6.18). This figure shows agreement of the rate
constant values at the low temperatures. At higher temperatures
the use of the SCB reactor yields smaller values.

This disagreement has to be explained in terms of the
difference in modes of operation of these two types of reactors.
The fact that the SCB reactor operates at the outlet concentration
means that all the catalyst particles are exposed to the high
outlet concentration of products, whereas in the tubular reactor
only the outlet portion of the catalyst bed is subjected to the
outlet conditions. In this way, an inhibition of the reaction
by the products would be more evident in the back-mix mode of
operation of the SCB reactor, whereas the same effect would be
strongly diminished under the plug flow mode of operation.

It is interesting to note that Ioffe and Lyubarskii (55)
detected a retarding effect of MAA on the rate of benzene disappearance
when using the flow circulation method to study the reaction.
SCS REACTOR
BENZENE DISAPPEARANCE

FIGURE 3.6.17 - SCBR, Benzene Disappearance Order Plots
FIGURE 3.6.13 - Comparison Between Benzene Disappearance Rates in Tubular and SCB Reactors.
3.7) **Kinetics of Maleic Anhydride Combustion**

3.7.1) **Introduction**

Studies reported in the previous sections show that although MAA combustion takes place rapidly in the presence of metal and almost any material which is used to pack the reactor, this does not produce a fall in the selectivity of the overall reaction even at the higher temperatures when only catalyst packs the reactor.

The difference found in the selectivities of the overall reaction in the tubular reactor as compared with those of the SCB reactor pointed out the necessity of a further study of the MAA combustion reaction.

3.7.2) **The Tubular Reactor; Kinetics of Maleic Anhydride Combustion**

Experiments were first conducted over the same catalyst (No. 5) used for the study of the overall reaction with a bed of 250 catalyst pellets in an aluminium reactor over the temperature range 400 to 470°C. Flowrate was varied between 0.5 and 3 l/min. Maleic anhydride inlet concentration was kept at 1.0 mole percent.

Fig. (3.7.1) shows the results presented as MAA converted as a function of space velocity at the different temperatures. It is seen that at about 415°C MAA combustion accelerates greatly at the longer contact times. The cause of this instability was thought to be probably due to the onset of 'runaway' producing a hot spot in the catalytic bed whose magnitude could not be evaluated. In order to confirm this, the flow through the reactor was reversed. In this way a large amount of empty tube was left at reaction conditions after the catalytic bed. If MAA was combusting very rapidly due to the high temperatures reached at 'runaway', the empty portion of the tube left after the catalyst bed would be
FIGURE 3.7.1 - Aluminium Tubular Reactor, MAA Combustion/Catalyst
relatively active only at the low temperatures before the rapid combustion of MA was initiated on the catalyst. The results, plotted in Fig. (3.7.1), showing the difference between a normal run and one in which free space was incorporated after the catalyst bed, show agreement with this assumption. This fact made the data for MA combustion obtained in the above experiments unsuitable for use in the analysis of the overall reaction scheme.

It was decided then to carry out the reaction in a glass reactor of 3/8 inch bore diameter, packed with a short bed of catalyst (11.6 gms.) in order to reduce large departures from isothermality and overoxidation on the walls.

Experiments were conducted using a MA inlet concentration of 0.66 mole % and flowrates were varied between 0.1 and 1.0 l/min. Runs were carried out over the temperature range 400 to 500°C. Full lists of results are given in Appendix B.

The results from these experiments confirm the fact that the catalyst itself is most inert to maleic anhydride combustion. Fig. (3.7.2) shows a plot of MA conversion versus space velocity and Fig. (3.7.3) shows the Arrhenius plot for this case. The activation energy taken from the slope of the Arrhenius plots yields $8.59 \pm 1.48$ kcal/mole. It later appeared that the rate velocity constants from these results were consistent with the selectivities to MA yielded by the overall reaction (vide infra).

The low value of the activation energy found for MA combustion suggests the existence of some physical rate-limiting mechanism. The low values of the rate constants found indicate that mass transfer is unlikely to be the controlling step. In the same way, pore diffusion can be safely ruled out since a catalyst with practically no interior surface was used.
FIGURE 3.7.2 - Glass Tubular Reactor, MAA Oxidation on Catalyst.
FIGURE 3.7.3 - Glass Tubular Reactor, Arrhenius Plot for MAA Oxidation / Catalyst.
The possibility exists of surface diffusion control, caused by the finite rate at which adsorbed MAA diffuses on the surface to an oxygen rich reaction site.

3.7.3) The SCB Reactor, Kinetics of MAA Oxidation

A) The SCB Reactor: Oxidation of MAA in the Presence of Catalyst

In order to obtain isothermal data for the combustion of MAA, experiments were next conducted using the SCB reactor. Although this reactor had rather a lot of metallic surface in the internals, its behaviour was considered to be isothermal and therefore very useful in the determination of MAA combustion kinetics.

The experiments were conducted over the temperature range 400 to 500°C with the MAA inlet concentration varying from 0.17 to 0.7 mole%. The flowrate was kept constant at 1.0 l/min. and the catalyst charge in the basket was 10.86 gms.

Order plots of rate of MAA disappearance versus MAA outlet concentration, Fig. (3.7.14), show a reaction order of about 0.64 at the different temperatures.

B) The SCB Reactor: Oxidation of MAA in the Absence of Catalyst

In order to isolate the contribution of the catalyst to the oxidation of MAA, blank runs were performed at the same conditions as those when catalyst was present.

The orders of reaction found in the plots of rate of MAA disappearance versus MAA outlet concentration were very much the same as those found when the basket contained catalyst. However, a small difference was found in the levels of conversion at the higher temperatures (see Fig. 3.7.4). This difference, which was the contribution of the catalyst to the oxidation of MAA, was too small to allow an accurate quantification. In fact, at
FIGURE 3.7.4 - SCBR, Order Plots for MAA Oxidation on Catalyst and on Empty Reactor.
SCB REACTOR
MAA OXIDATION

- Reactor/Catalyst
- Reactor Empty

FIGURE 3.7.5 - SCB R, MAA Oxidation on Catalyst and on Empty Reactor
the temperature of 400°C no difference was found in the levels of conversion between the runs with and without catalyst present, as can be seen in Fig. (3.7.5). The combustion of MAA then, under these conditions, was mainly due to the large amounts of metal present in the reactor. The catalyst on the other hand showed very little activity in good agreement with the results obtained in the glass tubular reactor with a short catalyst bed.

3.8) Discussion of Results

A) The Catalyst

The use of different catalyst formulations during this work gave the opportunity to look, although in a qualitative manner, upon the effects of some of the catalyst components on the selectivity of the reaction. The catalysts used consisted mainly of a mixture of $\text{V}_2\text{O}_5$, $\text{MoO}_3$ and $\text{P}_2\text{O}_5$. The basic difference between formulations being the relative amounts of $\text{P}_2\text{O}_5$ used. It is interesting to note that $\text{P}_2\text{O}_5$ has been reported (25) to increase the work function of the $\text{V}_2\text{O}_5$ catalysts in propene oxidation. Our results offer support to the theory that there is the possibility of suppressing complete combustion, and therefore of improving the selectivity of the catalyst, by increasing the catalyst work function. One is also led to point out the possibility of an optimum amount of $\text{P}_2\text{O}_5$ in the formulation of the catalyst. Since the activity of the catalyst could be reduced by a large amount of $\text{P}_2\text{O}_5$, high activity and selectivity would be ensured only at a strict optimum concentration of the $\text{P}_2\text{O}_5$ added to the formulation of the catalyst.

However, in view of the fact that the work here is oriented towards the prediction of the behaviour of the industrial reactor,
the above line of research was considered outside the scope of the present work.

The important fact in our case is that small alterations in the formulation and way in which the catalyst is prepared produce significant changes in selectivity, activity and even in the activation energy of the reaction. This is of great importance when predicting the behaviour of a large scale non-isothermal reactor since a change in activation energy could determine the difference between a stable or unstable operation of the reactor.

B) Incorporation of the Experimental Data in the Overall Scheme of Reaction

The detection of only benzene, maleic anhydride and carbon oxides at the outlet of the reactor and the absence of any significant heterogeneous-homogeneous interaction which could affect the reaction suggests that a triangular scheme of concurrent and consecutive catalytic reactions, shown below, can adequately describe the overall reaction:

\[
\begin{align*}
\text{Benzene} & \xrightarrow{1} \text{MAA} \xrightarrow{2} \text{C oxides} \\
& \xrightarrow{3}
\end{align*}
\]

Clearly, the results of the experiments using a tubular reactor, Figs. (3.6.12) and (3.6.13), show that benzene follows a first order rate law of disappearance. Although differences were found in the values of the rate constants between the experiments conducted in a Spinning Catalyst Basket reactor and a tubular reactor, the order of reaction for benzene disappearance obtained with the use of the former, shown in Fig. (3.6.17), also approaches unity.

The ratio between the routes 1 and 3 of the above scheme
can be obtained from the value of the initial selectivity of the reaction when no MAA has been formed. Fig. (3.6.14) shows this value to be about 0.75 and independent of temperature. This defines the value of \( \frac{k_1}{k_1 + k_3} \) which is the first important selectivity coefficient and indicates that routes 1 and 3 have the same activation energy.

Since a low area-low porosity (less than 1 sq. m/g) catalyst was used it was not surprising to find that the Arrhenius plots did not show any fall off in the activation energy due to diffusional process controlling the rate of reaction even at the high temperatures. The constant value of the activation energy found for benzene disappearance of about 23 kcal/mole over the entire range of temperatures studied suggests that chemical reaction controls the overall rate.

A more difficult task is to incorporate the results of MAA oxidation into the overall reaction scheme. This is because every experimental method which was used here to investigate this reaction by itself yielded different results. In observing the literature on MAA combustion (8) one finds that orders of reaction of 0, 0.5 and 1.0 have been reported by different workers. The data reported on the activation energy of the reaction show the same disagreement with values between 8 and 28 kcal/mole. It is not surprising then that our results change with the method used to study the reaction.

In order to find out the cause of these discrepancies and to decide on the true behaviour of the reaction, let us summarise the different results found by us and the reasons for its rejection or acceptance.
The oxidation of MAA carried in an aluminium tubular reactor with a 250 catalyst pellets bed, yielded unstable combustion too strong to be consistent with the selectivities found in the overall reaction. In other words, an activation energy of 37 kcal/mole and high values of the rate constants, higher than those of benzene disappearance, were considered enough to reject the validity of the data. As explained before, this was thought to be due to temperature runaway.

An attempt to study the rate of MAA combustion on the catalyst, at isothermal conditions, in a SCB reactor was frustrated by the high activity displayed by the metallic internals of the reactor. Since the SCB reactor operates isothermally or close to it the data, although overshadowed by the strong effect of the metal present, qualitatively show that the reaction only takes place to a very small extent on the surface of the catalyst.

Finally, the use of a glass reactor fitted with a short bed of catalyst, to avoid large departures from isothermality and eliminate the effect of metallic walls, confirmed the point that MAA oxidation is very low on the catalyst surface and quantitatively reliable data were extracted from these experiments. The activation energy of MAA combustion was found to be about 8.6 kcal/mole with pseudo first order rate constants plotting linearly in an Arrhenius plot. It might be because of this small extent of unselective MAA combustion that the different previous workers have been able to reproduce their product distribution curves. It is apparent that the oxidation of MAA takes place rapidly on most surfaces with the exception of the vanadium catalyst and it remains obscure as to why active metal tubular reactors when
packed with the catalyst show a very low activity under these circumstances when the overall reaction is taking place.

The data for MMA combustion obtained in the glass reactor were incorporated in the overall reaction scheme. Experimental and predicted selectivities to MMA, in two different diameters of reactor, are shown in Fig. (3.8.1 A,B) for the isothermal case, with rate constants data from Fig. (3.8.2). Since the data obtained in the glass tubular reactor for MMA combustion were free of the metallic wall effect, the actual values of the rate constant \( k_2 \) for metallic reactors will be expected to be slightly higher than those obtained in the glass reactor. However, the effect of the walls of the reactor, operating in the tubular reactor mode, is very small. This is confirmed by the fact that although stainless steel is more active to MMA combustion than aluminium, runs performed in a stainless steel reactor yielded the same selectivities to maleic anhydride as shown in Fig. (3.5.4).

Fig. (3.8.3) shows that the agreement obtained between experimental and predicted data at 480 and 500°C is satisfactory. Ultimately, the decision as to whether a reaction model is correct or not depends on the predictions of the isothermal reactor behaviour and even more significantly, on the prediction of the performance of a non-isothermal large scale reactor. The next part of this thesis deals with the non-isothermal case.
**Figure 3.8.1** - Tubular Reactor, Experimental (A) and Predicted (B) Selectivities to MAA

△ 400 °C, ○ 420 °C, ○ 440 °C, ▴ 460 °C, □ 480 °C, △ 500 °C

3/8 and 3/4 inch dia. Reactors
OVERALL REACTION

\[ B \xrightarrow{k_1} \text{MMA} \xrightarrow{k_2} \text{C. oxides} \]

**FIGURE 3.8.2** - Arrhenius Plots for the Steps in the Overall Reaction Scheme
FIGURE 3.8.3 - Tubular Reactor, Experimental and Predicted Concentration Profiles for Benzene and Maleic Anhydride at 480 and 500 °C.
Chapter 4

Characteristics of the Catalyst used in the Pilot Plant.

4.1) Introduction

4.2) Kinetics of Benzene Disappearance and Selectivities to MAA.

4.3) Maleic Anhydride Combustion

4.4) Conclusions
Characteristics of the Catalyst used in the Pilot Plant.

1.1) Introduction

It has been found during the course of this work that the mode of preparation of the catalysts used can influence their performance to the extent that two substantially identical catalyst batches differing only in minor variations of preparative procedure may give rise to significant variations in catalyst selectivity and rate.

Clearly, since we intend to model the behaviour of a large scale non-isothermal reactor, the characteristics of the catalyst to be used for this purpose have to be well known if the results are to be reliable.

In non-isothermal catalytic reactors, a small change for example in the activation energy of the reaction will, in some cases, significantly affect the behaviour of the reactor as has previously been pointed out by Carberry (204) in his analysis of the naphthalene oxidation reaction.

It is important to point out that the catalyst used in the pilot plant experiments (No. 6) had a slight difference in formulation compared with those previously used. In addition, this catalyst was the first to be prepared on a larger scale (2.0 Kg). Thus its parameters could not be assured and were re-determined.

Again, as in chapter 3, the results here are shown in the form of plots. Full tables of results are given in Appendix C.

4.2) Kinetics of Benzene Disappearance and Selectivities to MAA.

Since the pilot plant reactor was constructed in stainless steel, it was decided to conduct the kinetic measurements using the new catalyst in a 3/8 inch diameter stainless steel reactor, similar to the
one used before to assess the effect of reactor materials of construction.

The experiments were conducted over the temperature range 100 to 500°C and flow rates were varied between 0.5 and 2.0 l/min. The catalyst charge to the reactor was 16.7955 g, and the benzene inlet concentration was kept at approximately 1.0 mole percent.

A typical Arrhenius plot for the benzene disappearance step is shown in Fig. (4.1). A statistical least squares analysis of the points in this plot yields an activation energy of 17.6 ± 0.655 Kcal/mole.

Clearly, this activation energy is lower than the one found for catalyst No. 5 (23.0 Kcal/mole). A second difference between this catalyst (No. 6) and catalyst No. 5 is that the former is less active at the high temperatures. However, the selectivities exhibited by both catalysts do not differ greatly. A plot of reaction selectivity to MMA versus benzene converted is shown in Fig. (4.2). For this catalyst, the selectivity coefficient \( \frac{k_1}{k_1 + k_2} \) has a value of approximately 0.7.

It is important to point out that the closeness of the carbon balances to 100% diminished with increased conversion to values of around 85% at conversion levels also close to 85%. This was due to the formation of minor products from the MMA and benzene direct combustion routes. These minor products gave a very small signal in the chromatograph and were therefore difficult to evaluate. In fact, signs of them in the chromatograph appeared only at the high conversions.

The fact that the carbon balances departed from 100% at high conversions added to a changing ratio of CO to \( \text{CO}_2 \) in the products, presented a problem since knowledge of the heat evolution with reaction is a very important factor when modelling non-isothermal reactors.
Difficulties arose in plotting the CO/CO$_2$ ratio as a function of temperature due to the scatter of data, and compelled us to plot this ratio as a function of benzene converted to render a less significant relationship, see Fig. (4.3). Nevertheless, this type of plot allowed us to observe the trend of the CO/CO$_2$ ratio as the reaction proceeded and therefore made it possible to introduce an approximate correction for the heat release term.

Fig. (4.3) shows that, as reaction proceeds, the CO/CO$_2$ ratio tends to a value close to one. Thus, the CO/CO$_2$ ratio was adopted as the most convenient parameter to account for the presence of all partial combustion products. Hence, the heats of reaction shown in Appendix were calculated from the above and used in the modelling studies.

4.3). Maleic Anhydride Combustion

Although it has been shown that the oxidation of MA on the catalyst takes place only to a small extent under plug flow conditions, nevertheless, experiments were conducted here to look for a possible change in the mechanism of this reaction with the new batch of catalyst (No. 6).

Experiments were conducted over the temperature range 400 to 500$^\circ$C using a MA inlet concentration of about 0.5 mole %. Flowrate was varied over the range 0.6 to 2.0 l/min. and the charge of catalyst was the same as for the overall reaction experiments (16.7955 g.).

Figure (4.1) shows a typical Arrhenius plot for MA combustion. From the slope of this plot, an activation energy of 14.164 ± 0.734 Kcal/mole is obtained. This value of the activation energy appears high compared with the one obtained for MA combustion in a glass reactor. As before, it is believed that the data obtained in the glass reactor reflect more accurately the behaviour of the overall reaction.
FIGURE 4.1 - Arrhenius Plots for Benzene Disappearance and MAA Oxidation (Catalyst 6, SS Reactor).
FIGURE 4.2. - Stainless Steel Tubular Reactor, Reaction Selectivity vs Benzene Converted.

KEY: ○ 400 °C, △ 425 °C, ○ 450 °C, □ 475 °C, □ 500 °C
FIGURE 4.3 - CO/CO₂ Molar Ratio as a Function of Benzene Converted.
4.4) Conclusions

Clearly, the results obtained here with catalyst No. 6 do not point out any significant difference in the reaction scheme. Hence, the triangular scheme of three pseudo first order reactions remains valid and suitable to be used in the modelling of the large scale non-isothermal reactor.

In order to explain the lower activity and difference in activation energy of catalyst No. 6 as compared with catalyst No. 5, two factors may be invoked i.e., differences in formulation and/or differences in catalyst structure induced during the preparation stages. The fact that the change in activity was more apparent at the higher temperatures suggests that the catalyst did not react in the same way as catalyst No. 5 to an increase of temperature probably due to a different combination of oxide phases on the catalyst surface (a different oxidation state of the catalyst).

As mentioned earlier, phosphorous added to the catalyst formulation has been found to increase the work function of the catalyst (25). Thus lowering its oxidising power and preserving in this way the intermediate product (MAA). It is also believed that P$_2$O$_5$ has an optimum ratio in the catalyst which ensures high activity and selectivity. In order to give some relative numbers, let us look at the different catalyst formulations used during this work in terms of their differences in P$_2$O$_5$ content and the results obtained with each of them.

The ratio P$_2$O$_5$/V$_2$O$_5$ in catalysts 4, 5 and 6 goes in increasing order i.e., 1:21.7 for catalyst 4, 1:10.5 for catalyst 5 and 1:7.7 for catalyst 6. Catalyst 4 with the less amount of P$_2$O$_5$ gives a selectivity which drops rapidly from its initial value, see Fig (3.5.4).
Catalyst 5 shows high activity and a selectivity that is maintained at a high level as the reaction proceeds. Catalyst 6, on the other hand, shows a maintained selectivity with reaction but has a lower activity than catalyst 5. Hence, the possible optimum amount of $P_2O_5$ in the formulation, for best selectivity and higher activity, would be around a $P_2O_5/V_2O_5$ ratio of 1:10.5. However, the apparent connection between catalyst properties and $P_2O_5$ content has not been thoroughly evaluated and may indeed be spurious.
Chapter 5

Experimental Apparatus and Procedures (II)

5.1) The Reactor and Reactor Shell
5.2) The Fluidizing Air System
5.3) Delivery of Reactants
   5.3.1) The Air System
   5.3.2) The Benzene System
5.4) Control and Instrumentation
5.5) Analytical Equipment
5.6) Typical Experimental Schedule
Experimental Apparatus and Procedures (II)

Caldwell (148) designed this apparatus to study the theoretical findings on catalyst dilution applied to the o-xylene oxidation reaction and later Ellis (149) made slight modifications to the rig when testing models for the catalytic oxidation of o-xylene.

A thorough description of the rig is given elsewhere (148); only a brief description is given here. A standard flow diagram of the general arrangement of the equipment is shown in Fig. (5.1).

5.1) The Reactor and Reactor Shell

The reactor consisted of a 2.5 inch bore type 321 stainless steel tube, 0.16 cm wall thickness, shaped in a U form, with the axis of the two legs five inches apart. The height of the reactor was 2.54 m; see Fig. (5.2). A drilled stainless steel disc located close to the bend of the U tube supported the catalyst allowing in this way one of the legs to be used as a preheating section. The maximum bed length was approximately 2.0 metres. The depth of the bed used in the experiments was kept fixed at 80 cm.

Thermocouples installed, along the inside leg axis, at intervals allowed for temperature recordings in the centre of the catalytic bed; the exact positions are illustrated in Fig. (5.3).

The reactor was connected to the rest of the piping system by two 11.5 cm dia. flanges and 'Metaflex' gaskets.

At a distance of 7.62 cm. below the flanges a 27.5 cm. dia. mild steel plate was welded to the legs of the reactor to allow
the latter to be bolted to the upper reactor shell closing plate, bolted in turn to the upper reactor shell flange.

The reactor shell, illustrated in Fig. (5.4), was a two end flanged cylindrical vessel 45 cm. internal diameter, 2.75 metres long and 0.31 cm. wall thickness. This shell contained a heated fluidized bed of sand which provided constant jacket temperature. A 61.0 cm. dia. sintered disc, bolted between the lower reactor shell flange and the upper flange of the shell support drum, supported the sand. The sand in the reactor shell was "-120" sand supplied by A. L. Curtis (ONX) Ltd. of Cambridgeshire.

The reactor shell was provided with a take-off point near the bottom to allow the sand to be discharged if necessary.

The reactor shell support drum which was 3 ft. long had a side entrance for the fluidizing air. The fluid bed shell was lagged with a 7.6 cm. thick layer of high temperature asbestos-magnesia insulation and coated with plastic paint.

A 5.1 cm. dia. reactor was designed along the lines of the 2.5 cm. dia. reactor. A drawing of this larger reactor is presented in Fig. (5.6).
FIGURE 5.1 - Pilot Plant Flow Diagram
FIGURE 5.3 - Thermocouple Locations

FIGURE 5.2 - The One Inch Diameter Reactor
FIGURE 5.4
The Reactor Shell
FIGURE 5.5 - Heating Elements Arrangement.
FIGURE 5.6 - The Two Inch Diameter Reactor
5.2) The Fluidizing Air System

Air to the fluidized bed was fed from a TG 336 Holmes positive displacement Roots type blower, rated 75 cubic feet per minute at a discharge pressure of 7 p.s.i.g., driven by a \( \frac{5}{2} \) H.P. three phase motor. Part of the air supplied by the blower was discharged to the atmosphere by means of a 3 inch steam valve used to regulate the air required to fluidize the bed.

The air to the fluidized bed was monitored by a 65 X metric rotameter. The air monitored by the rotameter passed then through the shell side of a vertically mounted heat exchanger (121 tubes, 0.96 cm. O.D. x 16SWG., 2.13 metres in length) and from there to the reactor shell drum to be distributed in the bed by a 'Porosint' rigid mesh (40 micron) stainless steel disc. The air plus some sand entrained from the fluid bed was passed through the tube side of the heat exchanger mentioned earlier and from there to a cyclone, where the sand carried was collected, and through a vacuum cleaner bag to collect the fines before being vented to the atmosphere.

A plastic container was installed at the bottom of the cyclone to collect the sand which, at the end of the day, was returned to the sand shell through an entrance at the top of it provided for this purpose.

5.3) Delivery of Reactants

5.3.1) The Air System

The air to the reactor was delivered by an Edwards RB 10 high vacuum blower driven by a one H.P. motor. A filter packed with glass wool removed the traces of oil coming from the blower.
The air was monitored and controlled by a system of valve and rotameter (18 x metric rotameter). A bigger rotameter was fitted when the 5.1 cm. dia. reactor was used.

Before incorporating the air with the benzene, the air was preheated approximately to 400°C by passing it through a mild steel rectangular insulated box. Four 0.75 kilowatt Pyrobar heating elements were installed in the side wall of the box.

After the preheater, once the benzene was incorporated to the air, the stream was fed into the reactor. The major part of the air leaving the reactor was fed into a drum collector packed with steel fibre to collect the products and then vented to atmosphere.

A small sample was continuously taken from the outlet of the reactor to be analysed.

5.3.2) The Benzene System

Benzene was stored in a 100 or 200 ml. buretes to allow the volume of benzene used in each run to be measured. A Hughes positive displacement metering pump was used to feed the benzene. Two glass sintered filters were placed before and after the pump to avoid faulty operation of the small check ball valves installed in the pump head. The benzene feed rate was varied by adjusting the length of the stroke of the metering pump plunger by means of a graduated micrometric screw provided for this purpose in the back of the pump body.

The benzene was incorporated to the main air downstream of the preheater. All the piping of the benzene feed system was 0.64 cm. O.D. copper tubing.

For the experiments with the 2.5 cm. dia. reactor, a 105 ml. per hour (maximum delivery) rated pump was used, this
was changed for a 750 ml. per hour (maximum delivery) pump for the experiments with the 5.1 cm. dia. reactor.

5.4) Control and Instrumentation

The six Pyrobar heating elements in the reactor shell were connected in two different circuits with the three elements of each circuit wired in parallel. Independent on-off switches were provided for each circuit. In order to achieve a fine control of the fluid bed temperature the upper set of heaters were connected through a 7.5 kVA 'VARLAC'. The fluid bed heaters could only be activated when the Holmes blower was running in order to avoid damage to the heating elements. The four heating elements in the preheater were connected in a similar fashion, two elements wired through a 2 kVA 'VARLAC' and the other two direct. Both circuits connected through a contactor activated by the reactor air blower.

Providence was taken to ensure the stop of the hydrocarbon metering pump when the Holmes blower was not supplying air to the fluidized bed, avoiding in this manner overheating of the catalyst due to the heat of reaction not being able to be removed.

In order to measure the bed temperature, a set of chromel-alumel sheathed in 0.24 cm. O.D. stainless steel tubing thermocouples were installed in each reactor, see Figs. (5.5) and (5.6), to allow the axial catalytic bed temperature to be known. Two additional thermocouples were installed in the larger 5.1 dia. reactor to measure the wall temperature and the temperature halfway between the centre of the catalytic bed and the wall of the reactor. One thermocouple installed through the take-off
point of the fluid bed shell allowed the temperature of the fluid bed to be monitored.

All the above thermocouples were connected to a Kent Mark 3 twelve point recorder (range 350-500°C) in parallel with a ten channel Comark electronic thermometer (range -120°C to 1100°C). 'Araldite' was used to seal the point between the thermocouple and the steel tubing at the point where the latter terminated. An independent thermocouple allowed the temperature of the preheating reactor air box to be monitored.

In order to avoid damage to the Holmes blower supplying air to the fluidized bed a pressure switch set to trip the motor at a delivery pressure of 8 p.s.i.g. was installed.

5.5) Analytical Equipment

The same analytical equipment used for the experiments at small scale, already described, was used here.

5.6 Typical Experimental Schedule

All the runs were performed with undiluted catalyst and the 2.5 cm. dia. reactor was charged with 559 gms. of catalyst equivalent to 80 cms. bed height. Temperature along the axis of the bed was measured by six thermocouples. The 5.1 cm. dia. reactor was charged with 1560 gms. of the same catalyst. This was equivalent to 50 cms. of bed length. Five axial points were monitored for temperature in the bed.

The first thing to be switched on was the fluid bed air. After the air flow was stabilized at the required level (usually mark 5 in the rotameter) the heaters were switched on. Starting from cold the fluid bed would require approximately 15 hours to reach operating temperatures, therefore it was normally switched
on the day before the experiments were to be started. The air to the reactor was switched on as well as the preheater and the thermocords which heated the piping.

At the beginning of the experimental day, the fluid bed air and heaters were switched off and the sand carried over during the night was returned to the fluid bed shell. This operation caused a lowering in the fluid bed temperature of about 10-15°C. After this the air to the bed and heaters was turned on again. The mains to the analytical equipment was switched on and was kept in this way all the time to avoid fluctuations as explained earlier. The hydrogen and air flows to the flame ionization detector were turned on. The nitrogen flow to the chromatographic column was kept on all the time. The flame was ignited every day at the beginning of the experimental day. The electronic thermometer was switched on and once the temperature of the bed was within the range of the Kent recorder this was switched on as well.

Once all the units were at their required levels, the benzene metering pump would be switched on, initially at a lower level than required to avoid damage of the catalyst and only later judging by the recorded bed temperatures it was put to the level required for the run of the day.

Although steady state condition in the bed was achieved fairly quickly and, therefore, samples could be taken, methodic sampling only started after the reaction had been running for at least three hours. This time was given only at the start of the day runs. The time allowed when in between a run a change was made, in the flow rate or benzene
inlet concentration, was one hour. Normally, the operating
temperature in the fluid bed was not changed throughout the day.

Since the achievement of the steady state condition was
fast, no dynamic behaviour of the reactor is discussed in later
sections.

At the end of the experimental day the first thing to be
switched off was the benzene feed.

Monitoring of the catalytic bed temperature was continued
until all the thermocouples in the bed showed the same temperature
as the fluid bed. At this moment the electronic thermometer and
Kent recorder were switched off. In the same way the hydrogen
and air flows were only switched off until no peak appeared in
the recorder of the analytical equipment.

Once the above requirements were met, the air to the reactor,
the piping heating cords and the recorder of the analytical
equipment were switched off. As in the small scale runs the
mains to the flame ionization detector amplifier, chromatograph
oven and integrator were kept on all the time.

The air to the fluid bed and heaters was switched off to
allow for the entrained sand to be returned to the fluid bed.
After this they were switched on again and kept working overnight.
Chapter 6

A Mathematical Model of the Fixed Bed Catalytic Reactor

6.1) Introduction

6.2) Steady State Mathematical Model of the Fixed Bed Catalytic Reactor

6.2.1) Mass Transfer in Packed Beds

6.2.2) Heat Transfer in Packed Beds

6.2.3) Form of the model and simplifications introduced

6.2.4) Method of solution of the Mathematical Model
6) **A Mathematical Model of the Fixed Bed Catalytic Reactor**

6.1) **Introduction**

It is generally acknowledged in the chemical engineering field that the design and modelling of complicated equipment is not yet a straightforward operation. Catalytic packed bed tubular reactors are no exception and, indeed, there is no analytical method which explicitly yields design parameters.

For the case of non-isothermal catalytic packed tubular reactors, present practice involves the calculation of the conditions that would be obtained in the reactor for fixed sets of design parameters which are then allowed to vary within permissible limits. Thus, a set of parameters for the design may be deduced.

Clearly, the procedure outlined above becomes more simple and accurate as the number of known parameters increases or the intervals of uncertainty in these parameters is narrowed.

In general, the parameters which dictate reactor performance for a given reaction-catalyst system are:

- **A)** Operational Parameters, i.e. feed composition, pressure, coolant temperature etc.
- **B)** Transport Parameters, i.e. various heat and mass transport coefficients.
- **C)** Kinetic Parameters related to the chemical reaction taking place, i.e. rate constants, activation energies etc.

The operational parameters are well defined and normally experimentally available with precision. The transport and kinetic parameters, on the other hand, do not lend themselves to easy determination.
Because of the difficulty in obtaining kinetic parameters free of transport influences from experiments in a large non-isothermal reactor, these have to be independently determined under isothermal conditions in the laboratory. Ideally, heat transfer studies should be conducted to determine the heat transfer parameters in the system under consideration.

Obviously, if the system is complex, accurate determination of all the kinetic and transport parameters is difficult and therefore assumptions and simplifications, which may affect the final solution, have to be introduced.

To clarify the above considerations it seems pertinent at this point to recall the particular problem under investigation here and to outline the procedure used in its solution.

The catalytic oxidation of benzene in which both the desired intermediate product (maleic anhydride) and reactant itself are susceptible to complete combustion to undesired CO, CO₂ and H₂O offers a challenge to modelling not only because of the complexity of the reaction scheme but because of its high exothermicity. The first part of this thesis was concerned with obtaining the form of the reaction scheme and the determination of the kinetic parameters, under isothermal conditions. For the purpose of modelling the reactor, a problem arising out of this experimental work was the appearance of unidentifiable minor reaction products at high conversions and subsequent departure of the carbon balances from 100%. This made an exact evaluation of the heats of reaction difficult, and therefore an approximation based on the available data was introduced. This approximation is discussed in greater detail in Chapter Four of this work.
Independent experimental determination of the heat and mass transfer characteristics of the reactors used here was not available from previous work. Since to undertake such a task would be very time consuming, an alternative approach was necessary to model the reactor. The use of literature correlations for the prediction of heat and mass transfer parameters in packed beds seems possible. However, inspection of the published work in this field shows, particularly for heat transfer parameters, unsatisfactory scatter, thus making the choice of a correlation difficult.

An alternative approach which avoids the use of these literature correlations is the deduction of heat transfer properties of the system from the experimental axial temperature profile observed in non-isothermal packed bed reactors. This method assumes that the form of the rate equations is known and that the radial temperature profiles are flat. This approach was originally proposed by Wilson (157) and later used by Pasek and Pexidr (158). Beek (159) extended this procedure to an unknown form of the rate equation and relaxed the second assumption of flat temperature profiles by the less rigorous assumption that in a cross section of the reactor the temperature profile takes the form:

\[ T = C_0 + C_1 r^2 + C_2 \log r \]

where \( C \) varies with axial position

\( r = \) tube radius.

When the form of the rate equation is known, the above procedures are in effect a curve fitting scheme with the preliminary estimation of local rates as a device to make the fitting easier.

Using a similar device to the above, we propose to leave the overall heat transfer coefficient of our system as an adjustable
parameter and perform a sensitivity analysis on the kinetic and transport parameters of the system. Since the kinetic parameters have been experimentally determined, their interval of uncertainty is small and the above procedure becomes relatively simple.

Using this method it is possible to see if with the kinetic parameters determined previously, an assumed value of the heat transfer parameters can reproduce the experimental data. Failure to do this suggests a possible error in the kinetic parameters which may then be re-examined; a feedback trial and error solution to the problem. Once the experimental data has been reproduced by a set of parameters, these can be compared with the predictions from literature correlations to see if they have the right order of magnitude.

The application of this method requires the form of the mathematical reactor model to be chosen beforehand. Clearly, a high degree of complexity in the mathematical model would require a greater number of parameters to be determined. Thus, as mentioned earlier, a balance has to be reached between accuracy and practicability.

The following discussion considers both, the analytical structure of the mathematical reactor model and the important parameters therein. The relative importance of the parameters and their effect on the model solution is evaluated, particularly through examination of the literature. Finally, the method of solution of the model equations is discussed.

6.2) A Steady State Mathematical Model of the Fixed Bed Catalytic Reactor

In order to predict the behaviour of a fixed bed catalytic reactor, it is necessary to formulate a mathematical model to
describe the simultaneous occurrence of heat transfer, mass transfer and chemical reaction within the system.

When a highly endo or exothermic reaction takes place in the reactor, the changes in bed temperature are too wide to attempt to use an average temperature effectively. Thus, the conditions within the reactor have to be calculated step by step. This means that in order to know the outlet conditions, the conditions everywhere else in the reactor have to be calculated.

In general, two approaches have been proposed in the literature to describe the fixed bed reactor. These are,

A) Continuum models,
B) Cell models.

Each one of these models is in turn subdivided according to heterogeneity, i.e. pseudo-homogeneous and heterogeneous models.

Pseudo-homogeneous models assume no concentration or temperature differences between the flowing fluid and the stationary solid phase, while heterogeneous models make distinction between the solid and fluid phase. This gives a more realistic approach but also increases the number of parameters involved.

Continuum models allow the application of a differential balance over an element in the reactor and therefore can be stated in the form of differential equations whereas cell models regard the system as an array of interconnected cells, each one of these being perfectly mixed (202). Under these conditions the particle diameter becomes the natural measure of length, and the void volume associated with a particle is taken as the volume element for the balances. The steady state equations written for each stage are algebraic and seemingly more tractable than the differential equations yielded by the continuum model.
Valstar (160) has given a comparative discussion of both continuum and cell models. The continuum model is applied in this work. Thus, we assume that it is possible to define an elementary volume of uniform concentration and temperature, that is homogeneous but at the same time large enough to give statistical meaning to the average values considered inside the element.

This concept has been found to be satisfactory in some instances for reactors when more than 10 particles are packed across the tube and the number of particles exceeds six in the axial direction (161, 162). The second condition is normally fulfilled but industrial reactors do not always meet the first requirement.

When a tubular reactor exchanges heat with the surroundings, radial temperature and concentration gradients are created. Strictly speaking, a two dimensional model is then required to describe the bed but when the radial profiles are not very pronounced, a one dimensional model based on radial averages of the bed properties has been used with considerable success (165).

For the continuum model, where smooth gradients are considered, the transport of heat and mass may be described by a formula analogous to Fick's law of diffusion. These diffusional processes are then superimposed upon the convective transport of mass and heat induced by the overall flow. In the case of a packed bed, the proportionality constant in this law is called the "effective diffusivity" and "effective conductivity" for mass and heat transfer respectively.

Clearly, these effective diffusivity and conductivity referred to in this mode of mass and heat transfer are in reality complex functions of the bed characteristics (fluid plus solid) and the flow conditions.
Before the material and enthalpy balances are formulated it is useful to review briefly some aspects of the heat and mass transfer mechanisms involved in the treatment of packed bed reactors.

6.2.1) **Mass Transfer in Packed Beds**

For the flow conditions encountered in practice, it is generally assumed that diffusion is exclusively due to the deflection of gas by particles and that molecular diffusion is relatively insignificant. Transverse diffusion has been considered to result from a random walk of elements of fluid through the passages in the bed (164), or equivalently, from mixing of converging streams (165, 166). Essentially, the model assumes that when a fluid particle encounters a pellet it may deviate towards the left or the right with equal probability. If the distance between two consecutive deviations is known, a diffusivity coefficient may be obtained.

Based on the random walk theory, Baron (164) obtained an expression for the Peclet number \( (\frac{ud}{D_e}) \). Assuming deflections of the order of one half particle diameter he found the radial Peclet number should be between 5 and 13 for particle to tube diameter ratio of less than 0.1. In general, the results of the investigations on radial diffusion (167, 168, 169) restrict the Peclet number to 8 - 11 when the Reynolds number exceeds 50. Caldwell's (148) theoretical calculation of the Peclet number, using a three way matrix model free of wall effects, led to a value of 9.8. For practical design purposes, a Peclet number of 10 is usually chosen. It has been shown that computed profiles are relatively insensitive to this value (170, 171), and therefore a refined experimental approach in this direction is unnecessary.
Diffusion parallel to the flow primarily arises from the stagewise mixing in the interstices of the bed (172, 173) with some contribution from the variation of mass velocity with radial position.

In general, most of the work in this field (172, 174) reports a constant value of 2 for the Peclet number, for Reynolds numbers above 10. Although apparently the value of the Peclet number for longitudinal diffusion is small, it is based on the particle diameter. Thus, for a normal size of bed the Peclet number based on tube length is at least 100. Axial diffusive processes have been found to be insignificant in industrial reactors (169, 175, 176) and are normally neglected when building up a mathematical reactor model.

6.2.2) Heat Transfer in Packed Beds

The transfer of heat in packed beds is more complicated than mass transfer due to the participation of the solid phase and to a lesser extent to radiation effects. As in the case of mass transfer, the dispersion of heat in the axial direction has been found to be negligible, except for very shallow beds and low flow velocities (175). Thus we will focus our attention on the radial transport of heat.

The general recognized mechanisms (177, 178), which contribute to the overall flux of heat in the radial direction can be described as:

1) Molecular conduction through fluid phase.
2) Molecular conduction through solid phase.
3) Radiation from particle to particle.
4) A series mechanism from fluid to particle to fluid, etc.
5) Turbulent diffusion (convection) through the fluid phase.
Mechanism 4 and 5 become more important as the Reynolds number increases and in a static system mechanisms 1 to 3 only operate.

In order to deal with the complexity of a system in which all five mechanisms operate, it is customary to replace them by the single mechanism of conduction through a hypothetical homogeneous substance. The unreality of this concept is tolerated by permitting the thermal conductivity of this hypothetical substance to be a function of all those variables involved in each of the actual mechanisms operating in the bed; an effective thermal conductivity. Therefore the most logical method of estimating this effective thermal conductivity is to divide it into separate contributions, each of which corresponds to a mechanism of heat transfer (167, 178, 179). The effective thermal conductivity is also normally expressed in the literature in terms of a Peclet number. Most of the measurements in this field have been done under conditions where only the terms for eddy transport and conduction through the solid need to be considered, i.e. high Reynolds numbers. It is assumed that, by analogy with mass transport, the Peclet number increases as the Reynolds number decreases. All the experimental evidence (180 - 184) indicates that the conduction through the solid is at least as important as the eddy transport when the Reynolds number is less than 50, even for poorly conducting materials such as glass.

Because the transfer of heat is enhanced by the presence of the solid over the transport of mass, the Peclet number for heat transfer is expected to be smaller than for mass transfer at the low Reynolds numbers, and very similar at high Reynolds numbers. This has been confirmed experimentally by Singer and Wilhelm (167).
They found that the Peclet number for radial heat transfer is in the range 6 - 8 at low Reynolds numbers but tends to a value of 10 at Reynolds numbers higher than 100.

In general, the treatment of the effective thermal conductivity, considers it to be independent of radial position. However, when values of this effective thermal conductivity are experimentally measured at various points of a section perpendicular to the flow, it is found (177, 185) that it decreases strongly in the vicinity of the wall, as if an additional resistance was experienced there. In order to explain this decrease, it has been postulated that the presence of the wall interrupts the packing of the solid producing larger voids and less turbulence. Under the above conditions two attitudes are possible; either one may take a mean value of the effective conductivity over the whole section or introduce an additional coefficient accounting for the wall effect. This wall heat transfer coefficient \( (h_w) \) has been defined as follows:

\[
h_w (T_R - T_{\text{wall}}) = -k \frac{dT}{dr}
\]

Accordingly, this wall heat transfer coefficient becomes more important as the size of the particles packing the reactor becomes larger, for example, exceeding one tenth the diameter of the bed. The wall heat transfer coefficient is normally expressed in terms of a Nusselt number and its estimation is even more uncertain than is the effective thermal conductivity. The measurement of wall heat transfer coefficients depends either on an extrapolation of a temperature profile to the wall or on determining the resistance at the wall as the difference between a measured overall resistance and a calculated resistance within the packed bed.
Not surprisingly then, the exponent of the flowrate which represents the variation of the heat transfer coefficient at the wall with this parameter has been reported by Coberly and Marshall (162) as 0.33, by Calderbank and Pogorski (185) as 0.365, by Campbell and Huntington (182) as 0.47, by Aerov and Umnik (180) as 0.74, by Plautz and Johnstone (186) as 0.75 and by Quinton and Storrow (184) as 1.0. Hanratty (187), using the Higbie concept (188) of a systematic rate of fluid renewal at the wall, predicted a value of the flowrate exponent of 0.5. In the face of these discrepancies, the choice of a correlation to estimate the heat transfer coefficient at the wall becomes arbitrary to some degree.

Thoenes and Kramers (189) translated experimentally measured mass transfer rates from a particle of packing to the adjacent wall into the heat transfer analogue by substituting Nusselt and Prandtl numbers for Sherwood and Schmidt numbers. These authors suggest the use of three terms to represent conduction in laminar flow, eddy conduction and stagnant conduction, making the approach more realistic. It is important to point out that the correlations for both heat and mass transfer have been deduced for the case of non-reacting systems. It is however logical that the nature of a reaction taking place will affect to some extent the value of the heat and mass transfer parameters of the system. Petersen (190) points out that the heat transfer coefficients can be several fold larger than in the absence of chemical reaction. Therefore it behoves the designer to be aware of this fact and anticipate at least in a qualitative manner the consequences of the larger values of the overall heat transfer coefficient which may be anticipated in practice.
6.2.3) Form of the Model and Simplifications Introduced

Having briefly reviewed the transport processes which take place in a packed bed reactor, our attention is now turned to the mathematical form of the reactor model. Let us consider a catalytic packed bed reactor in which an irreversible first order reaction occurs. Under the continuum model assumption, no distinction is made between bulk gas and solid catalyst conditions, then for an elemental volume of annular cross section, assuming axial symmetry and a flat velocity profile (plug flow) the components of mass entering and leaving the element in unit time longitudinally and radially are:
Mass Entering

Longitudinal bulkflow:

\[ 2 \frac{\text{r} \Delta r \frac{G}{M}}{\frac{\frac{\text{PA}}{P}}{P_T^2}} \]

Mass Leaving

\[ 2 \frac{\text{r} \Delta r \frac{G}{M}}{\frac{\frac{\text{PA}}{P}}{P_T^2}} \text{Z + } \Delta \text{Z} \]

Transverse diffusion:

\[ - k_{e_r} 2 \frac{\frac{\Delta r}{\frac{\frac{\text{PA}}{P}}{\Delta z}}}{\Delta r} \]

\[ - k_{e_r} 2 \frac{\frac{\Delta r}{\frac{\frac{\text{PA}}{P}}{\Delta z}}}{\Delta r} \text{Z + } \Delta \text{Z} \]

Longitudinal diffusion:

\[ - k_{e_a} 2 \frac{\frac{\Delta r}{\frac{\frac{\text{PA}}{P}}{\Delta z}}}{\Delta r} \]

\[ - k_{e_a} 2 \frac{\frac{\Delta r}{\frac{\frac{\text{PA}}{P}}{\Delta z}}}{\Delta r} \text{Z + } \Delta \text{Z} \]

Mass of component consumed by chemical reaction:

\[ 2 \frac{\text{r} \Delta r \Delta z}{\frac{\Delta r}{\frac{\frac{\text{PA}}{P}}{\Delta z}}} \cdot P_B \cdot R(P_A, T) \]

where for a first order irreversible reaction:

\[ R(P_A, T) = A e^{-\frac{E_a}{RT}} P_A \]

In the steady state the algebraic sum of components will be zero. By expanding the terms evaluated at \((r + \Delta r)\) and \((Z + \Delta Z)\) about the points \(r\) an \(Z\) respectively and neglecting second order differentials, the mass balance equation can be
expressed as:

$$\kappa_{mr} \left( \frac{S^2 P_A}{\delta r^2} \right) + \frac{1}{r} \left( \frac{5P_A}{\delta r} \right) + \kappa_{ma} \left( \frac{S^2 P_A}{\delta z^2} \right) - \frac{G}{M \rho_T} \left( \frac{5P_A}{\delta z} \right) = \rho_B \left( -\Delta H \right) \frac{R(P_A,T)}{P_T} \quad (6.1)$$

Analogously, a heat balance equation yields:

$$\kappa_{hr} \left( \frac{S^2 P_A}{\delta r^2} \right) + \frac{1}{r} \left( \frac{5T}{\delta r} \right) + \kappa_{ha} \left( \frac{S^2 P_A}{\delta z^2} \right) - \frac{G}{M \rho_T} \left( \frac{5T}{\delta z} \right) = \rho_B \left( -\Delta H \right) \frac{R(P_A,T)}{P_T} \quad (6.2)$$

Equations (6.1) and 6.2 can be rearranged into a dimensionless form by introducing the coordinates

$$r^* = \frac{r}{D_p^*} \quad Z^* = \frac{Z}{D_p}$$

and the Peclet numbers:

$$Pe_{mr} = \frac{G D_p}{M \kappa_{mr} P_T} \quad , \quad Pe_{ma} = \frac{G D_p}{M \kappa_{ma} P_T}$$

$$Pe_{hr} = \frac{-G C_p D_p}{\kappa_{hr} M} \quad , \quad Pe_{ha} = \frac{-G C_p D_p}{\kappa_{ha} M}$$

Considering axial dispersion terms negligible, equation 6.1 and 6.2 become:

$$\frac{1}{Pe_{mr}} \left[ \left( \frac{S^2 P_A}{\delta r^2} \right) + \frac{1}{r^2} \left( \frac{5P_A}{\delta r^2} \right) - \frac{S^2 P_A}{\delta z^2} \right] - \frac{G}{M \rho_T} \left( \frac{5P_A}{\delta z} \right) = \frac{\rho_B D_p M (-\Delta H)}{G C_p} \frac{R(P_A,T)}{P_T}$$

$$\frac{1}{Pe_{hr}} \left[ \left( \frac{S^2 P_A}{\delta r^2} \right) + \frac{1}{r^2} \left( \frac{5T}{\delta r^2} \right) - \frac{5T}{\delta z^2} \right] = \frac{\rho_B D_p M (-\Delta H)}{G C_p} \frac{R(P_A,T)}{P_T}$$
with the boundary conditions:

at \( Z = 0 \); \( P_a = P_{\text{inlet}} \), \( T = T_{\text{inlet}} = T_{\text{wall}} \) for \( 0 < r < R \)

\[
\begin{align*}
  r = 0 : \left( \frac{6F_A}{\delta r} \right) &= 0, \left( \frac{6T}{\delta r} \right) = 0 \\
  r = R : \left( \frac{6F_A}{\delta r} \right) &= 0, -k_e h_r \left( \frac{6T}{\delta r} \right)_{r = R} = h w dp (T - T_{\text{wall}})
\end{align*}
\]

As mentioned previously, a one dimensional approximation to the above two dimensional model can be achieved by considering that all the resistance to heat transfer lies within a film localized near the wall. Thus, average concentration and temperature are considered in a cross section of reactor. Fig. (6.1) shows the difference between an actual radial temperature profile (203) and the one dimensional approximation of it.

\[\text{Fig. (6.1)}\]
Under the above considerations the one dimensional model follows as a reduced form of the more general two dimensional outlined above:

\[
\frac{dP_A}{dZ} = - \frac{\rho_B P_T D_P M}{G} R(P_A, T)
\]

\[
\frac{dT}{dZ} = \frac{\rho_B D_P M(-\Delta H)}{G \overline{C_p}} R(P_A, T) - \frac{h U D_P}{G \overline{C_p} Dt} (T-T_w)
\]

Where \( U \) is an overall heat transfer coefficient for this one dimensional model.

Experimental determinations of overall heat transfer coefficients were early performed by Colburn (191) and Leva (192-194) and later extended by Chu and Storrow (195) who found that the effect of column length ignored by Colburn and Leva, was important. Calderbank and Pogorski (185) later showed the influence of the \( L/Dt \) ratio on the overall heat transfer coefficient. Beek and Singer (196), Froment (197) and Crider and Foss (198) give relationships between the two dimensional parameters (\( \rho_{kr} \) and \( \rho_{rh} \)) to estimate the overall heat transfer coefficient.

Beek and Singer's correlation, as well as Froment's correlation

\[
\frac{1}{U} = \frac{1}{h_w} + \frac{R_o}{\frac{4}{3} \rho_{kr}}
\]

which can be deduced under the assumption that the radial temperature profiles are parabolic, give serious errors when the
bed resistance is controlling. Crider and Foss showed that Beek's equation is only appropriate when the wall resistance is controlling and suggest that their correlation,

$$\frac{1}{U} = \left( \frac{1}{h_w} \right) + \left[ \frac{R_0}{64\,133 \, k_{erh}} \right]$$

(based in the best estimate of bed resistance) leads to a maximum error of 5.7%.

Clearly, this overall heat transfer coefficient is a very complex entity since many contributions have been lumped in it. In addition it works with an artificial driving force based on average radial temperatures. Nevertheless, experience has shown this coefficient to be practically useful. For our particular case, with no previous independent determination of the heat transfer parameters of our system at hand, the use of a two dimensional model does not offer great advantages.

In addition, it has been shown (199, 200) that the form of the longitudinal temperature profiles yielded by the one and two dimensional models are analogous when the reactor operates in a stable region. The effect of the radial temperature distribution on the agreement between the two models on the other hand, can only be estimated. Therefore, if the reactor operates under conditions of low thermal sensitivity, that is, the rate of heat removal from every point is potentially larger than the rate of heat evolution, the radial temperature profiles are smooth with no inflection points. Under these conditions, the approximate one dimensional model is well satisfied and good agreement can be expected between the one and the two dimensional
model predictions. From the experimental runs one can detect if the reactor is working under conditions of high thermal sensitivity. In this case the inflection point on the radial temperature profiles, which results when the rate of heat evolution rises more rapidly with temperature than does the rate of heat removal, will be present and high parametric sensitivity will be exhibited. In the present work, parametric sensitivity was absent.

As mentioned earlier, the use of the one dimensional model would enable us to leave the overall heat transfer coefficient as an adjustable parameter to be obtained with the aid of the experimentally measured axial temperature profiles in the bed. Such a procedure would be very complex if treated in a two dimensional way and accurate separation of the bed and wall resistances would depend on accurate measurement of radial and axial temperature profiles. On the other hand, temperatures as measured by thermocouples do not offer the required precision if a two dimensional approach is used in this way.

In our particular case, temperatures in the centre of the bed were measured with normal size thermocouples sheathed in stainless steel tubing to give them strength. This could produce a smoothing of the true axial temperatures because of longitudinal heat conduction in the thermocouple making them more nearly comparable with the bulk mean computed values.

Although in our case the application of a one dimensional model appears suitable to describe the behaviour of the reactor, it is necessary to be aware that this approach is at least
uncertain in some areas which could be the source of possible error, viz: axial diffusion terms are neglected and all resistance to radial heat transfer is considered at the vicinity of the wall (flat radial temperature profiles). The suitability of this one dimensional model will be tested later on in this work when the accuracy between experimental and predicted axial temperature profiles for reactors of one and two inches diameter are analysed.

6.2.4) Method of Solution of the Mathematical Model

The integration of the one dimensional model mass and energy equations can be accomplished by standard numerical integration techniques. In our particular case use was made of available computer library subroutines based on the Adams-Baschoff-Adams-Moulton (ABAM) predictor-corrector method. A detailed theoretical elaboration of this method is given elsewhere (201). In general, these methods (predictor-corrector) make use of two algorithms, one which predicts a value and the other corrects or improves the predicted value. This process can be iterated until an acceptable error is found. A distinguishing feature of predictor-corrector methods is that in getting the next point they make use of prior points. Accordingly, they are not self-starting and use is made of a self-starting method, usually a Runge-Kutta to start the iterations.

In order to simplify the explanation, let us consider a second order predictor method to be:

\[ y_{m+1}^0 = y_{m-1} + 2h f(x_m, y_m) \]

where the superscript 'o' indicates the first "guess" at \( y_{m+1} \) - a predicted value.
Geometrically, see Fig. (6.2), the predictor amounts to finding the slope at \((x_m, y_m)\) and drawing a line \(L_1\) with that slope through \((x_m, y_m)\). A line \(L\) then is drawn parallel to \(L_1\), through \((x_{m-1}, y_{m-1})\). The point at which this line intersects the line \(x = x + 1\) is the predicted value, \(y_{0m+1}\).

The corrector method is then used to improve this first guess. Since \(y_{m+1}\) is known approximately, we can calculate an approximate slope at \((x_{m+1}, y^o_{m+1})\). This is line \(L_2\) in Fig. (6.3). The line \(L_1\) is the same as in Fig. (6.2). Line \(L\) is obtained from the average slope of \(L_1\) and \(L_2\). Finally, a line \(L\) is drawn parallel to \(L_1\) through the point \((x_m, y_m)\). Its intersection with the line \(x = x_{m+1}\) yields a new approximation to \(y_{m+1}\). We call this the corrected value \(y^1_{m+1}\) given by:

\[
y^1_{m+1} = y_m + \frac{h}{2} [f(x_m, y_m) + f'(x_{m+1}, y^o_{m+1})]
\]

A better estimate of \(f'(x_{m+1}, y_{m+1})\) can be obtained by using \(y^1_{m+1}\) and recorrecting the value of \(y_{m+1}\). Thus, in general, the \(i\)th approximation to \(y_{m+1}\) is given by

\[
y^i_{m+1} = y_m + \frac{h}{2} [f(x_m, y_m) + f'(x_{m+1}, y^{i-1}_{m+1})]
\]

for \(i = 1, 2, 3 \ldots\) the iterations are stopped when

\[
|y^{i+1}_{m+1} - y^i_{m+1}| < \epsilon
\]

for a positive specified \(\epsilon\).
FIGURE 6.2 - Geometrical Interpretation (Predictor).

FIGURE 6.3 - Geometrical Interpretation (Corrector).
Chapter 7

Experiments With and Modelling of the
Pilot Plant Reactor

7.1) Introduction

7.2) Results of Experimental and Modelling Work.
7.1) Introduction  

Following the method outlined in the previous chapter, this chapter deals with the prediction of the experimental axial temperature profiles in one and two inch diameter non-isothermal catalytic reactors. Thus, with the kinetic parameters determined previously and the bed properties incorporated in the model of the reactor, the overall heat transfer coefficients are adjusted to match the experimental temperature profiles. The heat transfer coefficients resulting from this exercise are then compared with those predicted by the available literature correlations and possible causes for the minor but significant discrepancies are analysed.

7.2) Results of Experimental and Modelling Work.  

As a result of detailed analysis in which the heat transfer coefficient was varied over a wide range of values in an attempt to fit the experimental reactor axial temperature profiles, it was found that the initial rise in temperature yielded by the model was too steep and the 'hot spot' temperature too high compared with the experimentally measured values. In fact, 'run-away' was predicted by the model at almost all the experimental conditions used in the one and two inch diameter reactors. Fig. (7.1) shows the difference between experimental and predicted temperature profiles using a value of the heat transfer coefficient $U = 95$ estimated from literature correlations (vide infra).

The temperature profiles yielded by the model showed that at the inlet section of the one inch diameter catalytic bed, the temperature gradient in a length equivalent to a particle diameter was about $20^\circ C$, anticipating very large gradients across a pellet for the two inch diameter reactor.
ONE INCH DIAMETER REACTOR
RUN 9

Experimental Profile
Predicted, $U^* = 95$ (run-away)

Kinetic Parameters as Obtained in Chapter 4 for Catalyst 6

FIGURE 7.1 - Difference Between Experimental and Predicted Axial Temperature Profiles. $U^*$ (Estimated from Literature
Correlations)
If these predicted temperature gradients existed in reality in the catalytic bed, the use of a pseudo-homogeneous model which assumes smooth gradients would be in gross error. Under these conditions a heterogeneous model using solid and fluid temperature for the predictions would probably be essential. However, inspection of the experimental axial temperature profiles did not exhibit this rapid increase in bed temperature and gradients across a pellet were only 1 - 2 °C, consistent with the pseudo-homogeneous model used. It was thought at the beginning that the difference between the predicted and experimental temperature profiles was possibly due to the one-dimensionality of the model used for the predictions. However, inspection of the radial temperature profiles measured in the two inch diameter reactor showed that these were remarkably flat and should be capable of being represented by a one dimensional model without introducing much error. This flatness of the measured radial temperature profiles can only be considered an approximation since the thermocouples used were too big for accurate measurements of this sort; there is also the possibility that the presence of the radial thermocouples may have disturbed the packing inducing a larger voidage in their vicinity and therefore reading a flatter radial temperature profile than actually existed. If the packing was disturbed, the above effect will be mainly felt by the thermocouple measuring the temperature midway between the centre of the bed and the wall. Fig. (7.2) shows several of the radial temperature profiles found in the two inch diameter reactor at different operating conditions.

During the course of finding the 'best fit' values of the overall heat transfer coefficient, it became apparent that the initial ascendent part of the temperature profile curve was mainly controlled by the kinetic parameters i.e., the values of the rate constants, and the tail
FIGURE 7.2. - Experimental Radial Temperature Profiles in the Two inch Diameter Reactor.
end of the curve was largely controlled by the heat transfer properties
of the system i.e., the overall heat transfer coefficient. Thus, although
the overall heat transfer coefficient was varied over a wide range, the
shape of the temperature-length curve was not reproduced. This indicated
that the cause of the great discrepancy between experimental and predicted
temperature profiles was incorrect kinetic parameters; that is, the
reaction was taking place less rapidly than indicated by the kinetic
parameters obtained previously at isothermal conditions. Thus, the
possibility of catalyst deactivation had to be explored. This possibility
had been in a way anticipated by the experiments in the small scale
reactors when tests were made on the effect of reactor diameter. As
mentioned earlier, the catalyst partially deactivated when the diameter
of the reactor was increased from $\frac{3}{4}$ to $\frac{3}{2}$ inch and stronger deactivation
was experienced when the reactor diameter was further increased to 1 inch
(see Fig. (3.6.15) chapter 3). Obviously, these two latter reactors did
not operate under strictly isothermal conditions. This shows that catalyst
deactivation takes place when large departures from isothermality occur
due to the increase in the tube to particle diameter ratio. Such
deactivation was not evident in the isothermal kinetic experiments conducted
below 550°C (vide infra) so that is apparently brought about by an initial
'run-away' at the hot spot of the order predicted in Fig. (7.1). The high
temperatures cause a reduction in catalyst activity which serves to reduce
them dramatically and stable operation is restored after a period in
which extensive combustion is evidenced by high CO$_2$ values at the outlet
of the reactor.

In order to confirm that catalyst deactivation had taken place,
experimental re-determination of the rate velocity constants of the
catalyst used was needed. To this end, the catalyst pellets in the two
inch diameter reactor were taken out and re-examined. It is necessary to
say at this point that the two inch diameter reactor contained the pellets used previously in the experiments with the one inch diameter reactor (560 g.) plus some fresh catalyst (1000 g.) added to give enough bed length.

Visual inspection of the pellets taken out of the reactor showed a difference in colour. Some of the pellets were black whereas others had the greenish coloration which was more characteristic of previous catalysts. The two types of pellets were separated and measurement of the rate velocity constants was made for a random sample of each batch of pellets. These tests were carried out in the \( \frac{3}{8} \) inch diameter stainless steel reactor, used previously to determine the characteristics of the original catalyst at isothermal conditions.

The rate velocity constants, measured over the temperature range 400-500°C, showed a different activity for each type of pellets. The black pellets showed an activity level of about half of the original value, whereas the green pellets had maintained the original level of activity, see Fig. (7.3). It is important to point out that the pellets taken out of the one inch diameter reactor and incorporated at random in the two inch diameter reactor bed were already black in colour. At the time this did not appear remarkable since the non-activated pellets were of a dark glossy colour and with the catalyst activated in situ it was difficult to anticipate its colour after activation had taken place. In addition, the modelling exercise was carried out after the experimental runs in the two reactors had ended. Although the experimentally measured temperature profiles were evidently unexpectedly low, it was difficult to decide if deactivation had taken place.
Most probably, it was thought, the catalyst in the one inch diameter reactor lost activity either during the initial ignition period or during the time the reactor was left running for the catalyst to settle at its normal activity level. The deactivation of the catalyst could have taken place also when at the beginning of the runs, as a result of a failure in the cooling system, the catalytic bed temperature reached 600°C. After this incident, the benzene metering pump was also wired to stop it from working if the cooling system failed.

The assumption that the catalyst in the one inch diameter reactor deactivated, was supported by the fact that the axial temperature profiles and outlet concentrations, in this reactor, could only be reproduced by assuming a lower catalyst activity.

The above facts led us to conclude that the one inch diameter reactor contained deactivated catalyst (black pellets) and the predicted axial temperature profiles for this reactor were successfully obtained by considering that the catalyst pellets had the low activity later observed in the subsequent kinetic re-determination.

It is interesting to mention that although this correction was introduced, the initial predicted rise in temperature was still slightly higher than the experimental profile. This suggested that the initial part of the one inch diameter bed had an even lower activity than the random sample of deactivated pellets used in the re-determination of the kinetics.

It was this low activity catalyst from the one inch diameter reactor which when mixed with fresh catalyst in the two inch diameter reactor bed produced a diluted bed preventing, in this way, what might have been a total deactivation.
Most probably the flat radial temperature profiles encountered in the two inch diameter reactor, which favoured the use of a one dimensional model, were a product of this involuntary bed dilution. Under the above conditions, the catalytic beds of the one and two inch diameter reactors operated with catalysts of different activities. The necessary correction was incorporated in the model.

Clearly, in order to give some meaning to the results from the two inch diameter reactor, it is necessary to know the ratio of active to less active pellets in the catalytic bed. Thus, various possibilities had to be explored.

If the inclusion of the low activity pellets from the one inch reactor prevented the deactivation of the fresh catalyst, an initial active to deactivated pellets ratio of 1.78 existed in the reactor. This assumption was supported by the fact that use of the lower activity failed to reproduce the initial temperature rise and resulted in very low benzene conversions. On the other hand, use of the maximum catalyst activity in the model resulted in high spot temperatures which could only be lowered to approach the experimental hot spot temperatures if unacceptably high heat transfer coefficients were used in the model. This in turn, deformed the shape of the predicted axial temperature profile showing that this latter assumption was incorrect. However, since the ratio of active to deactivated catalyst pellets at the end of the runs in the two inch diameter reactor was 1.12 rather than 1.78, obviously some extra deactivation had taken place during the two inch diameter reactor's operation. It is believed that this further catalyst deactivation took place during the runs performed to study the effect of benzene inlet concentration. During these runs, which intentionally were left at the end of the experimental program, the benzene concentration was increased in each run until bed
temperatures above 600°C were recorded. These temperatures are probably high enough to cause catalyst fusion (the melting point of the $P_2O_5$ is 580 - 585°C). This was confirmed by the fact that a subsequent and last run needed a heat transfer coefficient higher than acceptable to predict the temperature profiles from the assumed kinetics.

It is interesting to mention that a similar behaviour was reported by Ellis (149) in the study of the o-xylene oxidation reaction. His catalyst, which also had $V_2O_5$ as the main component and possibly some $P_2O_5$, suffered deactivation when the o-xylene inlet concentration was increased from 1.0 to 1.5 mole%. His experiments, which were conducted in the same rig as ours, revealed that despite the deactivation suffered by the catalyst, the selectivity levels were maintained. Clearly, this greatly resembles the behaviour exhibited by our catalyst. Thus, it appeared that the assumption of an active to less active pellets ratio of 1.78 was accurate for all the runs in the two inch diameter reactor prior to the experiments reaching 600°C in the bed. However, it is possible that an activity profile which was best approximated by the assumption of an homogeneous ratio of active to less active catalyst pellets of 1.78 was present in the bed.

Since the experimental temperature profiles in the one and two inch diameter reactors exhibited in some cases temperatures above 500°C, in order to avoid extrapolation of the original kinetic data, the temperature range for the determination of the rate velocity constants for the two sets of pellets was further extended to 550°C. This extension of the temperature range showed that the activation energy of the benzene disappearance step decreased at high temperatures, see Fig. (7.3), indicating the possible existence of a physical rate controlling step.
Values of the Arrhenius parameters (pre-exponential factor and activation energy) for the different regions were calculated using a simple least squares technique and are shown in table 7.2.1 for the benzene disappearance step.

Inspection of Fig. (7.3), shows that the change in activation energy may have been abrupt or more gradually with temperature, this being uncertain due to scatter in the data so that the ranges shown in table 7.2.1 are approximate.

Proper incorporation of the appropriate regions into the model is very important since a small change in the activation energy has a considerable effect on the value of the pre-exponential factor and therefore significantly affects the rate or reaction and consequently that of heat evolution.

In order to illustrate the difference in the prediction of the temperature profiles, depending on the kinetic parameters used, Fig. (7.4) shows the effect of using each of the four different regions of kinetic parameters shown in table 7.2.1 in the one inch diameter reactor, once the 'best fit' overall heat transfer coefficient had been found for the low activity catalyst pellets. This figure also shows that high temperatures, capable of causing catalyst deactivation are obtained with the original activity level of the catalyst pellets.

It is important to emphasize that the catalyst deactivation only reduces the rate of reaction while the selectivity levels are maintained. This amounts to a catalyst 'self-adjustment' which constrains the reactor to operate under stable conditions. The importance of this fact is that this may be a characteristic not only of our particular catalyst, but of many catalysts which promote exothermic reactions. Thus, the modelling of
FIGURE 7.3 - Arrhenius Plots for the Benzene Disappearance Step on Active (green) and Deactivated (black) Catalyst Pellets.
### Benzene Disappearance

<table>
<thead>
<tr>
<th>Pellets and Temperature Range</th>
<th>$A_1$</th>
<th>$EA_1$</th>
<th>$A_3$</th>
<th>$EA_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green Pellets (400 - 425°C)</td>
<td>$1.450779 \times 10^6$</td>
<td>24266</td>
<td>$0.621771 \times 10^6$</td>
<td>24266</td>
</tr>
<tr>
<td>Green Pellets (425 - 550°C)</td>
<td>$0.5663 \times 10^4$</td>
<td>17112</td>
<td>$0.2432 \times 10^4$</td>
<td>17112</td>
</tr>
<tr>
<td>Black Pellets (400 - 450°C)</td>
<td>$0.2927645 \times 10^6$</td>
<td>23321</td>
<td>$0.125470 \times 10^6$</td>
<td>23321</td>
</tr>
<tr>
<td>Black Pellets (450 - 550°C)</td>
<td>$0.284263 \times 10^3$</td>
<td>13324</td>
<td>$0.112528 \times 10^3$</td>
<td>13324</td>
</tr>
</tbody>
</table>

### Maleic Anhydride Combustion (From runs in glass reactor, see Chapter 3)

<table>
<thead>
<tr>
<th></th>
<th>$A_2$</th>
<th>$EA_2$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Active Pellets (400 - 550°C)</td>
<td>9.7639</td>
<td>8.589</td>
<td></td>
</tr>
<tr>
<td>Deactivated Pellets (400 - 550°C)</td>
<td>4.8819 *</td>
<td>8.589</td>
<td></td>
</tr>
</tbody>
</table>

* Approximated assuming that the MAA combustion rate was reduced by the same ratio as that of the benzene combustion rate.

Table (7.2.1)
ONE INCH DIAMETER REACTOR
RUN 3

1. $T_{\text{max}} = 1412^\circ C$ (run-away)
2. $T_{\text{max}} = 629^\circ C$
3. $T_{\text{max}} = 823^\circ C$ (run-away)
4. $T_{\text{max}} = 509^\circ C$

--o-- EXPERIMENTAL
-PREDICTED

FIGURE 7.4 - Effect of Kinetic Parameters on Reaction Behaviour. See Figure 7.3 to Identify Regions 1, 2, 3 and 4.
large scale non-isothermal reactors with kinetic parameters obtained from fresh catalyst under isothermal laboratory conditions would be an illusory theoretical exercise which would predict 'run-away' whereas the industrial reactor would operate in a stable region due to the catalyst 'self-adjustment'.

Clearly, it is important to review the possible causes leading to the observed changes in activation energy with temperature. Two possible mass transfer resistances could induce a change in the apparent energy of the reaction. The first, mass transfer from the fluid to the surface of the pellet was ruled out after comparison of the rate velocity constants with the gas phase mass transfer coefficients multiplied by the pellet area per unit volume (which were at least one order of magnitude bigger). In addition, if gas phase mass transfer were the controlling mechanism, the observed change in activation energy for both, the black deactivated and the active green catalyst pellets would occur at about the same value of the rate velocity constants. Inspection of Fig. (7.3) shows that for the black pellets the change in slope occurs at about 450°C with a rate constant value of 0.037. On the other hand, the change for the green pellets occurs at about 425°C with a value of the rate constant of 0.05. Therefore, external mass transfer influence can probably be dismissed as the cause for the observed change in activation energy. The second possibility is the existence of pore diffusion. Since a low surface-low porosity catalyst support was used, and as the method for the catalyst preparation further reduced the few available pores, it is very unlikely that pore diffusion influences the rate of reaction.

In theory (205), the effect of pore diffusion at one limit, of the values of the modulus $\phi$

$$\phi = \left( \frac{R^2}{D_{eff}} \right) \left( -\frac{1}{Vc} \frac{dn}{dt} \right) \left( \frac{1}{Cs} \right)$$

larger than 100 is that the observed value of the activation energy
would be approximately half its 'true' value. However, an estimate of the modulus $\phi$ in our case yields 1.03 and an effectiveness factor of 0.95 which indicates the absence of pore diffusion, although there is always the possibility of being in a region of complex effectiveness factors. The fact that the activation energies did not show any further decrease contradicted this possibility.

A third possible cause for the change in activation energy, is the presence of surface diffusion as an influential factor. Although it has been said (205) that surface diffusion may be unimportant in catalysis at elevated temperatures, nevertheless, there is little evidence one way or the other. The importance of surface diffusion in our case would be given by the magnitude of the finite rate of diffusion of an adsorbed benzene molecule to an active site. Since little is known about this process, the influence of surface diffusion remains a possible cause of the change in activation energies.

An extra possible cause for the apparent change in activation energies would be the incorrect assumption of first order kinetics and the existence of reaction inhibition by MAA. If MAA and benzene are combusted on similar active sites, an increased concentration of MAA would reduce the rate of benzene combustion as a result of more MAA molecules competing for active sites on the catalyst. This possibility was pointed out earlier when the results of benzene combustion in a SCBR and a tubular reactor were compared and may indeed be likely.

It is interesting to mention that a reversible decrease in the activation energy at high temperatures for the benzene oxidation reaction was observed by Vaydianathan and Dorayswami (48). In this case the
possible existence of physical rate controlling steps i.e., external mass transfer and pore diffusion control, was examined to explain a drop in activation energy from 23 Kcal/mole to about 2.0 Kcal/mole but it was concluded, after analysis of the physical processes, that these were not responsible and that the reaction was chemically controlled over the entire range of temperatures, the change in activation energy being probably induced by a reversible change in catalyst structure.

Similar changes in activation energy have also been reported for other hydrocarbon oxidations. Abo et. al. (206) reported a low activation energy for the o-xylene disappearance rate, albeit a dependency on the particle diameter was shown. Although no clear explanation was offered for this phenomenon, mass transfer did not appear to be cause of the observations.

Similarly, Pinchbeck (49) observed a decrease in the activation energy of the controlling rate process when studying the naphthalene oxidation. However, in this case possible intraphase and interphase diffusion effects were not completely ruled out.

The resemblance of our observations are not without connection with the above studies since in all cases, including our own, V₂O₅ based catalysts were used.

The difference in temperature at which the change in activation energy occurred in our case for the two different sets of catalyst pellets (black and green) could have been induced during the activation stage, since this was carried out in separate batches and different reactors (one and two inch diameter).
Incorporation of the appropriate kinetic parameters from table 7.2.1 into the reactor model allowed a good fit of the axial temperature profiles in the one and two inch diameter reactors; see Figs (7.5) to (7.23).

These figures show that the certainty in the determination of the overall heat transfer coefficients is about ± 5%. However, the predicted temperature profile is also dependent on the accuracy of the kinetic parameters whose values could be varied by 10% while maintaining a reasonable prediction.

The fitting of the axial bed temperature profiles alone is not sufficient to determine the accuracy of the reactor model. In addition, once an overall heat transfer coefficient which fitted the temperature profiles had been found, prediction of the concentration profiles in the reactor was carried out to assess the accuracy of the model. The accuracy of the concentration profiles along the bed cannot readily be evaluated but is expected to be within the limits found for the overall heat transfer coefficient (± 5%).

Clearly, the use of a one-dimensional model implies a certain degree of inaccuracy in the prediction of the concentration profiles due to the fact that it utilises radial average values of the bed temperature. However, although no sampling was made at various points along the catalytic bed, as this facility was not incorporated in the reactor, the prediction of the outlet reactor concentration of benzene and MAA at a variety of flowrates approached the experimentally measured values. Tables 7.2.2 and 7.2.3 show the experimental and predicted values of the outlet concentrations as well as the experimental and predicted selectivities.
### One Inch Diameter Reactor

<table>
<thead>
<tr>
<th>Run</th>
<th>G</th>
<th>B_{in}</th>
<th>B_{out}</th>
<th>B_{out} *</th>
<th>MAA_{out}</th>
<th>MAA_{out} *</th>
<th>Select.</th>
<th>Select. *</th>
<th>U</th>
<th>Tw</th>
<th>T_{in}</th>
<th>X_B</th>
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<td>0.4297</td>
<td>0.383</td>
<td>0.3759</td>
<td>60.6</td>
<td>60.6</td>
<td>100</td>
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<td>470</td>
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<td>0.360</td>
<td>0.3660</td>
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* Predicted value, $G = \text{Kg/hr-m}^2$, $B = \text{mole }\%$, $\text{MAA} = \text{mole }\%$, $U = \text{Kcal/hr m}^2 \degree C$, $T = \degree C$

Table 7.2.2.
## Two inch Diameter Reactor

<table>
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<tr>
<th>Run</th>
<th>G</th>
<th>B&lt;sub&gt;in&lt;/sub&gt;</th>
<th>B&lt;sub&gt;out&lt;/sub&gt;</th>
<th>MAA&lt;sub&gt;out&lt;/sub&gt;</th>
<th>Select.</th>
<th>U</th>
<th>T&lt;sub&gt;in&lt;/sub&gt;</th>
<th>X&lt;sub&gt;B&lt;/sub&gt;</th>
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<td>1</td>
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<td>0.535</td>
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</tbody>
</table>

* Predicted value, G = Kg/hr-m<sup>2</sup>, B = mole %, MAA = mole %, U = Kcal/hr-m<sup>2</sup>-°C, T = °C

Table 7.2.3
FIGURE 7.5. - One Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

*U (Estimated from Literature Correlations)
FIGURE 7.6 - One Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.
FIGURE 7.7 - One Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

*U (Estimated from Literature Correlations)
FIGURE 7-8 - One Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

- Experimental Profile

(1) Best Fit, \( U = 130 \)
(2) \( U^* = 99 \)
FIGURE 7.9 - One Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

(1) Best Fit, \( U = 105 \)

(2) \( U^* = 85 \)
RUN 9

Figure 7.10 - One Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

1. Best Fit, \( U = 95 \)
2. \( U = 75 \)

\( U^* \) (Estimated from Literature Correlations)
FIGURE 7.11 - One Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles. $U^*$ (Estimated from Literature Correlations)
FIGURE 7.12 - One Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.
FIGURE 7.13 - One Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

- Experimental Profile

1. Best Fit, $U = 100$
2. $U = 83$

$U^*$ (Estimated from Literature Correlations)
FIGURE 7.14 - One Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles. $U^*$ (Estimated from Literature Correlations)

RUN 13

- Experimental Profile
- (1) Best Fit, $U = 90$

RUN 14

- Experimental Profile
- (1) Best Fit, $U = 100$
- (2) $U = 68$
RUN 1

FIGURE 7.15 - Two Inch Diameter Reactor, Experimental and Axial Temperature Profiles.

U (Estimated from Literature Correlations)
FIGURE 7.16 - Two Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

U* (Estimated from Literature Correlations)
FIGURE 7.17 - Two Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

$U^*$ (Estimated from Literature Correlations)
FIGURE 7.18 - Two Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.
U° (Estimated from Literature Correlations)
FIGURE 7.19 - Two Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

Experimental
(1) Best Fit, \( u = 40 \)
(2) \( u' = 65 \)
FIGURE 7.20 - Two Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

U* (Estimated from Literature Correlations)
Figure 7.21 - Two Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

(1) Best Fit, $U = 35$
(2) $U = 48$

Estimated from Literature Correlations
FIGURE 7.22. - Two Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles.

U* (Estimated from Literature Correlations)
RUN 9

NOTE: During This Run, the Catalyst Deactivated and Therefore is not Strictly Correct to Model It with a Steady State Model.

FIGURE 7.23 - Two Inch Diameter Reactor, Experimental and Best Fit Axial Temperature Profiles. U* (Estimated from Literature Correlations)

(1) Best Fit, U= 43
(2) U* = 49
A comparison of the predicted temperature profiles and outlet concentrations shows that the proposed one-dimensional model predicts the behaviour of the one inch diameter reactor with a fair amount of accuracy which is not lost when the model is used to predict the behaviour of a two inch diameter reactor, provided the overall heat transfer coefficients are also determined for this latter reactor.

Clearly, the fact that the reaction became less temperature dependent at the higher temperatures together with the involuntary dilution of the two inch diameter reactor catalytic bed, made the reactor more stable and therefore more suitable for one-dimensional modelling. According to the model, this would have been different had the catalyst kept its high activity and temperature dependency and, indeed, the model predicts in this case 'run away' at some of the conditions used experimentally.

Having dealt with the prediction of concentration and temperature profiles, we now move on to compare the overall heat transfer coefficients which fitted the experimental temperature and concentration profiles with those predicted by the available semi-empirical correlations reported in the literature.

In order to estimate the overall heat transfer coefficient \((U)\), two possibilities are open. One is to compare our data with correlations such as the one by Leva (191) which yield overall heat transfer coefficients. A comparison of this type would not be very useful since this type of correlation is empirical and any agreement might be considered fortuitous. A second and more appropriate procedure is to build up the overall heat transfer coefficient from its contributing parts i.e., the effective radial conductivity \((k_{e_{lr}})\) and the wall heat transfer coefficient \((h_w)\)
To this end, use was made of the correlation derived by Froment (197) to which the contribution of the outside wall heat transfer coefficient \( (h_o) \), as estimated previously by Caldwell (148) for our rig, was added.

\[
\frac{1}{U} = \frac{1}{h_w} + \frac{R_c}{4 \cdot k_{e_{hr}}} + \frac{1}{h_o}
\]

Selection of a correlation for the estimation of the bed effective thermal conductivity requires more careful consideration since there are a large number of somewhat conflicting correlations and the choice is bound to affect the results.

The recently widely adopted correlation proposed by Yagi and Kunii (207) was chosen since this accounts for the various mechanisms contributing to the radial flux of heat.

\[
\frac{k_{e_{hr}}}{k_f} = \frac{\circ}{k_f} + \frac{Re}{Pr} \cdot \frac{C}{C}
\]

Agnew and Potter (208) made a detailed analysis of this correlation and found that the value of the constant \( C \) was dependent on the particle to tube diameter ratio, its value decreasing with the aspect ratio. Thus, from Agnew and Potter (208) the value of \( C \) is 6 and 8 for the one and two inch diameter reactors respectively.

The evaluation of \( k_e \), the stagnant contribution to the effective thermal conductivity, was made using the correlation proposed by Kunii and Smith (179)

\[
\frac{\circ}{k_f} = \frac{\beta}{\phi} \cdot \frac{(1-\epsilon)}{\phi + \alpha \frac{k_f}{k_s}}
\]
In order to estimate radiation effects, the simplified formula proposed by Damkoehler (209) was used.

\[ k_r = \varepsilon \left( \frac{4}{2\pi} \right) D_p (0.173) \frac{T_a^3}{100^4} \]

Although this formula does not take into account temperature gradients, it has been found (177) that the temperature level is more important in establishing \( k_r \) than the temperature gradient. In any case, the estimation of the solid emissivity is very uncertain; therefore no refined approach in this direction is justified. The radiation contribution at 450\(^\circ\)C incorporated into the stagnant component of the effective thermal conductivity contributed only about 10% to the net value and gave only a marginal increase of 2% in the predicted value of the overall heat transfer coefficient.

The choice of a correlation for the estimation of the heat transfer coefficient at the wall presented greater problems.

Since most of the correlations are based on the Higbie concept (188) of a systematic rate of fluid renewal at the wall, they give the wall heat transfer coefficient as a function of only Reynolds and Prandtl numbers, i.e.,

\[ h_w = F \cdot Re^n \cdot Pr^m \]

This would seem appropriate for the case of mass transfer but not for heat transfer since this would mean that at zero Reynolds numbers \( h_w \) becomes zero and therefore the resistance at the wall becomes infinite.

Clearly, this causes some error at the low Reynolds numbers, at which this work was carried out. Yagi and Kunii (210) used a different approach to arrive at a correlation for the heat transfer coefficient at the wall. They considered a mechanism of heat transfer at the wall which
included the following contributions:

1)- Heat transfer through solid phases i.e., contact points pellet wall.

2)- Radiant heat from pellet to wall.

3)- Heat transfer in void spaces independent of fluid flow i.e., molecular thermal conduction, radiant heat transfer void to void.

4)- Heat transfer in void spaces dependent on fluid flow i.e., heat transfer caused by the lateral mixing of the flowing fluid and heat transfer through the true boundary film.

Separation of the flow independent from flow dependent contributions allows the correlation to take the form:

\[
\frac{h_w D_p}{k_f} = \frac{h_w D_p}{k_f} + \epsilon \frac{Re}{Pr} \]

This new contribution \(h_w\) which could be called the 'stagnant component' accounts for the fact that at zero Reynolds numbers there is still some transfer of heat at the wall.

Although there is a lack of experimental measurements of \(h_w\) at Reynolds numbers below 100, some idea of the value of \(h_w\) can be obtained by extrapolating the data above \(Re = 100\) in order to obtain the intercept at the axis \(\frac{h_w D_p}{k_f}\).

Yagi and Kunii were able to reproduce Coberly and Marshall's data (162) by an equation of the above form leading to:

\[
Nu = \frac{h_w D_p}{k_f} = 20 + 0.069 Re Pr
\]

A correlation of the former type which was of interest to us was that of Calderbank and Pogorski (185).

\[
\frac{h_w D_p}{k_f} = 3.6 \frac{D_p G}{\mu \epsilon} 0.365
\]
This correlation was obtained using solids (alumina pellets) which had similar thermal properties to those of our catalyst pellets. In addition, this correlation showed a low dependency of $h_w$ on the Reynolds number, a feature exhibited by the overall heat transfer coefficients extracted from our modelling exercise. Thus, using a similar procedure as Yagi and Kunii, we obtained an approximation of Calderbank and Pogorski's correlation for low Reynolds numbers.

$$\text{Nu} = \frac{h_w D_p}{k_f} = 15 + 0.1145 \text{Re Pr}$$

Thus, the estimation of overall heat transfer coefficients was carried out as follows.

The effective thermal conductivities were estimated using Yagi and Kunii's correlation (297) in which the value of the constant $C$ was evaluated from Agnew and Potter's work (208). Radiation effects were ignored after evaluating the magnitude of their contribution to the overall heat transfer coefficient (2%). The wall heat transfer coefficient was estimated using Calderbank and Pogorski's correlation (185) approximated as explained above for the low Reynolds numbers. The outside wall heat transfer coefficient estimated by Caldwell (148) for our rig was also incorporated (250 Kcal/hr. m$^2$ °C).

Finally, Froment's correlation (197) was used to integrate all the above contributions into an overall heat transfer coefficient for the one dimensional reactor model used.

$$\frac{1}{U} = \frac{1}{h_w} + \frac{\text{Ro}}{4 \ k_e \ h_r} + \frac{1}{h_o}$$
Figure (7.24) shows plots of the heat transfer coefficients extracted from our experimental temperature profiles for the one and two inch diameter reactors compared with those predicted by the above mentioned correlations. Table 7.2.4 shows the various contributions to the predicted values of the overall heat transfer coefficient at various Reynolds numbers.

Inspection of Figure (7.24) reveals two main effects. The first is that the overall heat transfer coefficients extracted from the experimental temperature profiles are higher than expected in the one inch diameter reactor at the low Reynolds numbers, and those of the two inch diameter reactor are lower at the high Reynolds numbers.

A second important fact is the remarkably low dependency on Reynolds numbers exhibited by our overall heat transfer coefficients, especially in the case of the two inch diameter reactor. Let us then examine the possible causes for the above results. The fact that our heat transfer coefficients were insensitive to Reynolds numbers may be due to various possible causes.

If the main resistance to heat transfer is at the outside wall of the reactor, the overall heat transfer coefficient will be independent of the flow conditions inside the reactor. However, the estimated value of the outside wall heat transfer coefficient, 250 Kcal/hr. m² °C (148), suggests that this is not the case and therefore this possibility is dismissed.

A second possibility is that the flow independent contributions (stagnant) of the overall effective thermal conductivity are not accurately estimated by the available correlations. This could be due to the fact
OVERALL HEAT TRANSFER COEFFICIENTS

- BEST FIT (One inch dia. Reactor)

--- PREDICTED (One inch dia. Reactor)

- BEST FIT (Two inch dia. Reactor)

--- PREDICTED (Two inch dia. Reactor)

FIGURE 7.24 - Predicted and 'Best Fit' Overall Heat Transfer Coefficients for the One and Two inch Diameter Reactors.
<table>
<thead>
<tr>
<th>$G \times 10^{-3}$</th>
<th>$Re$</th>
<th>$Nu$</th>
<th>$h_w$</th>
<th>$1/h_w$</th>
<th>$1/h_o$</th>
<th>$\frac{0.025 h}{8 ke_1}$</th>
<th>$U_1 \times 10^{-3}$</th>
<th>$\frac{0.0508}{8 ke_2}$</th>
<th>$U_2 \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>37.49</td>
<td>18</td>
<td>183</td>
<td>0.00548</td>
<td>0.004</td>
<td>0.00795</td>
<td>57.5</td>
<td>0.0177</td>
<td>36.8</td>
</tr>
<tr>
<td>3000</td>
<td>112.0</td>
<td>23.95</td>
<td>242</td>
<td>0.00425</td>
<td>0.004</td>
<td>0.0044</td>
<td>80.0</td>
<td>0.0093</td>
<td>57.27</td>
</tr>
<tr>
<td>5500</td>
<td>206.0</td>
<td>31.50</td>
<td>320</td>
<td>0.00313</td>
<td>0.004</td>
<td>0.0025</td>
<td>104.0</td>
<td>0.00586</td>
<td>72.00</td>
</tr>
</tbody>
</table>

$h_w$; From Calderbank & Pogorski (185)

$ke$; From Agnew & Potter (208)

$ke$; From Yagi & Kunii (207)

$h_o$; From Caldwell (148)

Table 7.2.4.
that most of the experimental determinations of effective thermal conductivities have been made at the low temperatures (about 200° C) and at these conditions, the stagnant contributions which depend more on the temperature gradient and level of temperature (radiation) become underestimated. However, if this were the case, both the one inch and two inch diameter reactors would show similar trends. Since the discrepancy at the low Reynolds numbers is mainly encountered in the one inch diameter reactor, errors in the stagnant contributions cannot be wholly responsible for the observations.

Inspection of Table 7.2.4 reveals that it is likely that the internal bed resistance rather than that at the wall controls the transfer of heat. This appears to be the case for the two inch diameter reactor at all Reynolds numbers studied here and with a significant influence in the one inch diameter reactor. This would contribute to the constancy of the overall heat transfer coefficients needed to fit the experimental temperature profiles since the bed resistance is only weakly dependent on the Reynolds number.

Another factor which would contribute towards the constancy of the 'best-fit' overall heat transfer coefficients with Reynolds numbers arises from the possible existence of activity profiles in the catalytic bed.

Since the above heat transfer coefficients were the result of a fitting scheme, the presence of higher catalyst activity than assumed would call for lower 'best-fit' heat transfer coefficients in order to approximate the experimental temperature profiles and conversely, lower catalyst activity than assumed would call for higher transfer coefficients in the model. Thus, the presence of activity profiles in the bed, which are only approximated by the assumption made of a catalyst bed with homogeneous activity all along the reactor, would affect the values of the 'best-fit' heat transfer coefficients obtained.
These catalyst activity profiles would appear as a result of the catalyst 'self-adjusting' mechanism mentioned earlier. If axial activity profiles are developed in the bed, radial activity profiles must also be considered a possibility at least in the larger diameter reactors. This radial activity profiles would result in a tendency of the bed to operate as assumed in a one-dimensional model.

Finally, the possibility of experimental temperature measurements affected by the bulky thermocouples used cannot be discounted since accurate measurement of temperature profiles in reactors of small diameter (1.0 inch) would require finer thermocouples.

It is important to note that despite the fact that the bed resistance, as estimated from available correlations, seems to control the transfer of heat in the two inch diameter reactor and to be influential in the one inch diameter reactor, the one-dimensional model used to describe the reactor behaviour yielded satisfactory results and was able to predict closely the outlet concentrations of benzene and maleic anhydride.

This is important since it would imply that the use of a two dimensional model would only be called for when the bed resistance to heat transfer is large enough to produce significant temperature profiles across the bed when working at temperatures below the deactivation point of the catalyst.

Finally, since a change in scale was made during this work, it is interesting to analyse the results in terms of the similarity principle.

In the analysis of scale models of reactors, the rules for changing the scale without changing the course of the reaction were derived by
Damköhler (211) using dimensional analysis. In fact, a better criterion that can be applied to the case of catalytic tubular reactors, is the analysis of the coefficients present in the differential equations and boundary conditions describing the reactor behavior. Non-isothermal catalytic tubular reactors are complex and in some cases no analysis can be made. For example, if the reactions taking place are greatly affected by the pressure drop in the reactor or the temperature difference between solid and fluid, no useful model can be derived. On the other hand, if radial variations can be ignored, simpler and more useful models can be constructed. Thus, if we assume that the bed resistance is controlling the transfer of heat, the flux of heat as calculated from the overall heat transfer coefficient must be proportional to the flux of heat as calculated from all the contributions to the effective thermal conductivity of the bed and their ratio should be approximately constant for the one and the two inch diameter reactors.

In order to introduce the radius of the tube and the Peclet number a dimensionless group A defined as,

\[ A = \frac{R U \text{Pe}_{hr}}{C_p G D_p} \]

appears useful. A group like this in which \( h_w \) appears instead of \( U \) is obtained from the boundary condition of the reactor and is used when the analysis of change of scale requires the inclusion of the wall heat transfer coefficient \( (h_w) \).

Fig. (7.25) shows a plot of predicted Peclet numbers for the one and two inch diameter reactors. Thus, for \( G = 3000 \) from Fig. (7.25)

\[ \text{Pe}_{hr_1} = 4.7 \quad \text{and} \quad \text{Pe}_{hr_2} = 5.35 \]
FIGURE 7.25.- Estimated Peclet Numbers for the One and Two inch Diameter Reactors as a Function of Mass Velocity.
From Fig. (7.24); $U_1 = 100$, $U_2 = 40$ and considering that $C_p$ is approximately equal in both reactors, the ratio $A_1/A_2$ becomes

$$\frac{A_1}{A_2} = \frac{R_1 U_1 Pe_{hr}}{R_2 U_2 Pe_{hr}}$$

$$= \frac{(0.0254/2) (100) (4.7)}{(0.0508/2) (40) (5.35)} = 1.1$$

Although the above approximation is not exact since the one inch diameter reactor was apparently not fully controlled by the bed resistance, it nevertheless adds some weight to our earlier indications that the experimental overall heat transfer coefficients were strongly dependent on the bed radius and internal effective thermal conductivity.
Chapter 8

Conclusions and Suggestions for Further Work
8). **Conclusions and Suggestions for Further Work**

As a result of the study of the catalytic oxidation of benzene to maleic anhydride, the following main conclusions were reached.

Analysis of the effects of free space after the catalyst bed, catalyst dilution and packing after the bed, did not show evidence of the existence of important heterogeneous - homogeneous steps in the formation of maleic anhydride or in the total combustion of benzene. However, the methods used here were only capable of detecting effects whose magnitude would be of importance in the performance of a large reactor. Thus, the possibility of heterogeneous - homogeneous steps occurring in the vicinity of the catalyst pellet cannot be dismissed.

Experiments to detect a possible homogeneous chain oxidation of MAA initiated on the catalyst surface or on the walls of the reactor showed that MAA is mainly oxidised heterogeneously.

It was also found during the above experiments that MAA combusts readily, at reaction temperatures above 400°C, on almost any surface, the catalyst itself being one of the most inert materials in this respect. This was clearly evidenced by the fall in selectivity to MAA when extra packing was introduced in or after the catalyst bed.

Despite the fact that MAA appeared to combust rapidly on almost any surface with the exception of the vanadium catalyst, it remains obscure as to why active metal tubular reactors when packed with the catalyst show very little activity under these circumstances when the overall reaction is taking place and high selectivity levels (60%) are maintained to almost complete conversion of the reactant (benzene). This was evidenced by the fact that reactors of different materials of construction i.e., aluminium,
titanium and stainless steel yielded similar selectivities to MAA when packed with equal amounts of the same catalyst.

Study of the kinetics of the overall reaction showed that this can be adequately described, for the purposes of modelling the reactor, by a triangular scheme of three pseudo first order heterogeneous reactions.

\[ \begin{align*}
  &k_1 \\
  &\text{Benzene} \rightarrow MAA \rightarrow C. \text{ oxides} \\
  &k_2 \\
  &k_3
\end{align*} \]

However, there is some doubt concerning the exact nature of the MAA combustion reaction since this proved difficult to analyse due to the interference of overoxidation on the metallic walls of the reactors.

Comparison between the rates of benzene combustion in a SCBR and in a tubular reactor, both fabricated in aluminium, showed slower rates at high temperatures in the SCBR suggesting a possible inhibiting effect of MAA on the overall reaction, this effect being more apparent at backmix conditions and less important under the plug flow mode of operation. This retarding effect of MAA on the benzene combustion rate suggests the possibility that both, benzene and MAA, combust at similar active sites, the retarding effect being caused by a competition for active sites between molecules of MAA and benzene.

It was found that the selectivity at zero conversion varied slightly from one catalyst formulation to another but in general it was maintained at a level of about 70%. This selectivity, for a given catalyst, was independent of temperature indicating that routes 1 and 3 in the above reaction scheme have the same activation energy (about 23 Kcal/mole).
This value of the activation energy suggested that the rate of benzene combustion is chemically controlled. On the other hand, a value of 8.6 Kcal/mole found for the MAA combustion reaction using a glass tubular reactor to avoid wall effects suggested that this reaction is not wholly chemically controlled. External mass transfer and pore diffusion being unlikely causes of this observation, the existence of surface diffusion is left as a possible cause.

From the practical point of view, the difference in activation energies between the benzene oxidation routes 1 and 2 and the MAA combustion route 2 indicates no penalty in working at high temperatures under the plug flow mode, the only limitation being the temperature at which the catalyst suffers a decrease in activity. This temperature is believed to be above 550°C.

The above kinetic measurements which were carried out under isothermal conditions on the laboratory scale were applied to observations obtained with large non-isothermal reactors to arrive at a satisfactory model for large reactors. The model found adequate to describe non-isothermal reactor behaviour was of a one-dimensional type.

As a result of the modelling of one and two inch diameter reactors, which consisted in fitting overall heat transfer coefficients to reproduce the experimental axial temperature profiles, several important facts came to light.

It was first shown that extrapolation of the kinetic data obtained in the laboratory with fresh catalyst could not reproduce the performance of the large scale non-isothermal reactors. Variation of the heat transfer parameters over a wide range did not improve the fitting of
the experimental temperature profiles suggesting that the error was in the kinetic parameters used. Visual inspection of the catalyst pellets, part of which had been used in both reactors, revealed a change in colour, part having become black while the rest had remained green.

Further re-determination of the kinetics for each separate colour of catalyst pellets over a wider range of temperature than the one used in the experiments at isothermal conditions revealed two main factors.

Firstly, as suspected, the black catalyst pellets had partially deactivated and secondly, there was a fall in the activation energy of the reaction from 23 Kcal/mole to about 15 Kcal/mole at about 425-450°C.

It is important to note that although the catalyst partially deactivated, this did not change the selectivity of the overall reaction. Moreover this deactivation had a beneficial effect which constrained the reactor to operate under stable conditions which otherwise resulted in 'run-away'. The deactivation of the catalyst was believed to occur as a result of high temperatures reached in the catalyst bed.

This valuable catalyst 'self-adjusting' activity may be characteristic not only of our particular catalyst but of many other catalysts which promote exothermic reactions. Thus, the modelling of large scale non-isothermal reactors using kinetic parameters obtained with fresh catalyst under isothermal conditions would be an illusory theoretical exercise which would result in severe malprediction of the performance of the actual reactor.

Although it is difficult to point out the exact nature of the process leading to this catalyst 'self-adjusting' activity, the fact that the reaction selectivity was maintained at its original level suggests that
some of the active surface area of the catalyst was lost during this process. This loss of active area can occur in several ways, for example, at the high temperatures, some non-volatile minor products possibly of a polymeric nature may poison the catalyst. Another possibility is that some of the active components diffuse away from the catalyst surface, although in our case with well impregnated catalyst pellets and an almost non-porous catalyst, this seems unlikely. Catalyst self-poisoning can also occur in the case of mixed catalysts when as a result of high temperatures one of the less active components melts and covers part of the surface. However the two possibilities which seem more likely in our case are an irreversible change in the catalyst oxidation state which seems favoured by the observed change of colour between active and deactivated catalyst pellets or the occurrence of catalyst sintering leading to a loss in exposed area.

Although the extent of catalyst deactivation probably depends on the prehistory of the catalyst, this cannot be assessed from the experimental evidence at hand. During the experiments at isothermal conditions up to temperatures of $550\,^\circ C$, no catalyst deactivation was detected. However the behaviour of the non-isothermal reactor indicates that deactivation takes place in the neighbourhood of $600\,^\circ C$.

It is possible that the catalyst deactivates only as long as it is subjected to temperatures above the deactivation point and therefore, under a fixed set of operating conditions, a fall in catalyst activity at some point in the reactor bed may be brought about. This should be an interesting avenue for further work.
As regards the change in activation energy observed at high temperatures during the re-determination of the kinetics, it is suggested that a cause may be the finite rate of surface diffusion of adsorbed benzene molecules since it was found that external mass transfer and pore diffusion influences were not likely to control the rate of reaction under the conditions of the experiments. Another possible cause for the observations would be the incorrect assumption of first order kinetics and the existence of reaction inhibition by MAA since some slight evidence for the latter was found.

Use of the re-determined kinetics in the reactor model allowed a reasonably good fit of the experimental temperature profiles in the one and two diameter reactors. However, inspection of the 'best-fit' overall heat transfer coefficients found during the modelling exercise revealed a remarkably low dependency on Reynolds numbers within the range studied here. Two possible explanations offered themselves.

The first was that the internal bed resistance rather than that at the wall controls the transfer of heat. This assumption was supported by the fact that the values of the overall heat transfer coefficients from the one and the two inch diameter reactors were in a similar ratio to that of the theoretical bed resistances.

The second factor contributing to the constancy of the 'best-fit' overall heat transfer coefficients with Reynolds numbers arises from the possible existence of catalyst bed activity profiles. Thus, the above observations could be a result of the fitting method used to obtain the heat transfer coefficients, since higher catalyst activity than assumed in the bed would call for lower best-fit heat transfer coefficients in order to approximate the temperature profiles, and conversely, lower catalyst activity than assumed would call for higher heat transfer coefficients in the model.
Since the catalyst is expected to have a lower activity at the inlet side of the bed and higher at the end, those runs performed at high flowrates, in which the end part of the bed has higher catalyst activity than assumed and is being used to a greater extent, will require a lower heat transfer coefficient in the model to fit the experimental rise in bed temperature. Some experimental evidence of this behaviour was found in the two inch diameter reactor where for the runs at high flowrates the temperature rise in the earlier part of the bed was reasonably well predicted using published heat transfer coefficients and kinetics which apply to the mixed catalyst bed, whereas the temperature prediction was on the low side for the end part of the bed. The corresponding effect of a lower than predicted experimental temperature rise in the earlier part of the bed was not clearly detected. This may be due to the fact that the kinetics, as determined after the experiments in the two inch diameter reactor which contained the active and partially deactivated pellets, assumed a randomly distributed mixture of active and less active pellets in the bed and therefore would only approximately represent the average activity present in the bed.

Since the activity of active and less active pellets was determined in a random sample of only 100 pellets of each type, it is possible that the average activity assigned to the bed was approximately only. Also, it should be recognized that the temperature profiles in the earlier part of the bed are very abrupt and differences difficult to define with certainty.

Clearly, if there is a possibility that axial catalyst activity profiles are developed, one must also consider the existence of radial activity profiles which would result in a tendency of the bed to operate as is assumed in a one-dimensional model.
It would be interesting to see if, by using a more sophisticated curve fitting technique, one could predict both, the kinetic and heat transfer parameters from the experimental temperature and concentration profiles, given the form of the rate equation, so as to determine the catalyst activity as it varies along the reactor length.

The fact that several levels of exothermicity (bed excess temperature from 20°C to close to 100°C) were covered by the experiments indicates that the overall heat transfer coefficients found are not particular to the reaction studied and it is expected that the model, with similar heat transfer parameters, would also apply to other reactions, with other kinetics operating within these exothermicity levels.

Finally, a comparison between the model predictions using the 'best-fit' and the heat transfer coefficients obtained from available literature correlations does not produce a large difference in the outlet concentrations (± 5%) and temperature rises (± 20°C) and in this connection it must be pointed out that the accuracy and agreement between the different correlations to estimate heat transfer parameters is not high. Also some discrepancy must be due to the bulky thermocouples used for the measurements and it is suggested that finer thermocouples be used in further work of this type.
Appendices
Appendix A

A.1) Chemicals and Catalyst Support

The chemicals used to carry out the experimental runs, i.e. benzene, maleic anhydride and o-xylene, as well as the ones used in the preparation of the catalysts were as follows:

<table>
<thead>
<tr>
<th>Chemical Purity (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene 95.0</td>
<td>BDH</td>
</tr>
<tr>
<td>Maleic Anhydride 99.5</td>
<td>BDH</td>
</tr>
<tr>
<td>O-xylene 95.0</td>
<td>BDH</td>
</tr>
<tr>
<td>Vanadium Pentoxide 98.5</td>
<td>BDH</td>
</tr>
<tr>
<td>Molibdenum Trioxide 99.5</td>
<td>BDH</td>
</tr>
<tr>
<td>Phosphorous Pentoxide 98.0</td>
<td>BDH</td>
</tr>
<tr>
<td>Lithium Acetate 98.0</td>
<td>BDH</td>
</tr>
<tr>
<td>Nickel Acetate 98.0</td>
<td>BDH</td>
</tr>
<tr>
<td>Silver Carbonate 98.0</td>
<td>BDH</td>
</tr>
<tr>
<td>Hydrochloric Acid 35-38% w/w.</td>
<td>BDH</td>
</tr>
</tbody>
</table>

The carrier used in the preparation of the catalyst was a low surface area (less than 1 m²/gm.) Sä-201 3/16 inch diameter alundum spheres supplied by Norton Carriers Ltd. with the following properties:

Chemical Composition:

\[
\begin{align*}
\text{Al}_2\text{O}_3 & \quad 90.4\% \\
\text{SiO}_2 & \quad 8.16\% \\
\text{Fe}_2\text{O}_3 & \quad 0.26\% \\
\text{TiO}_2 & \quad 0.28\% \\
\text{CaO} & \quad 0.04\% \\
\text{MgO} & \quad 0.07\% \\
\text{Na}_2\text{O} & \quad 0.33\% \\
\text{K}_2\text{O} & \quad 0.09\% \\
\text{ZrO}_2 + \text{H}_2\text{O}_2 & \quad 0.05\%
\end{align*}
\]
Physical Properties:

- Apparent porosity: 39 - 45%
- H₂O adsorption: 18 - 24%
- Bulk density (gm/cc): 2.0 - 2.3
- Packing density (lb/ft³): 75 - 80
- Apparent specific gravity: 3.5 - 3.7
- Pore diameter range: 3 - 30 microns (90%)

A.2) Rotameter Capacities

<table>
<thead>
<tr>
<th>Stream</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0 - 70 ml/min</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0 - 115 ml/min</td>
</tr>
<tr>
<td>Dilution Air to Benzene</td>
<td>0 - 8.0 l/min</td>
</tr>
<tr>
<td>Maleic Anhydride</td>
<td>0 - 2.5 l/min</td>
</tr>
<tr>
<td>Dilution Air to MAA</td>
<td>0 - 2.5 l/min</td>
</tr>
</tbody>
</table>
Appendix B

Experimental Results from Chapter 3
### Tests to Detect the Existence of an Heterogeneous - Homogeneous Component in the Reaction.

**Undiluted Catalyst, 'O' Free space After the Bed**

$\frac{3}{8}$ inch. Diameter Aluminium Reactor, Flowrate = 1.0 l/min, $W = 14.4782$ g.cat. Bin = 0.9506 mole %.

| Temp. ($^\circ$C) | B.out | $X_B$ | (MAA)$_0$ (mole %) | $CO_2$ (mole %) | $CO^*$ (mole %) | Selectivity | C. Balance (%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>410</td>
<td>0.8455</td>
<td>0.1545</td>
<td>0.0552</td>
<td>0.22</td>
<td>-</td>
<td>0.3759</td>
<td>96.67</td>
</tr>
<tr>
<td>430</td>
<td>0.7650</td>
<td>0.2350</td>
<td>0.0846</td>
<td>0.36</td>
<td>-</td>
<td>0.3788</td>
<td>92.72</td>
</tr>
<tr>
<td>450</td>
<td>0.6537</td>
<td>0.3463</td>
<td>0.1159</td>
<td>0.50</td>
<td>-</td>
<td>0.3520</td>
<td>85.65</td>
</tr>
<tr>
<td>470</td>
<td>0.5517</td>
<td>0.4484</td>
<td>0.1415</td>
<td>0.70</td>
<td>-</td>
<td>0.3321</td>
<td>80.23</td>
</tr>
<tr>
<td>490</td>
<td>0.4616</td>
<td>0.5384</td>
<td>0.1507</td>
<td>0.85</td>
<td>-</td>
<td>0.2945</td>
<td>74.03</td>
</tr>
<tr>
<td>500</td>
<td>0.4449</td>
<td>0.5551</td>
<td>0.1494</td>
<td>0.90</td>
<td>-</td>
<td>0.2832</td>
<td>73.05</td>
</tr>
</tbody>
</table>

**Undiluted Catalyst, 21.5 inches tube length. Free Space.**, Bin = 0.9779 mole %

| Temp. ($^\circ$C) | B.out | $X_B$ | (MAA)$_0$ (mole %) | $CO_2$ (mole %) | $CO^*$ (mole %) | Selectivity | C. Balance (%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>410</td>
<td>0.8521</td>
<td>0.1479</td>
<td>0.0355</td>
<td>0.25</td>
<td>-</td>
<td>0.2457</td>
<td>93.82</td>
</tr>
<tr>
<td>430</td>
<td>0.7773</td>
<td>0.2227</td>
<td>0.0459</td>
<td>0.42</td>
<td>-</td>
<td>0.2109</td>
<td>89.77</td>
</tr>
<tr>
<td>450</td>
<td>0.6825</td>
<td>0.3175</td>
<td>0.0530</td>
<td>0.62</td>
<td>-</td>
<td>0.1708</td>
<td>83.97</td>
</tr>
<tr>
<td>470</td>
<td>0.5706</td>
<td>0.4294</td>
<td>0.0541</td>
<td>0.85</td>
<td>-</td>
<td>0.1288</td>
<td>76.52</td>
</tr>
<tr>
<td>490</td>
<td>0.4718</td>
<td>0.5282</td>
<td>0.0458</td>
<td>1.20</td>
<td>-</td>
<td>0.0886</td>
<td>71.82</td>
</tr>
<tr>
<td>500</td>
<td>0.4262</td>
<td>0.5738</td>
<td>0.0442</td>
<td>1.20</td>
<td>-</td>
<td>0.0788</td>
<td>67.04</td>
</tr>
</tbody>
</table>

* No CO meter available.
### 1:1 Diluted Catalyst

Flowrate = 1.0 l/min, 2 inches Free Space. \( W = 14.4782 \) g.cat. B.in = 0.945 mole %

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>B.out/B.in</th>
<th>( X_B )</th>
<th>(MAA) (_0) (mole %)</th>
<th>CO(_2) (mole %)</th>
<th>CO(^A) Selectivity ([\text{mols MAA/mols B.converted}])</th>
<th>C. Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>410</td>
<td>0.8205</td>
<td>0.1795</td>
<td>0.0513</td>
<td>0.30</td>
<td>-</td>
<td>0.3025</td>
</tr>
<tr>
<td>430</td>
<td>0.8205 (?)</td>
<td>0.1795 (?)</td>
<td>0.0787</td>
<td>0.42</td>
<td>-</td>
<td>0.4640</td>
</tr>
<tr>
<td>450</td>
<td>0.7114</td>
<td>0.2886</td>
<td>0.0891</td>
<td>0.62</td>
<td>-</td>
<td>0.3267</td>
</tr>
<tr>
<td>470</td>
<td>0.5911</td>
<td>0.4089</td>
<td>0.0900</td>
<td>0.90</td>
<td>-</td>
<td>0.2328</td>
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<tr>
<td>490</td>
<td>0.4488</td>
<td>0.5512</td>
<td>0.0524</td>
<td>1.10</td>
<td>-</td>
<td>0.1000</td>
</tr>
</tbody>
</table>

### 1:1 Diluted Catalyst, 10.5 inches Free Space, B.in = 0.8829

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>B.out/B.in</th>
<th>( X_B )</th>
<th>(MAA) (_0) (mole %)</th>
<th>CO(_2) (mole %)</th>
<th>CO(^A) Selectivity ([\text{mols MAA/mols B.converted}])</th>
<th>C. Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>410</td>
<td>0.8135</td>
<td>0.1866</td>
<td>0.0447</td>
<td>0.28</td>
<td>-</td>
<td>0.2715</td>
</tr>
<tr>
<td>430</td>
<td>0.7454</td>
<td>0.2546</td>
<td>0.0579</td>
<td>0.50</td>
<td>-</td>
<td>0.2577</td>
</tr>
<tr>
<td>450</td>
<td>0.6428</td>
<td>0.3572</td>
<td>0.0646</td>
<td>0.70</td>
<td>-</td>
<td>0.2049</td>
</tr>
<tr>
<td>470</td>
<td>0.5429</td>
<td>0.4571</td>
<td>0.0563</td>
<td>0.90</td>
<td>-</td>
<td>0.1396</td>
</tr>
<tr>
<td>490</td>
<td>0.4357</td>
<td>0.5643</td>
<td>0.0341</td>
<td>1.15</td>
<td>-</td>
<td>0.0685</td>
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</table>
Variable Free Space After the Bed

'O' Free Space After the Bed, Undiluted Catalyst, B.in = 0.8872

<table>
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<th>Temp (°C)</th>
<th>B.out / B.in</th>
<th>X_B</th>
<th>(MAA)_o (mole %)</th>
<th>CO₂ (mole %)</th>
<th>CO_-selection</th>
<th>C.Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>410</td>
<td>0.8626</td>
<td>0.1374</td>
<td>0.0455</td>
<td>0.18</td>
<td>-</td>
<td>0.3733</td>
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<tr>
<td>430</td>
<td>0.8075</td>
<td>0.1925</td>
<td>0.0699</td>
<td>0.26</td>
<td>-</td>
<td>0.4090</td>
</tr>
<tr>
<td>450</td>
<td>0.7231</td>
<td>0.2769</td>
<td>0.0991</td>
<td>0.40</td>
<td>-</td>
<td>0.4035</td>
</tr>
<tr>
<td>470</td>
<td>0.6348</td>
<td>0.3652</td>
<td>0.1233</td>
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<td>-</td>
<td>0.3806</td>
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<tr>
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<td>0.4451</td>
<td>0.1380</td>
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<td>-</td>
<td>0.3495</td>
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5 inches Free Space After the Bed, B.in = 0.93 mole %

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>B.out / B.in</th>
<th>X_B</th>
<th>(MAA)_o (mole %)</th>
<th>CO₂ (mole %)</th>
<th>CO_-selection</th>
<th>C.Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>410</td>
<td>0.8969</td>
<td>0.1031</td>
<td>0.0518</td>
<td>0.17</td>
<td>-</td>
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<tr>
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<td>0.8145</td>
<td>0.1855</td>
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<tr>
<td>450</td>
<td>0.7433</td>
<td>0.2567</td>
<td>0.1011</td>
<td>0.39</td>
<td>-</td>
<td>0.4233</td>
</tr>
<tr>
<td>470</td>
<td>0.6459</td>
<td>0.3541</td>
<td>0.1200</td>
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<td>-</td>
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<tr>
<td>490</td>
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<td>0.4487</td>
<td>0.1226</td>
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<td>-</td>
<td>0.2937</td>
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7 inches Free Space After the Bed, B.in = 0.93 mole %

<table>
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<th>X_B</th>
<th>(MAA)_o (mole %)</th>
<th>CO₂ (mole %)</th>
<th>CO_-selection</th>
<th>C.Balance</th>
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<tbody>
<tr>
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<td>0.0496</td>
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<td>-</td>
<td>0.3477</td>
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<tr>
<td>470</td>
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<td>0.3721</td>
<td>0.1004</td>
<td>0.72</td>
<td>-</td>
<td>0.2900</td>
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<tr>
<td>490</td>
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<td>0.4338</td>
<td>0.0962</td>
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<td>-</td>
<td>0.2385</td>
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</table>

* No CO meter available.
<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>B.out</th>
<th>X_B</th>
<th>(MAA)</th>
<th>CO₂</th>
<th>CO⁺</th>
<th>Selectivity</th>
<th>C.Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.in</td>
<td></td>
<td>(mole %)</td>
<td>(mole %)</td>
<td></td>
<td>mols MAA/mols. B. converted (%)</td>
<td></td>
</tr>
<tr>
<td>410</td>
<td>0.9037</td>
<td>0.0964</td>
<td>0.0435</td>
<td>0.35</td>
<td>-</td>
<td>0.4856</td>
<td>106.55</td>
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<tr>
<td>430</td>
<td>0.8312</td>
<td>0.1688</td>
<td>0.0543</td>
<td>0.55</td>
<td>-</td>
<td>0.3456</td>
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<tr>
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<td>0.4135</td>
<td>0.0544</td>
<td>1.00</td>
<td>-</td>
<td>0.1416</td>
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<tr>
<td>490</td>
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<td>0.4708</td>
<td>0.0314</td>
<td>1.20</td>
<td>-</td>
<td>0.0717</td>
<td>80.66</td>
</tr>
</tbody>
</table>

11.0 inches Free Space After the Bed, B.in = 0.93 mole %

<table>
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<tr>
<th>Temp. (°C)</th>
<th>B.out</th>
<th>X_B</th>
<th>(MAA)</th>
<th>CO₂</th>
<th>CO⁺</th>
<th>Selectivity</th>
<th>C.Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.in</td>
<td></td>
<td>(mole %)</td>
<td>(mole %)</td>
<td></td>
<td>mols MAA/mols. B. converted (%)</td>
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</tr>
<tr>
<td>410</td>
<td>0.8855</td>
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<td>0.0361</td>
<td>0.25</td>
<td>-</td>
<td>0.3476</td>
<td>102.59</td>
</tr>
<tr>
<td>430</td>
<td>0.8234</td>
<td>0.1767</td>
<td>0.0506</td>
<td>0.40</td>
<td>-</td>
<td>0.3081</td>
<td>99.32</td>
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<tr>
<td>450</td>
<td>0.7312</td>
<td>0.2688</td>
<td>0.0581</td>
<td>0.55</td>
<td>-</td>
<td>0.2323</td>
<td>92.63</td>
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<tr>
<td>470</td>
<td>0.6448</td>
<td>0.3552</td>
<td>0.0565</td>
<td>0.75</td>
<td>-</td>
<td>0.1711</td>
<td>86.82</td>
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<tr>
<td>490</td>
<td>0.5561</td>
<td>0.4440</td>
<td>0.0423</td>
<td>1.00</td>
<td>-</td>
<td>0.1024</td>
<td>80.74</td>
</tr>
</tbody>
</table>

18.0 inches Free Space After the Bed, B.in = 0.93 mole %

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<tr>
<th>Temp. (°C)</th>
<th>B.out</th>
<th>X_B</th>
<th>(MAA)</th>
<th>CO₂</th>
<th>CO⁺</th>
<th>Selectivity</th>
<th>C.Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.in</td>
<td></td>
<td>(mole %)</td>
<td>(mole %)</td>
<td></td>
<td>mols MAA/mols. B. converted (%)</td>
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<tr>
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<td>0.0999</td>
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<td>-</td>
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<td>100.90</td>
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<td>0.3796</td>
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<tr>
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<td>0.4862</td>
<td>0.0080</td>
<td>1.60</td>
<td>-</td>
<td>0.0176</td>
<td>84.48</td>
</tr>
</tbody>
</table>

* No CO meter available.
'Inert' packing After the Catalyst Bed. (25 Al₂O₃ spheres), B.in = 0.93 mole %

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>B.out</th>
<th>X_B</th>
<th>(MAA)_o</th>
<th>CO₂</th>
<th>CO</th>
<th>Selectivity</th>
<th>C.Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.in</td>
<td>(mole %)</td>
<td>(mole %)</td>
<td>(mole %)</td>
<td>(mole %)</td>
<td>mols MAA</td>
<td>mols B.converted (%)</td>
</tr>
<tr>
<td>410</td>
<td>0.8946</td>
<td>0.1054</td>
<td>0.0373</td>
<td>0.30</td>
<td>-</td>
<td>0.3802</td>
<td>104.24</td>
</tr>
<tr>
<td>430</td>
<td>0.8129</td>
<td>0.1871</td>
<td>0.0480</td>
<td>0.40</td>
<td>-</td>
<td>0.2760</td>
<td>98.02</td>
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<tr>
<td>450</td>
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<td>0.2873</td>
<td>0.0541</td>
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<td>-</td>
<td>0.2024</td>
<td>90.36</td>
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<tr>
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<td>0.0544</td>
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<td>-</td>
<td>0.1513</td>
<td>85.97</td>
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<tr>
<td>490</td>
<td>0.5077</td>
<td>0.4923</td>
<td>0.0420</td>
<td>1.10</td>
<td>-</td>
<td>0.0916</td>
<td>77.30</td>
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</tbody>
</table>

* No CO meter available.
### Effect of Reactor Materials of Construction

#### Titanium Reactor

Flowrate = 1.0 l/min, $W = 11.7725$ g catalyst, $B_{\text{in}} = \begin{cases} (1) 0.920 \text{ mole} \\ (2) 0.905 \text{ mole} \end{cases}$

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$B_{\text{out}}$</th>
<th>$X_B$</th>
<th>$(\text{MAA})_0$ (mole %)</th>
<th>$\text{CO}_2$ (mole %)</th>
<th>$\text{CO}$ (mole %)</th>
<th>Selectivity ($\frac{\text{mols MAA}}{\text{mols B Converted}}$)</th>
<th>C. Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>(1) 0.8152</td>
<td>0.1848</td>
<td>0.1162</td>
<td>0.41</td>
<td>0.260</td>
<td>0.6800</td>
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<tr>
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<td>(2) 0.8122</td>
<td>0.1879</td>
<td>0.1073</td>
<td>0.35</td>
<td>0.215</td>
<td>0.6309</td>
<td>108.04</td>
</tr>
<tr>
<td>425</td>
<td>(1) 0.6957</td>
<td>0.3044</td>
<td>0.1859</td>
<td>0.66</td>
<td>0.405</td>
<td>0.6600</td>
<td>108.30</td>
</tr>
<tr>
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<td>(2) 0.6851</td>
<td>0.3149</td>
<td>0.1776</td>
<td>0.60</td>
<td>0.380</td>
<td>0.6232</td>
<td>106.88</td>
</tr>
<tr>
<td>450</td>
<td>(1) 0.4348</td>
<td>0.5652</td>
<td>0.2542</td>
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<td>0.600</td>
<td>0.4900</td>
<td>92.85</td>
</tr>
<tr>
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<td>(2) 0.5249</td>
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<td>0.575</td>
<td>0.5759</td>
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<tr>
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<td>0.830</td>
<td>0.4700</td>
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</tr>
<tr>
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<td>0.4480</td>
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<tr>
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<td>0.2857</td>
<td>1.82</td>
<td>1.050</td>
<td>0.3500</td>
<td>84.60</td>
</tr>
<tr>
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<td>(2) 0.1547</td>
<td>0.8453</td>
<td>0.3044</td>
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<td>1.050</td>
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</table>

#### Aluminium Reactor

Flowrate = 1.0 l/min, $W = 11.7725$ g catalyst, $B_{\text{in}} = \begin{cases} (1) 0.92 \text{ mole} \\ (2) 0.93 \text{ mole} \end{cases}$

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$B_{\text{out}}$</th>
<th>$X_B$</th>
<th>$(\text{MAA})_0$ (mole %)</th>
<th>$\text{CO}_2$ (mole %)</th>
<th>$\text{CO}$ (mole %)</th>
<th>Selectivity ($\frac{\text{mols MAA}}{\text{mols B Converted}}$)</th>
<th>C. Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>(1) 0.8370</td>
<td>0.1631</td>
<td>0.0826</td>
<td>0.31</td>
<td>0.175</td>
<td>0.5503</td>
<td>105.74</td>
</tr>
<tr>
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<td>(2) 0.8333</td>
<td>0.1667</td>
<td>0.0809</td>
<td>0.31</td>
<td>0.170</td>
<td>0.5217</td>
<td>104.00</td>
</tr>
<tr>
<td>425</td>
<td>(1) 0.7533</td>
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<td>0.6493</td>
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</tr>
<tr>
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<td>(2) 0.7452</td>
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<td>0.5993</td>
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<td>94.62</td>
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<tr>
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<td>0.2569</td>
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<td>0.700</td>
<td>0.4629</td>
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<td>0.860</td>
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<td>90.50</td>
</tr>
<tr>
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<td>(2) 0.2151</td>
<td>0.7850</td>
<td>0.3114</td>
<td>1.65</td>
<td>0.940</td>
<td>0.4265</td>
<td>91.85</td>
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</table>
Stainless Steel Reactor

Flowrate = 1.0 l/min, W = 11.7725 g, catalyst, B.in = 0.91 mole %

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>B.out/B.in</th>
<th>X_B (mole %)</th>
<th>(MAA)_o (mole %)</th>
<th>CO_2 (mole %)</th>
<th>CO (mole %)</th>
<th>Selectivity [\text{mols MAA/mols B converted}]</th>
<th>C. Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.8077</td>
<td>0.1923</td>
<td>0.1076</td>
<td>0.3850</td>
<td>0.2350</td>
<td>0.6147</td>
<td>107.99</td>
</tr>
<tr>
<td>425</td>
<td>0.6648</td>
<td>0.3352</td>
<td>0.1805</td>
<td>0.5750</td>
<td>0.3900</td>
<td>0.5919</td>
<td>103.95</td>
</tr>
<tr>
<td>450</td>
<td>0.4780</td>
<td>0.5220</td>
<td>0.2657</td>
<td>0.7900</td>
<td>0.5700</td>
<td>0.5594</td>
<td>96.90</td>
</tr>
<tr>
<td>475</td>
<td>0.3132</td>
<td>0.6868</td>
<td>0.3312</td>
<td>1.5600</td>
<td>0.8350</td>
<td>0.5299</td>
<td>102.54</td>
</tr>
<tr>
<td>500</td>
<td>0.1484</td>
<td>0.8517</td>
<td>0.3544</td>
<td>1.6000</td>
<td>1.1000</td>
<td>0.4573</td>
<td>91.71</td>
</tr>
</tbody>
</table>
B.3). Tubular Aluminium Reactor; Benzene Oxidation/Catalyst.

Reactor Diameter = $\frac{3}{8}$ inch.

$W = 45.3175$ g.Cat., Flow rate = 0.5 l/min., Benzene in = 1.0 mole %

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$\frac{B_{\text{out}}}{B_{\text{in}}}$</th>
<th>$X_B$ (mole %)</th>
<th>(MAA)$_{\text{out}}$ (mole %)</th>
<th>CO$_2$ (mole %)</th>
<th>CO (mole %)</th>
<th>Selectivity $\left[\frac{\text{mols MAA}}{\text{mols B. converted}}\right]$</th>
<th>C.Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>380</td>
<td>0.3325</td>
<td>0.6675</td>
<td>0.3853</td>
<td>0.92</td>
<td>0.6</td>
<td>0.5773</td>
<td>84.27</td>
</tr>
<tr>
<td>400</td>
<td>0.1671</td>
<td>0.8329</td>
<td>0.5039</td>
<td>1.35</td>
<td>0.7650</td>
<td>0.6050</td>
<td>85.55</td>
</tr>
<tr>
<td>420</td>
<td>0.0511</td>
<td>0.9489</td>
<td>0.5392</td>
<td>1.50</td>
<td>0.8850</td>
<td>0.5683</td>
<td>80.81</td>
</tr>
<tr>
<td>460</td>
<td>0.0042</td>
<td>0.9958</td>
<td>0.4623</td>
<td>1.55</td>
<td>0.97</td>
<td>0.4642</td>
<td>73.23</td>
</tr>
</tbody>
</table>

Flowrate = 1.0 l/min., Benzene in = 0.94 mole %

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$\frac{B_{\text{out}}}{B_{\text{in}}}$</th>
<th>$X_B$ (mole %)</th>
<th>(MAA)$_{\text{out}}$ (mole %)</th>
<th>CO$_2$ (mole %)</th>
<th>CO (mole %)</th>
<th>Selectivity $\left[\frac{\text{mols MAA}}{\text{mols B. converted}}\right]$</th>
<th>C.Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.5283</td>
<td>0.4717</td>
<td>0.2493</td>
<td>0.92</td>
<td>0.4450</td>
<td>0.5621</td>
<td>98.08</td>
</tr>
<tr>
<td>420</td>
<td>0.3679</td>
<td>0.6321</td>
<td>0.3306</td>
<td>1.10</td>
<td>0.60</td>
<td>0.5563</td>
<td>92.72</td>
</tr>
<tr>
<td>440</td>
<td>0.1967</td>
<td>0.8033</td>
<td>0.3950</td>
<td>1.32</td>
<td>0.785</td>
<td>0.5232</td>
<td>86.26</td>
</tr>
<tr>
<td>460</td>
<td>0.0600</td>
<td>0.9401</td>
<td>0.4897</td>
<td>1.50</td>
<td>1.00</td>
<td>0.5542</td>
<td>85.43</td>
</tr>
<tr>
<td>480</td>
<td>0.0074</td>
<td>0.9926</td>
<td>0.4550</td>
<td>1.56</td>
<td>1.10</td>
<td>0.4877</td>
<td>80.22</td>
</tr>
<tr>
<td>500</td>
<td>0.0005</td>
<td>0.9995</td>
<td>0.3600</td>
<td>1.95</td>
<td>1.20</td>
<td>0.3832</td>
<td>81.43</td>
</tr>
</tbody>
</table>

Flowrate = 1.5 l/min., Benzene in = 1.0 mole %

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$\frac{B_{\text{out}}}{B_{\text{in}}}$</th>
<th>$X_B$ (mole %)</th>
<th>(MAA)$_{\text{out}}$ (mole %)</th>
<th>CO$_2$ (mole %)</th>
<th>CO (mole %)</th>
<th>Selectivity $\left[\frac{\text{mols MAA}}{\text{mols B. converted}}\right]$</th>
<th>C.Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.6092</td>
<td>0.3908</td>
<td>0.2534</td>
<td>0.64</td>
<td>0.390</td>
<td>0.6484</td>
<td>94.97</td>
</tr>
<tr>
<td>420</td>
<td>0.4588</td>
<td>0.5412</td>
<td>0.3494</td>
<td>0.83</td>
<td>0.540</td>
<td>0.6457</td>
<td>92.00</td>
</tr>
<tr>
<td>440</td>
<td>0.3154</td>
<td>0.6846</td>
<td>0.4278</td>
<td>1.00</td>
<td>0.665</td>
<td>0.6249</td>
<td>87.80</td>
</tr>
<tr>
<td>460</td>
<td>0.1739</td>
<td>0.8262</td>
<td>0.5079</td>
<td>1.10</td>
<td>0.795</td>
<td>0.6147</td>
<td>82.82</td>
</tr>
<tr>
<td>480</td>
<td>0.0525</td>
<td>0.9475</td>
<td>0.5470</td>
<td>1.32</td>
<td>1.000</td>
<td>0.5774</td>
<td>80.38</td>
</tr>
<tr>
<td>500</td>
<td>0.0049</td>
<td>0.9951</td>
<td>0.4900</td>
<td>1.50</td>
<td>1.100</td>
<td>0.4924</td>
<td>76.49</td>
</tr>
</tbody>
</table>

Flowrate = 2.0 l/min., Benzene in = 1.04 mole %

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$\frac{B_{\text{out}}}{B_{\text{in}}}$</th>
<th>$X_B$ (mole %)</th>
<th>(MAA)$_{\text{out}}$ (mole %)</th>
<th>CO$_2$ (mole %)</th>
<th>CO (mole %)</th>
<th>Selectivity $\left[\frac{\text{mols MAA}}{\text{mols B. converted}}\right]$</th>
<th>C.Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.6814</td>
<td>0.3186</td>
<td>0.2461</td>
<td>0.555</td>
<td>0.375</td>
<td>0.7428</td>
<td>96.20</td>
</tr>
<tr>
<td>420</td>
<td>0.5309</td>
<td>0.4691</td>
<td>0.3238</td>
<td>0.710</td>
<td>0.510</td>
<td>0.6637</td>
<td>91.35</td>
</tr>
<tr>
<td>440</td>
<td>0.3852</td>
<td>0.6148</td>
<td>0.4125</td>
<td>0.840</td>
<td>0.660</td>
<td>0.6452</td>
<td>87.52</td>
</tr>
<tr>
<td>460</td>
<td>0.2229</td>
<td>0.7771</td>
<td>0.4831</td>
<td>1.100</td>
<td>0.825</td>
<td>0.5977</td>
<td>83.24</td>
</tr>
<tr>
<td>480</td>
<td>0.0987</td>
<td>0.9013</td>
<td>0.5488</td>
<td>1.325</td>
<td>1.000</td>
<td>0.5854</td>
<td>81.92</td>
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<tr>
<td>500</td>
<td>0.0254</td>
<td>0.9746</td>
<td>0.5294</td>
<td>1.500</td>
<td>1.075</td>
<td>0.5223</td>
<td>77.63</td>
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</table>
Reactor Diameter = \( \frac{3}{4} \) inch.

Flowrate = 0.5 l/min., Benzene in = 0.985 mole %

<table>
<thead>
<tr>
<th>Temp. (^\circ\text{C})</th>
<th>B. out (\frac{\text{mols}}{\text{mols B. in}})</th>
<th>(X_B) (mole %)</th>
<th>(MAA) out (mole %)</th>
<th>(\text{CO}_2) (mole %)</th>
<th>(\text{CO}) (mole %)</th>
<th>Selectivity [mols MAA (\frac{\text{mols MAA}}{\text{mols B. converted}})]</th>
<th>C. Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>380</td>
<td>0.7300</td>
<td>0.2701</td>
<td>0.1844</td>
<td>0.500</td>
<td>0.300</td>
<td>0.6933</td>
<td>100.12</td>
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<tr>
<td>400</td>
<td>0.5308</td>
<td>0.4693</td>
<td>0.3054</td>
<td>0.740</td>
<td>0.490</td>
<td>0.6608</td>
<td>95.36</td>
</tr>
<tr>
<td>420</td>
<td>0.3687</td>
<td>0.6313</td>
<td>0.4146</td>
<td>1.000</td>
<td>0.665</td>
<td>0.5668</td>
<td>93.66</td>
</tr>
<tr>
<td>440</td>
<td>0.2433</td>
<td>0.7568</td>
<td>0.4892</td>
<td>1.120</td>
<td>0.800</td>
<td>0.6562</td>
<td>90.28</td>
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<tr>
<td>460</td>
<td>0.1302</td>
<td>0.8698</td>
<td>0.5072</td>
<td>1.300</td>
<td>1.000</td>
<td>0.5920</td>
<td>86.46</td>
</tr>
</tbody>
</table>

Flowrate = 1.0 l/min., Benzene in = 1.0 mole %

<table>
<thead>
<tr>
<th>Temp. (^\circ\text{C})</th>
<th>B. out (\frac{\text{mols}}{\text{mols B. in}})</th>
<th>(X_B) (mole %)</th>
<th>(MAA) out (mole %)</th>
<th>(\text{CO}_2) (mole %)</th>
<th>(\text{CO}) (mole %)</th>
<th>Selectivity [mols MAA (\frac{\text{mols MAA}}{\text{mols B. converted}})]</th>
<th>C. Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.6195</td>
<td>0.3806</td>
<td>0.2593</td>
<td>0.700</td>
<td>0.430</td>
<td>0.6814</td>
<td>98.06</td>
</tr>
<tr>
<td>420</td>
<td>0.4489</td>
<td>0.5511</td>
<td>0.3713</td>
<td>0.847</td>
<td>0.610</td>
<td>0.6737</td>
<td>93.92</td>
</tr>
<tr>
<td>440</td>
<td>0.2935</td>
<td>0.7065</td>
<td>0.4352</td>
<td>1.050</td>
<td>0.750</td>
<td>0.6161</td>
<td>88.36</td>
</tr>
<tr>
<td>460</td>
<td>0.1950</td>
<td>0.8050</td>
<td>0.4923</td>
<td>1.200</td>
<td>0.860</td>
<td>0.6115</td>
<td>86.65</td>
</tr>
<tr>
<td>480</td>
<td>0.1003</td>
<td>0.8997</td>
<td>0.5223</td>
<td>1.400</td>
<td>1.050</td>
<td>0.5805</td>
<td>85.68</td>
</tr>
</tbody>
</table>

Flowrate = 1.5 l/min., Benzene in = 0.9 mole %

<table>
<thead>
<tr>
<th>Temp. (^\circ\text{C})</th>
<th>B. out (\frac{\text{mols}}{\text{mols B. in}})</th>
<th>(X_B) (mole %)</th>
<th>(MAA) out (mole %)</th>
<th>(\text{CO}_2) (mole %)</th>
<th>(\text{CO}) (mole %)</th>
<th>Selectivity [mols MAA (\frac{\text{mols MAA}}{\text{mols B. converted}})]</th>
<th>C. Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>0.6475</td>
<td>0.3525</td>
<td>0.2638</td>
<td>0.72</td>
<td>0.475</td>
<td>0.7460</td>
<td>104.59</td>
</tr>
<tr>
<td>440</td>
<td>0.5034</td>
<td>0.4966</td>
<td>0.3850</td>
<td>0.84</td>
<td>0.625</td>
<td>0.7750</td>
<td>100.41</td>
</tr>
<tr>
<td>460</td>
<td>0.3643</td>
<td>0.6358</td>
<td>0.4474</td>
<td>0.94</td>
<td>0.750</td>
<td>0.7050</td>
<td>94.41</td>
</tr>
<tr>
<td>480</td>
<td>0.2446</td>
<td>0.7555</td>
<td>0.4879</td>
<td>1.20</td>
<td>0.885</td>
<td>0.6460</td>
<td>91.73</td>
</tr>
<tr>
<td>500</td>
<td>0.1818</td>
<td>0.8182</td>
<td>0.5169</td>
<td>1.25</td>
<td>0.950</td>
<td>0.6310</td>
<td>89.30</td>
</tr>
</tbody>
</table>
SCB Reactor: Benzene Oxidation/Catalyst

\[ W = 10.86 \text{ g.cat.} \]
\[ T = 400^\circ\text{C}, \quad Q = 1.113 \text{ l/min.} \]

<table>
<thead>
<tr>
<th>Bin (mole %)</th>
<th>B_out (mole %)</th>
<th>( k_p ) (g.mole/hr-g.cat-atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1942</td>
<td>0.1692</td>
<td>0.03795</td>
</tr>
<tr>
<td>0.2694</td>
<td>0.2318</td>
<td>0.04154</td>
</tr>
<tr>
<td>0.4762</td>
<td>0.4136</td>
<td>0.03882</td>
</tr>
<tr>
<td>0.6956</td>
<td>0.6016</td>
<td>0.04003</td>
</tr>
<tr>
<td>0.9588</td>
<td>0.8460</td>
<td>0.03416</td>
</tr>
<tr>
<td>1.1029</td>
<td>0.9713</td>
<td>0.03471</td>
</tr>
<tr>
<td>1.2283</td>
<td>1.0403</td>
<td>0.04630</td>
</tr>
</tbody>
</table>

\[ T = 425^\circ\text{C} \quad Q = 1.113 \text{ l/min.} \]

<table>
<thead>
<tr>
<th>Bin (mole %)</th>
<th>B_out (mole %)</th>
<th>( k_p ) (g.mole/hr-g.cat-atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1786</td>
<td>0.1504</td>
<td>0.04803</td>
</tr>
<tr>
<td>0.2444</td>
<td>0.2099</td>
<td>0.04206</td>
</tr>
<tr>
<td>0.3133</td>
<td>0.2657</td>
<td>0.04592</td>
</tr>
<tr>
<td>0.3860</td>
<td>0.3196</td>
<td>0.05325</td>
</tr>
<tr>
<td>0.4386</td>
<td>0.3697</td>
<td>0.04776</td>
</tr>
<tr>
<td>0.5013</td>
<td>0.4198</td>
<td>0.04971</td>
</tr>
<tr>
<td>0.5527</td>
<td>0.4762</td>
<td>0.04112</td>
</tr>
<tr>
<td>0.6893</td>
<td>0.5953</td>
<td>0.0404</td>
</tr>
<tr>
<td>1.0240</td>
<td>0.8598</td>
<td>0.04892</td>
</tr>
</tbody>
</table>

\[ T = 450^\circ\text{C} \quad Q = 1.113 \text{ l/min.} \]

<table>
<thead>
<tr>
<th>Bin (mole %)</th>
<th>B_out (mole %)</th>
<th>( k_p ) (g.mole/hr-g.cat-atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2005</td>
<td>0.1566</td>
<td>0.07174</td>
</tr>
<tr>
<td>0.2694</td>
<td>0.2118</td>
<td>0.06973</td>
</tr>
<tr>
<td>0.4010</td>
<td>0.3133</td>
<td>0.07174</td>
</tr>
<tr>
<td>0.4700</td>
<td>0.3697</td>
<td>0.06948</td>
</tr>
<tr>
<td>0.6580</td>
<td>0.5264</td>
<td>0.06405</td>
</tr>
<tr>
<td>0.7896</td>
<td>0.6266</td>
<td>0.06661</td>
</tr>
<tr>
<td>0.9400</td>
<td>0.7457</td>
<td>0.06674</td>
</tr>
</tbody>
</table>
\[ T = 475^\circ C \quad Q = 1.113 \text{ l/min.} \]

<table>
<thead>
<tr>
<th>( B_{\text{in}} ) (mole %)</th>
<th>( B_{\text{out}} ) (mole %)</th>
<th>( k_p ) (g.mole/hr-g.cat-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2180</td>
<td>0.1566</td>
<td>0.10043</td>
</tr>
<tr>
<td>0.3509</td>
<td>0.2456</td>
<td>0.10980</td>
</tr>
<tr>
<td>0.4950</td>
<td>0.3459</td>
<td>0.1047</td>
</tr>
<tr>
<td>0.6893</td>
<td>0.4988</td>
<td>0.09785</td>
</tr>
<tr>
<td>0.8209</td>
<td>0.5953</td>
<td>0.0970</td>
</tr>
<tr>
<td>1.1155</td>
<td>0.8084</td>
<td>0.09732</td>
</tr>
</tbody>
</table>

\[ T = 500^\circ C \quad Q = 1.113 \text{ l/min.} \]

<table>
<thead>
<tr>
<th>( B_{\text{in}} ) (mole %)</th>
<th>( B_{\text{out}} ) (mole %)</th>
<th>( k_p ) (g.mole/hr-g.cat-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2256</td>
<td>0.1316</td>
<td>0.1830</td>
</tr>
<tr>
<td>0.3509</td>
<td>0.2130</td>
<td>0.1657</td>
</tr>
<tr>
<td>0.4950</td>
<td>0.3008</td>
<td>0.1654</td>
</tr>
<tr>
<td>0.6893</td>
<td>0.4386</td>
<td>0.1464</td>
</tr>
<tr>
<td>1.0779</td>
<td>0.6893</td>
<td>0.1444</td>
</tr>
</tbody>
</table>
B5). - Glass Tubular Reactor; MAA Oxidation/Catalyst

W = 11.61 g.cat.

MAA = mole %, \( k_p \) = g.mole/hr-g.cat-atm.

Flowrate = 0.1 l/min.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>(MAA)\text{in}</th>
<th>(MAA)\text{out}</th>
<th>( X_{\text{MAA}} )</th>
<th>( k_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.7360</td>
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<td>0.5533</td>
<td>0.01735</td>
</tr>
<tr>
<td>425</td>
<td>0.7030</td>
<td>0.2807</td>
<td>0.6006</td>
<td>0.01976</td>
</tr>
<tr>
<td>450</td>
<td>0.6515</td>
<td>0.1765</td>
<td>0.7290</td>
<td>0.02812</td>
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<tr>
<td>475</td>
<td>0.6630</td>
<td>0.1501</td>
<td>0.7735</td>
<td>0.03198</td>
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<tr>
<td>500</td>
<td>0.6647</td>
<td>0.1010</td>
<td>0.8480</td>
<td>0.04057</td>
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Flowrate = 0.2 l/min.

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<th>(MAA)\text{in}</th>
<th>(MAA)\text{out}</th>
<th>( X_{\text{MAA}} )</th>
<th>( k_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.7440</td>
<td>0.4982</td>
<td>0.3303</td>
<td>0.01726</td>
</tr>
<tr>
<td>425</td>
<td>0.7015</td>
<td>0.4565</td>
<td>0.3492</td>
<td>0.01850</td>
</tr>
<tr>
<td>450</td>
<td>0.6480</td>
<td>0.4397</td>
<td>0.3213</td>
<td>0.01669</td>
</tr>
<tr>
<td>475</td>
<td>0.6247</td>
<td>0.3022</td>
<td>0.5162</td>
<td>0.03127</td>
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<tr>
<td>500</td>
<td>0.6477</td>
<td>0.2797</td>
<td>0.5681</td>
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<th>(MAA)\text{in}</th>
<th>(MAA)\text{out}</th>
<th>( X_{\text{MAA}} )</th>
<th>( k_p )</th>
</tr>
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<tbody>
<tr>
<td>425</td>
<td>0.7125</td>
<td>0.3765</td>
<td>0.4715</td>
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<tr>
<td>450</td>
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<td>0.5000</td>
<td>0.2512</td>
<td>0.01868</td>
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<tr>
<td>475</td>
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<td>0.3707</td>
<td>0.4012</td>
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<tr>
<td>500</td>
<td>0.6582</td>
<td>0.4295</td>
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Flowrate = 0.4 l/min.

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<th>(MAA)\text{out}</th>
<th>( X_{\text{MAA}} )</th>
<th>( k_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.7412</td>
<td>0.6437</td>
<td>0.1315</td>
<td>0.01214</td>
</tr>
<tr>
<td>425</td>
<td>0.7215</td>
<td>0.6132</td>
<td>0.150</td>
<td>0.01400</td>
</tr>
<tr>
<td>450</td>
<td>0.6557</td>
<td>0.5510</td>
<td>0.1846</td>
<td>0.01757</td>
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<tr>
<td>475</td>
<td>0.6435</td>
<td>0.4705</td>
<td>0.2688</td>
<td>0.02697</td>
</tr>
<tr>
<td>500</td>
<td>0.6822</td>
<td>0.5145</td>
<td>0.2458</td>
<td>0.02430</td>
</tr>
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</table>
Flowrate = 0.6 l/min.

<table>
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<th>(MAA)$_{in}$</th>
<th>(MAA)$_{out}$</th>
<th>$X_{MAA}$</th>
<th>$k_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.7475</td>
<td>0.6747</td>
<td>0.09732</td>
<td>0.01322</td>
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<tr>
<td>425</td>
<td>0.7067</td>
<td>0.6397</td>
<td>0.09480</td>
<td>0.01286</td>
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<td>0.6777</td>
<td>0.6017</td>
<td>0.1121</td>
<td>0.01536</td>
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<tr>
<td>475</td>
<td>0.6705</td>
<td>0.5757</td>
<td>0.1413</td>
<td>0.01968</td>
</tr>
<tr>
<td>500</td>
<td>0.6688</td>
<td>0.5827</td>
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<td>0.01763</td>
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</table>

Flowrate = 0.8 l/min.

<table>
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<tr>
<th>$T(°C)$</th>
<th>(MAA)$_{in}$</th>
<th>(MAA)$_{out}$</th>
<th>$X_{MAA}$</th>
<th>$k_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.7620</td>
<td>0.7112</td>
<td>0.0666</td>
<td>0.01187</td>
</tr>
<tr>
<td>425</td>
<td>0.7260</td>
<td>0.6747</td>
<td>0.07059</td>
<td>0.01261</td>
</tr>
<tr>
<td>450</td>
<td>0.6950</td>
<td>0.6395</td>
<td>0.07985</td>
<td>0.01433</td>
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<tr>
<td>475</td>
<td>0.6705</td>
<td>0.5757</td>
<td>0.1413</td>
<td>0.02224</td>
</tr>
</tbody>
</table>

Flowrate = 1.0 l/min.

<table>
<thead>
<tr>
<th>$T(°C)$</th>
<th>(MAA)$_{in}$</th>
<th>(MAA)$_{out}$</th>
<th>$X_{MAA}$</th>
<th>$k_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.7232</td>
<td>0.7170</td>
<td>0.008641</td>
<td>0.00186</td>
</tr>
<tr>
<td>425</td>
<td>0.7222</td>
<td>0.6727</td>
<td>0.06853</td>
<td>0.01528</td>
</tr>
<tr>
<td>450</td>
<td>0.6852</td>
<td>0.6235</td>
<td>0.09011</td>
<td>0.02033</td>
</tr>
<tr>
<td>475</td>
<td>0.6512</td>
<td>0.5957</td>
<td>0.08522</td>
<td>0.01918</td>
</tr>
<tr>
<td>500</td>
<td>0.6777</td>
<td>0.6150</td>
<td>0.09258</td>
<td>0.02092</td>
</tr>
</tbody>
</table>
The SCB Reactor; MAA Oxidation

**SCB Reactor; MAA Oxidation/Empty Reactor**

Flowrate = 1.0 l/min.

- $V_R =$ Reactor volume (60 cc.)
- $T =$ **400°C**

<table>
<thead>
<tr>
<th>$(\text{MAA})_{\text{in}}$ (mole %)</th>
<th>$(\text{MAA})_{\text{out}}$ (mole %)</th>
<th>$k_p$ (g.mole/hr-$V_R$-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1333</td>
<td>0.09542</td>
<td>0.09148</td>
</tr>
<tr>
<td>0.2800</td>
<td>0.2189</td>
<td>0.06415</td>
</tr>
<tr>
<td>0.3685</td>
<td>0.2890</td>
<td>0.06332</td>
</tr>
<tr>
<td>0.4417</td>
<td>0.3545</td>
<td>0.05665</td>
</tr>
<tr>
<td>0.6010</td>
<td>0.4902</td>
<td>0.05200</td>
</tr>
<tr>
<td>0.7547</td>
<td>0.6277</td>
<td>0.04657</td>
</tr>
</tbody>
</table>

$T =$ **425°C**

<table>
<thead>
<tr>
<th>$(\text{MAA})_{\text{in}}$ (mole %)</th>
<th>$(\text{MAA})_{\text{out}}$ (mole %)</th>
<th>$k_p$ (g.mole/hr-$V_R$-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1362</td>
<td>0.0677</td>
<td>0.2328</td>
</tr>
<tr>
<td>0.2965</td>
<td>0.1892</td>
<td>0.1304</td>
</tr>
<tr>
<td>0.4510</td>
<td>0.3117</td>
<td>0.1028</td>
</tr>
<tr>
<td>0.5365</td>
<td>0.3785</td>
<td>0.09609</td>
</tr>
<tr>
<td>0.6132</td>
<td>0.4450</td>
<td>0.08703</td>
</tr>
<tr>
<td>0.7690</td>
<td>0.5775</td>
<td>0.07633</td>
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</table>
### $T = 450^\circ C$

<table>
<thead>
<tr>
<th>(MAA)$_{in}$ (mole %)</th>
<th>(MAA)$_{out}$ (mole %)</th>
<th>$k_p$ (g.mole/hr$^{-1}$V$_R$-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1377</td>
<td>0.05625</td>
<td>0.3333</td>
</tr>
<tr>
<td>0.2927</td>
<td>0.1521</td>
<td>0.2128</td>
</tr>
<tr>
<td>0.4517</td>
<td>0.2550</td>
<td>0.1776</td>
</tr>
<tr>
<td>0.5285</td>
<td>0.3120</td>
<td>0.1597</td>
</tr>
<tr>
<td>0.6087</td>
<td>0.3662</td>
<td>0.1524</td>
</tr>
<tr>
<td>0.7725</td>
<td>0.4893</td>
<td>0.1331</td>
</tr>
</tbody>
</table>

### $T = 475^\circ C$

<table>
<thead>
<tr>
<th>(MAA)$_{in}$ (mole %)</th>
<th>(MAA)$_{out}$ (mole %)</th>
<th>$k_p$ (g.mole/hr$^{-1}$V$_R$-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2941</td>
<td>0.1180</td>
<td>0.3432</td>
</tr>
<tr>
<td>0.3772</td>
<td>0.1637</td>
<td>0.3000</td>
</tr>
<tr>
<td>0.4440</td>
<td>0.2075</td>
<td>0.2623</td>
</tr>
<tr>
<td>0.5955</td>
<td>0.2990</td>
<td>0.2202</td>
</tr>
<tr>
<td>0.7562</td>
<td>0.3985</td>
<td>0.2066</td>
</tr>
<tr>
<td>0.9085</td>
<td>0.4927</td>
<td>0.1942</td>
</tr>
</tbody>
</table>

### $T = 500^\circ C$

<table>
<thead>
<tr>
<th>(MAA)$_{in}$ (mole %)</th>
<th>(MAA)$_{out}$ (mole %)</th>
<th>$k_p$ (g.mole/hr$^{-1}$V$_R$-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2810</td>
<td>0.0886</td>
<td>0.4998</td>
</tr>
<tr>
<td>0.4407</td>
<td>0.1678</td>
<td>0.3744</td>
</tr>
<tr>
<td>0.5980</td>
<td>0.2445</td>
<td>0.3327</td>
</tr>
<tr>
<td>0.7575</td>
<td>0.3267</td>
<td>0.3034</td>
</tr>
<tr>
<td>0.9102</td>
<td>0.4110</td>
<td>0.2796</td>
</tr>
<tr>
<td>1.0397</td>
<td>0.4917</td>
<td>0.2565</td>
</tr>
</tbody>
</table>
### SCB Reactor: MAA Oxidation/Catalyst

Flowrate = 1.0 l/min. \( \dot{W} = 10.86 \text{ g.cat.} \)

\[ T = 375^\circ C \]

<table>
<thead>
<tr>
<th>(MAA)\textsubscript{in} (mole %)</th>
<th>(MAA)\textsubscript{out} (mole %)</th>
<th>( k_p ) (g.mole/hr-g.cat-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1133</td>
<td>0.0950</td>
<td>0.0444</td>
</tr>
<tr>
<td>0.2540</td>
<td>0.2137</td>
<td>0.0433</td>
</tr>
<tr>
<td>0.3997</td>
<td>0.3392</td>
<td>0.0410</td>
</tr>
<tr>
<td>0.4742</td>
<td>0.4022</td>
<td>0.0412</td>
</tr>
<tr>
<td>0.5342</td>
<td>0.4575</td>
<td>0.0386</td>
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</table>

\[ T = 400^\circ C \]

<table>
<thead>
<tr>
<th>(MAA)\textsubscript{in} (mole %)</th>
<th>(MAA)\textsubscript{out} (mole %)</th>
<th>( k_p ) (g.mole/hr-g.cat-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3157</td>
<td>0.2436</td>
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<tr>
<td>0.3857</td>
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<tr>
<td>0.4452</td>
<td>0.3537</td>
<td>0.0595</td>
</tr>
<tr>
<td>0.5085</td>
<td>0.4165</td>
<td>0.0508</td>
</tr>
<tr>
<td>0.6702</td>
<td>0.5467</td>
<td>0.0519</td>
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</tbody>
</table>

\[ T = 425^\circ C \]

<table>
<thead>
<tr>
<th>(MAA)\textsubscript{in} (mole %)</th>
<th>(MAA)\textsubscript{out} (mole %)</th>
<th>( k_p ) (g.mole/hr-g.cat-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2747</td>
<td>0.1630</td>
<td>0.1578</td>
</tr>
<tr>
<td>0.4190</td>
<td>0.2790</td>
<td>0.1155</td>
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<td>0.4875</td>
<td>0.3242</td>
<td>0.1159</td>
</tr>
<tr>
<td>0.5585</td>
<td>0.3815</td>
<td>0.1068</td>
</tr>
<tr>
<td>0.6522</td>
<td>0.4427</td>
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<tr>
<td>0.7235</td>
<td>0.5030</td>
<td>0.1009</td>
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### T = 450°C

<table>
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<tr>
<th>(MAA)$_{\text{in}}$ (mole %)</th>
<th>(MAA)$_{\text{out}}$ (mole %)</th>
<th>$k_p$ (g.mole/hr-g.cat-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2725</td>
<td>0.1225</td>
<td>0.2818</td>
</tr>
<tr>
<td>0.4295</td>
<td>0.2237</td>
<td>0.2114</td>
</tr>
<tr>
<td>0.5027</td>
<td>0.2735</td>
<td>0.1929</td>
</tr>
<tr>
<td>0.5747</td>
<td>0.3175</td>
<td>0.1865</td>
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<tr>
<td>0.7310</td>
<td>0.4200</td>
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</tr>
<tr>
<td>0.8777</td>
<td>0.5172</td>
<td>0.1604</td>
</tr>
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</table>

### T = 475°C

<table>
<thead>
<tr>
<th>(MAA)$_{\text{in}}$ (mole %)</th>
<th>(MAA)$_{\text{out}}$ (mole %)</th>
<th>$k_p$ (g.mole/hr-g.cat-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3037</td>
<td>0.1080</td>
<td>0.4172</td>
</tr>
<tr>
<td>0.4712</td>
<td>0.2023</td>
<td>0.3060</td>
</tr>
<tr>
<td>0.5487</td>
<td>0.2438</td>
<td>0.2877</td>
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<tr>
<td>0.6275</td>
<td>0.2897</td>
<td>0.2683</td>
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<tr>
<td>0.8000</td>
<td>0.3887</td>
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</tr>
<tr>
<td>0.9385</td>
<td>0.4725</td>
<td>0.2270</td>
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</table>

### T = 500°C

<table>
<thead>
<tr>
<th>(MAA)$_{\text{in}}$ (mole %)</th>
<th>(MAA)$_{\text{out}}$ (mole %)</th>
<th>$k_p$ (g.mole/hr-g.cat-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3107</td>
<td>0.0874</td>
<td>0.5878</td>
</tr>
<tr>
<td>0.4767</td>
<td>0.1600</td>
<td>0.4555</td>
</tr>
<tr>
<td>0.5515</td>
<td>0.1927</td>
<td>0.4283</td>
</tr>
<tr>
<td>0.6262</td>
<td>0.2226</td>
<td>0.4173</td>
</tr>
<tr>
<td>0.7835</td>
<td>0.3022</td>
<td>0.3665</td>
</tr>
<tr>
<td>0.9365</td>
<td>0.3805</td>
<td>0.3363</td>
</tr>
<tr>
<td>1.0710</td>
<td>0.4537</td>
<td>0.3131</td>
</tr>
</tbody>
</table>
Appendix C

Experimental Results from Chapter 4
### 1 inch Diameter Stainless Steel Tubular Reactor; Overall Reaction

$W = 16.7955$ g. (catalyst No. 6, to be used in Pilot Plant)

**Flowrate = 0.515 l/min., Benzene in = 1.0 mole %**

<table>
<thead>
<tr>
<th>$T(\degree C)$</th>
<th>$\frac{B_out}{B.in}$</th>
<th>$X_B$ (mole %)</th>
<th>(MAA) (mole %)</th>
<th>$CO_2$ (mole %)</th>
<th>$CO$ (mole %)</th>
<th>Selectivity</th>
<th>C.Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.6800</td>
<td>0.3200</td>
<td>0.2177</td>
<td>0.545</td>
<td>0.375</td>
<td>0.6804</td>
<td>97.85</td>
</tr>
<tr>
<td>425</td>
<td>0.4850</td>
<td>0.5150</td>
<td>0.3308</td>
<td>0.725</td>
<td>0.575</td>
<td>0.6424</td>
<td>92.22</td>
</tr>
<tr>
<td>450</td>
<td>0.3700</td>
<td>0.6300</td>
<td>0.4109</td>
<td>0.900</td>
<td>0.740</td>
<td>0.6523</td>
<td>91.73</td>
</tr>
<tr>
<td>475</td>
<td>0.2550</td>
<td>0.7450</td>
<td>0.4522</td>
<td>1.000</td>
<td>0.800</td>
<td>0.6070</td>
<td>85.69</td>
</tr>
<tr>
<td>500</td>
<td>0.1470</td>
<td>0.8530</td>
<td>0.4920</td>
<td>1.200</td>
<td>1.100</td>
<td>0.5768</td>
<td>85.83</td>
</tr>
</tbody>
</table>

**Flowrate = 0.850 l/min., Benzene in = 0.95 mole %**

<table>
<thead>
<tr>
<th>$T(\degree C)$</th>
<th>$\frac{B_out}{B.in}$</th>
<th>$X_B$ (mole %)</th>
<th>(MAA) (mole %)</th>
<th>$CO_2$ (mole %)</th>
<th>$CO$ (mole %)</th>
<th>Selectivity</th>
<th>C.Balance (%)</th>
</tr>
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<tbody>
<tr>
<td>400</td>
<td>0.7894</td>
<td>0.2105</td>
<td>0.1068</td>
<td>0.290</td>
<td>0.190</td>
<td>0.5329</td>
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<td>425</td>
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<td>0.3315</td>
<td>0.1844</td>
<td>0.440</td>
<td>0.325</td>
<td>0.5855</td>
<td>96.72</td>
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<td>450</td>
<td>0.5536</td>
<td>0.4463</td>
<td>0.2630</td>
<td>0.575</td>
<td>0.450</td>
<td>0.6202</td>
<td>94.72</td>
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<tr>
<td>475</td>
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<td>0.5768</td>
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<td>0.600</td>
<td>0.5978</td>
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<td>500</td>
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<td>0.800</td>
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<td>90.64</td>
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</table>

**Flowrate = 1.0 l/min., Benzene in = 1.01 mole %**

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<thead>
<tr>
<th>$T(\degree C)$</th>
<th>$\frac{B_out}{B.in}$</th>
<th>$X_B$ (mole %)</th>
<th>(MAA) (mole %)</th>
<th>$CO_2$ (mole %)</th>
<th>$CO$ (mole %)</th>
<th>Selectivity</th>
<th>C.Balance (%)</th>
</tr>
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<tbody>
<tr>
<td>400</td>
<td>0.8514</td>
<td>0.1485</td>
<td>0.09636</td>
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<td>0.180</td>
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<td>0.1735</td>
<td>0.410</td>
<td>0.275</td>
<td>0.6089</td>
<td>93.83</td>
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<tr>
<td>450</td>
<td>0.6089</td>
<td>0.3910</td>
<td>0.2515</td>
<td>0.540</td>
<td>0.410</td>
<td>0.6368</td>
<td>92.56</td>
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<tr>
<td>475</td>
<td>0.5099</td>
<td>0.4900</td>
<td>0.3316</td>
<td>0.655</td>
<td>0.530</td>
<td>0.6700</td>
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<tr>
<td>500</td>
<td>0.3811</td>
<td>0.6188</td>
<td>0.3937</td>
<td>0.790</td>
<td>0.665</td>
<td>0.6299</td>
<td>87.74</td>
</tr>
</tbody>
</table>
Flowrate = 1.5 l/min., Benzene in = 0.975 mole %

| T(°C) | B.out | X_B  | (MAA)_o (mole %) | CO_2  (mole %) | CO   (mole %) | Selectivity | C.Balance (%)
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>B.in</td>
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<td></td>
<td>mols MAA</td>
<td>mols B.converted</td>
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<td>0.8974</td>
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<td>0.0653</td>
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<td>425</td>
<td>0.7948</td>
<td>0.2052</td>
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<td>97.08</td>
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<tr>
<td>475</td>
<td>0.6256</td>
<td>0.3743</td>
<td>0.2349</td>
<td>0.500</td>
<td>0.417</td>
<td>0.6437</td>
<td>95.91</td>
</tr>
<tr>
<td>500</td>
<td>0.5205</td>
<td>0.4794</td>
<td>0.2894</td>
<td>0.635</td>
<td>0.560</td>
<td>0.6190</td>
<td>93.60</td>
</tr>
</tbody>
</table>

Flowrate = 2.0 l/min., Benzene in = 0.99 mole %

| T(°C) | B.out | X_B  | (MAA)_o (mole %) | CO_2  (mole %) | CO   (mole %) | Selectivity | C.Balance (%)
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>B.in</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>mols MAA</td>
<td>mols B.converted</td>
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<td>0.100</td>
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<td>0.1415</td>
<td>0.0934</td>
<td>0.250</td>
<td>0.175</td>
<td>0.6674</td>
<td>100.17</td>
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<tr>
<td>450</td>
<td>0.8030</td>
<td>0.1969</td>
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<td>0.255</td>
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<td>0.3010</td>
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<td>0.430</td>
<td>0.5804</td>
<td>92.28</td>
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</tbody>
</table>
C2) ¾ inch Diameter Stainless Steel Tubular Reactor

MAA Oxidation/Catalyst.

\[ W = 16.7955 \text{ g.catalyst (No. 6)} \]

Flowrate = 1.0 l/min.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>( X_{\text{MAA}} )</th>
<th>( k_p ) (g.mole/hr-g.cat-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.0441</td>
<td>0.0060</td>
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<tr>
<td>425</td>
<td>0.0824</td>
<td>0.0115</td>
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<td>450</td>
<td>0.1355</td>
<td>0.0195</td>
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<td>475</td>
<td>0.1742</td>
<td>0.0256</td>
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<tr>
<td>500</td>
<td>0.2210</td>
<td>0.03346</td>
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</tbody>
</table>

Flowrate = 2.0 l/min.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>( X_{\text{MAA}} )</th>
<th>( k_p ) (g.mole/hr-g.cat-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.0457</td>
<td>0.01255</td>
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<tr>
<td>425</td>
<td>0.0484</td>
<td>0.01331</td>
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<tr>
<td>450</td>
<td>0.0676</td>
<td>0.01875</td>
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<tr>
<td>475</td>
<td>0.0939</td>
<td>0.02642</td>
</tr>
<tr>
<td>500</td>
<td>0.1188</td>
<td>0.03390</td>
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</tbody>
</table>
C3).- Heats of Reaction

Reaction Scheme

C₆H₆ + 4 O₂ → C₄H₂O₃ + CO + CO₂ + 2H₂O \hspace{1cm} (1)

C₄H₂O₃ + 2 O₂ → 2CO + 2CO₂ + H₂O \hspace{1cm} (2)

C₆H₆ + 6 O₂ → 3CO + 3CO₂ + 3H₂O \hspace{1cm} (3)

Heats of formation

<table>
<thead>
<tr>
<th>Substance</th>
<th>Heats of formation (cal./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>19820</td>
</tr>
<tr>
<td>MAA</td>
<td>112430</td>
</tr>
<tr>
<td>CO₂</td>
<td>94050</td>
</tr>
<tr>
<td>CO</td>
<td>26416</td>
</tr>
<tr>
<td>H₂O</td>
<td>57797</td>
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</table>

Heats of reaction

ΔH₁ = -328672 cal./mole benzene converted

ΔH₂ = -186303 cal./mole MAA converted

ΔH₃ = -514975 cal./mole benzene converted.
Calculation of Rate Velocity Constants for the SCB and Tubular Reactors -

For a first order irreversible reaction: in a SCBR

Rate equation \[ r = k_c C_0 \] (1)

Mass balance \[ rW = Q(C_i - C_0) \] (2)

where \(Q\) and \(C_i\) are at reaction temperature \((T_R)\)

Now

\(C_M\) is concentration measured at chromatographic temperature \((T_c)\) and \(Q\) is measured at ambient temperature \((T_A)\)

\[ \Delta I = \text{Chromatographic Area of Peak} \]

\[ Q = Q_M \left( \frac{T_R}{T_c} \right), \quad C = C_M \left( \frac{T_c}{T_R} \right) \]

from (1) and (2)

\[ k_c = \frac{Q}{W} \left[ \frac{C_i}{C_0} - 1 \right] \]

\[ k_c = \frac{Q_M T_R}{W T_A} \left[ \frac{\Delta I}{\Delta_o} - 1 \right] \]

If partial pressures are used as driving force

the rate equation becomes, \( r = k_p P_0 \)

\[ P_0 = \frac{R}{V} R T_R = C_0 R T_R \]

\[ r = k_p R T_R C_0 = k_c C_0 \]

\[ k_c = k_p R T_R \quad k_p = \frac{k_c}{R T_R} \quad \frac{g \text{ mol.}}{g \text{ cat-min-atm}} \]

Thus

\[ k_p R T_R = \frac{Q}{W} \left[ \frac{\Delta I}{\Delta_o} - 1 \right] \]

\[ k_p = \frac{1}{R T_R} \frac{Q_M T_R}{W T_A} \left[ \frac{\Delta I}{\Delta_o} - 1 \right] \]
Similarly for an isothermal plug flow reactor

\[ r = k \frac{C}{c} \]  
\[ r \, dW = Q \, dC \]  
\[ k_c \, dW = Q \frac{dC}{C} \]  

\[ k_c \, W = Q \ln \left( \frac{C_0}{C_I} \right) \]  
\[ k_c = \frac{Q}{W} \left[ \ln \left( \frac{C_0}{C_I} \right) \right] \]  
\[ k_c = \frac{Q}{W} \frac{T_R}{T_A} \left[ \ln \left( \frac{C_0}{C_I} \right) \right] \]

and

\[ k_p = \frac{Q}{W} \frac{1}{RT_A} \left[ \ln \left( \frac{C_0}{C_I} \right) \right] \]  
\[ k_p = 2.5 \frac{Q}{W} \left[ \ln \left( \frac{C_0}{C_I} \right) \right] \]
Least Squares Calculation of Slopes and Intercepts of Straight Lines


For a straight line of form;

\[ y = a + bx \]  \hspace{1cm} (1)

\[ b = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2} \]  \hspace{1cm} (2)

\[ a = \frac{1}{n} \left( \sum y - b \sum x \right) \]  \hspace{1cm} (3)

where \( n \) = size of sample

In addition, the statistical variance of the slope \( b \) is given by

\[ S_b = \frac{S_{y/x}}{S_x \sqrt{n-1}} \]  \hspace{1cm} (4)

where \[ S_x = \sqrt{\frac{1}{n(n-1)} \left[ n \sum x^2 - (\sum x)^2 \right]} \]  \hspace{1cm} (5)

and \[ S_{y/x} = \sqrt{\frac{n-1}{n-2} \left[ S_y^2 - b^2 S_x^2 \right]} \]  \hspace{1cm} (6)

and \[ S_y = \sqrt{\frac{1}{n(n-1)} \left[ n \sum y^2 - (\sum y)^2 \right]} \]  \hspace{1cm} (7)

Procedure;

1) - from (2) calculate \( b \)
2) - from (5) and (7) calculate \( S_x, S_y \)
3) - from (6) calculate \( S_{y/x} \)
4) - from (4) calculate \( S_b \)
5) - with $b$ calculate $\bar{a}$

6) - with $b + S_b$ calculate $a$ upper limit

7) - with $b - S_b$ calculate $a$ lower limit

Focal Computer Program Listing (PDP-8 Computer)

Symbols:

\[ X_3 = \Sigma x \quad y_3 = \Sigma y \]
\[ X_2 = \Sigma x^2 \quad y_2 = \Sigma y^2 \]
\[ Z = \Sigma xy \]

$B_9$ \[ b = B_9 \quad S_b = S_6 \]

$A_9$ \[ a = A_9 \]

$a$ (upper limit) = $A_2$

$a$ (lower limit) = $A_1$
C— FOCAL 01969

C1.01 T "STATISTICAL ANALYSIS OF DATA"
C1.02 A "DATE"
C1.03 S Y3=G
C1.04 S X3=D
C1.05 S Y2=G
C1.06 S Z=G
C1.07 T "N"
C1.08 T "IF Y IS FED IN LINEAR FORM BUT IN CALC. USED AS LOGY"
C1.09 T "IF CALC IS ALSO IN LINEAR FORM TYPE 1"J
C1.10 F I=1,N-1; DO 2
C1.11 A "X"X(I)
C1.12 A "Y"Y(I)
C1.13 S Y(I)=FLOG(Y(I))
C1.14 S Y3=Y3+Y(I)
C1.15 S Y2=Y2+Y(I)
C1.16 S Z=Z+X(I)*Y(I)
C1.17 T !
C1.18 S B9=(N*Z-Y3*X3)/(N*X2-X3*D)
C1.19 S A9=(Y3-B9*X3)/N
C1.20 S S9=SQT((N*Y2-Y3*X3)/(N*(N-1)))
C1.21 S S7=SQT((N*Y2-Y3*X3)/(N*(N-1)))/S9
C1.22 S A1=(Y3-B9*S6)/N
C1.23 T !
C1.24 T !
C1.25 T !
C1.26 T !
C1.27 T !
C1.28 T !
C1.29 T !
C1.30 T !
C1.31 T !
C1.32 T !
C1.33 T !
C1.34 T !
C1.35 T !
C1.36 T !
C1.37 T !
C1.38 T !
Appendix F

Experimental Axial Temperature Profiles in the
One and Two inch Diameter Non-isothermal Reactors.
# One Inch Diameter Reactor

## Thermocouples temperature °C

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<th>FBT.</th>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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</tr>
</thead>
<tbody>
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<td>470</td>
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<td>474.5</td>
<td>479.5</td>
<td>482.5</td>
<td>479</td>
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</tr>
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</tbody>
</table>

*For location of the thermocouples see Fig (5.3)*
Two Inch Diameter Reactor

| Run No. | FBT. | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | *
<table>
<thead>
<tr>
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<td>464.5</td>
<td>430</td>
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<td>453</td>
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<td>434</td>
<td>418.5</td>
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<tr>
<td>9</td>
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<td>435</td>
<td>463</td>
<td>597</td>
<td>454</td>
<td></td>
</tr>
</tbody>
</table>

* For location of thermocouples see Fig (5.6).
Appendix G

Computer Listing Program for One-Dimensional Plug Flow Model.

Kinetic scheme:

\[
\text{Benzene} \rightarrow_{1} \text{MAA} \rightarrow_{2} \text{C. oxides} \rightarrow_{3}
\]

**R1DPF**

**Nomenclature**

- **AA1, AA2, AA3**: Pre-exponential factors
- **EA1, EA2, EA3**: Activation Energies
- **PT**: Total pressure
- **G**: Mass velocity
- **TW**: Wall temperature
- **CP**: Specific heat of fluid
- **RHOF**: Catalyst density
- **VOID**: Void fraction
- **R**: Universal gas constant
- **DEHL 1, DEHL 2, DEHL 3**: Heats of reaction
- **UW**: Overall heat transfer coefficient
- **TD**: Tube diameter
- **M**: Molecular weight of fluid
- **N**: Number of differential equations
- **N154**: Dimension factor for the subroutines, always equal to \((15 * N) + 4\)
- **E(1), E(2), E(3)**: Accuracy limit
- **NSF**: Number of digits in accuracy limit
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISW</td>
<td>Subroutine requirement, always equal to one</td>
</tr>
<tr>
<td>T</td>
<td>Initial time</td>
</tr>
<tr>
<td>DT</td>
<td>Initial step size for integration</td>
</tr>
<tr>
<td>TB</td>
<td>Interval size for printing</td>
</tr>
<tr>
<td>Y1(1)</td>
<td>Initial condition for temperature</td>
</tr>
<tr>
<td>Y1(2)</td>
<td>Initial benzene partial pressure</td>
</tr>
<tr>
<td>Y1(3)</td>
<td>Initial MAA partial pressure</td>
</tr>
<tr>
<td>D</td>
<td>Dimension subroutine requirement, always equal to $(15 \times N) + 4$</td>
</tr>
<tr>
<td>DY(1), DY(2), DY(3)</td>
<td>Derivatives of $Y(1), Y(2), Y(3)$ with respect to time.</td>
</tr>
<tr>
<td>Y(1), Y(2), Y(3)</td>
<td>Temperature, Benzene and Maleic anhydride.</td>
</tr>
</tbody>
</table>
LIST(RIDPF)
C TEB MENTET N U Associates, 1-D MODEL *******
DOUBLE PRECISION AA1, AA2, AA3, EA1, EA2, EA3, G, CP, KPDP, V01D, E,
DELH1, DELH2, DELH3, TW, UW, DT, Y(3), Y1(3), E(3), T, TB, TD, D(49), M, DY(3),
EQUIVALENCE(E(1), DY(1)), (Y(1), Y1(1))
C PARAMETERS OF THE SYSTEM
PT=1.0
AA1=284.263
AA2=4.8819
AA3=122.528
EA1=13324.0
EA2=8589.0
EA3=13324.0
G=2009030.0
TW=499.0
CP=0.237
KPDP=2893000.0
V01D=0.57
K=1.987
DELH1=-328672.0
DELH2=-186303.0
DELH3=-514975.0
UW=68000.0
TD=0.0254
M=29.0
N=3
N15A=(15*N)+4
C INITIAL CONDITIONS(Y(1) IS TEMP OF FLUID, Y(2) IS BENZENE,
C Y(3) IS MALIC ANH IN ATM.
Y1(1)=499.0
Y1(2)=0.0095
Y1(3)=0.0
SUBROUTINE REQUIREMENTS (T IS INITIAL TMS, TB IS INTERVAL SIZE)

FOR PRINTING, DT IS STEP SIZE FOR INTEGRATION, E=ACCURACY LIMIT

E(1)=0.000001
E(2)=0.000001
E(3)=0.000001
NSF=6
ISW=1
T=0.0
DT=0.0001
TB=0.05

CALL NLDEW(1,NSF,E,Y1,1,N,ISW,1B,1,DT,0,N154)

V1=(EA1/(K*(Y(1)+273.)))
V2=-(EA2/(K*(Y(1)+273.)))
V3=-(EA3/(K*(Y(1)+273.)))
V4=AA1*EXP(V1)*Y(2)*(-DELH1)
V5=AA2*EXP(V2)*Y(3)*(-DELH2)
V6=AA3*EXP(V3)*Y(2)*(-DELH3)
V7=(4.0*U0*(Y(1)-TU)/(G*CP*TD))

DY(1)=((K*OP*(1-V01D))/(G*CP))*(V4+V5+V6)-V7
V4=AA1*EXP(V1)*Y(2)
V5=AA2*EXP(V2)*Y(3)
V6=AA3*EXP(V3)*Y(2)

DY(2)=((-M*PT*K*OP*(1-V01D))/G)*(V4+V6)
DY(3)=((-M*PT*K*OP*(1-V01D))/G)*(V4-V5)

CALL NLDEW(2,NSF,E,Y1,1,N,ISW,1B,1,DT,0,N154)
GOTO(1,2,3,1)

1 CALL NLDEW(3,NSF,E,Y1,1,N,ISW,1B,1,DT,0,N154)
GOTO 2

3 WRITE(6,100)Y(1),Y(2),Y(3),TB
100 FORMAT(2X,16.8,2X,16.8,2X,16.8,2X,16.8,2X,16.8)

1F(1,8,GT,0.8)STOP
TB=TB+0.05
GOTO 1

END
SUBROUTINE NLDEQD(J, NSF, E, Y, I, N, ISW, TB, T, DT, D, N154)
REAL*8D(N154), E(N), Y(I), TB, T, DT
      DO10 K = 1, N
        DO20 K2 = 2*K + 1
          D(K2) = YI(K)
        END DO20
      D(K2) = E(K)
      D(1) = DT
      D(2) = T
      CALL NBAMD(J, NSF, D, I, N, ISW, TB, N154)
      DT = D(1)
      T = D(2)
      DO21 K = 1, N
        DO22 K2 = 2*K + 1
          E(K) = D(K2)
        END DO22
      E(K) = D(K2)
      RETURN
      END

SUBROUTINE NBAMD(J, NSF, D, I, N, ISW, TB, N154)
REAL*8DABS, TSAVE, D(N154), TB, H, HALFDT, DELTA, DENOM, ETA, XP, XC, T0BOLD, A00010003
      C
      DIMENSION OF D IS 15*N+4
      IF(J .LE. 4) GO TO 15
      PRINT999, J
      FORMAT(1X, 2HJ = , I3, 1 NUMBER OF ENTRY POINTS TOO LARGE, MAX IS 4)
      STOP
      GOTO(100, 101, 103, 104), J
      GOTCIO, (1, 12, 21, 26, 27, 28, 33)
      GOTCIP, (9, 34)
      N4P3 = N*4+3
      D0107 JJ = 1, N
      D(N4P3+JJ) = D(2*JJ+2)
      IXP = 2*N+2
      IK = 3*N+3
      IEX = 4*N+3
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<td>0054</td>
<td>D(I1+JJ) = D(2*JJ+2)</td>
</tr>
<tr>
<td>0055</td>
<td>IY = I1</td>
</tr>
<tr>
<td>0056</td>
<td>GOT0122</td>
</tr>
<tr>
<td>0057</td>
<td>D0125JJ=1,N</td>
</tr>
<tr>
<td>0058</td>
<td>D(I7+JJ) = D(2*JJ+2)</td>
</tr>
<tr>
<td>0059</td>
<td>IY = I7</td>
</tr>
<tr>
<td>0060</td>
<td>122 ASSIGN2TOII</td>
</tr>
<tr>
<td>0061</td>
<td>GOT01000</td>
</tr>
<tr>
<td>0062</td>
<td>2 ASSIGN3TOIR</td>
</tr>
<tr>
<td>0063</td>
<td>GOT02000</td>
</tr>
<tr>
<td>0064</td>
<td>3 IF(ISW=1)126,117,127</td>
</tr>
<tr>
<td>0065</td>
<td>126 IF(IRK=2)128,129,130</td>
</tr>
<tr>
<td>0066</td>
<td>128 IRK = IRK + 1</td>
</tr>
<tr>
<td>0067</td>
<td>GOT05</td>
</tr>
<tr>
<td>0068</td>
<td>129 IAM = 1</td>
</tr>
<tr>
<td>0069</td>
<td>G0104</td>
</tr>
<tr>
<td>0070</td>
<td>DO138JJ=1,N</td>
</tr>
<tr>
<td>0071</td>
<td>D(I5+JJ) = D(2*JJ+2)</td>
</tr>
<tr>
<td>0072</td>
<td>IY = I5</td>
</tr>
<tr>
<td>0073</td>
<td>GOT0135</td>
</tr>
<tr>
<td>0074</td>
<td>113 IF(IRK=1)131,130,132</td>
</tr>
<tr>
<td>0075</td>
<td>130 PRINT997,IRK</td>
</tr>
<tr>
<td>0076</td>
<td>997 FORMAT(2X,4,4IR(,I3,1) ERROR IN IRK1)</td>
</tr>
<tr>
<td>0077</td>
<td>STOP</td>
</tr>
<tr>
<td>0078</td>
<td>131 DO133JJ=1,N</td>
</tr>
<tr>
<td>0079</td>
<td>D(I4+JJ) = D(2*JJ+2)</td>
</tr>
<tr>
<td>0080</td>
<td>IY = I4</td>
</tr>
</tbody>
</table>
GOT0135
DC134 JJ=1,N
I(Y2+JJ)=D(2*JJ+2)
IY=I2
IYO=IY
ASSIGN7TOII
GOT01000
ASSIGN11TOIR
GOT02000
ASSIGN10TOID
I=2
RETURN
IF(ISW=2)139,117,140
DO141 JJ=1,N
D(I4+JJ)=D(2*JJ+2)
IY=I4
GOT0142
IRK=IRK+1
IF(IRQ=2)143,130,144
DO145 JJ=1,N
D(I3+JJ)=D(2*JJ+2)
IY=I3
GOT0142
DO146 JJ=1,N
D(I1+JJ)=D(2*JJ+2)
IY=I1
D(I7)=D(2)
DO147 JJ=1,N
D(I7+JJ)=D(2*JJ+1)
0110 IX=17
0111 ASSIGN12TOII
0112 GOTO1000
0113 12 ASSIGN13TOIR
0114 GOTO2000
0115 13 ASSIGN33TOID
0116 I=2
0117 RETURN
0118 33 DO31JJ=1,N
0120 ASSIGN14TOIC
0121 GOTO4000
0122 14 IF(IEQNEQ0)G010148
0123 149 IF(ID0NE0)GT0150
0124 151 D(1)=2.DO*D(1)
0125 IRK=0
0126 GOT01
0127 150 IF(ISW=2)152,117,153
0128 153 IRK=0
0129 GOT01
0130 152 IF(IRK=3)154,155,130
0131 154 IRK=IRK+1
0132 GOT01
0133 155 IAM=1
0134 GOT01
0135 148 D(1)=.5DO*D(1)
0136 IX=IK
0137 148 IF(ISW=2)157,117,158
0138 158 IX=15
0139   GOT032
0140   157 IF(IRK=2)159,130,160
0141   159 IY=I4
0142   GOT032
0143   160 DO161JJ=1,N
0144   161 D(I4+JJ)=D(I2+JJ)
0145   IY=I4
0146   32 IRK=0
0147   IX=IK
0148   GOT07
0149   111 DO162JJ=1,N
0150   162 D(IZ+JJ)=D(2*JJ+2)
0151   IY=IZ
0152   ASSIGN17TOII
0153   GOT01000
0154   17 DO163JJ=1,N
0155   K1=IXP+JJ
0156   D(K1)=D(IK+JJ)+D(1)/24,D0*(55,D0*D(IZ+JJ)=59,D0*D(I1+JJ)+37,D0*D(I01590000
0157   *2+JJ)=9,D0*D(I3+JJ))
0158   163 D(2*JJ+1)=D(K1)
0159   D(2)=D(IK)+D(1)
0160   ASSIGN28TOID
0161   RETURN
0162   28 DO164JJ=1,N
0163   D(2*JJ+1)=D(IK+JJ)+D(1)/24,*9,D(2*JJ+2)+19,*D(IZ+JJ)=5,*D(I1+JJ)01670000
0164   *+D(I2+JJ))
0164 164 CONTINUE
0165 165 IF(ISW)117,165,166
0166 165 IT=I3
0167 165 I3=I2
0168 165 I2=I1
0169 165 I1=IZ
0170 165 IZ=IT
0171 165 GOTO5
0172 166 ASSIGN18TOIC
0173 166 GOTO4000
0174 166 IF(IE,NE,0)GOTO167
0175 166 IF(IDB.EQ,0)GOTO170
0176 169 IAM=IAM+1
0177 169 IT=I7
0178 169 I7=I6
0179 169 I6=I5
0180 169 I5=I4
0181 169 I4=I3
0182 169 I3=I2
0183 169 I2=I1
0184 169 I1=IZ
0185 169 IZ=IT
0186 169 GOTO5
0187 170 IF(IAM.LT.5)GOTO169
0188 171 IAM=1
0189 171 D(1)=2.*D0*D(1)
0189 171 IT=I2
0190 171 I2=I3
0191 171 I3=I5
0192 171
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<td>0193</td>
<td>I5=I7</td>
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<td>0194</td>
<td>I7=I4</td>
</tr>
<tr>
<td>0195</td>
<td>I4=I7</td>
</tr>
<tr>
<td>0196</td>
<td>GOTO05</td>
</tr>
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<td>0197</td>
<td></td>
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<tr>
<td>0198</td>
<td>167</td>
</tr>
<tr>
<td>0199</td>
<td>D(1)=.5D0*D(1)</td>
</tr>
<tr>
<td>0200</td>
<td>IAM=1</td>
</tr>
<tr>
<td>0201</td>
<td>D0172JJ=1,N</td>
</tr>
<tr>
<td>0202</td>
<td>K=I6+JJ</td>
</tr>
<tr>
<td>0203</td>
<td>L=I2+JJ</td>
</tr>
<tr>
<td>0204</td>
<td>L1=I1+JJ</td>
</tr>
<tr>
<td>0205</td>
<td>L2=I2+JJ</td>
</tr>
<tr>
<td>0206</td>
<td>L3=I3+JJ</td>
</tr>
<tr>
<td>0207</td>
<td>L4=I4+JJ</td>
</tr>
<tr>
<td>0208</td>
<td>D(K)=.0390625D0<em>D(L)+.46875D0</em>D(L1)+.703125D0<em>D(L2)+.15625D0</em>D(L3)*3)</td>
</tr>
<tr>
<td>0209</td>
<td>D(K1)=.2734375D0<em>D(L)+1.09375D0</em>D(L1)+.546875D0<em>D(L2)+.21875D0</em>D(L3)*3)</td>
</tr>
<tr>
<td>0210</td>
<td>I5=I7</td>
</tr>
<tr>
<td>0211</td>
<td>I7=I4</td>
</tr>
<tr>
<td>0212</td>
<td>I4=I7</td>
</tr>
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<td>0213</td>
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</tr>
<tr>
<td>0214</td>
<td>I6=I1</td>
</tr>
<tr>
<td>0215</td>
<td>I4=I2</td>
</tr>
<tr>
<td>0216</td>
<td>I2=I7</td>
</tr>
<tr>
<td>0217</td>
<td>GOTO17</td>
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</tbody>
</table>
M = 1
HALFDT = 5D0 * D(1)
D(2) = D(IY) + HALFDT
DO2001 J = 1, N
D(2*J+1) = D(IY+J) + HALFDT * D(IY+J)
J = J + 1
ASSIGN25 TO ID
I = 2
RETURN
DO2002 J = 1, N
K = IY + J
D(K) = D(2*J+2)
D(2*J+1) = D(IY+J) + HALFDT * D(K)
ASSIGN26 TO ID
I = 2
RETURN
DO2003 J = 1, N
K = IY + J
D(K) = D(2*J+2)
D(2) = D(IY) + D(1)
ASSIGN27 TO ID
I = 2
RETURN
DO2004 J = 1, N
D(2*J+1) = D(IY+J) + D(1) * (D(IY+J) + 2 * D(IY+J+1) + 2 * D(IY+J+2)) / 6.D0
ASSIGN28 TO ID
I = 2
RETURN
G0T04014
4013 DENOM=XC
4014 ETA=DELTA/DENOM
4016 IF(32D0*ETA,GT,H)GOT04018
4017 GOT030
4018 ID81=1
30 CONTINUE
277 GOT030
1000 IF(TB.LE.D(2))GOT019
1002 IF(TB.GT.(D(2)+D(1)))GOT019
1003 SAVEDT=D(1)
TBOLD=TB
TSAVE=D(2)
D(1)=TB-D(2)
ASSIGN22TOIR
GOTO2000
20 D(1)=SAVEDT
1004 ASSIGN21TOID
I=2
RETURN
21 ASSIGN34TOIP
I=3
RETURN
34 D(2)=TSAVE
19 GOTOII,(2,7,9,12,17)
END
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<th>Volume</th>
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<td>127</td>
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<td>ibid,</td>
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<td>Vorotyntsev V.M., Shvets V.A., Kazanski V.B.</td>
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<td>676</td>
<td>(1971)</td>
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<td>134</td>
<td>Shvets V.A., Kazanski V.B.</td>
<td>ibid.</td>
<td>25</td>
<td>123</td>
<td>(1972)</td>
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<td>135</td>
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<td>(1972)</td>
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</table>
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Nomenclature

A  Pre-exponential factor in the Arrhenius expression.
B  Benzene.
C  Constant in the Yagi and Kunii equation, page 214.
Cp  Specific heat (Kcal/Kg - °C).
Cs  Concentration of reactant at the solid catalyst surface.
Dp, dp  Catalyst pellet diameter (m).
De  Effective mass diffusivity (m²/hr).
EA  Activation Energy (cal/g.mole).
FT  Fluid bed temperature (°C).
G  Mass Velocity (Kg/hr-m²).

h_w² Stagnant contribution to the inside wall heat transfer coefficient (Kcal/hr - m² - °C).

h_w² Heat transfer coefficient at the inside wall of a tubular reactor (Kcal/hr - m² - °C).

h_o² Heat transfer coefficient at the outside wall of a tubular reactor (Kcal/hr - m² - °C).

k_p, k_1, k_2, k_3  First order rate constant (g.mole/hr-g.cat-atm).
ke_mr  Radial effective mass diffusivity (Kmole/hr-m-atm).
ke_ma  Axial effective mass diffusivity (Kmole/hr-m-atm).
ke_ea  Axial effective thermal conductivity (Kcal/hr - m - °C).
ke_hr  Radial effective thermal conductivity (Kcal/hr - m - °C).
kek_r  Stagnant contribution to the effective thermal conductivity (Kcal/hr - m² - °C).

k_f  Thermal conductivity of fluid (Kcal/hr - m - °C).
k_s  Thermal conductivity of solid (Kcal/hr - m - °C).
M  Average molecular weight of fluid (Kg/Kg mole).
MAA  Maleic Anhydride.

P_A

Bulk reactant partial pressure (atm).

P_T

System total pressure (atm).

Pr

Prandtl Number (C_pμ/k).

Pe_{ha}

Peclet number for axial heat transport.

Pe_{hr}

Peclet number for radial heat transport.

Pe_{ma}

Peclet number for mass axial transport.

Pe_{mr}

Peclet number for mass radial transport.

Q_{F}

Flowrate (l/min).

Q_M

Measured flowrate (l/min).

R

Reaction rate function (Kmole/hr-Kg.cat).

R_g

Universal Gas Constant (cal/g.mol - °k).

Ro

Reactor tube radius (m).

Re

Reynolds Number (D G/μ).

Re_p

Reynolds Number (Dp G/μ).

S_{MAA}

Reaction selectivity to Maleic Anhydride (moles MAA Produced/moles Benzene converted).

S_b

Statistical Variance of b.

S_x

Statistical variance of x.

S_x/y

Statistical variance of x on y.

T

Bulk fluid temperature (°C).

T_A

Ambient temperature (°C).

T_w

Temperature at external reactor wall (°C).

T_R

Reaction Temperature (°C).

U

Reactor overall heat transfer coefficient (Kcal/hr - m² - °C).

V_R

Reactor Volume (cm³).

W

Catalyst weight (g).

X_B

Benzene fractional Conversion (1 - (B_o/B_I)).
Maleic Anhydride fractional Conversion \( (1 - \frac{\text{MAA}_o}{\text{MAA}_{in}}) \).

Distance along the reactor axis (m).

Parameters in the Kunii and Smith equation, page 214.

Bed voidage.

Packing density \( (\text{Kg/m}^3) \).

Catalyst bulk density \( (\text{Kg/m}^3) \).

Fraction of catalyst in oxidised state.

Thiele type Modulus, page 188.

Heat of reaction \( (\text{cal/g.mole}) \).

Chromatographic area of peak (inlet).

Chromatographic area of peak (outlet).

Emissivity of solid particles.

Viscosity of fluid \( (\text{Kg/m - hr}) \).

**Suffixes**

- \( i \) in
- \( o \) out