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SELECTIVE OXIDATION OF OLEFINS
IN STIRRED GAS FLUIDISED BEDS

by

EMMANUEL .S. FTENAKIS

A thesis is submitted for the
Degree of Doctor of Philosophy
The City University , London
July , 1979

I dedicate this work
to my family.

ACKNOWLEDGEMENTS

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E. Ftenakis

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SYNOPSIS

Experiments in the temperature range 390°C to 537°C have been carried out for the selective oxidation of propylene to acrolein and isobutylene to methacrolein quantitatively in a laboratory scale, shallow fluidised bed of bismuth-molybdate catalyst (particle size $60\text{--}80\ \mu\text{m}$), and the optimum operating conditions determined. Uniformity of fluidisation was achieved by use of a stirrer within the catalyst bed. The minimum fluidisation velocity was derived and oxidation experiments performed at this, and low superficial gas velocities.

Effects of bubble formation on conversion, selectivity to methacrolein, and yields of the by-products were measured. Kinetics of the reaction and catalyst studies and their part in the reactions were investigated. Carbon and oxygen mass balances were checked in order to determine the experimental error.

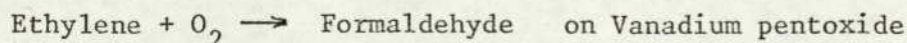
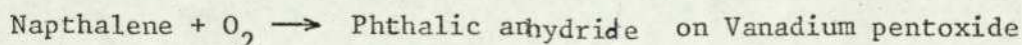
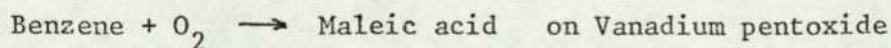
CHAPTER I

INTRODUCTION

Since the second world war industrial organic chemistry has seen two significant changes: completely different base materials have been used, and a large number of new products have been manufactured. Coal tar, the traditional base material, has yielded in importance to fractions derived from petroleum. This means that petrochemistry has become the most important part of industrial chemistry. The consumption of petroleum oil has increased tremendously during the last two decades (1), this increase being not only due to the use of oil as the main source of energy but also due to the growing demand for its middle distillates.

In this extensive part of industrial chemistry very important intermediates are the hydrocarbon derivatives containing oxygen or other hetero-atoms. The demand for these derivatives is very large and further increase is expected in the future. The oxidation of hydrocarbons by merely burning them is of course undesirable and the homogeneous gas phase oxidation is unfortunately unselective (2,3), and generally gives a complex mixture of molecules.

Only comparatively recently heterogeneous catalytic oxidation enabled the synthesis of new molecules selectively by changing the chemical structure of the hydrocarbons. Reactions leading to the formation of commercially important products include:



Ethylene + O₂ → Acetaldehyde on Vanadium pentoxide

Ethylene + O₂ → Ethylene-oxide on Silver metal

Propylene + O₂ → Formaldehyde on Vanadium pentoxide

Propylene + O₂ → Acrolein on Cuprous oxide

n-Butenes + O₂ → Buta-1,3-diene on Bismuth oxide

Isobutylene + O₂ → Methacrolein on Bismuth oxide

Since the catalytic process includes a number of consecutive elementary steps such as the formation and breaking of bonds in reactant molecules, and electron transfer between the molecules and the solid catalyst, the electronic properties of catalyst surfaces influence the adsorption processes and hence catalytic reactions.

In general, heterogeneous catalysts contain transition metals with open inner electronic shells, which however, do not function in the same way for different types of reaction. The oxidation catalysts, for example, often have an oxide, (MoO₂, Bi₂O₃, CuO Cu₂O), or a pair of these oxides that are readily interconvertible. Furthermore the ideal catalyst for commercial application should be very active, very robust, stable and reproducible.

In the large field of catalytic reactions fluidisation technology has seen numerous successful applications in the last

thirty years. Industrially, it has been found advantageous to use fluidised bed reactors for many solid catalysed reactions. In a fluidised bed a mass of solid particles is made mobile by means of an upward flow of gas or liquid, and the pressure drop through the bed balances its weight. The bed behaves like a fluid and thus the rather uniform agitation within it prevents the occurrence of hot spots and dead regions.

The major disadvantage of a fluidised system is that the catalyst may be broken by its constant motion, so that there is continual attrition of the particles requiring continual make-up of fresh catalyst.

The largest scale industrial application of fluidisation is in the fluid catalytic cracking of gas oil fractions to give gasoline components. During the early part of world-war II, there was a great demand for high octane aviation spirit as a fuel for the piston driven aircraft of the time. In this process by which oil is cracked over a catalyst it, carbon is deposited on the catalyst which soon becomes fouled and has to be regenerated. The techniques of fluidisation provided the means whereby the cracking and regeneration reactions could be carried out, and the problem of transferring the fouled catalyst from the reactor to the regenerator and back could be solved on a scale with the very large throughputs involved.

The fluid cracking process still remains the largest scale application of fluid bed reacting, but fluidised bed reactors have been developed for many other processes including : the Fisher-Tropsch synthesis of hydrocarbons, extraction of oil from

shale and bituminous sand, production of alkyl chloride, and phthalic anhydride by oxidation of naphthalene, and the oxidation of ethylene to ethylene-oxide, which is further used for preparation of ethylene glycol and other organic compounds.

The fluidisation techniques have also been widely used in physical operations such as the transportation of powdered solids, coating of plastic materials on metal surfaces, drying and sizing of powdery material, ore roasting; they provide a more efficient, convenient, and economical way for carrying out these processes over alternative methods.

However, the difficulties inherent in the design of large scale fluidised beds have undoubtedly inhibited their more widespread use, and the expensive failures which have occurred following scale-up from smaller units (4), have caused designers to exercise considerable caution in choosing them for new processes.

In addition, research in the past has given a great deal of important information related to fluidisation phenomena, but the fluidisation field still presents many little understood problems.

The difficulty of understanding these phenomena and their various applications can be attributed to the complex hydrodynamics of solids and fluids, to intrusion of physical phenomena on chemical rate processes in fluidised bed reactors and to complicated geometrical factors associated with fluidised beds.

The greatest problem, however, remains that most of the basic information on fluidisation has been obtained in a rather limited range of conditions, and for very few fluid-particle systems which cannot, generally, be applied in all scale-up situations.

CHAPTER II
LITERATURE SURVEY

CHAPTER II
LITERATURE SURVEY

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II.1 SOLID CATALYSED REACTIONS

In this part we will attempt to classify the reaction steps that are possibly involved when a gas phase chemical reaction actually occurs on the catalyst surface. The determination of the rate of the reaction depends upon the value at which each of these possible steps occurs. Although much effort is concentrated on the development of new catalysts and new catalytic processes the phenomena occurring during a catalytic reaction are not completely understood.

The selection and manufacture of catalysts for specific purposes is largely based on experience and most information remains secret to the manufacturers .

II.1.1 Physical aspects of catalysis

The investigation of catalytic reactions and catalytic processes is normally complicated by the fact that diffusion as well as chemical phenomena are usually involved; the two are not easy to separate so as to determine the factors affecting each.

i. The mass transfer of reactants to the gross exterior surface of the catalyst particles appears to be the first step of all solid catalysed reactions. The rate at which the transfer of reactant molecules to the catalyst surface occurs is determined by the mass velocity of the gas stream, the size of the particles, and the diffusional characteristics of the fluid. Transport normal to the surface is by molecular diffusion. The overall

process of transfer between catalyst and fluid is proportional to D_{lm}^n , where n varies between zero and unity. The diffusion coefficient for species 1 in the mixture is related to the binary coefficients by the general equation:

$$D_{lm} = (1 - Y_1) \left(\sum_{j=2}^n \frac{Y_j}{D_{1j}} \right)^{-1} \quad \text{equation II.1.1}$$

The best method of calculating the diffusion coefficients for binary gas mixtures is from the theoretical equation based on the modern kinetic theory and the Lennard-Jones expression for intermolecular forces (5). This is:

$$D_{12} = \frac{0.001858 T^{3/2} \left[(M_1 + M_2) / M_1 M_2 \right]^{1/2}}{P \sigma_{12}^2 \Omega_d} \quad \text{equation II.1.2}$$

where D_{12} is the diffusion coefficient for a binary mixture of gases 1 and 2.

T is the absolute temperature.

P is the total pressure.

M_1 is the molecular weight of gas 1

M_2 is the molecular weight of gas 2

Ω_d is the "collision integral" and is a function of KT/ϵ_{12}

ϵ_{12} , σ_{12} are the force constants in the Lennard-Jones potential function

Values of σ and ϵ , are usually obtained from viscosity data but where they are not reported they can be estimated by the empirical equations listed below:

$$\sigma_{12} = 1/2 (\sigma_1 + \sigma_2) \quad \text{equation II.1.3}$$

$$\sigma = 1.18 V_B^{1/3} \quad \text{equation II.1.4}$$

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2} \quad \text{equation II.1.5}$$

$$KT/\epsilon_{12} = KT/(\epsilon_1 \epsilon_2)^{1/2} \quad \text{equation II.1.6}$$

$$KT/\epsilon_1 = 1.30 T/T_c \quad \text{equation II.1.7}$$

where V_B is the molar volume at the normal boiling temperature.

K is the Boltzmann constant.

T_c is the critical temperature of gas 1.

For very fast reactions, it is possible that the overall rate may become limited by the rate of mass transfer to the surface. Wheeler (6,7), suggested that equation II.1.8 gives the first order constant K for external diffusion to the catalyst surface in a flow system where all the gases have the same viscosity and Schmidt number:

$$K_{\infty} = 10 (V_1 / \bar{M} a^3 P_t)^{1/2} \text{ sec}^{-1} \quad \text{equation II.1.8}$$

ii. When the catalyst is mostly porous and when the reaction takes place at interior interfaces, the degree of porosity of the catalyst, the dimensions of the pores, the size of the particles, and the diffusional characteristics will determine the rate at which the diffusional and flow transfer of the reactants in

the pore structure of the particle occur.

For catalyst particles with large pores the diffusion of liquids or relatively dense gases will fall in the category of bulk-diffusion. The bulk-diffusion coefficient per unit cross section of porous mass, $D_{12,eff}$, is given by the expression:

$$D_{12,eff} = D_{12} \theta / \tau \quad \text{equation II.1.9}$$

On the other hand if the gas density is low, and the catalyst pores very small, the molecules collide with the pore wall much more frequently than with each other. This type of diffusion is known as "Knudsen diffusion". The molecules hitting the wall are momentarily adsorbed and then given off in random directions. The gas flux is reduced by the wall "resistance" which causes a delay because of both the diffuse reflection and the finite time the molecule is adsorbed. Knudsen diffusion is not observed in liquids. The kinetic theory provides a relation for the Knudsen diffusion in gases in a straight round pore:

$$D_K = 9700 \tau_e (T/M)^{1/2} \quad \text{equation II.1.10}$$

In this equation τ_e is the pores in cm, T is the absolute temperature, and M is the molecular weight. The symbols refer to a single component; since molecular collisions are negligible, flow and diffusion are synonymous and each component of a mixture behaves as though it alone were present.

iii. The adsorption of reactants on the catalyst interface

will depend upon the characteristics of the catalyst surface, the extent of the surface and the specific catalytic activity of the various catalytic systems.

iv. The surface reaction of the adsorbed molecules will be determined by the activation energies required for the reaction on the surface and the nature of the catalyst surface.

v. Finally during all solid catalysed reactions the formation of adsorbed products will be followed by diffusional transfer of the products out of the pore structure of the catalyst particle and then mass transfer of the products away from the catalyst surface.

II.1.2 Adsorption

Although contact catalysis offers many practical advantages over homogeneous catalysis, its theoretical treatment was presented only recently. The basic reason lies in the fact that even though much was known about the active centres of the surface of solid catalysts, the role of these centres during adsorption has been explained only recently. In general, heterogeneous catalysis could include reactions proceeding at a variety of interfaces; however, the most interesting are those between gases and solids.

The first theory which attempted to explain the phenomena of heterogeneous catalysis was the theory of the intermediate compound. This proposed that the reaction takes place between the bulk solid and a reactant to form an intermediate compound which decomposed, or reacted to give the products of the main reaction and to regenerate the catalyst.

At the same time Faraday (8) and Mitcherlich (9) developed theories to explain the action of heterogeneous catalysts during a catalytic reaction.

The big change, however, came when Langmuir (10) first reported that hydrogen adsorption on the surface of metal wires involves a chemical reaction in which strong bonds are formed and the molecule which is adsorbed is dissociated. This type of adsorption was named chemisorption to distinguish it from physical adsorption. However, a clear distinction between them is rather difficult for some intermediate cases. With his two latest papers (11,12), Langmuir in 1916 applied a simple kinetic treatment to adsorption equilibria. He considered the adsorption of molecules without and with dissociation on crystal surfaces. When the adsorption occurs without dissociation, Langmuir supposed that on the surface of the crystal there is a definite number of sites capable of holding adsorbed gas molecules. If each site can adsorb just one molecule, a number of molecules greater than the number of sites can only be adsorbed by the formation of additional layers of molecules. Langmuir's conception of the chemisorption of molecules or atoms in monolayers led to the derivation of simple isotherms, connecting the fraction of the surface occupied with the pressure of the gas being adsorbed. The expression for equilibrium is:

$$\theta_A = b P_A / (1 + b P_A) \quad \text{equation II.1.11}$$

Where θ_A is the fraction of sites occupied by gas A

$b = a'K / v_1$ is the adsorption coefficient

P_A is the pressure of adsorbed gas A

When molecular adsorption occurs on crystal surfaces with dissociation, the above expression takes the different form:

$$\theta_A = (\alpha' P_A)^{1/2} / 1 + (\alpha' P_A)^{1/2} \quad \text{equation II.1.12}$$

Where $\alpha' = a' K / v_2$

This equation is applicable for a dissociative chemisorption in which two similar fragments are formed. However, recent statistical studies showed that the number of neighbouring sites around a given site need re-consideration (13,14), and hence Langmuir's equation should be slightly modified.

II.1.3 Kinetics

In general, the rate of heterogeneous catalytic reactions involving gases is often controlled by the reaction of the adsorbed molecules, and not by the adsorption/desorption processes. Relations between reaction rates and gas pressures were devised with the help of mechanisms which regarded a reaction step within the surface as the rate controlling step.

These mechanisms have become known as Langmuir-Hinshelwood mechanisms, and are generally based on the conception that for two molecules A and B to react they should be adsorbed on adjacent sites.

Thirty years later, Hougen and Watson (15), devised rate equations for gas adsorption based on Langmuir's theory relating the rate of reaction with the gas phase pressure of the reactants, assuming that the rate determining step is the surface reaction of

the molecules. Bearing this in mind the rate for an unimolecular decomposition reaction, $A \longrightarrow B$ taking place on the surface of the catalyst is:

$$-dP_A/dt = K_1 K_A P_A / (1 + K_A P_A + K_B P_B) \quad \text{equation II.1.13}$$

Various modifications, depending on the relative values of the terms in the denominator of the above expression can be applied.

If both the reactant A and the product B are weakly adsorbed the general equation becomes:

$$-dP_A/dt = K_1 K_A P_A \quad \text{equation II.1.14}$$

and the reaction kinetics are similar to those of a first order gaseous reaction.

If the reactant is adsorbed strongly, and the product rather weakly, the rate of the reaction will be given by:

$$-dP_A/dt = K_A P_A / (1 + K_A P_A) \quad \text{equation II.1.15}$$

and may well be first or zero order at low and high pressures, respectively.

In the case when the product is fairly strongly adsorbed and the reactant weakly, the rate will be proportional to either $K_1'' P_A K_A / P_B K_B$ or $K_1'' P_A K_A / (1 + P_B K_B)$.

II.2 OXIDATION OF PROPYLENE TO ACROLEIN

The succesful production of acrolein catalytically over cuprous oxide was discovered by Hearne and Adams(16) in the 1940's and subsequently used commercially by Shell Chemical company. However, the heterogeneous oxidation of olefins really started with the discovery of bismuth molybdate as an oxidation catalyst. Before this time acrolein has been produced by several different methods. In 1836 Hefs(17) and Redtenbacher(18), first isolated acrolein during the dry distillation of fats, and reported the presence of a highly toxic aldehyde. More recently aldol condensation of acetaldehyde and formaldehyde in the presence of "dehydrating catalysts", or the noncatalytic pyrolysis of diallyl-ether were used for its industrial preparation. Since the 1940's a number of different catalysts have been developed for its production.

Cuprous oxide used by Shell(19), bismuth-molybdate or phosphomolybdate(20) by Standard Oil of Ohio, and combinations of tin and antimony oxides by Distillers Company Limited.

Although many different types of catalysts can be used for this selective oxidation, the choice of the catalyst (type and composition), and reaction conditions (temperature, olefin/oxygen ratio, contact time, e t c) influence directly the reaction route of the end products. The oxidation of propylene will result mainly in acrolein, acrylic acid, acetone, propene oxide and carbon oxides, while the ammonoxidation will produce acrylonitrile as the main product.

In 1967 Rubanic and co-workers(21) studied extensively the specific catalytic activities of SnO_2 , Bi_2O_3 , Sb_2O_4 , MoO_3 , and their binary mixtures in the oxidation of propylene, and elucidated the relationship between the catalytic properties of the individual oxides and their mixtures.

The catalysts were prepared from their hydroxides by precipitation with ammonia, dried at 90°C , and then were converted by calcination in air into the corresponding oxides. The calcination was achieved when the temperature was raised from ambient temperature to 600°C over 2 hr and kept at this temperature for almost 2 hr. The tin and antimony hydroxides were calcinated additionally after this treatment for a further 2 hr at 1050°C , with the temperature previously raised from 600°C to 1050°C over 3 hr. The determination of the catalytic activity was carried out in the kinetic region. Propylene was oxidised in the temperature range $380^\circ\text{C} - 480^\circ\text{C}$, and conversions, selectivities and yields of the various products were reported.

The results obtained are summarised in figures II.2.a , II.2.b , II.2.c , II.2.d and II.2.e , where the specific rates of product formation, and selectivities towards the main product are given as functions of the composition of the catalyst. From these results it was proposed that the optimum binary oxide systems (those possessing a maximum activity with respect to the main products obtained) at 450°C fall into the sequences given in table II.2.a , of decreasing specific activity and selectivity.

They finally concluded that the most active and selective

Figure II.2.a Specific rates of formation of 1) acrolein 2) CO_2 3) acids and 4) CO at 400°C as functions of the atomic ratio of tin to molybdenum.

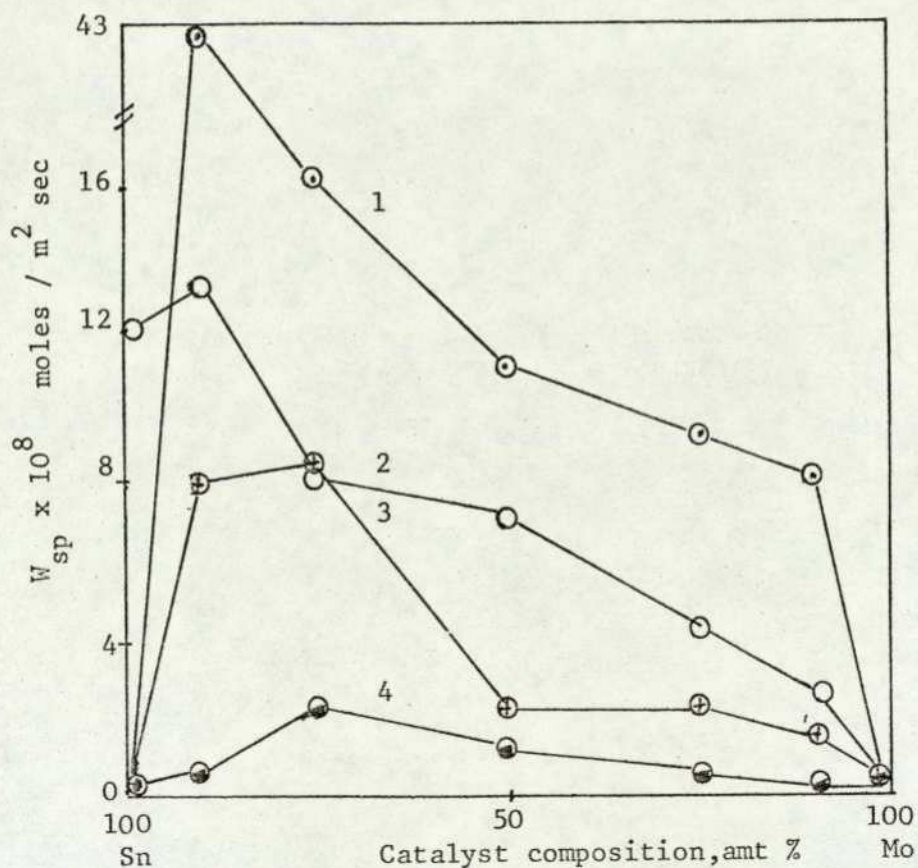


Figure II. 2 b Selectivity of the conversion of propylene into 1) acrolein and 2) acids as functions of the composition of tin-molybdenum oxide catalysts.

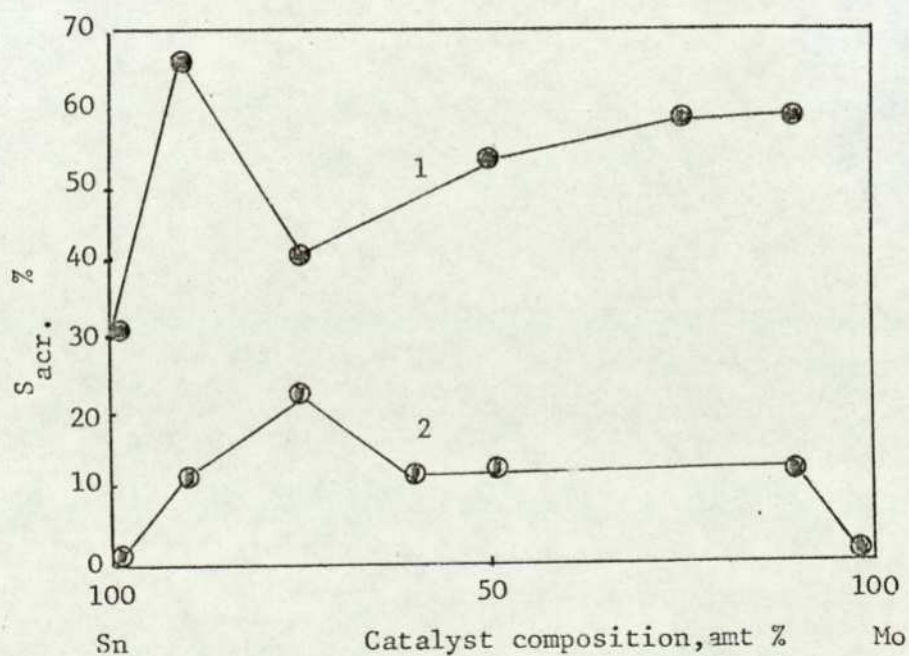


Figure II.2.c Specific rates of formation of 1) acrolein 2) CO_2 3) the selectivity of the conversion to acrolein as functions of the atomic ratio of Sn to Sb

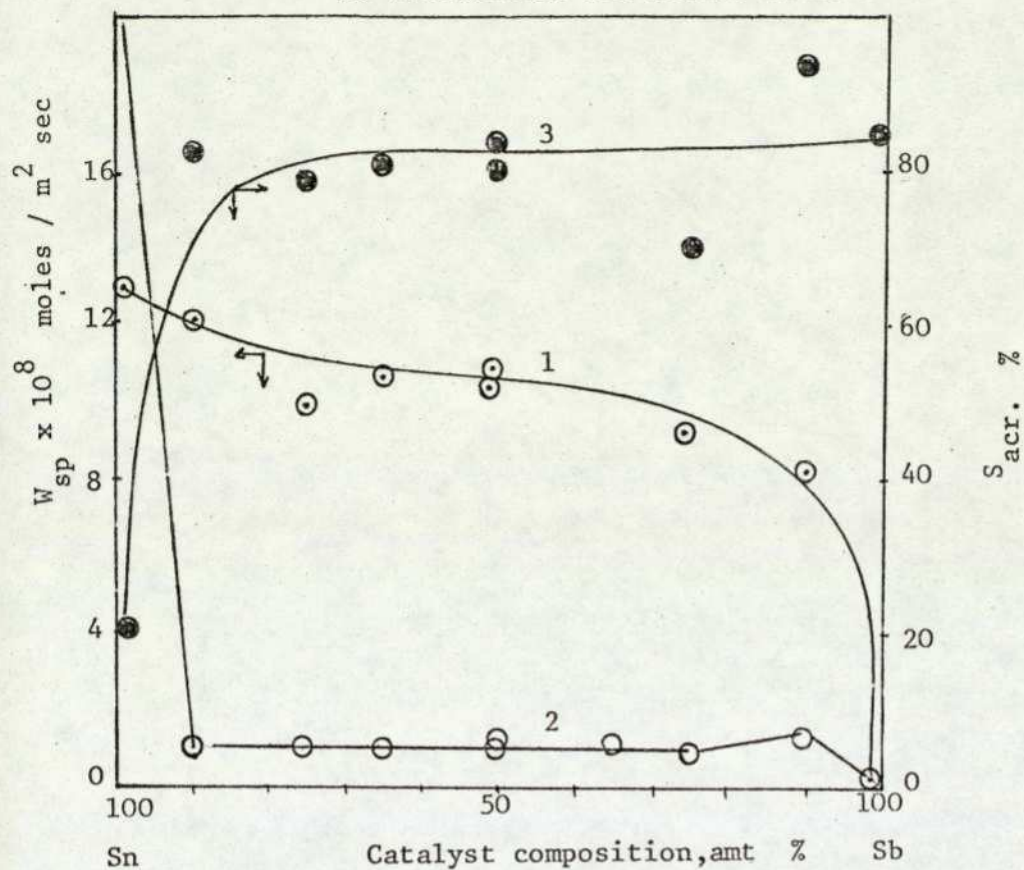


Figure II.2.d Specific rates of formation of 1) acrolein 2) CO_2 3) the selectivity of the conversion to acrolein as functions of the atomic ratio of Sb to Mo

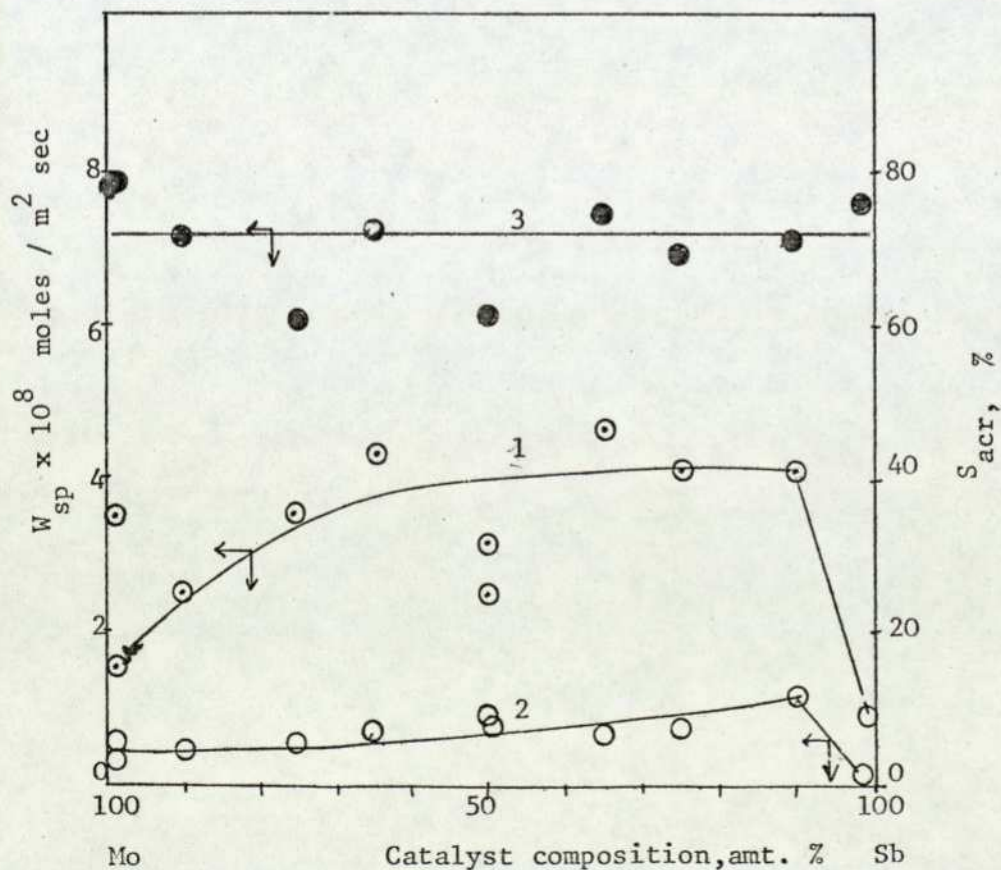


Figure II.2.e Specific rates of formation of 1)acrolein 2) CO_2
 3)the selectivity of the conversion to acrolein
 as functions of the atomic ratio of Sb to Bi

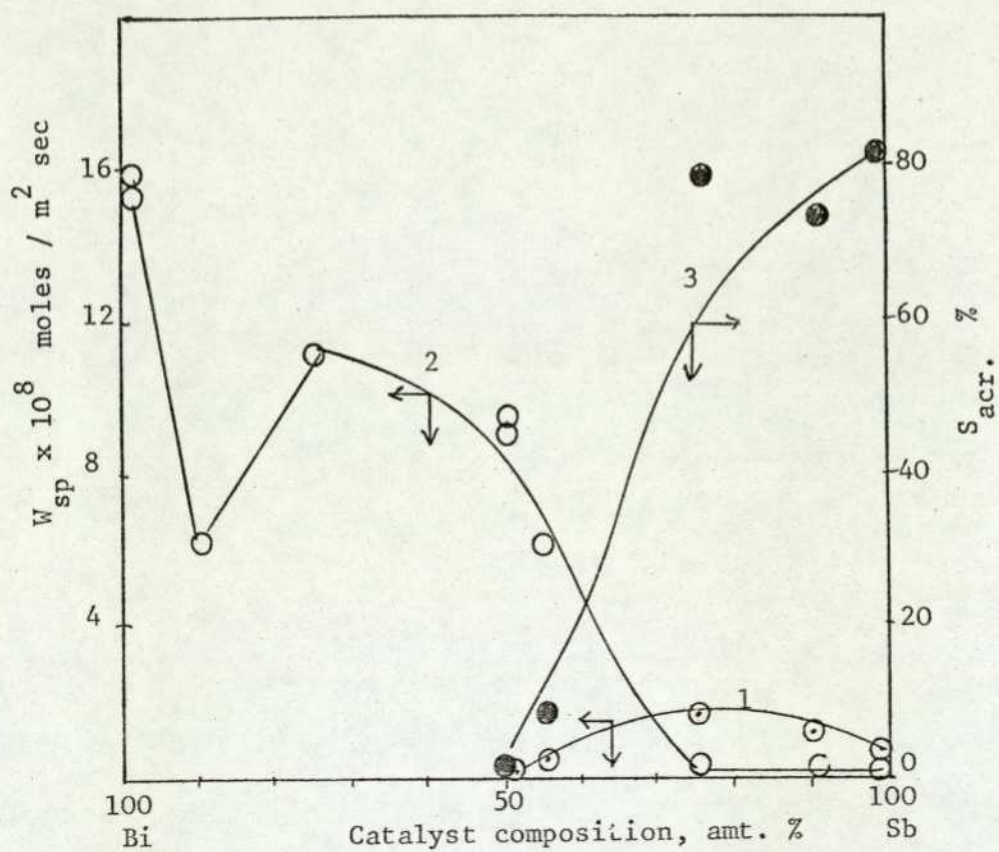


Table II.2.a Classification of catalysts by Rubanic (21)

With respect to the specific rate of propene consumption		With respect to the selectivity in the formation of products of incomplete oxidation	
CATALYST	$W \times 10^7$ moles/m ² sec	CATALYST	S %
Bi:Mo (1:1)	21.64	Bi:Mo (1:1)	94
Sn:Mo (9:1)	12.55	Sn:Sb (9:1)	94
SnO ₂	6.80	MoO ₃	87
Bi:Sn (1:1)	2.26	Mo:Sb (0.54:1)	86
[Bi ₂ O ₃	1.65	Sb ₂ O ₄	85
Sn:Sb (9:1)	1.41	Bi:Sb (0.33:1)	81
[Bi:Sb (3:1)	1.14	Sn:Mo (9:1)	79
[Mo:Sb (0.54:1)	0.64	SnO ₂	26
[MoO ₃	0.46	Bi:Sn (1:1)	7
Bi:Sb (0.33:1)	0.24	Bi:Sb (3:1)	0
Sb ₂ O ₄	0.13	Bi ₂ O ₃	0

mixed catalysts, the bismuth-molybdenum, tin-antimony, and tin-molybdenum are obtained by combining an active nonselective oxide with a selective oxide of low activity. The combination of two non-selective oxides (bismuth oxide and tin oxide) leads to a catalyst with low selectivity. Additionally combination of two selective oxides of low activity (antimony oxide and molybdenum oxide) gives a selective catalyst but one still with a low activity.

II.2.1 Cuprous oxide catalysts

The production of unsaturated aldehydes and ketones from $C_3 - C_6$ olefins started with the use of cuprous oxide catalyst by the Shell Chemical Company in the 1940's . However, product selectivity over copper catalyst is strongly dependent on the operating conditions.

Isaev and co-workers(1), and Popova and Vermell(2), have reported that the selectively active form of a copper catalyst appears to be a surface condition which leads to cuprous oxide in the bulk form. The steady-state condition of the catalyst may be changed easily due to reaction or oxidation at the temperatures in the range $300^{\circ}C$ to $400^{\circ}C$.

Shapovalova et al(3) reported that during the partial oxidation of olefins, change from one olefin to another causes changes in the catalyst steady-state condition to occur readily, thus it is not easy to obtain reliable data on selectivities, kinetics e t c. That the reaction could be contrasted with thermal vapor phase oxidation of propylene at $330^{\circ}C - 400^{\circ}C$ was investigated by Kamiya(21,22) in 1962 . It was reported that during the oxidation

of propylene over cuprous oxide catalyst at 12.8 % conversion the composition of the products was:

34 % acetaldehyde
24 % propene-oxide
12 % acrolein
5 % allyl-alcohol

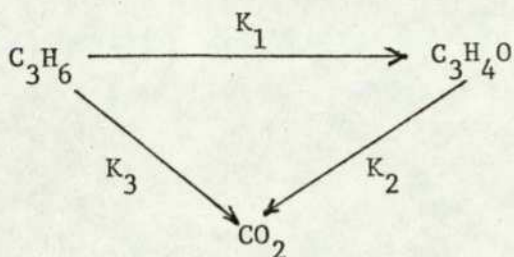
with the main product being carbon dioxide. He deduced that the catalyst is of crucial importance in making acrolein selectively.

In 1966 Ghorokhovatskii et al(23) attempted to identify the active phase in a selective copper oxide catalyst, and they suggested that selective catalysts were composed mainly of copper oxide or copper oxide plus copper metal.

Modified catalysts using a number of electronegative elements have been reported(24,25,26) to give higher yields of acrolein over the un-modified copper oxide catalyst. A highly selective catalyst was obtained by the use of SeO_2 in large amounts; however, introduction of a small amount of Mo and W has been reported by Russian workers(27,28) to have beneficial effects on catalyst selectivity.

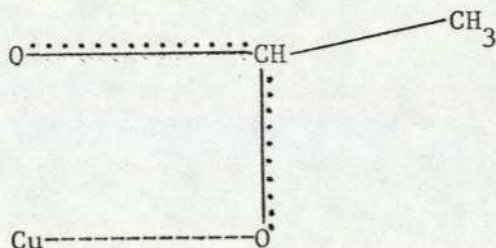
A. Mechanism

Earlier work(29) has shown that oxidation of propylene over copper oxide catalyst can be well described by a combination of parallel and consecutive reactions:

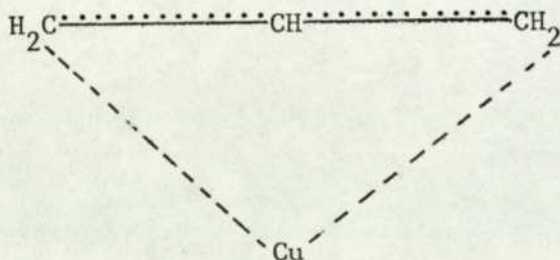


The rate determining step for K_1 is the abstraction of an allylic hydrogen from the olefin(30), which is followed by the formation of a π -bonded allylic surface intermediate(31,32).

In support, Zhdanova and co-workers(33) used i.r spectroscopy to study the chemisorption of propylene on cuprous oxide supported on high surface area ($200 \text{ m}^2 / \text{g}$) alumina. Two types of surface intermediates were found, one with adsorption corresponding to those of copper acetate

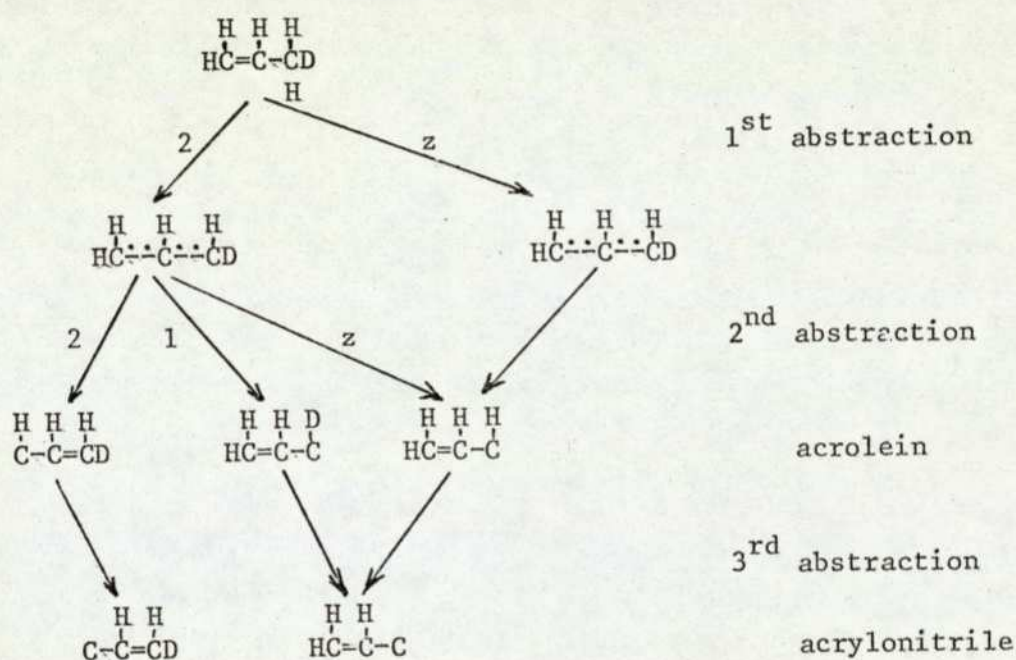


which was decomposed to give carbon dioxide and another compound of the type



which then gave acrolein.

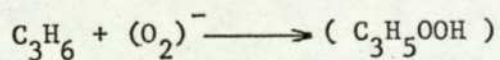
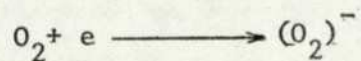
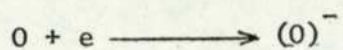
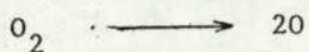
Confirmation and extension of this mechanism was reported by Adams and Jennings(32,34) using propylene labelled with deuterium in various positions. The following model which assumes that allylic hydrogen abstraction occurs to form an allylic intermediate followed by hydrogen abstraction from either end was in quantitative agreement with their results.



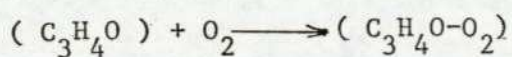
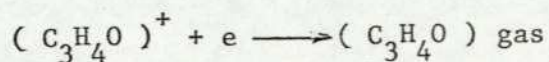
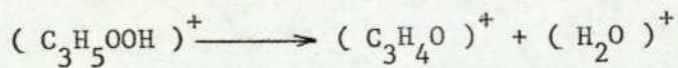
Here the numbers show the relative probability of the preceding species reacting along the indicated path, where z is the discrimination isotope effect (K_D / K_H) related to the probability of breaking a carbon-deuterium bond relative to that of breaking a carbon-hydrogen bond under the same conditions.

On the other hand, Margolis(35) has reported a different mechanism for propylene oxidation from that proposed by Adams and Jennings. He postulated an allyl hydroperoxide, $\text{C}_3\text{H}_5\text{OOH}$, as an intermediate. His following mechanism does not allow for

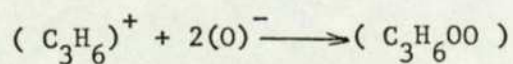
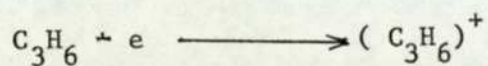
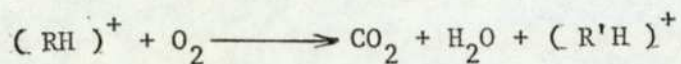
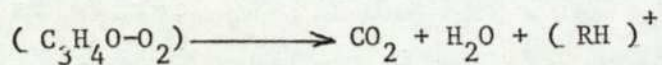
a symmetrical intermediate, nor for the required abstraction of two hydrogens before the symmetry is destroyed.



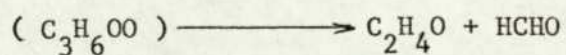
charged complex 1



charged complex 2



charged complex 3





B. Kinetics

Although many attempts have been made to elucidate the kinetics of the oxidation of propylene over cuprous oxide it has been proved difficult to obtain reliable kinetic data, due to the large exothermicity of the reaction, the changing character of the catalyst, and the pronounced inhibition of the reaction by the products.

Popova and Ghorokhovatskii(36,37) in 1964 examined the effect of steam during the oxidation of propylene. They have reported that at high steam concentrations (amounts up to 60 % of the feed mixture) the rate is approximately first order in olefin as well as in oxygen. The presence of water vapour has an inhibiting effect on both acrolein and carbon dioxide production rates. The rate equations proposed were:

$$\frac{d[C_3H_6O]}{dt} = \frac{K_1 [O_2]^{0.8} [C_3H_6] (1 + [H_2O]^{0.5})}{(1 + b' [C_3H_6O]) (1 + b_1 [H_2O])} \quad \text{equation II.2.1}$$

and

$$\frac{d[CO_2]}{dt} = \frac{K_2 [O_2] [C_3H_6]}{(1 + b'' [C_3H_6O]) (1 + b_2 [H_2O])} \quad \text{equation II.2.2}$$

In an earlier publication Isaev and Margolis(38) concluded that acrolein and carbon dioxide formation rates are proportional to oxygen concentration in the gas phase and independent of olefin and acrolein concentrations. They also suggested that carbon

dioxide is formed completely by post-oxidation of acrolein. In support of those workers Belousov et al(39) found that reaction rates could be described by:

$$\frac{d[C_3H_4O]}{dt} = \frac{K_1 [O_2]}{1 + b [Products]} \quad \text{equation II.2.3}$$

$$\frac{d[CO_2]}{dt} = \frac{K_2 [O_2]}{[C_3H_4O]^{0.7} [C_3H_6]^{0.2}} \quad \text{equation II.2.4}$$

On the other hand, Billingsley and Holland(40) studied the same reaction using a differential reactor at 240 °C. They reported that the reaction was limited by oxygen mass transfer. and proposed the following equations:

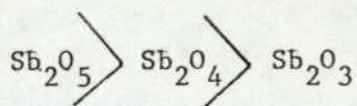
$$\frac{d[C_3H_4O]}{dt} = \frac{0.72K [C_3H_6] [O_2]}{0.72 [C_3H_6] + 4.5 [O_2]} \quad \text{equation II.2.5}$$

$$\frac{d[CO_2]}{dt} = \frac{3K [O_2]^2}{0.72 [C_3H_6] + 4.5 [O_2]} \quad \text{equation II.2.6}$$

II. 2.2 Tin oxide-Antimony oxide catalysts

Commercially, tin oxide and antimony oxide catalysts were developed by Hadley and co-workers (41,42,43,44) for the oxidation and ammonoxidation of propene and the oxidative dehydrogenation of butenes to butadiene. There is a considerable literature devoted to the investigation of the catalytic properties of tin and antimony oxides of various compositions in the oxidation of olefins.

For example, Belousov and Gershingorina (45) studied the catalytic properties of the following oxides; Sb_2O_5 , Sb_2O_4 , Sb_2O_3 , SnO_2 , and SnO . Their results showed that the catalytic activity of oxide catalysts, the selectivity of the process taking place on them, the quantitative composition of the reaction products, and the temperature at which the maximum quantity of strongly chemisorbed propylene is attained all depend on the valency of the cations of the oxide catalysts. The oxides were placed in the following order of decreasing catalytic activity.



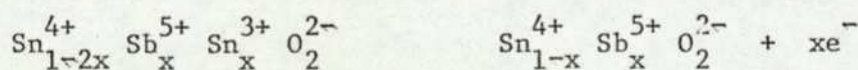
At low temperatures Sb_2O_5 was found more active than SnO_2 . Between the tin oxides, SnO was proved to be a more selective catalyst than SnO_2 but it was concluded that the catalytic properties of tin-antimony oxide catalysts are determined by the presence in them of the Sb^{5+} cation. Thus the presence of Sb^{5+} and Sb^{3+} leads to the formation of acids, Sb_2O_5 favours the formation of propionaldehyde, and although acrolein is formed in the presence of all oxides it was observed with Sb_2O_4 only at high temperatures.

In 1968 Godin et al (46) studied the air oxidation of propylene over tin-antimony oxide catalysts. The activation energies for propylene oxidation over various catalyst compositions were obtained and those are summarised in table II.2.b.

Table II.2.b Activation energies for various catalyst compositions (46)

Catalyst composn. (atom % Sb)	E _A (Kcal/mole)
6.8	12.2
21.4	16.3
50.0	17.1
78.6	13.1
93.7	13.0

They also reported that the addition of only 6.8 % Sb to SnO₂ increased the conductivity by three orders of magnitude to give a semiconductor with a very low temperature coefficient. This was explained by a mechanism which assumes that Sb⁵⁺ substitutes the Sn⁴⁺ ions in the SnO₂ lattice, creating firstly Sn³⁺ cations which act as electron donors thereby giving free electrons, and a rise in conductivity.

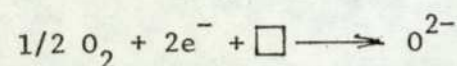
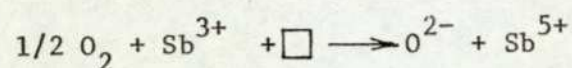
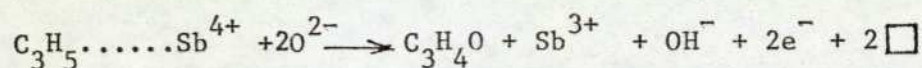
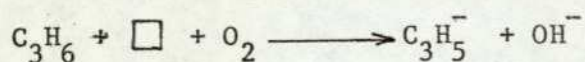


Margolis and co-workers (47) studied in detail the chemisorption of propylene and oxygen on SnO₂ and Sb₂O₄, aiming to elucidate the changes in electron work function, and electrical conductivity. At 200 °C they reported that propylene and oxygen are rapidly adsorbed on both surfaces. Adsorption of propylene on SnO₂ having already irreversibly adsorbed oxygen on its surface yields a surface complex having a negative charge

and containing an excess of oxygen over carbon. However, the adsorption on tin-antimony oxide mixtures yielded a surface complex with a positive charge and contained an excess of carbon relative to oxygen.

A. Mechanism

Studies using ^{13}C -labelled propylene have shown that the oxidation mechanism of propylene over tin-antimony oxide catalysts is similar to that over bismuth molybdate catalysts (46). The mechanism postulated involves the formation of a π -allyl species and can be described by:



where $\square$ = anion vacancy

Further evidence that the oxidation mechanism of propylene over tin-antimony oxides is similar to that over bismuth molybdate catalysts, involving a chemisorbed allylic intermediate formed through an allylic hydrogen abstraction from propylene, is given by many experimentalists (31,48,49,50,51,52).

In 1975 Pendleton and Taylor (53) used a static reaction

system to study the oxidation of propylene over tin-antimony oxides catalyst. The oxidation experiments were carried out in the temperature range $350^{\circ}\text{C} - 400^{\circ}\text{C}$, using isotopic oxygen containing 95 % $^{18}\text{O}_2$.

The percentage $\left[\begin{smallmatrix} 16 \\ 0 \end{smallmatrix} \right]$ acrolein content in the total acrolein formed was determined as shown in figure II.2.f.

It can be seen at the initiation of the reaction when the lattice contains no $^{18}\text{O}^{2-}$ anions, mainly $\left[\begin{smallmatrix} 16 \\ 0 \end{smallmatrix} \right]$ acrolein is formed, and the lattice is obviously the direct source of the oxygen in the aldehyde. As the reaction proceeds, reduction of the catalyst is followed by re-oxidation with $^{18}\text{O}_2$, and therefore the percentage of $\left[\begin{smallmatrix} 16 \\ 0 \end{smallmatrix} \right]$ acrolein decreases. Similar curves which, however, do not extrapolate to 100 % at zero conversions were obtained for the formation of carbon dioxide and given in figure II.2.g.

In agreement Cartlidge, Mc Grath, and Wilson (54) reported that during the oxidation of propylene to acrolein over tin-antimony oxides catalysts, the kinetic model which assumed that reactant molecules do not compete for active sites best correlates their experimental data. This suggests that chemisorbed oxygen does not directly oxidise adsorbed propylene.

B. Kinetics

It appears that the kinetics of propylene oxidation over bismuth molybdate and tin-antimony oxides catalysts are very similar. The order of the reaction with respect to olefin is first order, but there is also a dependence on oxygen. This has been postulated by Belousov and Gerghingorina (55) recently. The possible participation of lattice oxygen in propylene oxidation over $\text{Sb}_2\text{O}_5 / \text{SnO}_2$ and $\text{Sb}_2\text{O}_3 / \text{SnO}_2$ oxide catalysts was also examined but no evidence found to support this idea.

Figure II.2.f Percent $[^{16}\text{O}]$ acrolein in total acrolein formed in propylene + ^{18}O reaction on Sn:Sb (1:3) catalyst ($T = 623^\circ\text{K}$)

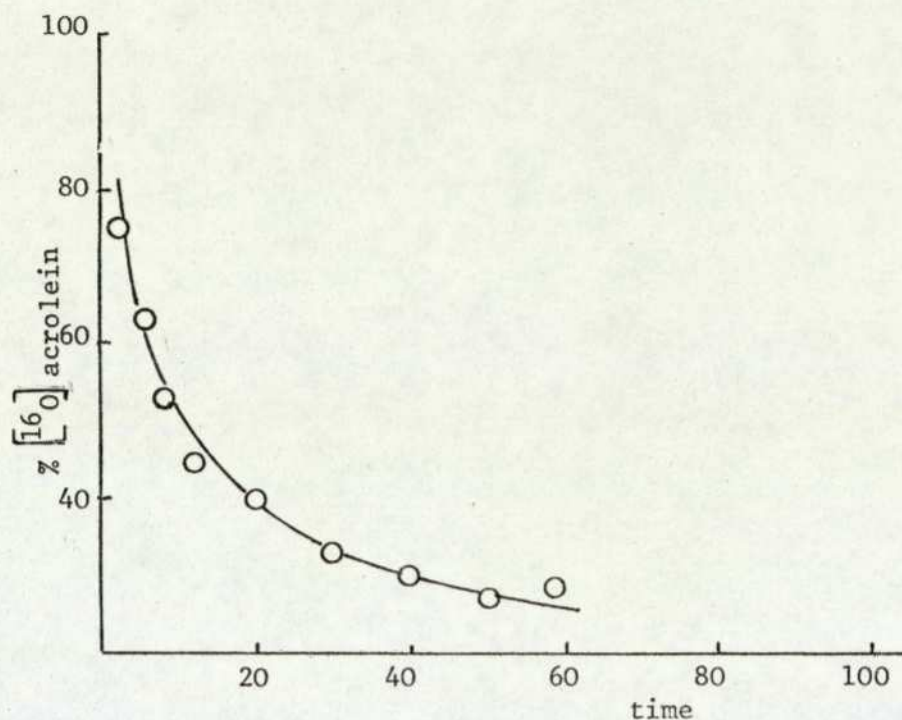
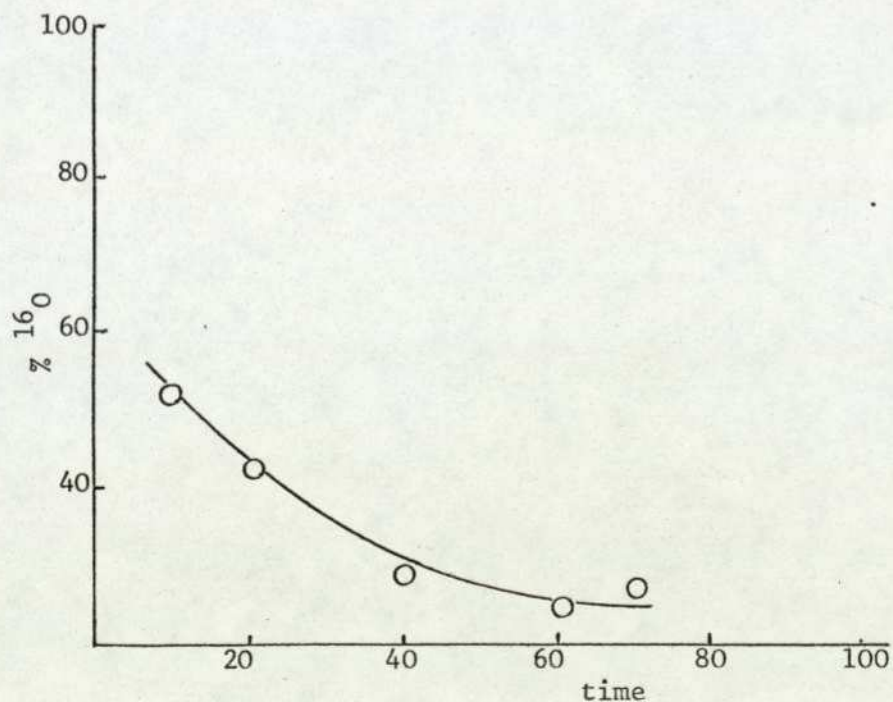


Figure II.2.g Percent ^{16}O in oxygen of CO_2 formed in propene + ^{18}O reaction on Sn:Sb (1:3) catalyst. ($T = 623^\circ\text{K}$)



Recently Cartlidge et al (54) have derived a model for the catalytic oxidation of propylene over tin-antimony oxides catalyst. The catalyst used was prepared by converting tin and antimony metals into oxides, mixing the oxides in the atomic ratio $\text{Sb}:\text{Sn} = 4:1$ and then calcining at 900°C . The experimental conversion data were fitted by means of a non-linear least squares procedure to several models based on Langmuir isotherms. The preferred model is given by the equation II.2.7

$$\frac{d[\text{C}_3\text{H}_4\text{O}]}{dt} = \frac{K K_{\text{C}_3\text{H}_6} K_{\text{O}_2} [\text{C}_3\text{H}_6] [\text{O}_2]}{(1 + K_{\text{C}_3\text{H}_6} [\text{C}_3\text{H}_6]) (1 + K_{\text{O}_2} [\text{O}_2])} \quad \text{equation II.2.7}$$

For its derivation it was assumed that there are two types of active sites, one with an affinity for propylene only and the other for oxygen only. It again assumes that each adsorbed molecule occupies only one active site, and thus the reactants do not compete for active sites. The degree of surface coverage with oxygen varied both with temperature and catalyst age.

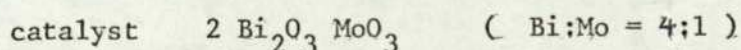
II.2.3 Bismuth Molybdate catalysts

Bismuth molybdate catalysts have a very high activity and produce acrolein with great selectivity with or without the presence of oxygen. Other products which are formed include carbon dioxide, carbon monoxide, acetaldehyde, formaldehyde and smaller amounts of propionaldehyde, propionic acid, formic acid and acetic acid.

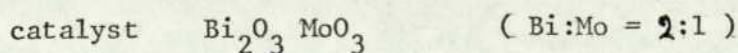
Adams (56) reported that propylene oxidation over bismuth

molybdate catalysts shows high selectivity towards the main product at conversion levels as high as 80 %. Addition of steam or hydrogen in the feed mixture had no effect on activity or selectivity of the catalyst.

The excellent catalytic properties of bismuth molybdate have been investigated in detail by Lippens and co-workers (57, 58,59). Earlier work (60,61) had indicated no connection between the presence of the two oxides separately on the catalytic activity, and this initiated a search for an explanation based upon the structural chemistry of the catalysts. Results from x-ray analysis, i.r. spectra and reflection spectroscopy suggested that the superior catalytic activity of the compounds $\text{Bi}_2\text{O}_3\cdot 2\text{MoO}_3$ and $\text{Bi}_2\text{O}_3\cdot \text{MoO}_3$ is connected to the presence of corner sharing Mo--O octahedra in the bulk of the solid, that give rise to tetragonal pyramidal Mo--O sites at the surface also sharing only corners with neighbors. The promoting influence of Bi_2O_3 , then reported, might also arise because of forcing this structure on the MoO_3 component. Thus if the $(\text{Bi}_2\text{O}_2)_n^{2+}$ layer is named the B-layer, and the $(\text{MoO}_2)_n^{2-}$ A-layer, the structure of bismuth molybdate catalysts may be schematically represented;



B O B O A O B O B O A O



B O A O B O A O B O A O

catalyst $\text{Bi}_2\text{O}_3 \cdot 2 \text{MoO}_3$ (Bi:Mo = 1:1)

B O A O A O B O A O A O

In compounds which are rich in molybdenum, ($\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3$, and $\text{Bi}_2\text{O}_3 \cdot 2 \text{MoO}_3$), the terminal oxygen will occupy the edges of A-layers. The presence of some O^{2-} ions will lead to some of the boundary molybdenum ions being present in a tetragonally pyramidal configuration, and this was suggested to be the active site. The absence of anion vacancies connected to molybdenum in the bismuth-rich compounds lowers the catalytic activity as the catalyst would show the type of activity associated with Bi_2O_3 .

A. Mechanism.

An excellent study on the mechanism of the vapour-phase oxidation of propylene to acrolein was made by Mc Gain and co-workers (62) in 1963. $1\text{-}^{13}\text{C}$ -propene-1 was oxidised over bismuth-molybdate catalyst in a closed system. The i.r spectra of the recovered propylene was used to determine the percentage ^{13}C on the methylene group, thus giving the extent of double-bond migration which had occurred. The position of the carbon-13 in the acrolein product was determined by mass spectrometer.

From their results given in table II.2.c, it can be seen that although the recovered propylene was only partially isomerised at 448°C , being 84 % $^{13}\text{CH}_2=\text{CH}-\text{CH}_3$ and 16 % $\text{CH}_2=\text{CH}-^{13}\text{CH}_3$, however under all reaction conditions the ratio $\text{CH}_2=\text{CH}-^{13}\text{CHO}$ / total ^{13}C -acrolein is 0.5. This result means that at about 450°C the isomerisation of acrolein is not due to a prior iso-

Table II.2.c Oxidation of 1-¹³C-propene-1 (62)

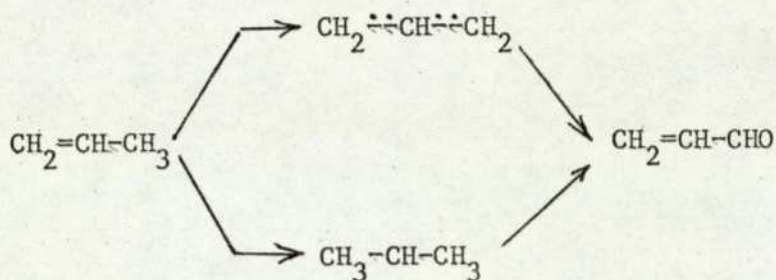
Moles reactants x 10 ³		Tempera- ture °C	Contact time sec	Labelling of products		
				Recovered propene		Acrolein
Propene	Oxygen			% ¹³ CH ₂ =CH-CH ₃	% CH=CH- ¹³ CH ₃	Ratio CH ₂ =CH- ¹³ CH ₃ Total ¹³ C acr
0.22	0.22	448	0.4	84	16	0.53
0.22	0.29	450	1.1	75	25	0.52
0.25	0.31	450	1.3	73	27	0.48
0.21	0.21	448	3.2			0.51
0.45	0.21	250	101	53	47	
0.22	0.21	251	217			0.51

Table II.2.d Oxidation of propene by a deuterated catalyst
at 450°C (62)

Moles reactants x 10 ³		Contact time sec	Labelling of products					
			Recovered propene			Acrolein		
Propene	Oxygen		% d ₀	% d ₁	% d ₂	% d ₀	% d ₁	% d ₂
0.11	0.15	0.09	99.6	0.4	-	99.1	0.9	-
0.11	0.15	0.34	95.7	4.1	0.2	97.1	2.9	-
0.11	0.15	1.29	89.1	10.2	0.7	95.8	4.1	0.1

merisation of the propylene, but must be due to the oxidation of propylene proceeding through a symmetrical intermediate.

They have suggested that the most probable symmetrical intermediate in the oxidation of propylene is allyl, but the possibility of isopropyl being involved was also considered.



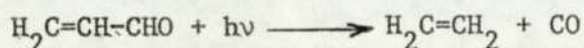
The results for the oxidation of propene- d_0 over a deuterated catalyst surface at 450°C (table II.2:d) showed that the acrolein was more than 95 % in the light form in support of the allyl route. The absence of acrolein- d_1 in larger amounts eliminates the possibility that a proton addition reaction occurs, during the formation of acrolein.

In support, Adams and Jennings (32,34) oxidised a deuterated propylene (1-propene- $3d$) with molecular oxygen over two catalysts, cuprous oxide and bismuth molybdate to give acrolein, and in the presence of ammonia to acrylonitrile.

Their results suggested that the reaction mechanism of propylene oxidation involves a formation of an allylic intermediate for both catalysts. This intermediate undergoes a second hydrogen abstraction before the incorporation of an oxygen atom to give acrolein.

Propylene samples, tagged with radioactive carbon, have been oxidised with molecular oxygen, on bismuth molybdate by Sachtler

and De-Boer (63). After an appropriate time, the oxidation run was stopped, the reaction products separated, and the specific radioactivities of acrolein, carbon monoxide and carbon dioxide were determined. The acrolein fraction was then decomposed photochemically in a quartz reactor (64,65) :

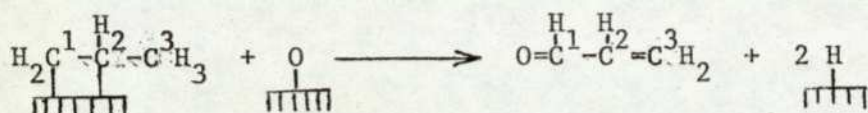


The decomposition products were separated by G.L.C. and their specific radioactivities were determined.

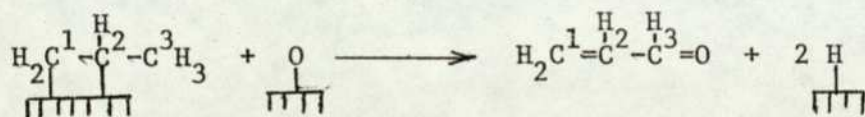
To study the mechanism of the reaction they assumed that for the rate determining adsorption on the surface, two possible mechanisms might be involved.

Mechanism A

Propylene is adsorbed on the catalyst surface by opening the double bond leading to:



or



Mechanism B

Propylene is adsorbed on the catalyst surface with dissociative chemisorption, resulting in an allylic adsorbate:

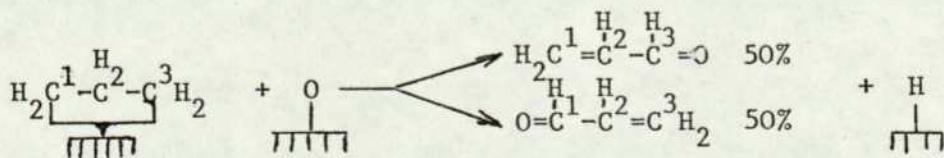


Table II.2.e Specific radioactivities r of CO and C_2H_4 ex photochemical decomposition of acrolein ex catalytic oxidation of propylene.

Propylene	$r_{C_3H_6}$	r_{CO}	$r_{C_2H_4}$	$R = r_{CO} / r_{C_2H_4}$			
				Expected from			Experimental
				Mech. A-1	Mech. A-2	Mech. B	
$H_2^{14}CCHCH_3$	0.99	0.447	0.490	∞	0.0	1.0	0.91
$H_2^{14}CCHCH_3$	0.99	0.437	0.483	∞	0.0	1.0	0.91
$H_2^{14}CCHCH_3$	0.40	0.168	0.185	∞	0.0	1.0	0.91
$H_2^{14}CCHCH_3$	0.252	0.008	0.243	0.0	0.0	0.0	0.03
$H_2CCH^{14}CH_3$	0.504	0.245	0.257	0.0	∞	1.0	0.95

Their results given in table II.2.e ,strongly suggest an allylic adsorbate as the true reaction intermediate.

Using a recirculation type of reactor Keulks (66,67,68) aimed at elucidating the mode of oxygen incorporation into the oxygen-containing products formed in the catalytic oxidation of propylene on bismuth-molybdate. The proposed mechanism was interpreted in terms of the layer structure of bismuth-molybdate catalyst as proposed by Batist et al (57,59) .For molybdenum-rich catalysts the oxygen boundary layers occur on $(\text{MoO}_2)_n^{2-}$ layers which creates anion vacancies on molybdenum atoms. The oxygen boundary layers serve as a source of oxygen that is incorporated into the products. The removal of oxygen from the boundary layers leaves the surface in the reduced state. Re-oxidation of these layers by a rapid diffusion to the surface of O_2^{2-} anions from the bulk rather than the gas phase oxygen was postulated to be the most probable mechanism.

B. Kinetics

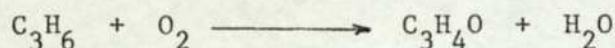
A general agreement for the kinetics of propylene oxidation over bismuth-molybdate catalyst exists, and the reaction is characterised by first order kinetics with respect to propylene, and zero order with respect to oxygen if the partial pressure of the latter is not very low.

Kinetic studies were carried out in the temperature range $410^\circ\text{C} - 500^\circ\text{C}$ using a circulating flow method (69), by Gel'bshtein and co-workers (70). The catalyst used was a mixture of bismuth oxide and molybdenum oxide with an atomic ratio of bismuth to molybdenum close to unity. Analysis of the reaction products for content of acrolein, acetaldehyde, carbon oxides, e t c was carried out

by standard chromatographic methods. The combination of the results of the kinetic investigation led to a simple equation for the total rate of conversion of propylene to acrolein and by-products as given by the equation II.2.8 .

$$r_1 = K_1 P_{C_3H_6} \quad \text{equation II.2.8}$$

Adams et al (29) studied the same reaction using a flow system at atmospheric pressure. The oxygen source was a mixture of 20 vol% oxygen and 80 vol% argon, while the exit gases from the reactor were analysed by mass spectrometer. For the reaction:



it was found that oxidation of propylene over bismuth-molybdate is first order in propylene and independent of oxygen and products, as illustrated in figure II.2.h. The curve is that calculated for first order kinetics, with the rate constant chosen to give the best visual fit. The apparent activation energy over the range 350 °C - 500 °C was estimated to be 20 Kcal/mole.

The effect of conversion on the selectivity of acrolein was also determined and the results are shown in figure II.2.i. The line drawn was calculated assuming all the reactions are first order and $K_3/K_1 = 0.10$ and $K_2/K_1 = 0.25$.

On the other hand, Cartlidge, Mc Grath, and Wilson (72) have taken a different approach in order to elucidate the kinetics of propylene oxidation over bismuth molybdate catalyst. Using an S.G.S reactor (71) , operating under no mass transfer gradients, they

Figure II.2.h Propene conversion variation with gas
volume per hour

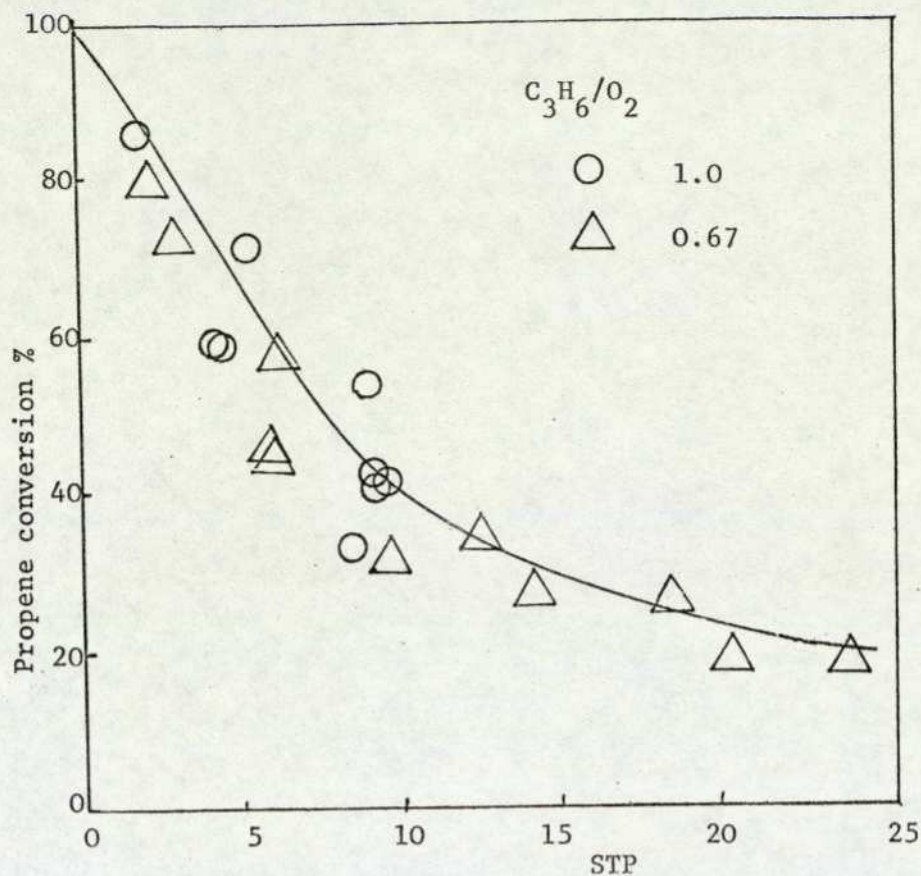
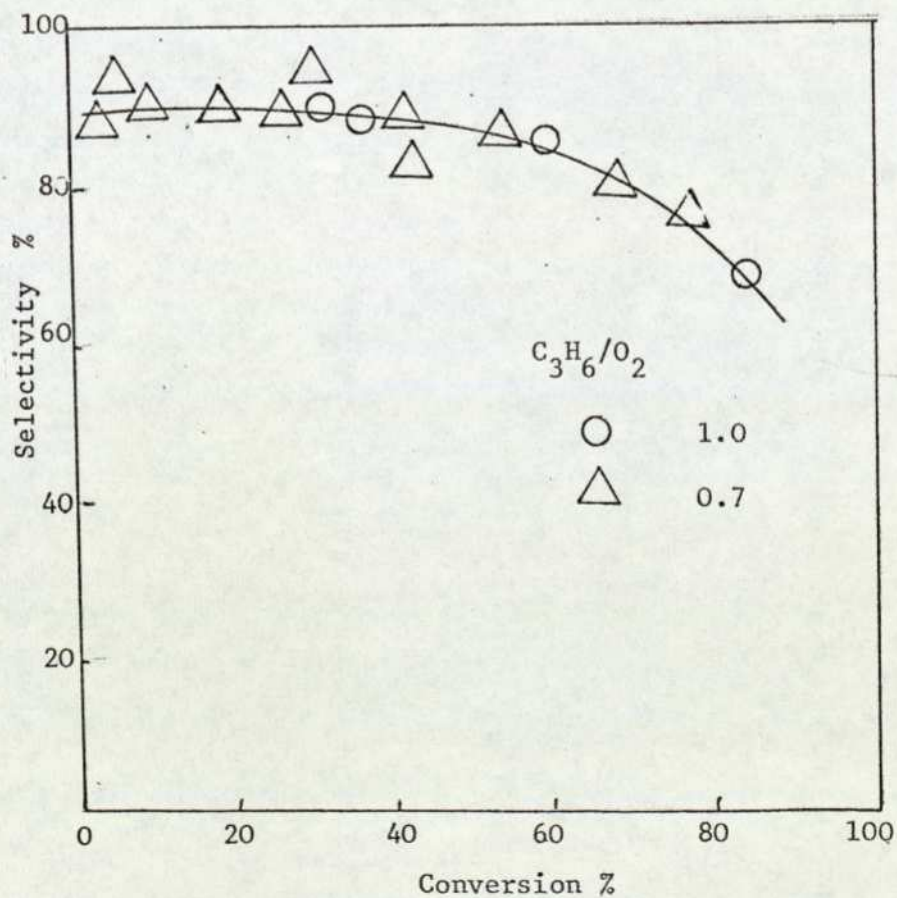


Figure II.2.i Variation of selectivity percentage with that
of conversion



obtained experimental conversion data, which have been fitted to a variety of models based on Langmuir isotherms.

The preferred model was that in which the goodness of fit most closely approached calculated values of the experimental error. For acrolein formation the model given in equation II.2.9 with a mean variance ratio of $\sigma_F^2 / \sigma_E^2 = 1.03$ correlate the experimental data most satisfactorily.

$$\frac{d[C_3H_4O]}{dt} = k \theta_{C_3H_6} = \frac{k K_{C_3H_6} [C_3H_6] W}{1 + K_{C_3H_6} [C_3H_6] + b K_{C_3H_6} [Product]} \quad \text{equat. II.2.9}$$

where b equals "average lifetime on the surface of propylene which desorbs unchanged" versus "average lifetime of propylene which reacts to give acrolein".

In deriving the above model the following assumptions were made;

- i. Propylene is adsorbed onto single oxidised sites only and most of this desorbs unchanged;
- ii. Propylene which reacts gives a reduced site and an acrolein molecule;
- iii. The average lifetime on the catalyst surface of molecules of propylene which desorbs unchanged is greater than the average lifetime of molecules on the surface which react to give acrolein;
- iv. The newly formed acrolein desorbs very rapidly due to its low affinity for reduced sites;

Furthermore the kinetics of carbon oxides formation by post oxidation of acrolein were determined, and the kinetic model derived:

$$\frac{d[\text{CO}_2]}{dt} = \frac{k (K_{\text{C}_3\text{H}_4\text{O}} [\text{C}_3\text{H}_4\text{O}])^{1/2}}{1 + (K_{\text{C}_3\text{H}_4\text{O}} [\text{C}_3\text{H}_4\text{O}])^{1/2} + (bK_{\text{C}_3\text{H}_4\text{O}} [\text{Product}])^{1/2}} \text{equat. II.2.10}$$

Similar assumptions in deriving the above model were also made:

- i. Acrolein is adsorbed on oxidised sites, either single sites or pairs of adjacent sites, most desorbing unchanged;
- ii. Acrolein which reacts gives a reduced site or sites and a molecule or molecules of oxygenated products;
- iii. The average lifetime on the catalyst surface of the acrolein which desorbs unchanged is greater than the average lifetime of acrolein on the surface which reacts to give oxygenated products.
- iv. The newly formed oxygenated products desorb very rapidly due to their low affinity for reduced sites; the reduced sites are again very rapidly re-oxidised; thus there is an increase of acrolein adsorption due to the surface reaction as there is for propylene.

II.3 OXIDATION OF ISOBUTYLENE TO METHACROLEIN

Methacrolein is an important raw material for the manufacture of plastics. The main source of its production is isobutylene which can be converted by gas-phase oxidation on certain catalysts to unsaturated products.

While demand is increasing a large number of research publications have appeared during the last decade describing various catalysts, and different oxidation processes for its production.

An extensive study on the catalytic oxidation of isobutylene

was made by Bretton, Wan and Dodge (73) in 1952. They used vanadium pentoxide, under conditions leading to complete oxidation. The air oxidation of isobutylene has been investigated by Mann and Rouleau (74) over several supported and unsupported copper oxide catalysts in an isothermal flow reactor. Mann and Yao (75, 76, 77, 78, 79) have also examined the effect of various modifiers such as, sulfur dioxide, selenium dioxide and halogen compounds with copper oxide catalyst to obtain a highly selective oxidation catalyst.

Recently Ray and Chanda (80) have reported their work on air oxidation of isobutylene over bismuth molybdate catalyst using an isothermal flow reactor. On the other hand Cartledge Mc Grath and Wilson (81) used an S.G.S. reactor for this reaction and succeeded in deriving the rate of the reaction over an unsupported bismuth-molybdate catalyst.

Furthermore many patents recommended and described the use of other catalysts for the same process. Generally the catalysts which are said to be suitable for the selective oxidation of isobutylene are the oxides of various transition metals (82, 83, 84, 85), and they are basically similar to those for the oxidation of propylene to acrolein. Although, similarity in the behaviour of both gases i.e. isobutylene and propylene, is a fact under conditions of catalytic vapour-phase oxidation, however, significant differences do exist. Straight chain C_4 -hydrocarbons do behave differently, and their catalytic oxidation leads to different products.

In table II.3.a some of the most important patented cata-

Table II.3.a Proposed catalysts for the selective oxidation of isobutylene to methacrolein

Catalyst composition	Carrier	Temp. °C	Feed-gas composition			Conversion %	Yield %	Select. %	Ref.
			i-C ₄ H ₈	O ₂	Steam				
Mo+Co+Te+Ca	-	440	7.5%	62.5%air	30%	28.2	-	82.5	86
Mo+Co+Te+Ca	-	460	7.5%	62.5%air	30%	39.8	-	80.8	86
Mo+Co+Te+Ca	-	460	7.5%	62.5%air	30%	42.2	-	81.4	86
Mo+Co+Te	-	435	7.5%	62.5%air	30%	38.5	-	35.6	86
Cu+Li	SiO ₂ -Al ₂ O ₃	-	-	-	-	-	"high"	-	87
AgNO ₃	Silicon-carbide	400	60	40 air	-	-	19	-	88
V+P+B	Alundum or SiC	490	1.1%	98.9%air	-	-	32	-	85
V ₂ O ₅ +Bi ₂ O ₃ + Mo(W)O ₃	Fused Al ₂ O ₃	-	-	-	-	-	20.1	-	89
Cr ₉ PMo ₁₂ O ₅₂	-	381	11.1%	58.9%air	30%	12.0	20	-	90
Cu ₉ TePV ₁₂ O ₄₄	Porous SiC	538	14.4%	73.2%air	12.4%	42.0	46	-	91
Ag ₂ O+P ₂ O ₅	Alundum	500	10%	10%	80%	-	61	-	92
Cu+P ₂ O ₅	Alundum	600	10%	7.5%	82%	-	72	-	93
VOSO ₄ +TeO ₂ + MoO ₃	-	450	1	14.3 air	9	-	38	49	94
Mo,Bi+ silic acid	-	450	1	9 air	-	91	35	-	95
Cu+Na+O	Celite	315	50	13	37	-	-	-	96
Sb ₂ O ₅ +P ₂ O ₅	-	450	6.8%	63.2%air	30%	-	30	-	96
Ni+Co+Fe+	-	345	1	2.2	5	98	70	-	97
Bi+P+K+Mo+O									

lysts for the selective oxidation of isobutylene to methacrolein are summarised.

II.3.1 Cuprous and copper oxide catalysts

The use of cuprous oxide catalysts for the selective oxidation of isobutylene is one of the first mentioned for this type of reaction.

The use of bulk metal in forms such as powder, gauze, film, shavings have been reported (98,99,100) extensively. However, supported catalysts have been used more frequently. Many supports have been adopted especially silicon carbide, celite, alundum e.t.c, which are mostly of high porosity.

The commercial use of this catalyst system began after the discovery by Hearne and Adams (16,19) that cuprous oxide is very effective in converting isobutylene to methacrolein selectively. The presence of a small amount, preferably 0.02-0.08 % of a volatile Cl-containing compound was found to increase the yield of methacrolein. When the catalyst was used in a finely-divided state, a fluidised bed technique was observed to improve the selectivity considerably.

Later the use of Cu catalyst, in the presence of S is mentioned in a British Patent (101) to Continental Oil Company in 1958. Furthermore, several patents (102,103,104,105,106) have recommended the use of copper oxide, supported on silica, silicon carbide or alumina as effective catalysts for the vapour-phase oxidation of isobutylene.

A. Mechanism

Experiments on the mechanism of the oxidation of olefins

with three and four atoms of carbon were carried out by Adams and Jennings (32). They reported that the reaction mechanism appears to be the same over both cuprous oxide, and bismuth molybdate catalysts. The proposed mechanism involves the formation of an allylic intermediate by abstraction of a hydrogen from the methyl group followed by further abstraction of this intermediate.

In order to determine the rate equation that best fitted their experimental data, Mann and Rouleau (74) in 1964 suggested that the surface reaction between adsorbed isobutylene and gaseous oxygen appears to be the rate controlling step in the reaction. The same authors, in agreement with Adams and Jennings, have suggested that the reaction mechanism of catalytic oxidation of isobutylene over cuprous oxide is the same as the reaction over bismuth molybdate catalyst. This conclusion was due to the fact that the rate equation for the catalytic oxidation of isobutylene over bismuth molybdate was similar to the rate equation over modified copper catalyst.

B. Kinetics

Mann and Rouleau (107), in 1964, studied the air oxidation of isobutylene to methacrolein over copper oxide catalyst supported on pumice in a flow system.

They reported that increase in temperature from 350 °C to 450 °C, results in a steady increase in the conversion of isobutylene, while the yield of methacrolein decreases with temperature. A similar effect of the oxygen (in the air) to isobutylene ratio on the conversion of isobutylene to methacrolein

lein, and the yield of methacrolein reported. They also found that the conversion was independent of the oxygen to isobutylene ratio and temperature, when the ratio g of catalyst to g-moles feed per hour was less than 0.2. They have concluded that the surface reaction between adsorbed isobutylene and gaseous or weakly adsorbed oxygen is the rate controlling step in the reaction. They also postulated that the rate of the reaction for the oxidation of isobutylene could be well described by the following equation;

$$r = \frac{a K_{iso} P_{iso} P_{ox}}{1 + K_{iso} P_{iso} + K_{meth} P_{meth}} \quad \text{equation II.3.1}$$

The maximum deviation between the predicted conversion values from the above equation and the experimental values was found to be less than $\pm 6\%$.

Ghorokhovatskii et al (108,109) studied the same reaction under a wide range of conditions. They determined the activation energies for methacrolein and carbon oxide formation to be 15 and 20 Kcal/mole respectively. They also reported that, apart from methacrolein as main product, acetaldehyde, propionaldehyde, carbon oxides and water were detected.

Similar studies were made by Popova (110) in 1951. Isobutylene was oxidised at $350^{\circ}\text{C} - 370^{\circ}\text{C}$ by oxygen in the presence of a catalyst consisting of 70% Cu_2O and 30% CuO . Experiments were carried out at an oxygen to isobutylene ratio 1:5.6 over a wide range of space velocities. It was found that with

a conversion of 3.8 % isobutylene to carbonyl compounds, 82.5 % was methacrolein, 7.2 % propionaldehyde, 6.2 % acetaldehyde and 4.1 % acrolein.

II.3.2 Bismuth-molybdate catalysts.

Recently much work has been carried out on the use of bismuth oxide and molybdenum oxide, and their various mixtures for the selective oxidation of isobutylene to methacrolein. A large number of patents (111,112,113,114,115) have described different methods of preparation and special heat treatment for obtaining highly selective bismuth molybdate catalysts.

Adams (56) reported that when propylene and butylenes were oxidised over bismuth molybdate catalyst, selectivities towards the main product were very high at rather high conversion levels. Contrarily other olefins containing more than four carbon atoms lose their selectivity at high conversions.

Tichy (116) in 1972 has studied the air oxidation of isobutylene to methacrolein over various bismuth molybdate catalysts. The specific surface area of each different catalyst was determined using x-ray diffraction analysis. It was observed that the maximum selectivity towards methacrolein was obtained when the catalyst had a bismuth to molybdenum ratio of 1.25. He also observed a rapid fall in activity as the ratio approached 2:1 which was attributed to a less well developed crystal structure by results from x-ray diffraction analysis.

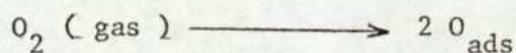
A. Mechanism

The mechanism of the oxidation of olefins with three and four atoms of carbon was reported (56) to be the same over both

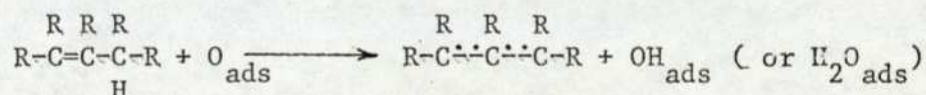
cuprous oxide and bismuth molybdate catalysts. The proposed mechanism involves the formation of an allylic intermediate by abstraction of a hydrogen from the methyl group, followed by further abstraction of this intermediate.

Adams (32) refers to a prior overall mechanism which the oxidation of olefins over bismuth molybdate should obey. This mechanism follows the steps:

- i. An olefin molecule comes in contact with the surface that is covered with chemisorbed oxygen atoms.

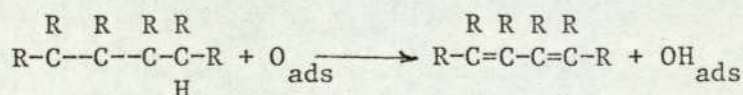


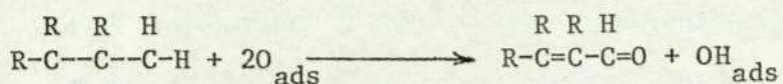
- ii. The abstraction of an allylic hydrogen atom by an oxygen atom causes the formation of a resonance stabilised allylic intermediate and an OH species.



The kinetic slow step is the formation of this intermediate; thence the speed of the reaction is an inverse function of the strength of an allylic $\text{C}^{\cdot\cdot}\text{H}$ bond.

- iii. Subsequent hydrogen abstraction from this intermediate yields a conjugated diene, or upon oxygen substitution, a conjugated unsaturated aldehyde.





where R represents either hydrogen or alkyl.

In addition, Uchijima and Oda (117) observed that both propylene's and isobutylene's oxidation rates are the same over bismuth molybdate catalyst and from this fact they concluded that the same mechanism is possibly involved in both oxidations.

Mann and Yao (118) have proposed a mechanism for the oxidation of isobutylene to methacrolein over bismuth molybdate catalyst based on the electron theory of catalysis. They have considered that the surface of the catalysts consist of two types of active sites, electron and positive holes on which oxygen and olefin adsorbed. The surface reaction was assumed to follow the next steps.

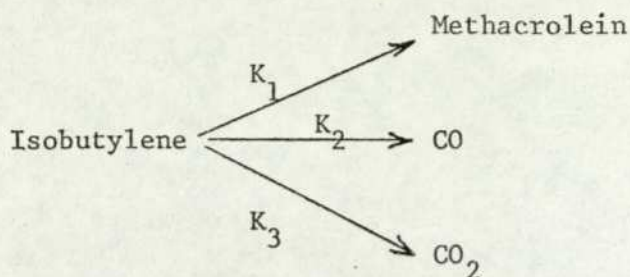
- i. Electron transfer from the catalyst to the reactants.
- ii. Homogeneous reaction i.e formation of activated complex and rearrangement of the charged particles on the surface.
- iii. Electron transfer from the products to the particles.

On the other hand Ray and Chanda (80) have adopted three criteria in order to discriminate the reaction mechanism as follows;

- i. Positive values for all rate constants.
- ii. Agreement with Arrhenius law in respect of temperature dependence of rate constants.
- iii. Small deviation between calculated and experimental conversions

All the possible reaction routes have been considered, i.e

parallel, consecutive and parallel-consecutive; only the following parallel scheme was in agreement with the adopted criteria.



B. Kinetics

An interpretation of the kinetics based on their experimental data for the selective oxidation of isobutylene over bismuth molybdate catalyst was attempted by Mann and Ko (119), in 1973. These experiments follow their previous work on isobutylene oxidation, with different catalyst systems using an isothermal integral flow reactor. For a space velocity equal to 3.75 and a temperature range $350^{\circ}\text{C} - 560^{\circ}\text{C}$, the selectivity for methacrolein was found to increase with increased oxygen/isobutylene ratios. They also observed that while the conversion of isobutylene increased steadily with temperature, the selectivity decreased at all space velocity values. Figure II.2.a illustrates graphically their findings.

The kinetic analysis of their experimental data was made using the approach suggested by Hougen and Watson (15). In this method, various mechanisms which could control the reaction were postulated based on a single site and two types of active sites. To determine the rate controlling step of the solid catalysed gas, the values for the highest temperature and the highest partial

Figure II.3.a Variation of conversion and selectivity with reactants feed ratio

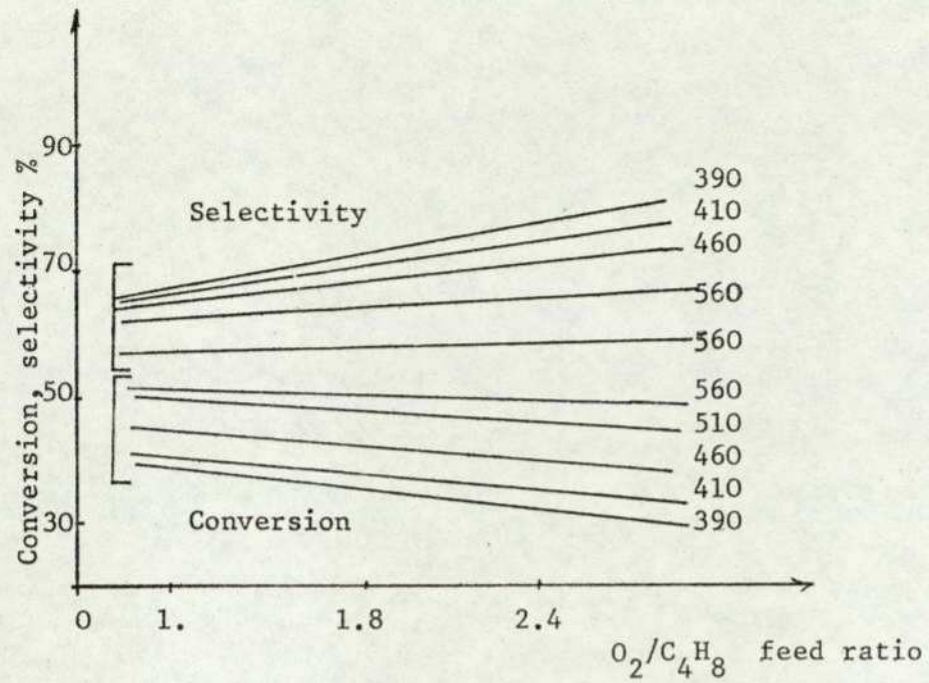
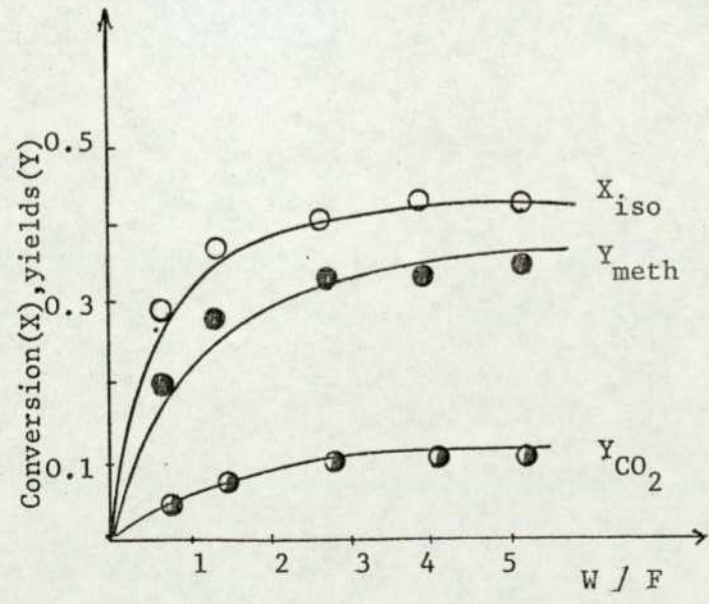


Figure II.3.b Effect of the reciprocal of the flow velocity on conversion and yields.



pressure gradient were calculated. From these values heat and mass transfer effects were considered as negligible.

Equations for these mechanisms relating the rate of formation of methacrolein and water, were postulated and checked against their experimental data. The mechanism which assumes that the rate controlling step is the surface reaction between charged adsorbed isobutylene and oxygen, was found to correlate the data most satisfactorily. The rate expression was:

$$r = \frac{K_S K_{iso} P_{iso}}{(1 + K_{iso} P_{iso} + K_{meth} P_{meth})} \frac{P_{ox} K_{ox}}{1 + K_{ox} P_{ox}} \quad \text{equation II.3.2}$$

where K_S , K_{iso} , K_{meth} and K_{ox} are temperature dependent and can be expressed by the following equations:

$$\ln K_{iso} = 5.18 + 17.79 \times 10^3 / T \quad \text{equation II.3.3}$$

$$\ln K_{meth} = 4.30 + 24.27 \times 10^3 / T \quad \text{equation II.3.4}$$

$$\ln K_{ox} = 0.75 + 3.64 \times 10^3 / T \quad \text{equation II.3.5}$$

$$\ln K_S = 7.44 - 7.32 \times 10^3 / T \quad \text{equation II.3.6}$$

In figure II.3.b the theoretical conversion values obtained from the rate equation are compared with the experimentally obtained values for a temperature of 410 °C, and an oxygen to isobutylene ratio of 1.2. The maximum deviation between these values was found to be only $\pm 4\%$ at low reciprocal space velocities.

Similar work was carried out by Uchijima and Oda (117) in 1968. A single pass flow reactor was operated at atmospheric pressure, and the reaction temperature varied between 400 °C and 520 °C. The analysis of the products was carried out using standard gas chromatography techniques. The kinetic analysis of their experimental data showed that isobutylene oxidation rates are first order with respect to the olefin and independent of oxygen concentration. Similar results were found during the catalytic oxidation of propylene over the same catalyst system. However, the oxidation rate of isobutylene was found to be greater than that of propylene.

Addition of a phosphorus promoter to the catalyst lowered the apparent activation energy of propylene oxidation but had no effect on the oxidation of isobutylene. The activation energy of isobutylene oxidation was calculated as being 27 - 28 Kcal/mole. They also reported that when the conversion of isobutylene was increased, the selectivity to methacrolein was steadily decreased, and that the reaction deviated markedly from their first order relationship when the conversions were higher than 30 %. This was attributed to product retardation caused by the reactivity of methacrolein.

In addition, Ray and Chanda (80) studied the air oxidation of isobutylene over bismuth molybdate catalyst, using an integral flow reactor, in the temperature range of 325 °C to 500 °C. They reported that the conversion of isobutylene and the yields for both carbon oxides increased with increasing temperature. The selectivity for methacrolein was found to increase up to 425 °C,

after which it decreased with further increase in temperature.

To obtain kinetic data the authors carried out experiments, studying the effect of contact time on the conversion of isobutylene at different temperatures and different feed ratios. They observed that oxygen to isobutylene moles ratios above 6.0 had no effect on conversion. The reaction scheme which assumes that methacrolein and carbon oxides are formed from a parallel route during the catalytic oxidation of isobutylene was closer to their experimental results. The integrated forms of the rate equations were given as:

$$\ln \left(1 - \frac{P_{I_0} - P_I}{P_{I_0}} \right) = -K_I t \quad \text{equation II.3.7}$$

$$\frac{P_M}{P_{I_0}} = (K_1/K_I) \left[1 - \exp(-K_I t) \right] \quad \text{equation II.3.8}$$

$$\frac{P_{CO}}{4P_{I_0}} = (K_2/K_I) \left[1 - \exp(-K_I t) \right] \quad \text{equation II.3.9}$$

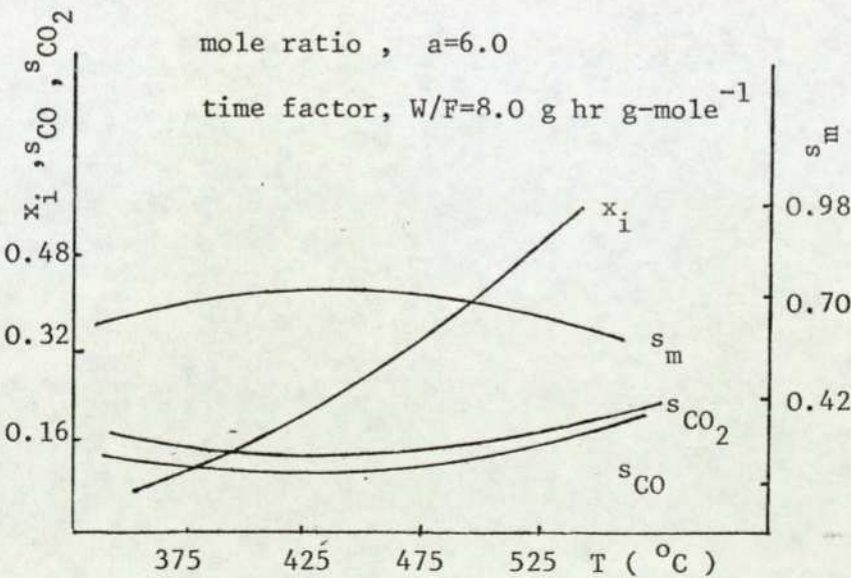
$$\frac{P_{CO_2}}{4P_{I_0}} = (K_3/K_I) \left[1 - \exp(-K_I t) \right] \quad \text{equation II.3.10}$$

where t is the time factor defined as the reciprocal of moles of isobutylene feed per hour per g of catalyst. K_I is the rate constant for the scheme leading to the formation of methacrolein, K_2 to the formation of CO, and K_3 to the formation of CO₂. K_I was chosen to be $K_1 + K_2 + K_3$. The values for these rate constants were obtained by linear regression from their experi-

Table II.3.b Activation energies and pre-exponential factors
for pseudo-first order kinetics (80)

	K_1	K_2	K_3
Activation energy Kcal / mole	10.87	15.11	15.06
Preexponential, g-moles / g h atm	62.05	196.4	330.9

Figure II.3.c Variation of conversion, x_i , and selectivities
 s_m , s_{CO} , s_{CO_2} , with temperature



mental data.

The values for activation energy and the pre-exponential factor of the Arrhenius equation for each of the reaction rate constants were determined and are shown in table II.3.b, while their results are illustrated in figure II.3.c.

The experimental values of conversions and the values calculated from the above equation gave a deviation at each temperature less than 6 % .

Recently Cartlidge, Mc Grath and Wilson (81) have attempted to model the oxidation of isobutylene to methacrolein and carbon oxides over bismuth molybdate catalyst. They used an S.G.S. reactor which is considered to operate under conditions of negligible heat and mass transfer effects.

Their experimental data were fitted to a number of kinetic models based on Langmuir's isotherms. The preferred model assumes that:

- i. The surface of the catalyst has a high affinity for isobutylene; hence K_{iso} is unity for all the experimental conditions. Oxygen and isobutylene are chemisorbed on different types of active sites and thus there is no competition for active sites.
- ii. Oxygen is chemisorbed on pairs of adjacent sites and most of it desorbs unchanged. The reaction occurs between oxygen and adjacently adsorbed isobutylene.
- iii. The average lifetime of oxygen on the surface which desorbs unchanged is greater than the average lifetime of oxygen which desorbs as oxygenated products.
- iv. The newly formed methacrolein desorbs very rapidly due to its

low affinity for the sites at which it is formed.

v. All the carbon oxides are formed by post oxidation of methacrolein.

The expression for the rate of the reaction which best fitted the experimental data was given by the following equation:

$$\frac{d [C_4H_6O]}{dt} = \frac{k K_{O_2} [O_2]^{0.5} W}{1 + (K_{O_2} [O_2]^{0.5} - b K_{O_2} [Products])^{0.5}} \quad \text{equation II.3.11}$$

where $[Products] = [C_4H_6O] + 1/4 [CO_2] + 1/4 [CO]$

$$b = \frac{\text{average surface lifetime of } O_2 \text{ which desorbs unchanged}}{\text{average surface lifetime of } O_2 \text{ which desorbs as products}}$$

W = Weight of the catalyst

The absence of an isobutylene term was explained considering that the surface has very high affinity for isobutylene under the conditions employed, and that the isobutylene and oxygen do not compete for active sites.

It should be emphasized that the above equation represents data for the reaction leading to methacrolein formation only over the range 356 °C - 370 °C . Above this temperature no equation has been found to represent the experimental data satisfactorily.

II.4 FLUIDISATION

Unfortunately, definition of fluidisation phenomena can lack a completeness due to the complications involved in a fluidised system. Instead, this phenomena can best be interpreted in terms of a simple operation by which a bed of fine solids is transformed to a fluidised stage. When a fluid is forced to pass upwards through a bed of solid particles, a pressure drop develops across the bed. With increasing flow-rate of the gas or liquid, the bed of particles will pass through the stages of a fixed bed, and expanded bed as illustrated in figure II.4.a. With further increase in the upward fluid velocity, the bed expands and a stage will be reached where the drag forces will be sufficient to support the weight of the particles. In this state, the fluid/particle system begins to behave like a fluid and it will flow under a hydrostatic head; the bed is then considered incipiently fluidised, or to be a bed at minimum fluidisation velocity (figure II.4.b).

In liquid solid systems an increase in flow rate above the minimum required to produce a fluidised bed usually results in a smooth, progressive expansion of the bed the particles spacing themselves evenly so that the liquid passes smoothly through the interstices. In this case the average distance between the particles will become much greater, (figure II.4.c) this type of fluidisation is referred to as "particulate".

In general, particulate fluidisation occurs with liquid-solid systems and with gas-solid systems when the particles are very



Figure II.4.a
Fixed bed

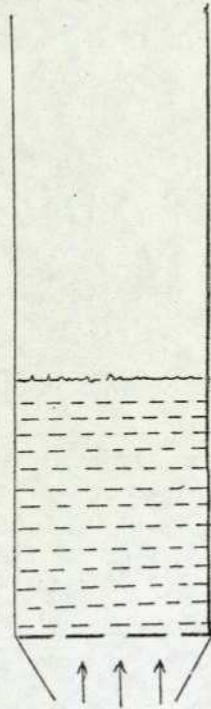


Figure II.4.b
Minimum fluidi-
ed bed

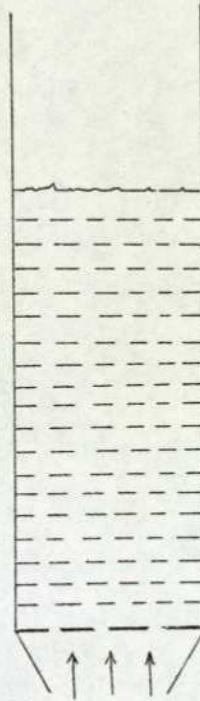


Figure II.4.c
Expanded bed

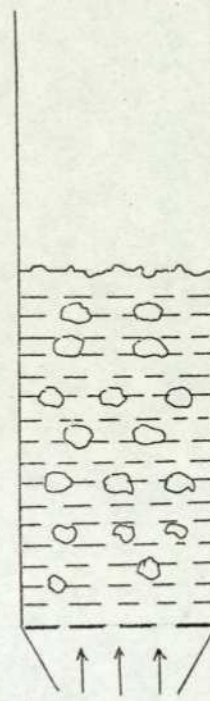


Figure II.4.d
Bubbling bed

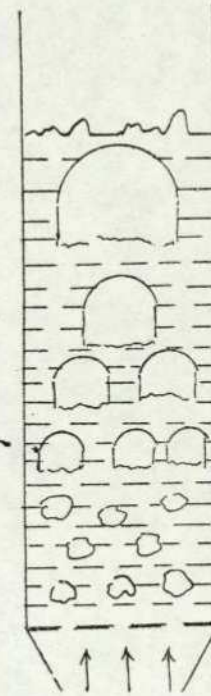


Figure II.4.e
Slugging bed

fine and over a limited range of velocities.

Gas-solid systems and sometimes liquid-solid systems, when the solids are of high density, behave in a quite different manner. With an increase in flow rate above the minimum fluidisation, the excess gas will pass through the bed in the form of bubbles. This type of fluidisation is referred to as "aggregative". The bed in this case is called an aggregative fluidised bed, a bubbling bed, or simply a gas fluidised bed (figure II.4.d).

When the flow rate is further increased, the bubbles agitate the bed and consequently its height fluctuates due to bubbles. With still greater flows the bubbles grow until their frontal diameters are reaching the size of the diameter of the containing apparatus; the bed is then said to be "slugging" (figure II.4.e).

Eventually at high flow rates the terminal velocity of the solids is exceeded, the upper surface of the bed disappears and particles are carried out of the apparatus. The voidage fraction is then very high and the phenomenon is that of pneumatic transport. In this last stage the bed is called a disperse, or dilute fluidised bed.

Gas fluidised beds of fine, irregular particles are prone to channeling. As the fluid velocity through the bed is increased, instead of the bed expanding uniformly, the fluid opens up channels through the bed. Then having created a path of low resistance, this path is enlarged with further increase in the fluid flow velocity. In the extreme case, with gas fluidised beds of fine particles the bed fails to fluidise at all.

Certain crystalline materials with axis very much longer than the others or a wheat grain, will not fluidise stably. However, they can be handled by spouted bed techniques in which the material is entrained in an air jet, which carries it up the centre towards the top of the bed, where it becomes deentrained and flows back down the walls of the bed so that vigorous circulation is maintained (120). These techniques are also of value when it is impractical to use a conventional distributor.

II.4.1 Advantages and disadvantages of fluidisation technique

The technique of fluidisation has been extensively used for operations involving solid/fluid contacting, especially whenever high rates of heat and mass transfer between the solid and fluid are required. However, the various disadvantages of a fluidised system should also be mentioned for the purpose of selecting an optimum overall design. The most important advantages are concerned with temperature control and heat transfer, continuity of operation, mass transfer and handling of fluidised beds.

i. Temperature control

The violent agitation of the particles disperses the heat throughout a fluidised bed and a temperature uniformity is quickly established. Since some catalytic reactions are highly exothermic, rapid heat removal and close temperature control is required and thus a fluidised bed reactor can be applied successfully for such catalytic reactions (105, 106). The heat transfer between the fluidised solids and an immersed surface is very high, hence heat exchangers within fluidised beds require relative-

vely small surface areas.

ii. Contacting efficiency.

An extremely large area of contact between solid and fluid gives rise to high overall rates of mass transfer between the solid and the fluid. This can often be a considerable asset in the design of reactors for some industrial processes. The drying of solid particles with the fluidisation technique has become widely used recently. Some liquids are dried also on inert bodies and the dry product is carried away as a fine powder. The usual operations of evaporation, crystallization, filtration, drying and pulverisation are replaced by a single process of drying in a fluidised bed.

iii. Continuity of operation

The behaviour of a fluidised system allows continuous controlled operations. The addition and withdrawal of solid particles from the process equipment can also be controlled and as a result many batch processes have been replaced by continuous ones, which have proved to be more economic.

Inherent within the technique are also some limitations:

- i. The process demands expenditure of power for fluidisation.
- ii. An excessive tendency for particle attrition is shown by some friable solids. This will produce too many fines by degradation of the particles which will be lost from the bed.
- iii. The formation of "agglomerated" particles too large to fluidise, can necessitate a lowering in temperature of operation, thereby reducing the rate of a chemical reaction quite significantly. Also there some materials of such irregular shape that

they can only be handled by the spouting bed technique.

iv. Operating parameters are limited to within the range over which the bed may be fluidised. If the fluid velocity is too low, the bed settles; if, on the other hand, the flow rate is too high, there is excessive loss of particles from the bed by carry over.

v. There is usually a limit to the size of particles which may be fluidised (6500 μm down to a few microns). This limit is particularly dependent on the fluid viscosity and particle/fluid density ratio as well as the fluid flow rate.

vi. The quick equilibration of temperature in a fluidised system is a disadvantage in those operations where thermal gradients are required.

vii. The formation of bubbles characteristic of most gas-solid beds may result in reduced contacting efficiency. This becomes possible when some of the gas within the bubbles by-passes the solids and that can be serious when high conversions of gaseous reactant are required.

viii. For catalytic reactions the movement of porous catalyst particles which continually capture and release reactant molecules contributes to a high degree of back mixing, resulting in lower conversions relative to those of an ideal plug-flow reactor.

ix. The dynamics of fluidised systems are not sufficiently well understood to permit confident scale-up to large scale units when reaction conditions are critical.

II.4.2 Pressure drop in gas fluidised beds, and minimum fluidisation velocity

When a gas is forced to pass vertically upwards through a bed of solid particles a pressure drop is caused across the bed. According to Ergun equation (121) a relationship between the pressure drop and gas velocity will exist.

$$\frac{\Delta P}{H} g_c = 150 \frac{(1 - \epsilon_m)^2 \mu U_o}{\epsilon_m^3 \phi_s^2 d_p^2} + 1.75 \frac{1 - \epsilon_m}{\epsilon_m^3} \frac{\rho_g U_o^2}{\phi_s d_p} \quad \text{equation II.4.1}$$

The pressure drop in equation II.4.1 represents two factors, the viscous losses which need to be considered at low Reynolds numbers, and the kinetic energy losses at high Reynolds numbers.

In the cases of low and high Reynolds numbers equation II.4.1 simplifies to equations II.4.2 and II.4.3 respectively.

$$\frac{\Delta P}{H} g_c = 150 \frac{(1 - \epsilon_m)^2 \mu U_o}{\epsilon_m^3 (\phi_s d_p)^2} \quad N_{Re} (P) < 20 \quad \text{equation II.4.2}$$

$$\frac{\Delta P}{H} g_c = 1.75 \frac{1 - \epsilon_m}{\epsilon_m^3} \frac{\rho_g U_o^2}{\phi_s d_p} \quad N_{Re} (P) > 10^3 \quad \text{equation II.4.3}$$

The linear relationship between the pressure drop and gas velocity was initially predicted by Kozeny (122) in 1927, and Carman (123) in 1937 based on work in fixed beds.

At the point of minimum fluidisation the gas velocity has reached such a value that the frictional pressure drop is equal to the weight per unit area of the particles (124), and thus;

$$\left[\begin{array}{c} \text{Pressure drop} \\ \text{across the bed} \end{array} \right] \times \left[\begin{array}{c} \text{Cross-sectional} \\ \text{area of tube} \end{array} \right] = \left[\begin{array}{c} \text{Specific weight} \\ \text{of particles} \end{array} \right] \times \left[\begin{array}{c} \text{Volume} \\ \text{of bed} \end{array} \right] \times \left[\begin{array}{c} \text{Fraction of} \\ \text{solids} \end{array} \right]$$

$$\text{or } \Delta P A_t = W = (A_t H_{mf}) (1 - \epsilon_{mf}) \left[(\rho_s - \rho_g) g/g_c \right]$$

$$\text{and } \Delta P = (1 - \epsilon_{mf}) (\rho_s - \rho_g) H_{mf} g/g_c \quad \text{equation II.4.4}$$

It is obvious that the evaluation of the pressure drop in the above equation necessitates a knowledge of the voidage fraction, ϵ_{mf} , at the point of minimum fluidisation. It is generally supposed that in a bed at the onset of fluidisation the voidage corresponds to the loosest state of a packed bed. In this case we would expect a bed of uniform spheres to take up the cubic mode of packing and therefore at the point of incipient fluidisation the voidage fraction will be $\epsilon_{mf} = 1/6 (6 - \pi) = 0.476$. This assumption is approximately correct, since voidages for uniform spherical particles have been observed (125,126) being between 0.4 and 0.5.

Combining the equation II.4.1 with equation II.4.4 the minimum fluidisation velocity can be determined from the resulting equations II.4.5 and II.4.6 (124,127)

$$\frac{1.75}{\phi_s \epsilon_{mf}^3} \left[\frac{d_p U_{mf} \rho_g}{\mu} \right]^2 + \frac{150 (1 - \epsilon_{mf})}{\phi_s^2 \epsilon_{mf}^3} \frac{d_p U_{mf} \rho_g}{\mu} = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2} \quad \text{equation II.4.5}$$

writing $N_{Re} = U_{mf} \rho_g d_p / \mu$

and $Ga = \text{Galileo number} = \frac{\rho_g (\rho_s - \rho_g) g d_p^3}{\mu^2}$

equation II.4.5 becomes:

$$Ga = 150 \frac{1 - \epsilon_{mf}}{\epsilon_{mf}^3} N_{Re} + 1.75 \frac{1}{\epsilon_{mf}^3} N_{Re}^2 \quad \text{equation II.4.6}$$

However, for small particles of small specific weight equation II.4.1 simplifies to equation II.4.2: thus equation II.4.5 gives:

$$U_{mf} = \frac{(\phi_s d_p)^2}{150} \frac{\rho_s - \rho_g}{\mu} g \frac{\epsilon_{mf}^3}{1 - \epsilon_{mf}} \quad N_{Re}(P) < 20 \quad \text{equation II.4.7}$$

For larger particles equation II.4.1 simplifies to equation II.4.3; thus equation II.4.5 gives:

$$U_{mf} = \left[\frac{\phi_s d_p}{1.75} \frac{\rho_s - \rho_g}{\rho_g} g \epsilon_{mf}^3 \right]^{1/2} \quad N_{Re}(P) > 10^3 \quad \text{equation II.4.8}$$

Assuming that for uniform spherical particles the voidage fraction at the point of incipient fluidisation is about 0.42, equation II.4.6 can be modified thus:

$$N_{Re} = 25.7 \sqrt{1 + 5.53 \times 10^{-5} Ga - 1} \quad \text{equation II.4.9}$$

which gives the minimum fluidisation velocity for the whole range of Reynolds numbers when the voidage fraction and the

sphericity are unknown. This was suggested by Wan and Yu (128) who reported that for 284 data points in the whole range of Reynolds numbers the expression predicts the minimum fluidisation velocity with a standard deviation of $\pm 34\%$.

Generally a pressure drop through the bed of particles versus gas velocity graph is used for the determination of the minimum fluidisation velocity. An ideal case of a well fluidised bed of uniformly sized particles is shown in figure II.4.f (124), established by Shirai (129).

At relatively low gas flow rates in a packed bed a linear relationship between pressure drop and gas velocity exists, and will be well described by equation II.4.2. At the point of minimum fluidisation, U_{mf} , the gas velocity will result in a pressure drop equal to the weight per unit area of the particles, $\Delta P = W/A_t$, and this pressure drop remains practically constant with further increase in gas velocity. However, ideal circumstances are very difficult to achieve and as a result a pressure drop versus gas velocity diagram would give a useful rough indication of the quality of fluidisation. In beds of small diameter, where the wall effects may be important, according to Richardson (127), "Because of the tendency of the particles to interlock with one another, partial bridging can occur; thus it is possible for pressure drop to exceed its theoretical value and the pressure drop velocity curve, will pass through a point of maximum pressure drop, ΔP_{max} ". On the other hand, non fluidised regions in a gas fluidised bed may exist if the structure of the bed is not completely uniform. As a result the minimum fluidising velocity is lower, than

Figure II.4.f Ideal pressure drop in fluidised beds (129)

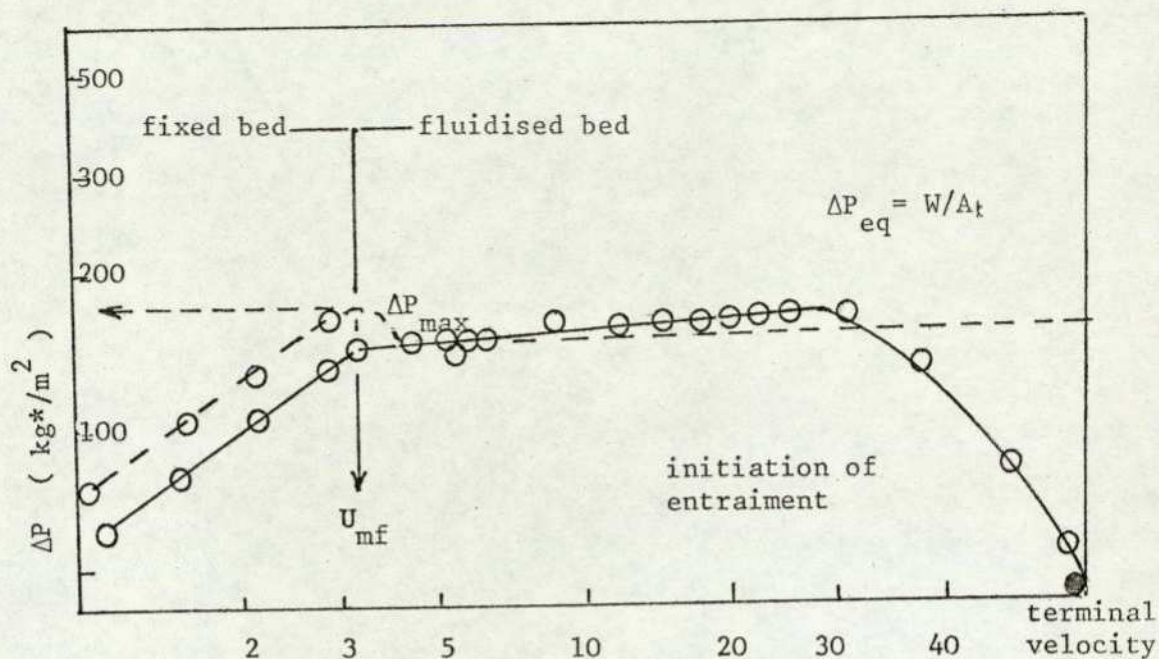


Figure II.4.g Effect of presence of non fluidised regions in bed (127)

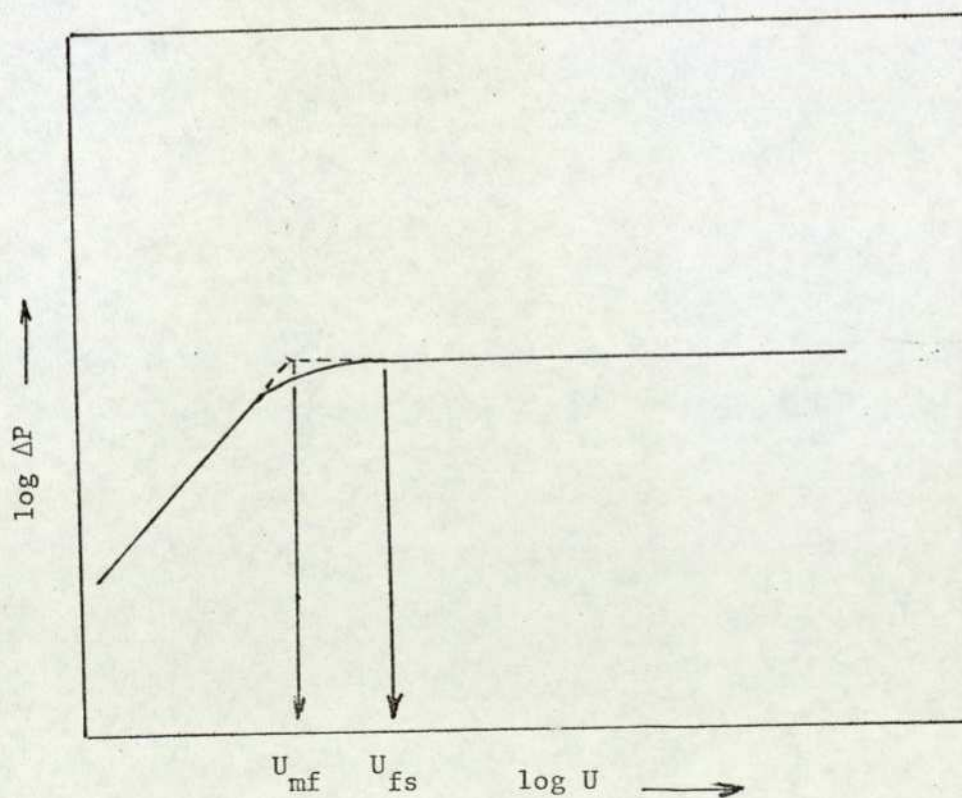
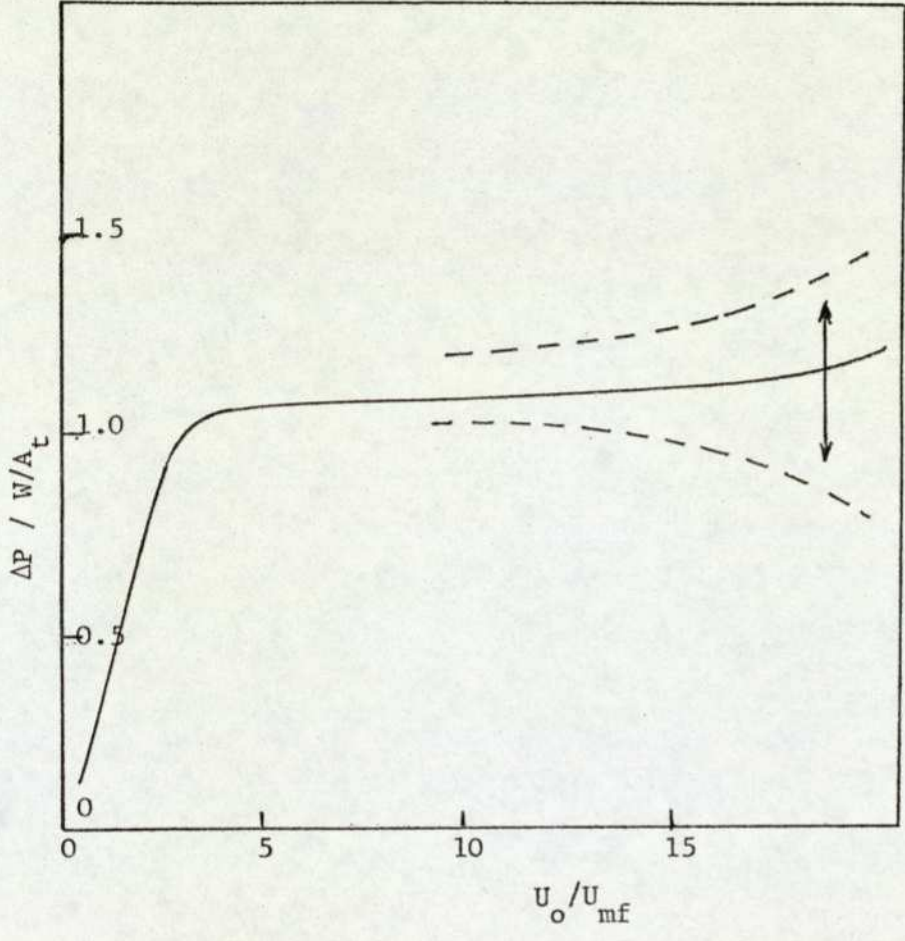


Figure II.4.h The slugging phenomenon (results by Hiraki (30))



the velocity at which the bed weight is fully supported by the fluid, U_{fs} , as shown in figure II.4.g (127). In deep narrow fluidised beds there is a tendency for bubbles to grow and coalesce as they rise through the bed until they occupy the whole cross-sectional area of the tube and so a slugging bed is formed; the slug rises through the tube carrying particles ahead of it and causes large pressure fluctuations within the bed, figure II.4.h (124).

II.4.3 Modes of fluidisation

Since the mode of fluidisation is basically dependent upon the properties of the particles and the gas velocity, many experimentalists attempted to relate the behaviour of a fluidised bed with the gas characteristics and particle properties.

Early studies by Wilhelm and Kwauk (131), suggested that the transition between particulate and aggregative behaviour as shown by non-bubbling, and bubbling beds, could be explained in terms of the Froude number, equation II.4.10. This implied that if the fluid could lift the particles, particulate fluidisation occurred, and that the gas passed through an "expanded bed" stage. If the gas was unable to lift and separate the particles then bubbles were formed throughout the bed.

$$N_{Fr} (U_{mf}) = U_{mf}^2 / d_p g \quad \text{equation II.4.10}$$

$$\text{If } N_{Fr} (U_{mf}) < 0.13 \quad \text{particulate fluidisation}$$

$$\text{If } N_{Fr} (U_{mf}) > 1.3 \quad \text{aggregative fluidisation}$$

When the ratio of solid to fluidising fluid does not exceed

two or three, particulate fluidisation generally takes place, until solid transport occurs. The régime of "particulate fluidisation", has been examined in detail by Richardson and Zaki (132,133). They showed that the ratio of superficial gas velocity of a particle, was a function of the voidage to a power n , where n is a function of the Reynolds number, depending on the range of the latter, equation II.4.11.

$$\frac{U}{U_i} = \epsilon^n \quad \text{equation II.4.11}$$

where $\log U_i = \log U_t - d/D$

Happel et al (134,135) showed that a modification was necessary for the very dilute phase. This means that the equation II.4.11 applies only up to a voidage of 0.95, which was the experimental range of Richardson and Zaki (132). It is mentionable also that this value is the upper limit in the most practical applications of fluidisation.

The above relationship has been found to apply to beds of fine particles, $d_p = 55 \mu\text{m}$, fluidised with air at values up to about three times the minimum fluidisation velocity by Richardson and Davies (136) in 1966. This is because beds of fine particles expand considerably before bubbles appear, and in the expanded state they are similar to liquid/solid beds, that is, they are behaving in a particulate manner (137).

On the other hand, when the ratio of the densities of solid and fluidising fluid is about 10 to 1, the nature of the fluidisation changes, the most obvious difference being the appearance

of bubbles containing 0.4 - 0.6 vol% of solids as suggested by Kunii et al (138). The remainder of the solids comprise the dense phase which has a voidage approximately that at minimum fluidisation. The dense phase is therefore similar in structure to a fixed bed, except that gross solids movement occurs as each bubble rises.

Geldart (139) in 1973 had classified solid particles into four characteristic groups. This classification enables identification of the mode of fluidisation according to the sizes, and density of particles, as shown in figure II.4.i.

Particles of group C have basically very high surface forces. Thus, fluidisation cannot occur or is extremely difficult. For the particles which belong to group A, fluidisation can occur. However, considerable dense phase expansion exists before bubbling commences. For such particles the bubble rising velocity is greater than the emulsion phase velocity and cross circulation of the powder occurs even when few bubbles exist. It is a fact that most of the information on fluidisation is based on particles of group B, indicating a need for additional investigation of particles belonging to other groups. The behaviour of a fluidised bed with particles of group B is different from that of a bed fluidised with particles of the other groups, and bubble correlations based on group B particles should not be extended to other types of particles without careful consideration of particle properties. Fluidisation in this group occurs easily, and little or no powder circulation exists due to convection effects. For most of the bubbles, the rising velocity is greater than the average gas velocity in the emulsion phase. Eventually, in group D we reach

Figure II.4.i Classification of solid particles by Geldart (139)

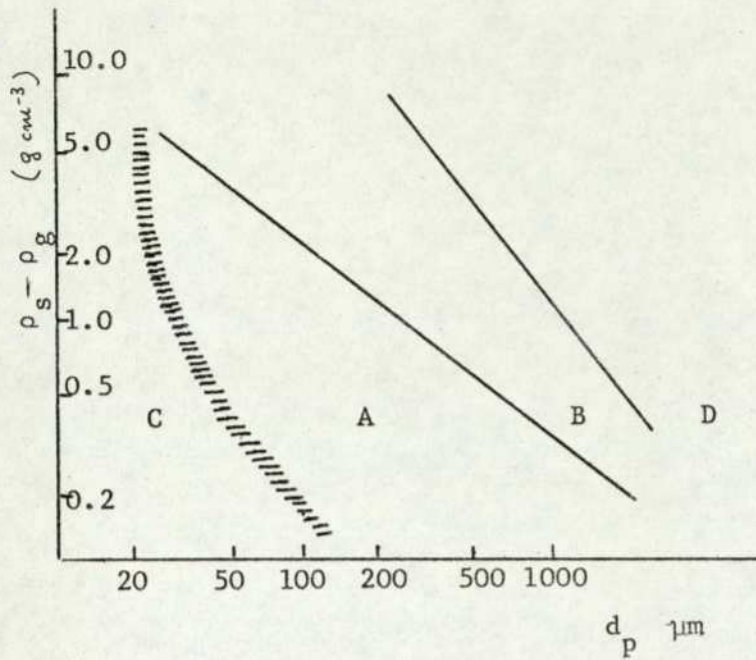
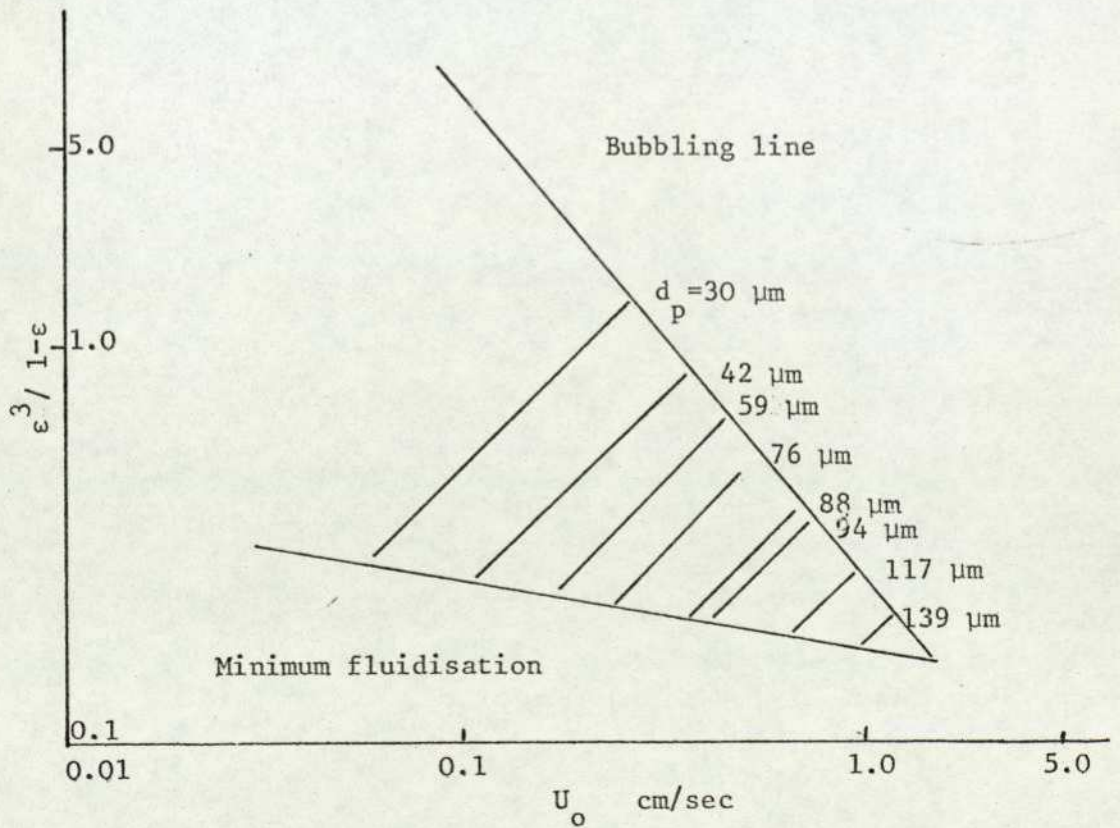


Figure II.4.j The bubble-free region (140)



the extreme where the bubble rising velocity is smaller than the average gas velocity in the emulsion phase.

As previously mentioned, the state of fluidisation will vary widely between systems of large and fine particles. A fluidised bed may be operated close to the particulate mode in some instances, or it can be operated in highly aggregative mode in many others.

Nomden and De-Jong (140) in 1974 observed that when fine particles are fluidised, there is a region in which the bed expands without formation of bubbles. Instead, when larger particles are fluidised this bubble free region disappears. Figure II.4.j illustrates graphically their findings. The relation between the gas velocity and the fraction $\epsilon^3 / 1 - \epsilon$ for different particle sizes is used to obtain this bubble-free region.

II.4.4 Fluidised bed reactor models

The difficulty of describing accurately the pattern of gas-flow through a bed of fluidised particles and the complexity of the physics of the fluidisation process does not help the derivation of realistic models of fluidised bed reactors. Only comparatively recently a number of models have been proposed to describe the behaviour of gas solid contacting and the fluid-mechanical behaviour within a fluidised bed.

The formation of gas-bubbles and the circulation of the solid particles will result in decreasing the overall reaction efficiency as compared to a fixed bed operating under the same conditions. In an ideal plug-flow reactor equation II.4.12 will predict theoretical conversions during gas solid catalytic reactions;

equation II.4.13 gives conversions in a completely-mixed flow reactor.*

$$X = 1 - e^{-K'} \quad \text{equation II.4.12}$$

$$X = 1 - 1/(1+K') \quad \text{equation II.4.13}$$

where, $K' = K_r P W / F$, is the dimensionless number of reaction units.

A. DISPERSION MODEL

Since the plug flow and the completely mixed models do not correlate fluidised bed data very well, various other models have been postulated to account for the deviations from these idealised cases.

The dispersion model developed by Danckwerts (141) assumes that the flow of gas through a bed involves some axial mixing which is characterised by an effective dispersion coefficient.

The steady state differential equation in dimensionless form is:

$$\frac{1}{N_{Pe}} \frac{d^2 f(z)}{dz^2} - \frac{df(z)}{dz} - R f(z) = 0 \quad \text{equation II.4.14}$$

where the dimensionless Peclet group contains the dispersion coefficient.

If the above equation solved analytically (142) for a first order catalytic reaction, the result is equation II.4.15 which predicts theoretical conversions in a catalytic reactor, where the gas flow involves some partial mixing in the dense phase.

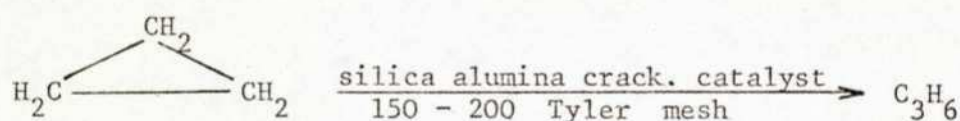
* All kinetics refer to a first order catalytic reaction

$$X = 1 - \frac{4a}{(1+a)^2 \exp \left[\frac{-FW(1-a)}{2E_g} \right] - (1-a)^2 \exp \left[\frac{-FW(1+a)}{2E_g} \right]} \quad \text{equat. II.4.15}$$

where
$$a = \sqrt{1 + 4 K_r \frac{W}{F} \left[\frac{E_g}{FW} \right]}$$

The two limiting cases, $E_g \longrightarrow 0$, and $E_g \longrightarrow \infty$, will result in solutions for equation II.4.15 identical with those of the plug flow and perfectly mixed models, respectively. This is illustrated graphically in figure II.4.k.

Ishii and Osberg (143) used equation II.4.15 to represent the performance of a fluidised bed packed with open-ended 14 mesh/in stainless steel screen cylinders (wire 0.024 in in diameter), of two sizes (0.2 x 0.2 and 0.4 x 0.4 in). The reaction studied was the catalytic isomerisation of cyclopropane to propylene.



The order of the reaction and the rate constants were determined from conversion data obtained in a fixed bed at different reactant flow velocities. They reported that the reaction follows approximately a first order process, and an overall activation energy of 15.7 Kcal/mole was calculated from the slope of the curve $\log K$ versus $1/T$. It was found that the dispersion model could not correlate unpacked fluidised bed conversion data, however, when packing was used the dispersion model been applied to correlate the conversion data obtained from the 6 in reactor.

In figure II.4.1 a comparison of their experimental data for two

Figure II.4.k Application of the dispersion model (170).

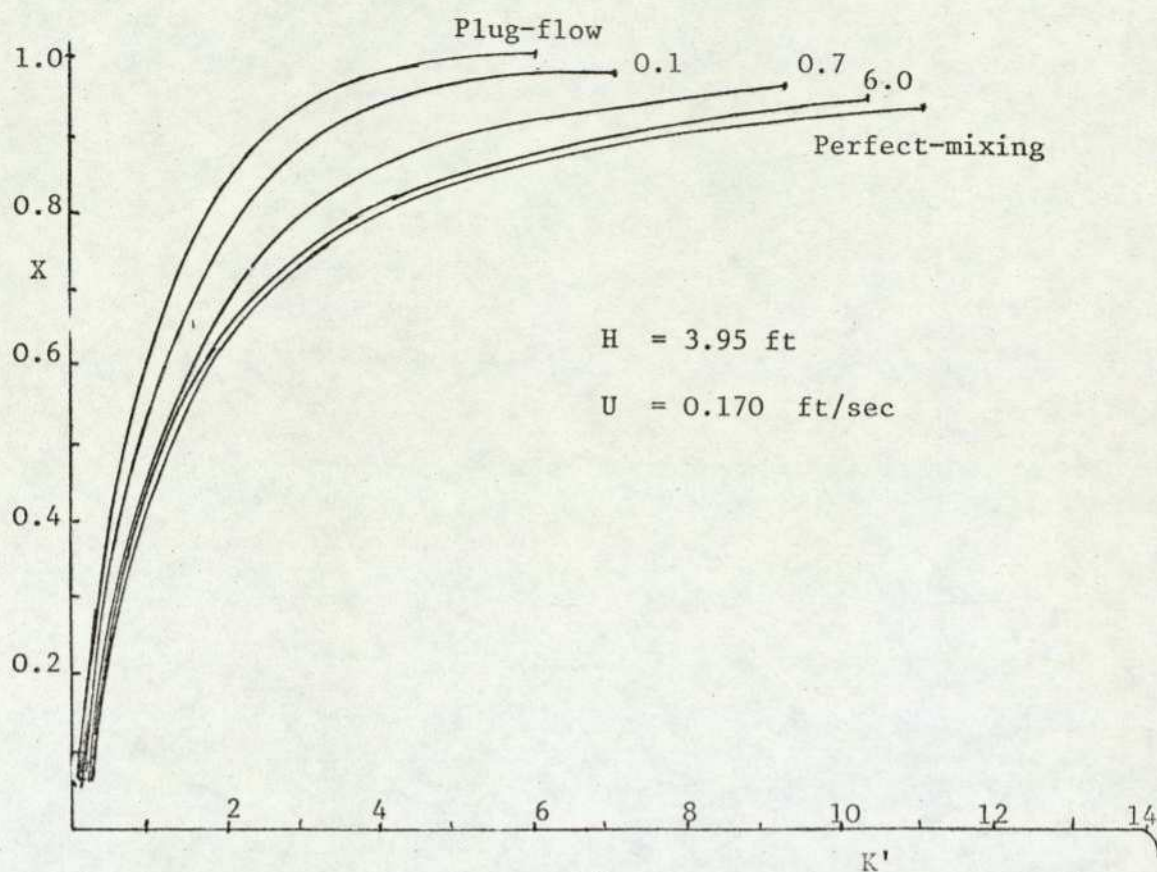
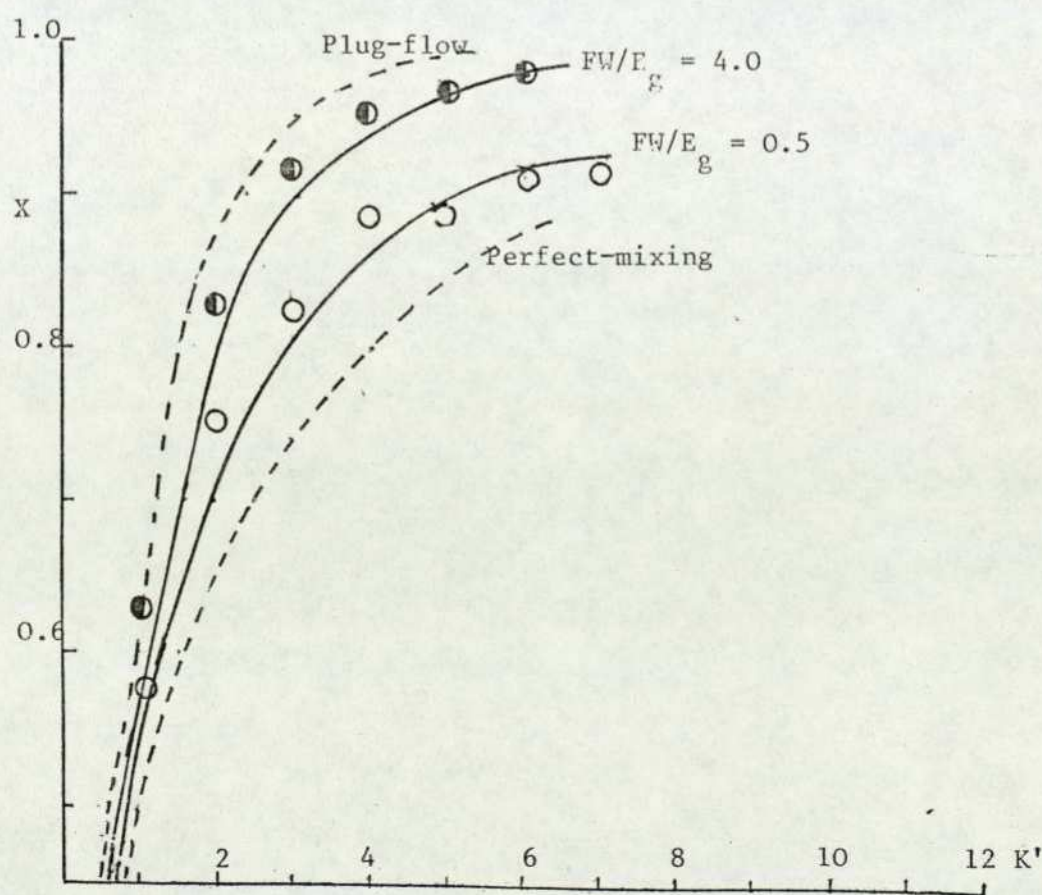


Figure II.4.1 Test of data with the dispersion model (143).



different settled bed heights, (1.8 and 10-11 in), and two gas velocity ranges , (0.03-0.2 and 0.1-0.52 ft/sec) ,with the dispersion model is well illustrated.

In a fluidised bed most of the early work showed that almost complete mixing of solids takes place. Singer and co-workers (144) showed almost perfect mixing of catalyst in a commercial catalytic cracking unit, and Overcashier, Todd and Olney (145) reported that the solids mixing observed in a 5-compartment baffled fluidised bed, was equivalent to that for three perfect mixers in series. Gilliland and Mason (146,147) showed that solids mixing was rapid enough in a gas fluidised bed, to maintain a uniform temperature distribution.

Furthermore Brammer et al (148) have applied Danckwerts model to correlate experimental data in a bubbling fluidised bed reactor ,but the agreement between the dispersion model and experiment was good only at low superficial gas velocities, where the average bubble size was very small.

B. ORCUTT-DAVIDSON-PIGFORD TWO PHASE MODEL

The simple two-phase model was first suggested by Toomey and Johnstone (149) in 1952 ,and it was developed by Johnstone et al (150,151,152) ,Mathis and Watson (153) ,Lewis et al (154) ,and May (155) . This model may be set up considering a fluidised bed system consisting of:

- i. A dense phase in which the flow rate is equal to the flow rate of the gas for minimum fluidisation i.e the voidage fraction is practically constant at ϵ_{mf} , and
- ii. A lean or bubble phase which carries the additional flow of fluidising fluid.

This situation is illustrated in figure II.4.m. The evidence of this picture of a fluidised bed is considerable, and it finds support for instance in the work of Morse and Ballou (156), Yasui and Johanson (157), Baumgarten and Pigford (158), and many others.

In 1961 Davidson (159) postulated that bubbles in a fluidised bed existed as if they were in an inviscid liquid. He derived a velocity potential for the particle motion and a stream function for the flow of fluidising fluid for both two and three dimensional beds.

In beds of coarse particles where bubbles rise at a velocity lower than the particulate phase fluid velocity, the theory predicted, that the bubble acts as a low resistance path for the particulate phase gas. The gas flows in at the base of the bubble, and out at the top, with no circulation. In beds of fine solids where bubbles rise at a velocity greater than the interstitial gas velocity, the theory predicted a circulation of gas from the nose to the base of the bubble within the limits of a spherical cloud. In particular for isolated bubbles rising in beds where the particles are smaller than about 400 μm in diameter, bubble gas contacts only particles within the cloud-overlap region, depending strongly upon the value of U_b / U_o , as illustrated in figure II.4.n.

Subsequently Orcutt, Davidson and Pigford (160), were the first to include the results on the relation between bubble rising velocity and the bubble size and the gas velocity in their two-phase fluidised bed reactor model.

In this model the bubble rising velocity is considered proportional to the square root of the bubble radius, $U_b = 0.711 (gD_e)^{1/2}$, following Davies and Taylor (161), where the equivalent bubble diameter,

$D_e = (6V / \pi)^{1/3}$. The upward velocity of the particulate phase above any bubble must be $U - U_{mf}$, so that the absolute rise velocity of each bubble will be:

$$U_a = (U - U_{mf}) + 0.711 \sqrt{g D_e} \quad \text{equation II.4.16}$$

It was also considered that all but the gas required to incipiently fluidise the bed passes through the bed as uniform and equally distributed bubbles. If the number of bubbles per unit volume is N and the bed expansion, $H - H_{mf}$, is due entirely to the presence of bubbles it was calculated that:

$$N V_b U_a = U - U_{mf} \quad \text{equation II.4.17}$$

$$\text{and } N V_b H = H - H_{mf} \quad \text{equation II.4.18}$$

Assuming that within each rising bubble there is complete mixing and no reaction, and there is an exchange of gas between the two phases, the following model was derived to give the conversion when a first order, catalytic reaction takes place in a fluidised bed where the dense phase gas is completely mixed:

$$X = 1 - \beta e^{-n_k} + \frac{(1 - \beta e^{-n_k})^2}{K' + (1 - \beta e^{-n_k})} \quad \text{equation II.4.19}$$

An analogous derivation, which assumes complete mixing within each rising bubble, but plug flow in the dense phase, gave a second order differential equation the solution of which is:

$$X = 1 - \left\{ \frac{1}{m_2 - m_1} \left[m_2 e^{-m_1} \left(1 - \frac{m_1 U_{mf}}{n_k U_o} \right) - m_1 e^{-m_2} \left(1 - \frac{m_2 U_{mf}}{n_k U_o} \right) \right] \right\}$$

equation II.4.20

where m_1 and m_2 are the roots of the quadratic equation:

$$m^2 - (n_k + K' / 1 - \beta) m + K' n_k / 1 - \beta = 0 \quad \text{equation II.4.21}$$

$$\text{where } \beta = 1 - U_{mf} / U_o \quad \text{equation II.4.22}$$

$$\text{and } n_k = q H / U_a V_b \quad \text{equation II.4.23}$$

If the gas exchange between the bubbles and the dense phase is described as a combination of the "cross flow" of the gas and convective diffusion (162), then the total gas exchange between the bubble and the dense phase is:

$$q = 3/4 U_{mf} \pi (D_e)^2 + 0.975 D_g^{1/2} (g/D_e)^{1/4} \pi D_e^2 \quad \text{equation II.4.24}$$

and thus equation II.4.23 becomes:

$$n_k = \frac{6.34 H_{mf}}{D_e (g D_e)^{1/2}} \left[U_{mf} + 1.3 D_g^{1/2} (g/D_e)^{1/4} \right] \quad \text{equation II.4.25}$$

The limiting conditions of equation II.4.19 and II.4.20 are:

$$\text{Lim } (K' \rightarrow \infty) \quad X = 1 - e^{-n_k} \quad (\text{fast reaction})$$

$$\text{Lim } (K' \rightarrow 0) \quad X = 0 \quad (\text{no reaction})$$

$$\text{Lim } (n_k \rightarrow \infty) \quad \begin{cases} X = 1 - 1/(1 + K') \\ X = 1 - e^{-K'} \end{cases} \quad \left(\begin{array}{l} \text{very fast} \\ \text{exchange} \\ \text{through bubbles} \end{array} \right)$$

Figure II.4.m The two phase model

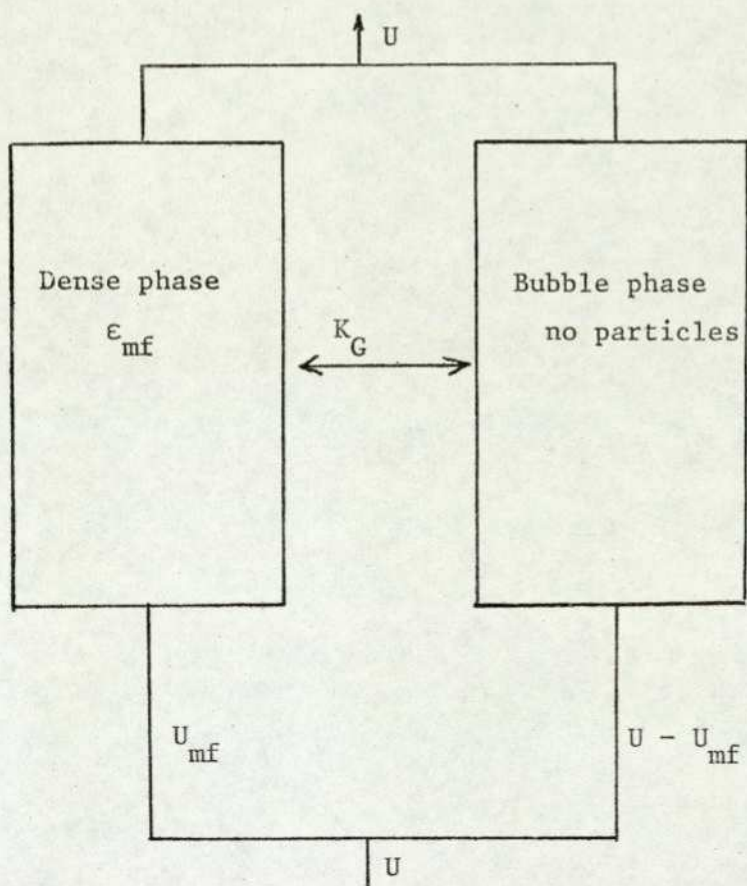


Figure II.4.n Flow of gas around a rising bubble in fluidised beds

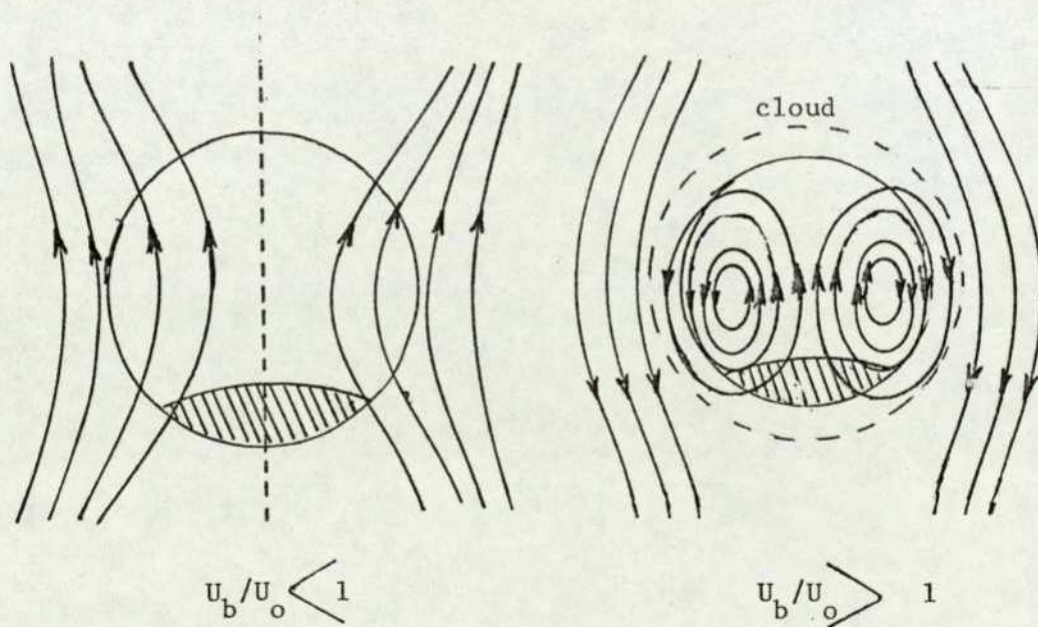


Figure II.4.o Test of Orcutt's results with the bubble model

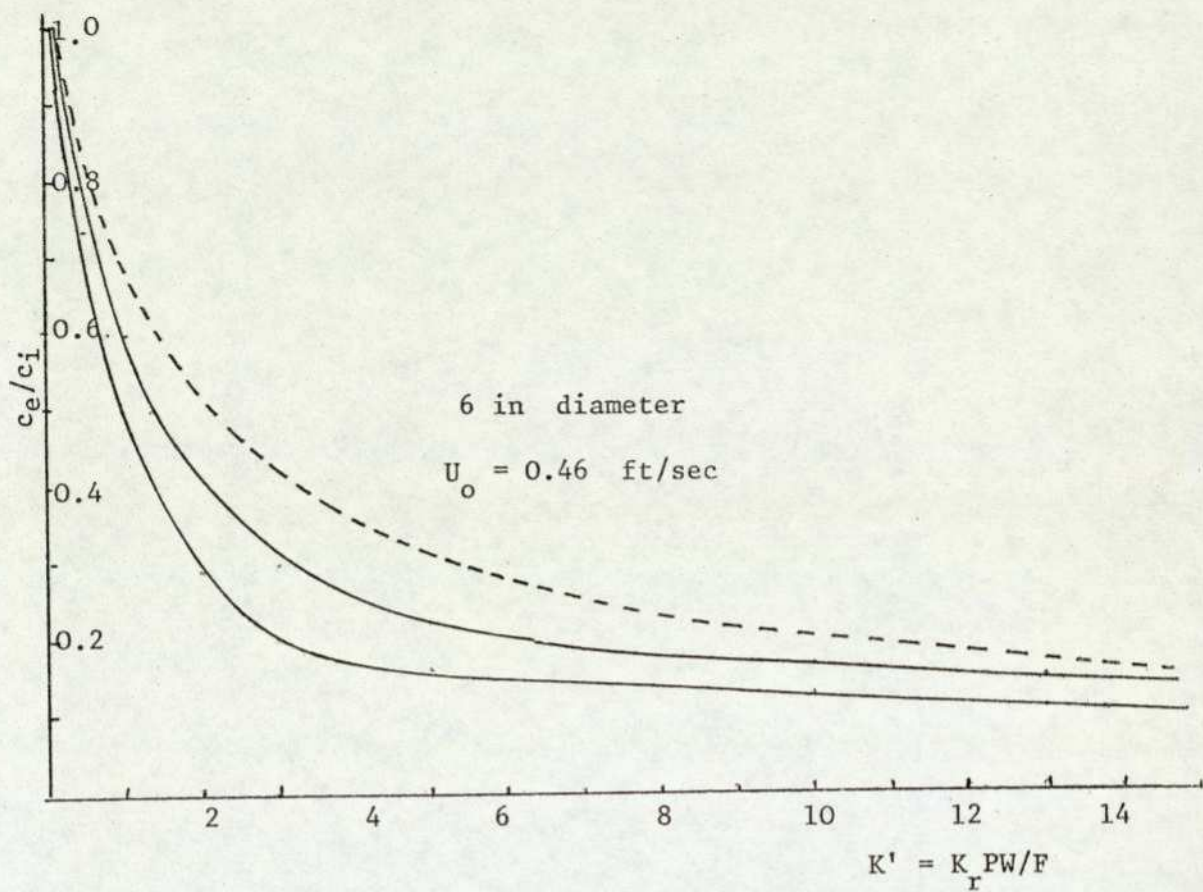


Figure II.4.p Test of Orcutt's results with the bubble model

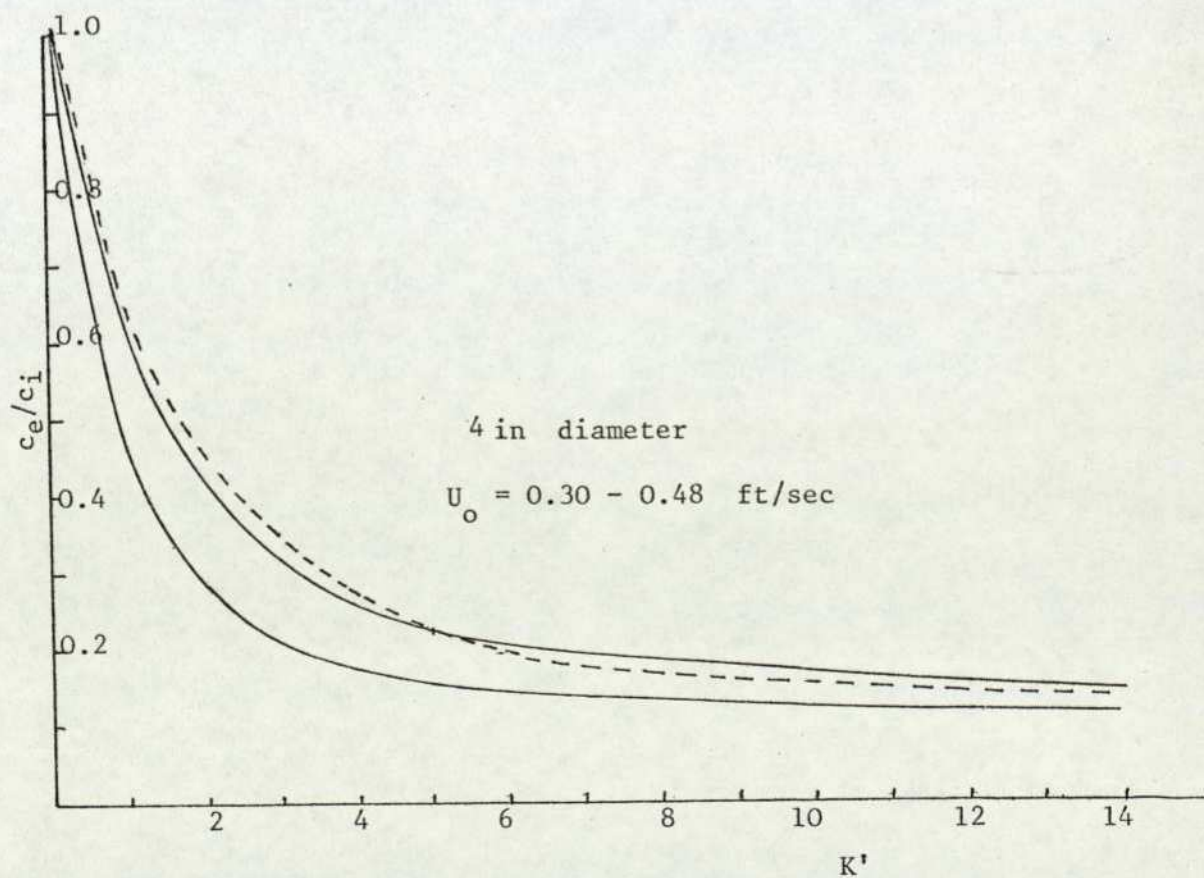


Figure II.4.q Test of Orcutt's results with the bubble model

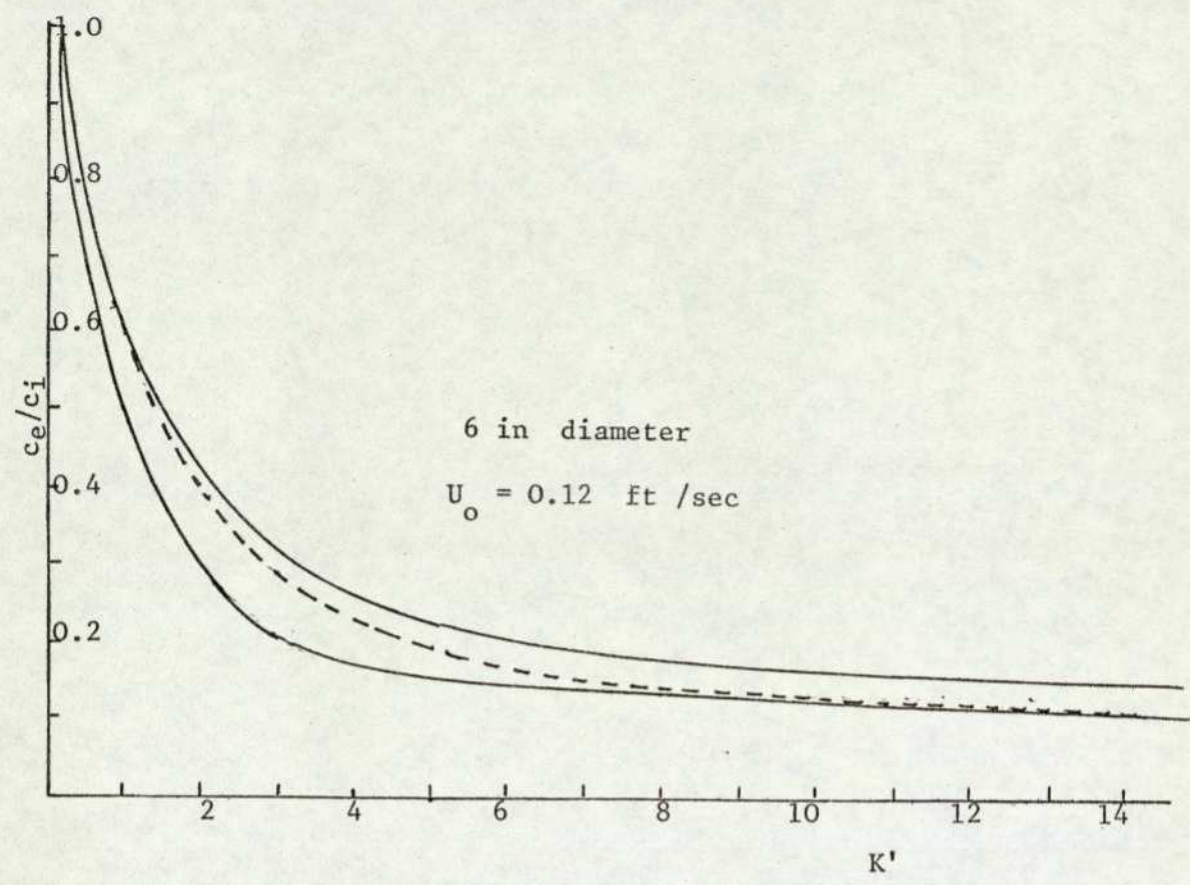
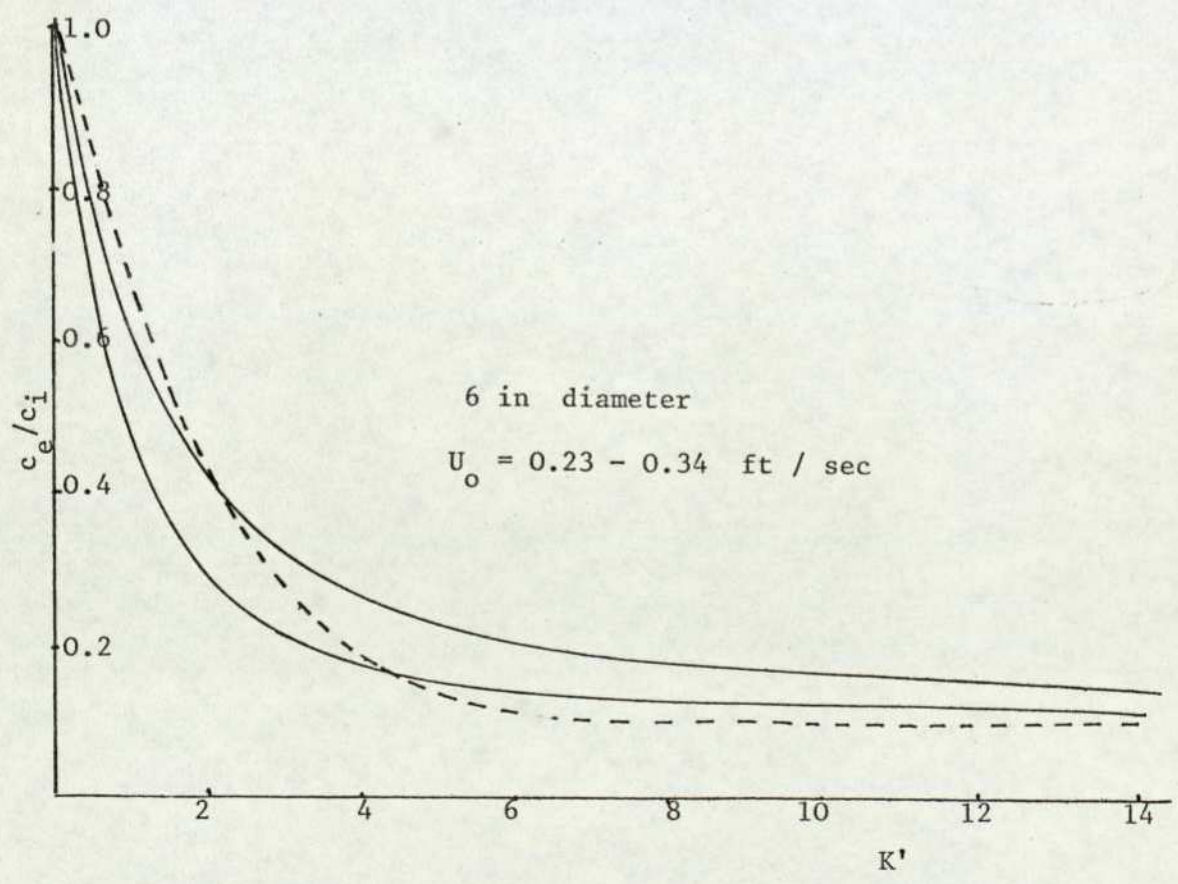


Figure II.4.r Test of Orcutt's results with the bubble model



These reactor models were compared with experimental conversions obtained by Orcutt (163), during the catalytic decomposition of ozone over iron-enriched silica alumina catalyst of particle size 20-60 μm . The results are illustrated in figures II.4.o, II.4.p, II.4.q and II.4.r, in the form of graphs showing the fraction of unconverted ozone, as a function of the dimensionless number of reaction units, K' . The dashed lines represent the best fit curve through his data points, while the solid lines represent theoretical conversions calculated from the bubble model assuming 1) Piston flow (equation II.4.20), and 2) Complete mixing (equation II.4.19) of the gas in the dense phase.

C. BUBBLE ASSEMBLAGE MODEL

Although the formation of a slug within a fluidised bed is an extreme case, however there is reasonable evidence (164, 165, 166), that coalescence of bubbles does occur; thus, bubbles increase in size as they rise through a fluidised bed.

Variations in bubble sizes were determined by measuring the bubble frequency at various flow rates and different bed levels in a 6 in diameter fluidised bed by both Lancaster (167) and Toor (168), using the experimental technique suggested by Angelino et al (169). They postulated that bubble frequencies were practically independent of the gas flow rates and could well be estimated from the following relationship.

$$fr = a_1 e^{-b_1 h} \quad \text{equation II.4.26}$$

Including the effect of bubble growth as described in the

above expression with the two-phase theory Calderbank and Toor (170) derived the "coalescence models". These fluidised bed reactor models predict the fractional conversions during a catalytic reaction within a fluidised bed where the gas is considered 1) completely mixed (equation II.4.27), and 2) in plug flow (equation II.4.28), while the bubble size increases as they rise through the bed mostly due to coalescence.

$$X = 1 - \left[\left(1 - \frac{U_{mf}}{U} \right) (c_b/c_i)_{h=H} + \left(\frac{U_{mf}}{U} \right) (c_p/c_i)_{h=H} \right] \text{ equat. II.4.27}$$

$$X = 1 - \left[\left(1 - \frac{U_{mf}}{U} \right) (c_b/c_i)_{h=H} + \left(\frac{U_{mf}}{U} \right) (c_p/c_i)_{h=H} \right] \text{ equat. II.4.28}$$

For equation II.4.28 the following boundary conditions were taken;

- i. $c_b = c_i$ at $h=0$
- ii. $dc_b/dh = 0$ at $h=0$

In deriving the above models the following assumptions were made;

- i. Bubbles within a fluidised bed are formed from the excess gas above the minimum fluidisation velocity.
- ii. The bubble size is increasing due to coalescence with rise through the bed, and the rate of bubble growth is given by equation II.4.26.
- iii. The bed expansion, $H - H_{mf}$, is due entirely to the presence of bubbles. The bubbles are completely devoid of particles and

therefore no reaction takes place in them.

iv. The absolute rise velocity of bubbles, U_a , is the sum of their natural velocity, U_b , and the upward velocity of the particulate phase between them.

v. The total gas exchange between the bubbles and the dense phase is attributed to a combination of the gas crossflow, and mass transfer from the bubble to the dense phase.

Experimental conversions obtained during the catalytic decomposition of ozone were compared directly with conversions predicted from the bubble assemblage model by Lancaster (167) and Toor (168). The variation of the unconverted fraction of ozone, c_e/c_i , in the fluidised bed reactor with the dimensionless number of reaction units, K' , is shown in figures II.4.s, II.4.t, II.4.u and II.4.v.

The solid lines were calculated from the models represented by equations II.4.27 and II.4.28, while the dashed line represents the best fit curve through the experimental points estimated from the following expression.

$$\frac{c_e}{c_i} = \frac{1}{1+K'} + \bar{a}_1 \left(\frac{K'}{1+K'} \right)^2 + a_2 \frac{K'^2}{(1+K')^3} + \dots + a_m \frac{K'^m}{(1+K')^{m+1}}$$

equation II.4.29

giving the limits $\lim (K' \rightarrow 0) \quad (c_e/c_i) = 1$

$$\lim (K' \rightarrow \infty) \quad \left(\frac{c_e}{c_i} \right) - \frac{1}{1+K'} = \bar{a}_1$$

In addition, many other more sophisticated models have been

Figure II.4.s Comparison between experimental data and the bubble assemblage model (170)

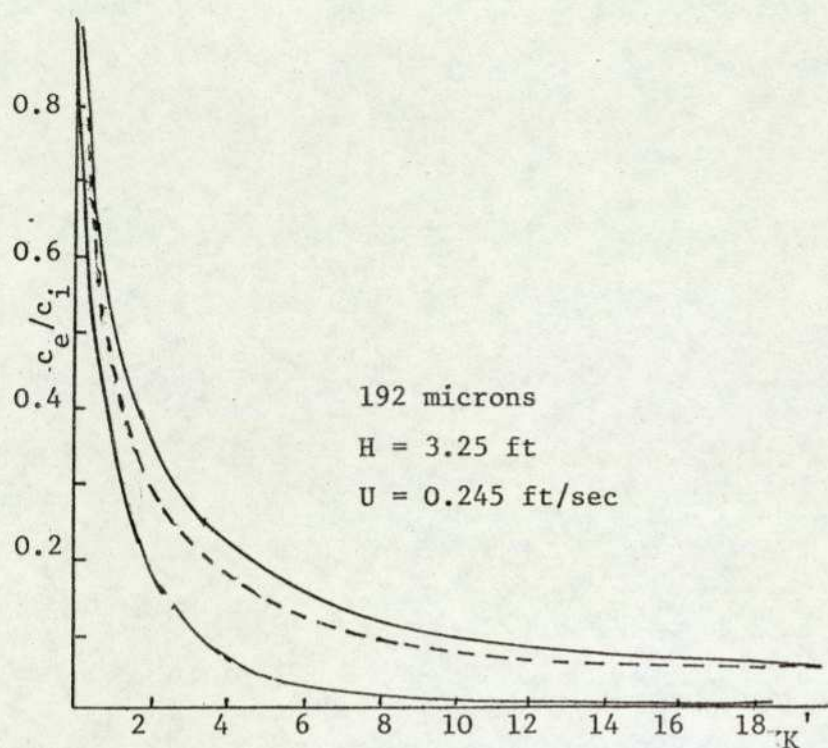


Figure II.4.t Comparison between experimental data and the bubble assemblage model (170)

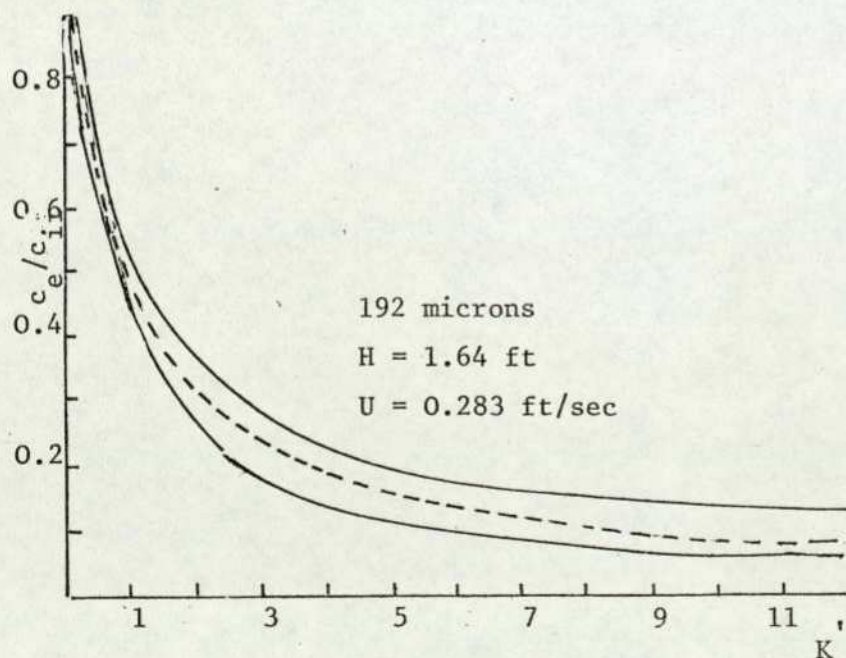


Figure II.4.u Comparison between experimental data and the bubble assemblage model (170)

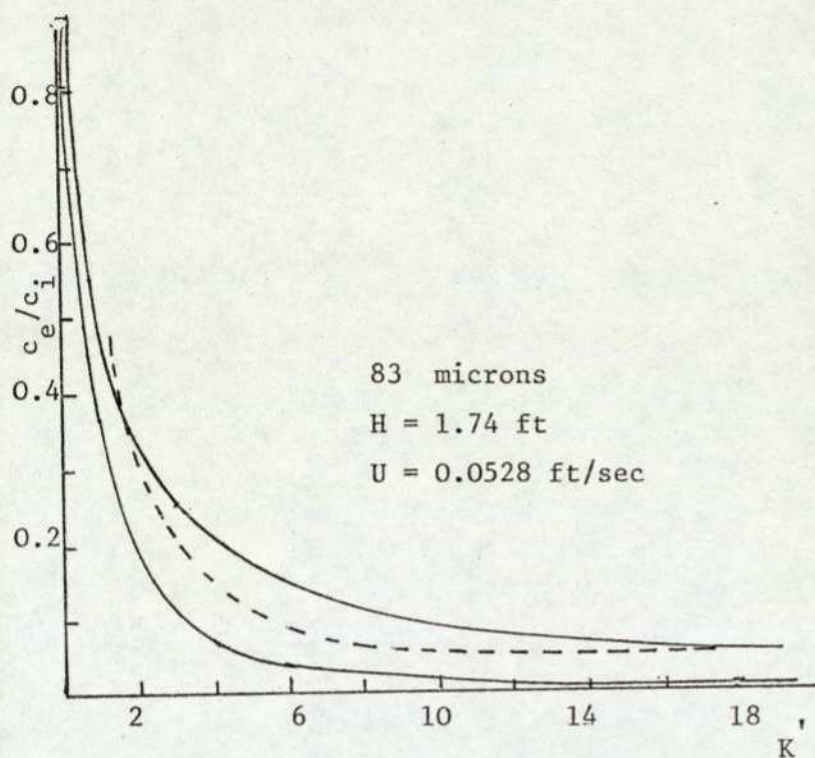
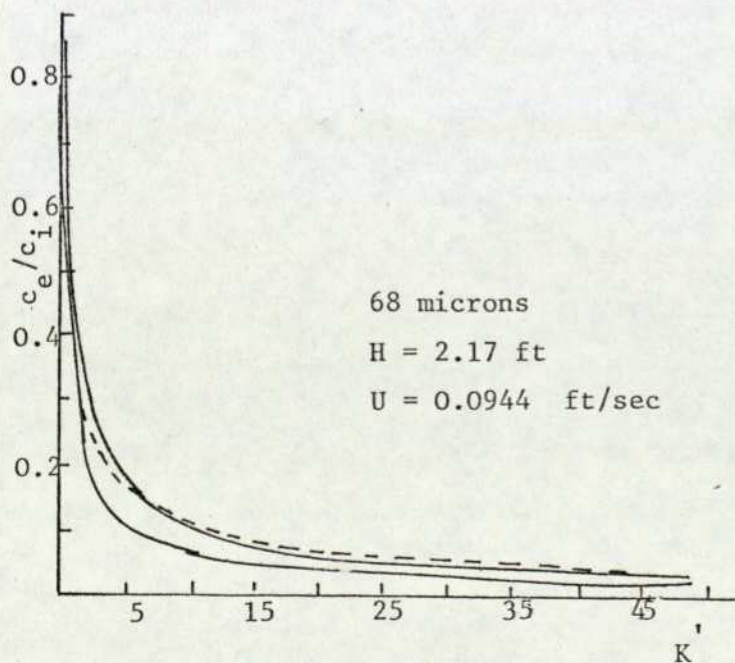


Figure II.4.v Comparison between experimental data and the bubble assemblage model (170)



proposed in the last ten years to describe the performance of fluidised bed reactors. These models may be classified according to their level of sophistication and complexity into two groups. In one group of models, a fluidised bed is considered to be composed of two parallel single phase reactors with cross-flow between them. Such models are basically variations of the two phase models containing more than three parameters, two of which specify the degree of back-mixing in the individual phases, and a third which defines the rate of cross-flow between them.

In the second group the models are based on the properties of single rising bubbles and normally the average bubble diameter becomes the key parameter in these models. The absolute and normal bubble rise velocity, cloud formation, throughflow of gas in the bubbles e.t.c , are also considered in certain models. A summary according to the above classification of the most important fluidised bed reactor models in the literature are given in tables II.4.a and II.4.b .

II.4.5 Mass transfer in fluidised beds

Reference has been made to the fact that mass transfer is accepted as one of the basic steps during solid catalysed reactions. Hougen and Marsall (171) proposed the first exhaustive treatment of mass transfer control for the process of adsorption from fluid streams by fixed beds.

Gamson , Thodos and Hougen (172) , and Wilke and Hougen (173) correlated experimentally measured mass and heat transfer for a bed of granular solids, as empirical functions of the Reynolds number and Schmidt number. This method was extended by Hurt (174) to cover heterogeneous catalytic reactions in a fixed bed by

Key to tables II.4.a and II.4.b

A. Gives the way of dividing the phases within the fluidised bed.

i. 3-phases bubble phase-cloud phase-emulsion phase

ii. 2-phases $\begin{cases} \text{bubble phase-(cloud phase+emulsion phase)} \\ \text{(Bubble phase+cloud phase)-emulsion phase} \end{cases}$

B. Describes the type of flow of the gas within the bubble phase

C. Describes the type of flow of the gas within the emulsion phase ,i.e the degree of back-mixing

D. Describes the gas exchange between the phases.

E. Considers the effect of jet formation in the model.

F. Considers the effect of cloud formation in the model.

G. Considers the bubble wake in the model.

Table II.4.a Fluid-bed reactor models " GROUP I "

MODELS	DESCRIPTION
Shen and Johnstone (151)	A. Two phases, bubble phase completely free of particles. B. The flow of the gas in the bubble phase is assumed to be the gas flow in excess of that required at minimum fluidisation. C. The gas flow is considered either in plug-flow or perfectly mixed. D. The mass transfer coefficient between the two phases is calculated on the basis of chemical reaction data. E. Is ignored F. Is ignored G. Is ignored
Mathis and Watson (153)	A. Two phases, dilute phase including solids but not specifically cloud or wake solids. B. The gas flow is assumed to be the gas flow in excess of that required at minimum fluidisation C. The gas is considered in plug flow D. The mass transfer coefficient between the two phases is calculated on the basis of chemical reaction data. E. Is ignored F. Is ignored G. Is ignored

MODELS	DESCRIPTION
Lewis et al (154)	A. Two phases, dilute phase including solids but not specifically cloud or wake solids. B. The gas flow is considered to be the entire flow through the bed. C. The gas flow is considered either in plug-flow or perfectly mixed. D. The mass transfer coefficient between the two phases is calculated on the basis of chemical reaction data. E. Is ignored F. Is ignored G. Is ignored
May (155)	A. Two phases, bubble phase completely free of particles. B. The gas flow is assumed to be the gas in excess of that required at minimum fluidisation C. The flow of the gas in the dense phase is characterised by an axial dispersion coefficient, E_g, and it is a variable parameter. D. The mass transfer coefficient is a variable parameter. E. Is ignored F. Is ignored G. Is ignored

MODELS	DESCRIPTION
Van Deempter (197)	A. Two phases, bubble phase completely free of particles B. The flow of the gas in the bubble phase is a variable parameter. C. The flow of the gas in the dense phase is considered either in plug-flow or a downward moving flow. D. The mass transfer coefficient is a variable parameter. E. Is ignored. F. Is ignored G. Is ignored.
Lanneau (198)	A. Two phases, dilute phase including solids B. The flow of the gas in the bubble phase is a variable parameter. C. A downflow of dense phase gas is permitted D. The cross-flow between the two phases is based on a mechanistic expression and is a variable parameter. E. Is ignored F. Is ignored G. Is ignored

MODELS	DESCRIPTION
Muchi (199, 200)	A.Two phases,bubble phase completely free of particles B.The gas flow is assumed to be the gas in excess of that required at minimum fluidisation. C.The flow of the gas in the dense phase is considered similar to that as Tanks in series model. D.The mass transfer coefficient is calculated on the basis of chemical reaction data. E.Is ignored F.Is ignored G.Is ignored
Kobayashi et al (201)	A.Two phases,dilute phase including solids. B.The flow of the bubble phase gas is considered either the excess gas of that required at minimum fluidisation or the entire flow of the gas. C.The gas flow is considered either in plug-flow or perfectly mixed. D.The mass transfer coefficient is a variable parameter E.Is ignored F.Is ignored G.Is ignored

MODELS	DESCRIPTION
Mireur and Biscoff (202)	A. Two phases, bubble phase completely free of particles. B. The gas flow is assumed to be the gas in excess of that required at minimum fluidisation. C. The flow of the gas in the dense phase is characterised by an axial dispersion coefficient, E_g, and it is a variable parameter. D. The mass transfer coefficient is obtained by independent gas mixing studies or it is calculated on the basis of chemical reaction data. E. Is ignored F. Is ignored G. Is ignored

Table 11.4.b Fluid-bed reactor models " GROUP II "

MODELS	DESCRIPTION
Orcutt-Davidson-Pigford (160)	A. Two phases, bubble phase completely free of particles B. The gas flow is assumed to be the gas in excess of that required at minimum fluidisation, and is considered perfectly mixed. C. The gas in the dense phase is considered either in plug flow or perfectly mixed. D. The mass transfer between the lean and the dense phase is attributed to a combination of the gas "cross-flow" and convective diffusion. The transfer across cloud-emulsion boundary is considered fast. E. Is ignored F. Is ignored G. The wake is ignored or treated as part of the overall dense phase.
Rowe (203)	A. Two phases; a cloud-unit phase which includes bubbles and their associated clouds, and an emulsion phase which includes the remainder of the dense phase. B. The gas flow is assumed to be the gas in excess of that required at minimum fluidisation. C. The gas in the dense phase is considered in plug flow

5/

MODELS	DESCRIPTION
	D. The mass transfer across bubble-cloud interface is very fast, and is assumed that there is no gas transfer across cloud-emulsion boundary. E. Is ignored F. The effect of cloud is considered, and the gas within the cloud is assumed perfectly mixed. G. The wake is treated as part of the cloud.
Toor and Calderbank (204)	A. Two phases, bubble phase completely free of particles. B. The gas flow is assumed to be the gas in excess of that required at minimum fluidisation, and is considered perfectly mixed. The bubble growth is accounted in the model. C. The gas in the dense phase is considered either in plug-flow or perfectly mixed. D. The mass transfer between the lean and the dense phase is attributed to a combination of the gas "cross-flow" and convective diffusion. The transfer across cloud-emulsion boundary is considered very fast. E. Is ignored F. Is ignored G. Is ignored

MODELS	DESCRIPTION
Kunii and Levenspiel (124)	A. Three phases; bubble, cloud and emulsion phase B. The flow of the gas in the bubble phase is assumed to be the gas in excess of that required at minimum fluidisation with through-flow between the phases. C. A downflow of the gas in the dense phase is permitted. D. The mass transfer across bubble-cloud interface is a combination of diffusion with throughflow. E. Is ignored F. The effect of the cloud is considered, and the gas flow within the cloud is assumed perfectly mixed. G. The wake is treated as part of the cloud.
Rowe and Partridge (205)	A. Two phases; a cloud-unit phase which includes bubbles and clouds, and an emulsion phase. B. The gas flow is assumed to be the gas in excess of that required at minimum fluidisation. C. The gas in the dense phase is considered in plug flow D. Mass transfer coefficient is calculated on the basis of chemical reaction data, and the transfer across bubble-cloud interface is assumed very fast. E. Is ignored

MODELS	DESCRIPTION
	F. The effect of cloud is considered, and the gas within the cloud is assumed perfectly mixed G. The wake is treated as part of the cloud.
Mori and Wen (206)	A. Two phases; the bubble + cloud ,and an emulsion phase. B. The flow of the gas in the bubble phase is considered to be the entire flow of the gas. C. The flow of the gas in the dense phase is considered similar to that as Tanks in series model. D. Mass transfer is a variable parameter. E. The effect of jet formation is considered in the model F. The effect of cloud formation is also considered G. Is ignored.
Chiba and Kobayashi (207)	A. Two phases; a cloud-unit phase which includes bubbles and their associated clouds, and an emulsion phase which includes the remainder of the dense phase. B. The gas flow is assumed to be the gas in excess of that required at minimum fluidisation. C. The gas in the dense phase is considered in plug flow

MODELS	DESCRIPTION
	 D. Mass transfer coefficient is calculated on the basis of chemical reaction data, and the transfer across bubble-cloud interface is assumed very fast. E. Is ignored F. The effect of cloud is considered, and the gas flow within the cloud is assumed perfectly mixed. G. The wake is treated as part of the cloud.

defining the height of a reaction unit equal to the sum of the height of transfer units, and height of surface reaction unit. Amundson (175,176), Kasten et al (177,178), and Rosen (179), developed mathematical treatments for successive mass transfer, and intraparticle diffusion in fixed beds.

In fluidised beds it is impractical to apply the fixed bed theories simply because the solids are always in a state of rapid movement, and mixing. As a result, all the solids become partially saturated with adsorbate gas as soon as the fluidisation process starts. The activity of adsorbate at the gas/solid boundary depends on the type of gas and solids mixing, and the postulates of the two phase theory of fluidisation make the kinetics more complicated.

Usually, in many physical and chemical operations occurring in fluidised beds, mass transfer is excellent, and therefore mass transfer steps are not generally the rate determining ones. However, in fluidised bed reactors, kinetic data can easily be misinterpreted unless knowledge of the mass transfer resistances are taken into consideration.

Although the formation of bubbles is the main characteristic of fluidised beds, however, the mass transfer between the wall, and the bed, and between particles and fluid have to be considered in the absence of phase segregation. On the other hand, mass transfer between the lean and the dense phase in fluidised beds has to be examined carefully during "aggregative fluidisation" where the bubble phase has an influence on the transport rate.

A. Mass transfer between a fluidised bed and a wall.

In particulate fluidisation, the mass transfer coefficient, K_{GW} , for bed-to-wall transfer can be predicted from the following equation:

$$\frac{K_{GW}}{U} \epsilon N_{Sc}^{2/3} = C \left[\frac{U_o d_p}{\nu(1-\epsilon)} \right]^{-m} \quad \text{equation II.4.30}$$

This relationship predicts that the product of the Stanton number, $N_{St} = K_{GW} / u$, and $N_{Sc}^{2/3}$, is a unique function of the Reynolds number, based on the voids and their mean hydraulic diameter (180). Mass transfer coefficients theoretically obtained from the above equation are in fair agreement with experimental values obtained by many investigators (181,182,183).

In aggregative fluidisation the particles do not follow the fluid turbulence at all, unlike small particles in a liquid fluidised bed. This difference in turbulent motion of the particles in both cases undoubtedly will have some influence on the overall mass transfer coefficients.

Gupta and Thodos (184) reported that during transfer to a packed bed of spheres, the formation of an "aggregative bed", resulted in measurable changes of the mass transfer rates.

Ziegler and Holmes (185) in 1956 measured mass transfer from a fixed vertical plate of naphthalene to a gas fluidised bed. Unfortunately their data are inconsistent with other reported data. This lies in the fact that possible adsorption of naphthalene on the particles increased the transfer rates considerably. Only at the point of minimum fluidisation were their mass transfer coefficients in agreement with other data. That can be

easily explained by the fact that at low gas velocities the particles are still restricted in their movement and are not free to migrate.

B. Mass transfer between the fluid and solids

A large number of reports deal with the mass transfer between the particles and the fluid. Most of the data obtained, are for particles somewhat larger than those usually employed with gases. In general the mass transfer coefficients for fine particles are very difficult to measure accurately.

The first step towards comparing fluidised bed mass transfer data with those of fixed beds, was presented by Chu, Kalik and Wetteroth (186), studying systems of naphthalene coated celite cylinders, and glass beads fluidised with air. When the mass transfer factors were plotted against Reynolds number, the fluidised bed data were lower than the fixed bed results, for the same system, and a characteristic line existed for each particle size in agreement with earlier reported work (187,188).

Gas to particle mass transfer, has been examined by many investigators (189,190,191), and their work suggests that the only diffusional resistance of importance, is between the walls of the bubble and the gas inside.

Richardson and Bakhtiar (192) reported that equilibrium between fluidised solids and effluent gas is very nearly reached when air containing toluene is passed at 0.3-6.0 cm/sec through only 0.2-7.0 cm bed depth of a fluidised granular toluene adsorbent in the size range mostly of 40 - 80 μm particles.

Correlations and statements of existing data on mass transfer in both fixed and fluidised beds are given by several

authors (193,194,195) .However,the problem is that in the correlations proposed not only the influence of the velocity is hidden But also the voidage fraction of the bed on the mass transfer coefficient.

Chu et al (186) suggested that a modified Reynolds number containing the voidage in the denominator plotted against the mass transfer factor,correlated their fluidised bed data with the body of fixed bed data. It is therefore unfortunate that voidage is a difficult parameter to determine accurately for low solids density beds,especially bubbling gas fluidised beds.

Richardson and Szekely (195) used the adsorption of carbon tetra-chloride from air streams in fluidised beds of activated carbon in a non-bubbling system. They showed that the mass transfer coefficient was a maximum at the start of the process and decreased as the resistance to transfer in the pores of the solid increased. It was established that the back-mixing was more important at low Reynolds numbers,probably due to the movement of gas in the boundary layers surrounding the individual particles,as bubbles were not present. They postulated the following correlation for the mass transfer coefficients.

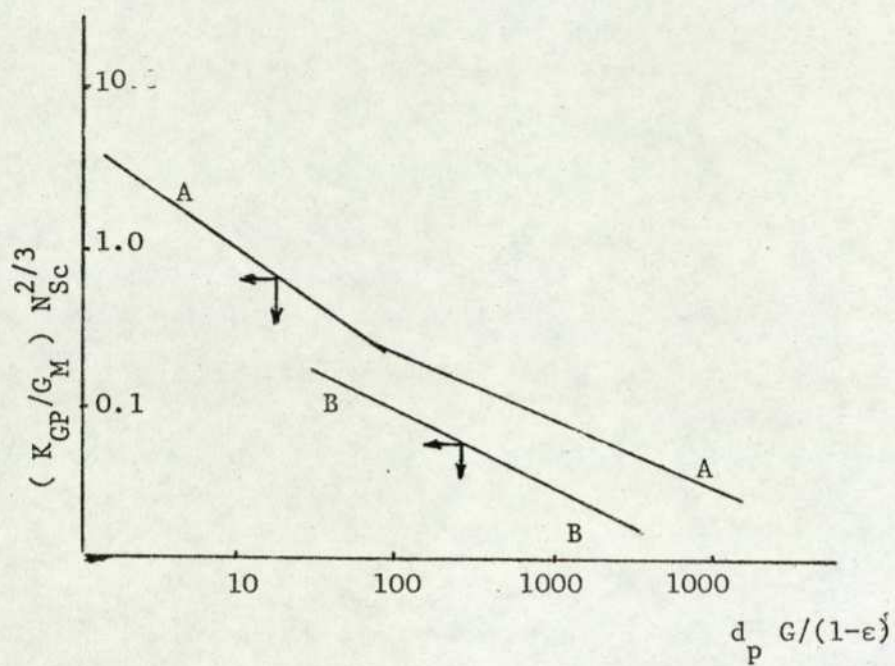
$$\frac{K_{GP} d_p Y}{D} = 0.374 \left[\frac{d_p U_o \rho}{\mu} \right]^{1.18} \quad \text{equation II.4.31}$$

$$\text{for } 0.1 < N_{Re}(P) < 15$$

$$\text{and } \frac{K_{GP} d_p Y}{D} = 2.01 \left[\frac{d_p U_o \rho}{\mu} \right]^{0.5} \quad \text{equation II.4.32}$$

$$\text{for } 15 < N_{Re}(P) < 250$$

Figure II.4.w Correlation of data on mass transfer.



Correlations of reported mass transfer data in both fluidised and fixed beds are given in figure II.4.w, which shows the abscissa, $(K_{GP} / G_M) N_{Sc}^{2/3}$, as a function of the Reynolds number, $N_{Re} = d_p G / \mu (1-\epsilon)$.

Line A-A is that of Chu et al (186), representing data from various sources on gas-solid and liquid-solid systems in fixed and fluidised beds. Line B-B represents a later correlation by Sen Gupta and Thodos (196).

The data of Fan, Yang and Wen (189) for expanded or partly fluidised beds of 8 - 24 mesh benzoic acid particles in water, fall considerably below line A-A, suggesting the possibility that figure II.4.w predict too large values of $j_D = K_{GP} / G_M$ for expanded beds. A recent correlation by Recetti and Thodos (190) using the same coordinates agrees closely with line A.

C. Mass transfer between lean and dense phase in fluidised beds

The way that phase segregation influences mass transfer rates between particles and fluid is rather complicated, and is mathematically difficult to express the transfer coefficient in terms of the exchange resistance between the two phases unless the relatively simple two phase theory is adopted. The two phase model assumes that:

- i. All particles are present in the dense phase.
- ii. The lean phase occupies a fraction ϵ_b of the bed and therefore a fraction $(1 - \epsilon_b)$ of the bed is occupied by the dense phase.
- iii. The fluid in the dense phase is considered to be in plug-flow
- iv. The lean phase does not contain any particles and is in

plug flow too.

v. The rate of exchange between the lean and the dense phases per unit volume and per unit of driving force is $K_G a_b$, where K_G is the exchange coefficient and a_b the surface area of the bubbles per unit volume.

For this simple model, the degree of equilibrium at the exit between the particles and the effluent, X , can be expressed in terms of the following four dimensionless groups (180):

$$1. \quad \alpha = U_{mf} / U_o \quad \text{equation II.4.33}$$

This parameter is the reciprocal of the fluidisation number. When a fluidised system is operated in the neighbourhood of the incipient fluidisation regime ($\alpha \rightarrow 1$) the influence of phase segregation on the transfer process can be neglected. Instead the degree of mixing in the dense phase becomes important. At high fluidisation numbers ($\alpha \rightarrow \infty$) the degree of mixing in the dense phase is irrelevant as long as the transfer resistance at the interface is still important.

$$2. \quad \beta = (1 - \epsilon_b) E_g / U_o H \quad \text{equation II.4.34}$$

The influence of dispersion in the dense phase on the transfer process is given by the parameter β , which is proportional to the dispersion coefficient, E_g .

$$3. \quad \gamma = U d / 6(1-\epsilon)K_{GP}H = U/K_{GP}aH \quad \text{equation II.4.35}$$

The parameter γ , is the reciprocal of the number of transfer units that would have been present in a uniformly fluidised bed. When a catalytic reaction is taken place in a fluidised bed, the mass transfer resistance between the fluid and the particles has to be replaced by the sum of this resistance, and the resistance due to chemical reaction at the particle. Consequently this parameter for a first order catalytic reaction of the type $A \longrightarrow B$ is given by:

$$\gamma = (U/H) (1/K_{GP}a + 1/K) \quad \text{equation II.4.36}$$

$$4. \quad \delta = K_G a_b / K_{GP} a \quad \text{equation II.4.37}$$

the ratio of the transfer resistance in the dense phase and the resistance between the two segregated phases is given by the parameter δ . Similarly this parameter in the case of a first order catalytic reaction will be modified to:

$$\delta = K_G a_b (1/K_{GP}a + 1/K) \quad \text{equation II.4.38.}$$

CHAPTER III
EXPERIMENTAL

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EXPERIMENTAL

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III.1 APPARATUS

The catalytic oxidation of isobutylene to methacrolein and other products was carried out in a bed of bismuth-molybdate catalyst fluidised with a gaseous mixture consisting of the olefin together with nitrogen and oxygen.

The inlet gases were taken from cylinders through molecular sieve drying columns, and the flow rate of each gas was adjusted using fine control needle valves, and measured by means of mercury manometers.

Back pressures across the reactor were measured with a CCL_4 manometer, fitted in the outlet of the reactor. The glass reactor was equipped with a stainless steel paddle stirrer with electric motor drive. The furnace in which the reactor was mounted vertically was fitted with a temperature controller, while the oven temperature was measured accurately by three Cr-Al thermocouples. Before passing to the analytical section the product gases were led through a cyclone system, where deposition of any entrained catalyst particles could be estimated.

Experiments in the temperature range 390-535 °C were carried out and percentage conversions, selectivities and yields of the products were determined using two PYE-UNICAM 104 chromatographs one fitted with a flame ionization detector, the other with a katharometer head.

The gas mixture was finally passed through a methacrolein trap and thence to the atmosphere. All parts of the apparatus were connected with copper tubing (1/4"), and the post-reactor part was

Key to the Figure III.1.a

O_2 , N_2 , C_4H_8 Gases from cylinders

A Molecular sieve drying columns

B Flow rate control needle valves

D Mixing chamber

E CCl_4 manometer

F Stainless steel stirrer

G Furnace

H Reactor

I Cyclone system

J Chromatographs

K Aldehyde trap

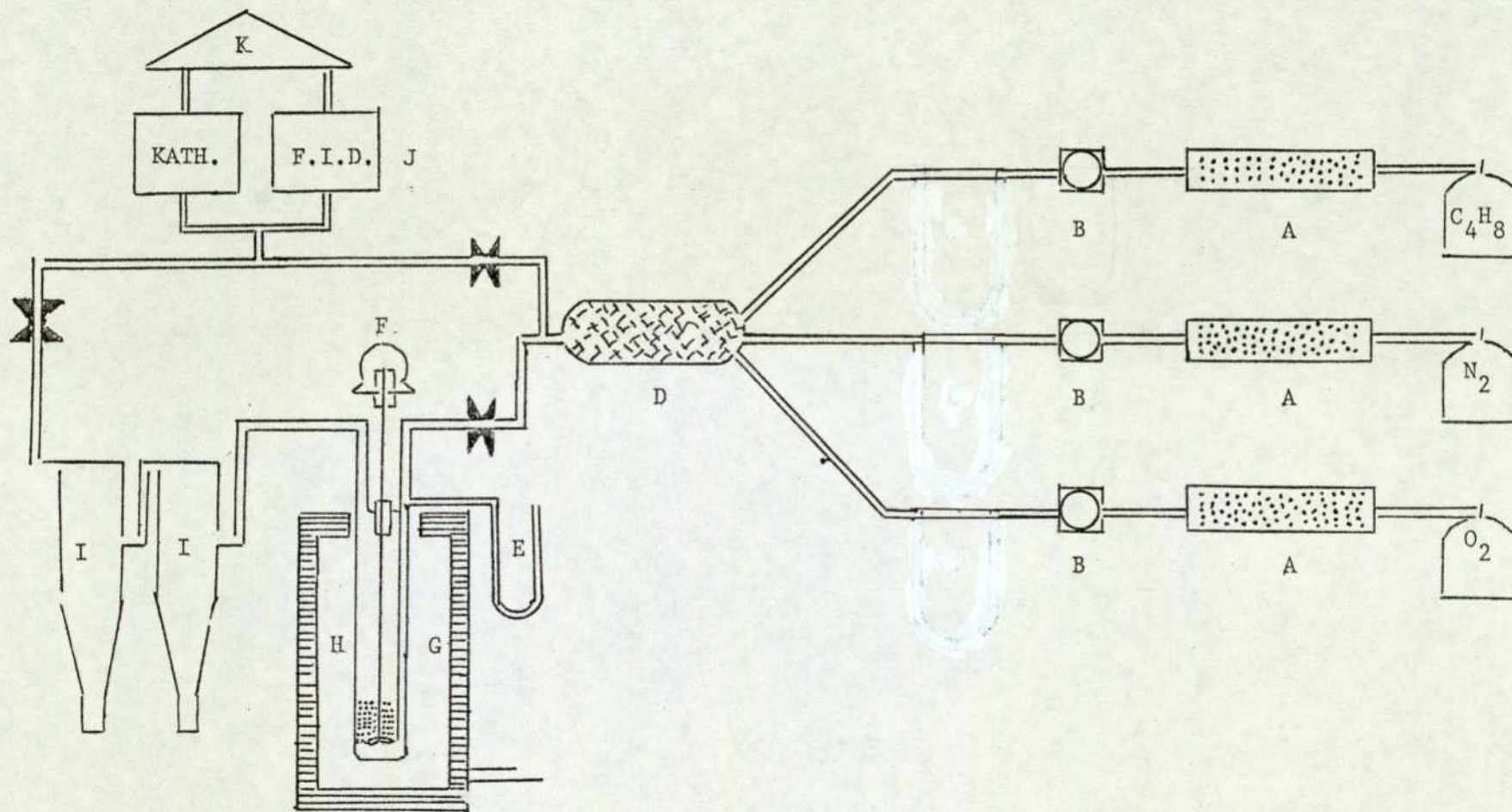


Figure III.1,a Schematic diagram of the experimental setup for the oxidation experiments

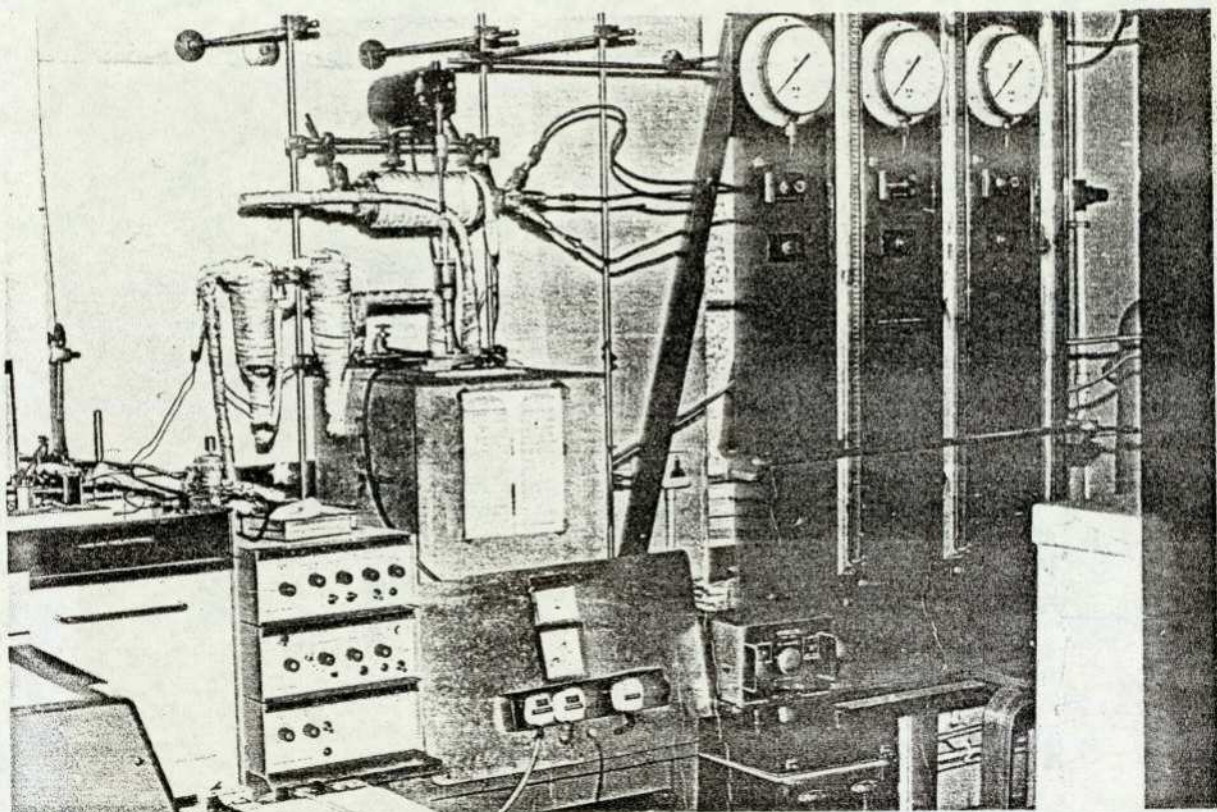


Plate III.1.a Laboratory layout of the apparatus.

bound with electrothermal heating tape and kept at a temperature of 120°C. This is required to prevent condensation of any polymer produced which can cause blockages. Heating tape at 70°C was also fitted to the reactor inlet to ensure homogeneity of the reactant upstream of the mixture.

The apparatus used are illustrated in the schematic diagram of figure III.1.a, while plate III.1.a shows the actual laboratory layout of the apparatus.

III.1.1 Inlet gases, drying columns

The inlet gases, oxygen free nitrogen and oxygen were supplied by the British Oxygen Company while analytical grade isobutylene was supplied by the British Petroleum Company.

The drying columns were made of pyrex glass tubing of dimensions 25"x1" and were fitted with molecular sieve 4A pre-activated at 450 °C for 24 hours.

III.1.2 Flow rates and control valves

The flow rates of the inlet gases were adjusted using fine control "MF" series needle valves, supplied by Negretti Aviation Ltd; equipped with digital meters in conjunction with three mercury manometers. These valves have been designed to operate at pressures down to 1×10^{-8} torr and up to 2000 lb/in². However, total pressures of 15 lb/in² for the oxygen and nitrogen and 10 lb/in² for the isobutylene was usually applied to each needle valve from the cylinders.

The calibration results for the three flow rate control valves are given in table III.1.a.

Table III.1.a Calibration table of the flow-rate control valves

Meter value	NITROGEN flow-rate ml/min	OXYGEN flow-rate ml/min	ISOBUT NE flow-rate ml/min
0	0.00	0.00	0.00
20	-	3.00	1.45
30	-	6.40	3.00
40	-	12.3	5.45
50	-	17.8	7.32
60	-	28.0	11.5
70	-	40.0	16.6
80	-	54.5	22.2
90	-	71.4	28.8
100	80.50	90.2	36.1
110	113.2	-	45.1
120	137.9	-	55.0
130	153.8	-	65.9
140	196.7	-	76.9
150	226.4	-	86.9
158	255.0	-	-
160	266.6	-	-
165	285.7	-	-
170	333.3	-	-

III.1.3 The reactor system

The reactor design was similar to the reactor "B" used previously to study the effect in the free board zone on the extent of conversion to acrolein and for kinetic measurements (208). It was made of pyrex glass tubing of 33mm diameter and 180mm long. The preheated homogeneous mixture of reactant gases passed through the inlet tubing (10mmx400mm) located into the furnace and thence was distributed uniformly within the catalyst bed.

The distributor was a pyrex glass sintered disc of porosity B.S No 2. At the top of the reactor an opening was especially designed for the stirrer and was located at the centre of the reactor, while the stirrer paddle was kept vertically within the catalyst bed 5mm above the distributor. The stainless steel stirrer was driven by a motor supplied by Citenco motors Ltd, which could rotate the stirrer in the range 0 to 300 r.p.m.

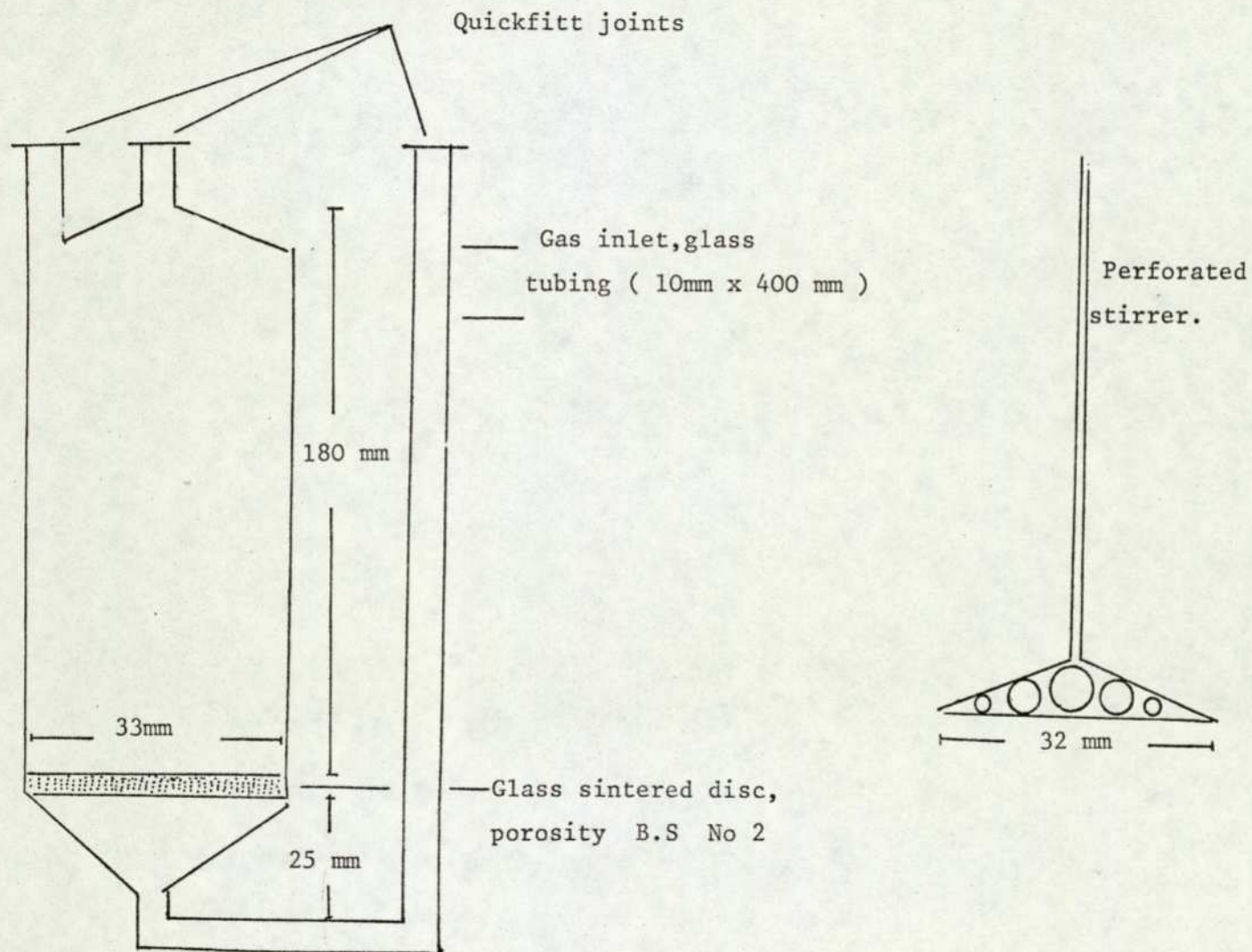
The reaction products were led for analysis through a second opening located at the top of the reactor after passing the cyclone system, where deposition of any entrained particles were collected and estimated.

The pressure drop across the reactor was measured with a CCL_4 manometer fitted in the inlet of the reactor. Usually the back pressure during experiments was constant; but unusual increases were caused from blockages of the sintered plate by fine powder.

The reactor system design is shown analytically in figure III.1.b.

III.2 ANALYSIS

Figure III.1.1.b The reactor system

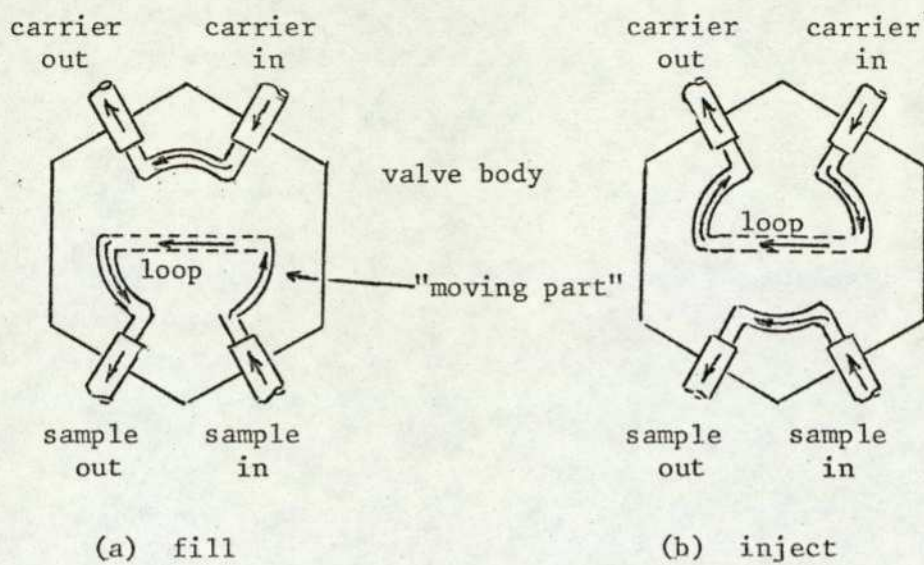


Analysis of feed and products were carried out using standard gas liquid chromatography techniques.

Two PYE UNICAM 104 chromatographs were used in the present studies. Initially the total effluent from the reactor (300ml/min) was passed through the two G.L.C. units. It was observed that high back pressures across the sampling loops were due to this high flow rate. To reduce anomalies on the exit flow rate, caused by changes in the back pressure, the exit gas mixture from the reactor was split before entering the sampling loops and the 1/8" copper tube was replaced with 1/4" tube. The size of the sample loops was selected to give the optimum sensitivity without overloading the columns. The chosen size was 0.5 ml but eventually those were replaced with 1 ml loops, in order to reduce errors in the amount of gas being injected, which could easily result from random changes in the back pressure or temperature of the sampling loops. The method by which standard volumes of gas samples were injected into the column packings is shown in figure III.2.a.

For quantitative analysis it is necessary to know accurately the volume of sample being injected. This has been achieved by determining the weight of mercury required to fill the loop. Furthermore, the maintenance of gas flow through all parts of the valve at all times, eliminates "dead volume". The operating knob was turned to the "fill" position ten seconds after the sample gas had been swept from the sample loop and into the column. This procedure was found to give generally better peak shapes for major components.

Figure III.2.a Functional diagram of gas sampling valve



To avoid condensation of liquid aldehydes, the sampling loops were heated with electrothermal heating tape at 120 °C. However, the high yields of methacrolein being produced often caused blockages in the loops. Acetone was forced through the loops and then air was passed until the solvent was completely removed. This cleaning procedure was found very effective and was used regularly to avoid blockages in the sampling system.

The output signals from the detectors were recorded with two Mitsui Rikadenki recorders and the areas of the peaks obtained were measured with a magnifier eye-piece which could give a good estimation of peak width.

The operating conditions for both chromatographs are summarised in the table III.2.a. A gas chromatography recorder chart for a typical run is given in figure III.2.b.

III.2.1 G.L.C. separation-columns

The empty glass columns were five feet in length and were supplied by PYE UNICAM.

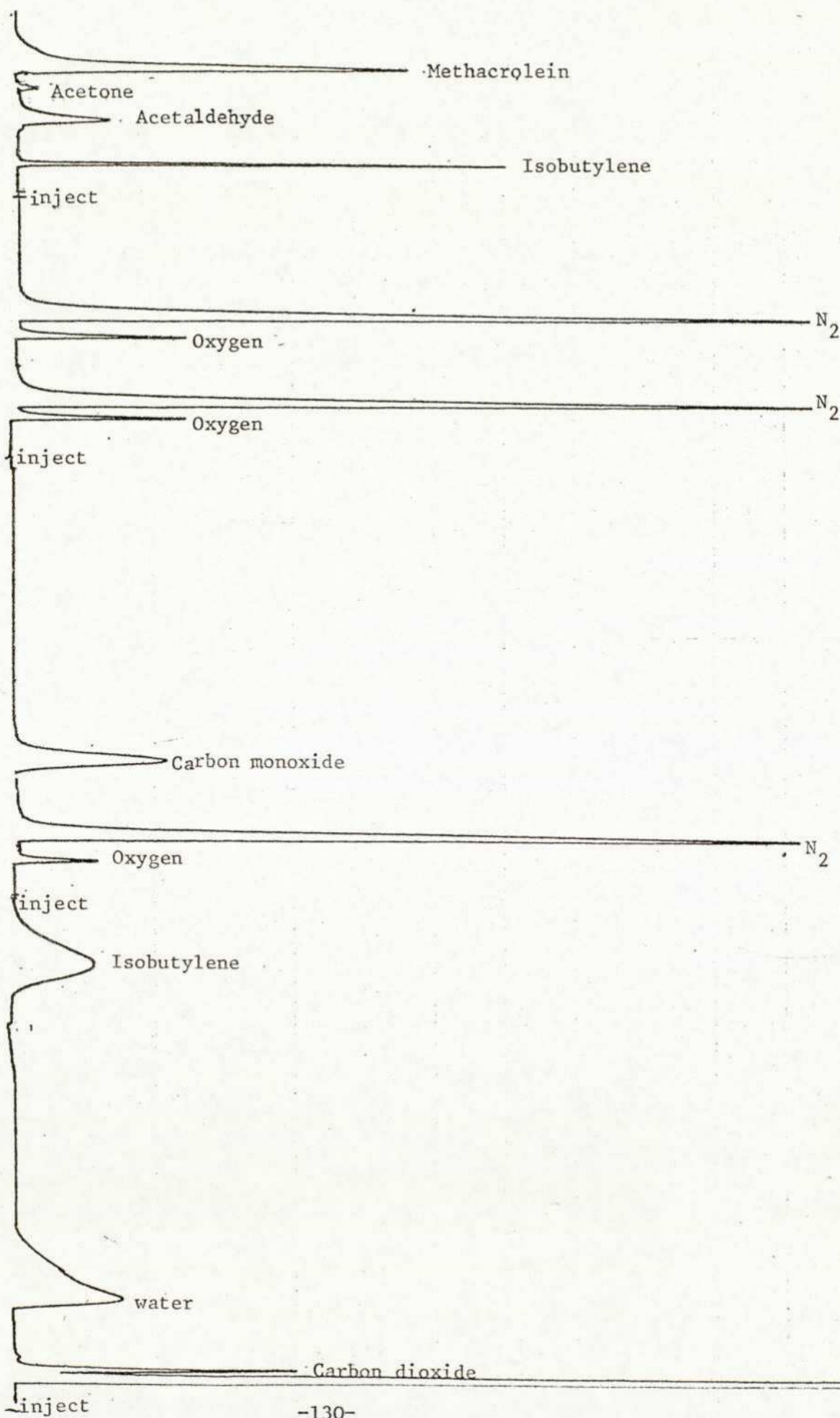
For the identification and analysis of the reactants and the oxidation products many column packings can be used satisfactorily. To obtain a good separation and identification in as short a time as possible, the following three column packings were adopted as the most suitable.

A. The column packing chosen for the analysis of the oxygen, nitrogen, and carbon monoxide was molecular sieve 5A(209) The column was packed under vacuum and activated at 475 °C for twelve hours(210) with nitrogen passing continuously at about 25 ml/min. Since many decomposition products may cause

Table III.2.a Operating conditions for the chosen column packings

Feature	F.I.D. head Column I	Katharometer head	
		Column 2	Column 3
Packing	15%, oxydiopropio- nitrile on Chromosorb P (80-100 Mesh)	Molecular sieve 5A	Porapak Q
Column oven temperature	70 °C	80 °C	80° C
Carrier gas	Nitrogen	Helium	Helium
Carrier gas flow rate	25 ml/min	40 ml/min	40 ml/min
Detector head temperature	200 °C	200 °C	200 °C
<u>Detector supplies:</u>			
Air.	600 ml/min	-	-
Hydrogen	25 ml/min	-	-
Bridge current	-	200 mA	200 mA

Figure III.2.b Typical chromatogram.



contamination of the packing the efficiency of the column was regularly checked and calculated from the chromatogram using the following formula:

$$\text{Efficiency} = 16 (Y/X)^2 \quad (211)$$

where X =width of base of peak

Y =retention time of peak

If the efficiency was smaller than the efficiency of a normal column i.e 500 theoretical plates, the packing was replaced with reactivated material.

B. From many Porapak column packings Porapak Q is thought to be the most suitable for the analysis and detection of propene, isobutene, carbon dioxide, and water. The column was packed under vacuum and activated by preheating to remove the residual low boiling materials before they could contaminate the detector and give rise to an unstable baseline.

The use of porous polymers beads as a packing material was reported by Hollins(212), and Cross(213) in 1966. They have used such columns for the separation of permanent gases and C_1 - C_2 hydrocarbons. Furthermore, Hollins and Hoynes(214) have independently described a procedure for separation of hydrogen-air-carbon dioxide-water and C_1 - C_4 hydrocarbons using Porapak Q packing with operating conditions similar to our own.

C. The column packing chosen for the analysis and detection of the olefins, and the other oxidation products (propene, isobutene, acrolein, methacrolein, formaldehyde, acetaldehyde, propion -

aldehyde, acrylic acid, methacrylic acid, methanol, ethanol and acetone) was β - β oxydipropionitrile 15% on Chromosorb P solid support.

This packing was prepared by dissolving β - β oxydipropionitrile (7.5 g) in methanol (150 ml) contained in a 500 ml flask. Chromosorb P (42.5 g), was then added followed by sufficient methanol to cover the solid. The mixture was shaken for several minutes and the flask was connected to a cold-trap i.e dry ice/acetone and a vacuum. The flask was heated gently to assist the removal of the solvent. Then the column was packed under vacuum and activated under the conditions of analysis.

III.2.2 Calibrations

From the three columns mentioned previously, the molecular sieve 5A, and Porapak Q columns were used with the chromatograph equipped with a katharometer detector, while the "ODPN" column was operated with the G.L.C. unit equipped with a flame ionization detector. Before the calibrations the operating conditions for both units were established and are summarised in table III.2.a.

Since, generally, detectors measure the number of molecules eluted from the columns and not percentages, the variables which can affect the number of molecules present in the sampling loops should be considered. The back pressure across the loops compresses the gas and hence the number of molecules increases. Thus the peak areas vary depending on the back pressure. The following relation was used to correct the peak areas obtained due to pressure within the apparatus:

$$\text{Corrected peak-area} = \text{measured peak-area} \times \frac{760}{760 + \text{back pressure}}$$

the similar relation:

$$\text{Corrected peak-area} = \text{measured peak-area} \times \frac{273 + \text{temp. of sample loops}}{273}$$

was applied to correct again the peak areas due to the heating of the sampling loops to a temperature considerably higher than the ambient temperature.

It is emphasized that if the above corrections have not been taken into consideration the error produced is greater than 9% .

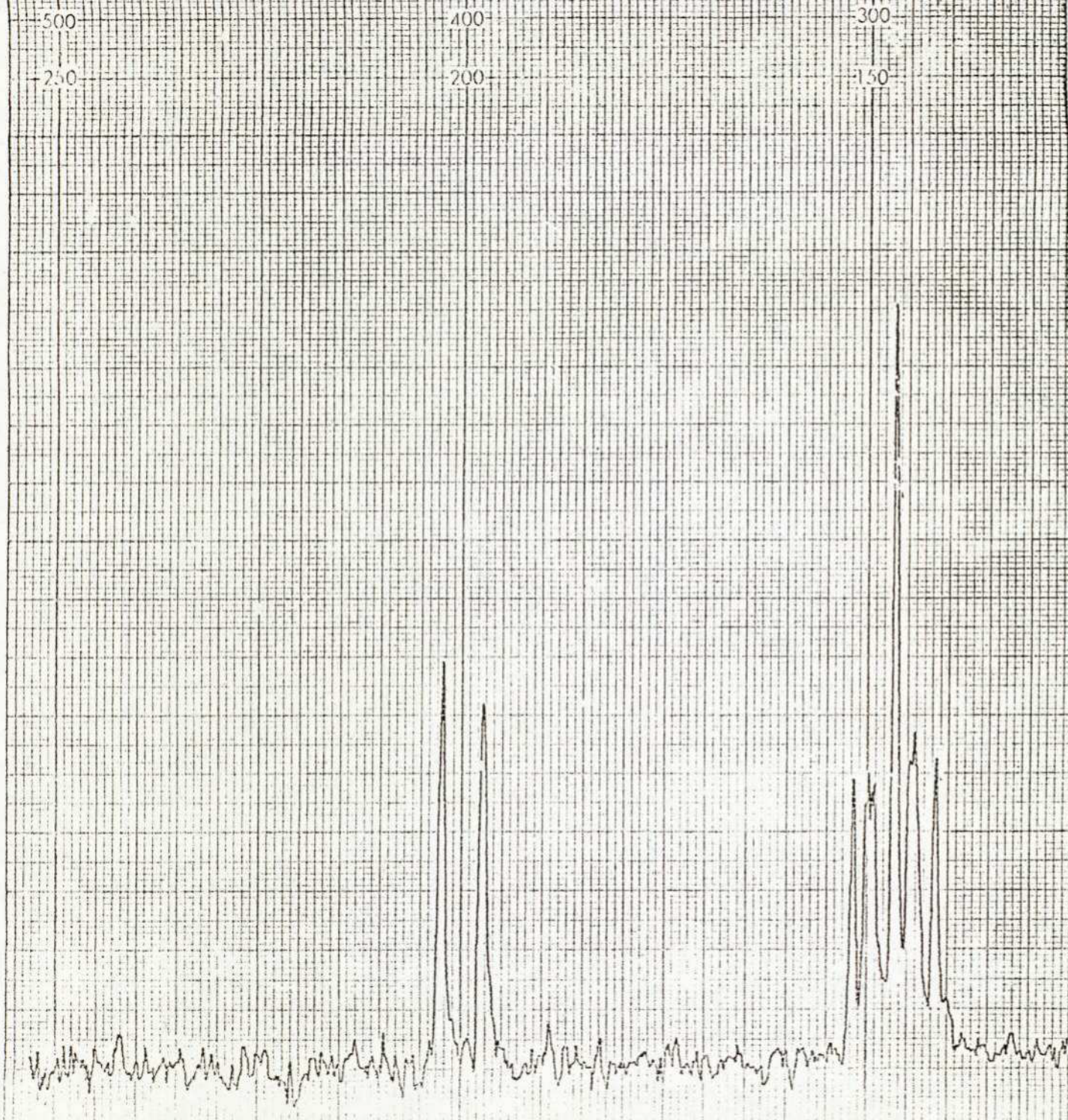
A. Calibration of the ODPN column.

Small quantities (30 ml) of methacrolein were purified by vacuum distillation over MgSO_4 .The product was confirmed to be pure by gas-liquid chromatography, and N.M.R. spectra.

Figure III.2.c shows the proton spectra obtained for distilled methacrolein.

Standarts consisting of 5% w/w, 10% w/w, and 15% w/w solutions of pure methacrolein in petroleum ether were prepared. The G.L.C. analyses of these solutions was performed immediately due to known instability of the methacrolein.

The standard methacrolein solutions (0.3, 0.5, and 0.8 μlit) were injected and analysed at different attenuations. Peak heights and peak areas were found to vary greatly for identical, consecutive injections. This inaccuracy was attributed to the sampling technique. Eventually the following procedure was found to give consistent peaks.



CONCENTRATION TMS
 REFERENCE amb
 TEMPERATURE amb

NUCLEUS

OBS. 13C
 LOCK ☒ D ☐ F ☐ H ()
 IRR. 1H

OFFSET

OBS. 35-80 KHZ
 IRR. 51.00 KHZ

PULSE ☒ SINGLE ☐ MULTI
 WIDTH 8 μ SEC. (45)
 INTERVAL 1 SEC.
 REPETITION 4 SEC.

DATA POINTS 4K
 WINDOW EX20
 NO. OF PULSES 1170

SPECTRAL WIDTH 4000 HZ
 RF GAIN 5
 AMPLITUDE 32

DECOUPLING

☒ CW ☐ NOISE ☐ PARTIAL
☐ HOMO ☐ HETERO ()
 POWER 57 dB

LOCK

RF LEVEL 4H
 RF GAIN 5
 AMPLITUDE 50

DATE 17.11.76
 OPERATOR XXXXXXXXXX
 REMARKS

Y61

- i. Regular check on flow rates
- ii. The syringe was cleaned between injections to avoid blockages from column packing or polymer deposits.
- iii. Before sampling, ensure that the syringe is not blocked by discharging some liquid.
- iv. Withdraw liquid into syringe (after flushing with sample 2 or 3 times), about 0.1 μ l more than required.
- v. Adjust to the required volume. Then if a bubble is in the end, remove it from the syringe exit.
- vi. Inject into the column packing and press the top of the syringe twice rapidly.
- vii. Rapid sampling was also preferred over a long term injection since the latter caused the solvent peak to broaden considerably and produce a slight difference on the methacrolein peak.

Similarly all the other aldehydes, ketones and acids were purified, identified and calibrated in order to obtain the retention time and the concentration in gmoles/mm^2 of each component.

B. Calibration of the molecular sieve 5A column.

The oxygen, nitrogen, and carbon monoxide were identified and calibrated on the molecular sieve 5A column. All the gases were supplied from standard gas cylinders (the gas cylinders contained mixtures of carbon monoxide, carbon dioxide with nitrogen and oxygen with nitrogen.). They were injected through the sampling loops and the retention times and the concentration of each compound were obtained.

C. Calibration of the Porapak Q column.

Table III.2.b Calibration factors for compounds identified
by F.I.D. gas chromatograph

Compound	Retention time sec	g-moles / mm ² 10 ⁻⁸	Attenuation	Column
Propylene	33		50x10 ⁴	15% β-β oxydipro- pionitrile on Chro- mosorb P (90mesh)
Isobutylene	36		50x10 ⁴	
Unknown	62	-	-	
Formaldehyde	125	0.9262	5x10 ⁴	
Acetaldehyde	134	1.3476	5x10 ⁴	
Propene-oxide	145	0.9379	5x10 ⁴	
Propionaldehyde	200-	1.1342	5x10 ⁴	
Acrolein	270	1.0110	10x10 ⁴	
Acetone	285	2.0930	10x10 ⁴	
Methacrolein	300	0.6135	10x10 ⁴	
Acrylic acid	340	3.2345	10x10 ⁴	
Methacrylic acid	420	2.5986	10x10 ⁴	

Table III.2,c Calibration factors for compounds identified
by katharometer gas chromatograph.

Oxygen	75	14,284	x20	Molecular- sieve 5A
Nitrogen	104	13,296	x20	
Carbon monoxide	252	0.73615	x1	
Nitrogen	60	10.655	x50	Porapak Q
Carbon dioxide	68	2,9553	x5	
Water	195	1,4396	x1	
Propylene	325	2,9876	x5	
Isobutylene	900	3,4732	x10	

The Porapak Q column was used for the identification of nitrogen, carbon dioxide, isobutylene, and water. The retention time and the concentration in gmol/mm^2 of each gas were calculated by injecting standard mixtures through the sampling loops. Liquid injections of distilled water were used for the identification and calibration of the water.

The calibration factors and retention times for compounds formed in the catalytic oxidation of isobutylene are summarised in tables III.2.b, and III.2.c.

III.3 COMPUTING PROCEDURE

FORTRAN IV computer programmes were developed and used for the calculations, statistical analysis and modelling of the experimentally obtained results.

A. Figure III.3.a shows the program used for the calculation of carbon mass balance, oxygen mass balance, conversion percentages, selectivity towards methacrolein, and yields of the various by-products.

The mean carbon mass balance and the mean oxygen mass balance were calculated for each temperature and a statistical analysis carried out on the calculated values.

The variance (equation III.3.1) for each set of experiments is the sum of squares of the deviations of the observed values from their mean, divided by one less than the total number of observations. The square root of the variance is the standard deviation (equation III.3.2), thus

$$\sigma^2 = \sum_{i=1}^N 1/N-1 (x_i - \bar{x})^2 \quad \text{equation III.3.1}$$

and $\sigma = \sum_{i=1}^N 1/N-1 (x_i - \bar{x})^2 \quad \text{equation III.3.2}$

The mean of the variances over the temperature range of the two balances, $(\sigma_c^2 + \sigma_o^2) / 2$, was taken to be the experimental error for a given block. For ease of reference, $(\sigma_c^2 + \sigma_o^2) / 2$ is represented by σ_E^2 .

The calculation of the conversion as percentages was based on the moles of olefin reacted over the moles of olefin in feed, while selectivities and percentage yields were calculated from the moles of compound formed over the moles of olefin reacted.

B. Determination of various physical quantities and other parameters involved in a fluidised bed reactor, or those reactor models being examined was obtained from the program given in figure III.3.b.

The input data for this program consist of the reactor temperature for each set of experiments, the partial pressure of olefin in feed, and the reciprocal of the olefin flow velocity.

The quantities calculated are:

- i. The rate constant of the reaction according to Arrhenius law (equation III.3.3), in respect of temperature dependence.

$$K_r = A e^{-E_a/RT} \quad \text{equation III.3.3}$$

- ii. The dimensionless number of reaction units, thus:-

$$K' = K_r PW / F$$

equation III.3.4

iii. The diffusion coefficient of olefin into air based on the Lennard-Jones expression for intermolecular forces (equ. III.3.5).

$$D_{12} = \frac{0.001858 T^{3/2} \left[(M_1 + M_2) / M_1 M_2 \right]^{1/2}}{P \sigma_{12}^2 \Omega_D} \quad \text{equation III.3.5}$$

iv. The equivalent mean bubble diameter (equation III.3.6) was estimated from bed expansion data, but this value was only initially used for the determination of the number of transfer units (equation III.3.7) in the Orcutt-Davidson-Pigford fluidised bed reactor model.

$$D_e = 1/g \left(\frac{H_{mf}}{H-H_{mf}} \frac{U-U_{mf}}{0.711} \right)^{1/2} \quad \text{equation III.3.6}$$

$$n_K = \frac{6.34 U_{mf}}{D_e \sqrt{g D_e}} \left[U_{mf} + 1.3 D_g^{1/2} (g/D_e)^{1/4} \right] \quad \text{equation III.3.7}$$

If all the above mentioned values are available then conversion can be predicted theoretically assuming different patterns of flow of the gas.

C. Two NAGF library subroutines were combined and modified in order to fit a set of experimental data points to chosen equations.

This routine performs a multiple linear regression in order to fit a curve of the form

$$Y = b_1 f_1(K) + b_2 f_2(K) + \dots + b_m f_m(K) \quad \text{equation III.3.8.}$$

to the following data points:-

$$\begin{aligned}
 & (f_{11}(K), f_{21}(K), \dots, f_{M1}(K), Y_1) \\
 & (f_{12}(K), f_{22}(K), \dots, f_{M2}(K), Y_2) \\
 & \cdot \\
 & \cdot \\
 & \cdot \\
 & \cdot \\
 & \cdot \\
 & (f_{1N}(K), f_{2N}(K), \dots, f_{MN}(K), Y_N)
 \end{aligned}$$

The input data consists of the number of cases, N (rows), on which the regression is based, the total number of variables dependent and independent in the regression, $(M+1)$, the number of independent variables in the regression, M , and finally the values of N observations for each of the variables given as an array:-

$$\begin{aligned}
 \left[f_{ij}(K) \right] \quad & i = 1, 2, \dots, N \quad (N \gg 2) \\
 & j = 1, 2, \dots, M \quad (M \gg 1)
 \end{aligned}$$

The quantities calculated are:-

i. Means:

$$\bar{f}_j(K) = \frac{1}{N} \sum_{i=1}^N f_{ij}(K) \quad j=1, 2, \dots, M+1$$

ii. Standard deviations:

$$\sigma_j = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (f_{ij}(K) - \bar{f}_j(K))^2} \quad j=1, 2, \dots, M+1$$

iii. Sums of squares and cross-products about zero:

$$\tilde{s}_{jk} = \sum_{i=1}^N f_{ij}(K) f_{ik}(K) \quad j, k = 1, 2, \dots, M+1$$

iv. Correlation-like coefficients:

$$\tilde{R}_{jk} = \frac{\tilde{s}_{jk}}{\sqrt{\tilde{s}_{jj} \times \tilde{s}_{kk}}} \quad j, k = 1, 2, \dots, M+1$$

if $\tilde{s}_{jj}$ or $\tilde{s}_{kk}$ is zero, $\tilde{R}_{jk}$ is set zero.

v. The inverse of the (MxM) partition of the matrix of correlation-like coefficients, RZ, involving only the independent variables:

vi. The modified inverse matrix, CZ = $[c_{ij}]$, where

$$c_{ij} = \frac{\tilde{R}_{ij} \tilde{r}^{ij}}{\tilde{s}_{ij}} \quad i, j = 1, 2, \dots, M$$

where $\tilde{r}^{ij}$ is the (i,j)th element of the inverse matrix of RZ as described above. Each element of CZ is thus the corresponding element of the matrix of correlation-like coefficients multiplied by the corresponding element of the inverse of the matrix, divided by the corresponding element of the matrix of sums of squares and cross-products about zero.

vii. The regression coefficients:

$$b_i = \sum_{j=1}^M c_{ij} s_{j(M+1)} \quad i = 1, 2, \dots, M$$

where $s_{j(M+1)}$ is the sum of cross-products about zero for the independent variable $f_j(K)$, and the dependent variable Y. The routine calculates the regression coefficients, $b_1, b_2, \dots$,

b_M , by minimising

$$\sum_{i=1}^N e_i^2$$

where $e_i = Y_i - (b_1 f_{1i}(K) + b_2 f_{2i}(K) + \dots + b_M f_{Mi}(K))$

ix. The sum of squares attributable to the regression, SSR,
the sum of squares of deviations about the regression, SSD,
and the total sum of squares, SST:

$SST = s_{(M+1)(M+1)}$, the sum of squares about zero
for the dependent variable, Y;

$$SSR = \sum_{j=1}^M b_j s_j(M+1)$$

$$SSD = SST - SSR$$

ix. The degrees of freedom attributable to the regression, DFR,
the degrees of freedom of deviations about the regression, DFD,
and the total degrees of freedom:

$$DFR = M$$

$$DFD = N - M$$

$$DFT = N$$

x. The mean square attributable to the regression, MSR,
and the mean square of deviations about the regression, MSD:

$$MSR = SSR / DFR$$

$$MSD = SSD / DFD$$

xi. The F-value for the analysis of variance:

$$F = MSR / MSD$$

xii. The standard error of estimate:

$$S = (MSD)^{1/2}$$

xiii. The coefficient of multiple correlation, R, the coefficient of multiple determination, R^2 , and the coefficient of multiple determination corrected for the degrees of freedom, $\bar{R}^2$:

$$R = (1 - SSD/SST)^{1/2}$$

$$R^2 = 1 - SSD/SST$$

$$\bar{R}^2 = 1 - SSD \times DFT / SST \times DFD$$

xiv. The standard error of the regression coefficients:

$$se(b_i) = (MSD \times c_{ii})^{1/2} \quad i=1,2,\dots,M$$

xv. The t-values for the regression coefficients:

$$t(b_i) = b_i / se(b_i) \quad i=1,2,\dots,M$$

The calculation of these statistical values determines how well the regression is performed, while the fitting error could be estimated from the values of the residual sums of squares according to the expression:

$$\sigma_F^2 = \sum_{i=1}^N \frac{1}{N-1} 100 \times \left[\begin{array}{c} V_F - V_C \\ V_F \end{array} \right]^2$$

and the "goodness of fit" relates to the ratio $\frac{\sigma_E^2}{\sigma_F^2}$.

This latest routine is given in figure III.3.c ,while computer plots were obtained with the GINO-F routine shown in figure III.3.d.

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C CARBON MASS BALANCE PROGRAMM
C OXYGEN MASS BALANCE PROGRAMM
C CONVERSION PROGRAMM
C SELECTIVITY PROGRAMM
C YIELDS OF CARBON MONOXIDE PROGRAMM
C YIELDS OF CARBON DIOXIDE PROGRAMM
C YIELDS OF FORMALDEHYDE PROGRAMM
C YIELDS OF ACETALDEHYDE PROGRAMM
C YIELDS OF PROPIONALDEHYDE PROGRAMM
C YIELDS OF ACETONE PROGRAMM
C CALCULATION OF MEAN CARBON MASS BALANCE
C CALCULATION OF MEAN OXYGEN MASS BALANCE
C DETERMINATION OF VARIANCE
C DETERMINATION OF STANDARD DEVIATION
C AFTER FTEJAKIS

REAL MEAN_C, METHA, MEAN_O
DIMENSION C4H8IC(45), UNISO(45), METHA(45), ACETAL(45), HCHO(45),
1 CO(45), CO2(45), PROPI(45), ACETO(45), SUMC(45), CARBMS(45), CARIC(
2 OXYIC(45), UNOXY(45), H2O(45), SUMO(45), OXYBMS(45), SUMSO(45),
3 CONVER(45), SELEC(45), PACETA(45), PHCHO(45), PCO(45), PCO2(45),
4 PROPOI(45), PACETO(45), SINC(45), SUMSX(45), SUMEV(45), OM(45), RAT
5 READ (1,1028)
1028 FORMAT(5H
1
WRITE(1,1028)
READ (1,90) L
80 FORMAT (12)
DO 16 I=1,L
READ (1,1000) C4H8IC(I), UNISO(I), METHA(I), ACETAL(I),
1 HCHO(I), CO(I), CO2(I), PROPI(I), ACETO(I),
2 OXYIC(I), UNOXY(I), H2O(I), CARIC(I)
1000 FORMAT (13 F8.0)
16 CONTINUE
DO 17 I=1,L
C CALCULATION OF MIXTURE COMPOSITION
OM(I)=(C4H8IC(I)/(CARIC(I)+C4H8IC(I)+OXYIC(I)))*100.0
RAT(I)=OXYIC(I)/C4H8IC(I)
C CALCULATION OF CARBON MASS BALANCE
SUMC(I) = UNISO(I)+METHA(I)+ACETAL(I)/2+HCHO(I)/4+CO(I)/4+
1 CO2(I)/4+0+0.75*PROPI(I)+0.75*ACETO(I)
CARBMS(I) = (SUMC(I)/C4H8IC(I)) *100.0000
C CALCULATION OF OXYGEN MASS BALANCE
SUMO(I) = UNOXY(I)+METHA(I)/2+ACETAL(I)/2+0+
1 HCHO(I)/2+0+CO(I)/2+0+CO2(I)+H2O(I)/2+0
OXYBMS(I) = (SUMO(I)/OXYIC(I)) *100.000
C CALCULATION OF CONVERSION
SINC(I) = C4H8IC(I)-UNISO(I)
CONVER(I)=((SUMC(I)-UNISO(I))/C4H8IC(I))

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22.      SELEC(I)=(METHA(I)/(SUMC(I)-UNISO(I)))*100.0
      C    CALCULATION OF YIELD OF CO2
23.      PCO2(I)=(CO2(I)/(SUMC(I)-UNISO(I)))*100.0*0.25
      C    CALCULATION OF YIELD OF CO
24.      PCO(I)=(CO(I)/(SUMC(I)-UNISO(I)))*100.0*0.25
      C    CALCULATION OF YIELD OF HCHO
25.      PHCHO(I) = (HCHO(I)/SIMC(I))*100.000*0.25
      C    CALCULATION OF YIELD OF CH3CHO
26.      PACETA(I) = (ACETAL(I)/SIMC(I))*100.000*0.5
      C    CALCULATION OF YIELD OF CH3CH2CHO
27.      PPROPI(I) = (PROPI(I)/SIMC(I))*100.000*0.75
      C    CALCULATION OF YIELD OF CH3COCH3
28.      PACETO(I) = (ACETO(I)/SIMC(I))*100.000*0.75
29.      17  CONTINUE
30.      DO 18 I=1,L
31.      WRITE (2,2000) CARBMS(I)
32.      2000 FORMAT(1X,35H CARBON MASS BALANCE OF RUN IS ,F7.4)
33.      18  CONTINUE
34.      DO 19 I=1,L
35.      WRITE (2,2001) OXYBMS(I)
36.      2001 FORMAT(1X,34H OXYGEN MASS BALANCE OF RUN IS ,F7.4)
37.      19  CONTINUE
      C    CALCULATION OF MEAN CARBON MASS BALANCE
38.      SUM = 0000.0000
39.      DO 20 I=1,L
40.      SUM = SUM + CARBMS(I)
41.      20  CONTINUE
42.      MEANC = SUM/FLUAT(L)
43.      WRITE(2,2002) MEANC
44.      2002 FORMAT(1X,25H MEAN CARBON BALANCE IS ,F7.4)
      C    CALCULATION OF MEAN OXYGEN MASS BALANCE
45.      SUM = 0000.0000
46.      DO 21 I=1,L
47.      SUM = SUM+OXYBMS(I)
48.      21  CONTINUE
49.      MEANO = SUM/FLUAT(L)
50.      WRITE (2,2003) MEANO
51.      2003 FORMAT(1X,32H MEAN OXYGEN MASS BALANCE IS ,F7.4)
      C    CALCULATION OF VARIANCE
52.      SUMQ = 000.000
53.      SUMX = 000.000
54.      DO 22 I=1,L
55.      SUMSQ(I) = (CARBMS(I)-MEANC)**2
56.      SUMSX(I) = (OXYBMS(I)-MEANO)**2
57.      SUMQ = SUMQ+SUMSQ(I)
58.      SUMX = SUMX+SUMSX(I)
59.      22  CONTINUE
60.      VAR =SUMQ / (FLUAT(L)-1)
61.      VARG = SUMX / (FLUAT(L)-1)
62.      WRITE (2,2004) VAR
63.      2004 FORMAT (1X,27H VARIANCE FOR CARBON IS ,F7.4)
64.      WRITE (2,2014) VARG
65.      2014 FORMAT (1X,27H VARIANCE FOR OXYGEN IS ,F7.4)
      C    CALCULATION OF STANDARD DEVIATION
66.      STD = VAR**0.5
67.      STDG = VARG**0.5
68.      WRITE (2,2005) STD

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69      2005 FORMAT (1X,37H STANDARD DEVIATION FOR CARBON IS      (F7.4)
70      WRITE (2,2015) STD
71      2015 FORMAT (1X,37H STANDARD DEVIATION FOR OXYGEN IS      (F7.4)
72      DO 23 I=1,L
73      WRITE (2,2006) CONVER(I)
74      2006 FORMAT(1X,25H CONVERSION OF RUN IS      (F7.4)
75      23 CONTINUE
76      DO 24 I=1,L
77      WRITE (2,2007) SELEC(I)
78      2007 FORMAT(1X,26H SELECTIVITY OF RUN IS      (F7.4)
79      24 CONTINUE
80      DO 25 I=1,L
81      WRITE (2,2008) PCO2(I)
82      2008 FORMAT(1X,29H PERCENT OF CO2 OF RUN IS      (F7.4)
83      25 CONTINUE
84      DO 26 I=1,L
85      WRITE (2,2009) PCO(I)
86      2009 FORMAT(1X,28H PERCENT OF CO OF RUN IS      (F7.4)
87      26 CONTINUE
88      DO 27 I=1,L
89      WRITE (2,2010) PHCHO(I)
90      2010 FORMAT(1X,30H PERCENT OF HCHO OF RUN IS      (F7.4)
91      27 CONTINUE
92      DO 28 I=1,L
93      WRITE (2,2011) PACETA(I)
94      2011 FORMAT(1X,32H PERCENT OF CH3COH OF RUN IS      (F7.4)
95      28 CONTINUE
96      DO 29 I=1,L
97      WRITE (2,2012) PPRPOI(I)
98      2012 FORMAT(1X,35H PERCENT OF CH3CH2CHO OF RUN IS      (F7.4)
99      29 CONTINUE
100     DO 30 I=1,L
101     WRITE (2,2013) PACETO(I)
102     2013 FORMAT(1X,34H PERCENT OF CH3COCHO OF RUN IS      (F7.4)
103     30 CONTINUE
104     CALCULATION OF EXPERIMENTAL ERROR
105     SUMV = 0.000000
106     DO 31 I=1,L
107     SUMV(I) = (((C4H8O(I)-SUOC(I))/(C4-H8O(I)))-
108     100((OXY(I)-SUHO(I))/OXY(I)))*2
109     SUMV = SUMV-SUMV(I)
110     VAREX = SUMV/(FLOAT(L)-1)
111     WRITE (2,2016) VAREX
112     2016 FORMAT(1X,45H EXPERIMENTAL VARIANCE IS      (F7.4)
113     31 CONTINUE
114     DO 32 I=1,L
115     WRITE (2,2017) OR
116     2017 FORMAT(1X,22H OLEFIN PERCENT IS      (F7.4)
117     32 CONTINUE
118     DO 33 I=1,L
119     WRITE (2,2018) RAI
120     2018 FORMAT(1X,23H O2/OLEFIN RATIO IS      (F7.4)
121     33 CONTINUE
122     READ(2,1952) R
123     1952 FORMAT(12)
124     IF (R.GT.0) GO TO 55
125     STOP

```


[illegible]

20/02/79 AT 18.09.01

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```

33      GR=981.0
34      DE=((HMF/(HO-HMF))*((UO-UMF)/0.711))**2.0)/981.0
      C   CALCULATION OF THE NUMBER OF TRANSFER UNITS
      C   IN ORCUTT-DAVINSON-PIGFORD MODEL
35      X(1)=(6.34*HMF/((GR*DE)**0.5)*DE)*(UMF+1.3*(D12(I)**0.5)*
      1((GR/DE)**0.25))
      C   CALCULATION OF THE FRACTIONAL CONVERSION FROM
      C   ORCUTT-DAVINSON-PIGFORD MODEL
      C   ASSUMPTION OF PLUG-FLOW REACTOR
36      R=1.5
37      W=0.8
38      S=(0.821+R)/0.64
39      Q=1.1997*R
40      X1=(-S+((S**2.0-4.0*Q)**0.5))/2.0
41      X2=(-S-((S**2.0-4.0*Q)**0.5))/2.0
42      CO=1.0-(((X1*(1.0+X2*W)*(2.7182**{X2*HO}))-
      1(X2*(1.0+X1*W)*(2.7182**{X1*HO}))))/(X1-X2))
      C   ASSUMPTION OF PERFECTLY MIXED REACTOR
43      CON=0.824-0.679/(R+0.824)
44      17  CONTINUE
45      DO 18 I=1,L
46      WRITE (2,2010) RU(I)
47      2010 FORMAT(1X,33H NUMBER OF REACTION UNITS IS ,F7.4)
48      18  CONTINUE
49      DO 19 I=1,L
50      WRITE (2,2011) PFF(I)
51      2011 FORMAT(1X,39H FRACTION FOR PLUG FLOW REACTOR IS ,F7.4)
52      19  CONTINUE
53      DO 20 I=1,L
54      WRITE (2,2012) PMF(I)
55      2012 FORMAT(1X,45H FRACTION FOR PERFECTLY MIXED REACTOR IS ,F7.4)
56      20  CONTINUE
57      DO 21 I=1,L
58      WRITE (2,2013) SEVAR(I)
59      2013 FORMAT(1X,24H SECOND VARIABLE IS ,F7.4)
60      21  CONTINUE
61      DO 22 I=1,L
62      WRITE (2,2014) THVAR(I)
63      2014 FORMAT(1X,24H THIERD VARIABLE IS ,F7.4)
64      22  CONTINUE
65      DO 23 I=1,L
66      WRITE (2,2015) D12(I)
67      2015 FORMAT(1X,30H DIFFUSION COEFFICIENT IS ,F7.4)
68      23  CONTINUE
69      DO 24 I=1,L
70      WRITE (2,2016) X(I)
71      2016 FORMAT(1X,33H NUMBER OF TRANSFER UNITS IS ,F10.6)
72      24  CONTINUE
73      WRITE (2,2017) DE
74      2017 FORMAT(1X,28H MEAN BUBBLE DIAMETER IS ,F7.4)
75      WRITE (2,2018) CO
76      2018 FORMAT(1X,27H CONVERSION FOR P.F IS ,F7.4)
77      WRITE (2,2019) CON
78      2019 FORMAT(1X,27H CONVERSION FOR P.M IS ,F7.4)
79      READ(2,1952) M
80      1952 FORMAT(I2)
81      IF (M.GT.0) GO TO 55

```

RKCA597F

20/02/79 AT 18.09.01

PAG

```

82.      STOP
83.      END

```


COMPILEATION BY #XFAT NK 6B DATE 14/06/79 TIME 18.40.41

```

SEND TO(GEOPSEMICOMP)
SEMICOMPILED(SUBGROUPPIANY,SUBRO %FIOLP)
LIBRARY(SUBGROUPNAGF)
LIST(LP)
WORK(ED)
PROGRAM(PROGRKCA597 )
COMPACT
INPUT 1,5= CRU
OUTPUT 2,6 = LPD
COMPRESS INTEGER AND LOGICAL
TRACE 2
END

```

MASTER FTENAKIS

C

```

REAL TITLE(7),SSP(5,5),CORR(5,5),RESULT(13),COEFFT(4,3),
* RINV(3,3),C(3,3),W(4,4),
* A(50,5),AMEAN(3),STD(3)
INTEGER NIN,NOUT,I,NV,NI,NC,J,IFAIL
DATA NIN /5/, NOUT /6/
READ (NIN,99999) TITLE
WRITE (NOUT,99998) (TITLE(I),I=1,6)
NV=3
NI=NV-1
NC=15
READ (NIN,88887) ((A(I,J),J=1,NV),I=1,NC)
WRITE (NOUT,88886) NV,NC, (J,J=1,NV), (I,(A(I,J),J=1,NV),I=1,
IFAIL=1
CALL G02BDF(NC,NV,A,50,AMEAN,STD,SSP,5,CORR,5,IFAIL)
CALL G02CHF(NC,NV,NI,SSP,5,CORR,5,RESULT,COEFFT,4,
* RINV,3,C,3,W,4,IFAIL)

```

C

C

C

```

TEST IFAIL
IF (IFAIL) 20, 40, 20
20 WRITE (NOUT,88885) IFAIL
GO TO 60
40 WRITE (NOUT,88884) (I,AMEAN(I),STD(I),I=1,NV)
WRITE (NOUT,88883) (I,I=1,NV), (I,(SSP(I,J),J=1,NV),I=1,NV)
WRITE (NOUT,88882) (I,I=1,NV), (I,(CORR(I,J),J=1,NV),I=1,NV)
WRITE (NOUT,99994) (I,(COEFFT(I,J),J=1,3),I=1,NI)
WRITE (NOUT,99993) (RESULT(I),I=1,13)
WRITE (NOUT,99992) (J,J=1,NI), (I,(RINV(I,J),J=1,NI),I=1,NI)
WRITE (NOUT,99991) (J,J=1,NI), (I,(C(I,J),J=1,NI),I=1,NI)

```



```

00 CONTINUE
STOP
99999 FORMAT (6A4, 1A3)
99998 FORMAT (4(1X/), 1H , 5A4, 1A3, 7HRESULTS/1X)
88887 FORMAT (3F10.5)
88886 FORMAT (32H,NUMBER OF VARIABLES (COLUMNS) =, 11/10H-NUMBER OF,
* 24H CASES (ROWS) =, 11/17H DATA MATRIX IS:-//1H ,
* 3112/(1H , 15, 3F12.4))
88885 FORMAT (22HROUTINE FAILS, IFAIL=, 12)
88884 FORMAT (28H, VARIABLE MEAN ST. DEV./(1H , 15, 2F11.4))
88883 FORMAT (46H,SUMS OF SQUARES AND CROSS PRODUCTS ABOUT ZERO/1H ,
* 3112/(1H , 15, 3F12.4))
88882 FORMAT (30H,CORRELATION LIKE COEFFICIENTS/1H , 3112/(1H , 15,
* 3F12.4))
99994 FORMAT (43H,VARIABLE COEFFT STD ERR T-VALUE/2(1H ,
* 15, 3F13.4/))
99995 FORMAT (32H,ANALYSIS OF REGRESSION TABLE :-//15H SOURCE,
* 55H SUM OF SQUARES D.F. MEAN SQUARE F-VALUE//
* 18H DUE TO REGRESSION, F14.4, F8.0, 2F14.4/14H ABOUT REGRES ,
* 4HSION, F14.4, F8.0, F14.4/18H TOTAL , F14.4,
* F8.0//29H STANDARD ERROR OF ESTIMATE =, F8.4/11H MULTIPLE C,
* 18H,CORRELATION (R) =, F8.4/29H DETERMINATION (R SQUARED) =,
* F8.4/29H CORRECTED R SQUARED =, F8.4/)
99992 FORMAT (50H,INVERSE OF CORRELATION MATRIX OF INDEPENDENT VARI,
* 6HABLES:/1H , 2110/2(1H , 14, 2F10.4/))
99991 FORMAT (25H,MODIFIED INVERSE MATRIX:/1H , 2110/2(1H , 14,
* 2F10.4/))
END

```

SEGMENT, LENGTH 381, NAME PTENAKIS

FINISH

COMPILATION - NO ERRORS

FILE: 15 BUCKETS USED

DOCUMENT REGR

, NUMREGR

: LP00 ON 14/06/79 AT 18.4

CONSOLIDATED BY XPCK 12K

DATE

14/06/79

TIME 18.41.08

PROGRAM PROG

COMPACT DATA (15AH)

COMPACT PROGRAM (DBM)

CORE 9088

SEG FTENAKIS
 SEG G02BDF
 SEG G02CHF
 SEG FLOAT
 SEG SQRT
 SEG P01AAF
 SEG F04ABF
 SEG G02CGZ
 SEG X02ACF
 SEG ABS
 SEG X02AAF
 SEG F03AEF
 SEG F04AFF
 SEG F04AGF
 SEG X03AAF
 SEG DBLE
 SEG SNGL
 SEG P01AAZ
 CLV SPFIL

DOCUMENT REGR

, NUMREGR

: LP00 ON 14/06/79 AT 18.4

G02CHF PROGRAM DATA RESULTS

NUMBER OF VARIABLES (COLUMNS) =3

NUMBER OF CASES (ROWS) =*15

DATA MATRIX IS:-

	1	2	3
1	0.8350	0.8470	0.8400
2	0.7560	0.7810	0.7800
3	0.3490	0.4640	0.4300
4	0.1560	0.3490	0.4100
5	0.2370	0.4100	0.3700
6	0.1460	0.3420	0.3100
7	0.1470	0.3420	0.3400
8	0.1350	0.3530	0.3200
9	0.1300	0.3490	0.3100
10	0.1250	0.3250	0.2700
11	0.0630	0.2060	0.2300
12	0.0380	0.2550	0.2000
13	0.0180	0.1990	0.1800
14	0.0180	0.1990	0.1600
15	0.0120	0.1810	0.1600

VARIABLE	MEAN	ST DEV.
1	0.2510	0.2540

2	0.3735	0.1959
3	0.3540	0.2042

SUMS OF SQUARES AND CROSS PRODUCTS ABOUT ZERO

	1	2	3
1	1.5769	1.8748	1.8354
2	1.8748	2.6292	2.5384
3	1.8354	2.5384	2.4635

CORRELATION LIKE COEFFICIENTS

	1	2	3
1	1.0000	0.9225	0.9330
2	0.9225	1.0000	0.9974
3	0.9330	0.9974	1.0000

VBLE	COEFFT	STD ERR	T-VALUE
1	0.1084	0.0575	1.8847
2	0.8882	0.0445	19.977

ANALYSIS OF REGRESSION TABLE :-

SOURCE	SUM OF SQUARES	D.F.	MEAN SQUARE	F-VALUE
DUE TO REGRESSION	2.4534	2.	1.2267	1584.2707
ABOUT REGRESSION	0.0101	13.	0.0008	
TOTAL	2.4635	15.		

STANDARD ERROR OF ESTIMATE	=	0.0278
MULTIPLE CORRELATION (R)	=	0.9980
DETERMINATION (R SQUARED)	=	0.9959
CORRECTED R SQUARED	=	0.9953

INVERSE OF CORRELATION MATRIX OF INDEPENDENT VARIABLES:

	1	2
1	6.7115	-6.1914
2	-6.1914	6.7115

MODIFIED INVERSE MATRIX:

	1	2
1	4.2723	-3.0465
2	-3.0465	2.5527

Figure III.3.d Computer plot routine

PRINT 447 PURM 040 IPO: ON 04/04/79 AT 18.00
 RUN COMPILATION BY JKEAT BK 6B DATE 04/04/79 TIME 18.00.15

```

1 SEND TO GEORGE SEMICOM
2 SEMICOMPILE (SUBROUTINE SUBRO XFINLP)
3 LIBRARY (SUBROUTINE GRA)
4 LIBRARY (SUBROUTINE SUR)
5 LIBRARY (SUBROUTINE IN)
6 LIST (LP)
7 WORK (E9)
8 PROGRAM (PRO:RKCA597)
9 COMPACT
10 INPUT 1,52,PU
11 OUTPUT 2,5 = LPO
12 TRACE 2,100
13 COMPRESS INTEGER AND LOGICAL
14 END
  
```

```

5 MASTER FTEHAKIS
6 DIMENSION W(109),K(109)
7 C SEE UP THE J AND K COORDINATES
8 F0N=0.4706
9 DO 10 I=1,109
10 P(I)=F0N
11 W(I)=0.0045+P(I)
12 1) F0N=F0N+0.1
13 C CALL THE PLOT ROUTINES
14 CALL H19346
15 CALL GRAPSR,W,109,0
16 CALL DEPEND
17 STOP
18 END
  
```

OF SEGMENT, LENGTH 60, NAME FTEHAKIS

CHAPTER IV

RESULTS

CHAPTER IV

RESULTS

	Page No
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IV.2 OPTIMIZING CONDITIONS OF THE FLUIDISED BED REACTOR	165-171
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IV.2.2 Attrition losses	
IV.2.3 Bed expansion and bubble diameters	
IV.3 HOMOGENEOUS REACTION IN THE CATALYST - FREE REACTOR	172-176
IV.4 KINETIC STUDIES AND DETERMINATION OF RATE OF REACTION	177-191
IV.4.1 Oxidation of isobutylene to methacrolein	
IV.4.2 Oxidation of propylene to acrolein	
IV.5 OPTIMIZATION OF CONDITIONS FOR THE SELECTIVE OXIDATION OF ISOBUTYLENE TO METHACROLEIN	192-219
IV.5.1 Conversion data at minimum fluidisation velocity	
IV.5.2 Conversion data at low superficial gas velocities	

TERMINOLOGY

$$\text{Conversion \%} = \frac{\text{moles of isobutylene reacted}}{\text{moles of isobutylene feed}} \times 100$$

$$\text{Selectivity \%} = \frac{\text{moles of methacrolein produced}}{\text{moles of isobutylene reacted}} \times 100$$

$$\text{Yield of CO \%} = \frac{\text{moles of CO produced}}{\text{moles of isobutylene reacted}} \times 1/4 \times 100$$

$$\text{Yield of CO}_2 \% = \frac{\text{moles of CO}_2 \text{ produced}}{\text{moles of isobutylene reacted}} \times 1/4 \times 100$$

$$\text{Yield of CH}_3\text{CHO \%} = \frac{\text{moles of acetone produced}}{\text{moles of isobutylene reacted}} \times 3/4 \times 100$$

$$\text{Yield of HCHO \%} = \frac{\text{moles of formaldehyde produced}}{\text{moles of isobutylene reacted}} \times 1/4 \times 100$$

$$\text{Yield of CH}_3\text{CHO \%} = \frac{\text{moles of acetaldehyde produced}}{\text{moles of isobutylene reacted}} \times 1/2 \times 100$$

Key to figures

	Conversion
	Selectivity
	Yield of carbon dioxide
	Yield of carbon monoxide
	Yield of acetone
	Yield of formaldehyde
	Yield of acetaldehyde

IV.1 CATALYST PREPARATION AND PROPERTIES

Most important considerations for the selection of a catalyst system are correct size and surface area.

The greater the surface area the greater the amount of reaction per unit weight. When the catalyst is porous the active surface area is not just the geometric surface but includes the surface inside the pores which is generally much greater than the geometric surface area. The smaller the pore size the greater the active surface area per unit volume, and hence the greater the activity. But the greater the activity the more likelihood pore diffusional effects will occur. Hence there is an optimum surface area for each chosen catalyst system.

Furthermore, a very important property of a catalyst is its selectivity. The selectivity of catalyst should be high and its heat treatment has a great effect on it. It is also necessary that the catalyst gives reproducible results.

Bismuth Molybdate catalyst of Bi:Mo = 1:1 was prepared by heating 125.36 g of ammonium molybdate; $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ with 135.85 g of bismuth nitrate; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, in air at 600 °C for 20 hours in a platinum crucible. The yellow oxide mixture was then ground and screened to give a fraction of B.S sieve 180-240 Mesh. The average size of the product solid particles was also estimated from photomicrographs. Randomly chosen samples were dispersed in methanol within glass plates and photographs were taken with a polaroid camera on different fields of the samples through a microscope. The average particle

Plate IV.1.a Photomicrograph of a sample of Bi:Mo catalyst
Magnification x 89.4

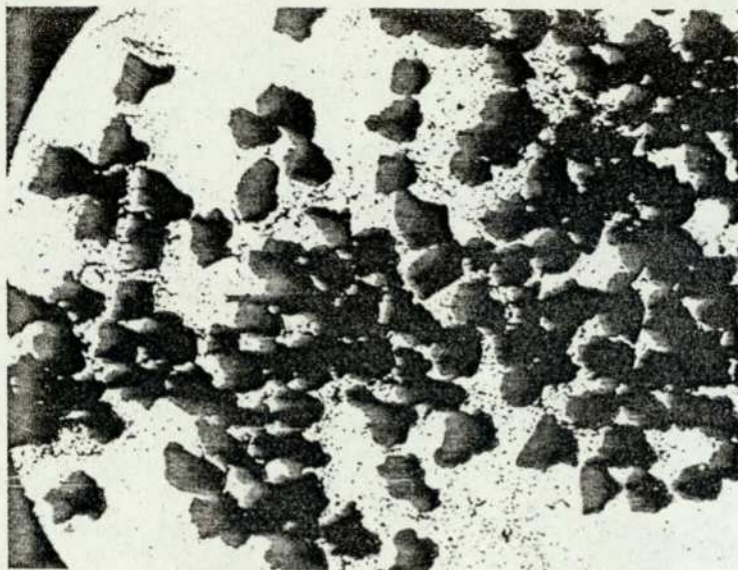
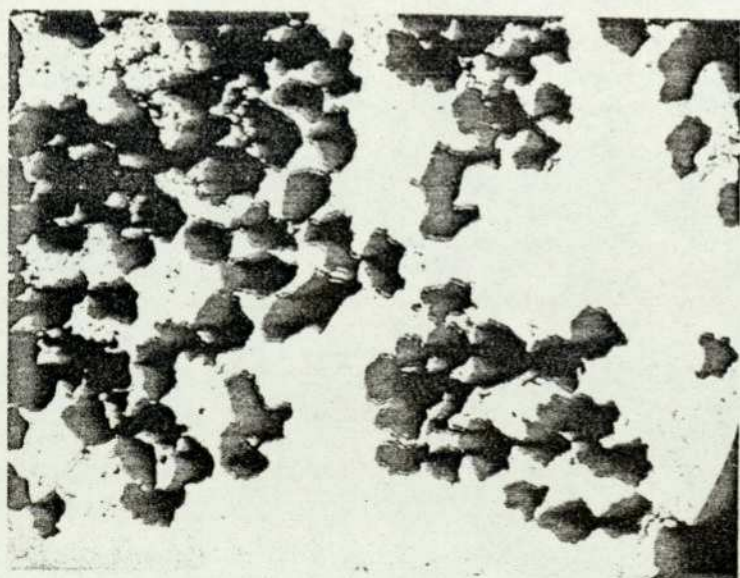


Plate IV.1.b Photomicrograph of a sample of Bi:Mo catalyst
Magnification x 103.8



diameter of 67 μm was determined after carrying out a statistical analysis on a number of particles, as shown in plates IV.1.a and IV.1.b.

Surface area measurements according to the method of Brunauer, Emmet, Teller and their collaborators in the 1930's (215, 216, 217, 218, 219) was carried out and linear regression of the obtained results was performed to calculate the specific surface area of the catalyst. The value which according to the following equation

$$\frac{P}{M_a(P_o - P)} = \frac{1}{M_a C} + \frac{C-1}{M_a C} \times \frac{P}{P_o} \quad \text{equation IV.1.1}$$

gave the best fit to the data points was 1.77 m^2/g , as given in table IV.1.a.

The voidage fraction of the particles at the point of minimum fluidization was experimentally found to be 0.58. The experiment was based on loading the reactor with a known weight of catalyst, it was momentarily fluidised and then allowed to slowly settle to the loosest packing case. By measuring the actual volume occupied by the catalyst the minimum fluidization porosity was determined by the formula

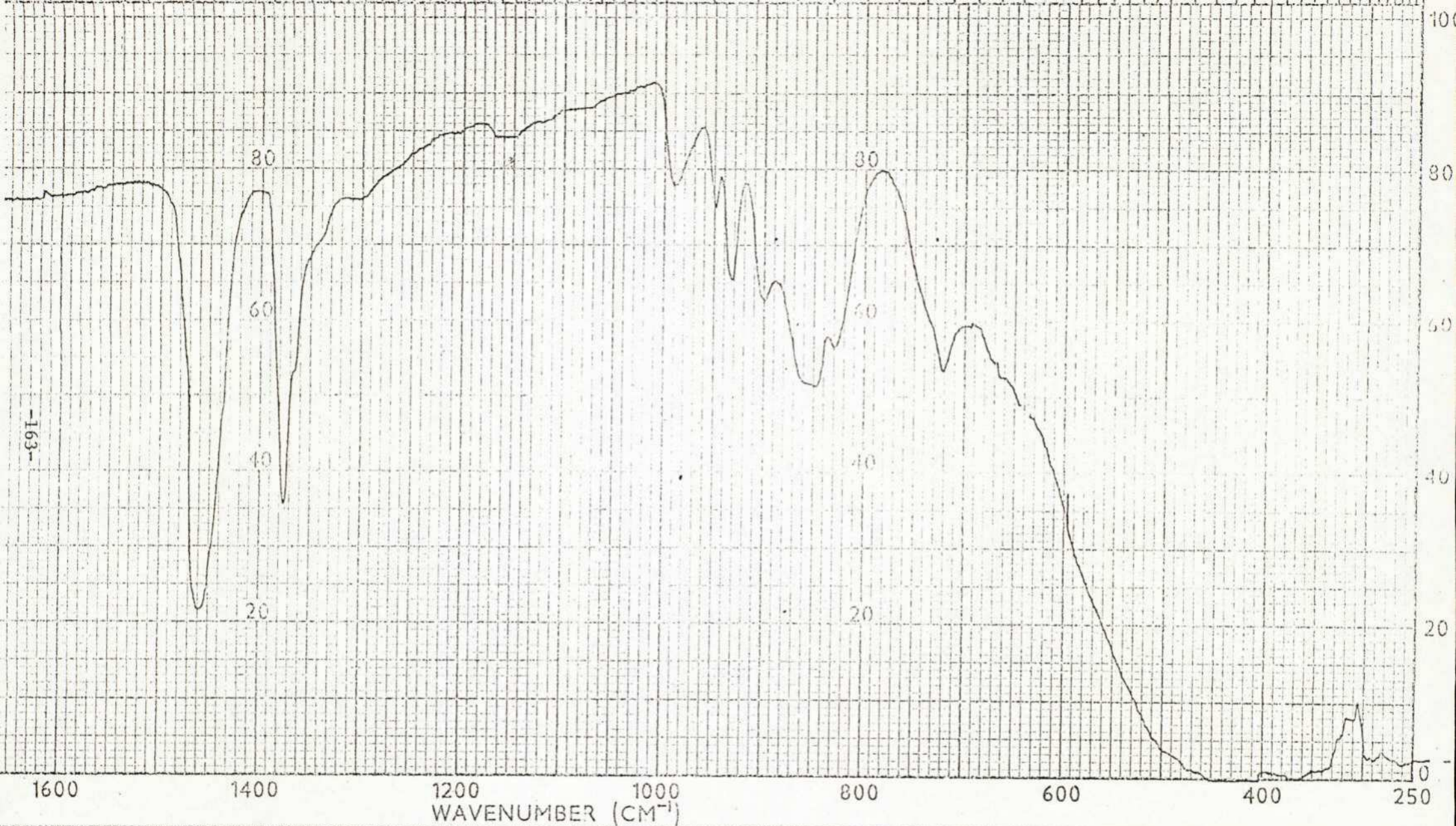
$$\epsilon_{mf} = 1 - \frac{\text{Weight} / \rho}{(\text{Height})(\text{Area})} \quad \text{equation IV.1.2}$$

Determining the voidage fraction for normal packing of the catalyst particles, the graphical correlation between sphericity and voidage fraction proposed by Brown et al (220), was used to achieve the value of 0.48 for the average spheri-

Table IV.1.a Determination of surface area.

Bi:Mo particles 67 μm

Values of $P/M_a (P_o - P)$		Catalyst weight after outgassing 144 mg Weight loss 0.16 mg	
OBSERVED	FITTED	DIFFERENCE %	GAS ADSORBED mg
0.671	0.614	8.555	0.08
1.450	1.500	-3.446	0.09
2.912	3.013	-3.477	0.10
3.771	3.677	2.486	0.10
SURFACE AREA 1.774 m^2/g			
STANDARD DEVIATION 4.977 %			



REMARKS

Figure IV.1.a i.r spectrum of Bi:Mo 1:1 catalyst (nujol mull)

SCAN SPEED

SLIT

OPERATOR M. Ftenakis

DATE 22-January 1978

RPK/219/1002 457-5001

GRAPHIC CONTROLS LIMITED

REF. No

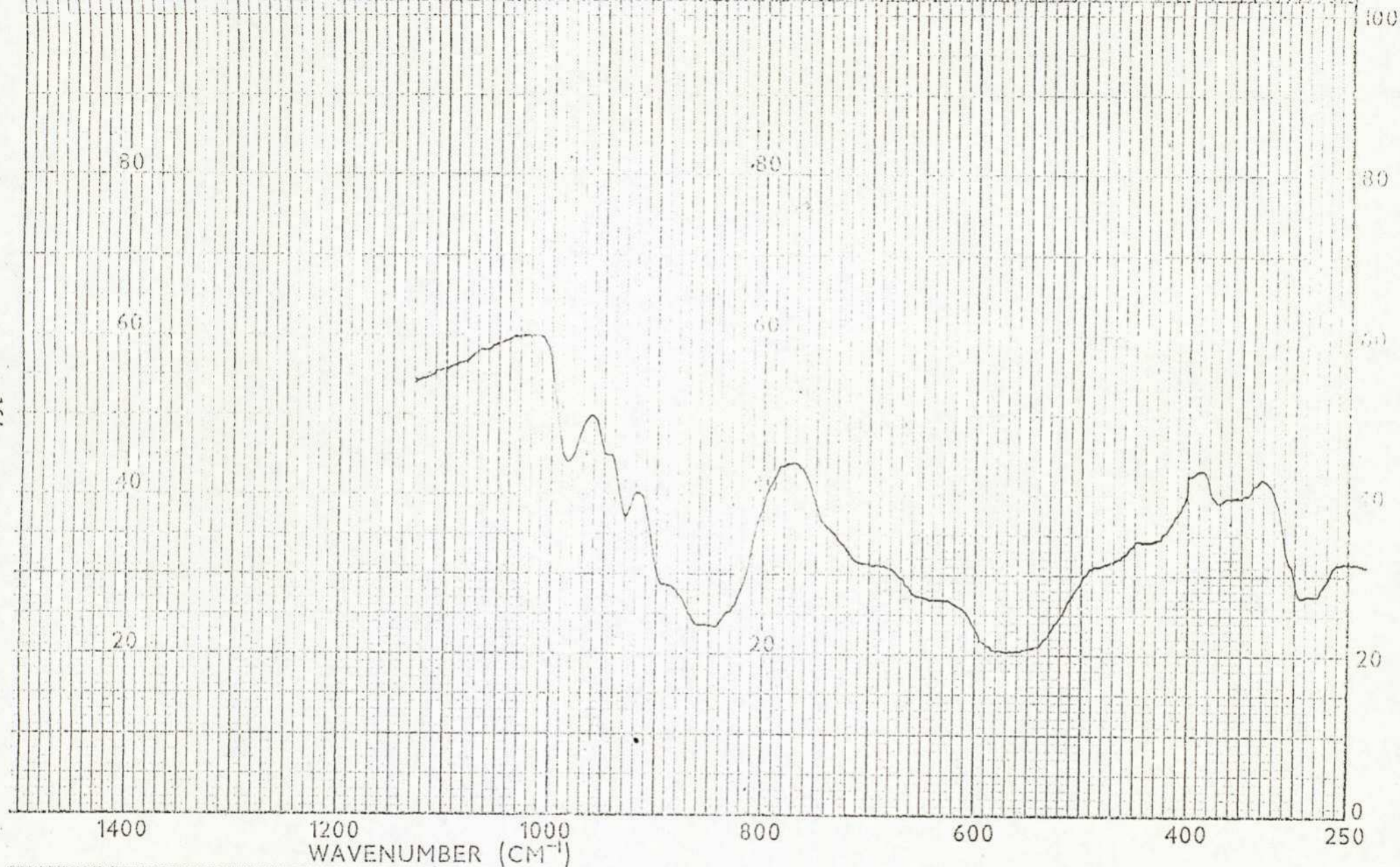


Figure IV.1.b i.r spectrum of Bi:Mo catalyst (KBr disc)

SCAN SPEED _____
SLIT _____

OPERATOR M. Ftenakis
DATE 22- January-1978

RPK/219/1002 457-5001
GRAPHIC CONTROLS LIMITED

REF. No. _____

city of the particles.

As shown in figures IV.1.a and IV.1.b the i.r spectra of the catalyst were also obtained to give an indication of the composition of the oxide mixture.

A summary of the particle studies on the bismuth molybdate catalyst are given in the following table.

Table IV.1.b Physical properties of Bi:Mo catalyst.

Average particle diameter	0.0067 cm
Particle density	5.44 g / cm ³
Bulk density	2.23 g / cm ³
Voidage fraction at U_{mf}	0.58
Average sphericity	0.48
BET surface area	1.775 m ² / g

IV.2 OPTIMIZATION CONDITIONS OF THE FLUIDISED BED REACTOR

IV.2.1 Minimum fluidisation velocity

Values for the minimum fluidisation velocity were determined by measuring the pressure drop across the catalyst bed for increasing and decreasing velocity of the gas mixture of composition $N_2:O_2:C_4H_8$ in the ratio 8:1:1. Table IV.2.a summarizes the results obtained at constant bed height, while figure IV.2.a illustrates the relationships and shows the effect of a stirrer within the catalyst bed.

When the gas velocity was increased above the minimum fluidising point, the stirred bed expanded without any observable

bubble formation until a gas flow-rate of 510 ml/min was reached, at which point a freely bubbling bed was obtained; the un-stirred bed gave rise to serious channelling. Moderate variation in stirrer speed did not affect seriously the results and therefore an average speed of 40 r.p.m which has been used previously (208), was adopted for the process.

When the catalyst bed was 30.12 g the minimum fluidisation velocity was observed to be 310 ml/min. For our reactor (33 mm diameter), the minimum fluidisation velocity in cm/sec is equal to;

$$U_{mf} \text{ (cm/sec)} = U_{mf} \text{ (cm}^3\text{/min)} / \text{cross sect. area (cm}^2\text{)} \times 60 \text{ (sec/min)}$$

$$\text{but cross sectional area} = \pi R^2 = 8.05$$

substituting this value in the above equation gave:

$$U_{mf} = 0.606 \text{ cm/sec}$$

Theoretically (124,128), for small uniform particles the gas velocity at the point of minimum fluidisation can be predicted from the equation:

$$U_{mf} = \frac{\epsilon_{mf}^3 \phi_s^2 d_p^2 (\rho_s - \rho_g) g}{150 (1 - \epsilon_{mf}) \mu} \quad \text{equation IV.2.1}$$

Our gas fluidised bed had the following physical properties:

$$d_p = 0.0067 \text{ cm}$$

$$\rho_s = 5.47 \text{ g / cm}^3$$

$$\rho_g = 0.001204 \text{ g / cm}^3$$

Figure IV.2.a Pressure drop variation with gas velocity

(Weight of catalyst 30.1 g)

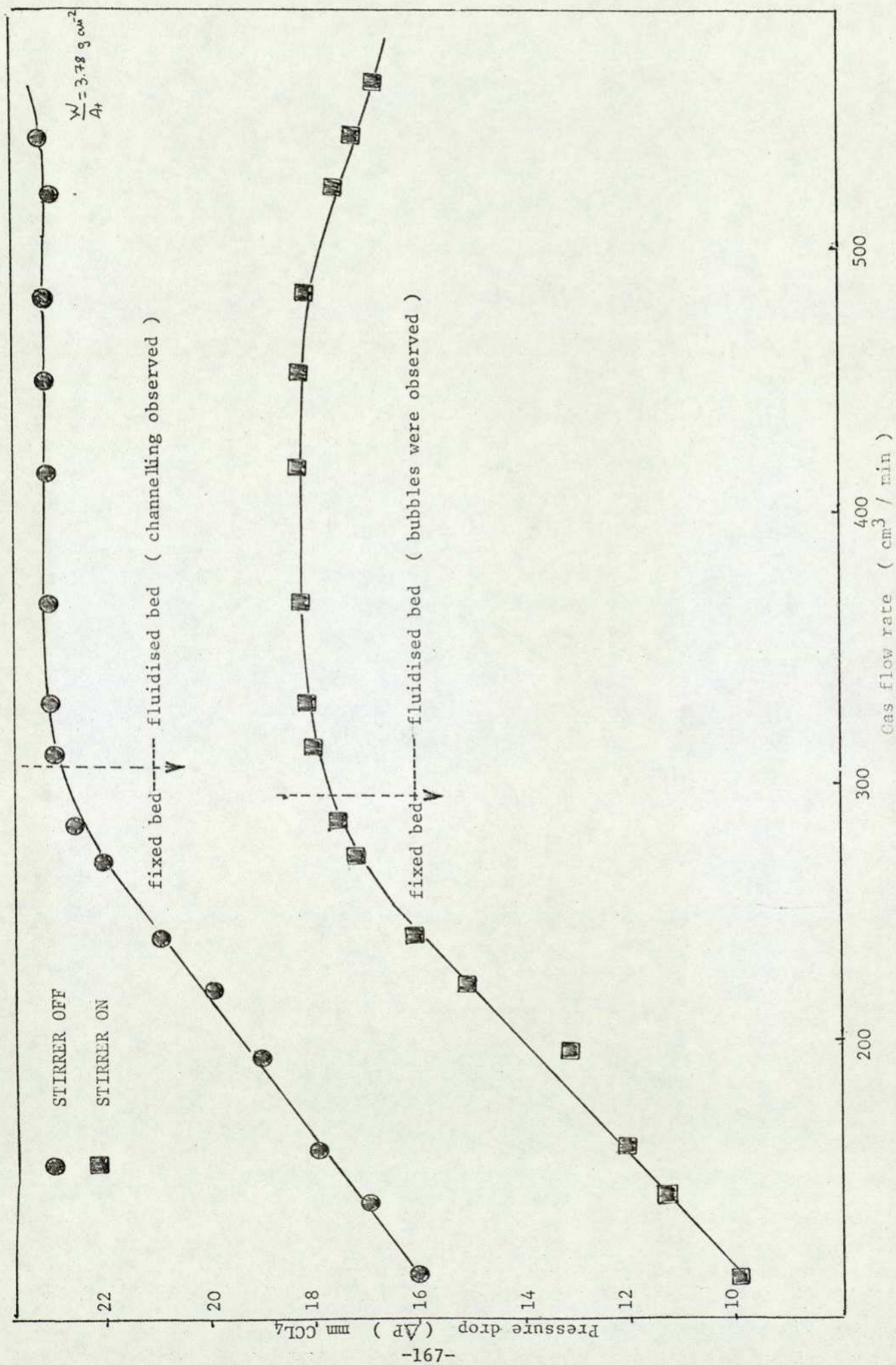


Table IV 2.a Effect of stirrer on bed behavior (Weight of catalyst 30.1 g)

Gas velocity ml/min	STIRRER ON				STIRRER OFF			
	Pressure drop mm CCL ₄	Minimum fluidisation velocity ml/min	Bubbling velocity ml/min	OBSERVATIONS	Pressure drop mm CCL ₄	Minimum fluidisation velocity ml/min	Bubbling velocity ml/min	OBSERVATIONS
86.9	9.0	290	510	FIXED-BED FLUIDISED-BED BUBBLING FLUIDISED BED	14.0	310	-	FIXED-BED FLUIDISED-BED CHANNELLED FLUIDISED BED
107.1	10.0				16.0			
131.8	11.0				17.0			
155.8	12.0				18.0			
190.4	13.0				19.0			
216.2	15.0				20.0			
235.3	16.0				21.0			
266.6	17.0				22.0			
279.0	17.5				22.5			
307.7	18.0				23.0			
324.0	18.0				23.0			
363.0	18.0				23.0			
413.8	18.0				23.0			
460.0	18.0				23.0			
480.0	18.0				23.0			
520.0	17.5				23.0			
540.0	17.0				23.5			
560.0	16.5				-			

$$\mu = 0.000185 \text{ g / cm x sec}$$

$$g = 981 \text{ cm / sec}^2$$

$$\epsilon_{mf} = 0.58$$

$$\phi_s = 0.46$$

Substituting these data into equation IV.2.1 gave a value for the minimum fluidisation velocity of 0.836 cm / sec.

Comparison of the theoretically obtained minimum fluidisation velocity with the experimentally obtained value gives an error of 27.5 % .

The generalised equation which predicts the minimum fluidisation velocity for the whole range of Reynolds numbers (all different sizes) has been devised by many authors (124 , 127). In general, this gives a quadratic in U_{mf} .

$$\frac{1.75 d_p^2 \rho_g^2}{\phi_s \epsilon_{mf}^3 \mu^2} U_{mf}^2 + \frac{150 (1 - \epsilon_{mf}) d_p \rho_g}{\phi_s^2 \epsilon_{mf}^3 \mu} U_{mf} - \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2} = 0$$

equation IV.2.2

Substituting the same data into equation IV.2.2 gave a value of $U_{mf} = 0.842 \text{ cm / sec}$.

Comparison of this value with the experimentally obtained value for the minimum fluidisation velocity gives an error of 28.02 % .

IV.2.2 Attrition losses

Transport of catalyst out of the reactor during the oxidation experiments was investigated by measuring changes in catalyst weight when the stirred bed was fluidised at different gas velocities. Results in table IV.2.b show that no appreciable

Table IV.2.b Catalyst transport at varying gas flow-rate
(Weight of catalyst 30.1 g)

Gas flow-rate ml / min	Time min	Mass transport % of total bed weight
248	60	0.00
266	60	0.00
307	60	0.00
363	60	0.03
413	60	0.04
514	60	0.07
620	60	0.10

particle transport occurred until a gas flow-rate of $363 \text{ cm}^3/\text{min}$ was attained.

IV.2.3 Bed expansion and bubble diameters.

On the basic assumption of the two phase theory, that the excess gas above that required to incipiently fluidise the bed by-passes the particles in the form of bubbles, many reactor models have been proposed to theoretically predict conversions during catalytic reactions within fluidised beds.

The main parameter in these models is the equivalent bubble diameter and its size determines the degree by which the reactant gases will by-pass the bed in the unreacted state.

Expansion in bed height as the gas flow rate increased above the minimum fluidisation point to about $500 \text{ cm}^3/\text{min}$. was measured employing a simple photographic technique (221, 222) . The bubble eruption diameter was also measured directly from the enlarged photographs (222, 223, 224) at this flow-rate and its value, 0.76 cm , was preferred to the value estimated from the bed expansion data, according to the method proposed by Davidson (159). This method has been considered inaccurate for our studies because of (1) the increase in bed height at these low superficial gas velocities is small and (2) the complications caused by the application of the stirrer.

Typical photographs used for the estimation of the average bubble diameter are shown in plates V.3.a , V.3.b , V.3.c and V.3.d .

IV.3 HOMOGENEOUS REACTION IN THE CATALYST-FREE REACTOR

Before any catalytic studies were attempted it was considered important to study the extent of the homogeneous reaction in the empty reactor. Three different gas mixtures with $C_4H_8:O_2$ mole ratios of 0.983, 0.467, and 0.272 were passed through the reactor at a velocity equal to the minimum fluidisation velocity at temperatures of 387, 420, and 437 °C. Figures IV.3.a, IV.3.b, and IV.3.c illustrate graphically the variation of conversion, selectivity and yields with temperature for all the three different ratios.

Table IV.3.a summarizes the results obtained for the gas phase oxidation of isobutylene at the different temperature levels.

From the results obtained it is observed that conversion increases steadily as the temperature increases at all feed ratios. At 0.983 feed ratio the total conversion increases from 1.700% to 3.055% as the temperature increases from 387 to 437 °C (Figure IV.3.a). For the ratio 0.467 the lowest conversion is 1.777% at 387 °C, the maximum observed being 2.551% at 437 °C. (Figure IV.3.b). The results for the third ratio, 0.272 showed that the conversion varied from 1.492% to 3.029% (Figure IV.3.c).

The main product of the homogeneous oxidation of isobutylene is acetone. It is formed in high yields which decrease with increasing temperature (figures IV.3.a, IV.3.b, and IV.3.c). The maximum observed yield of acetone was 81.1 % , while the minimum was 66.0 % . Instead the yield of acetone generally decreases when the reactant feed ratio decreases (Table IV.3.a).

Table IV.3.a Gas phase oxidation of isobutylene.

Temperature °C	Oxygen to Isobutene Molar Ratio	Total Conversion %	Yield of CH_3COCH_3 %	Yield of CH_3CHO %	Yield of HCHO %	Selecti- vity %	Yield of CO %	Yield of CO_2 %	Carbon mass balance	Oxygen mass balance
387	0,983	1.70	81.1	0,000	15,63	3.239	0,000	0,000	100.0	97.3
387	0,467	1,77	78.1	0,000	18,52	3,344	0,000	0,000	100.0	99.3
387	0,270	1.49	76.2	1,177	17,45	5.143	0,000	0,000	100.0	98.9
420	0,983	2,00	74,1	0,000	16,79	5.019	0,000	0,000	99.9	99.3
420	0,467	1.96	75.3	1,362	17,86	3.465	0,000	2,103	100.0	100.3
420	0,271	1,88	69,6	2,814	20,29	4,981	0,000	2,308	100.0	99.5
432	0,983	2,75	76,5	2,751	13,82	7.033	0,000	0,000	100.0	101.3
432	0,466	2,40	73,0	2,238	16,65	5,336	0,000	2,759	99.9	100.9
432	0,272	2,57	71,4	2,229	19,55	4,266	0,000	2,325	100.0	99.0
437	0,983	3,05	72,9	2,971	13,72	7,364	0,000	3,079	100.0	97.6
437	0,467	2,52	71,6	2,668	17,21	5,616	0,000	2,969	100.0	97.6
437	0,272	3,02	66,0	2,042	17,23	4,747	0,000	2,433	99.7	99.2

Figure IV.3.a Conversion, selectivity and yields variation
with temperature during the gas phase oxidation
of isobutylene. ($C_4H_8/O_2 = 0.983$)

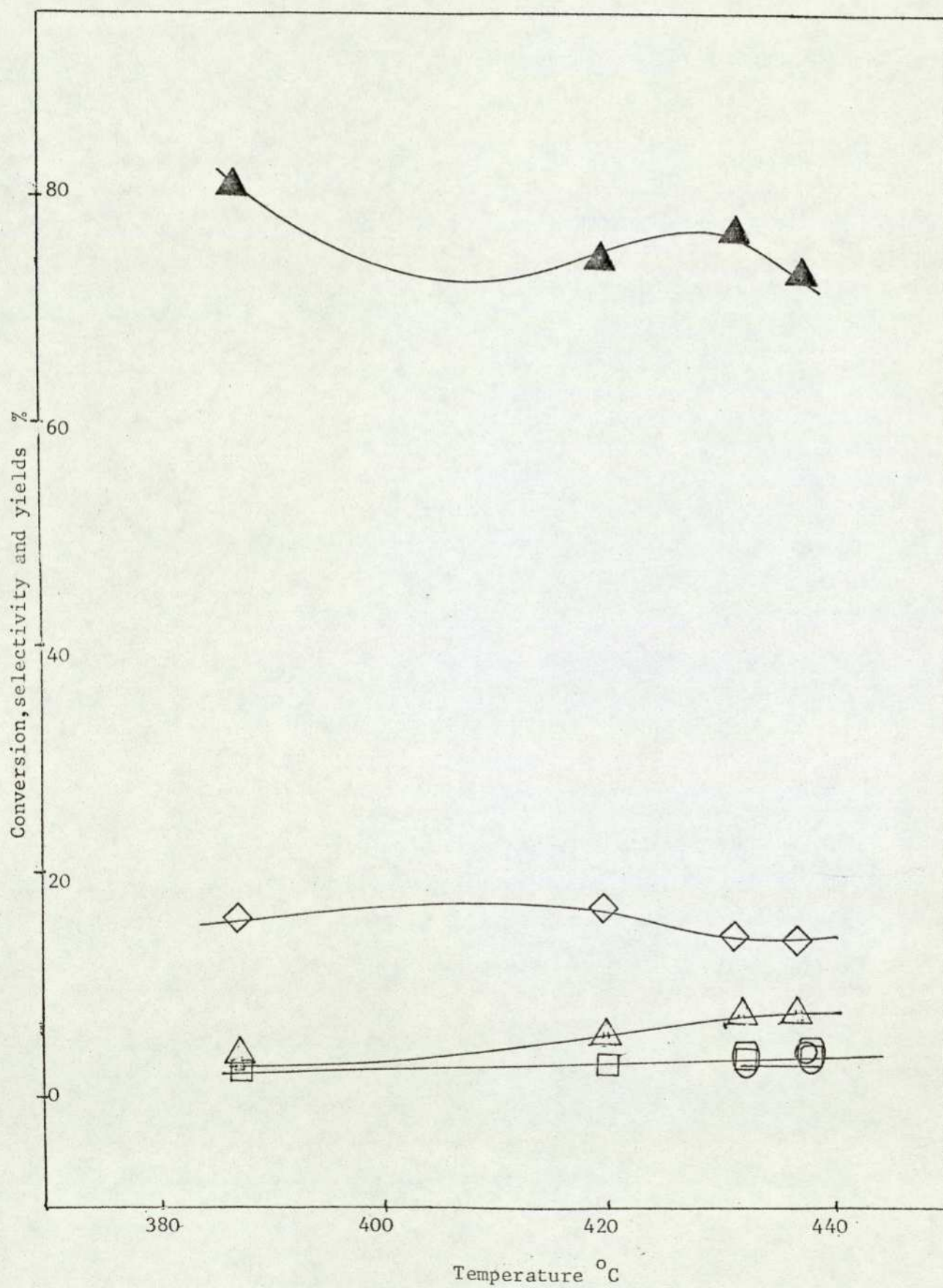


Figure IV.3.b Conversion, selectivity and yields variation
with temperature during the gas phase oxidation
of isobutylene. ($C_4H_8/O_2 = 0.467$)

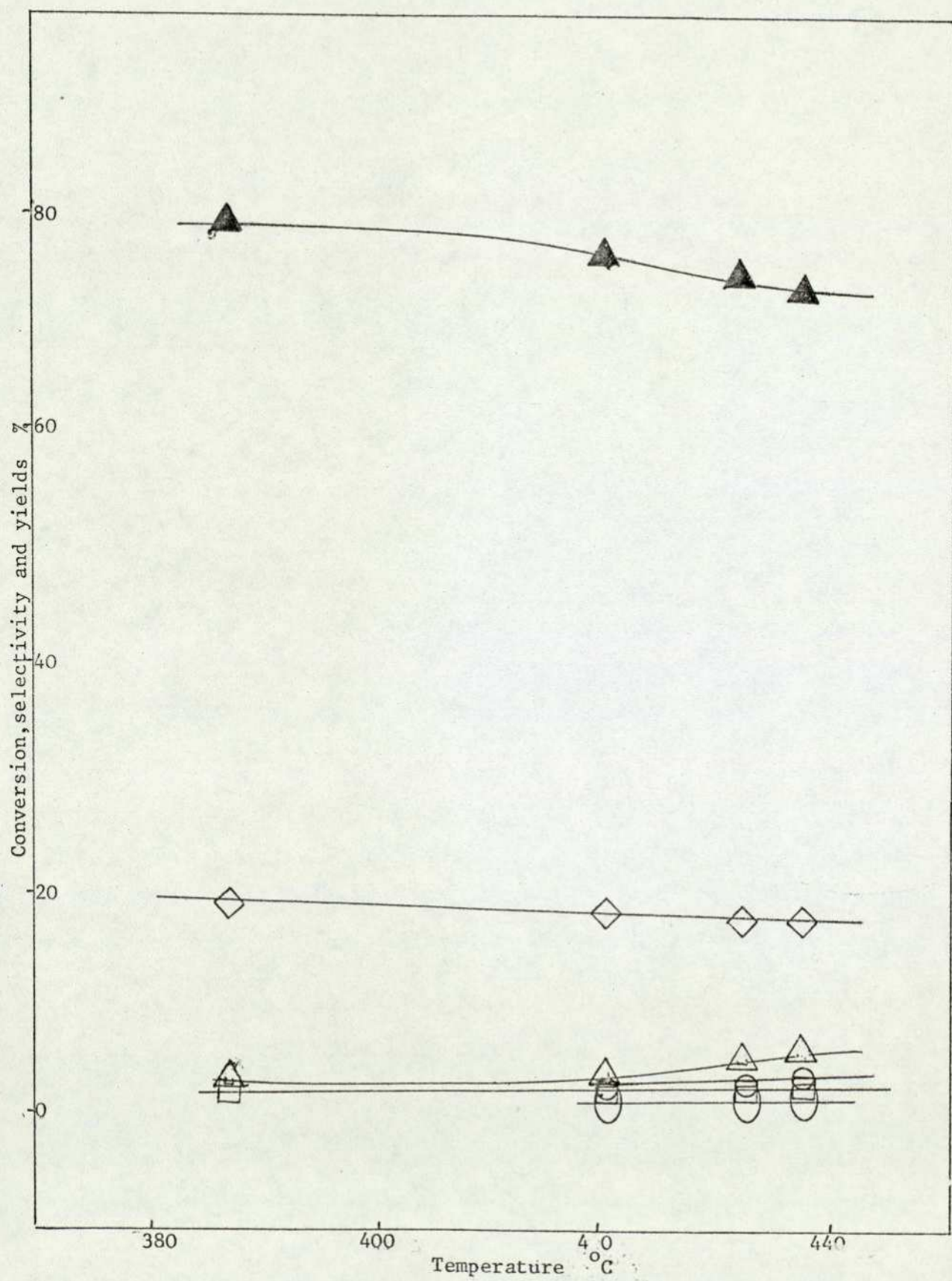
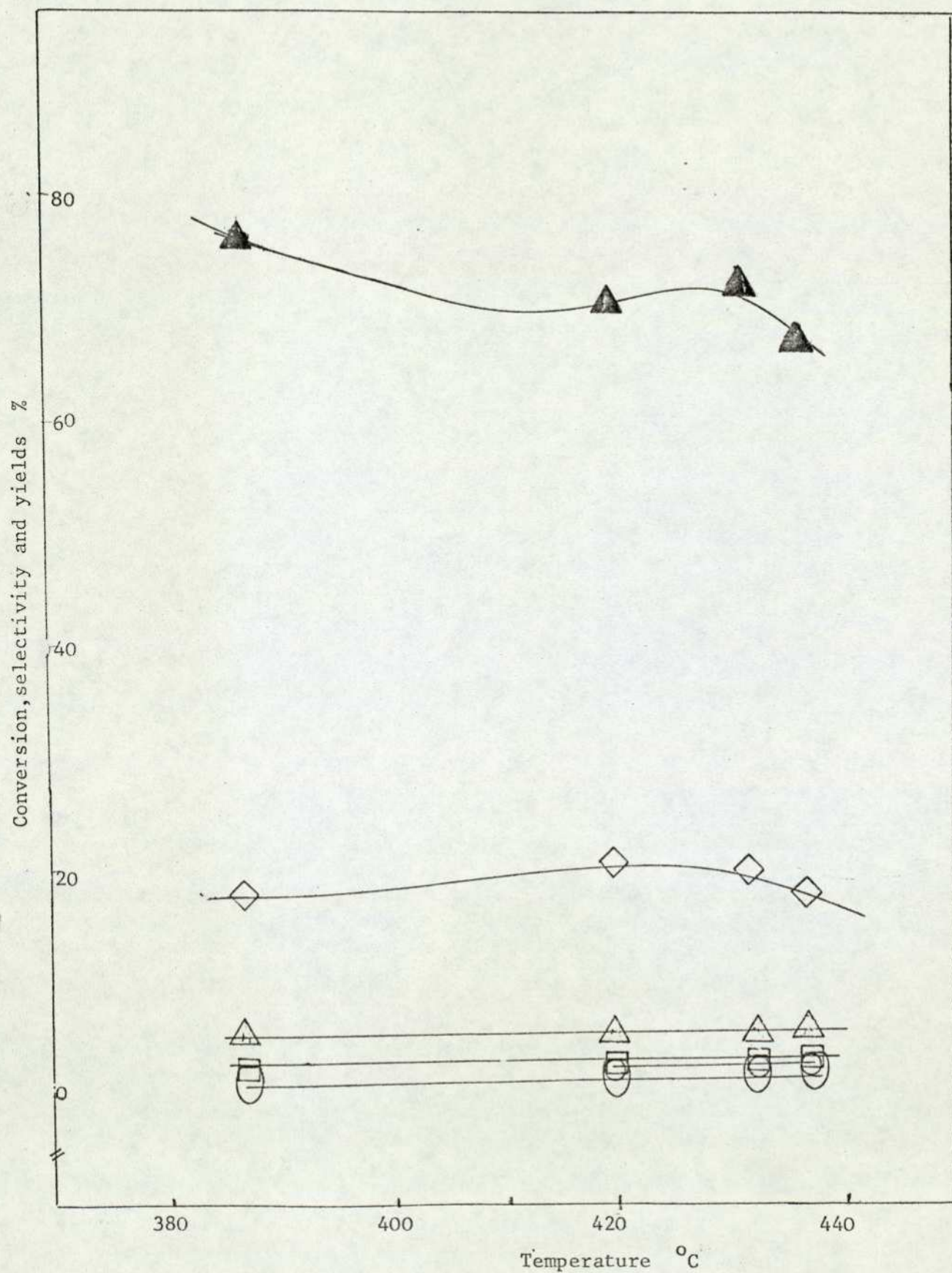


Figure IV.3.c Conversion, selectivity and yields variation
with temperature during the gas phase oxidation
of isobutylene. ($C_4H_8/O_2 = 0.272$)



On the other hand, formaldehyde is formed as a second main product. Its yield increases with decreasing olefin to oxygen ratio. This can be understood easily in relation to the variation of acetone formation.

The formation of methacrolein occurs in rather small yields. However, they increase slightly with temperature. The by-products are mainly acetaldehyde and carbon oxides, formed in very small yields and only at higher temperatures are they present in measurable quantities.

I.V.4 KINETIC STUDIES AND DETERMINATION OF THE RATE OF THE REACTION

Determination of the kinetics and the reaction rates for the oxidation of propylene and isobutylene, over mixed oxide catalysts to the corresponding unsaturated aldehydes has been achieved in this laboratory using the S.G.S type of reactors. Although S.G.S reactors have proved more suitable for kinetic measurements, an isothermal continuous flow reactor operating at atmospheric pressure has been used simultaneously with the fluidised bed for direct comparison of the conversion data obtained between the three different reactors.

The reaction system consisted of a pyrex-glass tube with a preheater, while the pre-reactor part is similar to that mentioned in page 118. The preheater was 1.5 m in length and 20 mm diameter pyrex glass tubing wound around the reactor. The catalyst bed (5 cm^3 volume), was placed in the centre of the reactor tube. Two chromel-alumel thermocouples measured

the temperature of the catalyst bed at the centre and adjacent to the reactor wall, respectively.

IV.4.1 Oxidation of isobutylene to methacrolein

All the experiments were carried out at a constant isobutylene : oxygen ratio of 1:1 . The ratio was chosen to avoid over-oxidation of isobutylene, and eliminate the possibility of catalyst reduction. A catalyst weight of 2.5 g diluted with glass spheres to give a total volume of 5 cm^3 was used in all the experimental runs. Conversion data were then obtained at different contact times, W / F . Three temperatures were investigated in the range 405 to 462 °C, and the results obtained are summarised in tables IV.4.a, IV.4.b, and IV.4.c .

The order of reaction in isobutylene was tested using the appropriate integrated forms of the zero, first and second order rate expressions.

Between them, the integrated form of a first order rate expression, $-\ln (1-X) = K_c W/F$, gave the best fit to the experimental conversion values as can be seen in figures IV.4.a, IV.4.b, and IV.4.c .

The values of the rate constants were obtained by a linear regression method from the experimental conversions, while the activation energy and the pre-exponential factor of the Arrhenius equation for each of the reaction rate constants were then determined by a linear estimation technique (Table V. 4. a).

In figures IV.4.a, IV.4.b, and IV.4.c computer plots for the relation between $-\ln (1-X)$, against contact time, W / F , are given. In each of these figures the solid straight

Table IV.4.a Oxidation of isobutylene to methacrolein

at 405 °C. (fixed-bed data)

Temperat., °C	W / F g hr/moles	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
405	7.56	6.25	98.5	0.92	0.0	98.5	96.2
	5.23	4.36	98.9	0.60	0.0	99.6	98.5
	3.42	2.90	100.0	0.0	0.0	103.5	102.1
	2.85	2.42	100.0	0.0	0.0	104.0	98.0
	1.61	1.36	100.0	0.0	0.0	97.2	103.6
	1.58	1.30	100.0	0.0	0.0	98.1	102.7
Mean carbon mass balance 100.1				Variance for carbon 8.4			
Mean oxygen mass balance 100.2				Variance for oxygen 9.2			

Table IV.4.b Oxidation of isobutylene to methacrolein
at 445 °C. (fixed-bed data)

Temperat., °C	W / F g hr/moles	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
445	12.93	22.0	96.7	2.700	0.089	103.2	96.5
	5.29	9.90	96.9	3.070	0.066	98.9	100.5
	4.48	8.40	97.3	1.985	0.043	100.5	97.2
	2.47	4.80	98.2	1.562	0.000	97.8	102.5
	2.27	4.40	100.0	0.000	0.000	99.3	96.8
	1.12	2.10	100.0	0.000	0.000	102.1	97.5
Mean carbon mass balance		100.3	Variance for carbon		4.16		
Mean oxygen mass balance		98.5	Variance for oxygen		5.92		

Table IV.4.c Oxidation of isobutylene to methacrolein
at 462 °C. (fixed-bed data)

Temperat., °C	W / F g hr/moles	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
462	11.56	27.0	95.6	3.92	0.105	97.5	96.2
	7.31	18.0	96.9	3.15	0.0890	102.5	97.5
	3.46	9.00	97.2	2.80	0.0710	99.5	104.6
	2.91	7.52	97.3	2.59	0.0680	97.2	102.5
	1.72	4.60	97.1	2.65	0.0650	100.0	97.2
Mean carbon mass balance 99.3				Variance for carbon 4.59			
Mean oxygen mass balance 99.6				Variance for oxygen 13.8			

Figure IV.4.a Isothermal first order plot for the oxidation
of isobutylene to methacrolein ($T = 405^{\circ}\text{C}$)

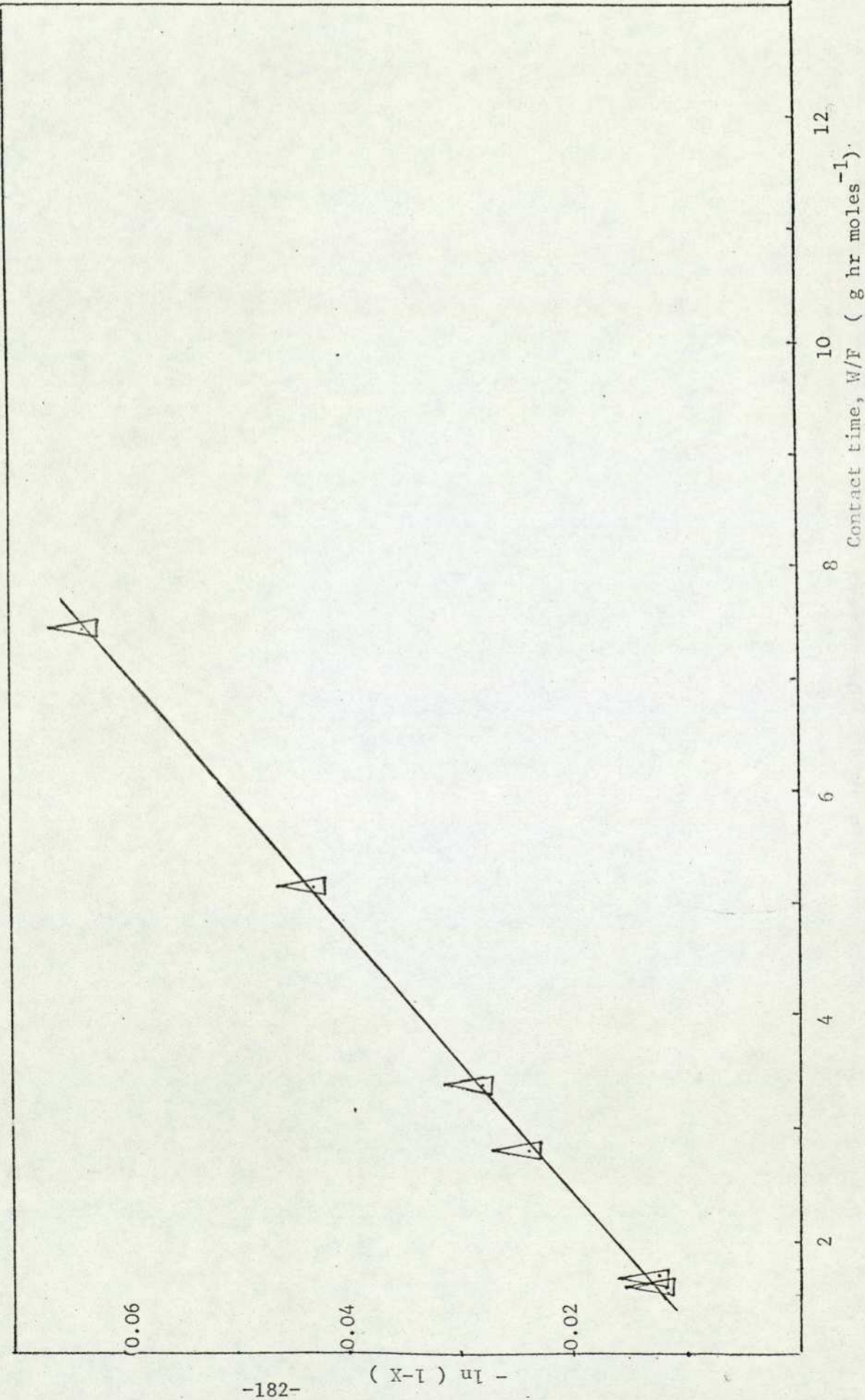


Figure IV.4.b Isothermal first order plot for the oxidation of isobutylene to methacrolein ($T = 445^{\circ}\text{C}$)

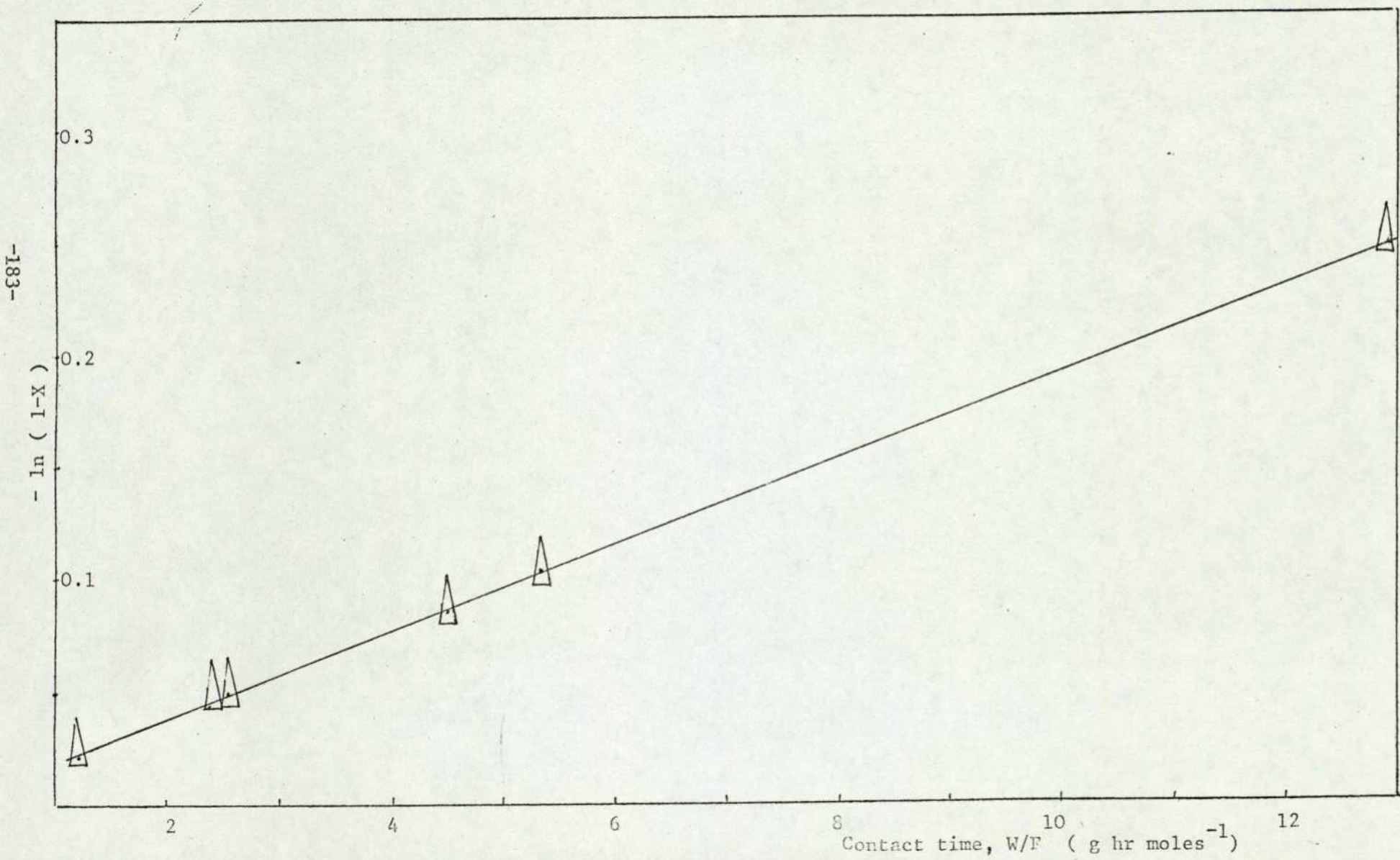
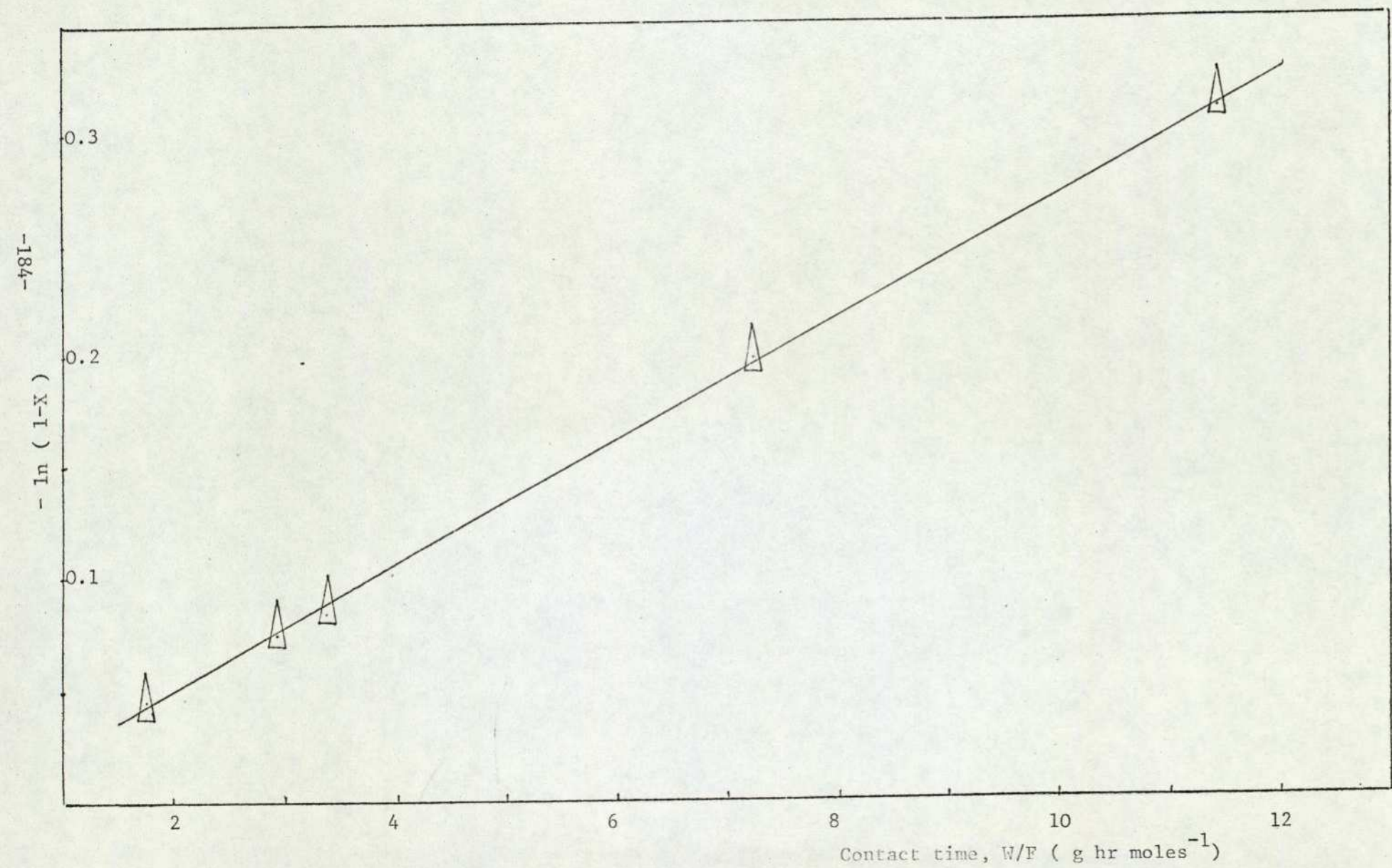


Figure IV.4.c Isothermal first order plot for the oxidation of isobutylene to methacrolein ($T = 462^{\circ}\text{C}$)



lines represent the best fit curve between the data points obtained by the method of least squares.

The reaction order in oxygen was tested where the oxygen partial pressure in the feed mixture was varied but no detectable difference in conversion was observed.

IV.4.2 Oxidation of propylene to acrolein

The same reactor and conditions, as reported above, were used to investigate the kinetics of the catalytic oxidation of propylene to acrolein over bismuth molybdate catalyst. In general conversions of propylene to acrolein were lower than those found for the oxidation of isobutylene under similar reaction conditions. Maximum conversion towards acrolein was 5.55 % ,while the highest value during the oxidation of isobutylene was 27.0 % ,both obtained at the highest temperature and longest contact time.

The amounts of carbon dioxide in these experiments were too small, (no carbon monoxide was detectable), to make quantitative comparisons possible between individual runs.

The results obtained are summarised in tables IV.4.d, IV.4.e, and IV.4.f . Again, linear regression technique was used to obtain the rate constants from conversion data, using the integrated form of a first order rate expression.

The first order plots $-\ln (1-X)$ against contact time, W/F , are given in figures IV.4.d, IV.4.e, and IV.4.f . Values of the apparent activation energy and the pre-exponential factor of the Arrhenius equation estimated for each of the reaction constants are given in table V.4.b .

Table IV.4.d Oxidation of propylene to acrolein
at 405 °C (fixed-bed data)

Temperat., °C	W / F g hr/moles	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
405	5.80	1.309	100.0	0.0	0.0	100.9	103.2
	4.60	1.158	100.0	0.0	0.0	102.5	96.5
	3.71	0.0880	100.0	0.0	0.0	98.5	97.5
	1.95	0.0462	100.0	0.0	0.0	99.6	100.9
	1.23	0.0293	100.0	0.0	0.0	97.5	96.5
	1.10	0.0000	-	-	-	-	-
Mean carbon mass balance 99,8				Variance for carbon 3.88			
Mean oxygen mass balance 98,9				Variance for oxygen 8.99			

Table IV.4.e Oxidation of propylene to acrolein
at 445 °C. (fixed-bed data)

Temperat., °C	W / F g hr/moles	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
445	6.20	4.23	97.4	1.234	0.0	98.7	99.6
	5.80	4.07	97.8	2.538	0.0	98.2	98.5
	4.48	3.04	100.0	2.173	0.0	100.5	102.5
	3.61	2.40	100.0	0.0	0.0	99.3	98.1
	2.24	1.50	100.0	0.0	0.0	100.0	96.2
	1.62	1.12	100.0	0.0	0.0	99.1	93.8
	1.50	1.00	100.0	0.0	0.0	99.8	97.5
Mean carbon mass balance 99.3				Variance for carbon 0.712			
Mean oxygen mass balance 98.4				Variance for oxygen 7.52			

Table IV.4.f Oxidation of propylene to acrolein
at 462 °C. (fixed bed data)

Temperat. °C	W / F g hr/moles	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
462	5.90	5.55	96.9	3.03	0.0	102.8	102.4
	5.00	4.52	97.5	2.85	0.0	100.5	96.2
	4.50	4.02	96.9	3.32	0.0	101.2	102.5
	4.20	3.96	96.7	3.22	0.0	101.8	98.6
	3.36	3.27	96.9	3.03	0.0	105.2	94.9
	2.20	1.98	100.0	0.0	0.0	100.4	94.8
	1.65	1.50	100.0	0.0	0.0	100.6	99.2
	1.48	1.45	100.0	0.0	0.0	99.5	101.5
Mean carbon mass balance 101.5				Variance for carbon 3.22			
Mean oxygen mass balance 98.7				Variance for oxygen 10.1			

Figure IV.4.d Isothermal first order plot for the oxidation
of propylene to acrolein ($T = 405^{\circ}\text{C}$)

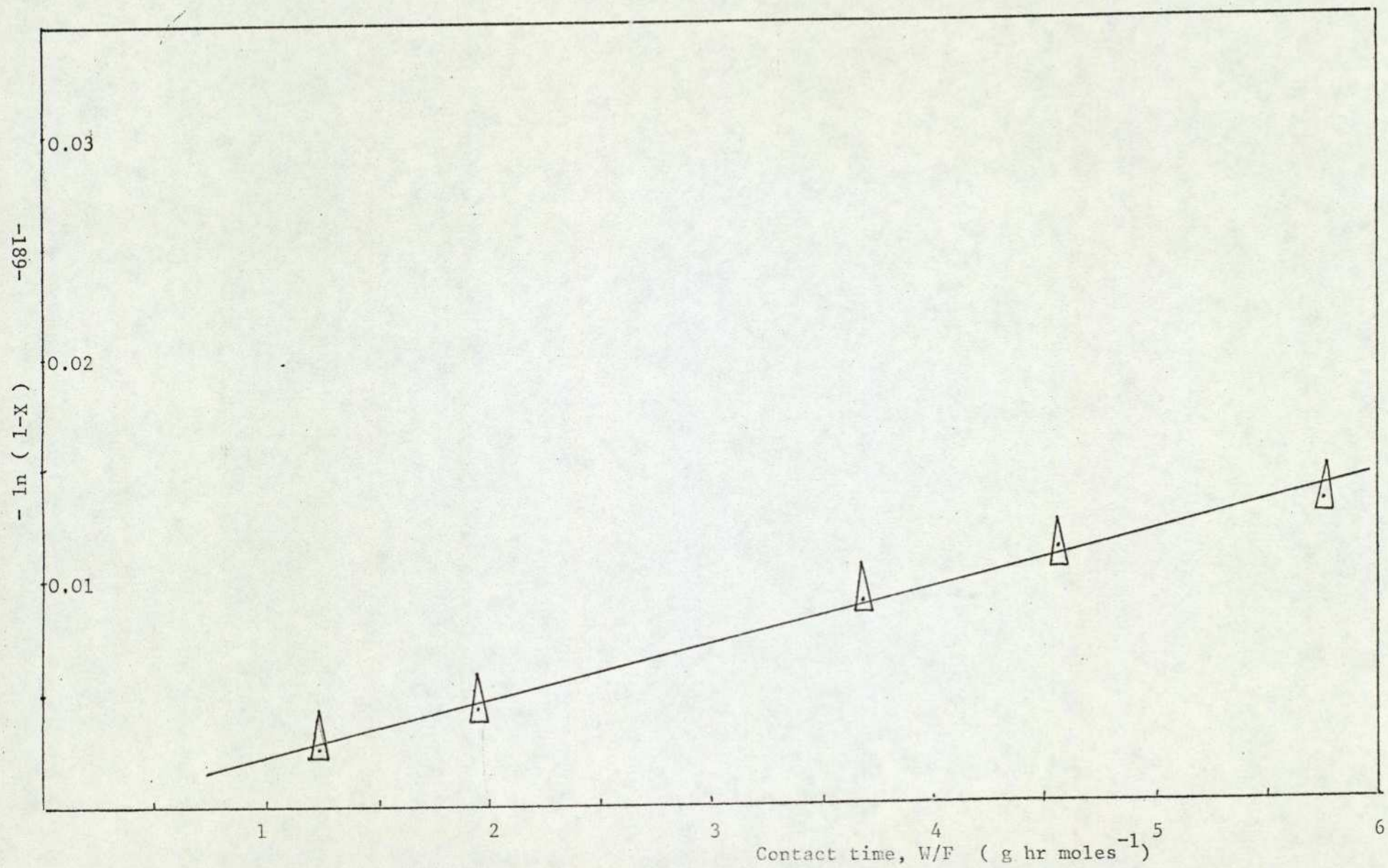


Figure IV.4.e Isothermal first order plot for the oxidation of propylene to acrolein ($T = 445^{\circ}\text{C}$)

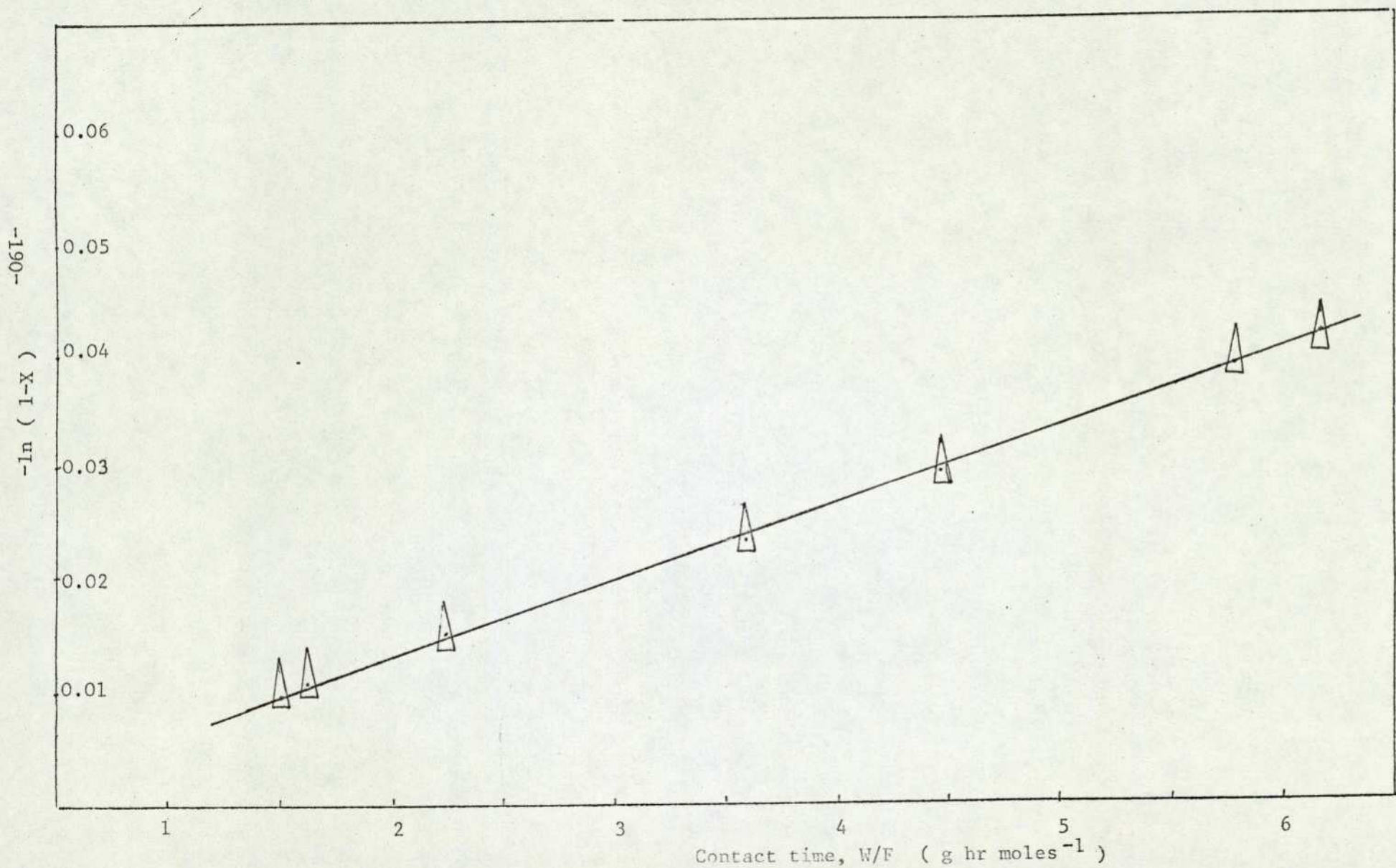
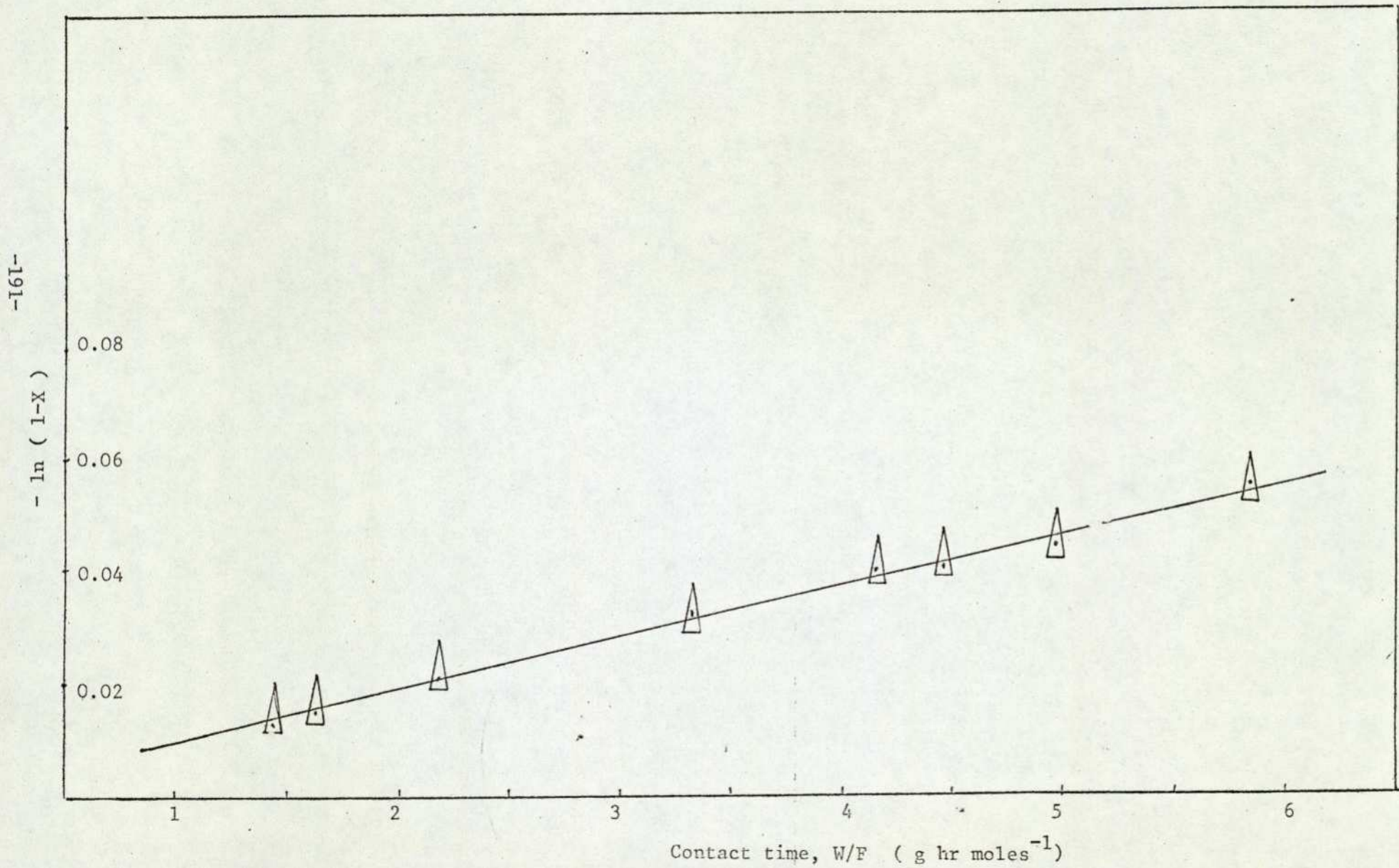


Figure IV.4.f Isothermal first order plot for the oxidation
of propylene to acrolein ($T = 462^{\circ}\text{C}$)



IV.5 OPTIMIZATION OF CONDITIONS FOR THE SELECTIVE OXIDATION OF ISOBUTYLENE TO METHACROLEIN

When the optimum fluidising conditions had been established and also other relevant parameters such as catalyst reactivity and reproducibility examined, attempts at isobutylene oxidation in respect of maximum conversion to methacrolein were then planned and carried out by varying isobutylene to oxygen ratio at different temperatures ranging from 387 to 535 °C. The catalytic bed was a shallow (H=1.2 cm), gas fluidised bed consisting of bismuth molybdate particles with an average diameter of 67 μm .

IV.5.1 Conversion data at minimum fluidisation velocity

Oxidation of isobutylene to methacrolein over bismuth molybdate catalyst varying the reactant feed ratio were carried out at different temperatures.

The temperatures examined were 402 °C, 442 °C, 453.5 °C, 463 °C, 469.5 °C, 471 °C, 500 °C, and 537 °C, and the results obtained are tabulated in tables IV.5.a, IV.5.b, IV.5.c, IV.5.d, IV.5.e, IV.5.f, IV.5.g, and IV.5.h.

Mathematical treatment of the results in the present work was based on the assumption that the catalytic oxidation of isobutylene to methacrolein and carbon oxides over bismuth molybdate catalyst is a first order reaction with respect to olefin concentration. Only those conversion data which justified the assumption of pseudo first order kinetics (208), were selected for subsequent

Table IV.5.a Oxidation of isobutylene by Bi:Mo at 402 °C

Temperature °C	Isobutylene to oxygen moles ratio	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
402	2.003	29.52	88.6	4.232	1.604	99.6	98.2
	1.040	28.34	88.9	4.675	1.452	99.0	101.6
	0.983	27.96	90.9	4.352	2.020	100.3	99.2
	0.707	19.23	90.4	4.520	1.893	100.5	97.4
	0.468	15.43	93.5	4.820	1.870	99.9	99.2
	0.419	15.15	92.6	5.030	2.016	100.3	100.0
	0.270	20.27	91.7	5.022	1.960	100.4	100.5
Mean carbon mass balance 99.9				Variance for carbon 0.290			
Mean oxygen mass balance 99.4				Variance for oxygen 1.840			

Tempera- ture °C	Isobutylene to oxygen moles ratio	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
442	2.025	81.3	88.5	12.76	2.604	100.9	96.5
	2.005	80.9	84.9	12.28	2.605	98.6	97.9
	1.036	81.0	85.5	11.75	2.506	102.5	99.5
	0.983	81.0	86.1	11.65	2.123	102.6	96.7
	0.701	68.3	85.8	11.64	1.850	104.5	99.0
	0.465	44.6	86.6	11.17	1.930	100.1	100.0
	0.269	25.0	85.2	11.90	2.253	99.5	101.2
	0.260	24.6	87.9	12.08	2.365	101.8	97.9
Mean carbon mass balance 101.3				Variance for carbon 3.712			
Mean oxygen mass balance 98.6				Variance for oxygen 2.395			

Table IV.5.b Oxidation of isobutylene by Bi:Mo at 442 °C.

Table IV.5.c Oxidation of isobutylene by Bi:Mo at 453.5 °C .

Tempera- ture °C	Isobutylene to oxygen moles ratio	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
453.5	2.015	85.6	85.2	13.62	2.701	100.0	98.5
	2.001	83.4	85.4	13.31	2.803	99.2	101.2
	0.983	83.2	86.6	12.92	2.750	98.4	100.5
	0.703	62.2	86.9	11.92	1.795	101.4	105.7
	0.465	41.3	88.0	10.57	1.624	99.6	95.1
	0.270	25.6	87.9	12.67	1.860	100.1	100.3
Mean carbon mass balance 99.7				Variance for carbon 1.018			
Mean oxygen mass balance 100.2				Variance for oxygen 12.01			

Tempera- ture °C	Isobutylene to oxygen moles ratio	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
463	2.000	74.8	80.0	14.43	3.658	99.2	101.9
	0.983	73.6	80.3	14.63	3.332	98.4	100.6
	0.710	58.2	80.8	13.02	2.200	101.3	110.6
	0.465	42.2	84.5	12.11	1.523	99.6	100.6
	0.420	36.03	85.1	12.65	1.650	100.1	98.8
	0.270	34.74	91.5	9.62	1.198	99.2	102.3
	0.210	34.01	90.4	6.010	1.304	102.2	102.5
Mean carbon mass balance 100.0				Variance for carbon 1.756			
Mean oxygen mass balance 102.5				Variance for oxygen 14.46			

Table IV.5.d Oxidation of isobutylene by Bi:Mo at 463 °C.

Temperature °C	Isobutylene to oxygen moles ratio	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
469.5	2.001	78.5	70.0	24.60	5.356	100.2	98.6
	0.983	75.7	80.7	15.22	3.920	101.5	99.2
	0.698	60.0	84.3	12.01	2.643	102.5	97.6
	0.465	41.3	85.5	11.65	2.730	100.5	98.2
	0.270	31.07	83.9	13.13	1.871	98.7	95.5
	0.234	27.24	85.0	11.23	1.462	99.4	99.0
Mean carbon mass balance		100.4	Variance for carbon		1.866		
Mean oxygen mass balance		98.0	Variance for oxygen		1.838		

Table IV.5.e Oxidation of isobutylene by Bi:Mo at 469.5 °C

Temperature °C	Isobutylene to oxygen moles ratio	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
471	2.005	78.5	87.6	12.46	3.032	102.3	97.3
	0.983	75.2	89.0	11.65	2.734	103.3	103.3
	0.703	60.0	89.9	10.63	2.862	102.0	102.0
	0.467	41.3	90.0	9.45	1.760	101.7	101.7
	0.270	31.05	91.2	7.49	1.480	101.2	101.2
	0.240	27.24	90.4	7.51	1.893	101.1	101.1
Mean carbon mass balance		101.9	Variance for carbon		0.660		
Mean oxygen mass balance		101.1	Variance for oxygen		4.098		

Table IV.5.f Oxidation of isobutylene by Bi:Mo at 471 °C.

Temperature °C	Isobutylene to oxygen moles ratio	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
500	2.001	72.3	73.5	21.66	5.87	107.2	99.8
	0.984	71.8	80.7	13.82	5.36	100.2	99.1
	0.930	70.2	81.0	14.53	4.37	106.5	95.4
	0.702	60.4	84.1	12.25	3.12	103.0	103.2
	0.465	45.2	86.2	11.11	2.81	101.5	101.5
	0.402	39.5	85.3	11.92	2.81	102.1	97.6
	0.270	25.3	86.2	11.11	1.47	100.2	99.0
	0.255	27.0	84.2	11.16	2.67	101.6	99.2
Mean carbon mass balance 102.7				Variance for carbon 7.09			
Mean oxygen mass balance 99.3				Variance for oxygen 5.59			

Table IV.5.8 Oxidation of isobutylene by Bi:Mo at 500 °C

Table IV.5.h Oxidation of isobutylene by Bi:Mo at 537 °C .

Tempera- ture °C	Isobutylene to oxygen moles ratio	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
537	2.085	73.2	66.6	25.06	8.05	105.7	100.2
	0.983	72.0	77.3	16.63	5.47	101.5	104.4
	0.730	60.6	84.9	10.86	3.62	100.3	106.2
	0.465	42.4	87.1	10.41	3.24	101.7	100.8
	0.270	24.7	86.0	10.45	2.63	99.5	100.8
	0.240	20.5	88.6	9.98	2.32	98.9	98.9
Mean carbon mass balance 101.2				Variance for carbon 5.94			
Mean oxygen mass balance 101.8				Variance for oxygen 7.81			

mathematical treatment.

Conversions experimentally determined for the incipiently fluidised bed are plotted in figure IV.5.a ,as a function of the dimensionless number of reaction units, $K_r W / F$,where K_r is the reaction rate coefficient determined from the Arrhenius equation, W is the weight of catalyst in g , and F is the molar rate of feed gas mixture in moles/hr . The two solid lines represent theoretical conversions calculated assuming 1) piston flow of the gas and 2) a perfectly mixed bed without by-passing. The dashed line represents the best fit curve for the data points. Goodness of fit and other statistical parameters are given in table V.5.a .

A. Effect of reactant feed ratio

The effect of reactant feed ratio on the conversion of isobutylene,selectivity to methacrolein,and yields of carbon oxides was examined at constant temperatures varying the molar ratio of isobutylene and oxygen in the feed. In general,the results show that the conversion of isobutylene increases with olefin to oxygen ratio,reaching a maximum value at higher ratios. The selectivity towards methacrolein decreases slightly while the yields of both carbon oxides increase steadily with increasing feed ratios.

Graphs showing decline in methacrolein selectivity with conversion are given in figures IV.5.b, IV.5.c, IV.5.d, IV.5.e, IV.5.f, IV.5.g, IV.5.h, and IV.5.i . It can be seen that selectivity decreases slightly with increasing conversion but at

Figure IV.5.a Comparison of experimental with theoretically predicted conversions (Results at minimum fluidisation velocity)

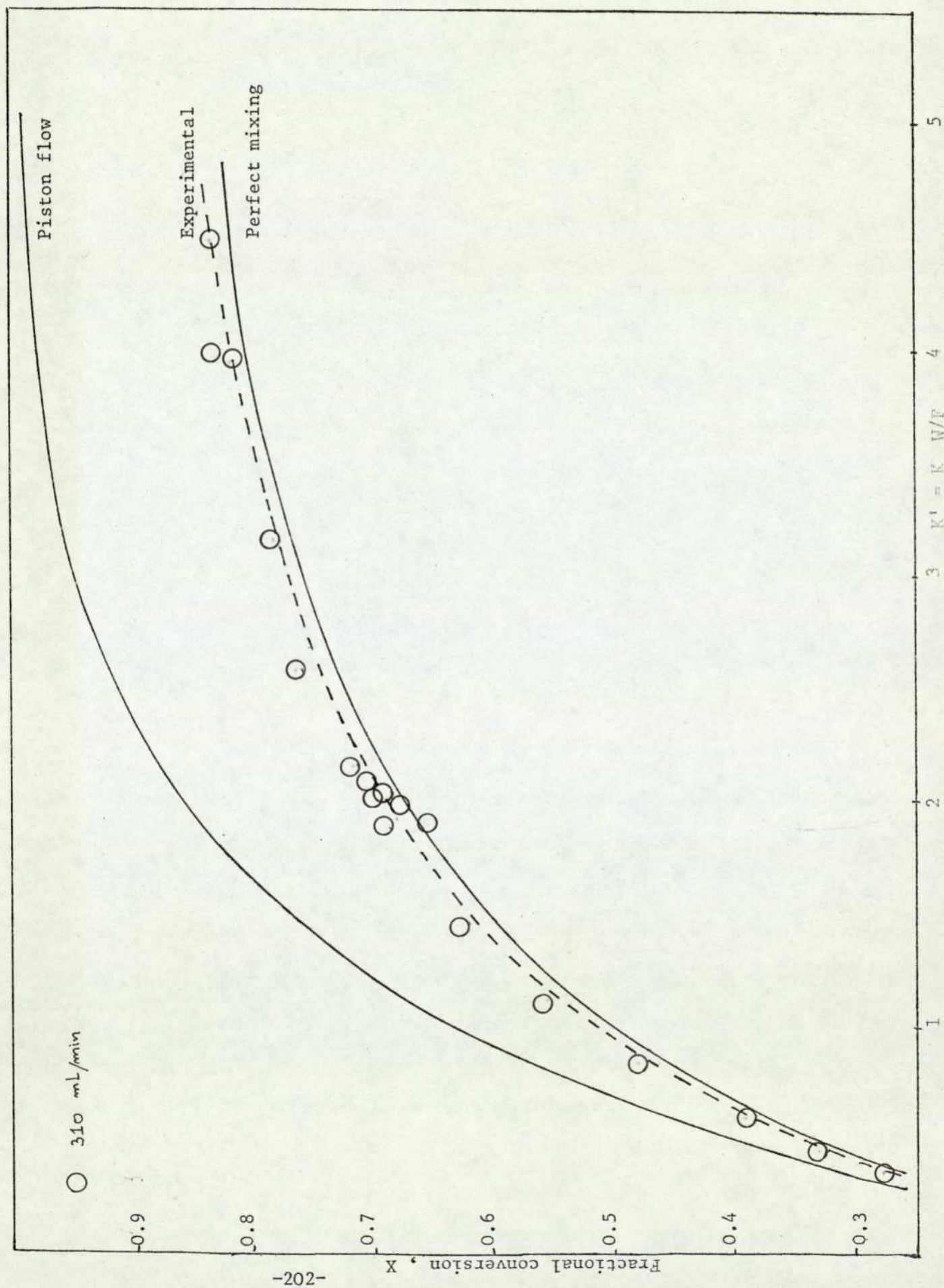


Figure IV. 5.b Effect of conversion on selectivity and yields

($T = 402^{\circ}\text{C}$)

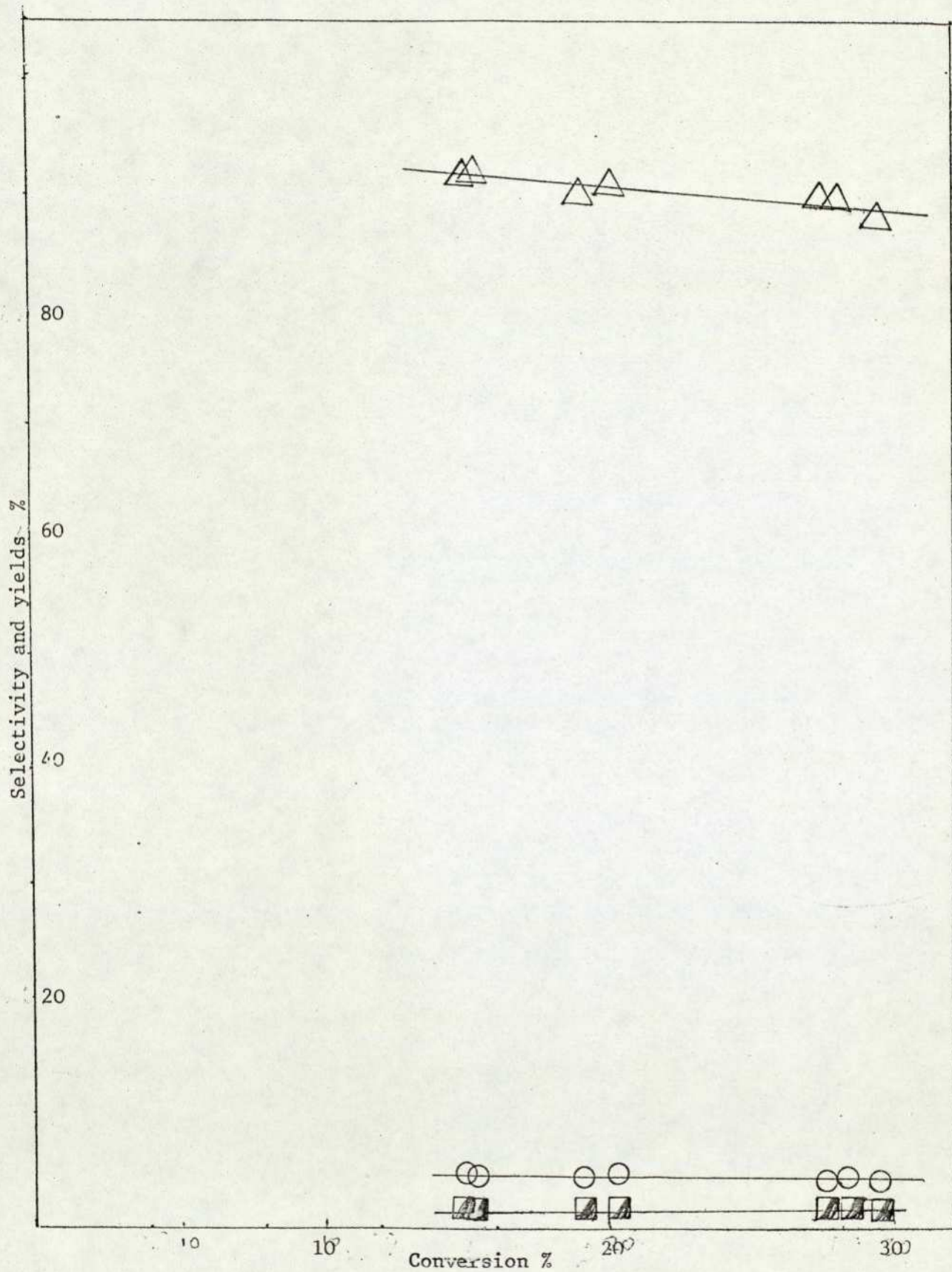


Figure IV.5.c Effect of conversion on selectivity and yields

($T = 442^{\circ}\text{C}$)

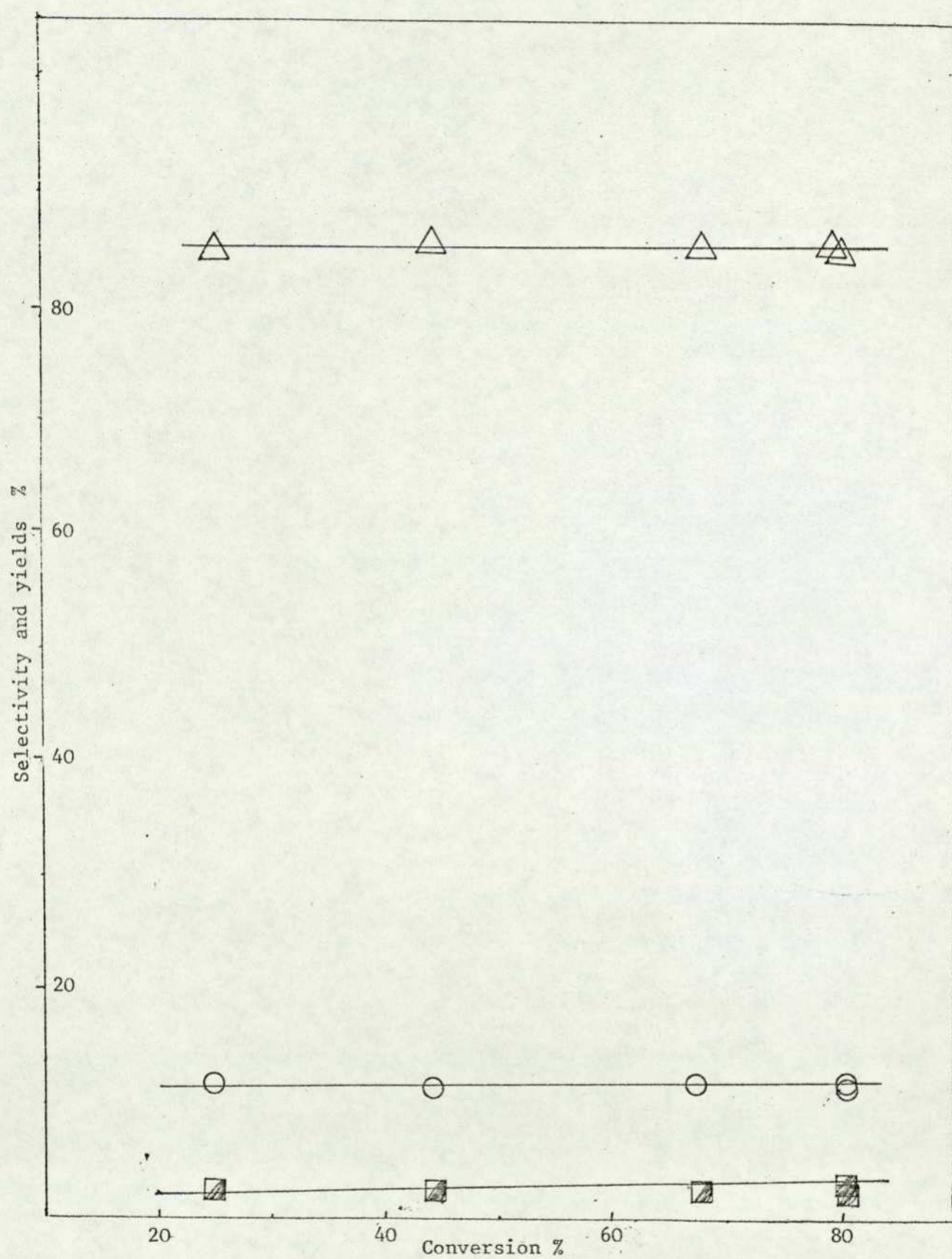


Figure IV.5.d Effect of conversion on selectivity and yields

($T = 453.5^{\circ}\text{C}$)

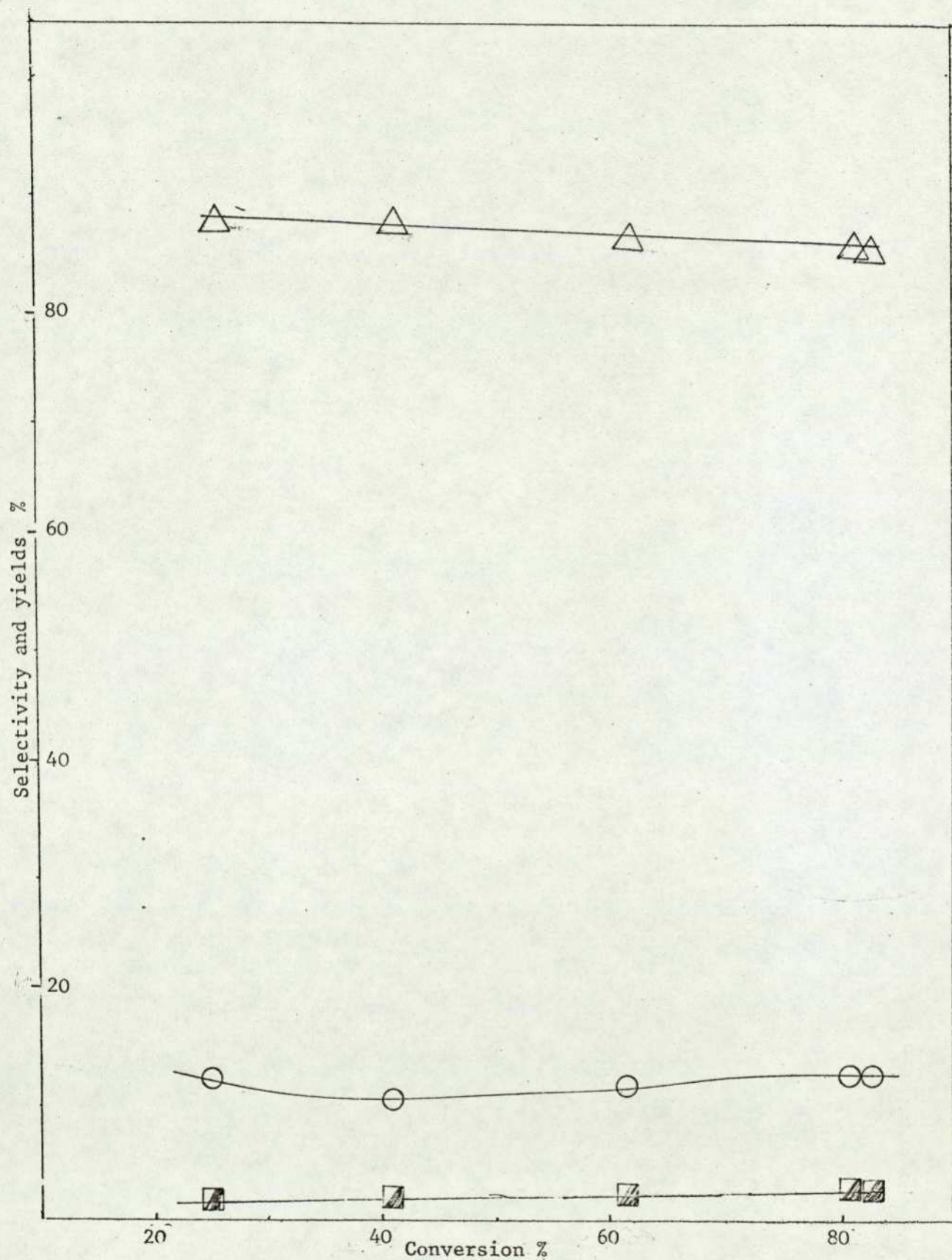


Figure IV.5.e Effect of conversion on selectivity and yields

($T = 463^{\circ}\text{C}$)

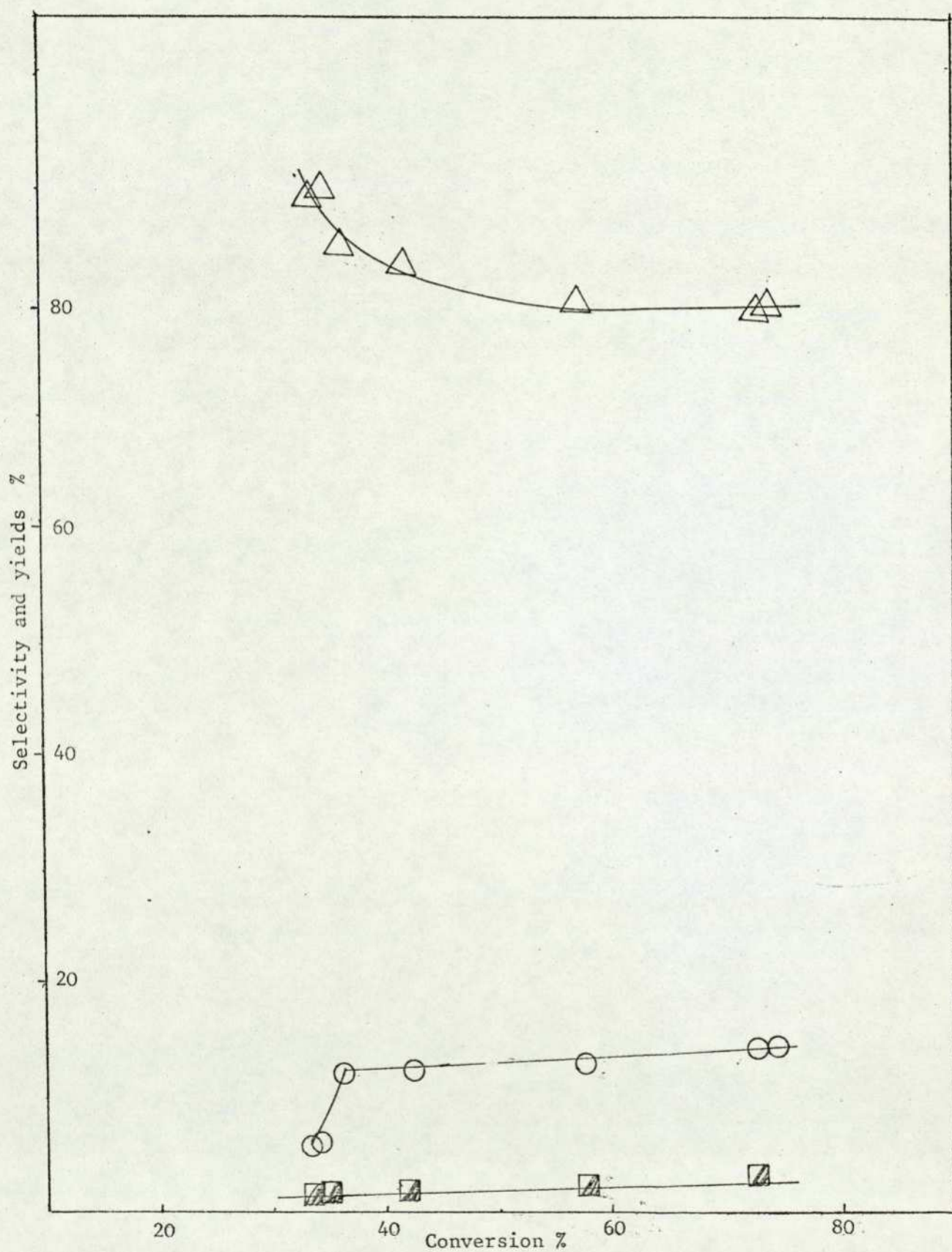


Figure IV.5.f Effect of conversion on selectivity and yields

($T = 469.5^{\circ}\text{C}$)

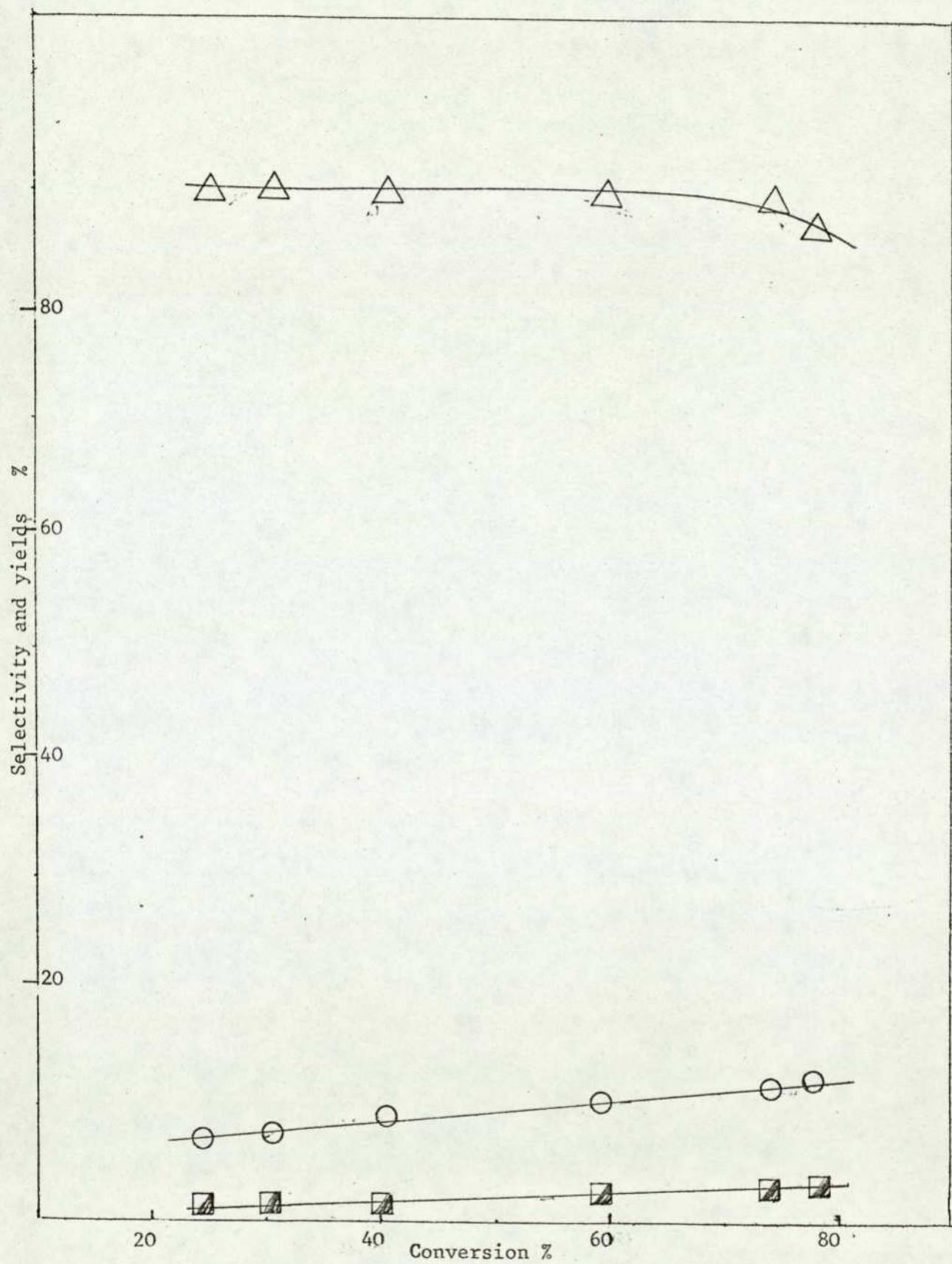


Figure IV.5.g Effect of conversion on selectivity and yields

($T = 471^{\circ}\text{C}$)

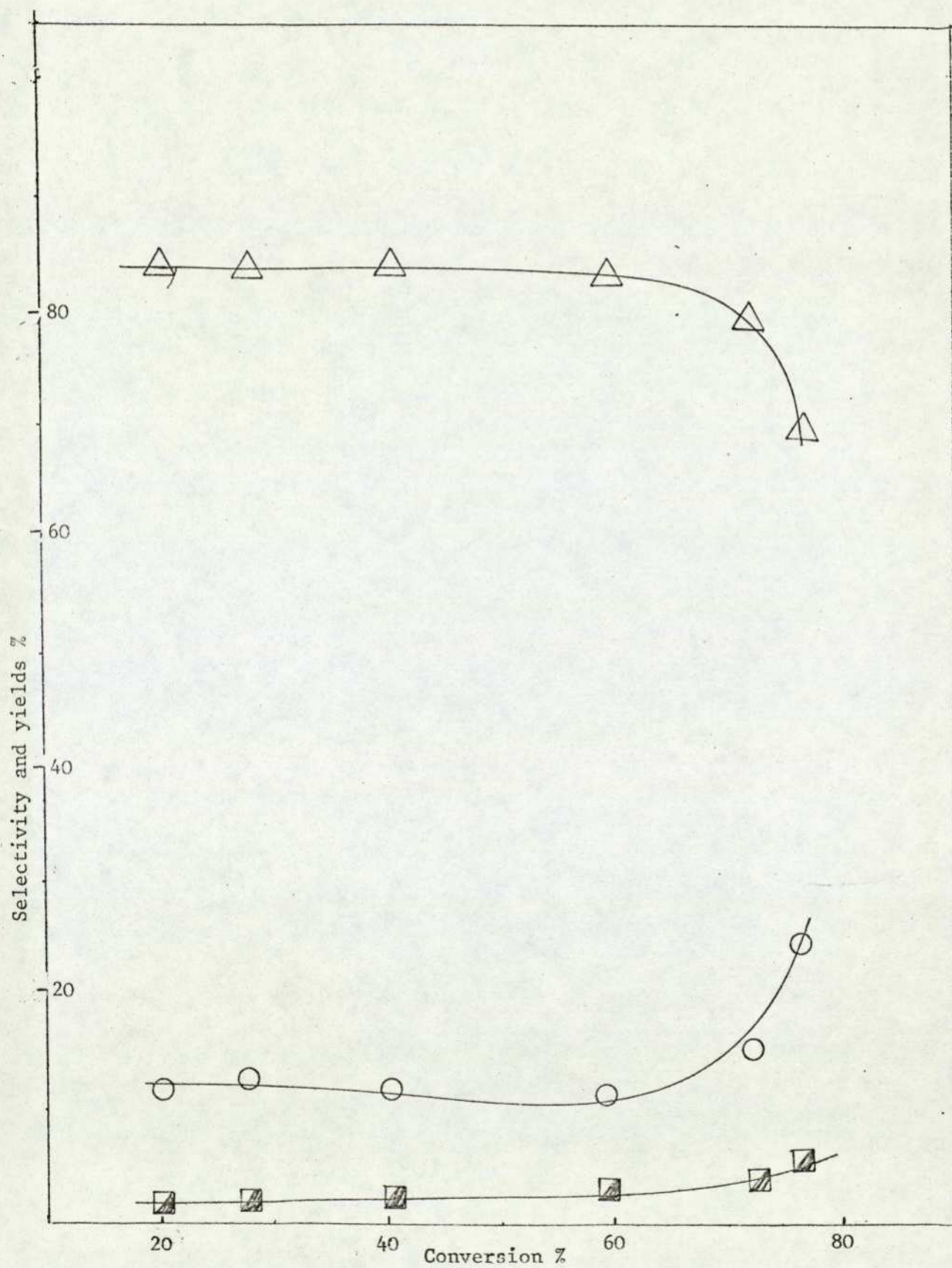


Figure IV.5.h Effect of conversion on selectivity and yields

($T = 500^{\circ}\text{C}$)

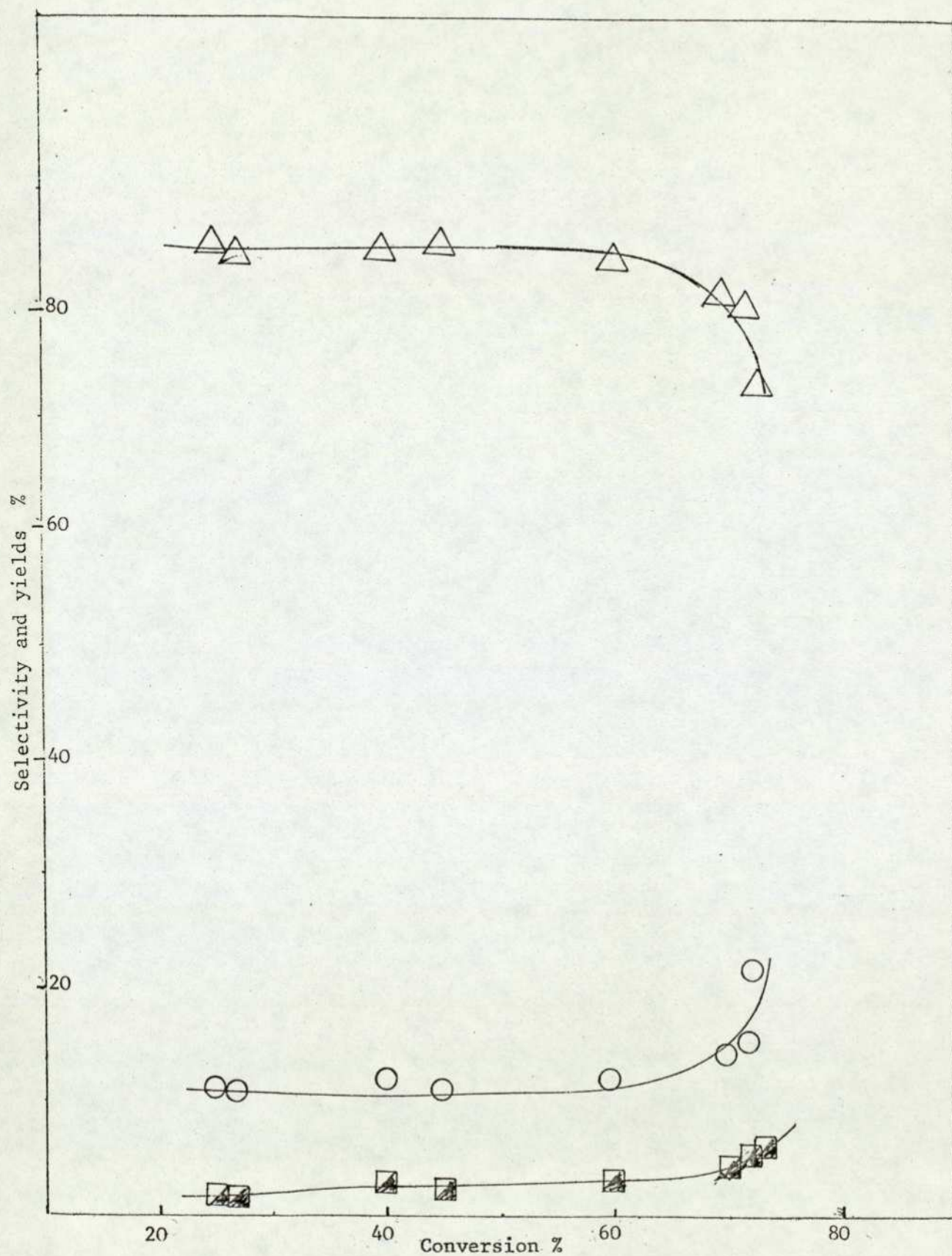
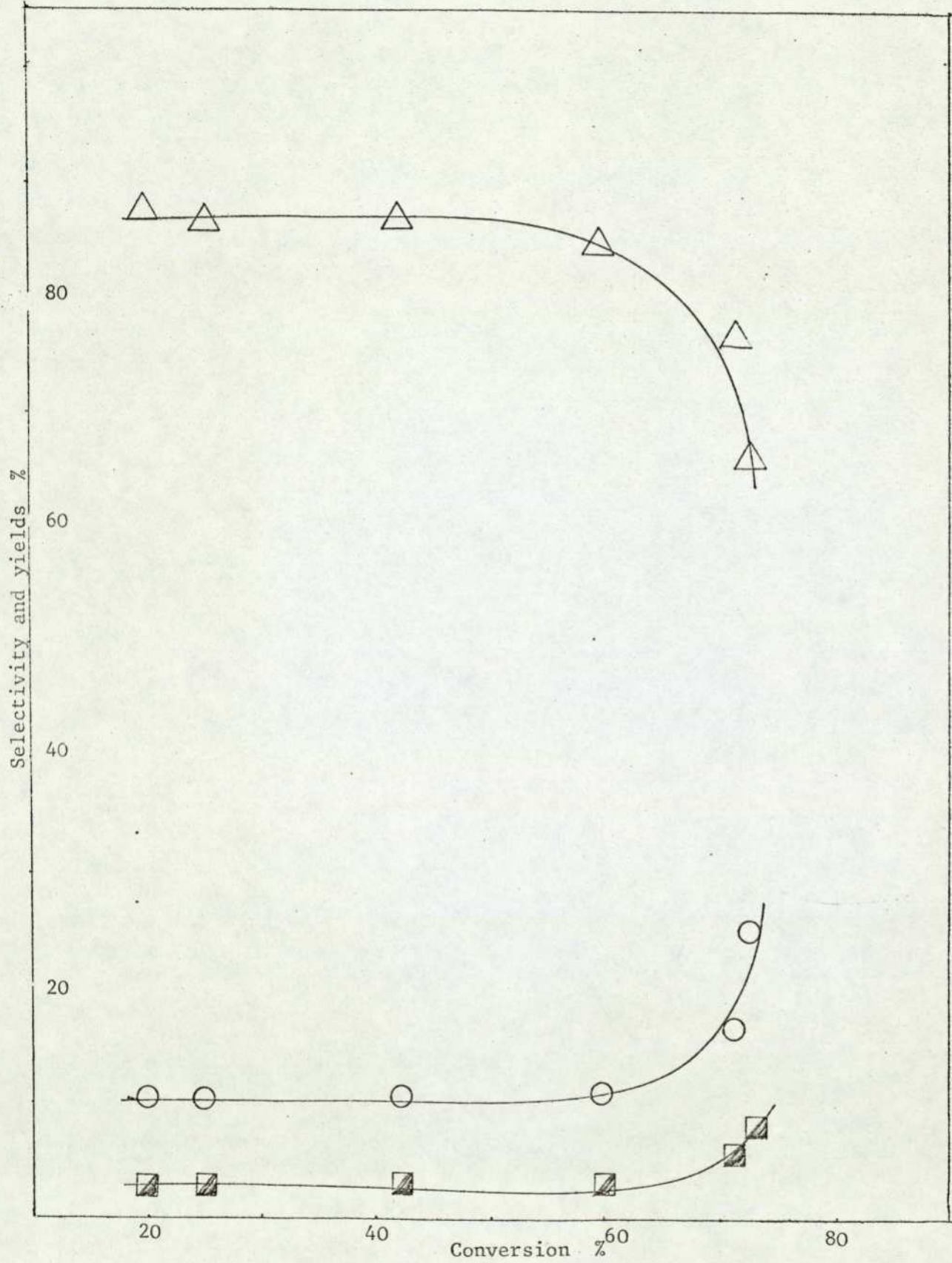


Figure IV.5.i Effect of conversion on selectivity and yields
($T = 537^{\circ}\text{C}$)



high conversion levels there is considerable decline in methacrolein yield

B. Effect of temperature

Variation in isobutylene conversion, methacrolein selectivity and yields of carbon oxides are given in figures IV.5.j, IV.5.k, and IV.5.l .

In figure IV.5.j, the selectivity towards the main product decreases from 91 % to about 77 % ,when the temperature increases from 400 °C to 537 °C. On the other hand, the yields of carbon oxides steadily increase with temperature. The conversion of isobutylene shows a sharp increase from 19 % to about 82 % ,when the temperature increases from 387 °C to 450 °C. At higher temperatures the conversion decreases slightly to reach a value of 72 % at temperatures higher than 500 °C.

In figure IV.5.k ,the maximum conversion is 44 % , however,the selectivity is slightly higher than quoted above, varying between 85 % and 93 % . The yield of carbon dioxide increases rapidly from 5 % to 12 % with increasing temperature,while carbon monoxide is formed in lower yields increasing from 1.8 % to about 3.5 % at higher temperatures.

In figure IV.5.l, the conversion of isobutylene increases smoothly from 17 % to 35 % , with a temperature increase from 400 °C to about 444 °C ; with the temperature continuing to increase the conversion decreases slightly to reach the value of 25 % at higher temperatures

Figure IV.5.j Effect of temperature on conversion,selectivity
and yields. ($C_4H_8/O_2 = 0.983$)

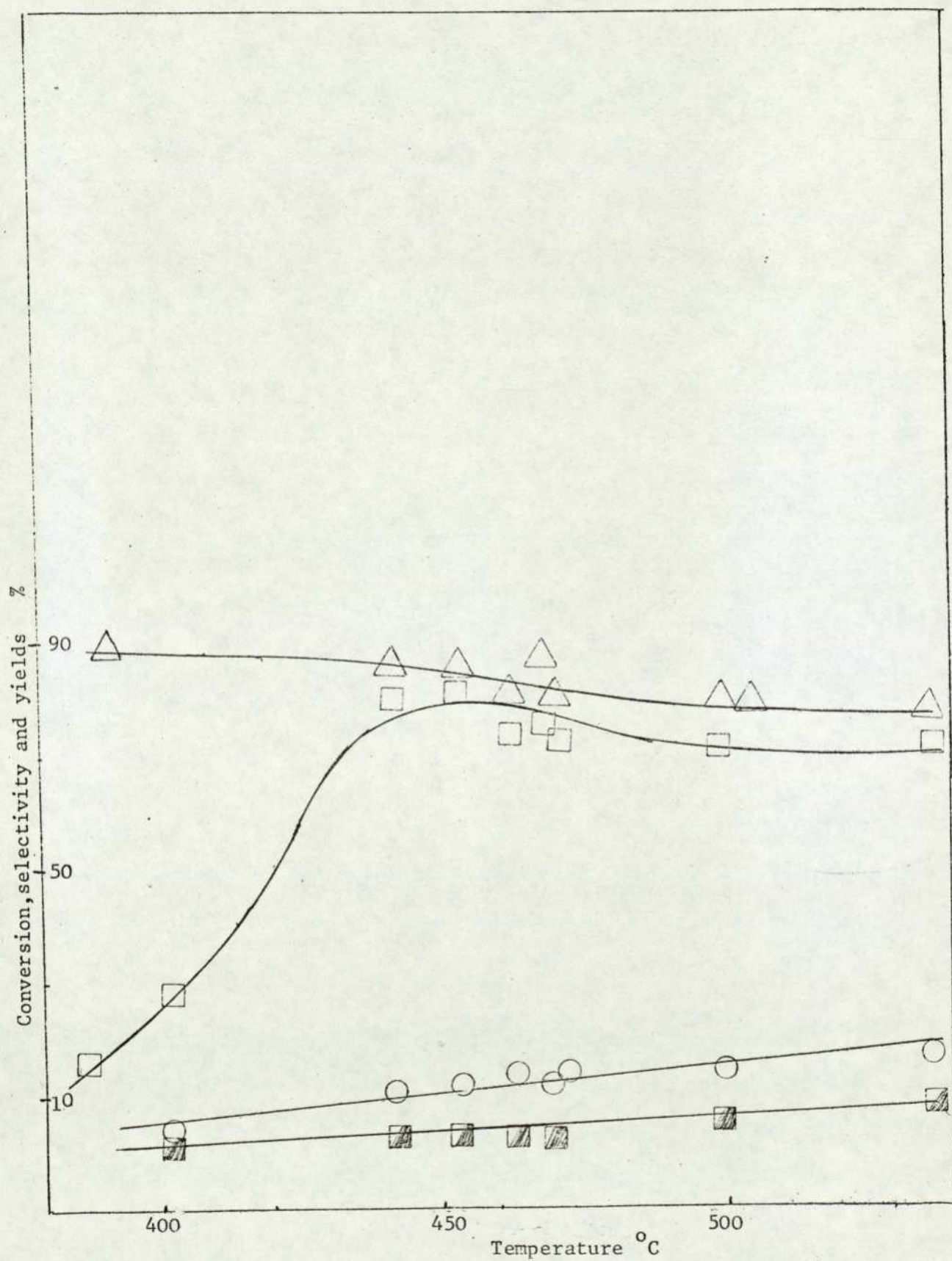


Figure IV.5.k Effect of temperature on conversion,selectivity
and yields. ($C_4H_8/O_2 = 0.465$)

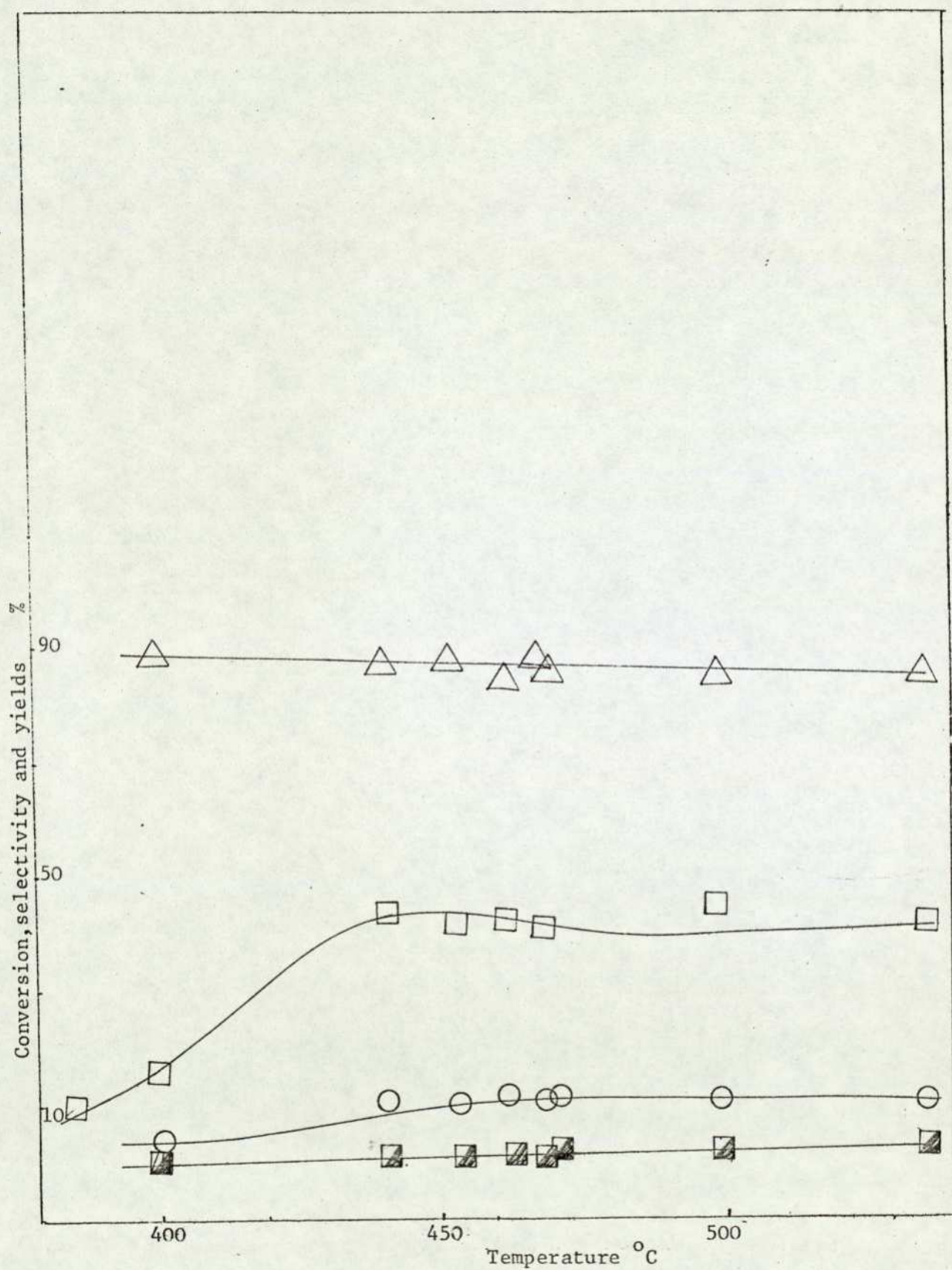
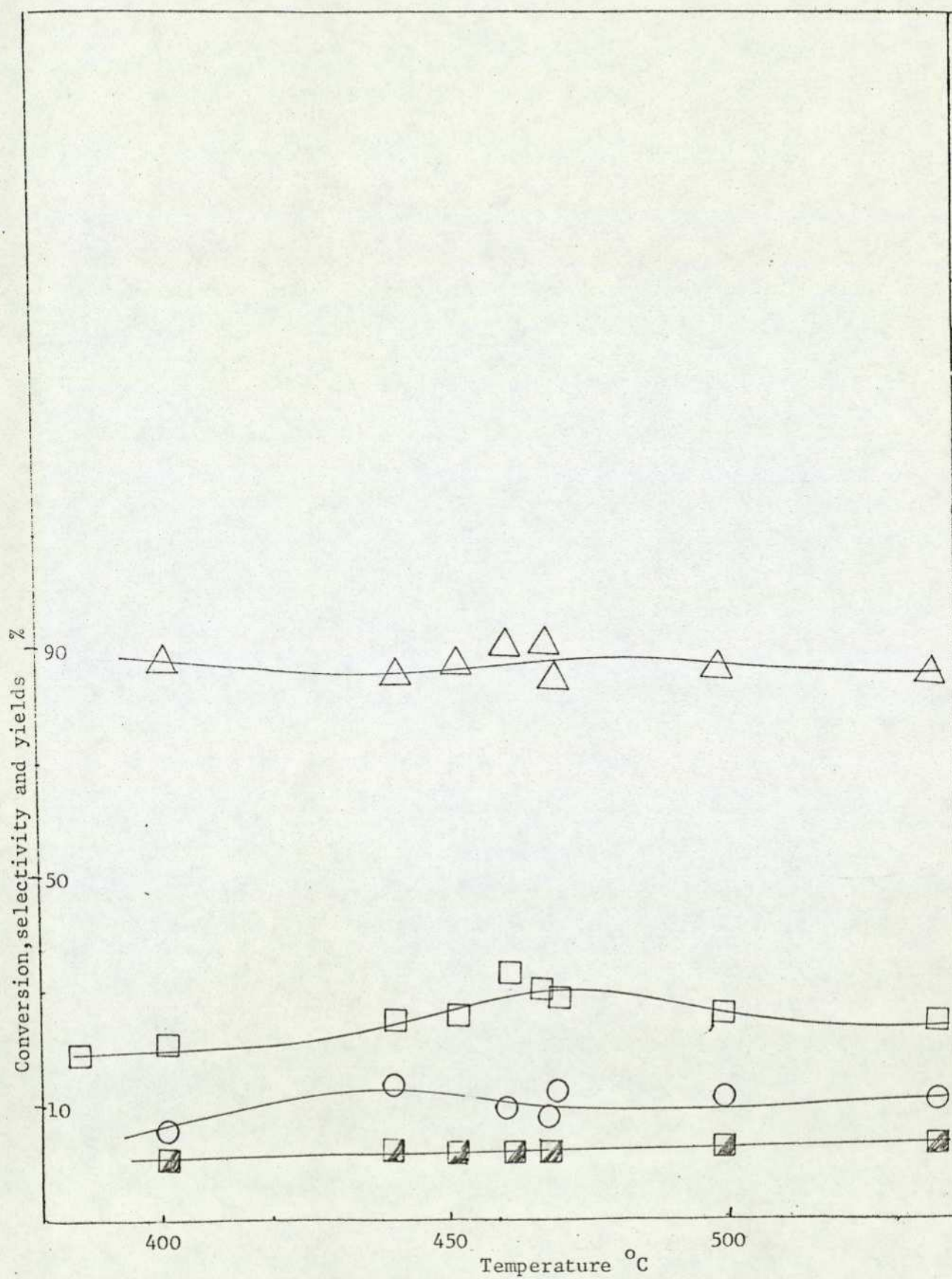


Figure IV.5.1 Effect of temperature on conversion, selectivity
and yields. ($C_4H_8/O_2 = 0.270$)



IV.5.2 Conversion data at low superficial gas velocities

Experimental conversions for two chosen reactant feed ratios were obtained at constant temperatures varying the velocity of the gas mixture. The gas mixture flow rate was varied from 100 ml/min to 500 ml/min, so the particle bed passed gradually through the stages of fixed bed, expanded bed, and bubbling fluidised bed.

The results for the three temperatures investigated are given in tables IV.5.i, IV.5.j, and IV.5.k . It is generally observed that the conversion of isobutylene decreases when the gas velocity increases above the point of minimum fluidisation. Similarly, the selectivity increases up to an optimum point and then remains practically constant as the gas velocity continues to increase.

Again, only those data which justified the assumption of pseudo first order kinetics were selected for subsequent mathematical treatment. Conversion results for two low superficial gas flow rates, 400 and 500 ml/min, are plotted as a function of $K' = \frac{K_p W}{F}$ in figure IV.5.m . The solid line represents conversions theoretically calculated assuming perfect mixing without by-passing , whilst the dashed line represents the best fit curve for the data points. Goodness of fit and other statistical quantities are shown in table V.5.b .

Table IV.5.i Catalytic oxidation of isobutylene by Bi:Mo
at various gas flow-rates ($T = 400^\circ\text{C}$)

Temperature $^\circ\text{C}$	Oxygen to Isobutene Molar Ratio	Gas Velocity ml/min	Conversion %	Selectivity %	Yield of CO_2 %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
400	1,118	100	26.89	72.9	27.23	11.30	104.8	97.7
400	1,118	300	26.74	85.3	10.70	4.206	100.0	98.5
400	1,118	310	25.00	90.1	5.326	2.126	99.6	99.2
400	1,117	400	11.53	86.3	11.25	4.673	100.0	98.6
400	1,118	500	7.69	82.3	11.26	7.023	99.5	98.7
400	2,126	100	23.10	64.6	29.07	12.52	105.3	99.5
400	2,126	300	20.51	73.3	18.47	7.669	99.8	98.5
400	2,124	310	25.93	77.5	17.56	7.002	98.5	100.4
400	2,125	400	15.38	72.3	18.27	10.52	100.1	100.5
400	2,126	500	14.28	71.3	17.38	9.019	99.6	100.4

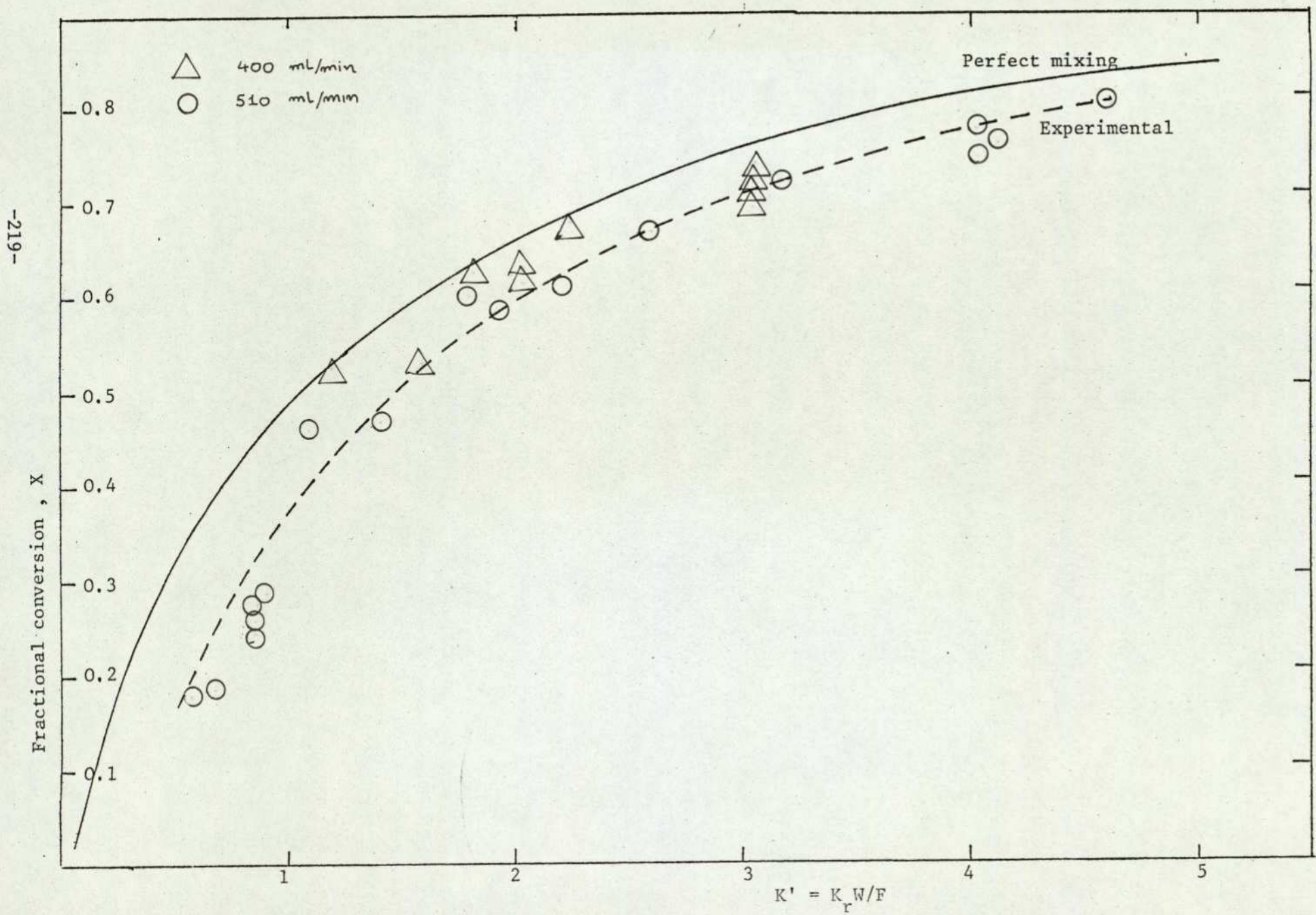
Table IV.5.j Catalytic oxidation of isobutylene by Bi:Mo
at various gas flow-rates (T = 463 °C)

Temperature °C	Oxygen to Isobutene Molar Ratio	Gas Velocity ml/min	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
463	1,050	100	73,5	78,4	23,72	10,51	101,4	99,5
463	1,050	300	75,7	75,5	14,34	9,67	99,7	98,7
463	1,050	310	75,6	78,5	16,81	5,336	102,8	100,7
463	1,050	400	58,7	76,5	12,28	7,866	98,0	101,2
463	1,050	500	48,7	80,3	13,86	6,216	100,7	98,9
463	2,060	100	66,6	71,9	17,43	9,92	99,6	99,5
463	2,060	300	69,6	69,3	21,80	9,61	100,5	96,6
463	2,063	310	76,6	77,3	16,81	9,50	103,8	97,2
463	2,064	400	62,8	77,5	12,74	10,27	99,7	98,4
463	2,059	500	56,6	69,6	17,43	9,92	98,3	100,8

Table IV.5.k Catalytic oxidation of isobutylene by Bi:Mo
at various gas flow rates (T = 505 °C) .

Tempe- rature °C	Oxygen to Isobutene Molar Ratio	Gas Velocity ml/min	Conversion %	Selectivity %	Yield of CO ₂ %	Yield of CO %	Carbon mass balance %	Oxygen mass balance %
505	1.043	100	66.2	60.1	29.44	7.334	97.9	98.6
505	1.045	300	68.6	80.9	13.25	8.208	101.6	98.7
505	1.043	310	71.9	81.0	14.55	4.370	99.9	99.0
505	1.043	400	66.8	85.1	9.21	4.337	99.8	96.5
505	1.044	500	62.2	74.8	20.55	6.765	102.5	96.9
505	2.086	100	66.4	39.0	43.77	17.04	99.9	99.9
505	2.086	300	69.1	70.2	19.85	11.04	100.7	99.6
505	2.086	310	72.3	72.4	21.58	5.863	99.9	98.7
505	2.087	400	65.8	63.1	20.61	15.51	99.5	96.7
505	2.087	500	62.3	61.2	28.94	10.64	99.8	99.2

Figure IV.5.m Comparison of experimental with theoretically predicted conversions (Results at low superficial gas velocities) .



CHAPTER V

DISCUSSION

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DISCUSSION

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V.1 CATALYST STUDIES

Although the surface area for the bismuth-molybdate catalyst used throughout the work is relatively small ($1.77 \text{ m}^2/\text{g}$) for particles with average diameter $67 \mu\text{m}$, the experimental results (Figures IV.5.b, IV.5.c, IV.5.d, IV.5.e, IV.5.f, IV.5.g, IV.5.h, and IV.5.i) showed that during the oxidation of isobutylene, methacrolein yields were very high at all conversion levels. Calcination of the catalyst in air at 500°C gives a catalyst with higher surface area, while the weight loss due to dehydration occurs in the temperature range below 500°C . Increasing the calcination temperature to 600°C for 20 hours leads to a considerable decrease in the surface area, however, without loss in weight.

An attempt to examine the chemical structure of the catalyst was made by means of its infra-red spectra. The spectra obtained are shown in figures IV.1.a and IV.1.b. The region above 1050 cm^{-1} shows some of the nujol absorption peaks, and the region below 1050 cm^{-1} shows the characteristic bismuth molybdate absorption peaks.

Bismuth oxide produces a broad absorption band around 400 cm^{-1} . The catalyst sample also shows a strong band at 840 cm^{-1} , and a smaller band at 720 cm^{-1} . The centre of the resonances at about 800 cm^{-1} possibly represents the tetrahedral MoO_4^{2-} , arrangement of the surrounding oxygen.

Clark and Doyle (25) have recorded similar infra red spectra on a number of molybdates and tungstates, either having the metal

ion in tetrahedral or in octahedral oxygen surroundings.

Batist et al (57,58,59,60,61) also used the KB_r disc technique to obtain the infra-red spectra of bismuth molybdate catalyst using different Bi:Mo ratios. The spectrum of the catalyst with similar heat treatment and a ratio Bi:Mo close to unity shows broad peaks; some of the absorption peaks of his spectra look quite similar to those obtained in the present work.

Previously used (208) tin-antimony oxide catalyst proved highly reactive towards acrolein; however, bismuth molybdate catalyst is more selective in the formation of products of incomplete oxidation. For olefin oxidation, MoO_3 , alone, shows a high activity but poor selectivity; Bi_2O_3 is relatively inactive and nonselective, but a combination of the two oxides gives a highly selective and active catalyst. The mixed oxides are active over a wide range of Bi:Mo ratios, but in agreement with our results, it has been reported (21,70) that bismuth molybdate catalysts, with an atomic ratio of bismuth to molybdenum close to unity, is the most active catalyst with respect to the specific rates of conversion of olefins and the most selective with respect to aldehyde formation.

Contrary to the behaviour of tin-antimony oxide catalyst, loss in reactivity and colour from yellow to dark brown were observed with bismuth molybdate. Studies using isotopic oxygen (57,59,66,67,68) have provided strong evidence for the participation of lattice oxygen during the oxidation of olefins. Although the diffusion of oxygen from the surface into the bulk and from the bulk back to the surface must be rapid, reduction of the catalyst with time is expected until all the lattice oxygen,

is totally consumed.

Nevertheless, the reduced catalyst regains part of its activity on replacement of the lattice oxygen which seems to take place by atmospheric oxygen to a certain extent, when the dark powder is treated at 500 °C for 2 hours; the catalyst regains its original colour, turning to a yellowish powder.

Highly reproducible values for the solid particle densities were obtained from different prepared batches, and this was a good indication that the method of preparation followed could well reproduce the same catalyst. Ray and Chanda (80) have reported the density of a differently prepared catalyst of the same composition, and their value, 5.66, lies very close to that obtained in these experiments (Table IV.1.b)

Studies of the microphotographs obtained (Plate IV.1.a and IV.1.b) showed that the oxide mixture consists of irregularly shaped particles, which were found to be very friable and thus susceptible to attrition. Attrition is a major disadvantage of some gas fluidised bed systems, since it results in a wider size distribution of solids leading to changes in the mode of fluidisation and may cause transportation of fines.

All these mechanisms resulting in reduction of the solid size, except those due to chemical reaction, are named particle attrition. The term includes abrasion among solid particles, bed walls and internals, and also abrasion caused by circulation of particles due to fluid-particle contact.

The spherical particles in general show the highest attrition resistance. Since the sphericity of the prepared bismuth molybdate particles was very low, 0.48, it was expected that

these particles would be susceptible to attrition. High size reduction, resulting wide size distribution was avoided by continual make-up of fresh material and replacement of the reduced catalyst particles, for the experiments carried out at gas velocities greater than the minimum fluidisation velocity.

It has been reported that in many instances a better "quality" of fluidisation can be achieved by using a wider range of particle sizes. Ikeda (226) pointed out that particles below $44\text{ }\mu\text{m}$ are especially important in maintaining smooth fluidisation, and called such particles the "good fraction".

However, there are a few design problems associated with the use of having a wide size distribution. Zenz (227) suggested that much particle/particle contact is likely to occur when beds of irregularly shaped particles of wide size distribution are fluidised. Also, although the minimum fluidisation velocity and the mode of fluidisation is quite clearly defined for closely sized, regularly shaped particles, it can never be so precisely determined for irregular material of wide size distribution.

Further studies (222) were attempted with larger size particles. Although conversion data were obtained only with the $\bar{d}_p = 67\text{ }\mu\text{m}$ particles, the greatly pronounced influence of particle size on the physical behaviour of the fluidised bed was examined by Iacovides (222) in combined studies. The physical properties of bismuth molybdenum particles employed in this exercise are given in table V.1.a .

Table V.1.a Physical properties of bismuth molybdate catalyst.

Physical Properties	B.S. 410 Mesh No.	60-85	85-120
Mean particle diameter, $\bar{d}_p$		239 μ	169 μ
Voidage fraction at fixed bed, ϵ_m		0.59	0.59
Voidage fraction at U_{mf} , ϵ_{mf}		0.60	0.62
Average sphericity, ϕ_s		0.54	0.53
Bulk density, ρ_s		1.966 ₃ g/cm ³	2.015 ₃ g/cm ³
Density, ρ_s		5.54 g/cm ³	

V.2 MINIMUM FLUIDISATION VELOCITY-STATE OF FLUIDISATION

Values for the minimum fluidisation velocity were determined by measuring the pressure drop across the catalyst bed, for increasing velocity of the gas mixture of composition $N_2:O_2:C_4H_8$ in the ratio of 8:1:1. The experimental value for the minimum fluidisation velocity without stirrer, $290 \text{ cm}^3/\text{min}$, was in reasonable agreement with the calculated from theoretical equations (124,127) in which an absolute error of $\pm 34\%$ is acceptable. Additionally to obtain reliable results, the pressure drop was measured as the gas flow rate through the bed was progressively reduced. Before hand, the bed was momentarily fluidised in order to break down any internal structures remaining from the fixed bed stage.

Experiments were also carried out with larger particles and various bed heights (222). For $\bar{d}_p = 169 \text{ }\mu\text{m}$, the minimum fluidisation velocity is found to be 2.04 cm/sec , while for $\bar{d}_p = 239 \text{ }\mu\text{m}$ the average U_{mf} for two bed heights used was 3.11 cm/sec .

Although the pressure drop versus gas velocity plot for the $\bar{d}_p = 67 \text{ }\mu\text{m}$ particles (Figure IV.2.a) suggested the presence of non-fluidised regions within the bed however, the plot for the bed of larger particles showed a characteristic "hump", which was more clearly defined for the greater bed depth. The observed values of the minimum fluidisation velocity for the two larger particle sizes (222) are considerably smaller than the theoretically calculated, exceeding the accepted deviation of $\pm 34\%$.

Bergougnou (228) reported that the presently existing correlations for minimum fluidisation velocity differ considerably from each other, and prediction errors, in certain cases, can be as much as 100 %.

Difference between predictions based on different correlations reflect the problem of making allowances for particle shape and size distribution effects, and all of the present correlations are inadequate in this respect.

Godart and Richardson (229) reported that the term minimum fluidisation velocity only has a meaning for those systems with a sharp transition from the fixed to fluidised bed state. It has also strongly been suggested (230) that with fine particles the transition is very indistinct or else the value indicated from pressure drop versus gas velocity plot is so high that severe channelling must already be occurring.

On the other hand, when there is a wide size distribution, the shape of the pressure drop versus gas velocity characteristic curve may exhibit several minor peaks.

Since the catalytic system bismuth oxide and molybdenum oxide used for the oxidation of olefins is of high density, the catalyst particle size is extremely important in order to achieve smooth fluidisation. Extra fine particles will lead to a considerable dense phase expansion before the onset of bubbling, and additionally it is possible that much gas will by-pass due to cloud formation (231). Instead, large particles will require a higher gas velocity to achieve fluidisation, which is certainly undesirable for the oxidation process.

The bismuth molybdate catalyst particles employed, $\bar{d}_p = 67 \mu\text{m}$,

gave rise to a condition in which the bed expanded above the minimum fluidisation without bubble formation. The appearance of this bubble-free region is in agreement with previous findings (136, 139, 140) .

Without stirring, a smooth bubbling regime was impossible to establish but preferential channelling of gas through the catalyst bed always occurred. As figure IV.2.a shows, the application of stirring enabled the formation of a freely bubbling bed at low superficial gas velocities.

It has been previously reported (232) that for large closely sized particles, the ratio between the minimum bubbling velocity, and that for minimum fluidisation is small; however, for smaller irregular particles it will be much longer, 2.8 , was the value for 55 μm particles.

Rowe (233) pointed out that it would require a 20 % increase above the minimum fluidisation, before there is sufficient gas flow to support a stream of bubbles of 5mm diameter in a bed of fine particles whereas, with bigger heavier particles, a much smaller percentage in the total gas flow would be sufficient to support free bubbling.

Geldart in 1973 (139) classified solid particles into four characteristic groups. This classification enables identification of the mode of fluidisation according to the size and density of the particles, as shown in figure II.4.i .

Groups A and B are the two groups most frequently encountered in fluid bed operations. For the particles belonging to group A considerable dense phase expansion exists before bubbling commences. Particles within group B exhibit much less stable bed

expansion, and free bubbling commences at or a little above minimum fluidisation velocity.

Geldart (139) also postulated that a simple relationship exists between the gas velocity through the bed at which bubbles begin to become apparent, U_{mb} , and the mean particle diameter, $\bar{d}_p$, thus:

$$U_{mb} = 0.095 \bar{d}_p \quad \text{equation V.2.1}$$

where the gas velocity is in mm/sec, and the mean particle diameter in μm .

Recently Baeyens and Geldart (234) reasoned that for a powder to belong to group B the U_{mb} must be greater than U_{mf} .

$$U_{mf} / U_{mb} < 1 \quad \text{equation V.2.2}$$

They also reported, using a correlation for the minimum fluidisation velocity from a range of published tests in small scale equipment, that a particle would belong to group B if:

$$(\rho_s - \rho_g)^{1.17} \bar{d}_p > 906,000 \quad \text{equation V.2.3}$$

with the densities expressed in kg/m^3 and the bed is fluidised by air at room temperature and atmospheric pressure.

Although two of the catalyst fractions used, $\bar{d}_p = 169 \mu\text{m}$ and $\bar{d}_p = 239 \mu\text{m}$, satisfy equations V.2.2 and V.2.3, and thus belong to group B, the $\bar{d}_p = 67 \mu\text{m}$ particles occupy a

place near the borderline of groups A and B ; however, equation V.2.1 predicts values for the U_{mb} lower than the values of minimum fluidisation velocity experimentally determined.

V.3 ONSET OF BUBBLING

The common method of calculating the equivalent mean bubble diameter from bed expansion data (159) proved inadequate for the shallow bed of fine particles and thus the only available technique was to measure the bubble eruption diameter as illustrated in plates V.3.a ,V.3.b ,V.3.c and V.3.d .

The bubble eruption diameter is assumed to be the size of the bubble in the fluidised bed, considering that the bubble size remains constant during their rise through the fluidised bed and that no bubble coalescence takes place. It is also assumed that there is only one bubble rising through the fluidised bed, i.e there is no interaction between rising bubbles and that during measurement, bubbles are considered as being spherical.

Bed expansion was determined for larger particles, $\bar{d}_p = 169 \mu m$ and $\bar{d}_p = 239 \mu m$, in combined studies (222). Data were taken at various air flow rates, increased in stages by about $76 \text{ cm}^3/\text{min}$ above the minimum fluidisation velocity up to about $5U_{mf}$, directly from the photographs obtained, since the reactor dimensions are exactly the same as those used in the experiments.

The excess gas velocities and the ratio of the expanded bed height to bed height at minimum fluidisation , H/H_{mf} , were also calculated, as it can be seen from the plots of figures V.3.a and V.3.b.

Geldart (235) and Streatfield (223) used expansion data to calculate bubble diameters from the two phase theory and they compared their results with measured bubble eruption diameters, as shown in figure V.3.c. The comparison of the ratio of surface eruption diameter, D_{bs} , to calculated bubble diameter, D_b , for fine, medium and coarse sand (235), in figure V.3.c shows that this ratio was greater than one for fine sand, approximately one for medium sand and less than one for coarse sand. The correlation implies that bed expansion data used to calculate bubble diameters, according to the two phase theory only give good agreement for particles of about $200 \mu\text{m}$. Further evidence on the applicability of the two phase theory for different size fluidised particles is given by Mc Grath and Streatfield, who classified solid particles in the categories of small, i.e. $> 200 \mu\text{m}$ and large particle systems, i.e. $< 200 \mu\text{m}$.

V.3.1 Small particle systems

For the catalyst particles 85 - 120 mesh of which the mean particle diameter is $\bar{d}_p = 169 \mu\text{m}$, the observed eruption diameter is about 2.6 times the theoretical one predicted by the simple two-phase theory. In this case the bubble rise velocity is greater than the dense phase velocity and recirculation of gas occurs to the bubble. Thus due to cloud formation it is likely that the eruption diameter is larger than the bubble diameter in the bed, because the cloud erupts with the bubble. Bubble diameter calculated from the two phase theory may well be a reasonable estimate in this case, but the measured bubble eruption diameter is too large as illustrated in figure V.3.d.

It can also be seen that for low excess gas velocities the ratio D_{bs}/D_b is very close to the two phase line which means that in this case the two phase theory applies more effectively.

V.3.2 Large particle systems

For the particle system $\bar{d}_p = 239 \mu m$, the observed bubble diameters were consistently smaller than the theoretically calculated (figure V.3. e). In this case, the bubble velocity is less than the dense phase gas velocity and the theory of Davidson (159) predicts a through flow of gas in the bubble equal to three times the minimum fluidisation velocity for a three dimensional bubble. Thus, a fraction of the excess gas does not contribute directly to the bubble phase volume.

In this flow regime the bubble is well defined because there is no recirculation of gas to the bubble. Thus, although, the values of calculated bubble diameters are too high and make the ratio shown in figure V.3.d and V.3.e less than unity, in agreement with the results quoted by McGrath and Streatfield (224), the bubble eruption diameter is probably a good estimate of the bubble diameter in the bed because of the well defined nature of the latter.

Finally it was generally observed (22) that the application of the stirrer driven at 40 r.p.m and located at 0.5 cm above the distributor, led to smaller bubble eruption diameters and was observed for all particle sizes investigated.

Figure V.3.a Relationship between bed expansion ratio and excess gas velocity for the $\bar{d}_p = 169 \text{ } \mu\text{m}$ (85-120 mesh)

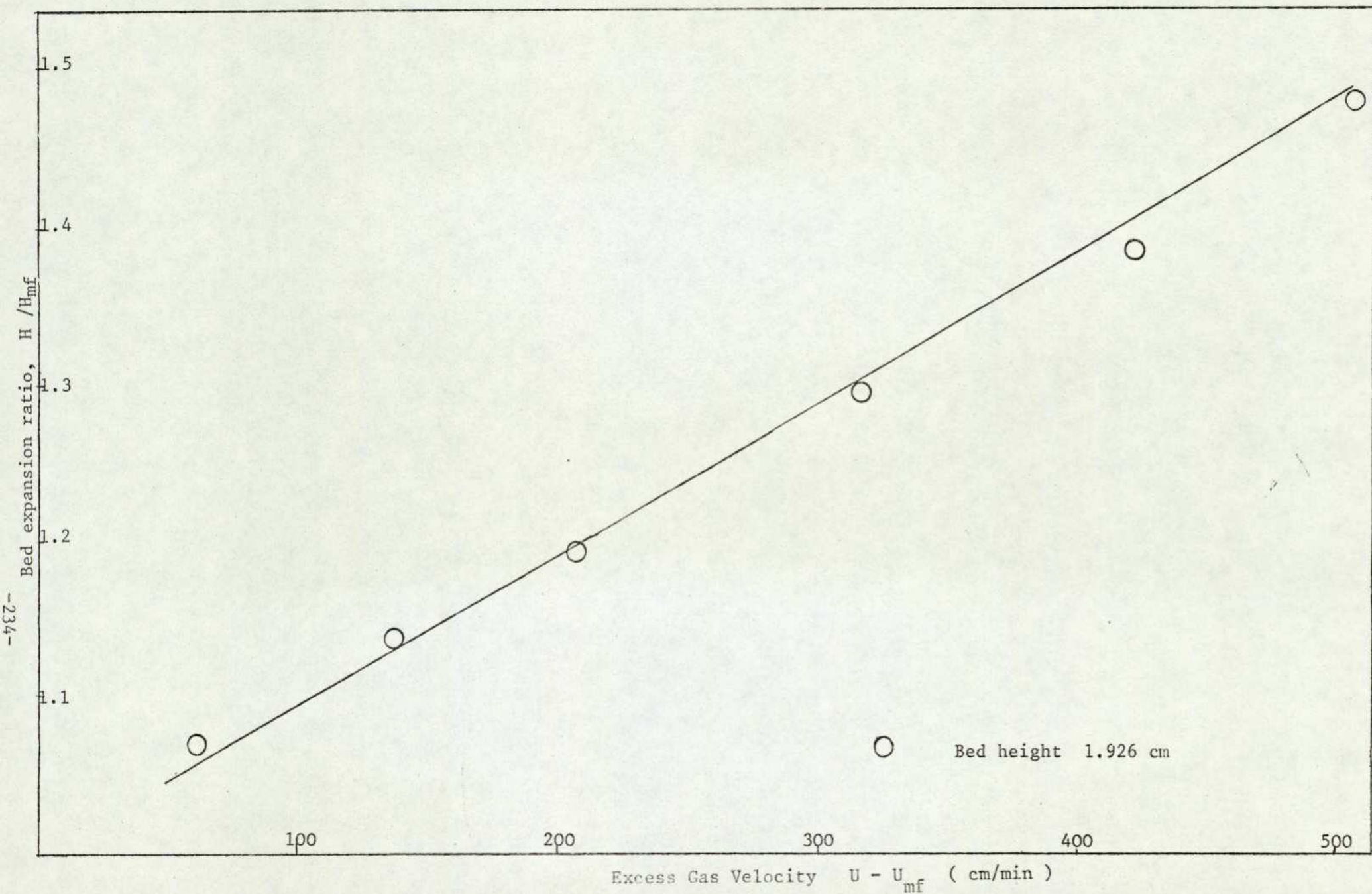
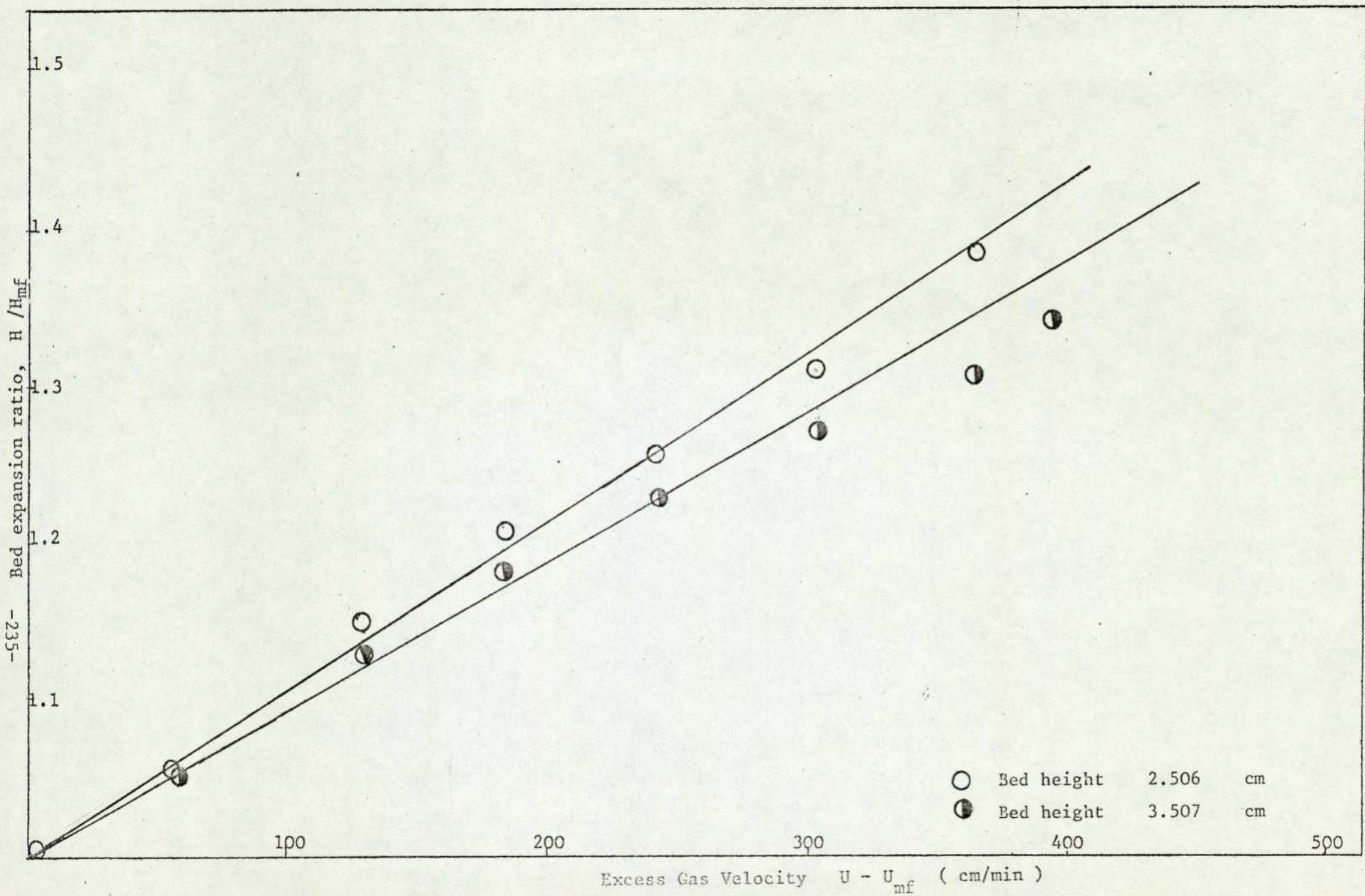


Figure V.3.b Relationship between bed expansion ratio and excess gas velocity for $\bar{d}_p = 239 \text{ }\mu\text{m}$ (60-80 mesh)



Geldart (1967)

Streathfield (1970)

As received

As received Grace

Hmf, cm:

Grace Material.

material:

5.0 ×
10.0 ●
15.0 Δ
20.0 +

Hmf, cms:

2.6 A 10.5 D
5.2 B 13.3 E
7.8 C

Hmf= 5.6 cms, F(1

Molecular sieve:

Hmf= 5.2 cms, G

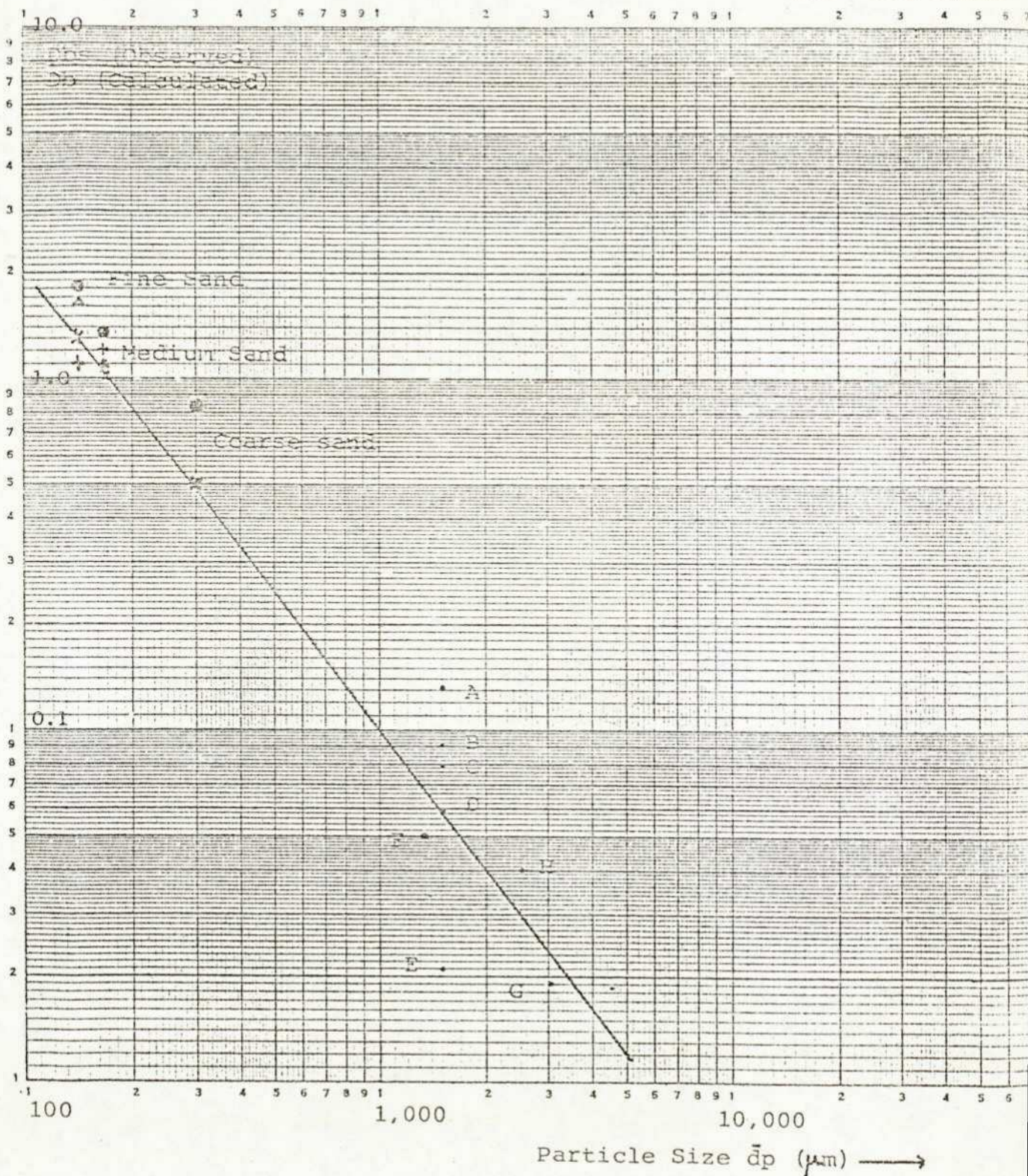
Activated Carbon:

Hmf= 5.3 cms, H

Log 3 Cycles x 3 Cycles

Graph Data Ref. 5333

WELL



$$U - U_{mf} = 420 \text{ cm/min}$$

Figure v.3.c Dependence of ratio of observed to calculated bubble diameter on particle size as shown by Geldart and Streathfield.

$\bar{d}_p = 169 \mu\text{m}$ (85-120 mesh)
Hmf = 2.031 cms

$\bar{d}_p = 239 \mu\text{m}$ (60-85 mesh)
Hmf = 2.087 cms

U-Umf (cm/min):

59.92 a 316.81 d
135.47 b 422.59 e
207.25 c 510.78 f

U-Umf (cm/min):

126.08 g 303.64 k
182.75 h 364.07 l
241.30 j

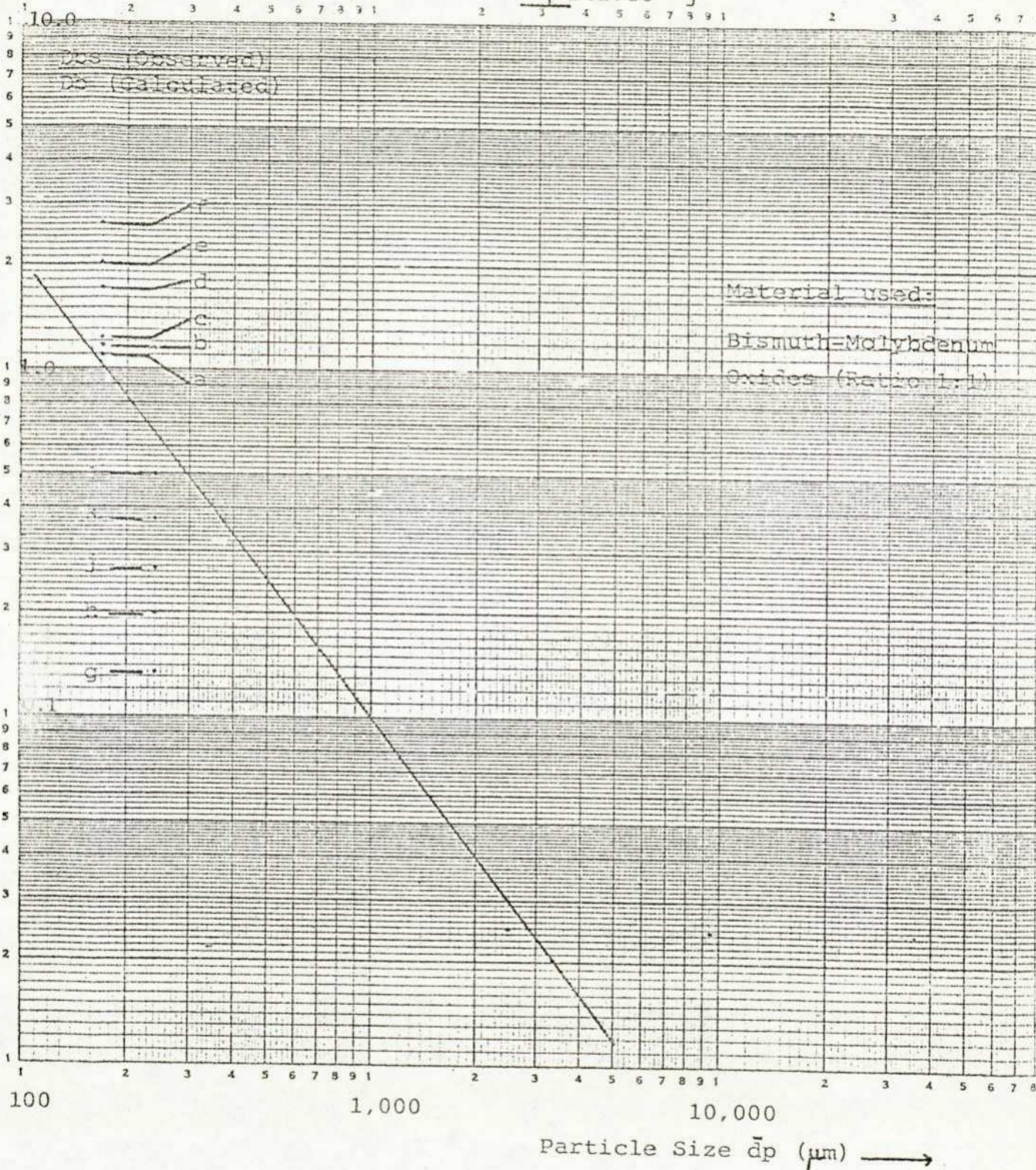


Figure V.3.d Dependence of ratio of observed to calculated bubble diameter on particle size.

$$\bar{d}_p = 239 \mu\text{m} (60-85 \text{ mesh})$$

$$Hmf = 35.60 \text{ mm.}$$

U-Umf (cm/min):

126.08 g' 303.64 k'

182.75 h' 364.07 l'

241.30 j' 397.42 m'

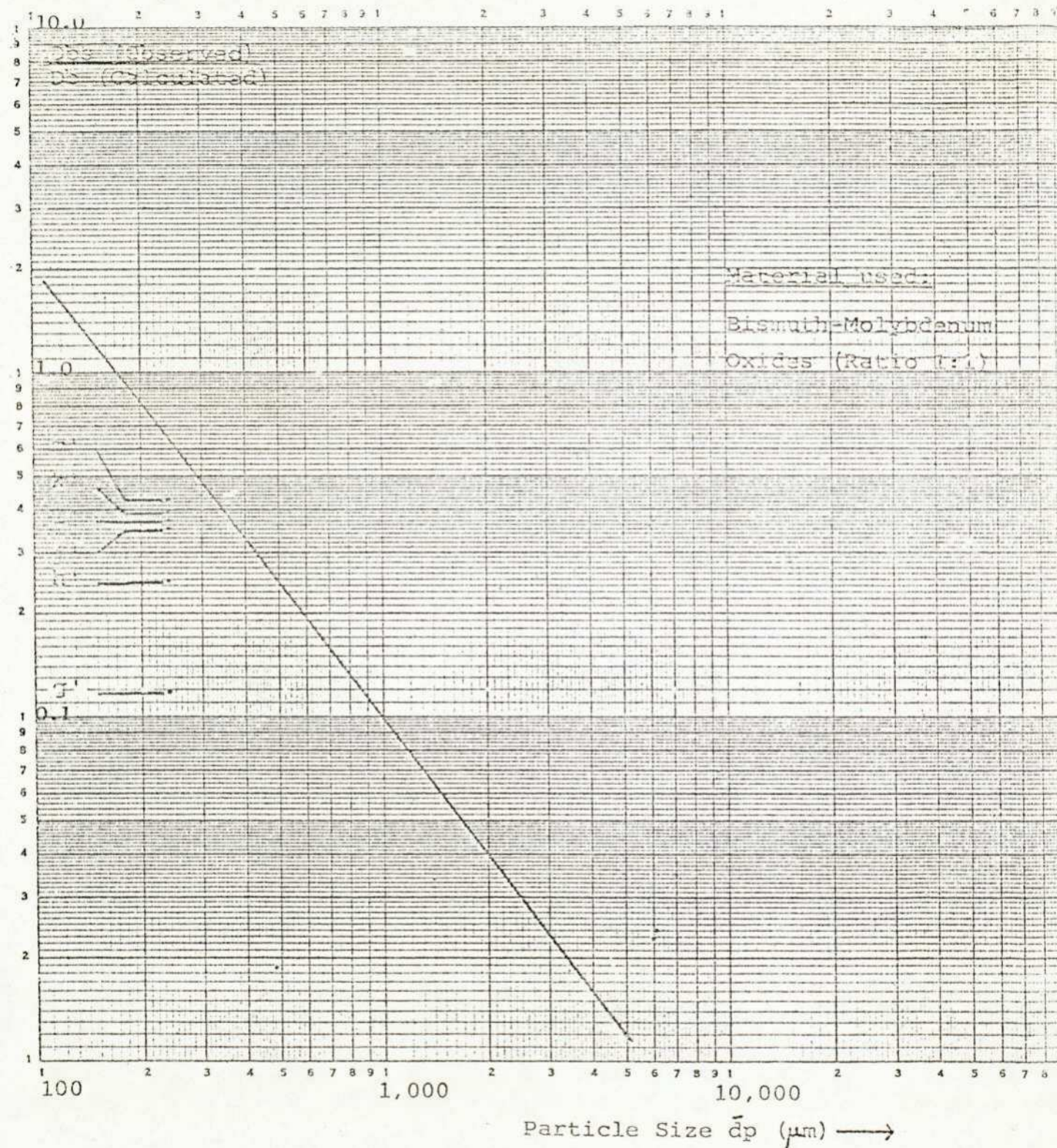
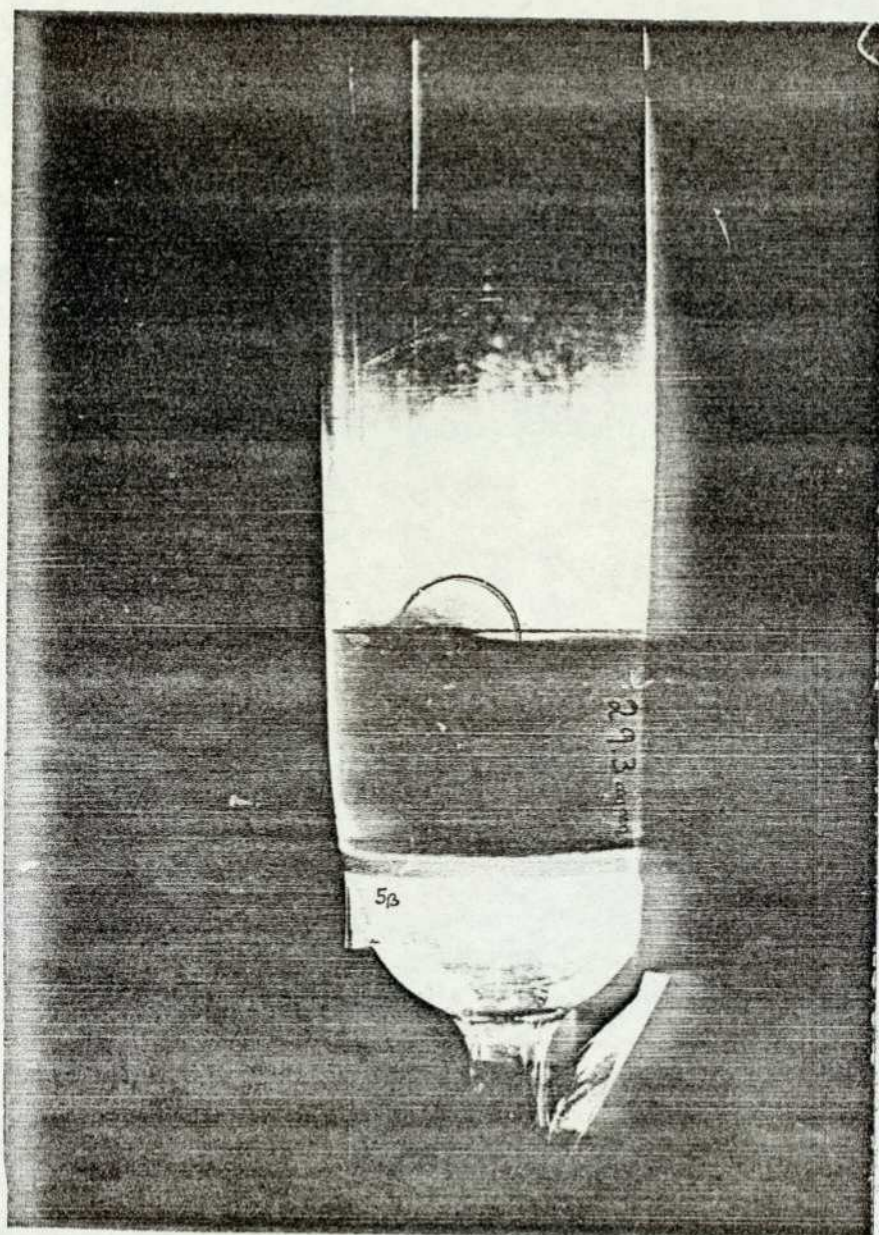


Figure V.3.e Dependence of ratio of observed to calculated bubble diameter on particle size.

Plate V.3.a Photograph No 3a ,particle diameter $\bar{d}_p = 169 \mu\text{m}$,
height of fixed bed 1.926 cm , $U-U_{mf} = 210 \text{ cm/min}$



Plate V.3.b Photograph No 5b ,particle diameter $\bar{d}_p = 239 \mu\text{m}$,
height of fixed bed 2.506 cm , $U - U_{mf} = 304 \text{ cm/min}$



LPlate V.3.c Photograph No 7a ,particle diameter $\bar{d}_p = 67 \mu\text{m}$,
height of fixed bed 3.855 cm , $U - U_{mf} = 80 \text{ cm/min}$

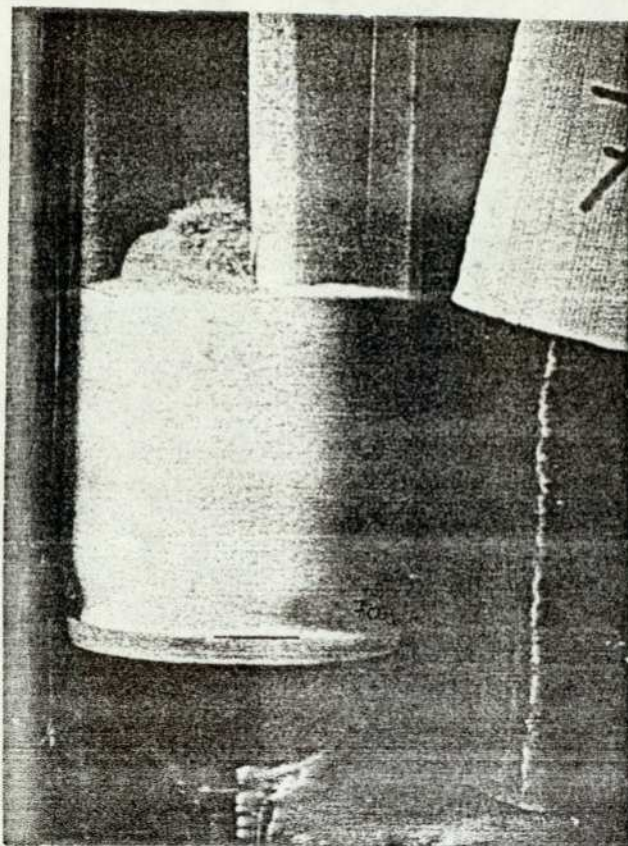
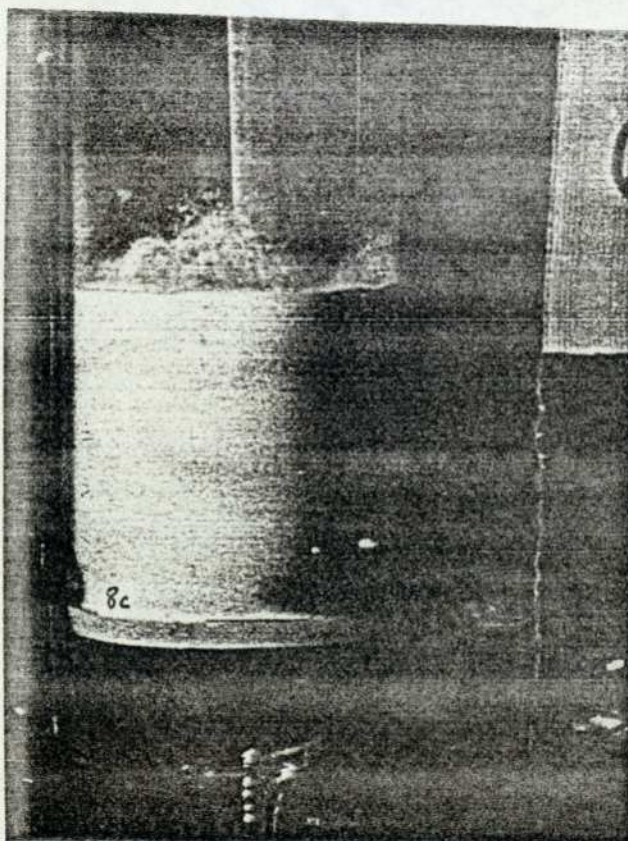


Plate V.3.d Photograph No 8c ,particle diameter $\bar{d}_p = 67 \mu\text{m}$,
height of fixed bed 3.855 cm , $U - U_{mf} = 135 \text{ cm/min}$.



V.4. STUDY OF THE KINETICS OF THE PARTIAL OXIDATION OF
PROPYLENE AND ISOBUTYLENE OVER BISMUTH MOLYBDATE
CATALYST.

The investigation of the kinetics for the catalytic oxidation of olefins is normally complicated by the fact that diffusion as well as chemical phenomena are usually involved; the two are not easy to separate so as to determine the factors affecting each. In addition, the large exothermicity of these reactions introduces the problem caused by the liberation and distribution of heat.

Studies in the chemical kinetics need to be acquired free of physical transport limitations, if possible, in order to interpret the results correctly, and have some knowledge of dealing with the data if mass transfer effects become important.

Kinetic models have been postulated without adequate appreciation of the problem (23, 6, 237), but recently, unconventional types of reactors have been postulated to operate under negligible heat and mass transfer effects.

Kinetic measurements have been carried out in this laboratory using an S.G.S. reactor, and mathematical models of olefin oxidation over oxide catalysts have been derived (54, 72, 81). A direct comparison of these models with experimental conversions obtained for a fixed and a fluidised bed was made in the present studies (pages 177 to 191).

Kinetic measurements were carried out in the temperature range $405^{\circ}\text{C} - 465^{\circ}\text{C}$ in a packed fixed bed by a continuous flow method. This guaranteed isothermicity of the catalyst layer,

in spite of the large heat effect of the processes. Preliminary experiments showed that it was difficult to achieve completely isothermal conditions within the bed. However, by the use of a diluent, glass spheres, temperature gradients were minimised within the bed. Radial temperatures were generally highest in the centre, decreasing towards the wall. The maximum recorded temperature difference between the bed centre and the wall was 4°C . The average temperature of the bed was taken as the mean of the three thermocouples readings. All experiments were performed at an olefin : oxygen ratio of 1.0. This ratio was chosen to avoid over-oxidation of the olefin and is well above the lowest possible oxygen level at which reduction of the catalyst can take place (page 178). The effect of the reciprocal of space velocity, W/F , on the conversion of both olefins was studied at different reactor temperatures. An increase in temperature increases the conversion, whereas an increase in the overall olefin flow rate causes the conversion to decrease (Tables IV.4.a, IV.4.b, IV.4.c, IV.4.d, IV.4.e, and IV.4.f).

Variation of the amount of oxygen in the inlet stream by a factor of three did not affect the rate of the reaction, and thus it was concluded that the reaction is independent (zero order) on oxygen concentration. This is an agreement with previous findings (80, 56, 72, 29).

However, during the catalytic oxidation of isobutylene over bismuth molybdate catalyst, Mann and Ko (119) reported that, while the selectivity for methacrolein increased with increasing oxygen: isobutylene ratios, the conversion decreased with increasing feed ratios, contrary to our experiments. The most probable explanation

for this was that their data were taken in a very small range of reactant feed ratios ($O_2 : C_4H_8 = 1.2 - 2.4$), where the differences between the recorded conversions were very small.

The order of reaction in olefin was tested using the appropriate integrated forms of zero, first and second order rate expressions, by the linear regression method from the experimental conversion data.

The rate equation for a catalytic reaction in a flow system may be written as:

$$-r_A = \psi F \left(\frac{dx}{dW} \right) = \psi \frac{dx}{d(W/F)} \quad \text{equation V.4.1}$$

Thus, the rate of conversion corresponding to any given value of W/F will be given by the slope of the tangent to the curve x_x versus W/F at that point.

On the assumption that the total moles of gas undergo no change during the reaction, the reaction follows first order kinetics for which the equation is:

$$r_A = -K (1 - x) \quad \text{equation V.4.2}$$

when the equation V.4.2 is substituted into equation V.4.1 and integrated for an idealised piston-flow reactor the rate constant will be given by:

$$\ln (1 - x) = -K (W/F) \quad \text{equation V.4.3}$$

The above expression gave the best agreement with the experimental

Table V.4.a Analysis of variance for the oxidation of propylene over Bi:Mo catalyst (fixed bed results)

Block No	Temperature °C	σ_C^2	σ_O^2	σ_E^2	σ_F^2	σ_E^2/σ_F^2	K_r mole g ⁻¹ hr ⁻¹
1	405	3.88	8.99	6.43	8.40	0.766	2.42 x 10 ⁻³
2	445	0.712	7.52	4.11	16.01	0.257	7.14 x 10 ⁻³
3	462	3.22	10.17	6.69	9.24	0.724	9.41 x 10 ⁻³
Activatin energy $E_a = 22.9$ Kcal / mole Pre-exponential factor A = 17.4 g⁻¹ sec⁻¹ mole $\sigma^2 = 13.9\%$ from the linearised equation							

Table V.4.b Analysis of variance for the oxidation of isobutylene over Bi:Mo catalyst (fixed bed results)

Block No	Temperature °C	σ_C^2	σ_O^2	σ_E^2	σ_F^2	σ_E^2/σ_F^2	K_r mole g ⁻¹ hr ⁻¹
1	405	8.23	9.40	8.80	12.2	0.712	8.6 x 10 ⁻³
2	445	4.16	5.92	5.04	7.10	0.709	19.3 x 10 ⁻³
3	462	4.59	13.8	9.19	11.13	0.825	27.3 x 10 ⁻³
Activatin energy $E_a = 20.12$ Kcal /mole Pre-exponential factor A = 7.29 g⁻¹ sec⁻¹ mole $\sigma^2 = 8.5\%$ from the linearised equation							

data, relative to those of zero, and second order expressions. However, the "goodness" of fit for the experimental data obtained during the catalytic oxidation of propylene is rather poor, relative to that of isobutylene oxidation. This is because the experimental error for propylene is smaller than that of isobutylene, which can be seen from the tables V.4.a and V.4.b.

It is mentionable that if the experimental error is too big any kinetic or reactor model can fit.

V.5 OPTIMIZATION OF CONDITIONS FOR THE SELECTIVE OXIDATION OF ISOBUTYLENE TO METHACROLEIN

To obtain high values for the selectivity of the conversion of isobutylene to methacrolein, the catalyst weight, stirring, fluid flow rate and total pressure in the reactor were kept constant, while the reaction temperature was varied in the range 400 °C - 537 °C and the fuel : oxygen moles ratio in the feed by a factor of 10.

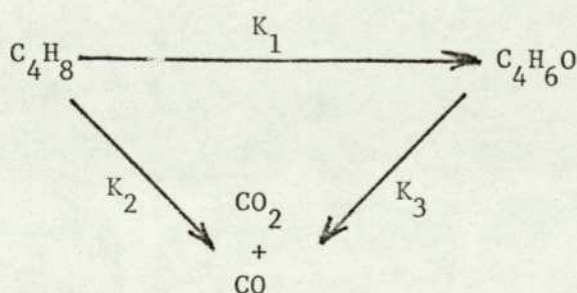
The maximum conversion recorded was 85.6 % at 453.5 °C, while the selectivity towards the main product was 85.2 % , with by products being mainly carbon oxides. Similar high values for selectivity to methacrolein were recorded at all conversion levels (Table IV.5.a , IV.5.b , IV.5.c , IV.5.d , IV.5.e , IV.5.f , IV.5.g, IV.5.h.

Combination of bismuth oxide and molybdenum oxide with an atomic ratio close to unity leads to a highly selective catalyst system, for the oxidation of olefins to unsaturated aldehydes in agreement with previous suggestions (57,59,60,29).

Furthermore the suitability of the reactor as previously investigated (208) ,did have a beneficial effect on the selectivity of the total conversion of isobutylene to methacrolein. The optimum ratio, bed height : total height of the reactor = 1 :7 , was established (208) to minimise the effect of the free board zone volume on the conversion of olefins to unsaturated aldehydes. It is important to state that,at the temperature range where maximum values of conversion and selectivity are attained,relatively high gas phase oxidation of olefins to mainly acetone and carbon oxides occurs. If the latter could have been avoided,it would result in even higher values of selectivity to the main product.

V.5.1 Effect of temperature and reactant feed ratios.

The conversion-selectivity plots given in figures IV.5.b , IV.5.c ,IV.5.d ,IV.5.e ,IV.5.f ,IV.5.g ,IV.5.h and IV.5.i ,show a general decline in selectivity at higher conversions,but they do not seem to extrapolate to 100 % at zero conversions. It is my hypothesis that if this is true the carbon oxides are formed by post oxidation of methacrolein as well as from the oxidation of the initial olefin . Thus,the proposed (56) combination of parallel and consecutive reactions for the oxidation of propylene appears to be the most probable reaction scheme for the vapour phase oxidation of isobutylene over bismuth molybdate catalyst.



With increasing $C_4H_8 : O_2$ moles feed ratio the conversion of isobutylene to products increases steadily, while the selectivity to methacrolein decreases up to the value $C_4H_8/O_2 = 2.0$. At higher feed ratios the conversion was observed to be unaffected although a steady increase of isobutylene consumption was expected. This can be explained in agreement with previous findings (58,59, 66,67,68), from the fact that the main source of oxygen for the reaction is the bismuth molybdate catalyst alone.

We suggest that, at low C_4H_8/O_2 ratio values, i.e. gaseous oxygen partial pressure is above the minimum point at which reduction of the catalyst is expected, the reaction proceeds through the lattice oxygen of bismuth molybdate, which leaves the catalyst in a reduced state. However, catalyst is fast re-oxidised by a rapid diffusion to the surface of O_2^{2-} anions from the chemisorbed oxygen.

With increasing reactant feed ratios the conversion increases steadily, as expected, due to the rate of the reaction dependence on the partial pressure of gaseous isobutylene (page 178).

We further suggest that as the value $C_4H_8/O_2 = 2.0$ is attained, i.e. gaseous oxygen partial pressure is about the lowest possible level at which reduction of the catalyst is avoided, re-oxidation of the temporarily reduced catalyst does not occur and thus the catalyst loses progressively its activity until the lattice oxygen is totally consumed.

With increasing temperature from $390^\circ C$ to $465^\circ C$ the conversion increases and selectivity to methacrolein decreases. Contrarily, the effect of temperature on the yields of carbon oxides is the opposite to that observed on the selectivity

(Figures IV.5.j ,IV.5.k and IV.5.l) . Nevertheless,much overoxidation does not occur as is evidenced by rather low yields of by-products.

With further increase in temperature above 400°C ,higher conversions of isobutylene to products were not obtained as could be expected.

The most probable explanation for this behaviour is that bismuth molybdate catalyst,strongly dependent upon the structure and the arrangement of the atoms within the crystal ,loses its activity,apparently because of structure collapse. A total loss of its activity was observed when the catalyst was heated above 650°C to support previous findings (29,30).

V.5.2 Effect of fluidisation behaviour

During previous investigations in this laboratory (208), kinetic data of propylene oxidation over mixed oxide catalysts in a fluidised bed reactor,within the temperature range 380°C - 545°C were obtained; mathematical treatment of the experimental data was not carried out . The reason lies in the fact that in fluidised bed reactors heat,diffusional and mass transfer effects should be considered,even though these effects could be limited to some extent,if the reaction is carried out in a one-phase model (fluidised bed at minimum fluidisation).

It was expected and subsequently found that in an incipiently fluidised bed no gross by-passing occurs. However,the effect of stirrer and reactor wall are considerable and lead to a rather high degree of back-mixing in the particulate phase. As a result all the conversion data at minimum fluidisation and below fall

on the same single curve approaching the completely mixed line (figure IV.5.a) . The data were fitted to a least-square curve according to equation III.3.8 ,where the right hand side of this equation was expressed as a combination of the following terms , $e^{-K'}$ (conversion for a plug flow reactor) ,and $1 / 1+K'$ (conversion for a perfectly mixed reactor) . The fitting error from the regression was tested over the experimental error calculated from the carbon and oxygen mass balances and the "goodness" of fit was related to the ratio , σ_E^2 / σ_F^2 , as given amongst other statistical quantities in table V.5.a .

Since the conversion values obtained for an incipiently fluidised bed are higher than conversions calculated assuming perfect mixing the degree of dispersion in the dense phase was estimated from Dankwert's dispersion model (141) ,which gives the degree of conversion assuming that the passage of gaseous reactants falls between the ideal states of piston flow and complete back-mixing. Axial mixing through the bed is assumed and is characterised by an effective dispersion coefficient. The modified equation for a pseudo-first order reaction is:

$$X = 1 - \frac{4a}{(1+a)^2 \exp -FW(1-a)/2E_g - (1+a)^2 \exp -FW(1+a)/2E_g} \quad \text{equat. V.5.1}$$

where $a = \sqrt{1 + 4 K_r (E_g / FW)}$

Values for the axial dispersion coefficient were assumed, and a figure of $72.3 \text{ g mole hr}^{-1}$ gave the best agreement for the experimental curve (dashed line) in figure V.5.a ,when compared with the ideal case of a perfectly mixed reactor (solid

Table V.5.a Analysis of variance and regression table
(Results at minimum fluidisation velocity)

$\sigma_C^2 = 6.94$	$\sigma_O^2 = 8.50$	
$\sigma_E^2 = 8.50$	$\sigma_F^2 = 7.81$	$\sigma_E^2 / \sigma_F^2 = 1.008$
Sum of squares total		9.030
Sum of squares of regression table		8.837
Sum of squares of residuals		0.194
Standard error of estimate		0.078
Corrected R^2		0.979

Table V.5 b Analysis of variance and regression table
(Results at low superficial gas velocities)

$\sigma_C^2 = 1.72$	$\sigma_O^2 = 9.35$	
$\sigma_E^2 = 5.5$	$\sigma_F^2 = 7.76$	$\sigma_E^2 / \sigma_F^2 = 0.709$
Sum of squares total		2.463
Sum of squares of regression table		2.453
Sum of squares of residuals		0.0101
Standard error of estimate		0.0278
Corrected R^2		0.9959

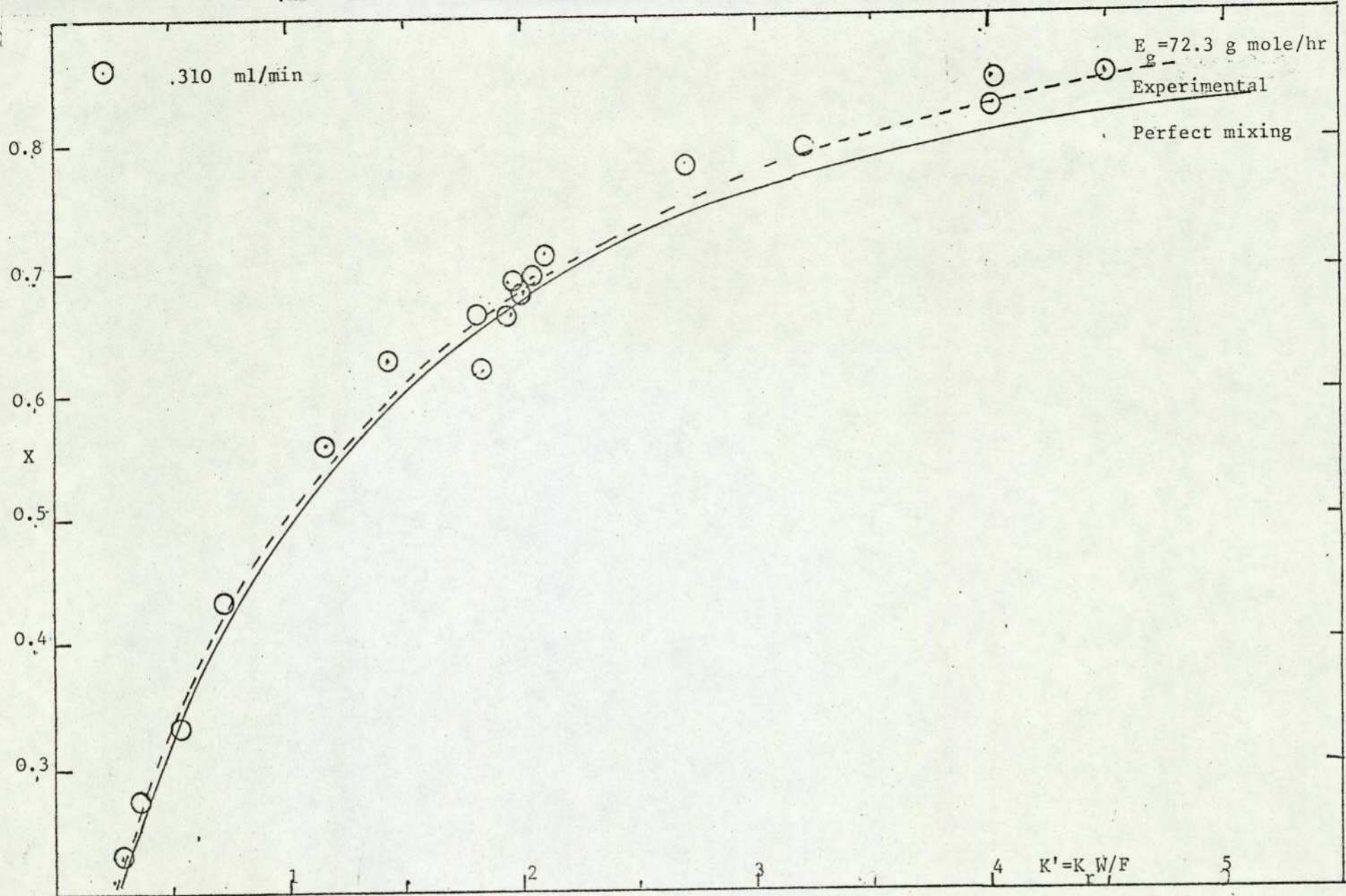


Figure V.5.a. Test of experimental data with the dispersion model

line) .

Since bubbling commenced at low gas velocities the experimental conversions were lower than those obtained from the incipiently fluidised bed otherwise operating under the same conditions, in agreement with Knudsen and Gilliland's (238) findings. The conversions were found to be 20 % less than the case of a perfectly mixed reactor indicating that the degree of by-passing is relatively high at the low superficial velocities used (figure IV.5.m) . Again the dashed line in figure IV.5.m represents the least squares curve with the data fitted according to equation III.3.8 , where the right hand side of this equation was expressed according to the simplified polynomial due to Calderbank and Torr (170) , initially suggested by Orcutt et al (160). "Goodness" of fit and other statistical quantities calculated from the regression table are given in table V.5.b.

As the formation and growth of bubbles lead to an overall lower efficiency of contacting in terms of selectivity, a less selective oxidation would naturally result at higher fluidising fluid velocities.

From the results obtained for the homogeneous oxidation of isobutylene (Figure IV.3.a , IV.3.b and IV.3.c) , it was found that acetone and formaldehyde are formed as the main products and some acetaldehyde, methacrolein and carbon oxides in smaller quantities, in agreement with published work (239, 240)

Since rising bubbles contain only a small amount of particulate material, it is expected that the reactant gases within the bubble will react homogeneously, and to a lesser extent heterogeneously, without considering any interchange between lean

and dense phases and consequently the overall selectivity is reduced. We suggest that, during the catalytic oxidation of olefins, the maximum selectivity of conversion to unsaturated aldehydes will be obtained by minimising the void volume within the bed, i.e. the size of the bubbles, and maximising the ratio volume of bed : total volume of the reactor. The application of internals or stirring devices will result in bubbles smaller in size, as combined work reported (222), in agreement with previous extensive studies (241, 242), and thus will increase the ratio conversion due to heterogeneous oxidation : conversion due to homogeneous oxidation and therefore increase the overall selectivity of the reaction. Additionally all fluidised bed reactor models combine the rate of the reaction with the rates of most of the physical phenomena involved in fluidised bed operation, but exclude the rate of the heterogeneous reaction. This may be significant if the rate of the gas phase oxidation is relatively high within the employed temperature range. Especially the probability of homogeneous reaction within a fluidised bed should be considered when the rate of the heterogeneous reaction is low.

The maximum proportion of propylene conversion in the gas phase at 437°C , using a fluidised bed reactor of total height : bed height = 7 : 1; and propylene to oxygen ratio of 3 : 1 was recorded at 5.9 % (208). Although, gas phase oxidation did not affect seriously the total conversion and selectivity of the reaction, however, the significance of the homogeneous reaction would be more pronounced if the reactor height is increased, i.e. the free board zone is extended. When the oxidation of olefins was carried out using a fluidised bed reactor of total

height : bed height = 16 : 1 a markedly reduced selectivity to unsaturated aldehydes was observed (208) .

The design of the laboratory reactor used does not allow formation of large bubbles due in part to the shallow catalyst bed and also, the use of a paddle stirrer. In this way, an equal distribution of bubbles throughout a uniformly fluidised bed was achieved.

The experimental conversions obtained were checked against those predicted by the bubble model of Orcutt et al (160), assuming pseudo first order kinetics. The fractional conversion taking place in the perfectly mixed gas in the particulate phase is given by:

$$X = 1 - \left[\beta e^{-n_k} + \frac{(1 - \beta e^{-n_k})^2}{K' + (1 - \beta e^{-n_k})} \right] \quad \text{equation V.5.2}$$

On the other hand, when the reactant gas is in plug flow through the particulate phase, the fractional conversion is:

$$x = 1 - \left[\frac{1}{m_2 - m_1} \left\{ m_2 e^{-m_1} \left(1 - \frac{m_1 U_{mf}}{n_k U_o} \right) - m_1 e^{-m_2} \left(1 - \frac{m_2 U_{mf}}{n_k U_o} \right) \right\} \right] \quad \text{equation V.5.3}$$

where m_1 and m_2 are the roots of the quadratic equation:

$$m^2 - (n_k + K'/1 - \beta)m + (K' n_k / 1 - \beta) = 0 \quad \text{equation V.5.4}$$

$$\text{where } \beta = 1 - U_{mf}/U_o \quad \text{equation V.5.4}$$

$$n_k = \frac{6.34 H_{mf}}{D_e (g D_e)^{1/2}} U_{mf} + 1.3 D_g^{1/2} (g/D_e)^{1/4} \quad \text{equation V.5.5}$$

and $K' = K W/F_r$

equation V.5.6

the limiting conditions of equations V.5.2 and V.5.3 are:

$\text{Lim } (K' \rightarrow \infty)$	$X = 1 - e^{-n_k}$	(fast reaction)
$\text{Lim } (K' \rightarrow 0)$	$X = 0$	(no reaction)
$\text{Lim } (n_k \rightarrow \infty)$	$X = 1 - 1/(1 + K')$ $X = 1 - e^{-K'}$	(very fast exchange through bubbles)

In figure V.5.b a comparison of the experimental fractional conversions (dashed line) is made with theoretical conversions calculated from Orcutt's fluid model assuming 1) piston flow and 2) perfect mixing (solid lines). The theoretical conversions were calculated at $\beta = 0.4$ whilst the number of transfer units was estimated using bubble diameters determined by experimental measurement of bubble eruption diameters in the same reactor.

The diffusion coefficient D_g for isobutylene into air over the temperature range used in the oxidation experiments was calculated using the Lennard-Jones relationship (5). Thus, values for the diffusion coefficient over the whole of the temperature range reduces the error for data correlation using Orcutt's flow model.

The assessment of the criterion of "goodness" of fit to data was made by means of the ratio σ_F^2 / σ_E^2 , and in calculating the experimental variance it is to be noted that the carbon variance is always lower than the oxygen variance due to the difficulty

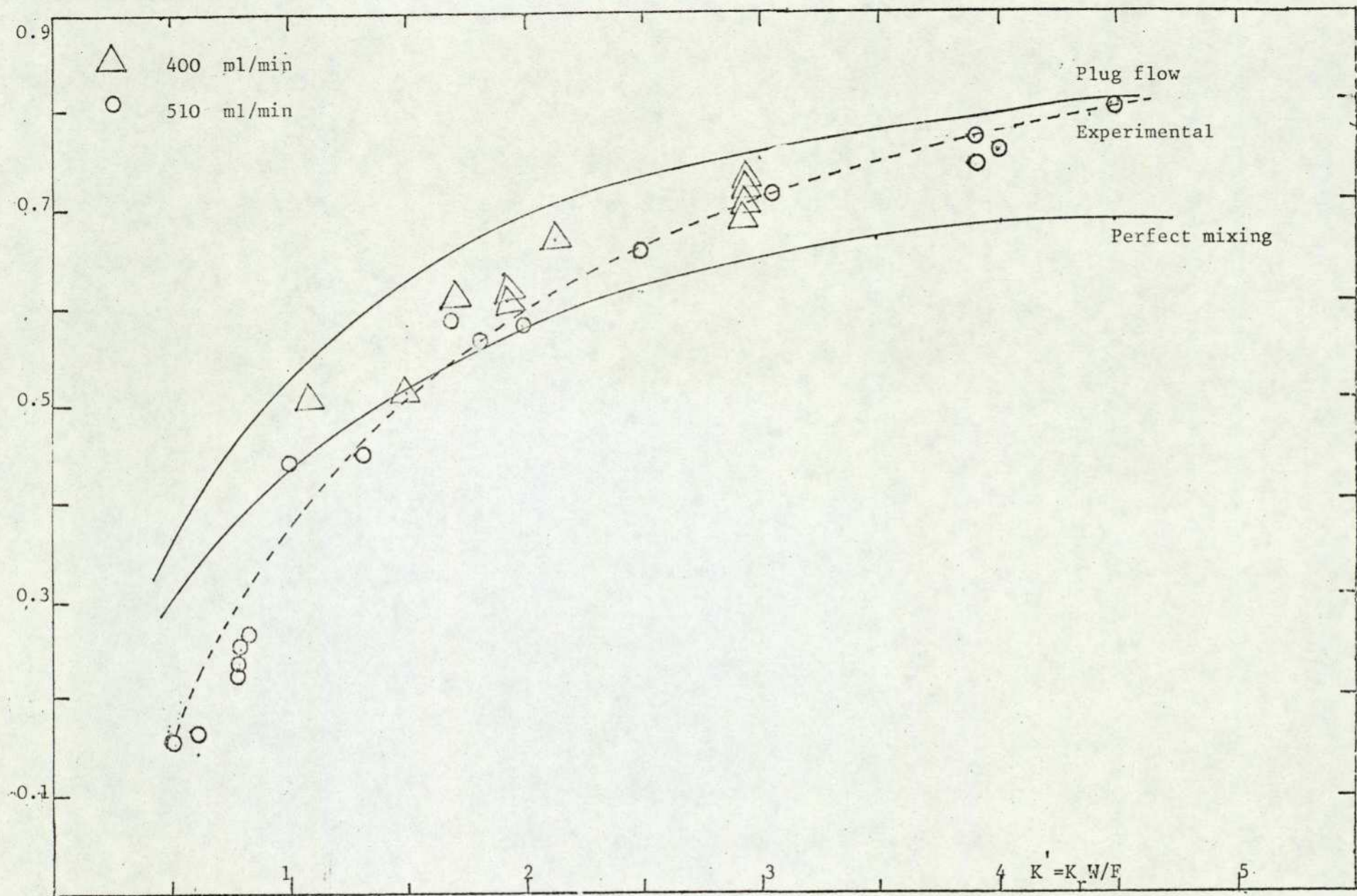


Figure V.5.b Test of experimental data with Orcutt's fluid-bed model

in determining the amount of water.

At low K_r values, small errors in predicted bubble diameters result in comparatively large deviations from predicted conversions based on the two phase model. This becomes more serious when the two phase theory is applied to the fluidisation of fine particles, as emphasised in an earlier study (223). Nevertheless, as is expected at high K_r values, i.e. high reaction temperatures, the degree of conversion due to gas phase oxidation will contribute more to the total conversion of the reaction, than at low K_r values. For this reason, it is not unexpected that the lower part of the experimental curve in figure V.5.b, falls outside the region bounded by the theoretically predicted curves.

V.6 FUTURE WORK

The selective oxidation of isobutylene to methacrolein has been carried out in a shallow gas fluidised bed. Aiming to obtain the highest olefin conversion and selectivities to unsaturated aldehydes, the optimum reaction conditions have been established.

Recently fluidisation technology has seen tremendous applications in a wide range of process industries. However, most of the design background on large scale fluidised bed reactors is based on earlier experience obtained empirically, seemingly without adequate theoretical understanding. This is due to the fact that with most gas-solid systems, achievement of comparable results between laboratory and large scale equipment is often difficult and sometimes even impossible.

For fluidised bed operation the following information

is needed if a confident scale-up is to be achieved.

- i. Tendency of solid particles to agglomerate.
- ii. Tendency of solids to sinter or brake.
- iii. Behaviour of the bed during exothermic reactions.
- iv. Tendency of solids to cover the wall of the free-board zone
- v. Transport of solid particles out of the reactor at high gas flow rates.
- vi. The kinetics and the rate constant of the reaction in the environment expected in the fluidised bed
- vii. Investigation of the explosion limits for the existing gas mixture in the operating temperatures of the bed.

If the experiments giving the above information are carried out correctly, then we should be able to proceed in the design of a pilot plant unit safely and certainly the laboratory results would be applicable when scale-up is attempted.

In some operations agglomeration of solid particles will cause accumulation on the distributor and will disrupt the proper distribution of gas in the bed. Therefore, special care should be given to the selection of a suitable distributor and to a method of discharge of agglomerates during steady state operation. A profile of heat of the reaction at different conversion levels is required to avoid hot spots and consequent agglomeration of fines.

Phenomena such as channelling and slugging were observed and overcome by controlling the behaviour of the bed with the use of a stirrer. The application of stirrers within fluidised

is the subject of present research (243, 244) ,however, the way it improves the bed behaviour to a fluidised, channelling-free and slugging-free bed where highest percentages of conversion and selectivities occur is yet to be examined.

The elucidation of the back-mixing of gaseous reactants in fluidised beds of fine particles needs further investigation, especially when stirring is applied within the bed. Minimising the degree of dispersion in the dense phase increases the efficiency of reactor operation quite considerably.

The simple kinetic investigation carried out during the present work enables a direct comparison for the reaction rates obtained from the fluidised bed and reactors operating under no mass transfer gradients; thus, determination of the overall mass transfer coefficient in fluidised beds is possible to be estimated indirectly.

Finally, further studies on the extent of the homogeneous reaction in the free-board zone region and the lean phase are presently being carried out in this laboratory and its mathematical treatment will complete the picture of such a complex system as a fluidised bed reactor.

V.7 CONCLUSIONS

A. Reaction within the bubble phase results in a less selective oxidation of olefins to unsaturated aldehydes.

B. Large bubbles within fluidised catalytic beds give rise to lower conversions and selectivities.

C. Application of stirring within fluidised bed of small particles leads to a smooth uniform régime.

D. The highest conversion value and selectivities to methacrolein are obtained in the temperature range 440°C - 460°C and a fuel:oxygen ratio close to unity.

CHAPTER VII

REFERENCES

VII. REFERENCES

1. Isaev, O.V., Kuchmerov, M.Ya., and Margolis, L.Ya., Dokl. Akad. Nauk SSSR 119, 104 (1958)
2. Popova, N.I., and Vermel, E.E., Dokl. Akad. Nauk SSSR 124, 842 (1959)
3. Shapovalova, L.P., Gorokhovatskii, Ya.B., and Rubanik, M.Ya., Ukr. Khim. Zh., 28, 1031 (1962); C.A 59-6237f
4. Geldart, D., Chem. Ind., 1474 (1967)
5. Hirschfelder, J.O., Curtiss, F.C., and Bird, R.B., "Molecular theory of gases and liquids", Wiley, New York, 1954.
6. Wheeler, A., Catalysis, 2, 105 (1955)
7. Wheeler, A., Advan. Catalysis, 3, 250 (1955)
8. Faraday, M., Phil. Trans., 114, 55 (1834)
9. Mitscherlich, E., Liebigs Ann., 44, 186 (1822)
10. Langmuir, I., F. Am. Chem. Soc., 34, 1310 (1912)
11. Langmuir, I., ibid , 38, 2221 (1916)
12. Langmuir, I., ibid , 40, 1361 (1916)
13. Miller, A.R., Proc. Camb. phil. Soc. math. phys. Sci., 43, 232 (1947)
14. Trapnell, B.M.W., "Chemisorption", Butterworths, London (1955)
15. Hougen, O.A., and Watson, K.M., "Chemical Process Principles", 5, Wiley, New York, 1947
16. Hearne, G.W., and Adams, M.L., U.S. Pat. 2,432,287 Dec. (1947); C.A 44-2012b

17. Annalen der Chemie, Vol XX., 9 (1836)
18. Annalen der Chemie, Vol LXVII., 8 (1843)
19. Hearne, G.W., and Adams, M.L., U.S. Pat. 2,451,458 (1948);
C.A 43-2222f
20. Callahan, J.L., Foreman, R.W., and Veatch, R., U.S. Pat.
2,941,007 (1960)
21. Lazukin, V.I., Belousov, V.M., and Rubanic. M.Ya., Ukrainskii
Khim. Zhurnal , 32 , 231 (1966)
22. Kamiya, Y., Sekiyu Gakkai Shi., 5, 18 (1962); C.A 57-9772a
23. Ghorokovatskii, Ya.B., Vovnyanko, I.I., and Rubanik, M.Ya.,
Kinetika i Kataliz, 7, 65 (1966)
24. Margolis, L.Ya., Advan. Catalysis 14, 429 (1963)
25. Kominami, N., Shibata, A., and Mikekawa, S., Kogyo Kagaku
Zasshi, 65, 1510 (1962)
26. Margolis, L.Ya., Enikeev, E.Kh., Isaev, O.V., Krylova, A.V.,
and Kushnerov, M.Ya., Kinetika i Kataliz 3, 181 (1962)
27. Popova, N.I., Stepanova, R.N., and Stukova, R.N.,
Kinetika i Kataliz 2, 916 (1961)
28. Popova, N.I., Vermel, E.E., and Mil'man, F.A., Kinetika i
kataliz 3, 241 (1962)
29. Adams, C.R., Voge, H.H., Morgan, C.Z., and Armstrong, W.E.,
J. Catal. 3, 379 (1964)
30. Adams, C.R., ibid., 3, 549 (1964)
31. Voge, H.H., Wagner, C.C., and Stevenson, D.P., J. Catal.
2, 58 (1963)
32. Adams, C.R., and Jennings, T.J., ibid., 2, 63 (1963)
33. Zhdanova, K.P., Filippova, A.A., and Popova. N.I.,

- Probl. Kinet. Katal. 12, 211 (1968)
34. Adams. C.R.,and Jennings, T.J., J. Catal. 3, 549 (1964)
35. Margolis, L.Ya., Advan. Catalysis 14, 429 (1963)
36. Popova, E.N.,and Gorokhovatskii, Ya.B., Dokl. Akad. Nauk SSSR 145, 570 (1962)
37. Popova. E.N.,and Gorokhovatskii, Ya.B., Kinetika i Kataliz 5, 134 (1964)
38. Isaev, O.V.,and Margolis, L.Ya., Kinetika i Kataliz 1, 237 (1960)
39. Belousov, V.M.,Gorokhovatskii, Ya.B.,and Rubanik, M.Ya., Kinetika i Kataliz 3, 221 (1962)
40. Billingsley, D.S.,and Holland, C.D., Ind. Eng. Chem., Fundamentals 2, 252 (1963)
41. Barclay, J.L.,Bethell, J.R.,Bream, J.B.,Hadley, D.J., Jenkins, R.H.,Stewart, D.G.,and Wood, B., British Pat. 864,666 (1960)
42. Bream, J.B.,Hadley, D.J.,Barclay, J.L.,and Stewart, D.C., British Pat., 876,446 (1961)
43. Barclay, J.L.,and Hadley, D.J., British Pat., 902,952 (1962)
44. Bethell, J.R.,and Hadley, D.J., U.S Pat., 3,094,565 (1963)
45. Belousov, V.M.,and Gershingorina, A.V., Kinetika i Kataliz 12, 614 (1971); Eng. Trans.
46. Gobin, G.W.,McGain, C.C.,and Porter, E.A., In "Proceedings of the 4th International Congress on Catalysis, Moscow, 1968" (D.A. Kazanaskii, ed.), Akademiai Kiado, Budapest,1971
47. Krylova, A.V.,Derlyukova, L.E., and Margolis,L.Ya., Dokl. Akad. Nauk SSSR 178, 79 (1968); Eng. Transl.

48. Germain, J.E., "Catalytic conversions of hydrocarbons"
Academic Press , 1969
49. Sampson, R.J., and Shooter, D., "Oxidation and Combustion
Reviews", 1, 223 (1965)
50. Chatt, J.,and Duncanson, L.A., J. Chem. Soc., 2939 (1953)
51. Peacock, J.M.,Ashmore, P.G.,Parker, A.J.,Sharp, M.,and
Hockey, J.A., J. Catal., 15, 379 (1970)
52. Dewing, J., "Chemical Society Symposium on Hydrocarbons
Oxidation", London, 1970
53. Pendleton, P.,and Taylor, D., J
54. Cartlidge, J.,McGrath, L.,and Wilson, S.H., Trans. I. Chem.
Engrs., 52, 222 (1974)
55. Belousov, V.M.,and Gershingorina, A.V., Kinet. Katal.,
11, 942 (1970); Eng. Transl.
56. Adams, C.R., "Proc. of the 3^d international congress
on catalysis", 240 (1964), Amsterdam.
57. Batist, Ph.A.,Derkinderen, A.H.W.M.,Leenwenburgh, Y.,
Metz, F.A.M.G.,and Schuit, G.C.A., J. Catalysis, 12,
45 (1968)
58. Batist, Ph.A.,Van der Moesdijk, C.G.A.,Matsura, I.,
and Schuit, G.C.A., *ibid.*, 20, 40 (1971)
59. Bleijenberg, A.C.A.M.,Lippens, B.C.,and Schuit, G.C.A.,
ibid., 4, 481 (1965)
60. Batist, Ph.A.,Lippens, B.C.,and Schuit, G.C.A., *ibid.*,
5, 55 (1966)
61. Batist, Ph.A., Kapteijns, C.J.,Lippens, B.C.,and
Schuit, G.C.A., *ibid.*, 7, 33 (1967)

62. McGain, C.C., Gough, G., and Godin, G.W., *Nature, London*,
198, 989 (1963)
63. Sachtler, W.M.H., *Rec. Trav. Chim., Pays-bas Belg.*,
82, 243 (1963)
64. Lossing, F.P., Marsdon, H.G.D., and Farmer B.J., *Can. J. Chem.*,
34, 701 (1956)
65. Harrison, G.A., and Lossing, F.P., *ibid.*, 37, 1696 (1959)
66. Keulks, G.W., Rosynek, M.P., and Daniel, C., *Ind. Engn.*
Chem., Prod. Res. Dev., 10, 138 (1971)
67. Keulks, G.W., and Rosynek, M.P., *Am. Chem. Soc., Div. Petrol*
Chem., 14, C55 (1969)
68. Keulks, G.W., and Krenzke, L.D., "6th Intern. Congress on
Catalysis" London, 1976
69. Gel'bshtein, I.A., Stroeve, S.S., Kul'kova, V.N., Bakshi,
M.Ya., Lapidus, L.V., Basil'ev, E.I., and Sevast'yanov, G.N.,
Neftekhimiya, 4, 906 (1964)
70. Gel'bshtein, I.A., Bakshi, M.Ya., Stroeve, S.S., Kul'kova,
V.N., Lapidus, L.V., and Zadovskii, S.A., *Kinetika i*
Kataliz, 6, 1025 (1965); Eng. Transl.
71. Brisk, M.L., Day, R.L., Jones, M., and Warren, J.B., *Trans. I.*
Chem. Engrs., 46, 3 (1968)
72. Cartlidge, J., McGrath, L., and Wilson, S.H., *Trans. I.*
Chem. Engrs., 53, 117 (1975)
73. Bretton, R.C., Wan, S.U., and Dodge, B.F., *Ind. Eng. Chem.*
46, 594 (1952)
74. Mann, R.S., and Rouleau, C., *Can. J. Chem. Engng.*, 43,
178 (1965)

75. Mann, R.S.,and Yao, K.C., Ind. Engng. Chem., Prod. Res.
and Dev., 6, 263 (1967)
76. Mann, R.S.,and Yao, K.C., Adv. Chem. Ser., 76, 276 (1968);
C.A 68-21457y
77. Mann, R.S.,and Yao, K.C., Ind. Engng. Chem., Prod. Res.
and Dev., 8, 331 (1969); C.A. 71-101233z
78. Mann, R.S.,and Yao, K.C., Ind. Engng. Chem., Prod. Res.
and Dev., 10, 25 (1971)
79. Mann, R.S.,Yao, K.C.,and Dosi, M.K., J. Appl. Chem. Biotechn.
22, 915 (1972)
80. Ray, S.K.,and Chanda, M., Ind. Eng. Chem., Prod. Des. Dev.,
15, 234 (1976)
81. Cartlidge, J.,McGrath, L.,and Wilson, S.H., Trans. I.
Chem. Engrs., 55, 164 (1977)
82. Ohara, T.,Ueshima, M.,Nishinomiya, H.,and Yanigisawa, I.,
Ger. Offen., 2,125,032 (1971)
83. Adams, C.R., Ind. Eng. Chem., 61, 30 (1969)
84. Mitsubishi Rayon Co., Jap., 7019,485 (1970)
85. Etherington, Ir., R.W., U.S Patend, 3,254,035 (1966)
86. Takayama, Y.,Ikeda, T.,and Sunaoka, R., Jap., 6810,603 (1968)
87. Narita, T.,and Nisijima, Y., Jap., 6914,928 (1969)
88. Masaki, S.,and Kuwata, T., Jap., 6929,045 (1969)
89. Izawa, M.,Ono, I.,and Noguchi, J., Jap., 6803,164 (1968)
90. Cahoy, R.P.,and Coyne, D.M., U.S. Pat., 3,417,144 (1968)
91. Cahoy, R.P.,and Coyne, D.M., U.S. Pat., 3,499,936 (1970)
92. Brill, W.F.,and Besozzi, A.J., U.S. Pat. 3,271,459 (1966)
93. Besozzi, A.J.,and Brill, W.F., U.S. Pat., 3,301,906 (1967)

94. Rohmu.Haas G.m.b.H., Fr. Pat., 1,554,240 (1969)
95. Oda, Y.,Uchijima, K.,and Fumami, F., Jap., 6913,488 (1969)
96. Nakayama, Y.,Ogawa, Y.,and Uchida, T., Jap. 6913,129 (1969)
97. Takenaka, S.,Shimizu, H.,and Yamamoto, K., Ger. Offen.,
2,155,411 (1972)
98. Isaev, O.V.,and Kushnerev, M.Ya., Proc. Accad. Sci. USSR ,
Phys. Chem. Sec., 124, 129 (1958); Engl. Transl.
99. Kernos, Yu.D.,and Moldavskii, B.C., J. Appl. Chem. USSR ,
33, 2555 (1960); Engl. Transl.
- 100.Rienacker, G.Z., Acta Chim. Acad. Sc. Hung., 14, 173 (1958)
- 101.Continental Co. Ltd., British Pat., 805,776 (1958); C.A 53-17905g
- 102.Farbenfabriken Bayer, A.G., British Pat., 839,808 (1960)
- 103.Hadley, D.J.,and Heap, R., (to Distillers Co Ltd.) British
Pat., 704,388 (1954)
- 104.Mantecatini, G., British Pat., 847,564 (1960)
- 105.Hadley, D.J.,and Distillers Co Ltd., British Pat., 648,386
(1951); C.A 45-7134c
- 106.Distillers Co Ltd.,Hadley, D.J.,Head, R.,and Nichol, R., British
Pat., 655,210 (1951); C.A 46-6668c
- 107.Mann, R.S.,and Rouleau, C., Ind. Eng. Chem., Prod. Res.and Dev.,
3, 94 (1964)
- 108.Gorokhovatskii, Ya.b.,and Vovyanko, I.I., Katal. Katal. Akad.
Nauk. SSSR , Resp. Mez. Sb., 5, 18 (1969); C.A 72-48003s
- 109.Gorokhovatskii, Ya.B., Katal. Katal. Akad. Nauk. SSSR ,
Resp. Mez. Sb., 1, 71 (1965); C.A 64-4894f
- 110.Popova, N.I.,Mil'man, F A.,and Latysheva, L.E., (Inst. Chem.
Irkutsk) Izves. Sibir. Otdel. Akad. Nauk. SSSR , 7, (1961)

111. Oda, Y., Uchijima, K., and Fumani, F., Jap. 6913,488 (1969)
112. Hagiwara, K., Ger. Offen. 2,038,998 (1971)
113. Nariya, T., and Nisijima, Y., Jap. 6914,928 (1969)
114. Deutsche Erdoel A-G., Fr. Pat., 1,558,233 (1969)
115. Shell International Res. Maatsh. N. V., Neth. Appl.
6,605,325 (1966)
116. Tichy, J., and Zavodsky, P., Chem. Prum. 22, 348 (1972)
117. Uchijima, K., and Oda, Y., Asahi Gvasu Kenkyu Hokoku
18 , 11 (1968); C.A 70-67334a
118. Mann, R.S., and Yao, K.S., Dech. Monogr. Band, 68 ,329 (1971)
119. Mann, R.S., and Ko, D.W., J. Catalysis, 30 , 276 (1973)
120. Mathur, N.B., In " FLUIDISATION " (Davidson & Harrrison, eds)
Academic press, London and New York (1971) .
121. Ergun, S., Chem. Eng. Prog. 48 , 89 (1952)
122. Kozeny, J., Uber Kapillare Leitung des Wassers im Boden
S. B. Akad. Wiss. Wien, Adt. IIa, 136, 271 (1927)
123. Carman, P.C., Tran. Inst. Chem. Eng. London, 38 ,79 (1937)
124. Kunii & Levenspiel " Fluidisation Engineering " J. Wiley
& sons , New York, (1969).
125. Leva, W.K., " Fluidisation " , Mc Graw Hill, New York, (1959).
126. Zenz, F.A., " Encyclopedia of Chemical Technology " .
first supplement volume, ed. Kirk, R.E.
127. Richardson, J.F., In " FLUIDISATION " (Davidson & Harrison, eds)
Academic Press, London and New York , (1971) .
128. Wen, C.Y., and Yu, Y.H., A.I.Ch. Engrs. Jl., 12 , 610 (1966)
129. Shirai, T., Ph. D thesis, Tokyo Institute of Technology,
(1954).

130. Hiraki I., Personal communication. from Kunii & Levenspiel (124)
131. Wilhelm, R.H., and Kwauk, M., Chem. Eng. Progr., 44 , 201 (1948)
132. Richardson, J.F., and Zaki, W.N., Trans. Inst. Chem. Eng.
32 , 35 (1954)
133. Richardson, J.F., and Zaki, W.N., Chem. Eng. Sci. 3 , 65 (1954)
134. Adler, I.L., and Happel, J., Chem. Eng. Prog. Symposium
Series, 58 , 98 (1962).
135. Happel, J., A.I.Ch.E. Jl., 4 , 197 (1958)
136. Richardson, J.F., and Davies, L., Trans. Inst. Chem. Eng.,
44 , 293 (1966)
137. Rowe, P.N., Partridge, B.A., Cheney, A.G., Henwood, G.A., and
Lyall, E., Trans. Inst. Chem. Eng., 43 , 271 (1965).
138. Kunii, D., Yoshida, K., and Hiraki, I., "Proceedings of Interna-
tional Symposium and Fluidisation, Amsterdam 1967 , (Nether-
lands University Press.)
139. Geldart, D., Powder Techn., 7 , 285 (1973)
140. De-Jong, J.A.H., and Nomden, J.F., Powder Techn., 9 , 91 (1974)
141. Danckwerts, P.V., Chem. Eng. Sci. 2 , 1 (1953)
142. Wehmer, J.F., and Wilhelm, H.R., Chem. Eng. Sci., 6 , 89 (1956)
143. Ishii, T., and Osberg, G.L., A.I.Ch.E. Jl., 11 , 279 (1965)
144. Singer, E., Todd, D.B., and Guinn, V.P., Ind. Eng. Chem.
49 , 11 (1957)
145. Overcashier, R.H., Todd, D.B., and Olney, R.B., A.I.Ch.E. Jl.,
5 , 54 (1959)
146. Gilliland, E.R., and Mason, L.A., Ind. Eng. Chem., 41 , 1191 (1949)
147. ibid. , 44 , 218 (1952)
148. Brammer, K.R., Schugerl, K., and Schiemann, G., Chem. Eng. Sci.
22 , 573 (1967)

149. Toomey, R.D., and Johnstone, H.F., Chem. Eng. Prog.,
48 , 290, (1952).
150. Johnstone, H.F., Bachelor, J.D., and Shen, C.Y., A.I.Ch.E. Jl.,
1 , 318 (1955)
151. Shen, C.Y., and Johnstone, H.F., A.I.Ch.E. Jl., 1 , 349 (1955)
152. Toomey, R.D., and Johnstone, H.F., Chem. Eng. Prog.,
48 , 5 (1952)
153. Mathis, J.F., and Watson, C.C., A.I.Ch.E. Jl., 2 , 518 (1956)
154. Lewis, W.K., Gilliland, E.R., and Glass, W., A.I.Ch.E. Jl.,
5 , 419 (1959).
155. May, W.G., Chem. Eng. Prog., 55 , 49 (1959)
156. Morse, R.D., and Ballou, C.O., Chem. Eng. Progr., 47 , 199 (1951).
157. Yashui, G., and Johanson, L.N., A.I.Ch.E. Jl., 4 , 445 (1958).
158. Baumgarten, P.K., and Pigford, R.L., A.I.Ch.E. Jl.,
6 , 115 (1960).
159. Davidson, J.F., Trans. Inst. Chem. Engrs., 39 , 230 (1961).
160. Orcutt, J.C., Davidson, J.F., and Pigford, R.L., Chem. Eng.
Progr. Symposium Series, 58 , 1 (1962).
161. Davies, R.M., and Taylor, I.G., Proc. Roy. Soc., A200,
375 (1950).
162. Baird, M.H.I., and Davidson, J.F., Chem. Eng. Sci., 17 , 87 (1962).
163. Orcutt, J.C., Ph. D. thesis, University of Delaware.,
Newark, Delaware (1960).
164. Harrison, D., and Leung, L.S., Trans. Insts. Chem. Engrs.,
40 , 146 (1962).
165. Rowe, P.N., Partridge, B.A., Lyall, E., and Arden, G.M.,
Nature , 195 , 278 (1962).

166. Toei, R., and Matsumo, R., "Proceedings of International Symposium on Fluidisation " ,Amsterdam, 1967, (Netherlands University Press.).
167. Lancaster, F.H., Ph. D. thesis, University of Edinburgh (1965).
168. Toor, F.D., Ph. D. thesis, University of Edinburgh (1967).
169. Angelino, H., Charzal, C., and Williams, R., Chem. Eng. Sci. 19 , 289 (1964).
170. Calderbank, P.H., and Toor, F.D., In "FLUIDISATION" (Davidson & Harrison, eds.) Academic Press, London and New York, 1971
171. Hougen, O.A., and Marshall, W.R., Chem. Eng. Progr., 43 , 197 (1947)
172. Gamson, B.W., Thodos, G., and Hougen, O.A., Trans. Am. Inst. Chem. Eng., 39 , 1 (1943)
173. Wilke, C.R., and Hougen, O.A., Trans. Am. Inst. Chem. Eng. 41 , 445 (1945).
174. Hurt, D.M., Ind. Eng. Chem., 35 , 522 (1943)
175. Amundson, N.R., Journal Physical and Colloid Chemistry, 52 , 1153 (1948)
176. ibid., 54 , 812 (1950)
177. Kasten, P.R., and Amundson, N.R., Ind. Eng. Chem., 42 , 1341 (1950)
178. Kasten, P.R., Lapidus, L., and Amundson, N.R., Journal of Physical Chemistry , 56 , 683 (1952).
179. Rosen, J.B., Journal of Applied Physics , 20 , 387 (1952).
180. Beek, J.W., In "FLUIDISATION" (Davidson & Harrison, eds) Academic Press, London and New York , (1971)
181. Jottrand, D., and Grunchard, F., Third Congress of the Eur. Fed, of Chem. Engrs., London , 74 (1962)
182. Jaganadharaju, G.I., and Rao Venkata, C., Indian Jl. of Techn. 3 , 201 (1965).

183. Coeuret, F., Le Goff, P., and Vergens, F., Proc. of the International Symposium on Fluidisation, 537, Eindhoven (1967).
184. Gupta, A.S., and Thodos, G., A.I.Ch.E. Jl., 9 ,751 (1963).
185. Ziegler, E.N., and Holmes, J.T., Chem. Eng. Sci.
21 , 117 (1966)
186. Chu, J.C., Kalil, J., and Wetteroth, W.A., Chem. Eng. Progr.,
49 , 141 (1953)
187. Gamson, B.W., and Thodos, G., Trans. Am. Inst. Chem. Eng.,
38 , 1 (1943)
188. Mc Cune, L.K., and Wilhelm, R.H., Ind. Eng. Chem., 41 ,1124 (1949)
189. Fan, L.T., Yang, Y.C., and Wen, C.Y., A.I.Ch.E. Jl.,
6 , 482 (1960).
190. Riccetti, R.E., and Thodos, G., A.I.Ch.E. Jl., 7 , 442 (1961)
191. Petrovic, J.J., and Thodos, G., Can. J. of Chem. Eng.
46 , 2 (1968)
192. Richardson, J.F., and Bakhtiar, A.G., Trans. Inst. Chem. Eng.
36 , 283 (1958).
193. Chu, J.C., "Fluidisation" (Othmer, D.E., eds), New York ,1956
194. Thones, D., and Kramers, H., Chem. Eng. Sci., 8 , 271 (1958).
195. Richardson, J.F., and Szekely, J., Trans. Insts. Chem. Eng.
39 , 212 9(1961).
196. Gupta, S.A., and Thodos, G., Chem. Eng. Progr., 58 , 58 (1962).
197. Van Deempter, J.J., Chem. Eng. Sci. 13 , 143 (1961)
198. Lanneau , J.F., Trans. Inst. Chem. Eng. 38 ,125 (1960)
199. Mamuro, T., and Muchi, I., Intern. Chem. Eng.
5 , 732 (1965)
200. Muchi. I., Memories of the faculty of engineering,
Nagoya University, 17 , 79 (1965)

201. Kobayashi, H., Arai, F., Chiba, T., and Tanaki, Y.,
Kagaku Kogaku, 33 , 274 (1969)
202. Mireur, J.P., and Bischoff, K.B., A.I.Ch.E. Jl., 13 , 839 (1967)
203. Rowe, P.N., Chem. Eng. Progr. 60, 75 (1964)
204. Toor, F.D., and Calderbank, H.P., In "Proceedings of the International Symposium on Fluidisation" 373 , Netherlands University Press, Amsterdam (1967)
205. Partridge, B.A., and Rowe, P.N., Trans. Inst. Chem. Eng.,
44 , 335 (1966)
206. Mori, S., and Wen, C.Y., Paper presented at International Fluidisation Conference. Pacific Grove , III-5 (1975)
207. Chiba, T., and Kobayashi, H., Chem. Eng. Sci. 25 , 1375 (1970)
208. Mekewi, M., Ph. D. thesis, The City University , London 1977.
209. Papic, M., Jl. of Gas Chr., 6 , 493 (1966)
210. PYE UNICAM Technical Manual, Booklet 14 , 9 .
211. Ambrose, D., "Gas chromatography" , Buterworth , London , 1971
212. Hollins, O.L., Anal. Chem., 38 , 309 (1966).
213. Cross, R.A., Nature, 211 , 409 (1966)
214. Hollins, O L., and Haynes, W.V., " Gas Chromatography ",
Littlewood, A.B., Elsevier , 1967 .
215. Brunaer, S., Emmet, P., and Teller, E., J. Am. Chem. Soc.
60 , 309 (1938)
216. Brunaer, S., Deming, L.S., and Teller, E., J. Am. Chem. Soc.
62 , 1723 (1940) .
217. Brunaer, S., "The Adsorption of Gases and Vapours" v.1
Princeton University Press, New Jersey (1945).
218. Emmet, P.H., Advances in Colloid Sci. 1 , 1 (1942)
219. Emmet, P.H., and Brunaer, S., J. Am. Chem. Soc.
59 , 1553 (1937)

220. Brown, G.G., "Unit Operations" , J. Wiley & sons New York ,1957
221. Dev, , Project report , The City University, London, 1978 .
222. Iacovidies, A., Project report, The City University, London
1979 ,
223. Streatfield, R. E., Ph. D. thesis , The City University,
London , 1970 .
224. Mc Grath, L.,and Streatfield,R .E ., Trans. Inst. Chem. Eng.,
49 , 70 (1971)
225. Clark. G.M.,and Doyle, W.P., Spectrochim. Acta 22 ,1441 (1966)
226. Ykeda, Y., Chem. Eng. Tokyo , 34 , 1013 (1970)
227. Zenz, F.A., Hydrocarbon Processing , 46 , 171 (1967)
228. Bergougnou, M.A., A.I.Ch.E. ,Symposium Series , 70 ,7 (1971)
229. Godard, K.,and Richardson, J.F., In Pirie, "Fluidisation" ,
Trip. Chem. Eng. Conference, Mondreal ,114., Inst. Chem. Engrs.
London, 1968
230. Alferson, P.G.,and Doig, I.D., In "Chemica 70" , s1 ,117,
Butterworths and Inst. Chem. Engrs., 1970
231. Rowe, P.N.,Partridge, B.A.,and Yates, J.G. in Drinkenburg,A.H.H.,
eds, "Proceedings of the International Symposium on fluid-
disation", Eindhoven 1967 , p711 (Amsterdam: Netherlands
University Press)
232. Godard, K., and Richardson, J.F., Chem. Eng. Sci. 24 ,663 (1969)
233. Rowe, P.N., Chem. Eng. Sci., 24 , 415 (1969)
234. Baeyens, I.,and Geldart, D., "La Fluidisation et ses
Applications" , Toulouse 182, Societe Chimie Industrielle (1973)

235. Geldart, D., Powder Technol. , 1 , 335 (1967)
236. Gagbiostro, D.E., Ph. D. thesis , University of California ,1968
237. Margolis, L..a.,Malvarova,E.P.,and Roginskii, S.Z.,
Invest. Akad. Nauk S.S.S.R , Otdel. Khim. Nauk, 6 ,958 (1954)
238. Gilliland, E.R., and Knudsen, C.W., A.I.Ch.E. Symposium
Series, 67 ,168 (1971)
239. Skirrow, G.,and Williams, A., Proc. Roy. Soc. (London) ,
1962, A268,p537 .
240. Hay,J.,Knox, J.H.,and Turner, M.C., 10th Symposium on
Combustion, 331 (1965)
241. Godard, K.,and Richardson, J.F., Chem. Eng. Sci., 24 ,194 (1969)
242. Volk, W.,Johnson,C.A.,and Statler, H.H., Chem. Eng. Progr.,
58 , 44 (1962)
243. Klöpsch, H.,and Weinspach, P., Chem. Ing. Techn. 49 , 511 (1977)
244. Novosad, J.,Šmid, V.,and Šmid, J., Chem. Ing. Techn., 49 ,915 (1977)

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LIST OF SYMBOLS

a	Catalyst pellet size (equation II.1.8) , cm
a_1	Constant of bubble frequency relationship (equation II.4.26)
A_t	Cross sectional area of bed , cm^2
b_1	Constant of bubble frequency relationship (equation II.4.26)
c_b	Gas concentration in the bubble phase
c_e	Exit gas concentration
c_i	Inlet gas concentration
c_p	Gas concentration in the particulate phase
d_p	Particle diameter , cm
$\bar{d}_p$	Average particle diameter , μm
D	Diffusion coefficient , $\text{cm}^2 \text{sec}^{-1}$
D_{12}	Diffusion coefficient for bulk diffusion of species 1 in a mixture of species 1 and 2 , $\text{cm}^2 \text{sec}^{-1}$
D_{1m}	Diffusion coefficient for bulk diffusion of species 1 in a multicomponent mixture , $\text{cm}^2 \text{sec}^{-1}$
$D_{1,\text{eff}}$	Effective diffusion coefficient for a porous solid under conditions of bulk or ordinary diffusion, based on total cross section of porous solid normal to direction of diffusion , $\text{cm}^2 \text{sec}^{-1}$
D_b	Calculated bubble diameter from the simple two phase model , cm
D_{bs}	Observed bubble eruption diameter , cm
D_K	Knudsen diffusion coefficient for a straight round pore , $\text{cm}^2 \text{sec}^{-1}$
E_g	Axial dispersion coefficient , g mole hr^{-1} or $\text{cm}^2 \text{sec}^{-1}$
F	Molar velocity , mole hr^{-1}

g	Acceleration due to the gravity , 980 cm sec^{-2}
g_c	Conversion factor , $980 \text{ g cm sec}^{-2} \text{ g}^{-1}$
G	Mass velocity , $\text{g sec}^{-1} \text{ cm}^{-2}$
Ga	Galileo number (equation II.4.6) , dimensionless
G_M	Molar velocity , M/G , $\text{g sec}^{-1} \text{ cm}^2$
H	Bed height , cm
H_{mf}	Bed height at minimum fluidisation , cm
K	Rate constant
K'	Number of reaction units , dimensionless
$K_1, K_2 \dots$	Rate constants
K_∞	First order rate constant (equation II.1.8) , sec^{-1}
$K_A, K_B \dots$	Adsorption coefficients
K_G	Overall mass transfer coefficient , cm sec^{-1}
K_{GP}	Mass transfer coefficient between fluid and particles , cm sec^{-1}
K_{GW}	Mass transfer coefficient between wall and bed , cm sec^{-1}
K_{iso}	Adsorption coefficient for isobutylene
K_{meth}	Adsorption coefficient for methacrolein
K_{ox}	Adsorption coefficient for oxygen
K_r	First order rate constant , $\text{mole g}^{-1} \text{ hr}^{-1}$
M	Molecular weight
$M_1, M_2 \dots$	Molecular weights
$\bar{M}$	Average molecular weight for diffusing species (equation II.1.8)
n_k	Number of transfer units (equation II.4.23)
N_{Fr}	Froude number , dimensionless
N_{Pe}	Peclet group , dimensionless
N_{Re}	Reynolds number , dimensionless

N_{Sc}	Schmidt number , dimensionless
N_{St}	Stanton number , dimensionless
P	Pressure , at or $g^* \text{ cm}^{-2}$
P_o	Initial pressure , at or $g^* \text{ cm}^{-2}$
$P_A, P_B, \dots$	Partial pressure for component A,B... , at or $g^* \text{ cm}^{-2}$
P_t	Total pressure in the reactor (equation II.1.1) , at
q	Total rate of interface gas exchange
T	Absolute temperature , $^{\circ}\text{K}$
T	Temperature of the reaction , $^{\circ}\text{C}$
T_c	Critical temperature , $^{\circ}\text{K}$
$\bar{u}$	Interstitial velocity , cm sec^{-1}
U	Superficial gas velocity , cm sec^{-1}
U_a	Absolute rise velocity of bubbles , cm sec^{-1}
U_b	Natural rise velocity of bubbles , cm sec^{-1}
U_i	Value of fluid velocity at voidage of unity (equation II.4.11) , cm sec^{-1}
U_{fs}	Minimum velocity at which the bed is fully supported , cm sec^{-1}
U_{mf}	Gas velocity at the point of minimum fluidisation , cm sec^{-1}
U_{mb}	Minimum bubbling velocity , cm sec^{-1}
U_o	Gas velocity through a bed of particles , cm sec^{-1}
U_t	Terminal free-falling velocity of particles (equation II.4.11) , cm sec^{-1}
V_b	Bubble volume , cm^3
V_l	Linear velocity (equation II.1.8) , cm sec^{-1}
W	Weight of particles , g
X	Fractional conversion , dimensionless
Y	Mole fraction , dimensionless
Y	Logarithmic mean fraction of inert nondiffusing component in a mixture (equation II.4.31)

Greek symbols

α	Dimensionless number defined in page 114
β	Dimensionless number defined in page 114
γ	Dimensionless number defined in page 115
δ	Dimensionless number defined in page 115
ΔP	Pressure drop , mm CCL ₄ or g* cm ⁻²
ϵ	Void fraction ,dimensionless
ϵ_{12}	Lennard-Jones force constant (equation II.1.5),dimensionless
ϵ_m	Void fraction for a packed bed , dimensionless
ϵ_{mf}	Void fraction at minimum fluidisation , dimensionless
θ	Porosity of the catalyst (equation II.1.9) cm ³ pores / cm ³ pellet
$\theta, \theta_A \dots$	Fraction of sites occupied by adsorbed gas,dimensionless
μ	Viscosity of the fluid , g sec ⁻¹ cm ⁻¹
ρ	Density , g cm ⁻³
ρ_s	Density of solids , g cm ⁻³
ρ_g	Density of gases , g cm ⁻³
σ	Variance ,dimensionless
σ_c	Variance for carbon , dimensionless
σ_o	Variance for oxygen , dimensionless
σ_E	Experimental variance , dimensionless
σ_F	Fitting variance ,dimensionless
σ_{12}	Lennard-Jones force constant (equation II.1.2), Å
τ_e	Radius of the pores (equation II.1.10) , cm
τ	Tortuosity factor,an empirical factor to correct for "turtuosity" and non uniformity of pores cross section
ϕ_s	Average sphericity of particles ,dimensionless
Ω_0	"Collision integral" (equation II.1.2) ,dimensionless