MODELLING OF THREE PHASE CATALYTIC REACTORS

A THESIS
SUBMITTED TO THE
UNIVERSITY OF POONA
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BY
RENGASWAMY JAGANATHAN

NATIONAL CHEMICAL LABORATORY
PUNE – 411 008 (INDIA)
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DEDICATED TO MY FATHER (LATE) SHRI J.RENGASWAMY.

CONTENTS

FORM - A

CERTIFIED that the work incorporated in thesis 'Modelling of Three Phase Catalytic Reactors' submitted by Shri R. Jaganathan was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

[R.V.Chaudhari]
Supervisor.

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[R. Jaganathan].

SUMMARY AND CONCLUSIONS

Three phase catalytic reactors are extensively used in several industrial scale chemical processes. Some of the well known examples are : hydrogenation and oxidation of organic compounds, hydroprocessing coal derived and petroleum oil, Fischer-Tropsch synthesis and polymerisation reactions. These reactions involve various steps such as gas-liquid mass transfer, liquid to particle mass transfer, intraparticle diffusion, adsorption, surface reaction and desorption of products. The relative rates of these processes under the operating conditions decide the overall rate of these multiphase reactions. Three phase reactors can be mainly divided into two categories: (a) slurry reactor in which the solid particles are suspended by means of mechanical or gas induced agitation and (b) fixed bed reactors where the catalyst is stationary with cocurrent or countercurrent flow of gas and liquid phase. The various design and modelling aspects of these reactors have been reviewed by Ramachandran and Chaudhari, (1983), and Shah (1979).

Most of the investigations in the literature relate to single reactions and simplified kinetics. However, many industrial processes involve multistep consectuvie and /or parallel reactions often represented by complex rate equations. The aim of the present work was to study the modelling of three phase slurry reactors with particular interest in complex reactions. The following reaction systems were investigated.

1. Hydrogenation of phenylacetylene to styrene and ethylbenzene over Pd/C catalyst.

2. Hydrogenation of butynediol to butenediol, butanediol and other side products over Pd/C catalyst.
3. Performance of a continuous bubble column slurry reactor as applied to the selective hydrogenation of butynediol to butenediol using Pd-Zn-$CaCO_3$ catalyst.

CHAPTER 1 : Introduction to Three Phase Reactors : Literature Survey

In this chapter a literature survey on the types of slurry reactors, analysis of three phase catalytic reactions and aspects of modelling of slurry reactors with simple and complex reaction systems has been presented. The objectives and scope of the present work are also outlined.

CHAPTER 2 : Effect of Catalyst Pretreatment in Phenylacetylene Over Pd/C Catalyst.

The hydrogenation of phenylacetylene was studied in a mechanically agitated autoclave using Pd/C catalyst. It is well known that the activity and selectivity of supported noble metal catalysts, are strongly dependent on the method of catalyst preparation, pretreatment conditions, type of support used and metal dispersion characteristics. There is very little information in the literature on the effect of catalyst pretreatment for hydrogenation reactions in the liquid phase.

In the present study the effect of catalyst pretreatment with phenylacetylene, styrene and hydrogen, as well as the conditions of pretreatment such as temperature and

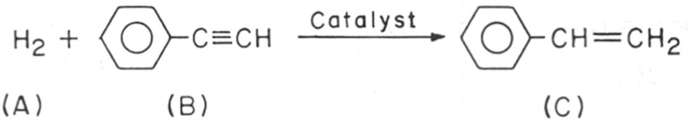
H_2 pressure, on the activity and selectivity was investigated and the important conclusions are given below:

1. Hydrogen pretreatment increases the activity for hydrogenation of phenylacetylene and styrene, but results in a decrease in selectivity of styrene.
2. Temperature of pretreatment showed no significant effect on the activity or selectivity.
3. The activity depended on the duration of hydrogen pretreatment and there exists a minimum time of pretreatment to achieve maximum activity.
4. Treatment with phenylacetylene showed no effect on the activity but resulted in a higher selectivity to styrene.
5. The pretreatment effects were found to be irreversible.

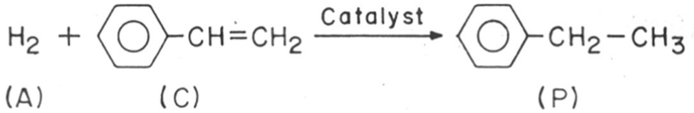
The present work implies that selectivity of hydrogenation of acetylenes to olefins can be achieved by pretreatment of the catalyst with acetylenes before exposure to H_2.

CHAPTER 3 : Kinetic Modelling of Complex Consecutive Reaction in a Slurry Reactor : Hydrogenation of Phenylacetylene.

In this chapter the kinetics of hydrogenation of phenylacetylene to styrene and ethylbenzene using Pd/C catalyst has been presented. The reaction scheme is :



(i)



(ii)

The experiments were carried out in a mechanically agitated autoclave over a temperature range of 15-45°C. Effect of catalyst loading, H_2 pressure, concentrations of reactants and products on the rate of hydrogenation as well as the concentration profile in a batch reactor were investigated. The analysis of initial rates showed that the data were in kinetic regime for 0.1% Pd/C catalyst. For interpretation of the kinetics, the observed concentration time data were directly used and the rate parameters evaluated using a simulation model for the batch reactor. It was found that the rate of hydrogenation was strongly inhibitted in the presence of phenylacetylene, while styrene and ethylbenzene showed negligible effects. Several rate models were examined and the following rate equation was found to represent the data satisfactorily.

$$R_A = \frac{w\,k_1\,AB + w\,k_2\,AC}{(1 + K_B\,B + K_c C)^2} \qquad \ldots(1)$$

where, A, B, and C are concentration and phenylacetylene, styrene and ethylbenzene respectively, kmol/m^3, w is the catalyst loading, kg/m^3, k_1 and k_2 are the rate constants for reactions (i) and (ii) respectively, (m^3/kg/s) (m^3/kmol), and K_B and K_C are the adsorption equilibrium constants for phenylacetylene and styrene respectively, m^3/kmol.

CHAPTER 4 : Kinetic Modelling of Hydrogenation of Butynediol using 0.2% Pd/C Catalyst in a Slurry Reactor.

Hydrogenation of butynediol over Pd/C catalyst was studied with the objective of identifying and characterising the various reaction products and kinetic modelling of this complex, consecutive/parallel reaction system.

The reaction products were separated by gas chromatographic and column chromatographic techniques and characterised by MS, NMR, IR and elemental analysis. The products identified and characterised were, butenediol butanediol, γ-hydroxy butyraldehyde n-butanol and acetal. The following reaction scheme explains the formation of these products :

$$A + B_3 \longrightarrow B_2 \tag{iii}$$

$$A + B_2 \longrightarrow B_1 \tag{iv}$$

$$B_2 \longrightarrow C_1 \tag{v}$$

$$C_1 + B_1 \longrightarrow C_2 \tag{vi}$$

$$2A + C_1 \longrightarrow C_3 \tag{vii}$$

where A, B_3, B_2, B_1, C_1, C_2 and C_3 represent, hydrogen, butynediol, butenediol, γ-hydroxylbutyraldehyde, acetal, and n-butanol respectively.

For kinetic modelling of the reaction system, the hydrogenation of butynediol was studied over 0.2% Pd/C catalyst. Several experiments were carried out in a high pressure slurry reactor over a temperature range 30-80°C. Effect of catalyst loading, H_2-pressure, initial butynediol concentration and agitation speed on the rates as well as concentration-time behaviour was studied. The initial rates were found to be first order dependent on catalyst loading and hydrogen pressure, while with respect to butynediol, an inhibition in the rate was observed. The kinetic parameters for the various reaction steps involved in this complex reactioin system were evaluated by simulation of the experimental concentration-time data, at various temperatures. The following rate equations were found to represent the kinetics of reaction steps (iii) to (vii).

$$r_1 = \frac{w\ k_1\ A^*}{(1 + K\ B_3^2)} \qquad \ldots(2)$$

$$r_2 = \frac{w\ k_2\ A^*\ B_2}{(1 + K\ B_3^2)} \qquad \ldots(3)$$

$$r_3 = \frac{w\ k_3\ B_2}{(1 + K\ B_3^2)} \qquad \ldots(4)$$

$$r_4 = k_4 \qquad \ldots(5)$$

$$r_5 = \frac{w\ k_5\ A^*}{(1 + K\ B_3^2)} \qquad \ldots(6)$$

The agreement between the experimental and predicted results was found to be within 6% error. The activation energies of reactions (iii) and (iv) were found to be 34.4 and 24.1 kJ/mol respectively.

CHAPTER 5 : Performance of a Continuous Bubble Column Slurry Reactor for Hydrogenation of Butynediol.

A mixing cell model has been developed for a continuous slurry reactor based on a rate equation applicable to the selective hydrogenation of butynediol to butenediol. In this model, the three phase slurry reactor is visualised as a number of backmixed reactors (N, Cells) in series. N=1 corresponds to the case of complete backmixing of the liquid, while $N > 20$ will correspond to the plug flow of liquid.

The conversion of the liquid phase reactant has been theoretically predicted, as a function of liquid phase mixing parameter N, gas and liquid velocity, H_2-pressure, catalyst loading and temperature. The suitability of literature correlations for gas-liquid mass transfer coefficients has also been discussed by comparison of the experimental results with model predictions. Theoretically, higher conversions of the liquid phase reactant were predicted for backmixed flow than for the plug flow, unlike the case where substrate inhibition is not observed.

Experiments were carried out in a continuous pressure bubble column reactor, 1 m long and 4.2×10^{-2} m diameter at various liquid and gas flow rates in a temperatures range

of 50-90°C. The experimental data agreed with the model predictions for $N = 1$, indicating a complete backmixing of the liquid phase for the case studied. The conversion of butynediol predicted using different literature correlations for gas-liquid mass transfer coefficients, (k_La) were found to vary widely. However, the prediction of the reactor performance using the k_La correlation of Akita and Yoshida, (1973) was found to agree well with the experimental data.

CHAPTER - 1

INTRODUCTION TO THREE PHASE REACTORS: A LITERATURE SURVEY

CHAPTER - 1

INTRODUCTION TO THREE PHASE REACTORS : A LITERATURE SURVEY

1.1 GENERAL BACKGROUND

Three-phase reactors have many diverse applications in chemical industries and particularly in catalytic processes. Some of the well known examples are : hydrogenation and oxidation of organic compounds, hydroprocessing of coal derived and petroleum oils, Fischer-Tropsch synthesis and polymerisation reactions. Due to the presence of three phases, the problem of reactor design is often important to achieve effective heat and mass transfer as well as a mixing pattern favourable to the particular process. Three phase reactors can be mainly divided into two categories (a) slurry reactors in which the solid particles are suspended by means of mechanical or gas induced agitation and (b) fixed bed reactors wherein the catalyst is stationary with cocurrent or countercurrent flow of gas or liquid phases. The various design and modelling aspects of three phase reactors have been reviewed by Ramachandran and Chaudhari (1983) and Shah (1979). A rigorous treatment and analysis of three phase reactions for a generalised case has been described in a review by Chaudhari and Ramachandran (1980).

The slurry reactors have a number of advantages over other three phase reactors, such as trickle bed or packed bubble bed reactors and these are given below:

1) As small particle size of the catalyst can be used in a slurry reactor, the intraparticle diffusional resistance is less in comparison to that in a trickle or packed bubble bed reactor. The trickle bed reactors normally employ larger catalyst particle sizes at which the intraparticle diffusion may be significant.
2) The external mass transfer coefficients in slurry reactors are higher than in trickle or packed beds, which leads to better utilization of the catalyst.
3) Slurries have higher heat capacities and higher heat transfer coefficients. Due to this, temperature control of exothermic reactions is better in slurry reactors, and the formation of hot spots can be avoided. Slurry reactors are relatively safer for reactions with temperature runaway. The large liquid volume is also an advantage in maintaining isothermal conditions.
4) In trickle bed reactors, partial wetting of the catalyst surface may exist for a certain range of liquid flow rates, and in such cases the entire catalyst may not be utilised (Ramachandran and Smith, 1979). In slurry reactors, this problem is not encountered.
5) In view of the pelletizing difficulties and the high cost involved, slurry reactors may prove to be more useful in some cases.

In spite of these several advantages of slurry reactors, they pose some practical problems. The major problems are the difficulty in separating the catalyst from the products and handling of the slurry. Because of this, the application of slurry reactors in continuous processes has been limited.

While our understanding of the design of slurry reactors has been considerably advanced, most of the investigations in the literature relate to single reactions with simplified kinetics. Many important chemical processes involve multistep, consecutive or parallel reactions, often represented by complex rate forms. The aim of the present work was to study the modelling of three phase slurry reactors with particular reference to complex reactions. It is important to give careful attention to the reliability of the rate equations used for design purpose. This question has been addressed by experimental investigations of the following systems in a three phase slurry reactor.

1. Hydrogenation of phenylacetylene to styrene and ethylbenzene over Pd/C catalyst
2. Hydrogenation of butynediol to butenediol, butanediol and other side products, over Pd/C catalyst.

Some aspects of continuous reactor modelling have also been investigated, using selective hydrogenation of butynediol as a reaction system.

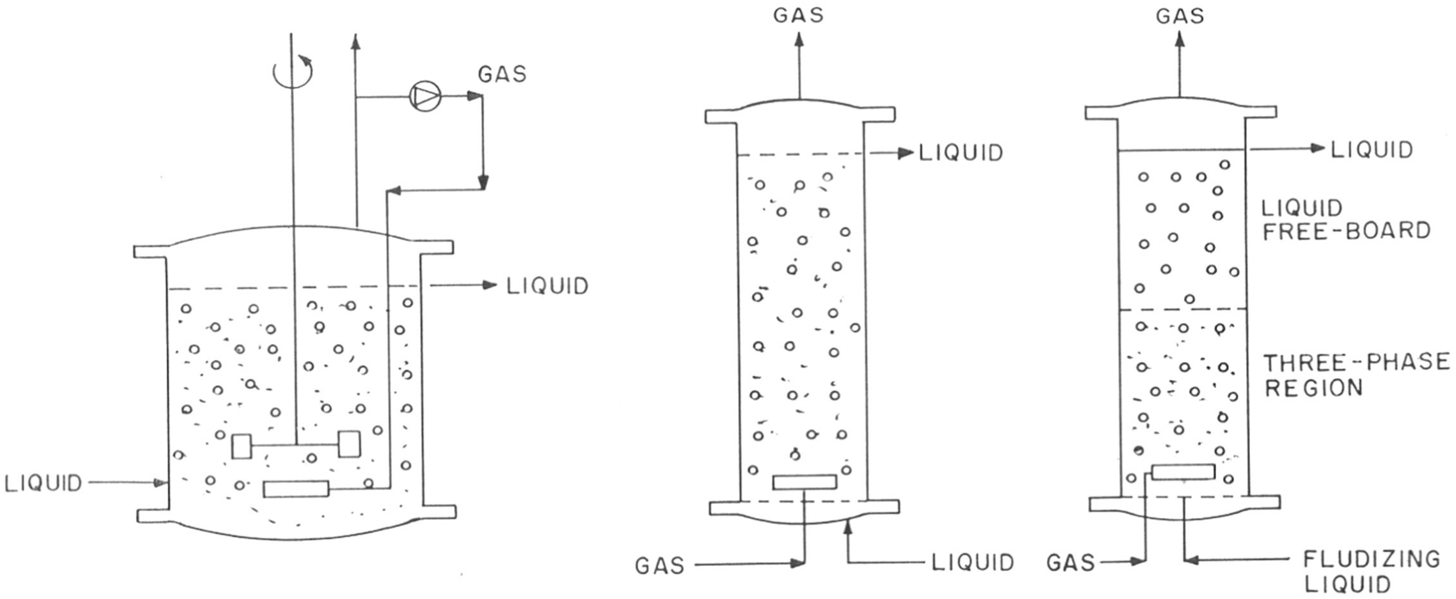
In the following sections a literature survey on the types of slurry reactors, analysis of three phase catalytic reactions and aspects of modelling of slurry reactors with simple and complex reaction systems have been presented.

1.2 TYPES OF SLURRY REACTORS

In slurry reactors, the catalyst particles are kept in suspension and depending on the mode of suspension the reactors are classified as, mechanically agitated slurry reactor, bubble column slurry reactor, three phase fluidized bed reactor and loop recycle reactor. Schematic of all these reactors are presented in Figures (1.1) and (1.2).

In mechanically agitated slurry reactors, the catalyst particles are suspended by means of mechanical agitation. Different types of impellers are used to achieve effective agitation. In bubble column slurry reactors, the solids are suspended by means of gas induced agitation and relatively small particles are used. In three phase fluidized bed reactors, the particles are suspended by the combined action of the gas bubble movement and liquid flow. The main difference between the fluidised bed and the bubble column slurry reactors is that in the former, the particles are suspended mainly due to the liquid flow and hence relatively larger particles can be used.

The mechanically agitated slurry reactor has higher heat and mass transfer rates compared to the bubble column reactors and the three phase fluidized bed reactors. As there are no moving parts, the mechanical design of the bubble column and the three phase fluidized bed reactors is simpler than the mechanically agitated slurry reactor, which requires suitable provision for stirrer seals. Catalyst attrition can be significant in the mechanically agitated reactors,



MECHANICALLY AGITATED REACTOR

BUBBLE COLUMN SLURRY REACTOR

THREE-PHASE FLUIDIZED BED REACTOR

FIGURE 1·1: DIFFERENT TYPES OF THREE-PHASE SLURRY REACTORS

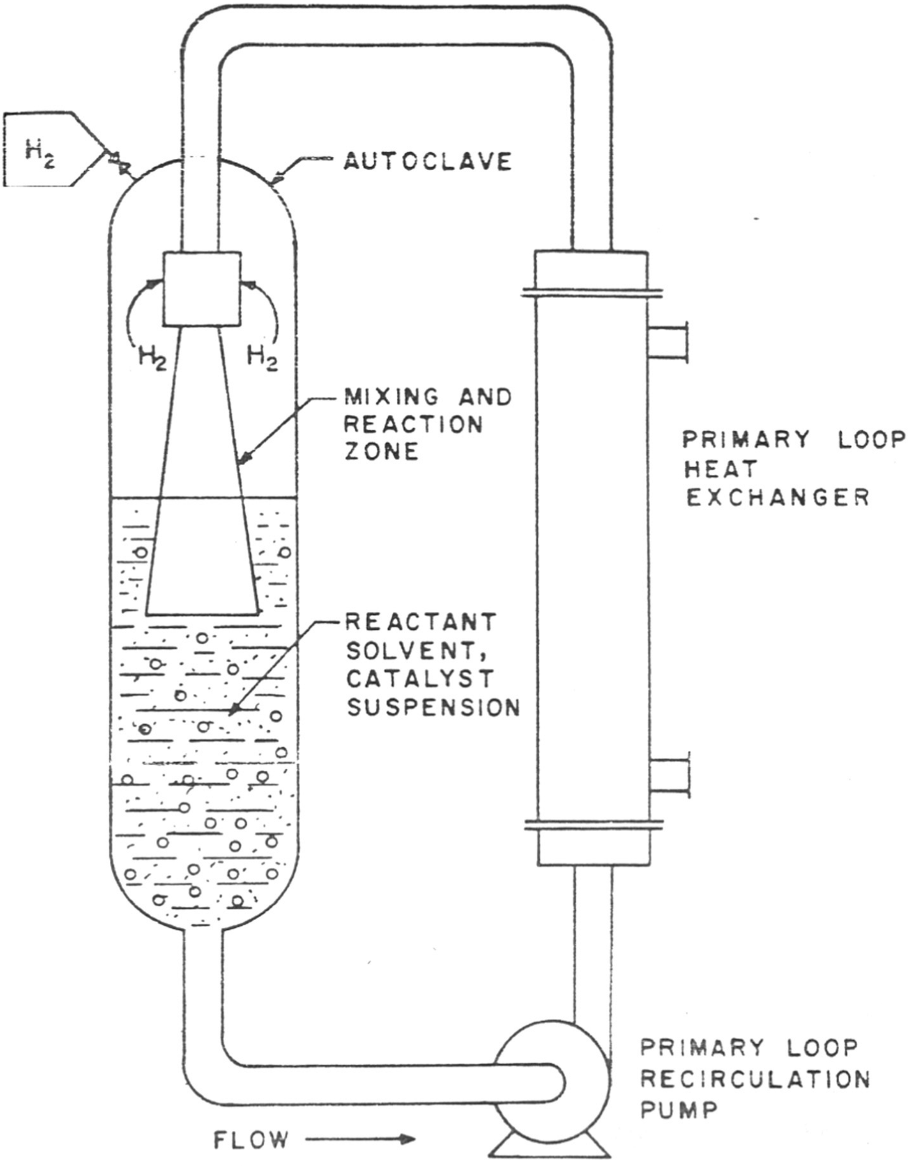


FIGURE 1-2 : SCHEMATIC OF A JET LOOP REACTOR than in the other types. Catalyst separation can also be a problem in the mechanically agitated and the bubble column slurry reactors, whereas it is relatively easy in the fluidized bed reactors where larger catalyst particles are used. The catalyst distribution is uniform in the mechanically agitated reactor while the bubble column and the fluidized bed reactor can have a non-uniform catalyst distribution.

The slurry reactors described above are frequently modified to achieve a certain specific objective like better heat and mass transfer rates, higher catalyst efficiency, better reactor performance, selectivity etc. These novel gas-liquid solid reactors are becoming important for both academic and industrial applications. Recently Chaudhari et al. (1986) have critically reviewed the design aspects of these reactors and their applications. Some examples of the novel reactors are : loop recycle reactors, multi stage slurry or packed bed reactors, column reactors with sieve trays or multiple agitators and horizontal packed bed reactors. The loop recycle reactor is the most important of these and is widely used in hydrogenation of castor oil and fatty acids and production of single cell protein by fermentation.

1.3 ANALYSIS OF SLURRY REACTORS : SINGLE REACTIONS

A simplest form of three phase catalytic reaction can be represented by the following reaction scheme:

$$A + \nu_B B \xrightarrow{\text{Catalyst}} \nu_E E \qquad (1.1)$$

The species A is generally a reactant present in the gas phase and B a non volatile reactant present in the liquid phase. ν_B and ν_E are the stochiometric coefficients for B and E respectively. A number of steps have to occur before species A and B can be converted to products by reaction at the catalyst surface.

1. Transport of A from bulk gas phase to the gas liquid interface,
2. Transport of A from gas-liquid interface to bulk liquid.
3. Transport of A and B from bulk liquid to the catalyst surface.
4. Intraparticle diffusion of the reactants in the pores of the catalyst.
5. Adsorption of the reactants on the active sites.
6. Surface reaction of A and B to yield products.

The concentration profile of species A as it diffuses from the bulk gas to the interior of the catalyst is shown in Figure(1.3). for a case wherein B is in large excess. In the case of reversible reactions and volatile products, additional steps such as desorption of products and transport from catalyst surface to the bulk liquid, and to bulk gas phase for volatile products, should also be taken into consideration.

Generally, not all these steps are important

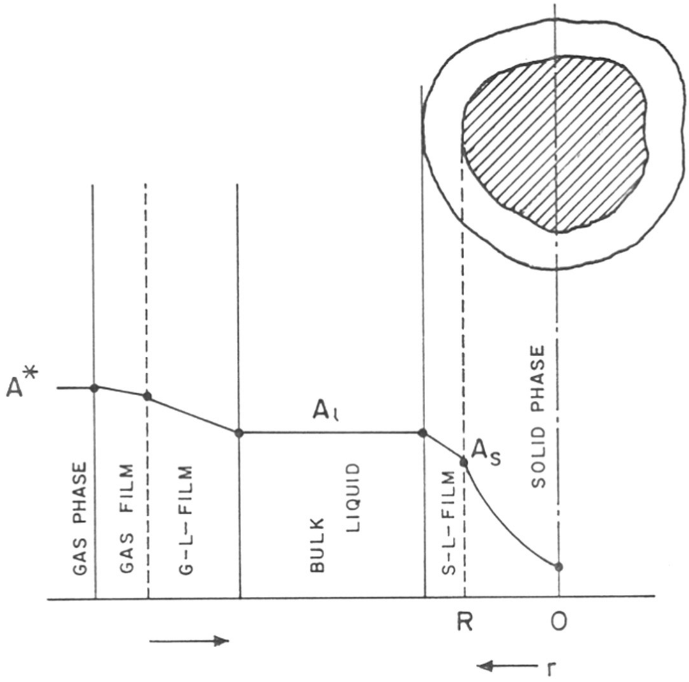


FIGURE 1·3 : CONCENTRATION PROFILE FOR A SLURRY CATALYSED REACTION in every reaction. For example, in most three phase reactors, gas side mass transfer resistance is small, if pure gas or high concentration of the gas phase reactant is used. In slurry reactors, the intraparticle diffusional resistance is negligible, as very fine catalyst particles are generally used. However, to interpret the laboratory data correctly and apply them to design an understanding of all the transport steps is essential.

1.3.1 Overall Effectiveness Factor

The concept of an overall effectiveness factor is useful in simplifying the calculation of the rate of chemical reaction in a slurry reactor. Ramachandran and Chaudhari (1979) defined the overall effectiveness factor as actual rate of reaction divided by the rate in the absence of diffusional resistances and based on inlet gas concentration.

$$\eta = \frac{R_A}{w\,\Omega(A^*)} \qquad (1.2)$$

where R_A is the observed rate of reaction, k mol/m^3/s

Ω is local rate of reaction per unit weight of the catalyst, kmol/g/s

w, catalyst loading per unit volume of the reactor, kg/m^3

and A^*, concentration of A in the liquid in equilibrium with the gas, kmol/m^3

For mth order reaction, η is defined as

$$\eta = \frac{R_A}{w\ k_m\ (A^*)^m} \tag{1.3}$$

Also, under steady state conditions, the overall rate of mass transfer of A, R_A, is given as (Chaudhari and Ramachandran, 1980).

$$R_A = M_A\ [A^* - A_s] \tag{1.4}$$

with

$$M_A = \left[\frac{1}{(k_L\ a_B)} + \frac{1}{(k_s\ a_p)} \right]^{-1} \tag{1.5}$$

Equation (1.4) gives the total rate of mass transfer from the gas phase to the catalyst surface. It includes gas to liquid and liquid to solid mass transfer contributions.

To obtain an analytical solution for η in terms of known parameters, the surface concentration, A_s has to be eliminated. This can be done by combining equation (1.3) and (1.4) to obtain

$$\eta = \frac{\left(1-\frac{\eta}{\sigma_A}\right)^{(m+1)/2}}{\phi_o} \left[\coth\left\{3\phi_o(1-\eta/\sigma_A)^{(m-1)/2}\right\} - \frac{1}{3\phi_o(1-\eta/\sigma_A)^{(m-1)/2}}\right] \tag{1.6}$$

where σ_A and ϕ_o are defined as

$$\sigma_A = \frac{A^* \quad M_A}{w\,\Omega(A^*)} \tag{1.7}$$

$$\phi_o = \frac{R}{3}\left[\frac{(m+1)\ \rho_p \quad k_m\ (A^*)^{m-1}}{2 \quad D_e}\right]^{0.5} \tag{1.8}$$

Chaudhari and Ramachandran (1980) have also developed expressions for the overall effectiveness factor for zero order reaction, reversible reactions, L-H kinetics and reaction between two gaseous reactants.

1.3.2 Models for Semibatch Reactors

Semibatch reactors are generally operated such that, the gas flows continuously and there is no net flow of the liquid phase into or out of the reactor. Some of the examples of industrial semibatch slurry reactors are: hydrogenation of fatty oils, nitrocompounds, and butynediol to butanediol. In a semibatch slurry reactor, the concentration of the liquid reactant changes with time, and hence the relative contributions of reaction and mass transfer resistances also vary. The design problem is to predict the batch time of operation for a required conversion of the liquid reactant. Theoretical analysis of semibatch slurry reactors is presented by Ramachandran and Chaudhari, (1980 b, 1983) for (1,0) order, (1,1) order and also general m, n th order kinetics. The equations for batch time for (1,0) and (1,1) order kinetics are :

(1,0) Order Reaction

$$t_B = \frac{Bl_i \; X_B}{\gamma \; A^*} \left[\frac{1}{K_L a_B} + \frac{1}{k_s \; a_p} + \frac{1}{\eta_c \; w k_1} \right] \qquad (1.9)$$

where

$$\eta_c = \frac{1}{\phi} \left[\mathrm{Coth} \; (3 \phi - \frac{1}{3\phi}) \right] \qquad (1.10)$$

and

$$\phi = \frac{R}{3} \left[\frac{\rho_p \; k_1}{D_e} \right]^{1/2} \qquad (1.11)$$

(1,1) Order Reaction

$$t_B = \frac{B_{1i} \; X_B}{\gamma \; A^*} \left[\frac{1}{K_L a_B} + \frac{1}{k_s \; a_p} \right] + \frac{B_{1i} \; R^2 \; p \; I}{3A^* \; w \; D_e} \qquad (1.12)$$

where,

$$I = \frac{2}{\phi_i^2} \; \ln \left[\frac{\phi_i \; \mathrm{Cosh} \; \phi_i - \mathrm{Sinh} \; \phi_i}{\phi_i \sqrt{1 - X_B} \; \mathrm{Cosh} \; \phi_i \sqrt{1 - X_B} - \mathrm{Sinh} \phi_i \sqrt{1 - X_B}} \right] \qquad (1.13)$$

with

$$\phi_i = R \left[\frac{\rho_p \; k_{11} \; B_{1i}}{D_e} \right]^{1/2} \qquad (1.14)$$

Chaudhari and Ramachandran (1980) have also pointed out that the solubility of the gas phase reactant may change with change in the composition of the liquid phase. This will affect the batch time for a given conversion. Lemcoff (1977) has observed significant solubility changes for hydrogenation of acetone in a slurry reactor, while Komiyama and Smith (1975) reported that the solubility of O_2 is reduced with increasing product concentration in their study on SO_2 oxidation. Chaudhari and Ramachandran (1980) have derived equations for semibatch reactors incorporating the solubility changes.

1.3.3 High Pressure Batch Reactors

Batch autoclave reactors under pressure are commonly used for kinetic studies of three phase reactions. In a batch operation, the pressure of the gas phase reactant, concentrations of liquid phase reactant and products vary simultaneously as a function of time. Thus, in a single experiment, it is possible to vary the concentrations of all the species over a wide range. Therefore, the kinetics can be evaluated with a minimum number of experiments. For a reaction between a gas phase reactant A, and a liquid reactant, B, [equation (1.1)] the mass balance equations are:

$$- \frac{1}{R_g T} \frac{d P_g}{dt} = \frac{V_L}{V_g} w \Omega (P_g, B_l) \tag{1.15}$$

$$-\frac{dB_1}{dt} = \gamma w \Omega (P_g, B_1) \qquad (1.16)$$

From these equations the following relationship between B_1 and P_g can be obtained.

$$B_1 = B_{1i} - \frac{\gamma V_g}{V_L R_g T}(P_{gi} - P_g) = B_{1i} - \frac{1}{\alpha}(P_{gi} - P_g) \qquad (1.17)$$

Here, $\Omega(P_g, B_1)$ represents the rate of reaction depending on the kinetic model and mass transfer effects. By substituting the relation for B_1 in terms of P_g in equation (1.15), we get an expression only in terms of P_g. This equation can be solved for a given set of parameters to predict P_g vs. time data. Similarly, the kinetic parameters can be evaluated by fitting the experimental data with model predictions. In this approach, the direct observations of pressure drop vs. time can be used and hence is more accurate for evaluation of kinetic parameters. Chaudhari et al.(1985) have demonstrated this approach to evaluate kinetics and mass transfer parameters for the hydrogenation of butynetiol to butenediol.

1.3.4 Continuous Reactor Models

In continuous slurry reactors, in addition to the mass transfer and kinetic steps, the variation of the reactant concentration caused due to mixing of the various phases need to be considered. Goto and Smith (1978), Goto et al (1976) Ramachandran and Smith (1979) and Ramachandran and Chaudhari (1980 a) have described approaches to model continuous slurry reactors, and a review of these is presented in Chapter 5 (Section 5.2).

1.3.5 Homogeneous and Heterogeneous Reactions

In some situtations, reaction of A can occur homogeneously in the liquid phase (non-catalytic) and also on the solid catalyst. Some examples of this category are : hydration of propylene oxide and ethylene oxide to their respective glycols using ion exchange resin as catalyst, and chlorination of toluene using $FeCl_3$ as the catalyst. In such cases, the contribution of the homogeneous liquid phase reaction must also be considered while predicting the overall rate of reaction. For a first order reaction (both homogeneous and heterogeneous), the rate per unit volume of the slurry is then given by the following set of equations.

$$R_A = k_L a_B \; (A^* - A_l) \qquad (1.18)$$

$$= k_H A_l + k_s a_p \; (A_l - A_s) \qquad (1.19)$$

and

$$k_s \; a_p \; (A_l - A_s) = w \; k_1 \eta_c \; A_s \qquad (1.20)$$

where k_H is the rate constant for homogeneous reaction, s^{-1}, and η_c is the catalytic effectiveness factor, [see equation (1.10) and (1.11)]. Eliminating A_l and A_s, the following expression for the overall rate of reaction is obtained for the case when both homogeneous and heterogeneous reactions are involved.

$$R_A = A^* \left[\frac{1}{k_L a_B} + \frac{1}{k_H + k_s a_p [w k_1 \eta_c / (k_s a_p + w k_1 \eta_c\}} \right]^{-1} \qquad (1.21)$$

The above theory is valid when there is no appreciable homogeneous reaction of A in the gas-liquid film.

Jaganathan et al. (1984) studied the hydration of propylene oxide in a slurry reactor using ion exchange resin as a catalyst,and derived an expression for the overall effectiveness factor for this homogeneous-heterogeneous reaction.

1.3.6 Reactions with Small Catalyst Particles

Very small catalyst particles of the order of 5 μm are often used in industrial slurry reactors. For particles less than 40 μm the reaction may occur predominantly on the outer surface of the catalyst (Gorokhovatskii , 1972). This is because of the proportionately larger external area of the smaller catalyst particles compared to the internal area. Verghese et al. (1978) analysed the effectiveness factor as a function of external area of the catalyst (as a fraction of total area). This analysis should be incorporated in predicting the rate of reaction for small particles having low porosity and low internal surface area.

For a special case, wherein very fine catalyst particles are used in a slurry reactor, it is possible to have a situation in which a significant reaction of a dissolved gaseous reactant may occur in the liquid film near the gas-liquid interface. In this case, an enhancement in the gas absorption rate is expected to be observed. A requirement for this situation to exist is that the film thickness has to be very much greater than the particle diameter and the rate of reaction is fast enough to deplete the concentration of A in the gas-liquid film. For the case of a non-catalytic three phase reaction Ramachandran and Sharma (1969) have reported a mathematical analysis. The criteria under which the reaction in the film can be significant for a catalytic three phase reaction are discussed by Ramachandran and Chaudhari (1983).

1.4 ANALYSIS OF SLURRY REACTORS - COMPLEX REACTIONS:

Many industrial three phase catalytic reactions involve complex reaction schemes such as consecutive and parallel reactions or combinations thereof. In this section, a review has been made regarding the studies of complex reactions in three phase catalytic reactors.

The complex reactions generally encountered in three phase systems can be classified into the following main types.

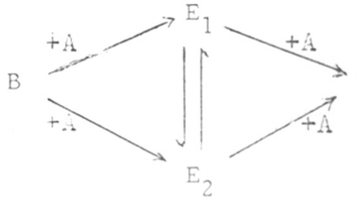
Type I : $A + B \rightarrow C$ (1.22)

$A + C \rightarrow P$ (1.23)

Type II : $A + B \rightarrow E$ (1.24)

$E + B \rightarrow P$ (1.25)

Type III :



(1.26)

Some of the important examples are given below:

Type I Scheme : Hydration of propylene oxide to mono and di-propylene glycol and hydrogenation of phenylacetylene.

Type II Scheme : Ethynylation of formaldehyde

Type III Scheme : Hydrogenation of unsaturated oils.

A summary of reaction engineering studies of the complex three phase reactions investigated in the literature is presented in Table (1.1).

Kawakami and Kusunoki (1976) investigated the effect of intraparticle diffusion on the yield of intermediate compound (styrene) in the hydrogenation of phenylacetylene using 0.5% Pt-Al_2O_3 catalyst in a stirred basket reactor. The intraparticle diffusion effects have been modelled theoretically and a numerical solution presented. They found that the yield of styrene is lower in the presence of intraparticle diffusion. Zwicky and Gut (1978) have studied the hydrogenation of o-cresol to 2-methyl cyclohexane to 2-methyl-cyclohexanol. This reaction follows type I scheme. They proposed rate equations for intrinsic kinetics represented by a mechanism in which hydrogen and reactants are adsorbed on different sites of the catalyst.

Cordova and Harriott (1975) and Tsuto et al.(1978) have studied hydrogenation of methyl linoleate using 1%

TABLE - 1.1

SUMMARY OF COMPLEX THREE-PHASE CATALYTIC REACTIONS INVESTIGATED

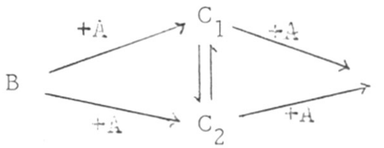
Type of Reaction	Reactants			Reactor type	Catalyst	Investigator
	A	B	C			
1	2	3	4	5	6	7
$A + B \rightarrow C$ $A + C \rightarrow P$	H_2	Phenylacetylene	Styrene	Slurry and Stirred basket	$Pt-Al_2O_3$	Kawakami and Kusunoki, (1976)
	H_2	Chlorobenzene	Benzene	Slurry	Pt-Carbon	Kawakami and Kusunoki, (1975).
	H_2	O-Cresol	2-methyl cyclohexanone	Slurry	Pd-Carbon	Zwicky and Gut,(1978) Kut et al. (1983).
	H_2	Methyl lineolate	Methyl oleate	Slurry	Pd-Carbon	Cordova and Harriot (1970). Tsuto et al. (1978).
	H_2	Butynediol	Butenediol	Tricklebed	Cu-Ni (supported)	Appleyard and Gartshore (1946).
	H_2	Butynediol	Butenediol	Slurry	$Pd-CaCO_3$	Fukuda and Kusama (1958)
	H_2	Acetylene	Ethylene	Slurry	Pd	Heck and Smith (1970)
$A + B \rightarrow C$ $C + B \rightarrow P$	C_2H_2	Formaldehyde	Propargyl alcohol	Tricklebed	Cu_2C_2 silicagel	Appleyard and Gartshore, (1946).
	C_2H_2	Formaldehyde	Propargyl alcohol	Slurry	Cu_2C_2 silicagel	Kale and Chaudhari

1.	2	3	4	5	6	7
Type III	H_2	Linoleicacid	Oleic acid (Cis and trans)	Slurry	Ni supported	Hashimoto et al.(1971). Gut et al.(1979).
$A + B \rightarrow E_1$ $A + C \rightarrow E_2$	H_2	Ethylene	Propylene (C)	Slurry	Pt-Carbon	Kawakami et al.(1976)
$B + C \rightarrow E_1$ $A + E_1 \rightarrow E_2$	H_2	Acetone (B) Aniline (C)	Schiff's (E_1) base	Slurry	Pd-Alumina	Kholer and Richarz (1986).

Pd/C catalyst. The kinetics of both steps were studied using rate data in regions where, only one of the steps dominated. They found the reaction to be first order with respect to hydrogen for first step and half order for the second step. Interestingly, they found the ratio of effective diffusivities D_{H_2}/D_L around 100. For such cases, the diffusion limitation to the liquid phase reactant is several times higher than that of the dissolved hydrogen. The unusual formation of final product in initial region of lower conversion has been explained on the basis of a rate model assuming non-equilibrium adsorption mechanism.

Hashimoto et al (1971) have studied the hydrogenation of unsaturated oils and proposed a detailed mechanism assuming that the catalyst surface is sparsely covered by adsorbed components. A detailed case study of oil hydrogenation based on this model has been discussed by Rase (1977).

Gut et al. (1979) studied the hydrogenation of sunflower seed oil using a nickel catalyst. The following simplified scheme was considered to interpret the kinetic data.



(1.27)

An interesting case of a parallel hydrogenation of ethylene and propylene was studied by Kawakami et al.(1976). The reaction was found to be controlled by mass transfer of olefins and the selectivity was determined by the ratio of the mass transfer rates of olefins.

Kut et al. (1983) developed L-H models for the hydrogenation of O-cresol and O-ethylphenol. They assumed adsorption of hydrogen and organic species on different active sites of the catalyst. Models were also developed, when surface reaction and transport of hydrogen or substrate control the kinetics and when surface kinetics and desorption of the intermediate product control the kinetics. In each case, simulated conversion time curves were compared with the experimental data. The effects of the reaction conditions on the selectivity of the intermediate product, as predicted by these models are also discussed in detail.

Recently Kohler and Richarz (1986) studied the reductive alkylation of aniline by acetone and hydrogen on a commercial palladium catalyst, supported on alumina, and proposed an L-H model. The external and internal mass transfer resistances were found to be negligible.

These studies indicate that the kinetics of complex reactions is often complicated due to the multi-component adsorption/desorption processes and simple power law models may not be adequate to explain the kinetic behaviour. Even in the range of conditions used in the slurry reactors, pore diffusion can be significant as indicated in some of the earlier studies. However, a detailed analysis of pore diffusion effects for L-H models and non isothermal reactions has not been attempted. Many of the hydrogenation reactions are exothermic in nature and this aspect needs further consideration. Also, there is in general a need to evolve an approach for kinetic modelling of complex three phase reactions. In this work, studies on some of these aspects will be undertaken.

1.5 OBJECTIVE AND SCOPE OF PRESENT WORK

As can be seen from the discussions in the previous section, complex reactions in three phase catalytic reactors involve several complications arising due to multi-component adsorption, desorption and mass transfer processes. Only a few attempts on detailed analysis of such systems have been made before. The main objective of this work was to investigate the various aspects of complex consecutive multiphase reactions that would be useful for design applications. In the first step, the intrinsic kinetics and approaches for developing suitable rate models will be studied. It would be ensured that in evaluating kinetic parameters, either rate data in kinetic regime only will be used or the effect of diffusional resistances will be accounted for. For this purpose, various known criteria will be used to evaluate the data. From the experimental concentration-time data, the selectivity of various products as a function of different operating variables will be evaluated. In order to achieve these objectives the following two reaction systems were chosen.

1. Hydrogenation of phenylacetylene to styrene and ethylbenzene over Pd/C catalyst.
2. Hydrogenation of butynediol to butenediol, butanediol and other products on Pd/C catalyst.

Hydrogenation of phenylacetylene to styrene and ethylbenzene was chosen as a model system, since it is known that for this system no side products are formed. On the other hand, hydrogenation of butynediol is known to form many reaction products involving combination of parallel and consecutive reaction schemes. The following aspects of these two systems are studied in the present work.

1. Effect of catalyst pretreatment on the activity and the selectivity of hydrogenation of phenylacetylene over Pd/C catalyst in an agitated slurry reactor.
2. Kinetic modelling of hydrogenation of phenylacetylene in a slurry reactor using Pd/C catalyst.
3. Product identification, characterisation and selectivity for hydrogenation of butynediol over Pd/C catalyst,
4. Kinetic modelling of hydrogenation of butynediol in an agitated slurry reactor using Pd/C catalyst,
5. Performance of a bubble column slurry reactor for the selective hydrogenation of butynediol using Pd-Zn-$CaCO_3$ catalyst.

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CHAPTER - 2

EFFECT OF CATALYST PRETREATMENT IN HYDROGENATION OF PHENYLACETYLENE OVER Pd/C CATALYST

CHAPTER - 2

EFFECT OF CATALYST PRETREATMENT IN HYDROGENATION OF PHENYLACETYLENE OVER Pd/C CATALYST

2.1 INTRODUCTION

Hydrogenation of acetylenic compounds is commonly encountered in many petrochemical processes. Some important examples are : hydrogenation of acetylene to ethylene, hydrogenation phenylacetylene to styrene, and hydrogenation of butynediol to butenediol and butanediol. Hydrogenation of acetylenic compounds is also important in the trace removal of acetylenic compounds in olefin streams.

In general, all Group VIII metal catalysts like Ni, Ru, Rh, Pt or Pd are suitable for hydrogenation of acetylenes. However, supported Pd catalysts are preferred in the selective hydrogenation of organic compounds and in particular alkynes, and dienes. It is well known that the activity and selectivity of these catalysts are strongly dependent on the method of catalyst preparation, pretreatment conditions, the type of support and the metal dispersion characteristics within the support. As one of the objectives of the present study was to investigate the kinetics of hydrogenation of phenylacetylene over Pd/C catalyst, it was thought important to undertstand the effect of catalyst pretreatment on its activity and selectivity before proceeding to investigate the intrinsic kinetics of this reaction.

2.2 LITERATURE SURVEY

It is believed, that under the conditions of hydrogenation over supported Pd catalysts, Pd-hydride is formed as an intermediate species, and the nature of the hydride species is responsible for the activity and selectivity of these catalysts. Generally, two types of hydrides, namely, α-Pd-H and β-Pd-H are formed (Pall and Menon, 1983). The pretreatment of Pd catalysts is expected to lead to either α or β hydride formation with different characteristics. The relevant literature on the pretreatment studies of Pd catalysts used for hydrogenation is presented below.

Borodzinski et al. (1976) studied hydrogenation of acetylene using, Pd wire (99.99%) and 0.3%, 1% and 5% Pd/γ-Al_2O_3 as catalysts and particularly investigated the α and β phase transformations in the catalyst using X-ray diffraction and small angle X-ray scattering techniques. They found that the β-Pd-H phase was less selective for ethylene formation, and α-~~Pd~~-H resulting from the decomposition of β-hydride phase, is more selective. In the case of a highly dispersed Pd catalyst, β-Pd-H was not formed and hence a higher selectivity of ethylene was achieved. They have also proposed a possible mechanism of hydrogenation of acetylene over Pd/γ-Al_2O_3 catalysts. Caga et al. (1971) studied the behaviour of PdO as a catalyst precursor for hydrogenation of phenylacetylene with and without prereduction of the PdO. They observed that the prereduction of PdO leads to a higher activity of hydrogenation and also different trends in the kinetic behaviour with respect to the catalyst weight, in comparison to the catalyst which is not prereduced. The X-ray diffraction study of the reduced PdO catalyst indicated the presence of PdO, Pd and β -Pd-H, the latter being produced rapidly from PdO and hydrogen.

Weiss et al. (1977) investigated the selective removal of traces of acetylene from ethylene, using deuterium, over 0.35% Pd, on Al_2O_3, carbon, and silica supports. They found that the catalyst activity did not change with the support, but the selectivity depended on the nature of the support.

Janko et al (1980), carried out the hydrogenation of acetylene over Pd films and single Pd crystals, recording the profiles of Pd and β-Pd-H phase. They found that the β -Pd-H phase was highly active but less selective towards ethylene formation.

Carturan et al.(1982), prepared several Pd metal dispersions on various supports, and studied the hydrogenation of phenylacetylene. The metal particle size distribution was studied by small angle and wide angle X-ray scattering. It was observed that the degree of dispersion was dependent on the nature of the support. The conclusion reached was that the selective hydrogenation of alkynes with Pd catalysts was favoured by very high metal dispersions, and low hydrogen pressures, good selectivity could be achieved when α -Pd-phase was present while the selectivity was less when β -Pd phase was present.

Moses et al. (1984) investigated the hydrogenation of acetylene in an artificial acetylene-ethylene-deuterium mixture on three types of Pd catalysts with 0.04% Pd on alumina. The effect of regeneration with oxygen, temperature, ethylene fouling, and deuterium was studied. The selectivity behaviour was explained on the basis of the formation of ethylidyne species, which aided the formation of alkanes, resulting in reduced selectivity.

Leonte et al. (1984) used transmission electron microscopy (TEM) and extended X-ray absorption fine structure (EXAFS) technique to characterize 0.5% Pd/Al_2O_3 catalyst, used in the hydrogenation of alkylnes and alkenes. The investigations were performed on samples of fresh catalyst, spent catalyst, regenerated catalyst, reduced catalyst, sintered catalyst, and sintered catalysts subjected to treatments in oxidizing and reducing atmospheres. The various treatments were found to change the redispersion and sintering of Pd particles in the support, affecting the activity and selectivity.

Weiss et al. (1984) hydrogenated ethylene streams containing 4000 ppm acetylene over 0.04% Pd on γ-Al_2O_3. They found that dispersing Pd to avoid formation of PdH phase almost eliminated the Pd catalyzed formation of ethane from acetylene. They proposed that the hydrogenation of ethylene proceeded separately on the support by means of "Spill Over" hydrogen atoms. Added copper reduced the rate of hydrogenation on the support, by providing desorption sites for spillover hydrogen. They also reported that traces of carbon monoxide, (50 ppm) almost stopped ethylene hydrogenation.

Foger and Jaeger (1985) studied the effect of chlorine treatment on the dispersion of Pt metal particles supported on silica and γ-alumina, using, XRD, TEM, and TPD techniques.

As can be seen from the literature survey, while some published information is available for the gas phase hydrogenation of acetylene, little is available for the liquid phase hydrogenations. Also, most of the work on catalyst pretreatment effects is mainly concerned with the effect of H_2, O_2 and CO treatment of Pd/C catalysts for acetylene hydrogenation. But, no information is available on the effect of acetylene pretreatment, and particularly on pretreatment effects in hydrogenation of phenylacetylene. Since, the problem of removal of traces of phenylacetylene from styrene is also of considerable importance, it was the objective of this work to systematically study the effect of pretreatment conditions on selectivity of Pd/C catalysts. The effect of catalyst pretreatment with phenylacetylene, styrene, and hydrogen, as well as the conditions of pretreatment, such as temperature and H_2 pressure on the activity and selectivity has been investigated.

2.3 EXPERIMENTAL

2.3.1 Reactor

All the hydrogenation experiments were carried out in a 6×10^{-4} m^3 (600 ml) capacity stirred pressure autoclave supplied by Ms.Parr Instrument Co., USA. The reactor was provided with a glass liner, automatic temperature control, heating mantle, variable stirrer speeds, sampling arrangement for gases and liquids, cooling coil, thermocouple and a pressure gauge. An intermediate vessel of 10^{-3}, m^3 capacity, with a two stage pressure regulator was used as H_2 reservoir in order to carry out the experiments at constant pressure. A schematic diagram of the experimental set up is shown in Figure (2.1), while the actual set up is shown in Figure (2.2) and (2.3). (The total volume of the reactor with the glass liner was 5.4×10^{-4}, m^3).

2.3.1 **Materials**

Phenylacetylene, supplied by Fluka AG, Switzerland was used. Stabilized styrene monomer was obtained from M/s.Sisco Research Laboratory, Bombay. Stabiliser was removed from styrene by treating it with 20% NaOH solution, followed by water washings to make it alkali free. Phenylacetylene and styrene were vacuum distilled and dried before use. The solvent ethanol was also distilled before use. Hydrogen gas with a stated purity $>$ 99% was used directly from cylinders supplied by M/s. Indian Oxygen Limited. Palladium chloride purchased from M/s. Loba Chemie, was used for the preparation of Pd/C catalysts. Activated carbon from M/s. High Purity Chemicals, New Delhi was used as a catalyst support. Before actual preparation of the catalyst, the carbon support was given on acid treatment to remove adsorbed impurities. About 0.5 kg of carbon was added

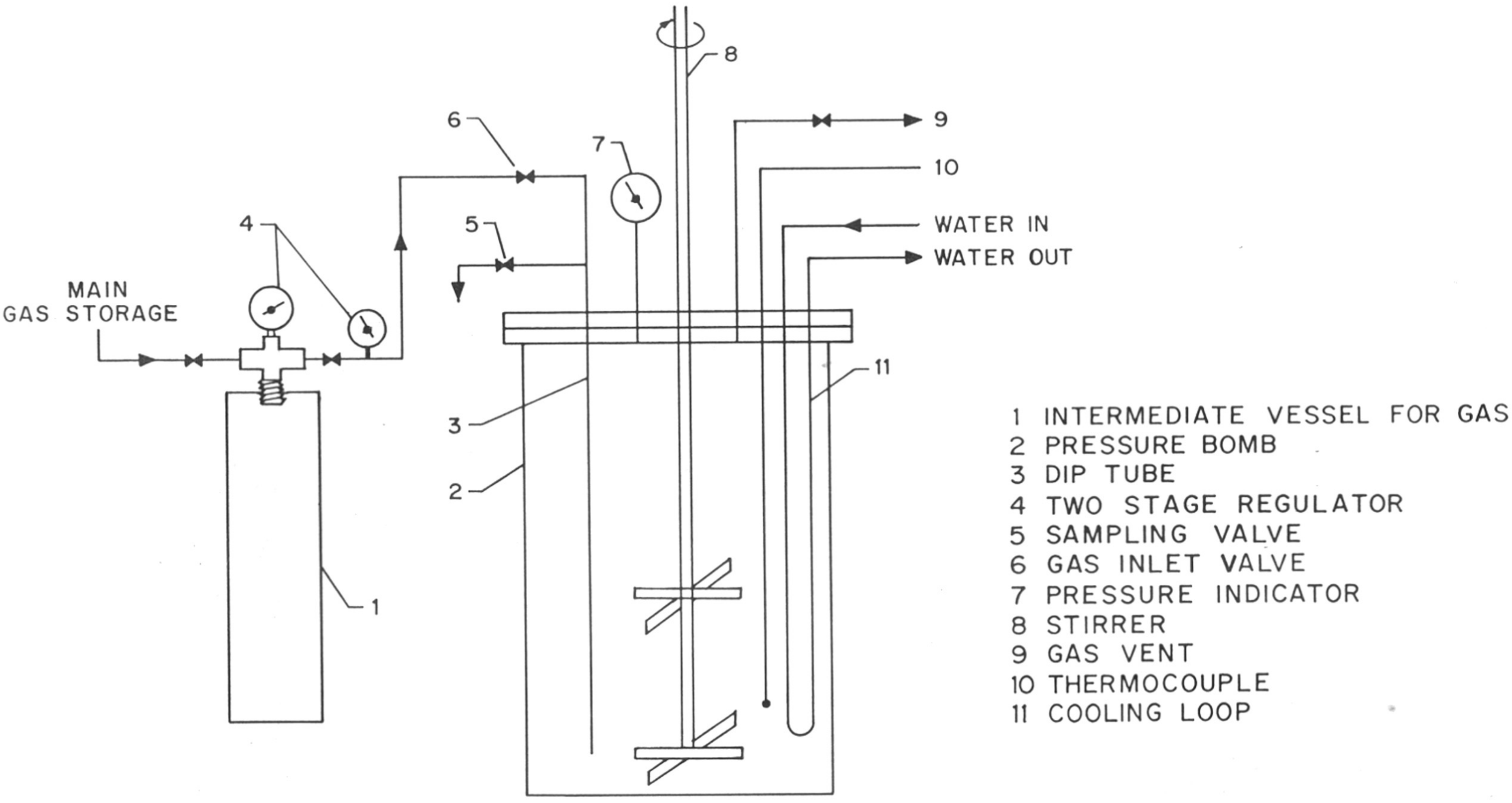

FIGURE 2·1: SCHEMATIC OF EXPERIMENTAL REACTOR SET-UP

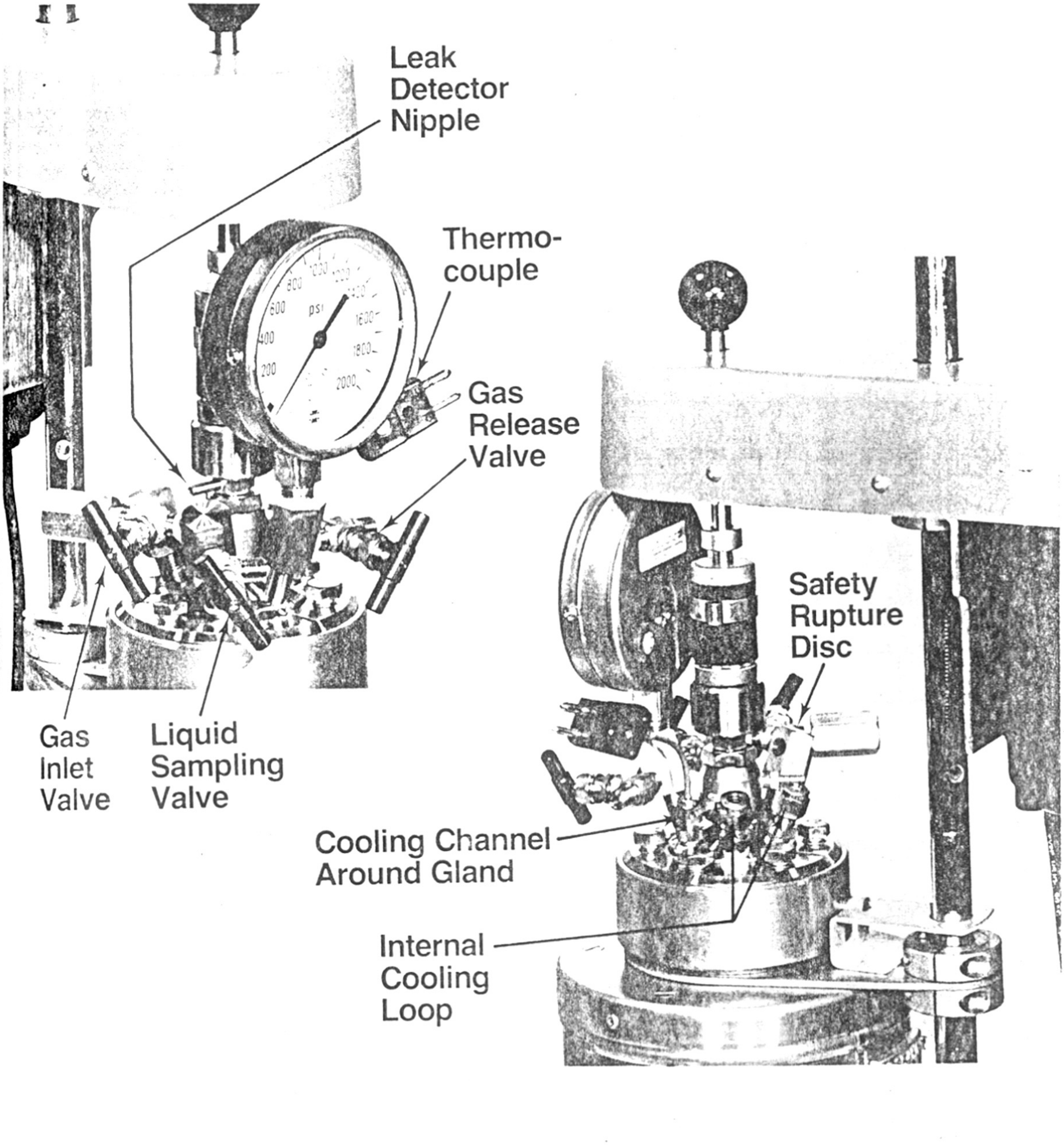

FIGURE 2·3 : EXPERIMENTAL SET-UP

to 10% nitric acid solution. The slurry was heated on steam bath for about 2-3 hours. Then it was cooled, filtered, and washed with distilled water till it was acid free. Filtered carbon was dried in an oven at 100-110°C and was used in the preparation of Pd/C catalysts.

2.3.3 **Preparation of the Catalyst**

The catalyst was prepared by a method described by Mozingo (1956). In a typical example, 2% Pd/C catalyst was prepared by dissolving 5g of palladium chloride in 10 ml of concentrated hydrochloric acid and 40 ml of distilled water. The mixture was warmed in steam bath till $PdCl_2$ completely dissolved. Then, 145 g of acid treated carbon was taken in a 2 litre beaker and about 1000 ml distilled water was added to form a slurry. The slurry was heated on water bath to 80°C with constant stirring for about an hour. To this, the $PdCl_2$ solution and 10 ml of 27% formaldehyde were added under stirring. The suspension was made alkaline (pH 8-10) using 30% NaOH solution. The slurry was stirred for some more time, then cooled, filtered and washed with distilled water till it was alkali free. The filtered catalyst was first dried in air at room temperature, and then under vacuum in an oven at 50°C. The dry catalyst was stored in a tightly stoppered bottle. In a similar way, catalysts with different Pd content were prepared by suitably changing the amount of $PdCl_2$ taken. The specifications of the catalyst are given in Table (2.1).

TABLE - 2.1

SPECIFICATION OF HYDROGENATION CATALYST Pd/C

Catalyst particle size (d_p)	:	10 micron
Particle density (ρ_p)	:	1.8 - 2.0 x 10^3,kg/m^3
Pore volume	:	4.5 x 10^{-4},m^3/kg
Porosity	:	0.90
Surface area	:	7.7 x 10^5, m^2/kg
Pd content (wt%)	:	2% and 0.1%

2.3.4 Experimental Procedure

In a typical hydrogenation experiment, known quantities of Pd/C catalyst and solvent ethanol were charged into the reactor. The contents were flushed with nitrogen and heated to a desired temperature. The phenylacetylene was charged and the reactor was flushed with hydrogen twice, and pressurised to a desired level. During an experiment, the pressure of hydrogen was maintained constant. Liquid samples(1 ml) were withdrawn at different time intervals and analysed for phenylacetylene, (PH) styrene (ST) and ethylbenzene. (EB) In all the experiments the liquid volume was 2.5 x 10^{-4}, m^3.

2.3.5 Analysis

The analysis was carried out by using DANI 3800 Gas chromatograph, coupled to a Spectraphysics 4100 computing integrator. A 3 m long column of 6 mm diameter packed with 5% carbowax 20M on chromosorb was used. The other conditions of the GC analysis were :

Column temperature	:	140°C
Detector (FID) temperature	:	350°C
Injector temperature	:	200°C
Carrier Gas (N_2) flow rate	:	25 cm^3/min.

A typical chromatograph of phenylacetylene hydrogenation products is shown in Figure (2.4). The quantitative analytical procedure was found to be within 3-4% of relative accuracy. In each experiment, concentration of phenylacetylene,

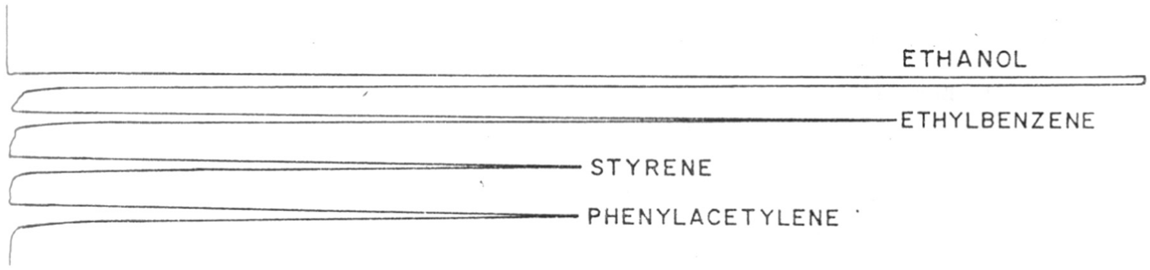

FIGURE 2·4: TYPICAL CHROMATOGRAPH OF PHENYLACETYLENE HYDROGENATION styrene and ethylbenzene were observed as a function of time.

2.4 RESULTS

The pretreatment experiments were carried out using 0.1% and 2.0% catalysts. It was important to ensure, that the catalyst does not deactivate during the course of a run. To confirm this, a few experiments on the reusability of the catalyst were carried out. The reusability of 0.1% Pd/C catalyst was studied by carrying out the hydrogenation of phenylacetylene in a batch reactor until both phenylacetylene and styrene were copmpletely consumed. At this stage, fresh phenylacetylene was added to the reactor and the hydrogenation continued. The concentration profiles are compared in Figure (2.5), which clearly indicates that the activity of the catalyst remains constant during a run. A similar observation was also made for 2.0% Pd/C catalyst. It was independently checked in this case that ethylbenzene had no effect on the activity and selectivity.

The concentration profiles in Figure (2.5) indicate that after phenylacetylene is completely consumed, styrene hydrogenation rate increases several fold indicating a strong influence of phenylacetylene on styrene hydrogenation kinetics. Generally, the maximum of the intermediate in a consecutive reaction coincides with the inflection point for the final product concentration. The deviation from this trend implies a case of complex adsorption mechanism. Another interesting feature noted was, that in the very beginning of the reaction,

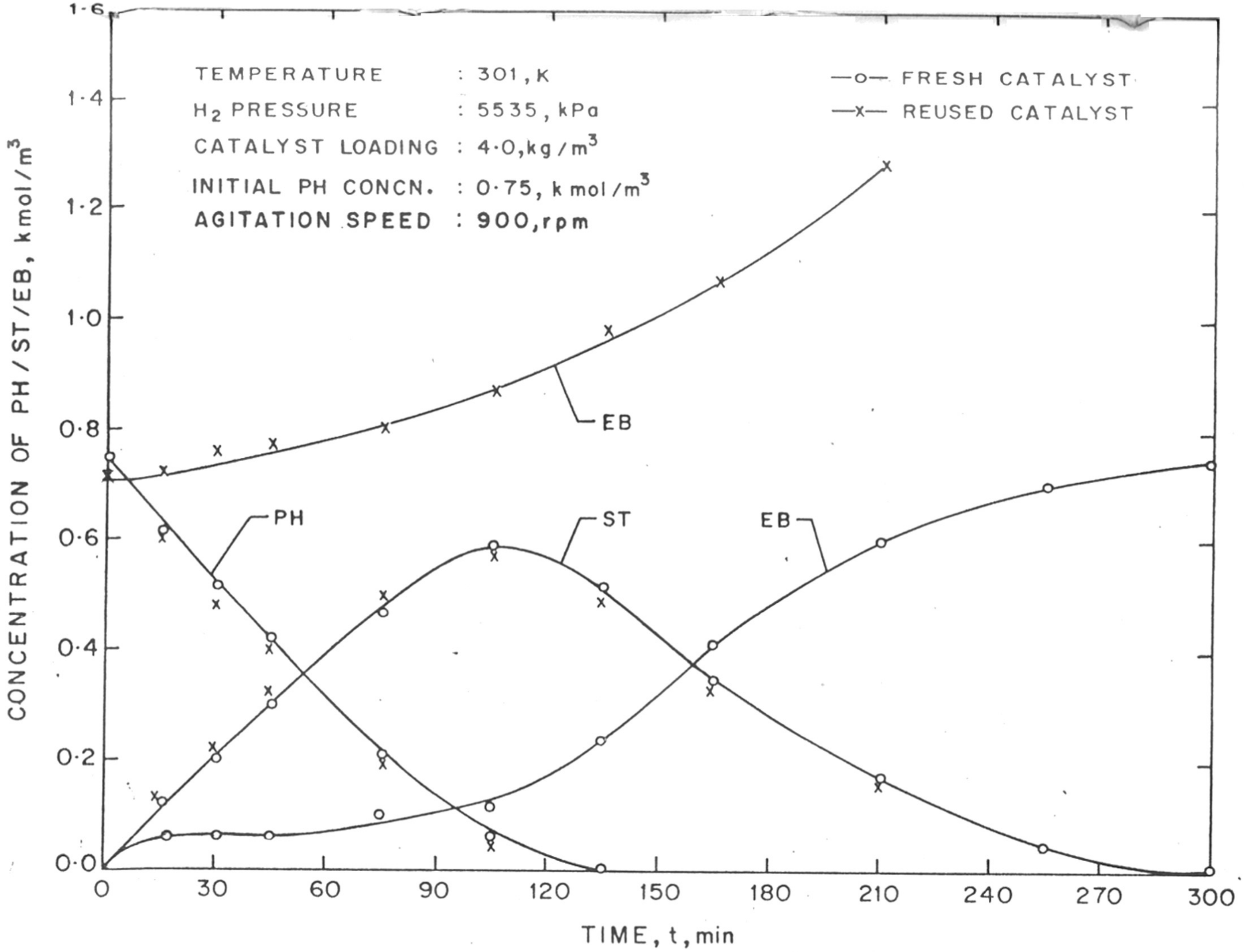

FIGURE 2·5 : CONCENTRATION PROFILES FOR A FRESH AND REUSED CATALYST (0·1 % Pd/C) a significant amount of ethylbenzene was formed only under certain conditions (see also Figure (2.9)), leading to lower initial selectivity. This behaviour, however, was found to be dependent on the pretreatment conditions and is disucssed later.

The experimental results on the effect of catalyst pretreatment have been expressed in terms of activity and selectivity of the catalysts. The activity, N, was expressed as moles of phenylacetylene converted per unit weight of Pd metal per hour. This was an average quantity calculated over a time duration required for complete conversion of phenylacetylene, and can be calculated from the following equation,

$$N = \frac{C_1 \times V_L}{t \times w'}$$

where,

C_1 = initial concentration of PH, mol/cm^3

V_L = volume of the reactants, cm^3

t = time required for complete conversion of PH, hr,

and

w' = weight of Pd in the catalyst, g

For example, with reference to Figure(2.5),

C_1 = 7.5×10^{-4} mol/cm^3

V_L = 250 cm^3

w' = 0.001 g

$t = 2.5 \text{ hr}$

$w' = 0.001 \text{ g}$

$$\text{Activity}, N = \frac{7.5 \times 10^{-4} \times 250}{2.5 \times 0.001}$$

$$= 75 \text{ mol/g.Pd/hr}$$

Similarly, the selectivity, S, was defined as the ratio of moles of styrene formed to the moles of phenylacetylene reacted.

$$S = \frac{\text{moles of Styrene formed}}{\text{moles of PH reacted.}}$$

With reference to Figure (3.5), after 30 minutes,

$$S = \frac{2 \times 10^{-4}}{(7.5 - 5.2) \times 10^{-4}} \simeq 0.87 \text{ or } 87\%$$

In order to compare the activity of pretreated catalysts with that of a fresh one, it is essential to test the catalysts under identical conditions. The following testing conditions were used in all the experiments, for catalyst pretreated under various conditions:

Hydrogen pressure : 5535, kPa

Temperature : 301, K

Catalyst loadings : 4.0, kg/m^3

Initial concentration of PH/ST : 0.75 $kmol/m^3$

2.4.1 Effect of H_2 Pretreatment

For H_2 pretreatment, the catalyst and solvent ethanol were stirred under hydrogen atmosphere for a certain duration. Then, phenylacetylene was charged under H_2 atmosphere, H_2 pressure adjusted to 5535 kPa and the experiment continued. The effect of pretreatment conditions such as duration of H_2 treatment, temperature and hydrogen pressure on activity and selectivity of the catalyst was observed. It was found that for hydrogenation of phenylacetylene, the pretreatment duration showed influence on the catalyst activity. Hence experiments were carried out by pretreating the catalyst with H_2 for 20, 60, 100, 120, and 240 minutes, and the results are shown in Figure (2.6), as a plot of activity vs. pretreatment time. It can be seen from this figure that the activity reaches a maximum value after a pretreatment time of nearly 100 minutes. The activity discussed in the following sections refers to the maximum activity. (pretreatment time : 120 min). The results for H_2 pretreatment studies for 0.1% Pd/C are presented in Table (2.2).

The effect of temperature of pretreatment with hydrogen was studied, in a temperature range 301-353 K, and the results are given in Table (2.2). It was observed that the temperature of pretreatment did not have any significant effect on the activity.

The pressure of H_2 pretreatment showed a significant effect on the activity. Increase in the pretreatment pressure resulted in an increase in the activity of the catalyst.

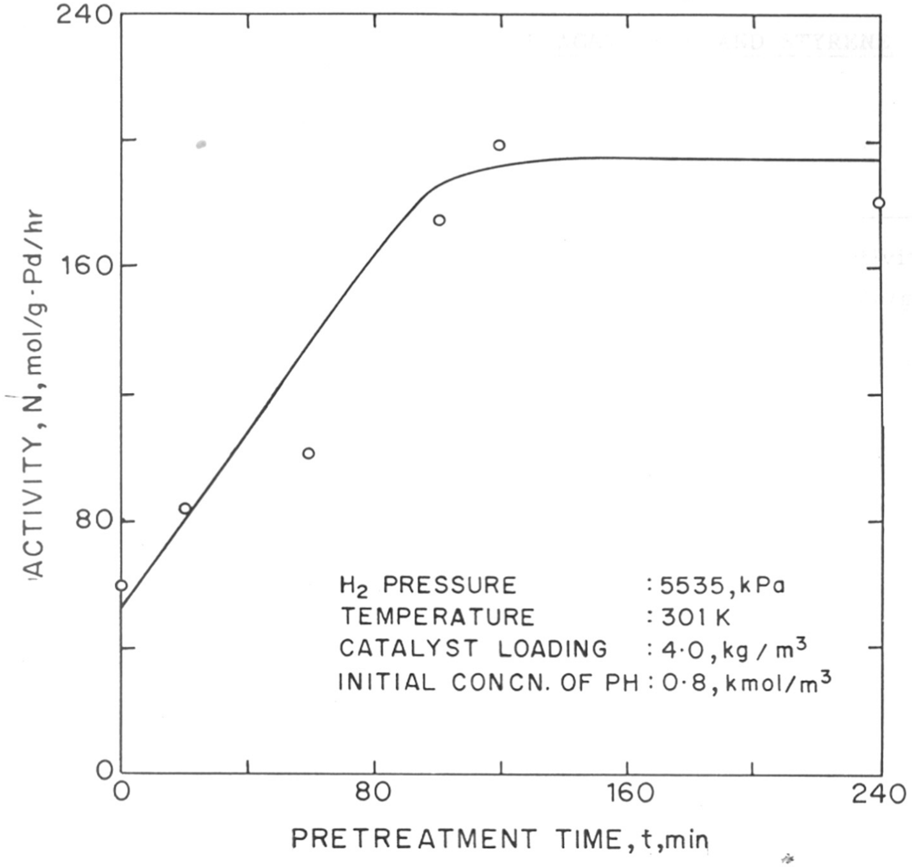

FIGURE 2·6 : EFFECT OF H_2 PRETREATMENT TIME ON THE ACTIVITY OF 0·1% Pd/C CATALYST

TABLE - 2.2

EFFECT OF H_2 PRETREATMENT ON ACTIVITY OF 0.1% Pd/C CATALYST FOR PHENYL ACETYLENE AND STYRENE HYDROGENATION

Sr.No.	Pretreatment Conditions			Activity, N molo/g Pd/hr
	Duration	Temperature K	H_2 pressure kPa	
A	Phenyl Acetylene Hydrogenation			
1.	0	-	-	59.3
2.	20	301	5535	84.0
3.	60	301	5535	100.0
4.	100	301	5535	175.0
5.	120	301	5535	200.0
6.	240	301	5535	180.0
7.	120	323	5535	192,0
8.	120	353	5535	210.0
9.	120	301	2814	190.0
10.	120	301	6556	799.0
11.	120	301	7576	1110.0
12.	120	301	9616	1145.0
B.	Styrene Hydrogenation			
13.	0	-	-	72.0
14.	120	301	5535	1600.0

Catalyst testing conditions H_2 pressure : 5535 kPa., Temp.:301K Catalyst loading : 4.0, kg/m^3, Initial concentration of phenylacetylene/styrene : 0.75, $kmol/m^3$

The results for the pressure effect are presented in Table (2.2) and Figure (2.7). In general, H_2 pretreatment leads to an increase in the hydrogenation activity by 2 to 20 folds depending on the pretreatment conditions.

Also, the activity of H_2 pretreated catalyst for hydrogenation of fresh styrene was studied. The activity for the fresh catalyst for styrene hydrogenation was 72 mol/g. Pd/hr, while that for H_2 pretreated catalyst was 1600 mol./g. Pd/hr indicating that H_2 pretreatment results in a drastic increase in the activity of the catalyst, for hydrogenation of styrene.

Effect of H_2 pretreatment on the selectivity of styrene in hydrogenation of phenylacetylene is shown in Figure (2.8). It was observed, that for the fresh catalyst, the selectivity of styrene vs. conversion of phenylacetylene shows a maxima. The initial lower styrene selectivity is mainly due to the formation of ethylbenzene in the very beginning of the reaction. Pretreatment of the catalyst with H_2 results in further lowering of the selectivity at all conversion levels. This suggests that hydrogen pretreatment leads to the formation of highly active sites for hydrogenation of alkylenes to alkanes.

2.4.2 **Effect of Phenylacetylene Pretreatment**

For studying the effect of phenylacetylene pretreatment on the activity of the catalyst, the fresh catalyst along with the solvent and a known quantity of phenylacetylene were stirred under N_2 atmosphere for two hours. Then,

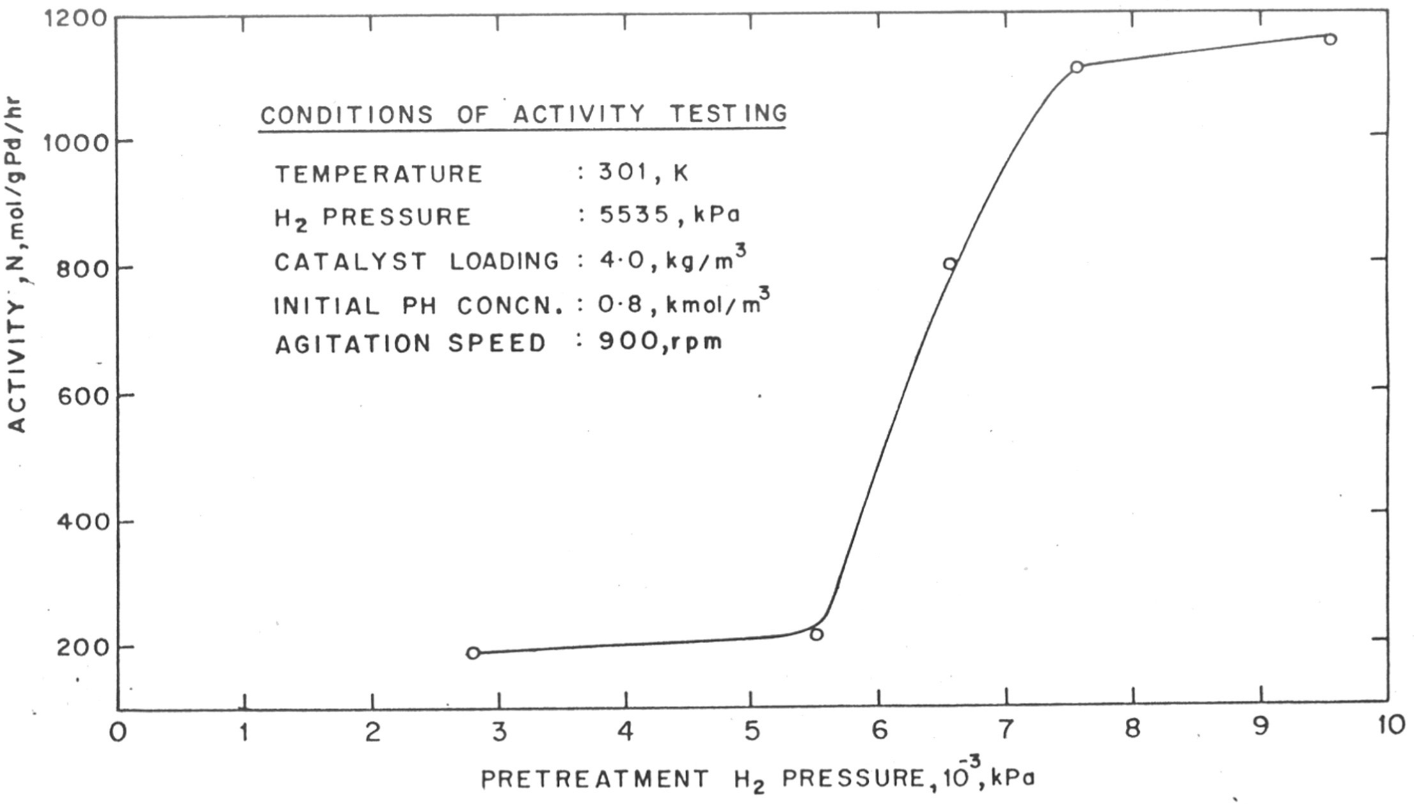

FIGURE 2·7: EFFECT OF H_2 TREATMENT PRESSURE ON THE ACTIVITY OF 0·1% Pd/C CATALYST

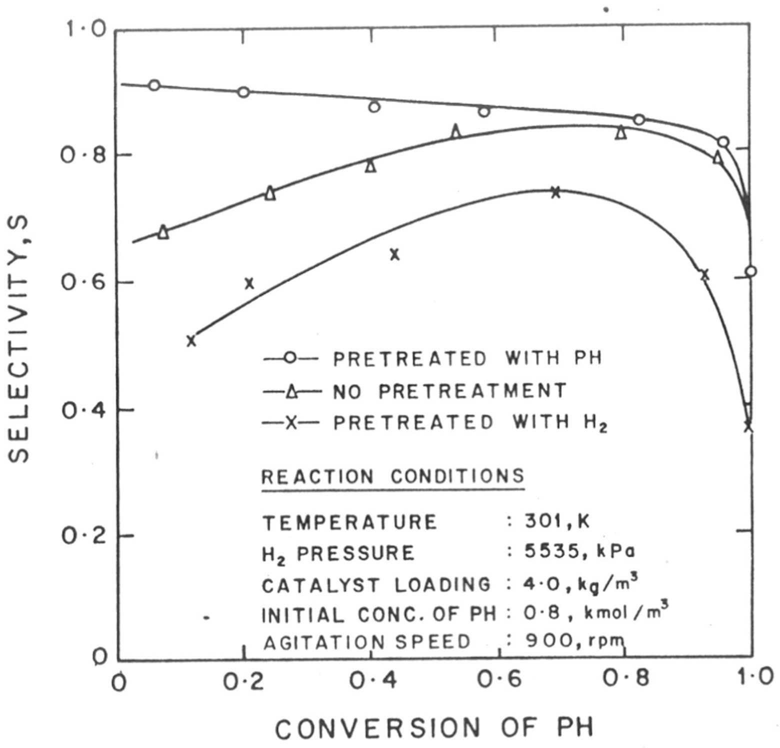

FIGURE 2·8 : EFFECT OF CATALYST PRETREATMENT ON STYRENE SELECTIVITY FOR 0·1% Pd/C CATALYST

H_2 introduced and the reaction continued under the test conditions. The results are compared with the experiments without pretreatment in Figure (2.9). It was observed that the average activity of hydrogenation was not influenced by the above pretreatment. However, there was an important difference in the nature of ethylbenzene concentration profile in the initial region, wherein, the formation of ethylbenzene was considerably reduced, when catalyst pretreated with phenylacetylene was used. This has important implication on the selectivity vs. conversion plot (see Figure 2.8), which suggests that the pretreatment with phenylacetylene improves the selectivity of styrene.

2.4.3 Reversibility of Pretreatment Effects

In order to check the reversibility of the pretreatment effects with respect to both H_2 and phenylacetylene, the following key experiments were carried out :

a) The experiment using the catalyst pretreated with phenylacetylene was carried out until both phenylacetylene and styrene were completely converted. Then the catalyst was treated with H_2 at 301, K, 5535 kPa, for two hours in the same reactor. After this phenylacetylene was added and the reaction carried out as usual.

b) The experiment using catalyst pretreated with H_2 was completed and then the catalyst was treated with phenylacetylene under N_2 atmosphere for two hours. This

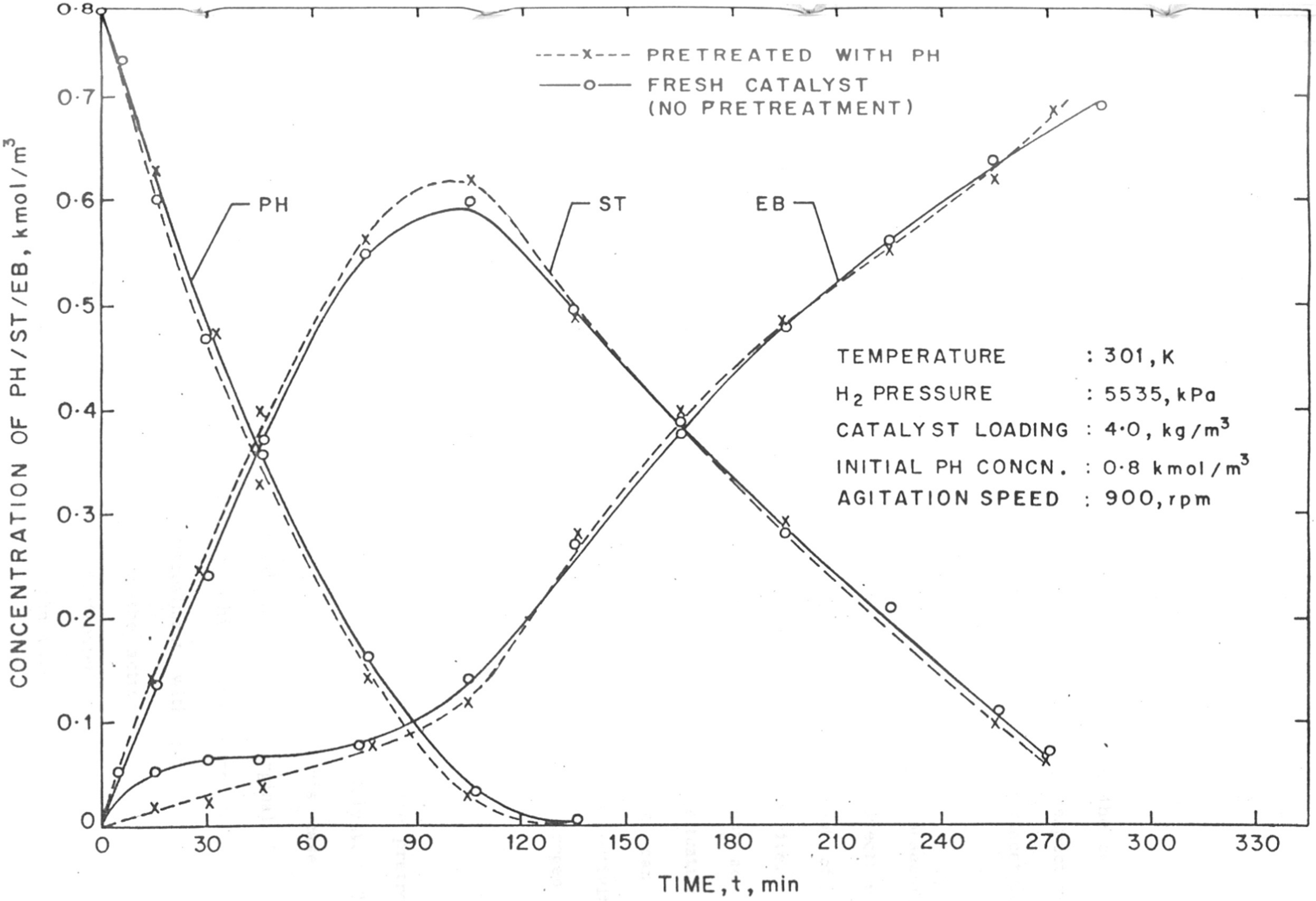

FIGURE 2·9: EFFECT OF PHENYLACETYLENE PRETREATMENT ON THE PERFORMANCE OF 0·1% Pd/C CATALYST was followed by the addition of H_2 to the required pressure and testing of the catalyst till the completion of the reaction.

In case (a), the activity, N, values for the consecutive experiments were 59 and 65 mol/g.Pd/hr, respectively indicating that the pretreatment effect of phenylacetylene was almost irreversible.

In case (b), the activities for the consecutive experiments were 200 and 185 mol/g.Pd/hr respectively. These observations suggest that the H_2 pretreatment of the fresh catalyst also leads to irreversible changes i.e. the sites activated by H_2 for alkane formation, do not adsorb PH. Also, it is implied that in a practical situation, pretreatment of the catalyst with phenyacetylene can be advantageously used to achieve higher styrene selectivity, while any exposure of the fresh catalyst to hydrogen is likely to lead to a poor selectivity.

2.4.4 Effect of Pd Content

Some experiments on H_2 and phenylacetylene pretreatment were also carried out using 2% Pd/C catalyst. The results are presented in Table (2.3). In this case, the pretreatment with H_2 resulted in only a marginal increase in the hydrogenation activity which was found to increase from 40 to 62. The pretreatment with phenylacetylene showed no significant effect on the activity (N = 37). The selectivity behaviour with pretreated catalysts is shown in Figure (2.10). It can be seen that for 2% Pd/C catalyst

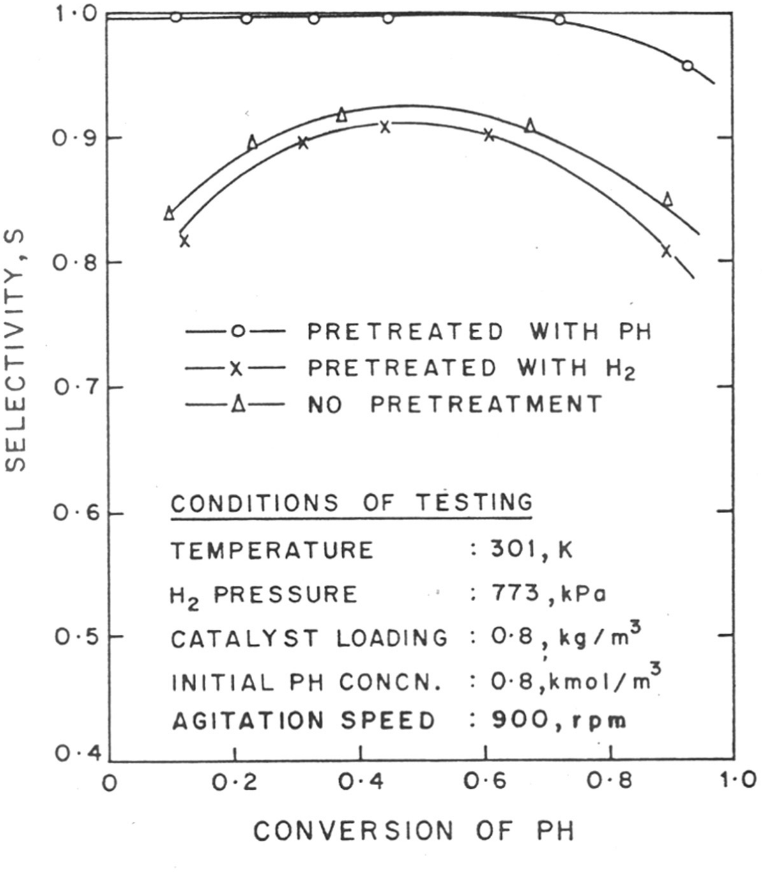

FIGURE 2·10 : EFFECT OF CATALYST PRETREATMENT ON STYRENE SELECTIVITY FOR 2% Pd/C CATALYST.

TABLE - 2.3

EFFECT OF H_2 AND PHENYL ACETYLENE PRETREATMENT ON ACTIVITY OF 2.0% Pd/C CATALYST

Type of pretreatment	Pretreatment conditions			Activity, N, mol/gPd/hr
	Duration, min	Temperature, K	H_2 pressure, kPa	
1. Fresh Catalyst (No pretreatment)	-	-	-	40
2. Hydrogen pretreatment	120	301	5535	62
3. Phenyl acetylene pretreatment	120	301	-	37

Catalyst testing Condicitions: H_2 pressure : 773, kPa;

Temperature 301 K; loading : 0.8, kg/m^3

Initial Phenylacetylene concentration : 0.8, kmol/m^3

also the pretreatment with phenylacetylene leads to almost 100% selectivity. The relatively mild effect of H_2 pretreatment on the activity of the 2% Pd/C catalyst may be due to the mass transfer limitation for hydrogen. It has been generally observed that for the consecutive reactions the starvation of H_2 on the surface, which can occur under conditions of mass transfer limitations, leads to higher selectivity of the intermediate species (Ramachandran and Chaudhari, 1983). Since, the fresh catalyst itself showed mass transfer limitations, as shown by the agitation speed effect (Table 2.4), an increased activity due to H_2 treatment is not likely to be observed for 2% Pd/C catalyst. The data for 0.1% Pd/C catalyst, was in kinetic regime as a change in the agitation speed showed no effect (See Table 2.4). This explains the difference in the pretreatment effect on the activity of the two catalysts.

2.5 DISCUSSION

The pretreatment studies in this work indicated some interesting features of Pd/C catalysed hydrogenation of phenylacetylene such as, (a) increase in activity of catalyst with H_2 pretreatment, (b) increase in selectivity, especially at low conversion levels, with phenylacetylene pretreatment, and (c) irreversibility of H_2 and phenylacetylene pretreatment effects. From previous studies (see Section 2.2), it is well known that the nature of the active species in supported Pd catalysts changes depending on the catalyst pretreatment

TABLE - 2.4

EFFECT OF AGITATION SPEED ON THE ACTIVITY OF FRESH CATALYSTS AT 301K

Catalyst	Catalyst loading kg/m^3	H_2 pressure kPa	PH Concn. $kmol/m^3$	Agitation speed rpm	Activity , N mol/g.Pd/hr
0.1% Pd/C	4.0	5535	0.75	400	58.5
				700	58.7
				900	59.3
2% Pd/C	0.80	773	0.8	400	14.7
				700	30.5
				900	40.0

and the metal dispersion characteristics, leading to changes in the activity and the selectivity. From analogous studies of hydrogenation of acetylene, it is believed that two types of Pd-hydride (α and β) complexes are formed during the hydrogenation, and also there is a possibility of continuous transition of β-Pd-H to α-Pd-H. It is also believed that α-sites are selective for olefin formation, while β-sites favour alkane formation. The substantial increase in the activity on H_2 pretreatment with a drop in styrene selectivity observed in this work can be due to a likely formation of β-Pd-H during H_2 pretreatment.

Another important observation made in this work was the irreversibility of the H_2 pretreatment effect. As pointed out earlier (Paal and Menon, 1983), the phenomena such as formation of α- or β-Pd hydrides, redispersion of Pd on the surface, and H_2 spillover of chemisorbed hydrogen, (particularly in catalysts with low Pd content) are likely to occur during pretreatment and hydrogenation reactions. One or more of these phenomena are likely to occur, simultaneously, resulting in changes in activity and selectivity of the Pd/C catalysts. The irreversible effect of H_2 pretreatment on hydrogenation activity may be attributed to a possible redispersion of Pd metal or formation of the active β-Pd-H species.

The observation that the catalyst first pretreated with phenylacetylene showed no effect of subsequent H_2 treatment on the activity indicated irreversibility of the phenylacetylene effect. This is likely to be due to the formation of relatively stable allyl type of complexes of Pd with phenylacetylene. The improved selectivity of styrene with phenylacetylene treated catalysts suggests that this treatment inhibits the formation of active β-Pd-H species responsible for alkane formation on exposure to hydrogen. This is similar to the already known effect of CO (McGown et al. 1978, Al-Ammar and Webb, 1979, Weiss et al. 1984) blocking certain active sites on Pd/C catalysts to achieve the selective hydrogenation of acetylene to ethylene. It is interesting to note (Figure 2.9) that with phenylacetylene pretreated catalyst the initial formation of ethylbenzene is reduced compared to the untreated and H_2 treated catalysts. This has direct implication in the operation of a commercial reactor, in which phenylacetylene pretreatment can be advantageously used to enhance the styrene selectivity. This is particularly attractive since phenylacetylene pretreatment effect is irreversible.

2.6 CONCLUSIONS

The effect of catalyst (0.1% Pd/C) pretreatment with H_2 and Phenylacetylene has been investigated for hydrogenation of phenylacetylene. It has been observed that H_2 pretreatment increases the activity for both hydrogenation of phenylacetylene and styrene but results in a decrease in the selectivity of styrene. Temperature of pretreatment showed no significant influence on the catalytic activity. Treatment with phenylacetylene showed no effect on the average hydrogenation activity but reduced the formation of ethylbenzene in the initial period, thus resulting in a higher selectivity. These effects were found to be irreversible.

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CHAPTER - 3

KINETIC MODELLING OF COMPLEX CONSECUTIVE REACTION IN A SLURRY REACTOR: HYDROGENATION OF PHENYLACETYLENE

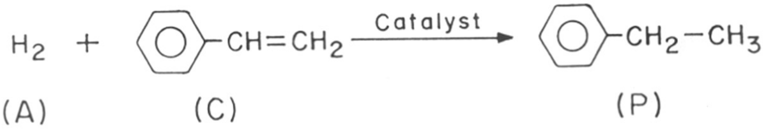
CHAPTER - 3

KINETIC MODELLING OF COMPLEX CONSECUTIVE REACTION IN A SLURRY REACTOR : HYDROGENATION OF PHENYLACETYLENE

3.1 INTRODUCTION

The objective of the present work was to study the kinetics of a consecutive reaction using a slurry reactor. For this purpose, the hydrogenation of phenylacetylene to styrene and ethylbenzene, was chosen as a model system. This reaction is an interesting example of a consecutive reaction, which is usually carried out in the presence of a catalyst in a slurry reactor. It is also industrially important in the removal of traces of phenylacetylene from styrene streams, which is used as a raw material for the manufacture of polystyrene. The stochiometric reactions are :

(i)



(ii)

Generally, this reaction is carried out using supported Ni, Pt, Ru or Pd catalysts. However, Pd catalysts are the most commonly used ones because of their high activity and selectivity. In the present work, hydrogenation of phenylacetylene using 0.1% Pd/C cataltst was studied, with the aim of developing a rate model representing the intrinsic kinetics.

3.2 LITERATURE SURVEY

The relevant literature on the hydrogenation of phenylacetylene is summarised in Table (3.1). Some of the important studies are discussed below.

Sheheglov et al. (1962) studied the selective hydrogenation of phenylacetylene in alcohol solution at 20,30 and 40°C, over skeletal Ni and Ni promoted with Ti catalysts. They found that the addition of pyridine did not affect the rate of triple bond hydrogenation, but decreased the hydrogenation of double bonds, resulting in an increased selectivity for the intermediate product (Styrene).

Sokol'skii et al. (1970) studied the hydrogenation of phenylacetylene in a flow system using tris (acetylacetonato) iron-triethylaluminium catalyst, and found, its activity decreased due to the accummulation of triphenylbenzene in the system. Increasing the molar ratio of Et_3Al to the Fe-acetylacetonate increased the activity.

Shutt and Winterbottom (1971) hydrogenated phenylacetylene, using reduced palladium oxide catalyst, in a vibrating flask. They studied the effect of catalyst

TABLE - 3.1

LITERATURE ON HYDROGENATION OF PHENYLACETYLENE

S.No.	Catalyst	Remarks	Investigators
1.	2.	3.	4.
1.	Ni and Ni promoted with Ti	Effect of pyridine on the rate of reaction. Kinetic curves and changes of catalyst potential are given	Sheheglov et al.(1962).
2.	$Pd/CaCO_3$	Influence of Hg and pyridine on hydrogenation of phenylacetylene in aq. alcoholic solution.	Sokol'skii and Beisekov (1968).
3.	tris(acetylacetobato) irontriethylaluminum	Catalyst activity study in phenylacetylene hydrogenation, changing molar ratio of Et_3Al to the Fe acetylacetonate in catalyst.	Sokol'skii et al.(1970).
4.	Pt/Al_2O_3	Selectivity study	Shohichi et al. (1972).
5.	Pt and Pd blacks	Effect of hydrogen pressure on the mechanism of hydrogenation of phenylacetylene.	Zhubanov and Maksimova (1975).

1.	2.	3.	4.
6.	0.5% Pt/Al_2O_3	Kinetic study. Role of mass transfer	Kawakami and Kusunoki (1976). (1976).
7.	Pd/Al_2O_3	L-H model proposed and aspects of mass transfer and selectivity studied.	Mochizuki and Matsui (1976). (1976),
8.	Rh_2O_3	Reaction was zero order with respect to phenylacetylene. Selectivity 65 - 78%.	Nurgozhaev and Omarkulov (1977),
9.	Ni/Al_2O_3	Selection of an optimum route for hydrogenation.	Sadykov and Zhubanov (197 (1978).
10.	Pt/C	Kinetics and mechanism was studied. Reaction order zero with respect to phenylacetylene. Increasing the temperature increased the selectivity. Activation energy 10 and 11 K cal/mol. for triple and double bond respectively.	Bizhanov et al. (1979).
11.	PdO	Effect of solvents and reaction conditions.	Shutt and Winterbottom (1971).
13.	Thin film of Pd	Kinetic study in a rotating disc reactor	White and Litt (1975)

1.	2.	3.	4.
14.	PdO	X-ray diffraction studies of the catalyst	Caga et al. (1976).
15.	Pd-$SnCl_2$ complex	Effect of solvents	Dorfman et al. (1976)
16.	Polymer bound Pd	Study of reaction mechanisms	Teresawa et al. (1979).
17.	Pd-Acetyl acetonate	Selectivity studies	Levkoskii et al. (1980).
18.	Pd-$BaSO_4$	Effect of poisons like Hg, pyridine and unithiol	Sokol'skii et al.(1982).
19.	Raney Ni	Electrocatalytic hydrogenation of PH	Bekenova et al. (1983).
20.	Raney Pt	Activity and selectivity of Pt-Cu alloy catalysts	Kuzora et al. (1983).
21.	Supported Pd,Pt and Pd-Pt alloy	Effect of Pt-Pd ratio on activity	Carturan et al.(1984).
22.	Polynuclear complex of Pd.	Kinetic study	Min'kov et al. (1984).
23.	Pd,Pt,Rh,Ni, Cu and Fe	Isotopic studies on reaction mechanism	Sokol'skii et al. (1984).
24.	$Pd(AcAc)_2$ PPh_3	Kinetic study	Mironova et al. (1985).

loading, frequency of vibration and various solvents (MeOH, EtOH, nPrOH, nBuOH) on the reaction rate and evaluated activation energies for phenylacetylene and styrene hydrogenation.

Shohichi et al. (1972) studied the kinetics of phenylacetylene hydrogenation using Pt catalysts supported on Al_2O_3, to evaluate the effect of diffusion on the selectivity of the reaction. They found the first and second step of the consecutive hydrogenation reaction to be zero order with respect to phenylacetylene and styrene concentration and 1st and 0.87 order with respect to H_2 concentration respectively. They also found that the selectivity of styrene decreased with increasing intra- and interparticle diffusional resistances.

Kawakami and Kusunoki (1976) investigated the effects of intraparticle diffusion on the liquid phase hydrogenation of phenylacetylene in a stirred basket reactor using 0.5% Pt/Al_2O_3 catalyst. They found that in the presence of intraparticle diffusion effects, the yield of styrene was lower when compared to the conditions under which the kinetics was controlling. Also, under these conditions the yield was found to increase with increasing phenylacetylene concentration and decreasing hydrogen concentration.

Mochizuki and Matsui (1976) investigated the hydrogenation of phenylacetylene (in a concentration range of 500 to 7000 ppm) in a packed bed reactor with cocurrent up-flow of gas and liquid. The catalyst used was 0.35 x 0.35 cm cylindrical pellets coated with palladium. They evaluated the effect of mass transfer resistances on selectivity and the overall rate of reaction and proposed a L-H model to explain the kinetics, assuming that the reaction occurred between the adsorbed phenylacetylene or styrene and dissociated hydrogen atoms competing for the same active sites.

Bizhanov et al. (1979) found that with Pt/C catalyst, the selectivity of styrene decreased with increase in hydrogen pressure, while increase in temperature increased the selectivity.

Carturan et al (1984), used palladium, platinum and palladium-platinum alloys as catalysts for the hydrogenation of phenylacetylene, and investigated the effect of platinum-palladium ratio, on catalytic activity and selectivity. They found that for hydrogenation of phenylacetylene to styrene, the specific activity of the alloy catalysts was lower than the sum of activity of individual palladium and platinum catalysts. The selectivity of Pd-Pt alloy catalyst was independent of the degree of dispersion.

From the literature survey presented here, it may noted that there are very few attempts to study the intrinsic kinetics of this reaction. A knowledge of the reaction kinetics is essential in designing of reactors, as well as understanding the mechanistic features of the reaction. Considering the complexities due to competitive adsorption of multicomponents in such consecutive reaction systems, it is important to study the overall kinetics of this reaction in detail. For supported Pd catalysts, which are more commonly used commercially, there is very little information on the kinetics of the reaction. Hence, the primary objective of this work was to study the intrinsic kinetics of this reaction using 0.1% Pd/C catalyst. A suitable rate equation will be proposed, that can be reliably used for reactor design purpose. Also, a detailed consideration to the consistancy of catalytic activity during a kinetic run has been given in obtaining intrinsic kinetic data. The effect of catalyst loading, agitation speed, H_2 pressure, initial phenylacetylene concentration and concentration of styrene and ethylbenzene, on the rate, as well as the overall concentration profile has been studied.

3.3 EXPERIMENTAL

The details of reactor, catalyst, reactants and analytical methods were the same as described in the previous chapter (see Section 2.3).

In a typical experiment, known quantities of Pd/C catalyst, phenylacetylene and solvent ethanol were charged into the reactor and stirred for one hour in order to pretreat the catalyst with phenylacetylene. The contents were flushed with nitrogen and then heated to a desired temperature. Then the reactor was flushed with hydrogen twice and pressurised to a desired level. The experiment was started by switching the stirrer on. During an experiment, the pressure of hydrogen in the reactor was maintained constant. Liquid samples, (approx. 1 ml) were withdrawn at different time intervals and analysed for phenylacetylene, styrene and ethylbenzene.

For calculating the rate of reaction at any given time, the concentration-time data observed under different conditions were fitted by a third degree polynomial as:

$$C_i = a_1 + b_1 t + c_1 t^2 + d_1 t^3 \qquad (3.1)$$

where, C_i is the concentration of i th component, kmol/m^3; t the time, sec. and a_1, b_1, c_1 and d_1 are constants. These constants were evaluated by linear regression procedures for different curves. The rate of reaction at any time can then be calculated as

$$r_i = \frac{dC_i}{dt} = b_1 + 2c_1 t + 3d_1 t^2 \qquad (3.2)$$

Initial rate of reaction r_{io} can then be calculated by substituting t = 0 in the above equation as

$$r_{io} = \left.\frac{dC_i}{dt}\right|_{t=0} = b_1 \qquad (3.3)$$

3.4 RESULTS AND DISCUSSION

3.4.1 Preliminary Experiments

Before proceeding for the kinetic study, experiments were carried out to examine the following aspects:

a) Material balance and reproducibility

b) Possibility of homogenous non - catalytic reactions.

It was found that the material balance of the liquid phase components was as per the stochiometry given by equation (i) and (ii) for all conversion levels. Also, no side products were detected in the range of conditions studied. A few experiments were repeated under identical conditions to check the reproducibility. It was found that the reproducibility was within 3% error. To study the possibility of a homogeneous reaction, phenylacetylene and ethanol were charged into the reactor, pressurised with hydrogen and the reaction continued. The liquid sample when analysed did not contain any styrene or ethylbenzene, indicating that no hydrogenation was taking place in the absence of Pd/C catalyst.

Initially some experiments were done using 2.0% Pd/C catalyst. The results showed significant external mass transfer resistance. The typical results of rate vs. agitation speed at two different catalyst loadings are shown in Figure (3.1). At higher catalyst loading, (1.6 kg/m^3), the rate shows a strong dependence on agitatioin speed indicating significance of gas-liquid mass transfer resistance. The results at lower catalyst loading (0.4 kg/m^3) indicate relatively mild influence of the agitation speed which suggests that the data are in the transition regime. With 0.1% Pd/C, the rate of hydrogenation was found to be independent of agitation speed and therefore the kinetic experiments were carried out using 0.1% Pd/C catalyst.

Some experiments on hydrogenation of styrene

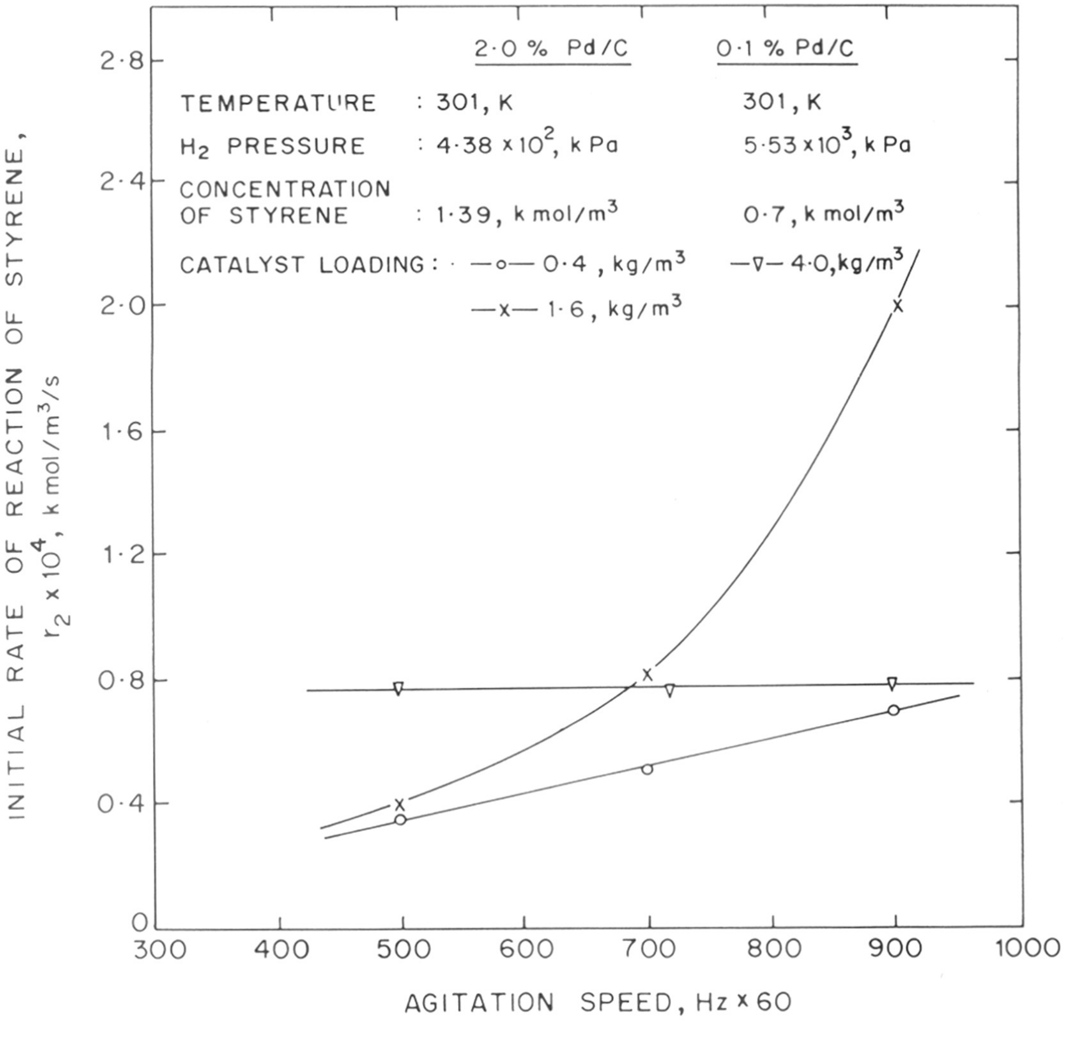


FIGURE 3·1: EFFECT OF AGITATION SPEED ON r_2

were also carried out independently. For this, styrene, catalyst, and solvent (ethanol) were charged into the autoclave, and pressurised with H_2 to a desired level, and the reaction continued. It was observed that, for a given set of conditions, the rate of hydrogenation of styrene during a consecutive reaction was slower by three times compared to the rate of hydrogenation of styrene studied independently. This can be due to catalyst deactivation or modification of the catalyst sites on exposure to phenylacetylene. To resolve this question, the following experiments were carried out.

(a) After both phenylacetylene and styrene were completely consumed in a run, fresh phenylacetylene was added to the reaction vessel and hydrogenation carried out.

(b) After both phenylacetylene and styrene were consumed, fresh styrene was added and reaction carried out.

(c) Styrene hydrogenation carried out with fresh catalyst.

The results of experiment (a) have already been discussed (see Section 2.4). The results shown in Figure (2.5) clearly indicate that the catalyst activity remains constant during the course of a run. The results of experiments (b) and (c) are shown in Figure (3.2). Styrene hydrogenation over the reused catalyst was found to proceed at comparable rates in the main parts of the curves with the original run (see curves A and B). However, styrene hydrogenation over a fresh catalyst, (not exposed before to phenylacetylene) proceeds at much faster rate (see curve C). These results conclude that the catalyst does not deactivate during a given experiment, and the lower

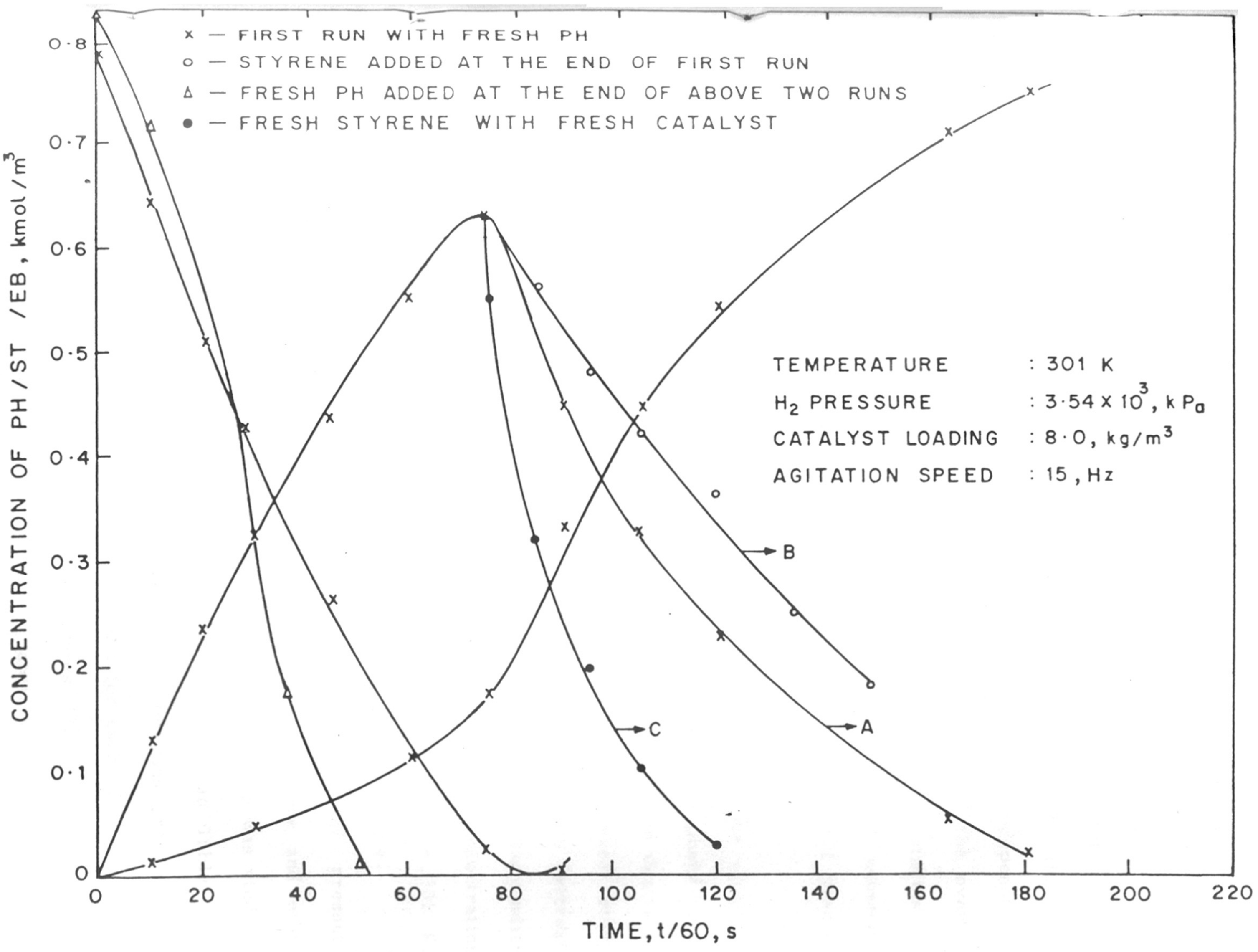


FIGURE 3·2: CATALYST ACTIVITY TEST

rate of styrene hydrogenation observed during a consecutive reaction compared to the independent hydrogenation is likely to be due to modification of the nature of the active sites on exposure to phenylacetylene. This suggests that the kinetics of styrene hydrogenation studied independently may not be useful in quantitative evaluation of the overall rate of a consecutive reaction. Therefore, in studies on such systems, rate from integral data obtained from consecutive reaction runs only can be useful for the purpose of precise kinetic modelling.

As already discussed in the previous chapter, (Section 2.4.2) pretreatment of the catalyst with phenylacetylene increases the selectivity to styrene, which is desirable in practical situations. Therefore, for the present study all the kinetic runs were carried out with catalysts pretreated with phenylacetylene under identical conditions. The conditions of pretreatment were: duration, 1 hour, concentration of phenylacetylene, 0.8 kmol/ m^3 and temperature, 301 K. The pretreatment was done under nitrogen atmosphere.

Effect of catalyst loading, partial pressure of H_2, concentration of phenylacetylene, styrene and ethyl benzene and temperature on the rate of reaction was studied. The range of parameters studied is given in Table (3.2). The concentration-time data for all the runs are presented in Appendix I. The typical result for each of the temperature studied, are shown in Figures (3.3) to (3.5). For each experiment, the initial rates were also calculated as described earlier. The general trends of the effect

TABLE - 3.2

RANGE OF PARAMETERS STUDIED FOR PHENYLACETYLENE HYDROGENATION USING 0.1 % Pd/C CATALYST

Catalyst Loading	: 4.0 - 20.0 kg/m^3
Agitation speed	: 5.0 - 15.0, Hz.
H_2 - Pressure	: 700 - 9600, kPa
Phenylacetylene concentration	: 0.15- 1.5, $kmol/m^3$
Temperature	: 288 - 318, K
Volume of liquid phase	: 2.5×10^{-4}, m^3

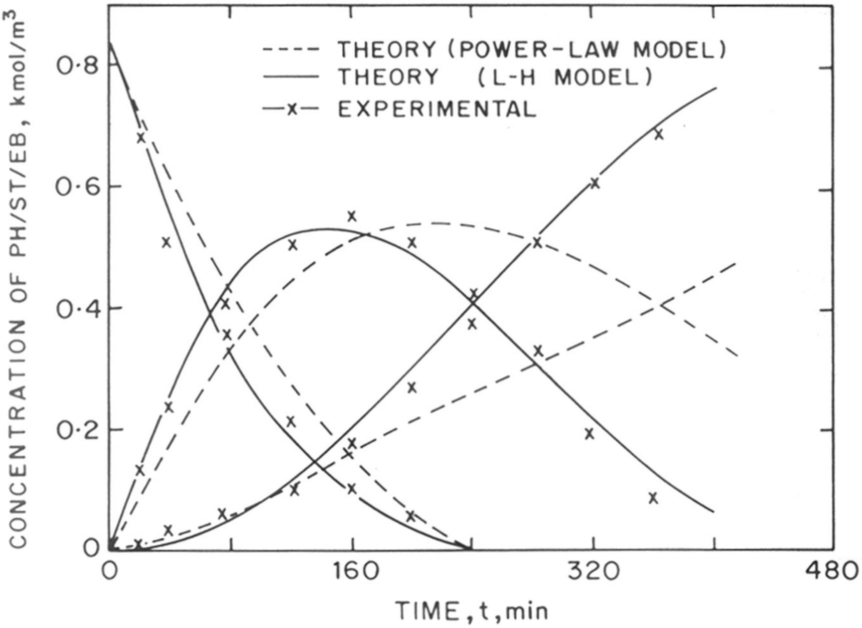


FIGURE 3·3 : CONCENTRATION - TIME PLOT

TEMPERATURE : 288, K
H_2 PRESSURE : $3·54 \times 10^3$, kPa
PH CONCENTRATION : 0·82, kmol/m^3
CATALYST LOADING : 12·0, kg/m^3
AGITATION SPEED : 15, Hz

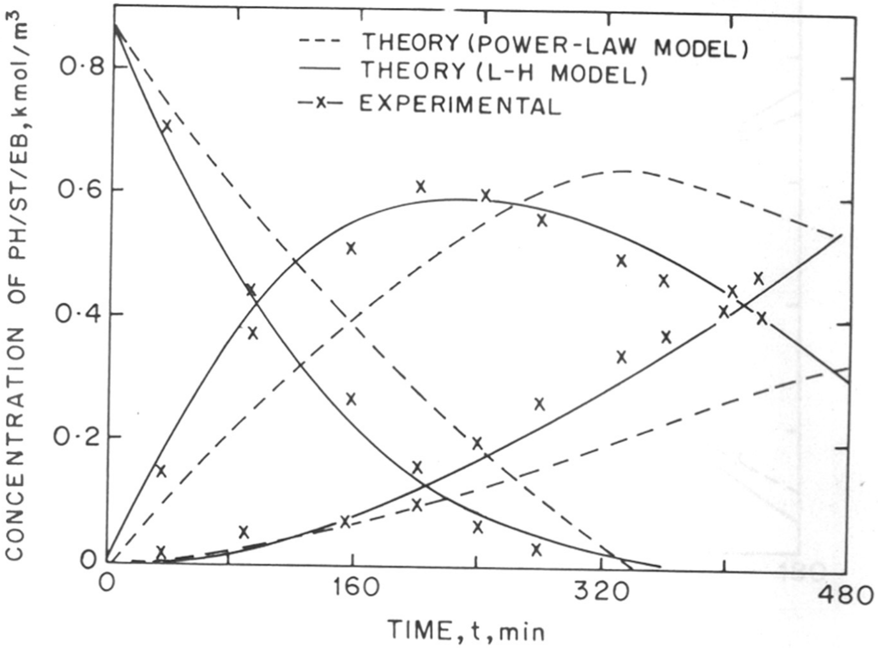


FIGURE 3·4: CONCENTRATION – TIME PLOT

TEMPERATURE : 301, K
H_2 PRESSURE : $2{\cdot}85\times10^3$, kPa
PH CONCENTRATION : 0·86, kmol/m^3
CATALYST LOADING : 4·0, kg/m^3
AGITATION SPEED : 15, Hz

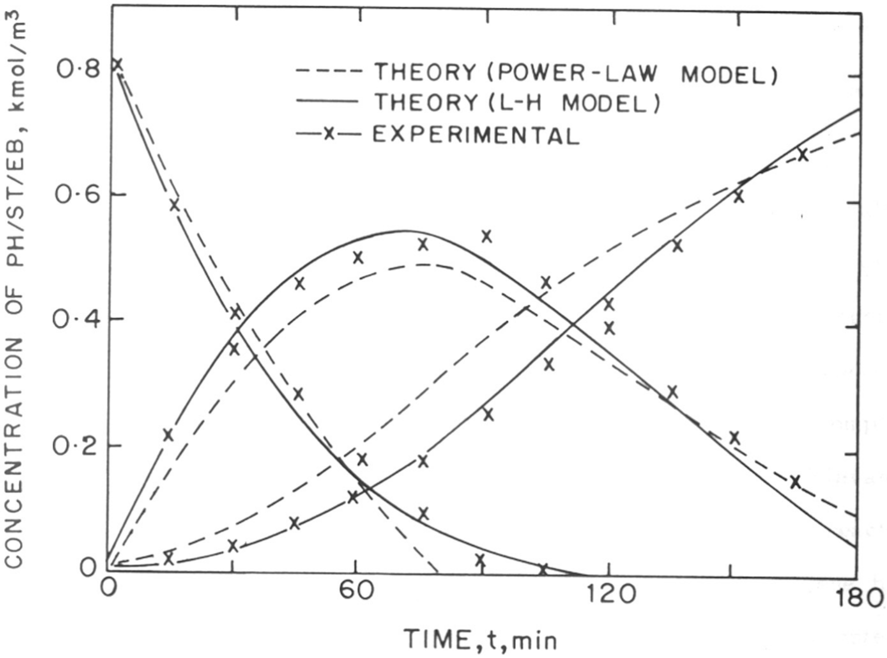


FIGURE 3·5: CONCENTRATION-TIME PLOT

TEMPERATURE : 318, K
H_2 PRESSURE : $3{\cdot}54 \times 10^3$, kPa
PH CONCENTRATION : 0·82, kmol/m^3
CATALYST LOADING : 4·0, kg/m^3
AGITATION SPEED : 15, Hz

of various operating conditions and contributions of various mass transfer steps have been discussed based on the initial rate data. However, the kinetic parameters were evaluated from the observed concentration-time data using a standard optimization programme.

3.4.2 **Analysis of Initial Rate Data with 0.1% Pd/C Catalyst**

The analysis of initial rates is always useful in understanding the dependency of the reaction rate on individual parameters and also in the evaluation of the significance of mass transfer effects. For hydrogenation of styrene, the rates were calculated from the concentration profile region in which phenylacetylene was completely consumed, as this approach would be more relevant to obtain meaningful kinetics of the consecutive reactions. The initial rates for both phenylacetylene and styrene hydrogenation, calculated from all the runs are presented in Table (3.3).

3.4.2.1 **Effect of Catalyst Loading**

Figures (3.6) and (3.7) show the effect of catalyst loading on the initial rate of hydrogenation of phenylacetylene and styrene for 288, 301, and 318 K. It is clear from these data, that for both the steps, the rate is linearly dependent on catalyst loading at all temperatures. This observation also suggests that gas-liquid mass transfer resistance may not be important under these conditions.

TABLE - 3.3

INITIAL RATE DATA FOR PHENYLACETYLENE HYDROGENATION

CATALYST, 0.1% Pd-CARBON

VOLUME OF LIQUID PHASE : 2.54×10^{-4}, m^3

Run No.	Catalyst Loading, $w \times 10^{-1}$ kg/m^3	H_2-Pressure, kPa	Initial Concn. of PH, $[PH] \times 10$ $kmol/m^3$	Initial Concn. of ST, $[ST] \times 10$ $kmol/m^3$	Initial rate of reaction of PH $r_1 \times 10^4$ $kmol/m^3/s$	Initial rate of reaction of ST $r_2 \times 10^4$ $kmol/m^3/s$
1.	2.	3.	4.	5.	6.	7.
TEMPERATURE : 288, K						
187	0.800	3541	8.20	5.90	1.003	0.400
185	1.200	3541	8.20	6.00	1.330	0.830
186	2.000	3541	8.20	5.80	2.280	1.210
189	1.200	1812	8.20	5.60	1.250	0.420
188	1.200	5255	8.20	5.75	2.700	1.197
190	1.200	6987	8.20	5.75	3.650	1.460
192	1.200	3541	4.10	2.95	2.160	0.920
191	1.200	3541	1.53	1.00	2.810	1.106
TEMPERATURE: 301, K						
214	0.400	2851	8.50	6.85	0.667	0.347
215	0.800	2851	8.50	6.60	1.570	0.660
216	1.200	2851	8.50	5.85	2.400	1.040
217	0.400	4220	8.50	6.60	1.060	0.520
218	0.400	5535	8.50	6.75	1.680	0.831
219	0.400	2851	15.80	13.0	0.58	0.280

TABLE - 3.3 Continued

1.	2.	3.	4.	5.	6.	7.
TEMPERATURE : 318, K						
174	0.400	1470	8.20	6.50	1.102	0.650
178	0.800	1470	8.20	5.85	1.980	1.190
182	1.200	1470	8.20	6.05	2.710	1.670
176	1.600	1470	8.20	5.40	4.440	2.600
171	0.400	780	8.20	6.75	0.710	0.450
175	0.400	2851	8.20	5.35	2.450	0.920
173	0.400	3541	8.20	6.00	3.560	1.160
172	0.400	4906	8.20	5.25	4.480	1.602
179	0.400	1470	15.73	-	0.752	-
181	0.400	1470	4.20	3.00	1.105	0.485
180	0.400	1470	1.65	1.00	1.623	0.693

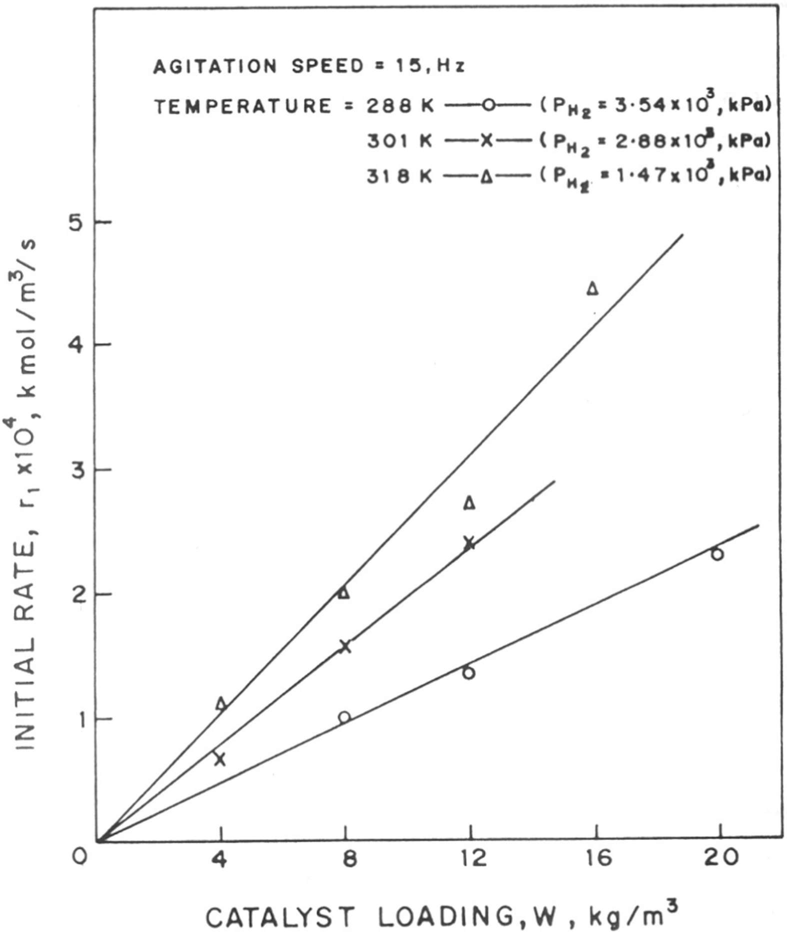


FIGURE 3·6: EFFECT OF CATALYST LOADING ON r_1.
(0·1% Pd / C).

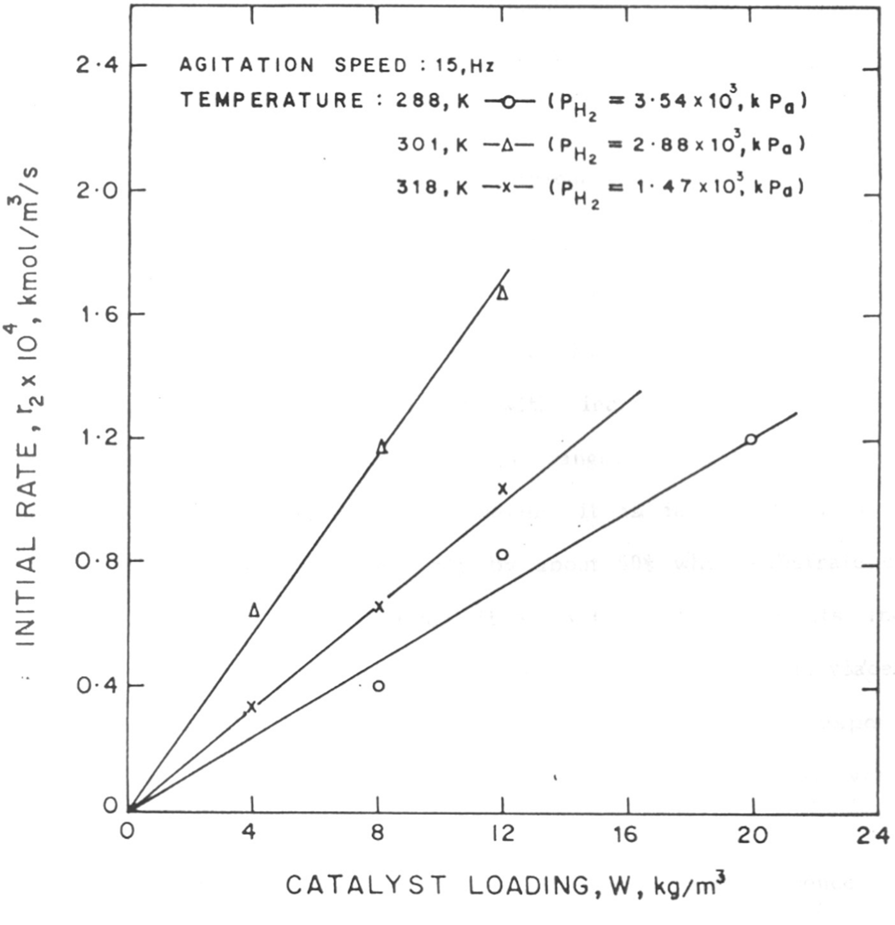


FIGURE. 3·7: EFFECT OF CATALYST LOADING ON r_2 (0·1 % Pd/C)

3.4.2.2 Effect of H_2 Pressure

The effect of H_2 pressure on the reaction rate is shown in Figures (3.8) and (3.9) for both steps for 288, 301 and 318 K. These results show that the rate of hydrogenation is first order with respect to H_2 pressure for both the steps.

3.4.2.3 Effect of Phenylacetylene Concentration

Figure (3.10) shows the influence of initial phenylacetylene concentration on the initial rate of reaction (first step) for 288 and 318 K. In this case, the rate was found to decrease with increase in phenylacetylene concentration in a certain range, indicating a substrate inhibitted kinetics. However, it is important to note that the rates decreased only by about 50% when substrate concentration increased over five fold. These results indicate an approximate -0.4th order. The nature of phenylacetylene concentration-time profile in almost all the experiments shows a nearly zero order kinetics except at very low concentrations.

Phenylacetylene has a strong influence on the rate of hydrogenation of styrene (second step) as evidenced from the observation that only after phenylacetylene is completely converted, styrene hydrogenation rate increases by several fold.

3.4.2.4 Effect of Styrene Concentration (on Second Step)

The effect of styrene concentration on the rate of hydrogenation of styrene (second step) is shown in Figure (3.11) for 288 and 318 K. Here, the rate was found to

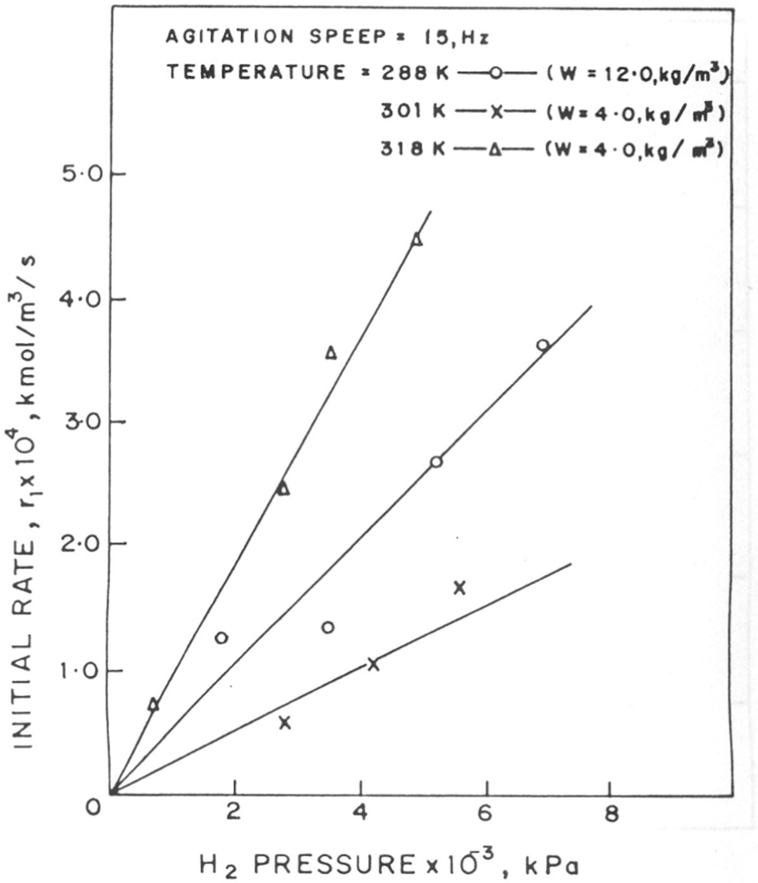


FIGURE 3·8: EFFECT OF HYDROGEN PRESSURE ON r_1
(0·1 % Pd/C).

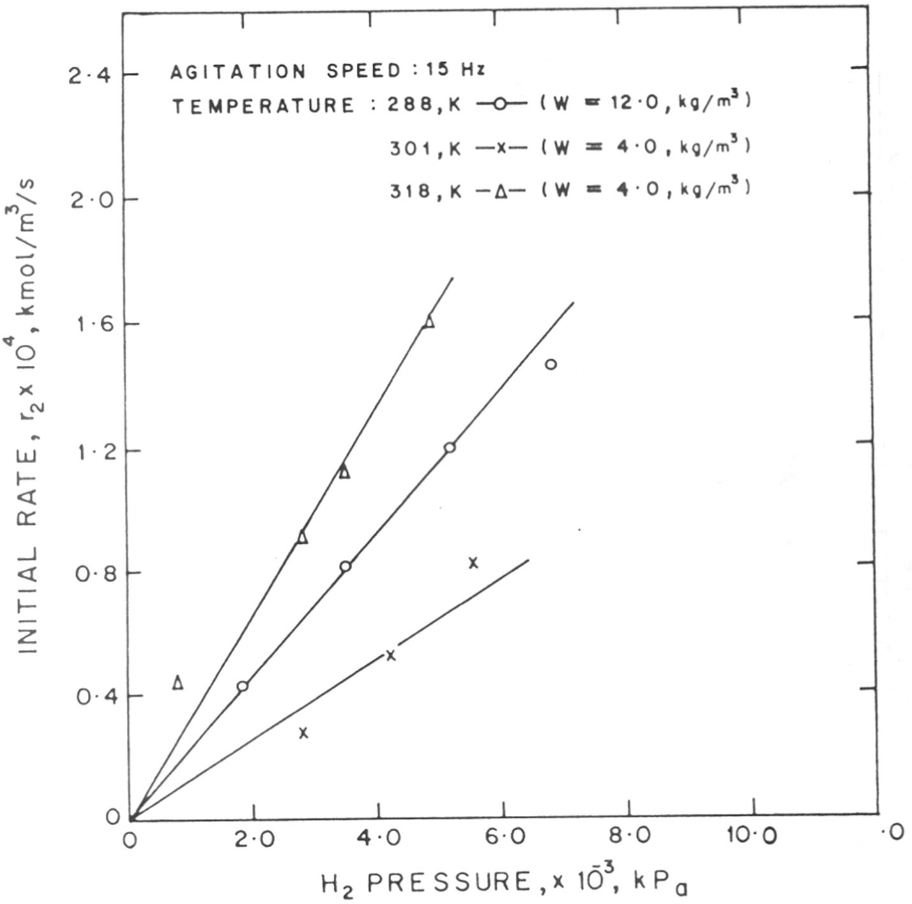


FIGURE 3·9: EFFECT OF HYDROGEN PRESSURE ON r_2

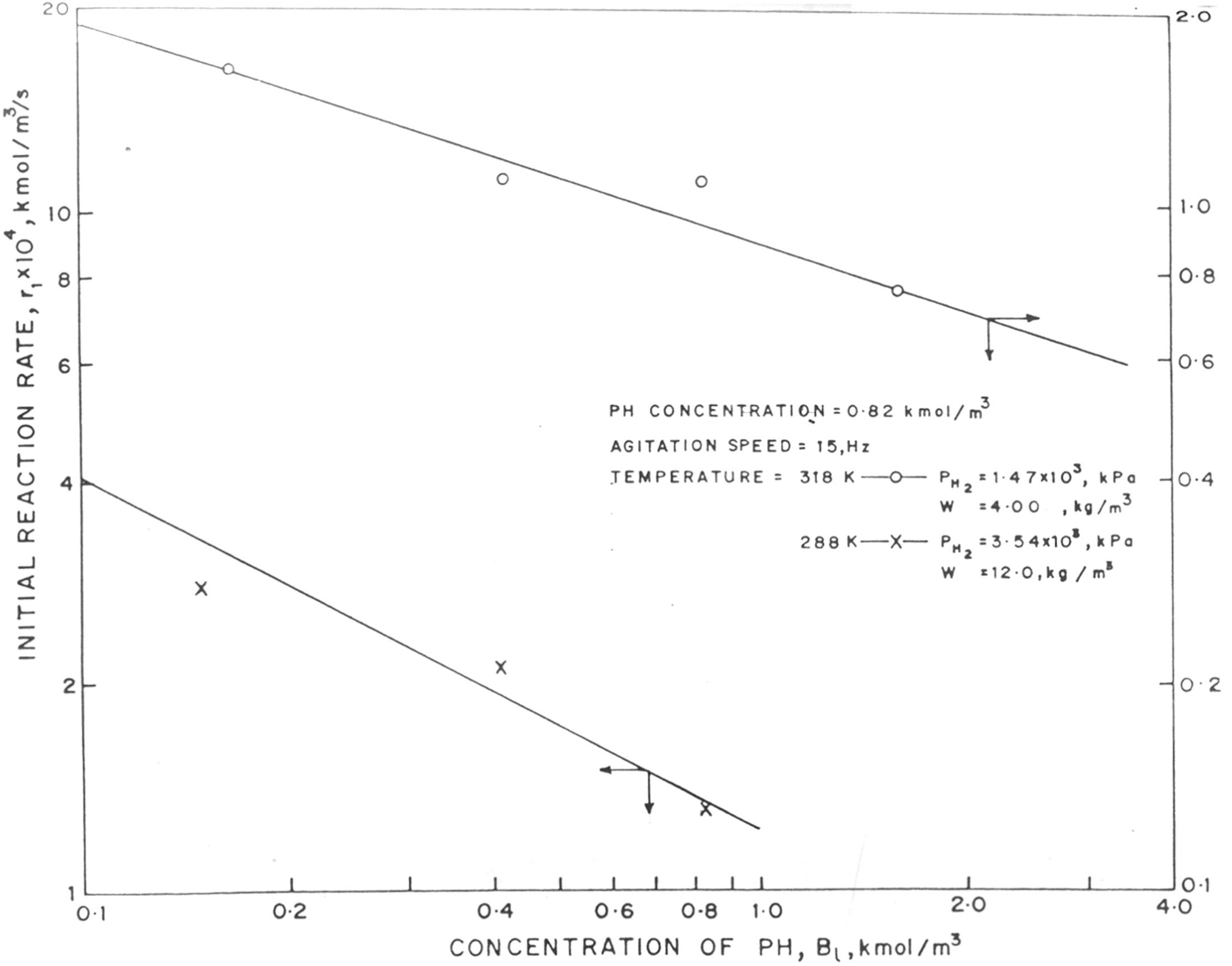


FIGURE 3·10: EFFECT OF INITIAL CONCENTRATION OF PHENYL ACETYLENE ON r_1 (0·1 % Pd/C).

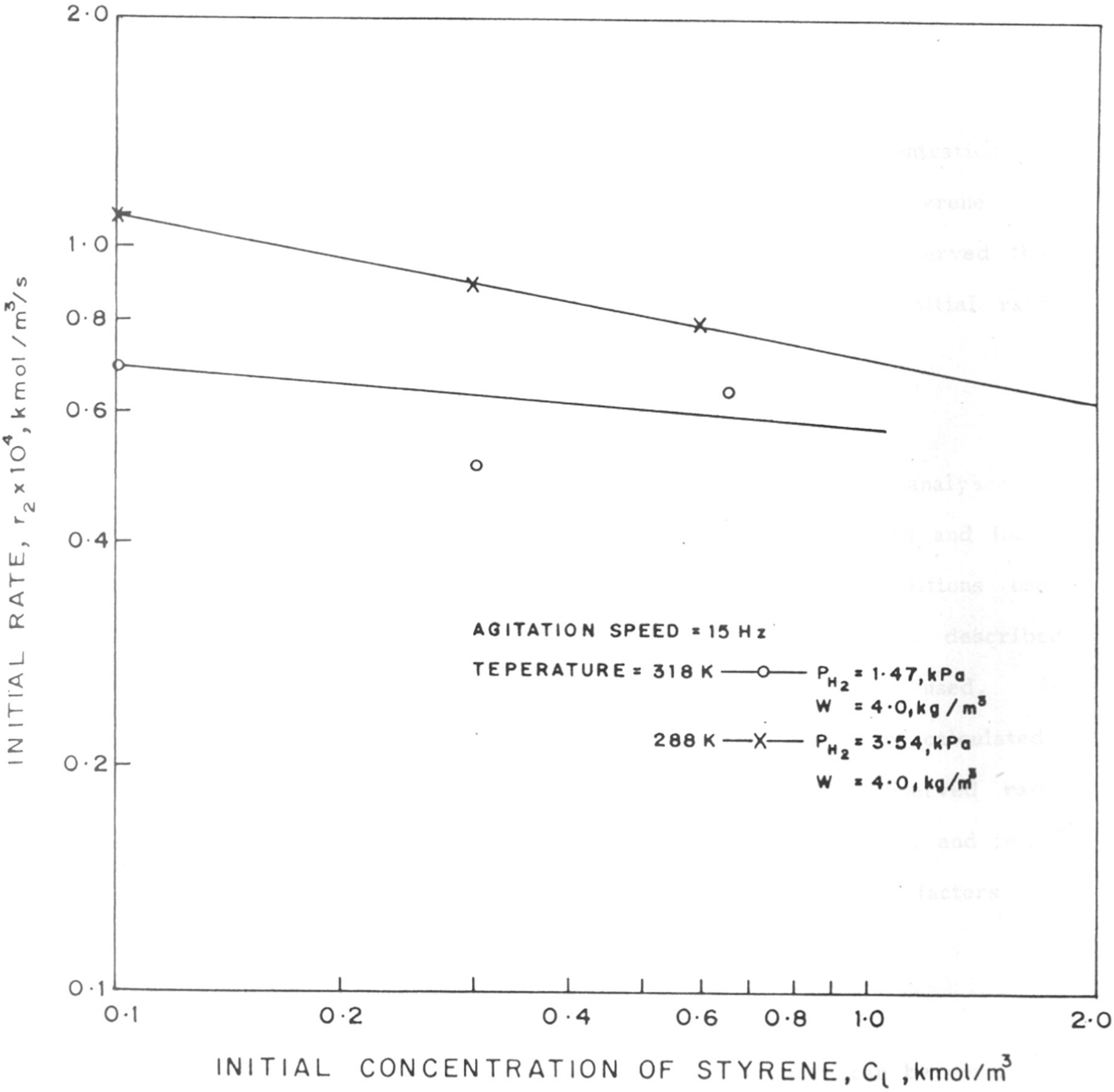


FIGURE 3·11: EFFECT OF INITIAL STYRENE CONCENTRATION ON r_2 (0·1 % Pd / C) be a mild function of styrene concentration with an approximate order of -0.15.

3.4.2.5 Effect of Ethylbenzene Concentration

The effect of ethylbenzene concentration on hydrogenation of both phenylacetylene and styrene was studied at 301 K (see Figure 3.12). It was observed that ethylbenzene had no significant effect on the initial rates of both the steps.

3.5 ANALYSIS OF MASS TRANSFER EFFECTS

The initial rate data were also analysed to check the significance of gas-liquid, liquid-solid and intraparticle mass transfer effects under the conditions used in this work. For this purpose the criteria described by Ramachandran and Chaudhari (1983) were used. In these criteria, factors α_1, α_2, and ϕ_{exp}, are calculated , which are defined as the ratios of the observed rates to the maximum rates of gas-liquid, liquid solid, and intraparticle mass transfer . respectively. These factors are given below.

3.5.1 Gas-Liquid Mass Transfer

The gas to liquid mass transfer can be considered unimportant if,

$$\alpha_1 = \frac{r_i}{k_L a_B P_A H_A} < 0.1 \qquad (3.4)$$

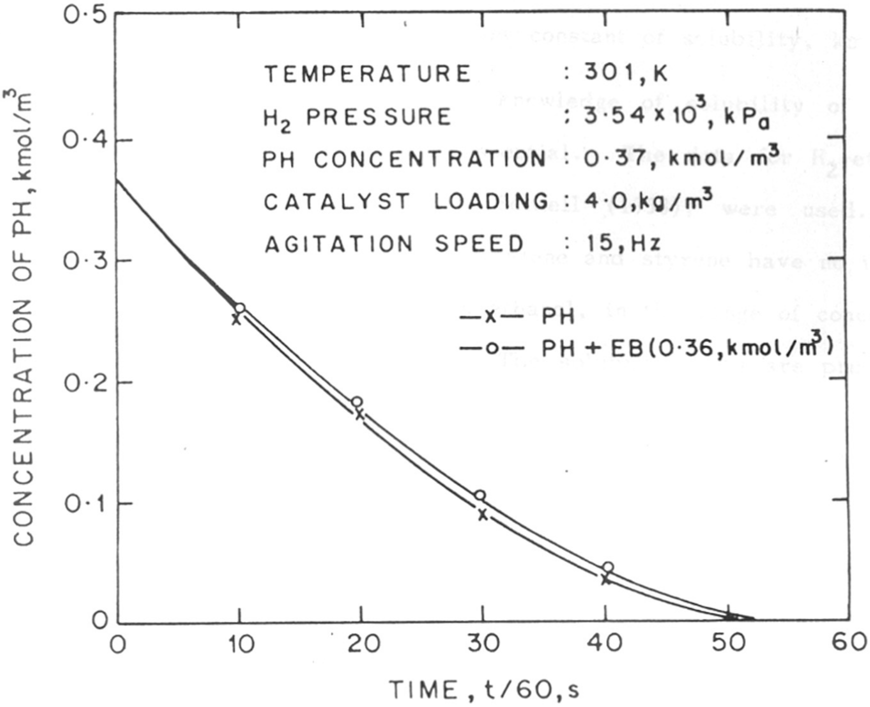


FIGURE 3·12: EFFECT OF ETHYL BENZENE CONENTRATION ON HYDROGENATION OF PHENYLACETYLENE where

r_i = rate of hydrogenation, kmol/m^3/s

k_L = gas-liquid mass transfer coefficient, m/s

a_B = effective gas-liquid interfacial area, m^2/m^3

H_A = Henry's law constant of solubility, kmol/m^3/kPa

For calculation of α_1. a knowledge of solubility of H_2 in the reaction medium is essential. The data for H_2-ethanol system, as reported by Seidell (1958), were used. It was assumed that phenylacetylene and styrene have no influence on the solubility of H_2 in ethanol, in the range of concentrations used in this work. The solubility data are presented in Table (3.4).

The values of k_La_B, the gas-liquid mass transfer coefficient can be calculated from the correlations described in the literature. However, in this work k_La_B values determined experimentally [Chaudhari, et al. (1986)] for the stirred reactor were used in the calculation of α_1. The k_La_B values are presented in Table (3.5).

3.5.2 **Liquid-Solid Mass Transfer**

The liquid-solid mass transfer resistance can be considered to be negligible, if,

$$\alpha_2 = \frac{r_i}{k_s a_p P_H H_A} < 0.2 \qquad (3.5)$$

where

k_s = liquid-solid mass transfer coefficient, m/s.

TABLE - 3.4

HENRY'S CONSTANT FOR HYDROGEN - ETHANOL SYSTEM

(from Seidell [958])

Temperature K	$H_A \times 10^5$ $kmol/m^3/kPa$
288	3.40
301	3.60
318	3.82

TABLE - 3.5

GAS-LIQUID* AND LIQUID-SOLID** MASS TRANSFER COEFFICIENTS

Agitation speed N x 60, Hz	Gas-Liquid Mass Transfer Coefficient $k_L a_B$, s^{-1}			Liquid-Solid Mass Transfer Coefficient, $k_s \times 10^2$, m/s		
	15°C	28°C	45°C	15°C	28°C	45°C
300	0.014	0.016	0.019	0.059	0.080	0.118
500	0.031	0.036	0.042	0.072	0.096	0.141
700	-	-	-	0.075	0.102	0.153
900	0.195	0.226	0.268	0.082	0.111	0.163

* Chaudhari et al. (1986).

** From the correlation of Sano et al.(1974).

$a_p = \frac{6\ w}{\rho_p d_p}$, effective liquid-solid interfacial area per unit volume of slurry m^2/m^3.

w = catalyst loading kg/m^3

ρ_p = particle density, kg/m^3

d_p = particle diameter, m

For calculation of k_s, the following correlation proposed by Sano et al (1974) was used

$$\frac{k_s\ a_p}{DF_c} = 2 + 0.4 \left[\frac{e\ d_p^4\ \rho_L^3}{\mu_L^3}\right]^{1/4} \left[\frac{\mu_L}{\rho_L D}\right]^{1/3} \tag{3.6}$$

where, F_c, the shape factor can be assumed to be unity for spherical particles. The energy supplied to the liquid, e, was calculated as (Calderbank, 1958)

$$e = \frac{N_P\ N^3\ d_I^5\ \psi}{\rho_L\ V_L} \tag{3.7}$$

where

N_P = power number

N = agitation speed, H

d_I = diameter of agitator, m

ρ_L = density of liquid, kg/m^3

V_L = volume of liquid, m^3

Here ψ is a correction factor for the presence of gas bubbles and is given as (Calderbank, 1958)

$$\psi = 1.0 - 1.26 \left[\frac{Q_g}{N\, d_I^3} \right] \quad \text{for} \quad \frac{Q_g}{N\, d_I^3} < 3.5 \times 10^{-2} \qquad (3.8)$$

$$\psi = 0.62 - 1.85 \left[\frac{Q_g}{N\, d_I^3} \right] \quad \text{for} \quad \frac{Q_g}{N\, d_I^3} > 3.5 \times 10^{-2} \qquad (3.9)$$

where, Q_g is the volumetric flow rate of gas, m^3/s. As in this work, a batch autoclave was used, gas was not continuously bubbled, but was supplied as per the consumption to maintain a constant pressure. Therefore, in the above calculations, Q_g, the volumetric flow rate of the gas was calculated as,

$$Q_g = r_{max} \quad V_L \quad V_m \qquad (3.10)$$

where

r_{max} = maximum rate of hydrogenation, $kmol/m^3/s$

V_m = molar gas volume, $m^3/kmol$.

For actual calculations, Q_g, was taken as 20% excess of that calculated by equation (3.10). The values of k_s calculated using the above equations are presented in Table (3.5).

3.5.3 Intraparticle Diffusion

The significance of intraparticle diffusion can be evaluated using the criteria based on experimental Thiele parameter, ϕ_{exp} (Satterfield, 1970, Chaudhari and Ramachandran, 1980) defined as :

$$\phi_{exp} = \frac{d_p}{6} \left[\frac{\rho_p \; r_i}{D_e \; w \; A_s} \right]^{0.5} \qquad (3.11)$$

For $\phi_{exp} < 0.2$, the intraparticle diffusion can be assumed to be negligible. The effective diffusivity, D_e was calculated as:

$$D_e = \frac{D \; \epsilon}{\tau} \qquad (3.12)$$

where

D = diffusion coefficient, m^2/s

and ϵ = porosity of the catalyst

τ = tartuosity factor

The molecular diffusion coefficients were calculated from Wilke-Chang equation (1955), and the tortuosity factor was assumed as 3.0, the value observed for carbon particles (Satterfield, et al. 1968, Komiyama and Smith, 1975). The diffusivity data are presented in Table (3.6). The values of A_s the surface concentration of disolved hydrogen was considered to be equal to A^* ($= P_H H_A$), since external mass transfer resistances were found to be negligible in this work.

The factors α_1, α_2 and ϕ_{exp} calculated from the above equations for all the runs are presented in

TABLE - 3.6

DIFFUSIVITY OF H_2 IN ETHANOL

Temperature K	Molecular Diffusivity $D \times 10^9$ m^2/s	Effective Diffusivity $D_e \times 10^9$ m^2/s
293	3.04	0.51
303	3.66	0.61
313	4.69	0.78
323	5.59	0.93

Table (3.7). It can be seen that the values of α_1, α_2 and ϕ_{exp} were less than 0.03, 0.0014 and 0.09 respectively. This clearly indicates that the rate data obtained with 0.1% Pd/C catalyst is in the kinetic regime and can be reliably used to evaluate the intrinsic kinetic parameters.

3.6 KINETIC MODEL

The kinetic modelling of complex multiphase catalytic reactions needs a careful consideration of various complexities of adsorption and desorption of reactants and products. In such cases, the kinetic models developed based on the initial rate data may not be adeuqate to explain the integral batch reactor performance. Considering the complexities already noted for this system based on catalyst pretreatment work (Chapter 2) it was thought appropriate to use mainly the integral rate data for developing a suitable kinetic model. Two types of models were examined.

In the first analysis, a power law type of kinetics was assumed for both the reaction steps as follows:

$$r_1 = w\ k_1\ A^*\ B^m \qquad (3.13)$$

and

$$r_2 = w\ k_2\ A^*\ C^n \qquad (3.14)$$

As the initial rate data showed first order dependence with respect to hydrogen over a wide range of conditions, in both reactions, the orders for H_2 were taken as unity. It is also important to note that, in a given batch reactor experiment, at a constant pressure, the dependency of the

TABLE - 3.7

LIST OF α_1, α_2, AND ϕ_{exp} FOR KINETIC DATA ON HYDROGENATION OF PHA USING 0.1% Pd/C-CATALYST

Run No.	PHENYLACETYLENEE			STYRENE		
	$\alpha_1 \times 10^3$	$\alpha_2 \times 10^4$	ϕ_{exp}	$\alpha_1 \times 10^3$	$\alpha_2 \times 10^4$	ϕ_{exp}
1.	2.	3.	4.	5.	6.	7.
TEMPERATURE : 288 K						
187	4.32	4.29	0.031	1.73	1.71	0.019
185	5.74	3.79	0.029	3.58	2.37	0.023
186	9.84	3.90	0.029	5.18	2.05	0.021
189	10.51	6.94	0.039	3.36	2.33	0.022
188	7.83	5.18	0.034	3.51	2.32	0.023
190	7.98	5.27	0.034	3.06	2.02	0.021
192	9.32	6.16	0.037	3.97	2.62	0.024
191	12.08	7.98	0.042	4.75	3.14	0.027
TEMPERATURE -301 K						
214	2.88	4.93	0.038	1.51	2.59	0.028
215	6.85	5.87	0.042	2.88	2.47	0.027
216	10.48	5.96	0.042	4.54	2.59	0.028
217	3.12	5.34	0.040	1.53	2.62	0.028
218	3.73	6.39	0.044	1.84	3.15	0.031
219	2.53	4.34	0.036	1.22	2.09	0.025
TEMPERATURE - 318 K						
174	7.43	10.18	0.067	4.39	6.02	0.052
178	13.37	9.16	0.064	8.04	5.51	0.049
182	18.30	8.36	0.062	11.28	5.15	0.048
176	29.99	10.27	0.069	17.56	6.06	0.052
171	8.89	12.17	0.074	5.71	7.82	0.059
175	8.55	11.71	0.072	3.21	4.39	0.044
173	10.00	13.71	0.078	3.25	4.47	0.044
172	9.06	12.41	0.075	3.23	4.43	0.045
179	6.54	9.53	0.071	-	-	-
181	7.76	10.64	0.069	3.52	4.81	0.046
180	1.12	17.52	0.088	4.42	6.03	0.049

rate of reaction on liquid phase reactant/products concentrations can change due to complex adsorption mechanism. Thus, the parameters, k_1, k_2, m and n evaluated using above equations would be empirical in nature. In the second case a Langmuir-Hinshelwood type model (L-H model) was derived based on the assumption of a dual site mechanism, which will be discussed in the subsequent section. This was based on the observed trends of the initial rate data which indicated a negative order dependence with respect to phenylacetylene concentration and first order with respect to hydrogen concentration. In such cases the dual site mechanism is more appropriate. In order to check the validity of these kinetic models, the observed concentration-time data were simulated by a trial and error procedure. The simulation model for the batch reactor for constant H_2 pressure and isothermal conditions used is

$$-\frac{d\,[PH]}{dt} = r_1 \tag{3.15}$$

$$-\frac{d\,[ST]}{dt} = r_2 - r_1 \tag{3.16}$$

$$\frac{d\,[EB]}{dt} = r_2 \tag{3.17}$$

with the initial conditions that

$$\text{at } t = 0,\ [PH] = [PH]_o,\ [ST] = [ST]_o$$
$$[EB] = [EB]_o \tag{3.18}$$

For the present work $[ST]_o$ and $[EB]_o$ were equal to zero. The above set of equations were solved by using Runge-Kutta method to obtain, the concentration of phenylacetylene, styrene and ethylbenzene as a function of time.

3.6.1 **Power Law Model**

In order to test the applicability of rate equations (3.13) and (3.14), the initial trial values of k_1, k_2, m, and n were calculated from the integral rate data by a linear least-square analysis. For this purpose, the concentration-time profile was divided into two regions as shown in Figure (3.13): (a) the region in which ethylbenzene formation rate was negligible (region A) and (b) the region in which phenylacetylene concentration is zero (region B). The data in these regions were fitted by equations (3.13) and (3.14) respectively.

Using the trial values of k_1 k_2, m, and n, equations (3.13) to (3.17) were solved and the results compared with experimental concentration-time data. This procedure was repeated to obtain optimum values k_1, k_2 m, and n, and these values are given in Table (3.8). The results for typical runs at 288, 301, and 318 K are shown in Figures (3.3) to (3.5). It can be seen that for the best values of parameters, the rate equations (3.13) and (3.14) predicted the concentration-time behaviour of phenylacetylene satisfactorily, but not that of styrene and ethylbenzene. This indicates that the power law kinetics is not adequate to represent the kinetics of a consecutive

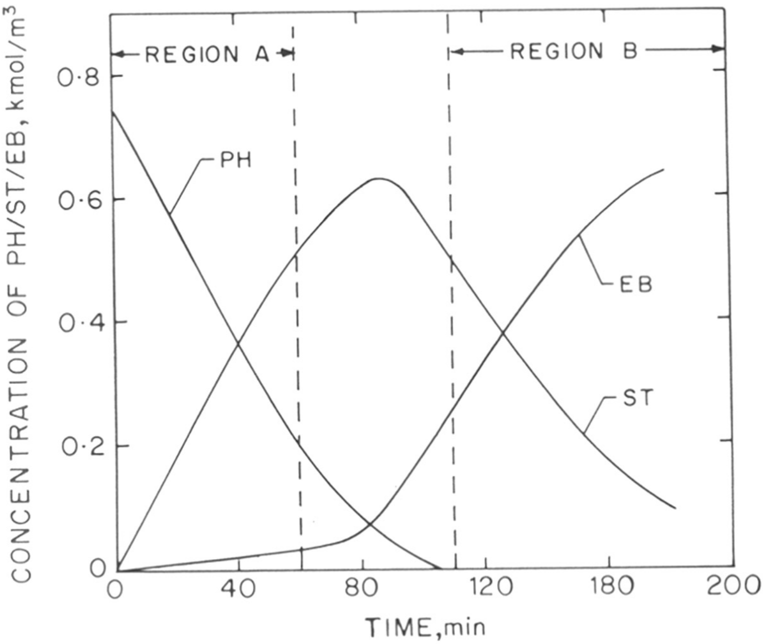


FIGURE 3·13 : A TYPICAL CONCENTRATION-TIME PLOT FOR PH HYDROGENATION

TABLE - 3.8

KINETIC PARAMETERS FOR POWER-LAW MODEL

Temperature, K	$k_1 \times 10^4$, $(m^3/kg/s)$ $(m^3/kmol)^m$	$k_2 \times 10^4$, $(m^3/kg/s)$ $(m^3/kmol)^n$	m	n
288	0.6310	0.1619	0.40	0.29
301	1.4226	4.4050	0.25	0.49
318	4.3065	3.1210	0.19	0.75

reaction of this type. This is also evident from the form of equations (3.13) and (3.14) which do not account for the observed fact that until phenylacetylene is completely consumed, no significant styrene hydrogenation occurs.

3.6.2 L-H Type Model

A Langmuir-Hinshelwood type model was derived based on the assumption of a dual site mechanism which seems to be appropriate based on the general trends observed for the initial rate data. Also, the fact that the rate of reaction of styrene picks up only after phenylacetylene is completely consumed indicates that both the reaction rates are strongly dependent on the concentration of phenylacetylene and styrene. Since, the total number of active sites available for the reaction are fixed, the component with strong adsorption characteristics (e.g. phenylacetylene) is likely to occupy most of the sites.

If we consider that the first reaction occurs between adsorbed hydrogen and adsorbed phenylacetylene and second between adsorbed hydrogen and adsorbed styrene, the following steps would be involved.

$$A + s \leftrightharpoons As \qquad \text{(iii)}$$

$$B + s \leftrightharpoons Bs \qquad \text{(iv)}$$

$$As + Bs \longrightarrow Cs + s \qquad \text{(v)}$$

$$As + Cs \longrightarrow Es + s \qquad \text{(vi)}$$

$$Cs \leftrightharpoons C + s \qquad \text{(vii)}$$

$$Es \leftrightharpoons E + s \qquad \text{(viii)}$$

If we assume that the steps (v) and (vi) as rate controlling and E (EB) is very weakly adsorbed, the following rate equations can be derived (Perry and Chilton, 1983):

$$r_1 = \frac{wk_1 \; [H_2] \; [PH]}{(1 + K_A \; [H_2] + K_B \; [PH] + K_C \; [ST])^2} \tag{3.19}$$

and

$$r_2 = \frac{wk_2 \; [H_2] \; [ST]}{(1 + K_A \; [H_2] + K_B \; [PH] + K_C \; [ST])^2} \tag{3.20}$$

The consistent observation of the first order dependence of the rates for both steps on hydrogen pressure allows us to assume that $K_A[H_2] << 1$. Thus, the overall rate of hydrogenation is given as:

$$\frac{d \; [H_2]_{Total}}{dt} = \frac{w \; k_1 \; [H_2] \; [PH] + w \; k_2 \; [H_2] \; [ST]}{(1 + K_B \; [PH] + K_C \; [ST])^2} \tag{3.21}$$

In order to simulate the experimental concentration-time data, equations (3.15) to (3.17) were solved with r_1, and r_2 given by equation (3.19) and (3.20). For this purpose, the trial values of the rate parameters k_1, K_B, k_2 and K_C are required,and these were evaluated using the data in the two regions of the concentratioin profile in a batch reactor (see Figure 3.13). For the data in region A, where the conversion of phenylacetylene is low, it can be assumed that K_C [ST] is negligible compared to $(1 + K_B [PH])$ to give

$$r_1 = \frac{w\, k_1\, [H_2]\, [PH]}{(1 + K_B\, [PH])^2} \tag{3.22}$$

Similarly, in region B, where phenylacetylene is completely consumed and [PH] = 0, r_2 can be taken as

$$r_2 = \frac{w\, k_2\, [H_2]\, [ST]}{(1 + K_C\, [ST])^2} \tag{3.23}$$

Equations (3.22) and (3.23) can be rearranged as:

$$\sqrt{\frac{(PH)}{r_1}} = \frac{1}{\sqrt{w\, k_1 [H_2]}} + \frac{K_B\, [PH]}{\sqrt{w\, k_1 [H_2]}} \tag{3.24}$$

and

$$\sqrt{\frac{(ST)}{r_2}} = \frac{1}{\sqrt{w\, k_2 [H_2]}} + \frac{K_C\, [ST]}{\sqrt{w\, k_2\, [H_2]}} \tag{3.25}$$

The typical plots of $\sqrt{[PH]/r_1}$ vs. [PH] and $\sqrt{[ST]/r_2}$ vs. [ST] for 288 and 318 K are shown in Figure (3.14). From the slopes and intercepts of these plots, approximate values of the constants k_1, k_2, K_B and K_C were estimated. For example, at 288 K, the values were, 2.62×10^{-3}, 0.42×10^{-3}, 4.17 and 1.96 respectively.

Using these trial values, the batch reactor equations (3.15) to (3.18) were solved by the Runge-Kutta method combined with an optimization programme to simulate the experimental concentration-time curves and obtain the rate

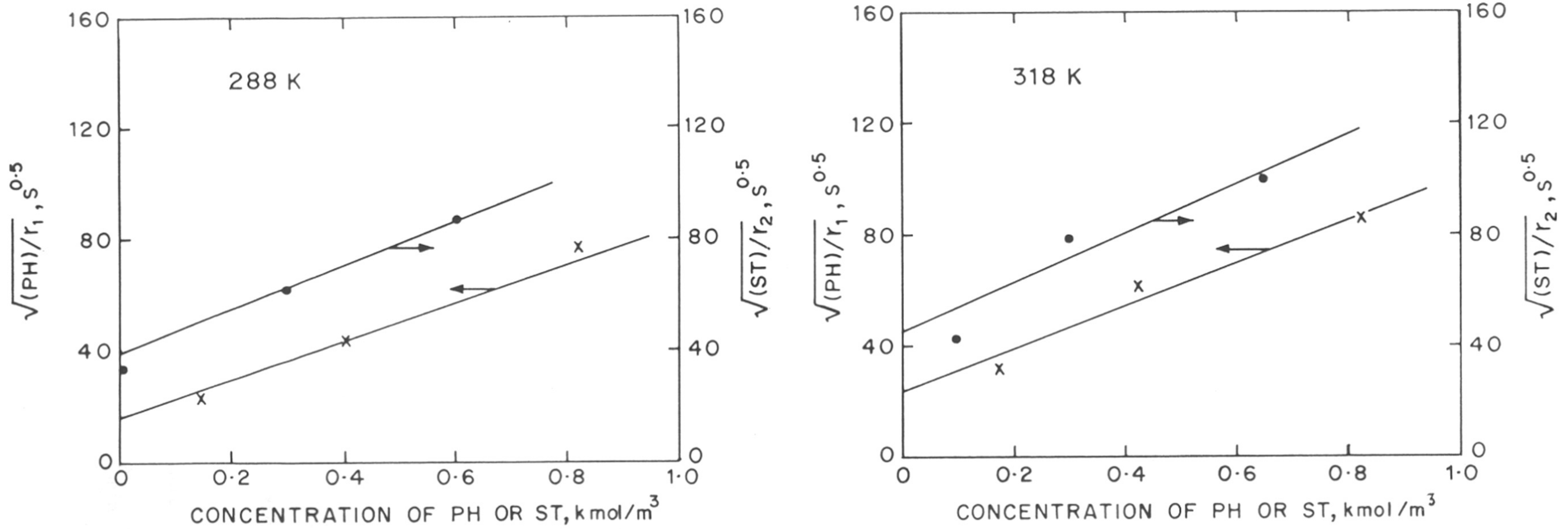


FIGURE 3·14: PLOTS OF $\sqrt{(PH)/r_1}$ vs. (PH) AND $\sqrt{(ST)/r_2}$ vs. (ST) parameters. All the data at 288, 301 and 318 K, at different catalyst loadings and H_2 pressures were simulated and the best common set of values of k_1, k_2, K_B and K_C obtained are presented in Table (3.9).

The results comparing the experimental and the predicted concentration-time behaviour for typical runs at each of the temperature studied, are also shown in Figures (3.3) to (3.5). It can be seen that the rate model [equation (3.21)] is satisfactory to explain the entire range of concentration profiles at different temperatures.

The temperature dependence of the rate parameters is shown in Figure (3.15) from the slopes of which the activation energy and heat of adsorption were calculated. These results are presented in Table (3.10).

3.6.3 Other Models

The rate data were also fitted to other types of rate equations, some empirical and some corresponding to L-H models. The list of equations considered along with the best parameters obtained are presented in Table (3.11). A nonlinear least square regression analysis was used with each equation in Table (3.11) to determine the best parameters for each model. The value of $\emptyset_{min}$, the minimised sum of squares of the difference between the observed and predicted concentrations are also given in Table (3.11).

It was found that, only for the rate equation discussed above (equation 3.21), $\emptyset_{min}$ was the lowest for

TABLE - 3.9

KINETIC PARAMETERS FOR L-H MODEL

Temperature K	$k_1 \times 10^3$, $(m^3/kg,s)$ $(m^3/kmol)$	$k_2 \times 10^3$, $(m^3/kg,s)$ $(m^3/kmol)$	K_B, $(m^3/kmol)$	K_C, $(m^3/kmol)$
288	1.006	0.21	2.618	1.787
301	3.354	0.576	2.743	2.153
318	8.882	1.812	3.337	2.317

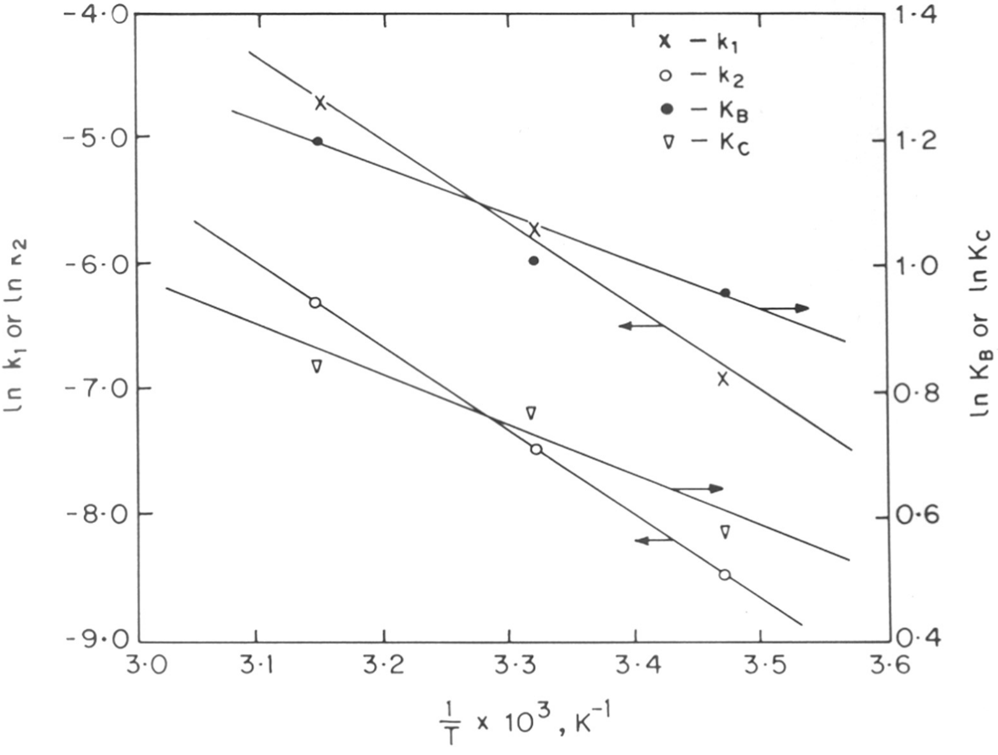


FIGURE 3·15: TEMPERATURE DEPENDENCE OF RATE PARAMETERS

TABLE - 3.10

ACTIVATION PARAMETERS

Activation Energy E_1 = 55.02 kJ/mol

Activation Energy E_2 = 54.69 kJ/mol

Heat of adsorption of ohenyl acetylene ΔH_B = 6.25 kJ/mol

Heat of adsorption of styrene ΔH_C = 6.50 kJ/mol

TABLE - 3.11

RATE EQUATIONS USED AND PARAMETERS OBTAINED

No.	Rate Equation	Temperature	$k_1 \times 10^3$. (m^3/kgs) ($m^3/kmol$)	$k_2 \times 10^3$ ($m^3/kg.s$) ($m^3/kmol$)	K_A' ($m^3/kmol$)	K_B' ($m^3/kmol$)	K_C' ($m^3/kmol$)	$\emptyset_{min} \times 10^4$ $(kmol/m^3)^2$
1.	2.	3.	4.	5.	6.	7.	8.	9.
1.	$\frac{wk_1AB + wk_2AC}{(1+K_BB+ K_CC)^2}$	288	1.0061	0.210		2.618	1.787	0.3968
		301	3.3540	0.576		2.743	2.153	0.0761
		318	8.882	1.812		3.337	2.317	0.3910
2.	$\frac{wk_1AB + wk_2AC}{(1+K_AA + K_BB +K_CC)^2}$	288	1.056	0.181	0.108	2.873	1.661	23.90
		301	3.424	0.395	-0.178	4.046	0.909	1.29
		318	6.444	1.329	-0.048	2.776	1.871	0.102
3.	$\frac{wk_1AB + wk_2AC}{(1 + K_BB)^2}$	288	0.769	0.069		3.029		14.30
		301	2.688	0.161		3.564		14.10
		318	2.393	0.412		1.471		1.25

TABLE 3.11 Continued..

1.	2.	3.	4.	5.	6.	7.	8.	9.
4.	$\frac{wK_1AB + wk_2AC}{(1 + K_BB)^3}$	288	0.413	0.062		0.964		6.77
		301	0.384	0.167		2.464		3.56
		318	2.574	0.438		0.985		1.67
5.	$\frac{wk_1AB + wk_2AC}{(1+K_BB)^2(1+K_CC)}$	288	0.902	0.204		1.954	4.049	0.798
		301	2.854	0.343		2.633	2.080	0.653
		318	6.080	1.200		2.011	3.709	0.083
6.	$\frac{wk_1AB + wk_2AC}{(1+K_BB)^2\ (1+K_CC)^2}$	288	1.167	0.191		2.714	1.282	0.456
		301	2.864	0.419		2.386	1.144	2.42
		318	4.535	0.873		1.966	0.860	2.18

all temperatures indicating that among the models considered equation (3.21) is the best.

3.7 CONCLUSIONS

The hydrogenation of phenylacetylene with 0.1% Pd/C catalyst was studied with the objective of developing a suitable rate equation to represent the intrinsic kinetics. The initial rate data were analysed for the significance of mass transfer effects, which showed that all the rate data, were in the kinetic regime. It was also observed that:

a) The rates for both steps were first order with respect to H_2 pressure at 288, 301 and 318°C.

b) The effect of catalyst loading on the initial rates was also found to be linear under all conditions.

c) The rate of first reaction showed negative order dependence with phenylacetylene; however, the dependence was not strong.

d) The rate of second reaction was almost independent of styrene concentration.

For kinetic modelling, power law, L-H, and some empirical rate equations were examined. The intrinsic kinetics of the consecutive hydrogenation of phenylacetylene was found to be satisfactorily represented by the following expression.

$$\frac{d\,[H_2]_{Total}}{dt} = \frac{w\,k_1\,[H_2]\,[PH] + w\,k_2\,[H_2]\,[ST]}{(1 + K_B\,[PH] + K_C\,[ST])^2} \qquad (3.21)$$

The kinetic parameters, the activation energies and heats of adsorption have been evaluated.

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CHAPTER - 4

KINETIC MODELLING OF HYDROGENATION OF BUTYNEDIOL USING Pd/C CATALYST IN A SLURRY REACTOR

CHAPTER - 4

KINETIC MODELLING OF HYDROGENATION OF BUTYNEDIOL USING Pd/C CATALYST IN A SLURRY REACTOR

4.1 INTRODUCTION

Hydrogenation of butynediol is important in the manufacture of butenediol and butanediol*. Butenediol is a raw material for insecticides and Vitamin B6, while butanediol is a major raw material for engineering plastics and tetrahydrofuran manufacture. This system is yet another case of a complex multiphase reaction involving several steps. Generally, Ni and Pd based catalysts are used for this reaction system. The modified Pd catalysts with Zn and Pb acetates and aqueous ammonia as inhibitors have been successfully used in the selective hydrogenation of butynediol to butenediol (Lindlar, 1966). In the absence of inhibitors, several side products are known to form along with butenediol and butanediol. Because of the commercial importance of butanediol, the selectivity of unpoisoned catalysts becomes an important problem. The relevant literature on this subject is presented in the next section. However, practically no attempts to investigate the product distribution and selectivity in hydrogenation of butynediol have been made so far. The objective of the present work was to investigate the product distribution

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* In this thesis, 2-butyne-1,4 diol, 2-butene-1,4 diol and 1,4 butanediol will be referred as, butynediol, butenediol & butanediol respectively.

and kinetics of hydrogenation of butynediol over Pd/C catalyst in a slurry reactor. The following aspects have been investigated.

a) Identification and characterization of products to arrive at a suitable reaction scheme.

b) Analysis of initial rate data and significance of mass transfer effects.

c) Intrinsic kinetics of the reaction steps involved

d) Modelling of the batch slurry reactor for the complex reaction system.

e) Effect of operating parameters on selectivity of various products.

4.2 LITERATURE SURVEY

A summary of the investigations reported in the literature on hydrogenation of butynediol is presented in Table (4.1). The first commercial process for hydrogenation of butynediol, described by Applyard and Gartshore (1946), employed Ni-Cu-Mn on silica as a catalyst. The reaction was carried out at 40-130°C and 200-300 atmosphere hydrogen pressure. This catalyst system was the basis of the well known Reppe process for the manufacture of butanediol.

Fukuda and Kusama studied the effect of the addition of lead acetate, quinoline, pyridine and piperidine to Pd/$CaCO_3$ in the partial hydrogenation of butynediol. They found that these inhibitors had no effect on the first stage of the Pd catalysed reduction of butynediol. However, hydrogenation of the resultant butenediol was slowed down a little by pyridine,

TABLE - 4.1

LITERATURE ON HYDROGENATION OF BUTYNEDIOL

S.No.	Butynediol %	Solvent	Catalyst	Inhibitor	Temperature °C	Pressure atm.	Yield of butene-diol.	Investigator
1.	2.	3.	4.	5.	6.	7.	8.	9.
1.	-	-	Ni	-	-	-	-	Farbenindustic (1939).
2.	-	Organic solvent	Zn	NaOH, Amines.	-	-	-	Farbenindustic (1939).
3.	-	-	Ni-Cu-Mn/ Silica	-	40-130	200-300	-	Appleyard and Gartshore (1946).
4.	5	MeOH	Pd/$CaCO_3$	-	20	1	-	Johnson (1946)
5.	-	EtOH	Raney Nickel	-	-	-	-	Valette (1948)
6.	40	-	Zn-Sponge	-	100	200	-	Friedrich et al.et (1953).
7.	23	MeOH	Cu-Kiselghur	-	100	130	-	Suwa (1956).
8.	17	Water	Pd/$CaCO_3$	Lead-acetate Quinoline, Piperidine Pyridine.	15	1	-	Fukuda and Kusama (1958)

1.	2.	3.	4.	5.	6.	7.	8.	9.
9.	–	MeOH EtOH	Ni	Quinoline	20	–	–	Freidlin et al. (1959).
10.	30	Pyridine	Lindlar	–	–	1.1	91	Feit (1960)
11.	36	Water	Raney nickel	–	90	2	45	Hort (1960a).
12.	38	Water	$Pd/CaCO_3$ with Cu-acetate	–	40	5	90	Hort (1960b)
13	–	EtOH, Dioxane, Water	Raney nickel	Pyridine	20	–	–	Freidlin et al. (1960).
14.	25	MeOH Water	$Pd/CaCO_3$ with Zn-acetate	NH_3,amines	40-80	1-100	–	BASF (1961).
15.	–	Alcohol, Water	Raney nickel or Ni-10% Cu	NH_3, Pyridine piperidine	35-100	1-21	86	Hort and Graham (1962).
16.	–	–	Iron	–	–	–	75	Tairi (1962).
17.	36	Water	Ni-Cu	NH_3	40	5	86	GAFC (1962).
18.	36	Water	Raney Nickel with copper	NH_3	50	20	83	GAFC (1963). GAFC (1964)
19.	–	Water	$Pd/CaCO_3$ with Zn-acetate	NH_3, pyridine, piperidine	25-100	1-21	Quantitative	SNAM (1964)

1.	2.	3.	4.	5.	6.	7.	8.	9.
20.	-	Water EtOH	5% Pd/$CaCO_3$	$Zn(OAc)_2$, NH_3 or triethanolamine.	20-30	1	-	Movsisyan et al. (1968).
21.	-	Water	5% Pd/$CaCO_3$	-	0^o and 60^o	-	-	Movsisyan et al. (1970).
22.	-	MeOH	Pd/Al_2O_3	-	-	1	-	Jardine et al. (1969).
23.	-	EtOH	Pt,Pd or their 1:1 mixture	-	20,30,40	-	-	Sokol'skii et al. (1971 a).
24.	-	EtOH	Pt,Pd,Os-blacks, Pt,Oa,Pd-Os mix.	NH_3 24%, $BuNH_2$	20-40	-	95	Sokol'skii et al. et (1971 b)
25.	-	-	Ni - Cr	-	150	200	-	Sivakova (1973)
26.	-	-	Ni-Cu-Mn/Al_2O_3	-	-	-	-	Rudoff and DeThomas (1975).
27.	-	Water	PdO,ZnO/Al_2O_3 and one of CdO Bi_2O_3 or TeO_2	-	-	-	-	Hoffman et al. (1976).
28.	-	-	5% Pd/Al_2O_3	-	-	-	-	Wodd and Reitz (1976 a)
29.	-	-	Pd/$BaSO_4$ Pd/Al_2O_3, Pd/C	-	-	-	-	Wood and Reitz (1976 b)

1.	2.	3.	4.	5.	6.	7.	8.	9.
30.	-	Water	5% Pd/Al_2O_3 or Pd/C	$Pb(OAc)_2$ or Pb_3O_4	-	-	-	Hort (1978).
31.	-	Water	5% Ru/C promoted with Pd and alkali	-	90	25	-	DelRosso et al.(1984).
32.	-	Water	Pd/Zn-$CaCO_3$	-	30-70	8-35	-	Chaudhari et al.(1985).
33.	-	-	Pd/C and Pd black	Pb and Te	-	-	-	Cerveny et al. (1983).
34.	-	-	Pd-Ru alloy membrane	-	-	-	-	Karavanov et al. (1985).
35.	-	30% benzene 70% methanol	Polymer bound Pd	-	-	-	-	Nayak et al. (1985).
36.	-	-	Step I : Ni Step II: Ni/Al_2O_3	-	80 100	1.0 MPa 24.5 MPa	-	Turek et al.(1985).

more markedly by piperidine and almost completely by quinoline treated catalyst. This effect is due to the fact that butynediol is more strongly bonded to the active sites of the catalyst than butenediol. The stronger inhibitory effect of a more basic nitrogen compound was shown by Fukuda and Kusama (1958), in the more pronounced retarding effect of piperidine over pyridine in the second stage of the reduction of acetylenes.

Hort and Graham (1962) hydrogenated butynediol with Raney nickel or Ni containing 10% copper, to butenediol in aqueous or alcoholic solution over a temperature range of 25-100°C, and 1-21 atmosphere pressure in the presence of bases such as ammonia, pyridine and piperidine. They reported an yield of 86% of butenediol.

Rudoff and DeThomas (1975) have reported an improved catalyst consisting of Ni-Cu-Mn on high surface alumina for hydrogenation of butynediol to butanediol. This catalyst contained 15% Ni, 7.8% Cu, and 0.5% Mn.

Hort (1978) investigated partial hydrogenation of butynediol over 5% Pd/Al_2O_3 and Pd/C catalysts and $Pb(OAC)_2$ and Pb_3O_4 poisons to give cis- and trans- butenediol with only small amounts of butane end butenediol-hydroxy-butyraldehyde-acetal.

The formation of butanediol by the hydrogenation of butynediol on a Ru based catalyst has been studied in a slurry reactor by Del Rosso et al. (1984). The reaction was performed in the aqueous phase in a stirred autoclave of stainless steel, and the influence of reaction parameters e.g. hydrogen pressure, amount of catalyst and temperature was determined. They proposed a reaction scheme describing various products formed, however, no quantitative data on identification of side products were presented.

A kinetic study of hydrogenation of butynediol has been recently reported by Chaudhari et al. (1985) using Pd-Zn-$CaCO_3$ catalyst in a slurry reactor. This catalyst was highly selective for butenediol formation. The effect of catalyst loading, butynediol concentration, temperature, hydrogen partial pressure and agitation speed on the rate of hydrogenation has been studied. They have proposed a L-H type rate equation based on the rate data.

Turek et al. (1985) have described a two step process to hydrogenate butynediol to butenediol. In the first step butynediol was hydrogenated in a stirred reactor, at 80°C and 1 MPa pressure using a Ni based catalyst. The second step was carried out in a fixed bed reactor at 100°C and 24.5 MPa pressure using 18% Ni/Al_2O_3 catalyst.

From the literature presented in Table (4.1), it can be seen that a limited information is available on this subject. Nevertheless, the following general observations can be made. The catalysts normally used for this reaction are the conventional hydrogenation catalysts such as Ni, Ru and Pd. Palladium catalysts are commonly used, as they are active at milder operating conditions. In order to obtain higher yields of the intermediate product butenediol, in most cases, the catalysts are weakened in their activity by addition of special ingredients such as lead acetate, zinc acetate, copper, chromium and barium salts. It has also been reported that addition of ammonia or basic amines such as quinoline, pyridine on piperidine during the hydrogenation process, helps hydrogenating the triple bond selectively to double bond. Hydrogenations have been reported in the presence of methanol, ethanol, water and sometimes an amine as a solvent. With Pd catalyst in alcoholic solution, hydrogenations are essentially carried out at ambient conditions, while aqueous phase hydrogenation is carried out at 1-100 atmosphere pressure and 40-100°C. With Raney nickel catalysts hydrogenations have been reported at 10-100 atmospheric pressure and 20-20-100°C temperature. Inconsistent results and low yields have been reported with Ni catalysts, while high yields and very high stereo selectivity have been obtained with Pd catalysts.

4.3 EXPERIMENTAL

4.3.1 Materials

The catalysts 0.2% Pd/C and 2% Pd/C were prepared by the same procedure given in Section (2.3.3) and the specifications are given in Table (2.1). Hydrogen gas, supplied by M/s. I.O.L., Bombay, with stated purity of > 99% was directly used from cylinders. Butynediol was obtained from M/s. Fluka, Switzerland and was vacuum distilled before use. The solvent used was demineralized water.

4.3.2 Apparatus

All the hydrogenation experiments were carried out in a stirred pressure autoclave described in detail in Section (2.3.1).

4.3.3 Experimental Procedure

In a typical experiment, known quantities of Pd/C catalyst, and aqueous solution of butynediol were charged into the reactor and the contents flushed with nitrogen. After the required temperature was attained, the reactor was flushed with hydrogen and pressurised to a desired level. A sample of liquid was withdrawn and the run started by switching the stirrer on. During the course of reaction, the pressure of hydrogen in the reactor was maintained constant, by supplying hydrogen from the reservoir at the rate of consumption using a constant pressure regulator. Liquid samples were withdrawn at different time intervals and analysed for reactant and product concentrations.

4.3.4 Analysis

The analysis of liquid phase components were carried out using DANI 3800 GC and Spectra-Physics 4100 computing integrator. A 1.2 m long column of 6 mm diameter packed with 5% PEG 1500 on chromosorb was used as the stationary phase. The other conditions of GC analysis were:

Column temperature : 110-170°C (Programmed at a rate of 20°C min).

Detector (FID) temperature : 350°C

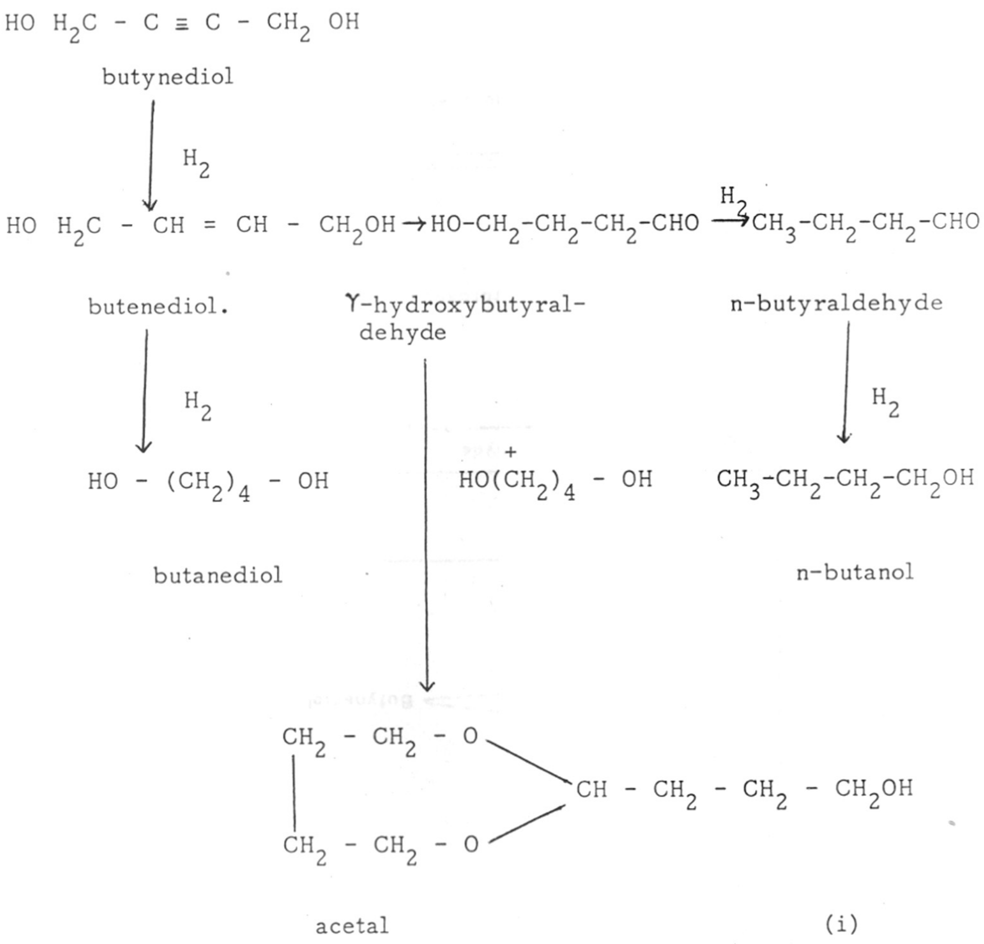
Injection temperature : 300°C

Carrier gas (N_2)flow rate : 40, cm^3/min

The products, butenediol, butanediol, n-butyraldehyde and n-butanol were identified by comparing with standard samples in G.C., while other side products were characterised using GC-MS, column chromatography and IR techniques. GCMS analysis was carried out using Varian-MS 30 instrument. The side products separated by column chromatography were used to prepare standard samples for quantitative analysis.

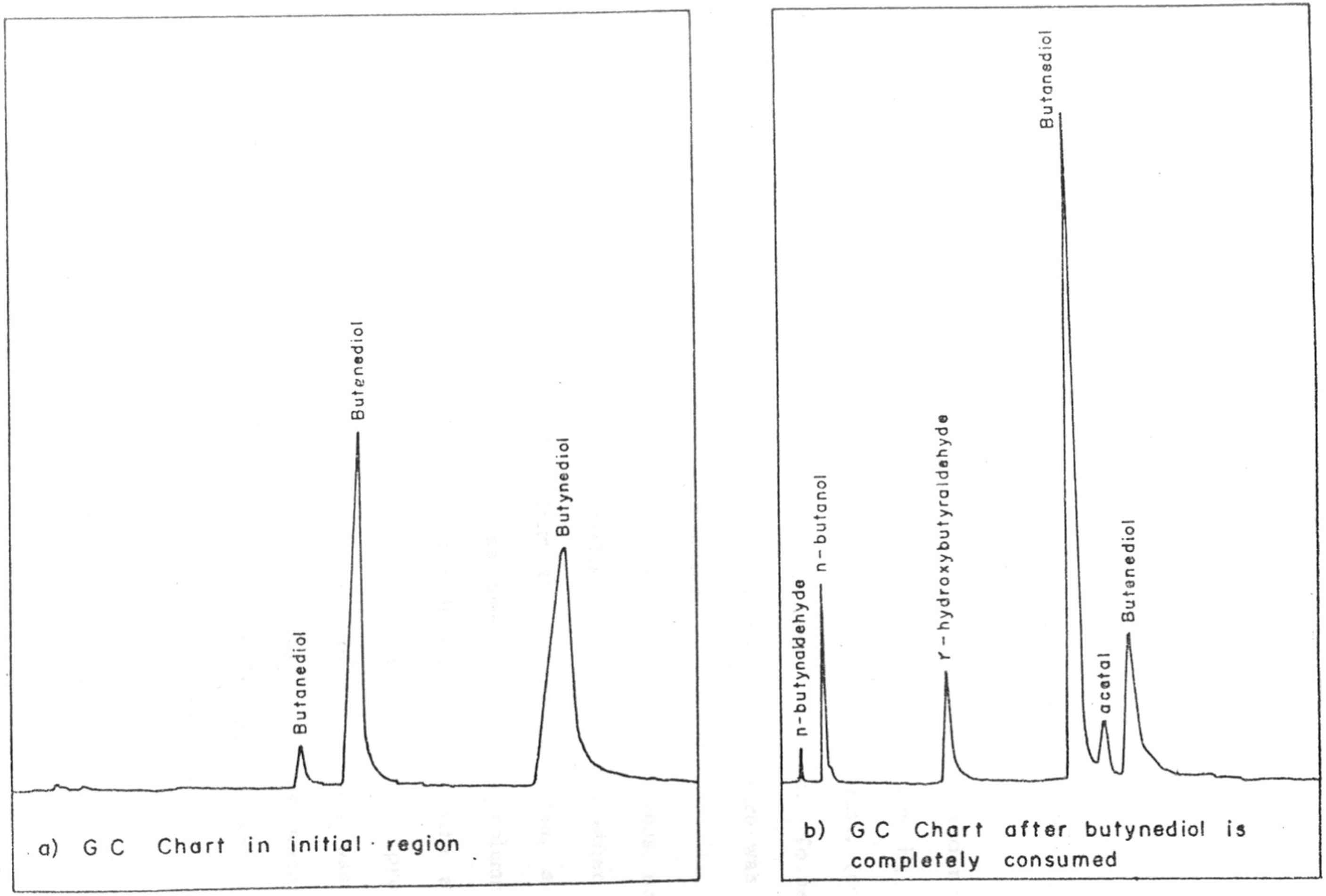
4.4 PRODUCT IDENTIFICATION

The preliminary experiments in which liquid samples were analysed, indicated that in addition to butenediol and butanediol, n-butyraldehyde, n-butanol and other side products were formed. The following reaction scheme can describe the various side reactions taking place during the hydrogenation of butynediol.



(i)

Several samples were analysed by GC and GCMS and a typical gas-chromatograph is shown in Figure (4.1). The formation of n-butyraldehyde and n-butanol was confirmed by comparison with GC and MS of standard samples. The other two products formed in significant quantities, suspected to be γ-hydroxy butyraldehyde and acetal (a condensation product of γ-hydroxybutyraldehyde and butanedi~~u~~ol), were identified by the following procedure.



a) G C Chart in initial region.

b) G C Chart after butynediol is completely consumed

FIGURE 4·1: G C CHARTS OF PRODUCTS IN HYDROGENATION OF BUTYNEDIOL

The product mixture obtained from butynediol hydrogenation was fractionated. Initially, some low boiling impurities were separated. After this, an azeotropic mixture of γ-hydroxybutyraldehyde and water was separated at 82°C, and this aqueous layer was stored in a separate flask for further characterization.

Other components like n-butyraldehyde and n-butanol were separated by vaccum distillation at 10 mm Hg. The residual product mixture contained butanediol, acetal, (condensation product), and other high boiling impurities. To separate acetal from the above mixture, the residual mixture was dissolved in ether and extracted with water.

Butanediol was extracted as an aqueous solution, while acetal and other organics remained in the ether phase. To separate the acetal from the other impurities, a column chromatography technique was used. A glass column of 25 mm diameter and 1 m length was loaded with a slurry of silica gel in pet ether. The proportion of product to silica gel was 1:40. Silica gel in the column was always kept under solvent to avoid drying. It was washed with a mixture of pet ether and benzene to remove any adsorbed impurities. After this, the product mixture containing the acetal and the other high boiling impurities was loaded in the column. Initially, 1% ethylacetate in benzene was used as an eluent and the eluted fractions were collected. Then the concentration of ethylacetate in benzene was increased to 5, 10, 15, 20, 30, 50 and 100%. Each time the eluted fractions were stored in separate stoppered flasks. Each fraction was then distilled out to concentrate the eluted products. These concentrated products were tested by TLC. The single and identical components separated on TLC were mixed together. For example 30, 50 and 100% ethylacetate fractions were found to contain a major quantity of acetal (as also tested by GC). This acetal component was stored separately for further analysis.

The components thus separated were characterised by GC, GCMS, NMR, IR and elemental analysis. The mass spectra of γ-hydroxybutyraldehyde is shown in Figure (4.2). Since the molecular ion peak of γ-hydroxybutyraldehyde was found to be weak, a derivative of this product with 2,4 dinitrophenylhydrazine was prepared. Melting point of this derivative was found to be 118°C which also agrees with the literature report (Meyers et al. 1973). The mass spectrum of the derivative is shown in Figure (4.3). It showed the expected strong molecular ion peak at M/z = 268, a peak at m/z = 252 (M^+ - 0) and m/z = 250 ($M^+ - H_2O$). This confirmed the formation of γ-hydroxybutyraldehyde.

The suspected acetal compound separated as discussed above was analysed by MS, IR and elemental analysis. The MS analysis indicated a molecular weight of 160, while the IR spectrum of acetal (Figure 4.4) showed the presence of -OH group (3044 cm^{-1}). The following structure can be assigned to this product, which is consistent with the molecular weight of 160.

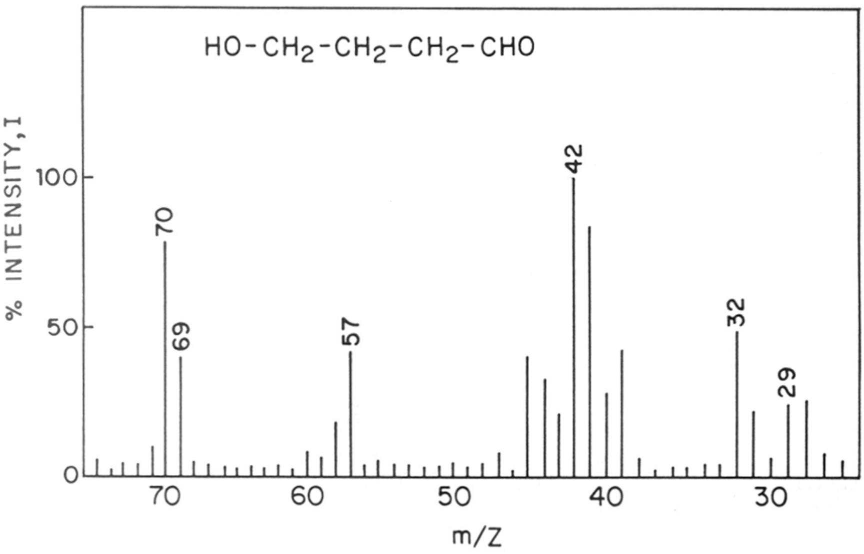


FIGURE 4·2: MASS SPECTRUM OF γ-HYDROXYBUTYRALDEHYDE

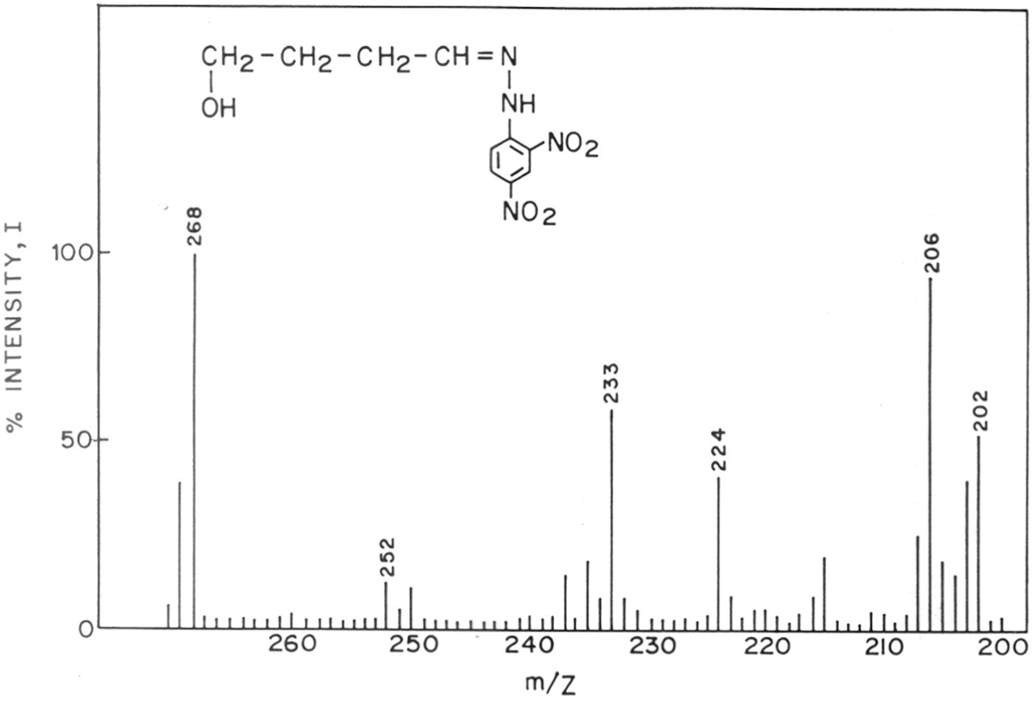


FIGURE 4·3: MASS SPECTRUM OF 2,4 DNP DERIVATIVE OF γ-HYDROXYBUTYRALDEHYDE

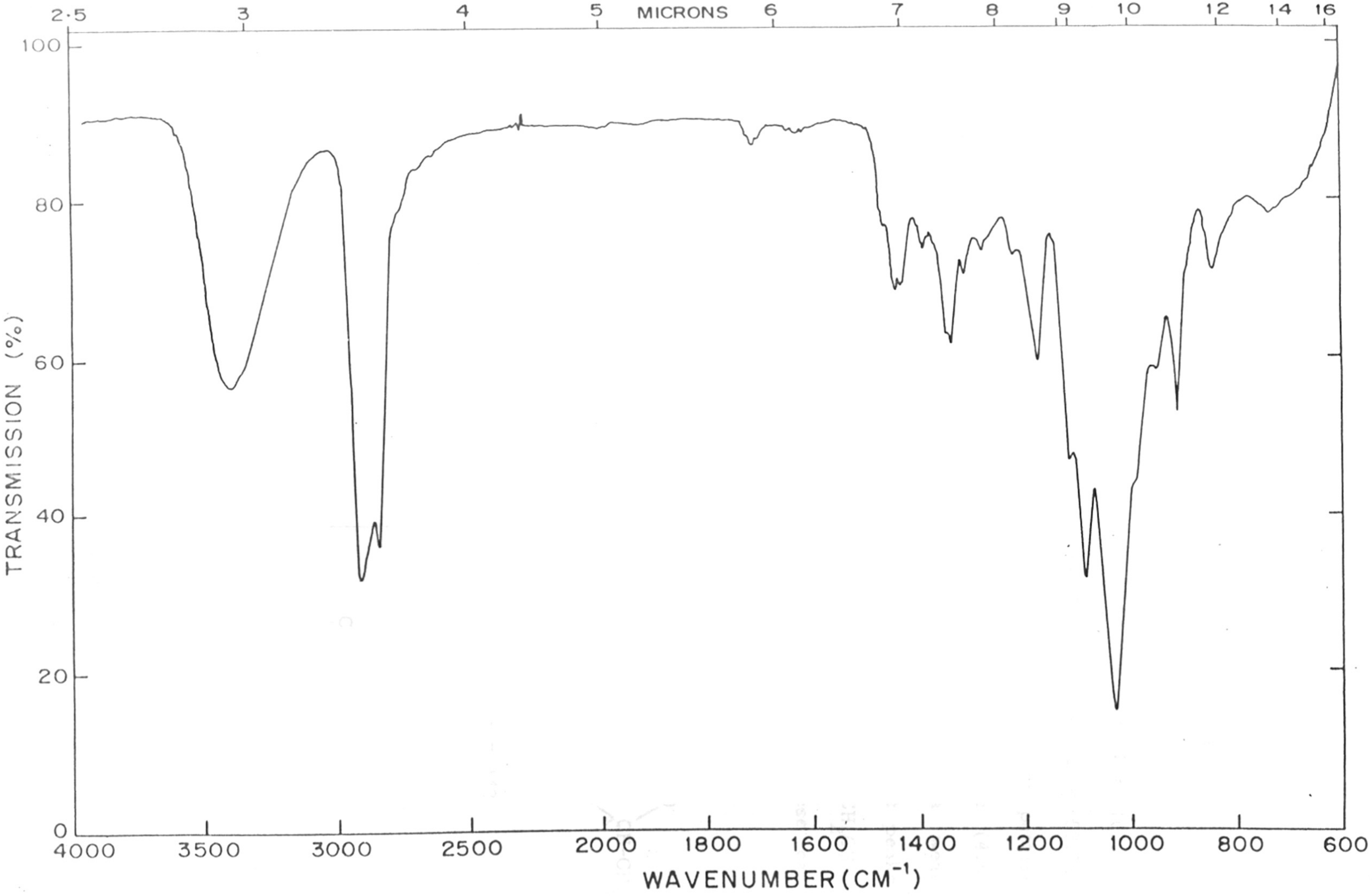
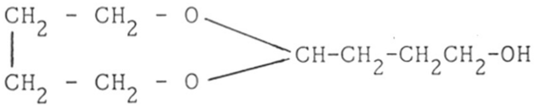
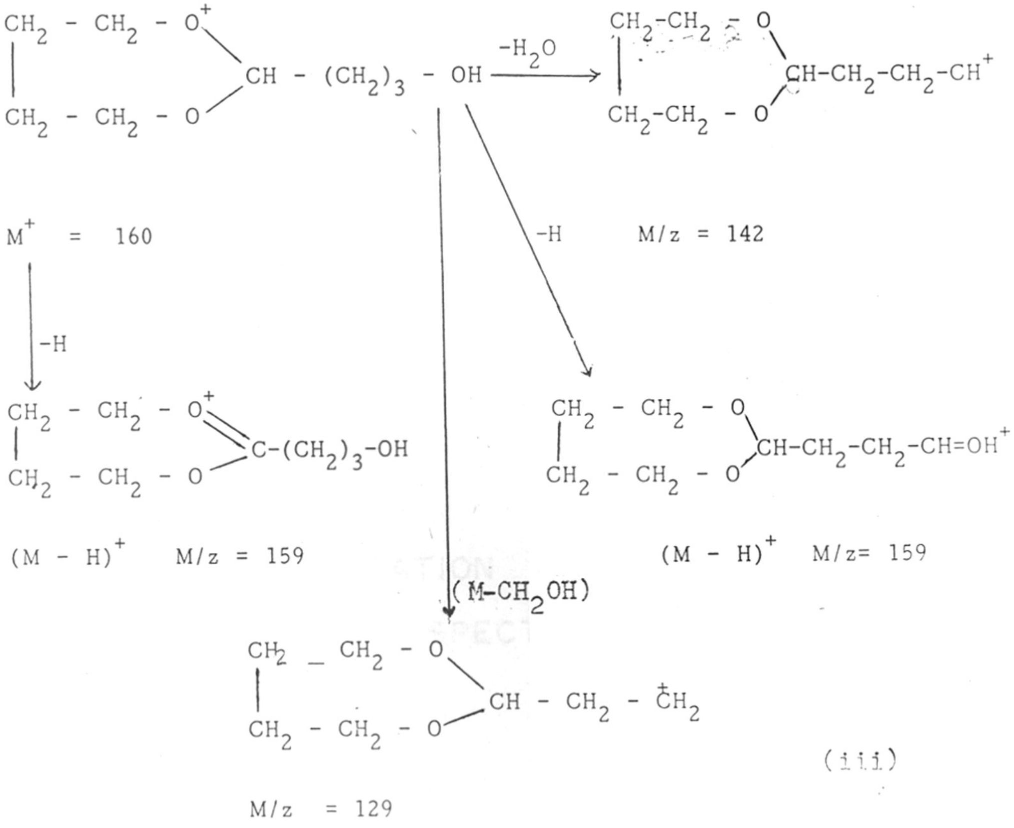


FIGURE 4·4: IR SPECTRUM OF THE ACETAL



(ii)

The elemental analysis showed C = 59.98% and H = 10.01%, which agrees well with the theoretical values (C = 58.72% and H = 10.10%) of the compound. The fragmentation pattern of the MS of the above product is shown in Figure (4.5) which indicates the following characteristics: (a) a weak molecular ion peak of m/z of 160; (b) other significant peaks at m/z, of 159 $(M - H)^+$, 142 $(M - H_2O)$ and 129 $(M - CH_2OH)$, which are consistent with the above structure. These can be best explained as follows:



(iii)

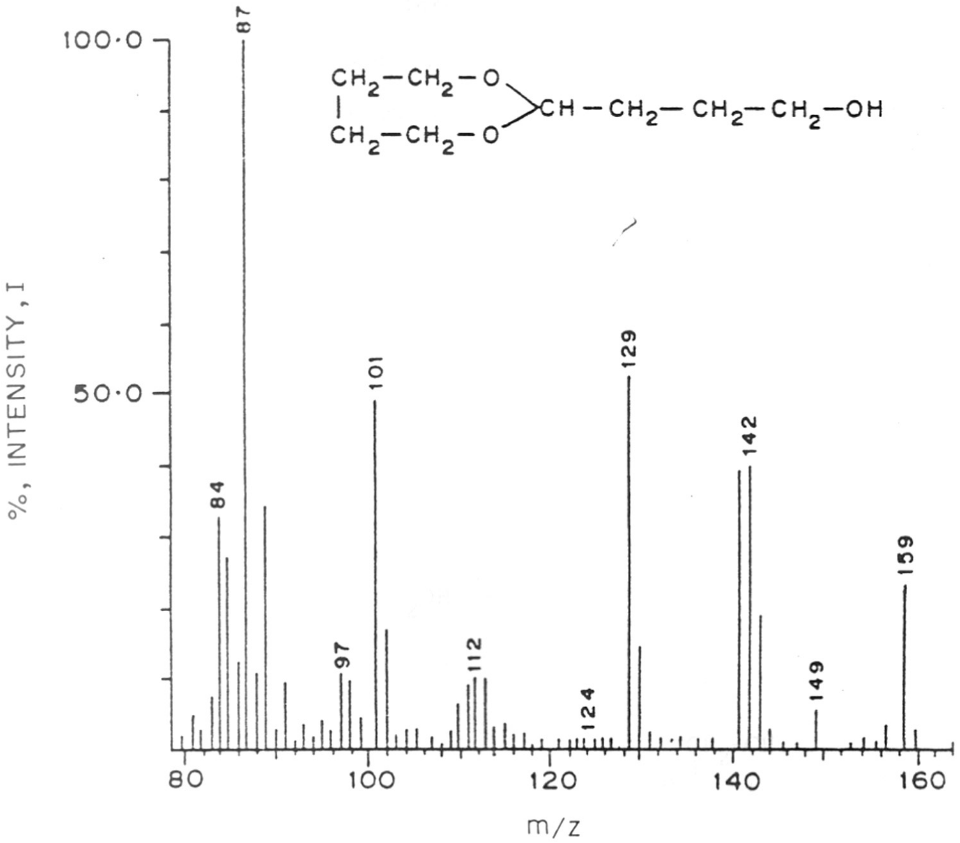


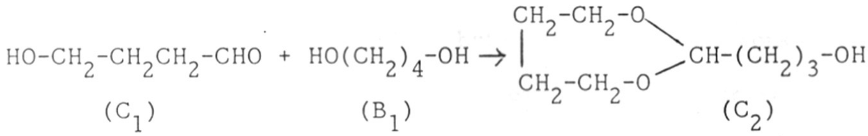
FIGURE 4·5: FRAGMENTATION PATTERN OF THE MASS SPECTRUM OF ACETAL

The NMR spectra of the isolated sample showed a peak corresponding to δ value at 5.06 which confirms the presence of $>$CH and therefore confirms the above structure. These products account for almost 95-98% of the material balance in hydrogenation of butynediol and therefore the following reaction scheme is proposed.

$$\underset{(A)}{H_2} + \underset{(B_3)}{HO\text{-}H_2C\text{-}C{\equiv}C\text{-}CH_2} \longrightarrow \underset{(B_2)}{HO\text{-}H_2C\text{-}CH{=}CH\text{-}CH_2OH} \qquad (iv)$$

$$\underset{(A)}{H_2} + \underset{(B_2)}{HO\text{-}H_2C\text{-}CH{=}CH\text{-}CH_2OH} \longrightarrow \underset{((B_1)}{HO\text{-}(CH_2)_4\text{-}OH} \qquad (v)$$

$$\underset{(B_2)}{HO\text{-}H_2C\text{-}CH{=}CH\text{-}CH_2OH} \longrightarrow \underset{(C_1)}{HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CHO} \qquad (vi)$$



$$\underset{(C_1)}{HO\text{-}CH_2\text{-}CH_2CH_2\text{-}CHO} + \underset{(B_1)}{HO(CH_2)_4\text{-}OH} \rightarrow \underset{(C_2)}{\left.\begin{matrix} CH_2\text{-}CH_2\text{-}O \\ | \\ CH_2\text{-}CH_2\text{-}O \end{matrix}\right\rangle CH\text{-}(CH_2)_3\text{-}OH}$$

(vii)

$$\underset{(A)}{2\ H_2} + \underset{(C_1)}{HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CHO} \longrightarrow \underset{(C_3)}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2OH}$$

(viii)

4.5 RESULTS AND DISCUSSION

4.5.1 Product Distribution and Selectivity

The likely formation of γ-hydroxybutyraldehyde and acetals with noble metal catalysts was speculated earlier (Rylander 1967 and Del Rosso et al. 1984), however , this is the first attempt wherein, these products have been isolated, characterised and estimated quantitatively. Several experiments were carried out under various H_2 pressures, butynediol concentrations and catalyst loadings. The range of conditions studied is given in Table (4.2). In a few experiments, concentration-time data were observed and these are presented in Appendix II. For most experiments, initial rates were calculated by the method described in Section (3.3) and these data are presented in Table (4.3). Some typical results of concentration-time data are shown in Figures (4.6) to (4.9), for 0.2% Pd/C catalyst, for different temperatures. It is clear from these data, that in hydrogenation of butynediol, several consecutive and parallel reactions are involved leading to a lower selectivity of butanediol. It has been generally observed that below 30-40% conversion range, butenediol was the major product with $>$ 95% selectivity. At the stage of complete conversion of butynediol, the selectivity of butenediol was in the range of 60 to 75%, the remaining product being mainly butanediol. It was only after the complete conversion of butynediol, that the rate of hydrogenation of butenediol to butanediol and the side reactions leading to the formation of n-butyraldehyde,

TABLE - 4.2

RANGE OF VARIABLES

Temperature = 303 to 353, K

H_2 pressure = 1.47×10^3 to 6.98×10^3, kPa

Catalyst loading = 2 to 12, kg/m^3

Initial concentration of butynediol = 0.5 to 2.85, $kmol/m^3$

Agitation speed = 9.13 to 15, Hz

TABLE - 4.3

INITIAL RATE DATA FOR HYDROGENATION OF BUTYNEDIOL USING 0.2% Pd/C CATALYST

Volume of liquid phase : 2.5×10^{-4}, m^3

Run No.	Agitation speed H_z	Catalyst loading w, kg/m^3	H_2-Pressure $P_H \times 10^{-3}$ kPa	Initial concentration of B_3, kmol/m^3	Initial rate of reaction $r_1 \times 10^4$,
1.	2.	3.	4.	5.	6.
	Temperature : 303 K				
29	15	4.0	3.541	1.977	0.419
23		12.0	3.541	1.977	1.26
22		12.0	6.987	1.977	2.48
	Temperature : 313 K				
14	15	4.0	3.541	1.977	0.60
15		12.0	3.541	1.977	2.30
16		12.0	6.987	1.977	4.32
18		12.0	1.473	1.977	0.90
20		4.0	3.541	1.177	1.80
31		4.0	3.541	0.50	3.30
19		4.0	3.541	2.85	0.35
37	12.25	12.0	3.541	1.977	2.40
38	9.13	12.0	3.541	1.977	2.15

1.	2.	3.	4.	5.	6.
	Temperature : 333 K				
12	15	2.0	3.541	1.977	0.74
6		4.0	3.541	1.977	1.477
11		8.0	3.541	1.977	2.95
27		12.0	3.541	1.977	4.43
10		4.0	1.473	1.977	0.60
9		4.0	5.263	1.977	2.19
8		4.0	6.987	1.977	2.91
13		4.0	3.541	1.163	3.28
32		4.0	3.541	2.850	1.01
	Temperature : 353 K				
26	15	2.0	3.541	1.977	1.60
25		4.0	3.541	1.977	2.45
24		12.0	3.541	1.977	7.75
28		4.0	6.987	1.977	5.30
33		8.0	3.541	1.977	5.95
34		4.0	1.473	1.977	1.25
35	12.25	12.0	3.541	1.977	7.50
36	9.13	12.0	3.541	1.977	6.50

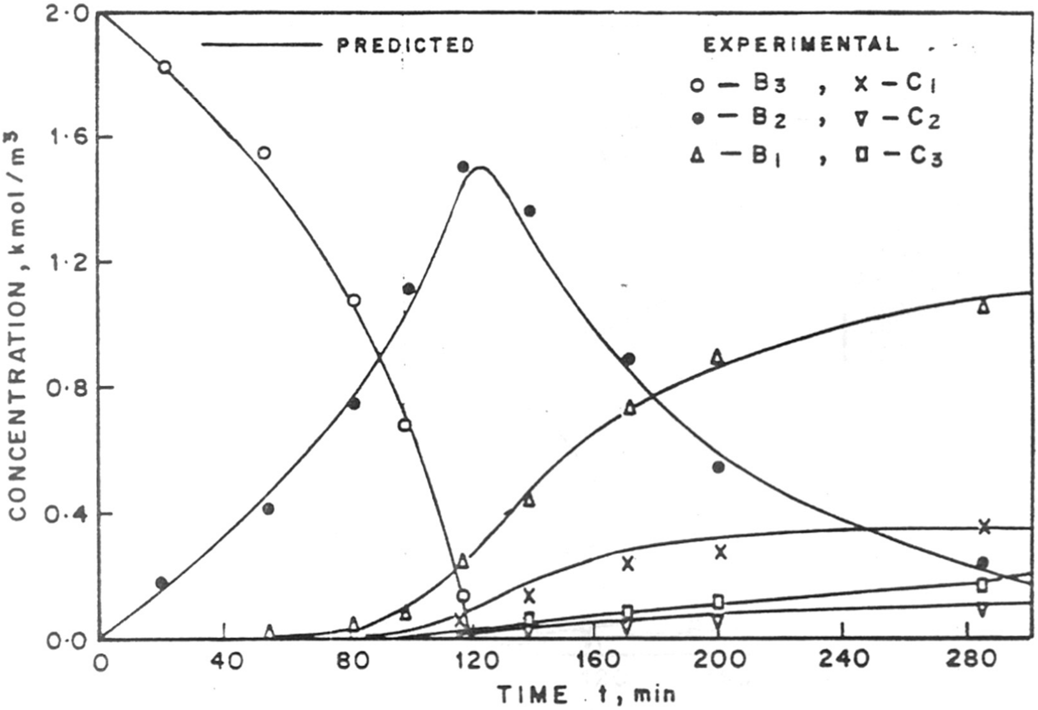


FIGURE 4·6: CONCENTRATION-TIME PLOT

Temperature = 303,K

H_2 Pressure = $3·54 \times 10^3$, kPa

Initial B_3 = 1·977, kmol / m³

Catalyst loading = 12·0, kg / m³

Agitation speed = 15, Hz

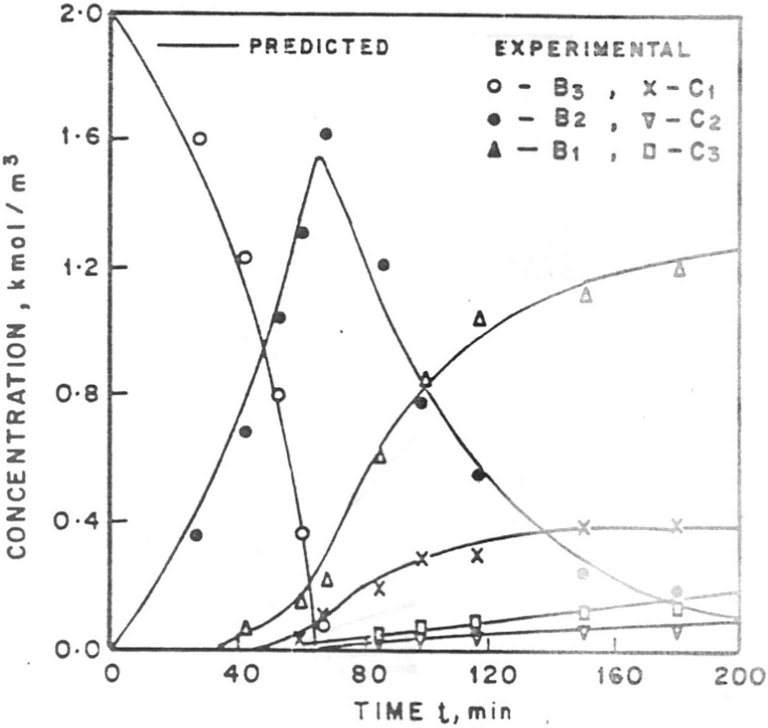


FIGURE 4.7 CONCENTRATION - TIME PLOT

Temperature = 313, K
H_2 Pressure = 3.54×10^3, kPa
Initial B_3 = 1.977, kmol / m^3
Catalyst loading = 12.0, kg / m^3
Agitation speed = 15, Hz

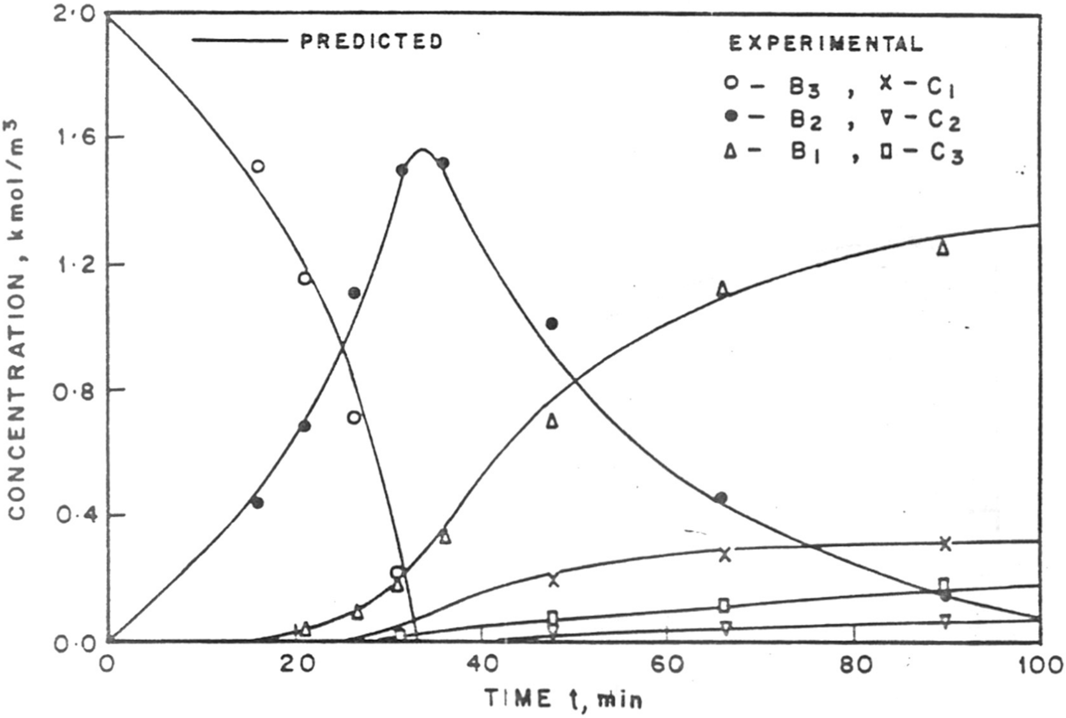


FIGURE 4·8: CONCENTRATION – TIME PLOT

Temperature = 333, K

H_2 Pressure = $3{\cdot}54 \times 10^3$, kPa

Initial B_3 = 1·977, kmol/m^3

Catalyst loading = 12·0, kg/m^3

Agitation speed = 15, Hz

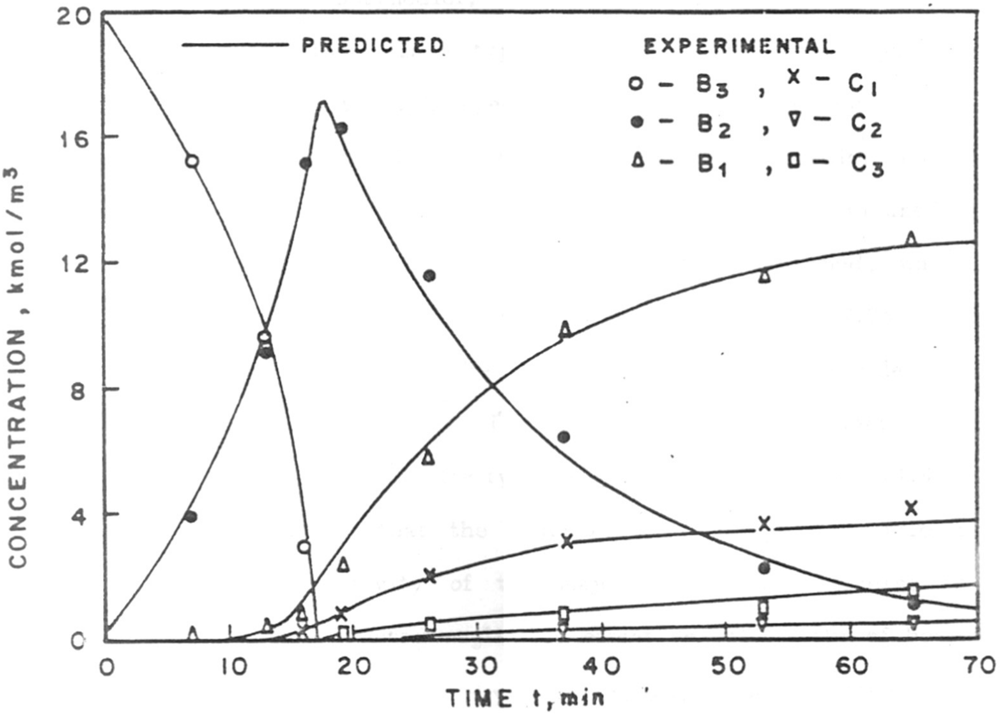


FIGURE 4·9:CONCENTRATION–TIME PLOT

Temperature = 353 ,K
H_2 Pressure = $3 \cdot 54 \times 10^3$, kPa
Initial B_3 = 1·977 , kmol / m^3
Catalyst loading = 12·0 , kg / m^3
Agitation speed = 15 ,Hz

n-butanol, γ-hydroxybutyraldehyde, and the acetal were significant. It appears that due to the strong adsorption characteristics of butynediol, these reactions are inhibited in the initial region. In a typical case, at 40°C (see Figure (4.7) the selectivity of butenediol at complete conversion of butynediol was found to be 85%, with 11.5% butanediol and 5.47% γ-hydroxybutyraldehyde. The selectivity of butanediol at a stage where butenediol was completely consumed, was found to be 67.6% with 21.6% γ-hydroxybutyraldehyde, 7.7% n-butanol, and 5-6% acetal. The formation of n-butyraldehyde in most cases was negligible. The results showing the effect of reaction conditions on selectivity are presented in Table (4.4). It was observed that the reaction conditions had a mild effect on the selectivity of the major products. Increase in the temperature showed negligible effect on selectivity of butenediol, butanediol and γ-hydroxybutyraldehyde. Increase in H_2 pressure showed decrease in selectivity of γ-hydroxybutyraldehyde. Variation in the catalyst loading and initial butynediol concentration also showed no significant effect on the selectivity of these products. This indicates that the selectivity of butanediol cannot be improved by change in the operating conditions, and may require modification of the catalyst by selective poisoning techniques.

4.5.2 Analysis of Initial Rate Data

For the purpose of kinetic study, initial experiments were carried out with 2% and 0.2% Pd/C catalysts. In the

TABLE - 4.4

EFFECT OF REACTION CONDITIONS ON SELECTIVITY

Run No.	Temperature K	Catalyst loading, w, kg/m^3	H_2 Pressure, P_{H_2}, kPa	Initial B_3. $kmol/m^3$	Selectivity, %		
					B_2^*	B_1^+	C_1^+
1.	2.	3,	4.	5.	6.	7.	8.
23	303	12.0	3.54×10^3	1.97	81.5	60.7	20.4
15	313	12.0	3.54×10^3	1.97	85.3	67.6	21.6
27	333	12.0	3.543×10^3	1.97	85.8	68.5	22.4
24	353	12.0	3.54×10^3	1.97	81.9	69.35	22.8
22	303	12.0	6.98×10^3	1.97	81.5	67.66	16.4
18	313	12.0	1.47×10^3	1.97	86.8	61.26	27.2
25	353	4.0	3.54×10^3	1.97	83.0	54.6	27.9
28	353	4.0	6.98×10^3	1.97	84.1	58.3	22.8
11	333	8.0	3.54×10^3	1.97	82.9	55.3	28.9
13	333	4.0	3.54×10^3	1.16	74.9	50.50	29.2
6	333	4.0	3.54×10^3	1.97	81.2	55.8	24.6

* Selectivity at 100% conversion of B_3 , + Selectivity at 100% conversion of B_2

case of 2% Pd/C catalyst, the rate of hydrogenation was found to be strongly dependent on agitation speed as shown in Figure (4.10), for two catalyst loadings. Even for the lower loading (2.0 kg/m^3) the agitation has a pronounced effect on the rate of reaction, indicating that gas-liquid mass transfer resistance was significant. On the other hand, for 0.2% Pd/C catalyst, the rate of hydrogenation was found to be independent of agitation speed. The effect of agitation speed for 0.2% Pd/C catalyst is shown in Figure (4.11) for temperatures 303 and 353K for a catalyst loading of 12.0 kg/m^3 (highest loading studied). It can be seen from Figure (4.11) that for the highest temperature and catalyst loading studied in the present work, the agitation speed does not show any influence on the initial rate of reaction, beyond 12.5 Hz. Hence for kinetic modelling all the experiments were carried out using 0.2% Pd/C catalyst at an agitation speed of 15Hz.

The initial rates of hydrogenation mainly representing the conversion of butynediol to butenediol were calculated under different conditions and the results are discussed below. In general, the analysis of initial rates, indicates general trends and can be useful for the first evaluation of mass transfer effects, if any.

4.5.2.1 Effect of Hydrogen Pressure

The effect of hydrogen pressure on the initial rate of hydrogenation of butynediol is shown in Figure (4.12) for temperatures 313, 333 and 353 K. It can be seen that the rates vary linearly with hydrogen pressure.

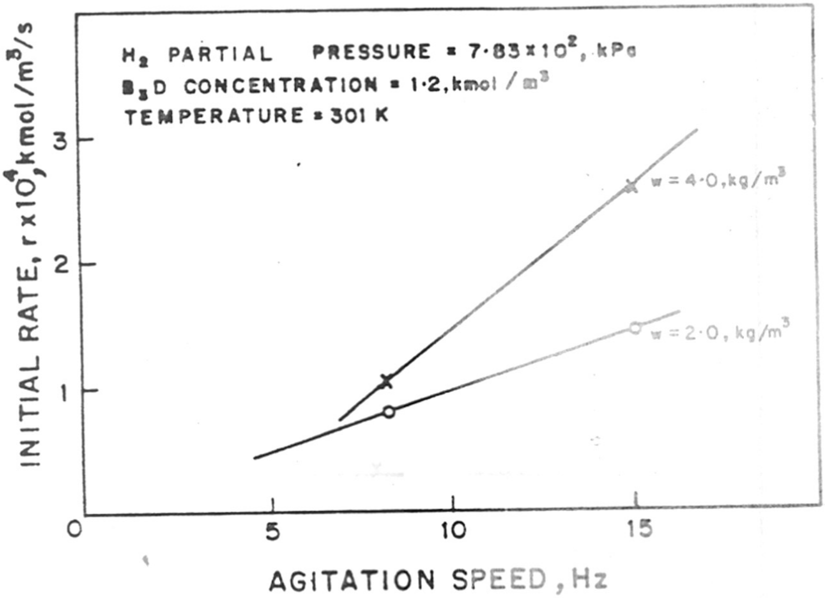


FIGURE 4·10: EFFECT OF AGITATION SPEED ON r_1.
(FOR 2 % Pd/C CATALYST)

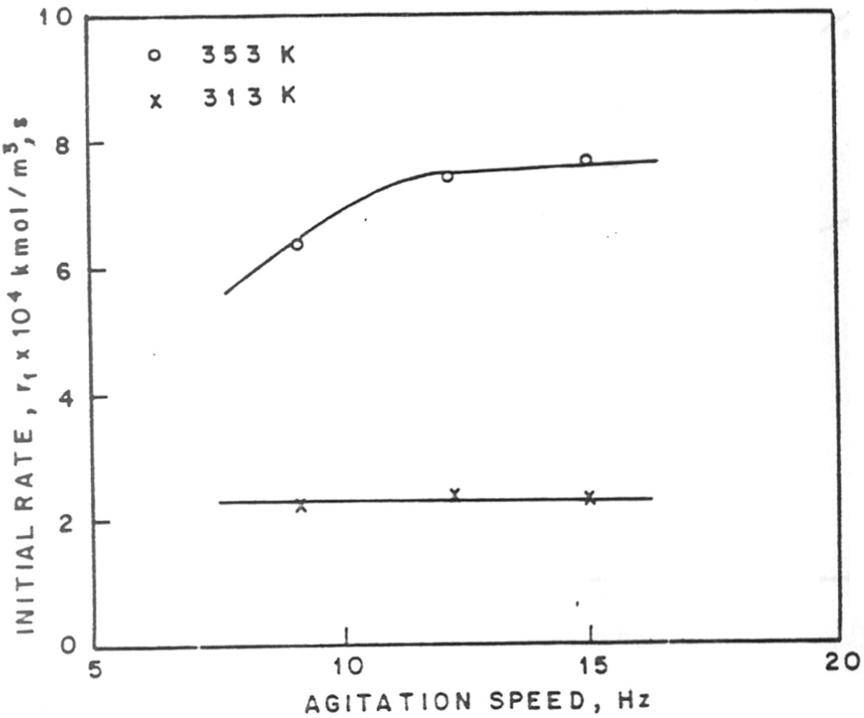


FIGURE 4·11: EFFECT OF AGITATION SPEED ON r_i FOR 0·2 % Pd/C CATALYST

H_2 Pressure = $3{\cdot}54 \times 10^3$, kPa
Initial B_3 = 1·977, kmol/m^3
Catalyst loading = 12·0, kg/m^3

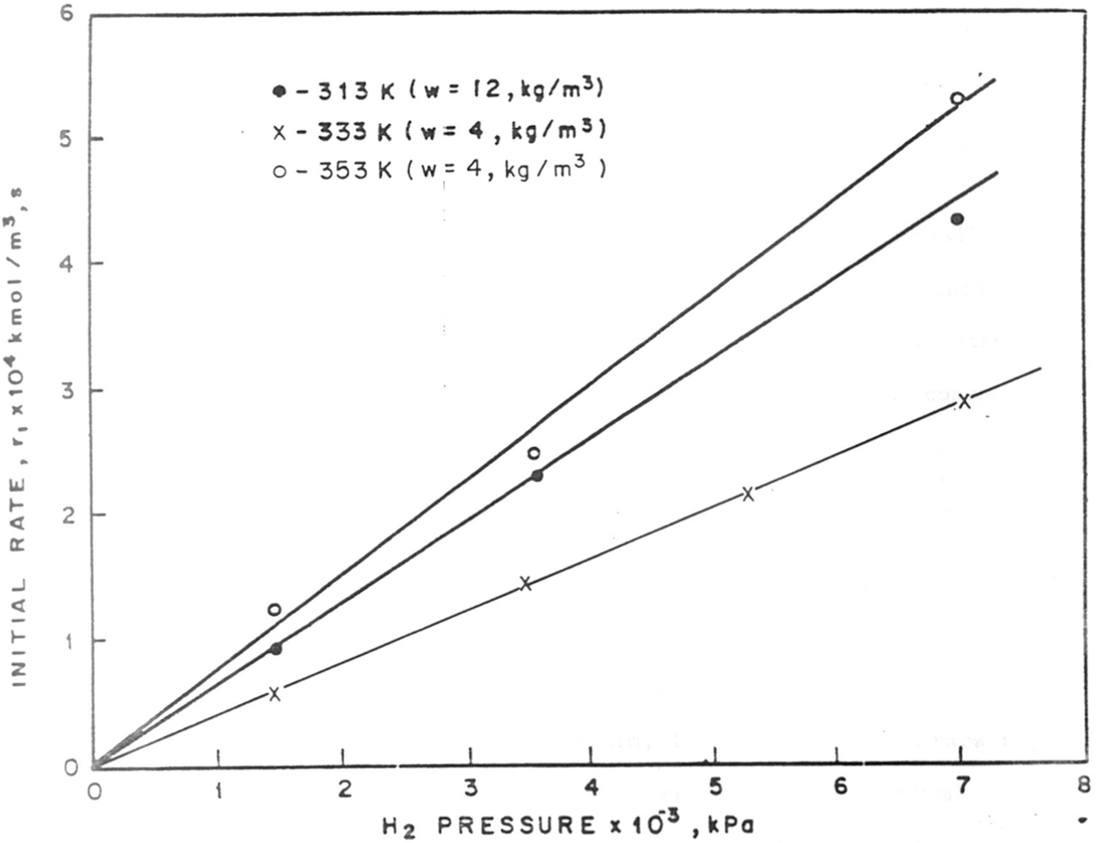


FIGURE 4·12: EFFECT OF HYDROGEN PRESSURE ON r_1

(FOR 0·2 % Pd/c CATALYST)

Agitation speed = 15, Hz

Initial B_3 = 1·977, kmol/m^3

4.5.2.2 Effect of Catalyst Loading

The effect of catalyst loading on the initial rate, is shown in Figure (4.13). Here, again the initial rate was found to vary with the catalyst loading.

4.5.2.3 Effect of Initial Concentration of Butynediol

The effect of initial butynediol concentration on the rate is shown in Figure (4.14). This figure clearly indicates, that hydrogenation of butynediol to butenediol is a case of substrate inhibitted kinetics, especially at higher concentrations of butynediol.

4.5.3 Analysis of Mass Transfer Effect

Since with 0.2% Pd/C catalyst, a change in agitation speed showed no effect on the initial rate of reaction, gas-liquid mass transfer resistance was considered to be absent. To further ensure that gas-liquid, liquid-solid and intraparticle mass transfer resistances were negligible, the initial rates were compared with the maximum rates of each mass transfer process, and the factors, α_1, α_2 and ϕ_{exp} as discussed by Satterfield (1970) and Ramachandran and Chaudhari (1983) were evaluated. (For a detailed discussion, see Section (3.5)). These factors were found to be in the range 0.006 to 0.11, 0.001 to 0.006 and 0.04 to 0.11 respectively, which clearly indicate, that the present reaction was in the kinetic regime.

For calculation of parameters, α_1, α_2 and ϕ_{exp} a knowledge of solubility of H_2 in the reaction mixture, gas-liquid and liquid-solid mass transfer coefficients and effective

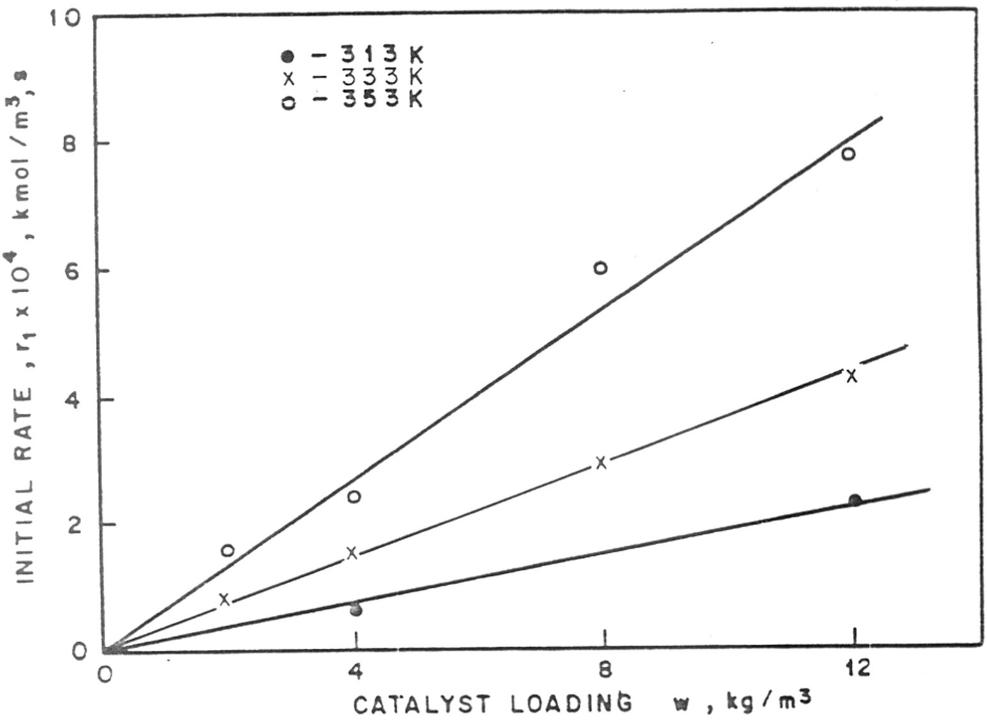


FIGURE 4·13: EFFECT OF CATALYST LOADING ON r_1 (FOR 0·2 % Pd/C CATALYST)

H_2 Pressure = $3 \cdot 54 \times 10^3$, kPa
Initial B_3 = 1·977, kmol / m^3
Agitation speed = 15, Hz

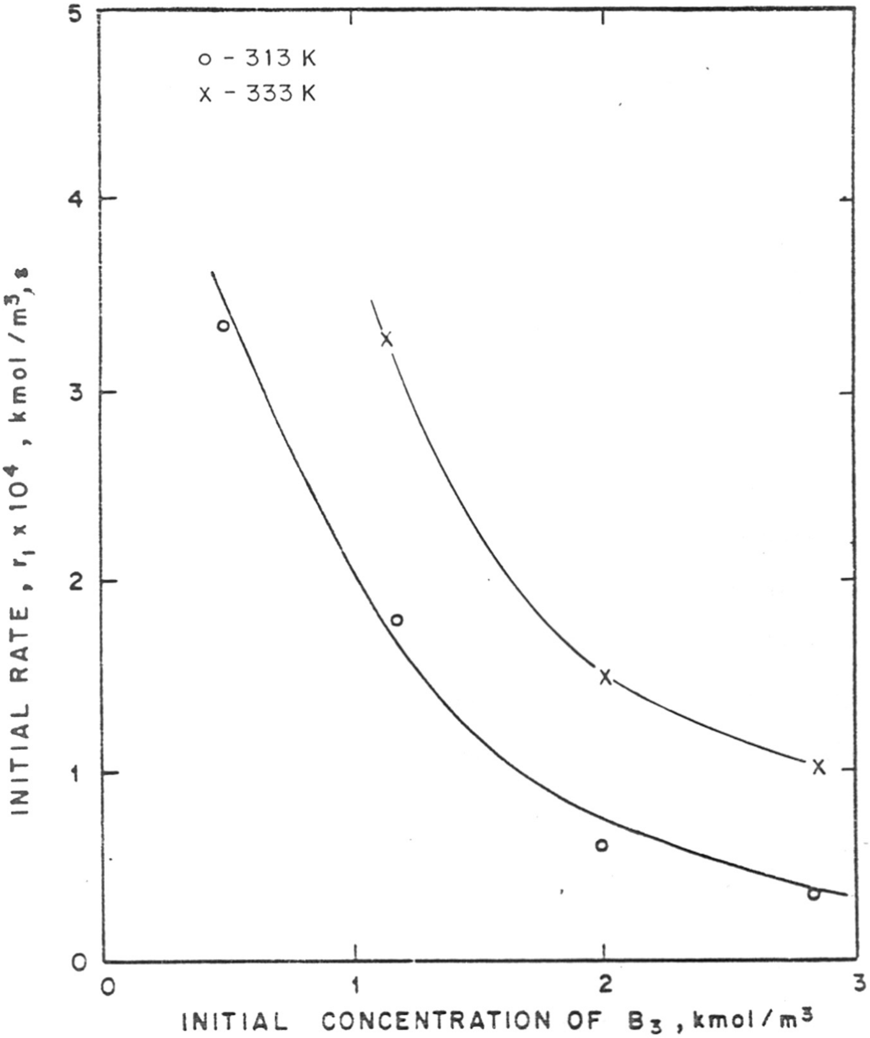


FIGURE 4·14: EFFECT OF INITIAL CONCENTRATION OF B_3 ON r_1 (0·2 % Pd/C CATALYST)

H_2 Pressure = $3 \cdot 54 \times 10^3$, kPa
Catalyst loading = 4·0, kg/m³
Agitation speed = 15, Hz

diffusivity is essential. The solubility data were used from the work of Brahme et al. (1981), and these are given as Henry's constants in Table (4.5). Liquid-solid mass transfer coefficient, molecular diffusivity and effective diffusivity were calculated from the literature correlations of Sano et al; (1974), Wilke and Chang (1955) and Satterfield (1970) respectively.

4.6 KINETIC MODEL

For the purpose of kinetic modelling, it was thought more appropriate to fit the observed concentration-time data to a batch reactor model, since several products are formed during hydrogenation of butynediol. The material balance of the various species can be represented by the following set of equations based on the reactions (iv) to (viii).

$$-\frac{d\,B_3}{dt} = r_1 \tag{4.1}$$

$$-d\,B_2/dt = -r_1 + r_2 + r_3 \tag{4.2}$$

$$-d\,B_1/dt = -r_2 + r_4 \tag{4.3}$$

$$-d\,C_1/dt = -r_3 + r_4 + r_5 \tag{4.4}$$

$$-d\,C_2/dt = -r_4 \tag{4.5}$$

$$-d\,C_3/dt = -r_5 \tag{4.6}$$

TABLE - 4.5

SOLUBILITY DATA FOR H_2 - BUTYNEDIOL - WATER SYSTEM

Temperature K	Henry's Constant, H_A kmol/m^3 kPa
303	6.82×10^{-6}
313	7.907×10^{-6}
333	8.55×10^{-6}
353	9.09×10^{-6}

With the initial conditions that at

$$t = 0, \; B_3 = B_{03}, \; B_2 = B_1 = C_1 = C_2 = C_3 = 0 \qquad (4.7)$$

The following rate equations were assumed.

$$r_2 = \frac{w\, k_1\, A^*}{(1 + K\, B_3^2)} \qquad (4.8)$$

$$r_2 = \frac{w\, k_2\, A^*\, B_2}{(1 + K\, B_3^2)} \qquad (4.9)$$

$$r_3 = \frac{w\, k_3\, B_2}{(1 + K\, B_3^2)} \qquad (4.10)$$

$$r_4 = k_4 \qquad (4.11)$$

$$r_5 = \frac{w\, k_5\, A^*}{(1 + K\, B_3^2)} \qquad (4.12)$$

where r_1, r_2, r_3, r_4, and r_5 represent the rates of reaction steps (iv) to (viii) respectively.

The basis of choice of the above rate equations deserves comments. If we observe the nature of the concentration profiles shown in Figures (4.6) to (4.9), the following points emerge regarding the trends of individual reactions.

1. The rate of reaction of butynediol (B_3) increases with decrease in B_3 and ultimately shows a zero order dependence at lower concentrations. Therefore the rate equation (4.8) was chosen which is consistent with the observed trend.

2. The rate of consumption of butenediol shows a first order type curve, but negligible reaction occurs until B_3 has disappeared. Equation (4.9) is consistent with this trend.
3. All catalytic reactions except reaction (4.1) occurs at very low rates until B_3 has disappeared, which indicates the strong adsorption characteristics of butynediol. Hence, in all these steps, an inhibition term $(1 + KB_3^2)$ in the denominator has been considered. This explains negligible formation of other products until B_3 is finite.
4. The rates of acetal (C_2) and butanol (C_3) formation in all the cases were constant (beyond $B_3=0$), though the concentrations of B_2, B_1 and C_1 vary substantially with time. This behaviour is consistent with zero order dependence and hence rate equations (4.11) and (4.12) were chosen. Thus, instead of randomly discriminating several rate forms, above rate models were chosen for fitting the experimental data based on the observed trends.

In order to simulate the experimental concentration time data, initial trial values of the rate parameters are required. These were estimated from the data in different regions. For example, in the initial region, only reaction (iv) was dominant, and hence, the rate evaluated at different times can be represented by equation (4.8). This equation can be rearranged to give

$$\frac{1}{r_1} = \frac{1}{w\ k_1 A^*} + \frac{K\ B_3^2}{w\ k_1 A^*} \qquad (4.13)$$

Hence from the slope and intercept of a plot of $1/r_1$ vs. B_3^2 , k_1 and K were evaluated. Typical plots of $1/r_1$ vs. B_3^2 for 313 and 333 K are shown in Figure (4.15). Similarly, the trial values of k_4 and k_5 were directly evaluated from the rates of formation of acetal and butanol in a certain range. Once k_4 and k_5 are known, k_2 and k_3 were obtained from the rates of formation of butanediol (B_1) and γ-hydroxybutyraldehyde (C_1). For example, the guess values of k_1, k_2,k_3,k_4,k_5 and K obtained for 313 K were, 3.72×10^{-3}, 8.2×10^{2}, 7×10^{-3}, 2×20^{-9}, 6×10^{-2} and 1.29 respectively.

The approximate values of the rate parameters obtained as discussed above, were used as initial guesses, and the batch reactor equation (4-1) to (4.6) were solved by Range-Kulta method, combined with a non linear optimization programme to simulate the experimental concentration-time curves and obtain the rate parameters. The best values of the rate parameters are presented in Table (4.6), for different temperatures. The experimental and predicted results were found to agree well for most of the experiments within the experimental error of 8%. Some typical results are shown in Figures (4.6) to (4.9).

The temperature dependence of the rate parameters k_1 and k_2, and k_3 and k_4 and k_5 and K are shown in Figures (4.16) to (4.18) respectively as Arhenious plots. From the slopes of these plots, the activation energies and heat of adsorption were calculated. These values are presented in Table (4.7). The activation energies of reaction (iv) and (v) were found to be 34.4 and 24.1 kJ/mol respectively. The activation energy values are rather low and such observations

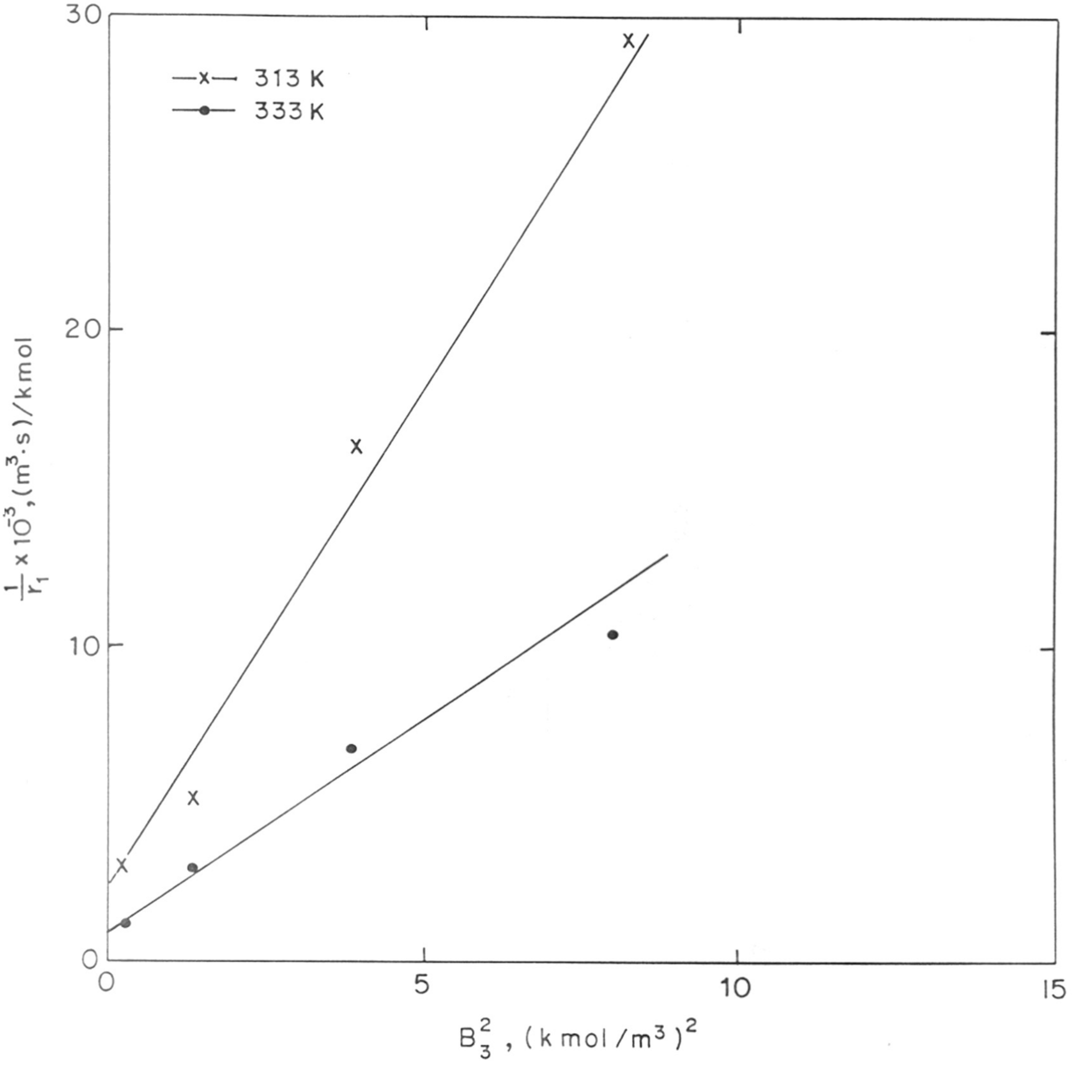


FIGURE 4·15: PLOTS OF $1/r_1$ vs. B_3^2

TABLE - 4.6

THE RATE CONSTANTS FOR VARIOUS STEPS IN HYDROGENATION OF BUTYNEDIOL

Temperature K	$k_1 \times 10^3$, $m^3/kg,s$	$k_2 \times 10^4$, $(m^3/kg,s)$ $(m^3/kmol)$	$k_3 \times 10^6$, $m^3/kg,s$	$k_4 \times 10^6$, $kmol/m^3,s$	$k_5 \times 10^5$, $m^3/kg,s$	K, $(m^3/kmol)^2$
303	2.30	0.45	5.8	7.3	4.6	1.1
313	4.15	0.69	9.0	7.9	5.5	1.3
333	7.56	1.32	15.0	10.0	11.0	1.35
353	15.0	1.65	22.0	15.0	13.0	1.60

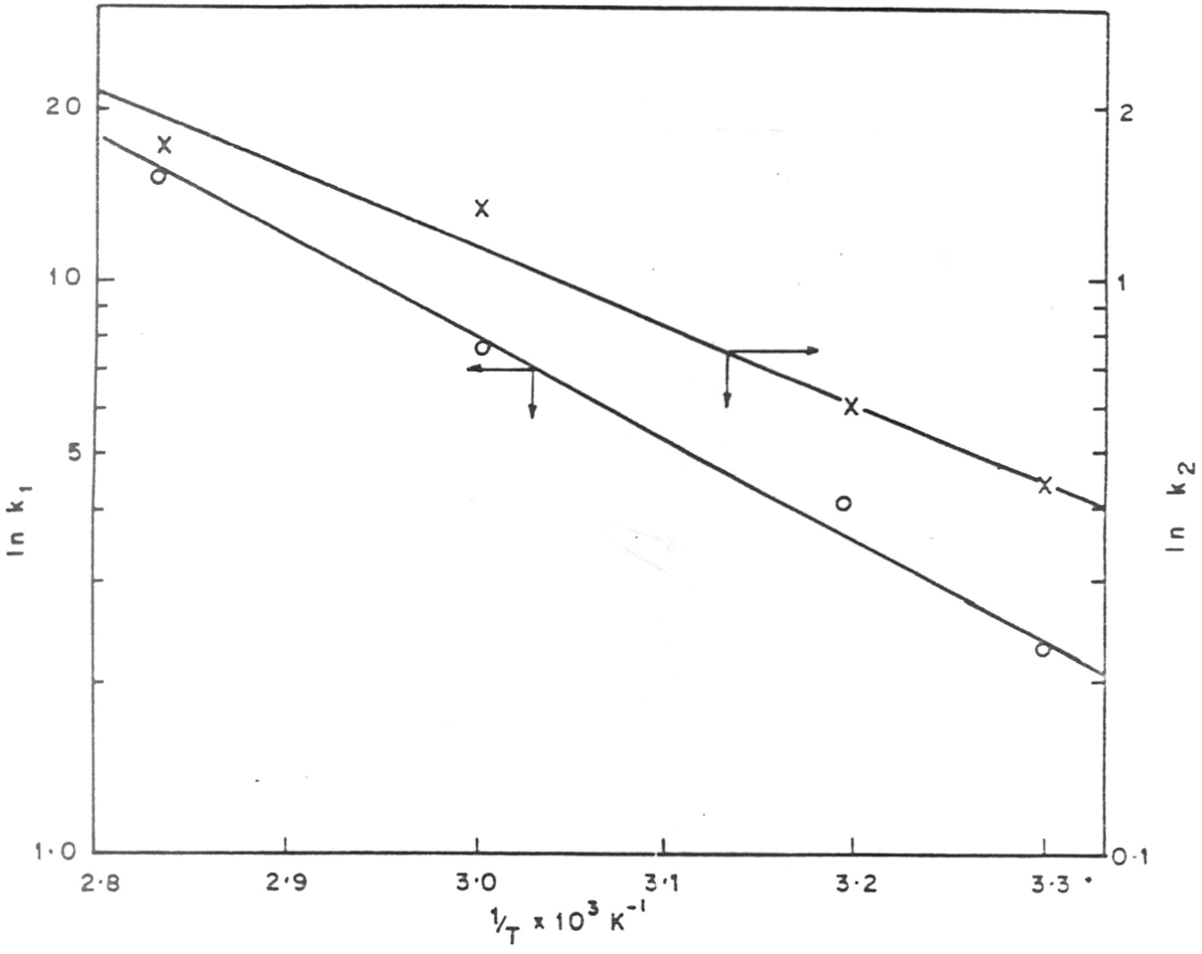


FIGURE 4·16: TEMPERATURE DEPENDENCE OF THE RATE CONSTANTS k_1 AND k_2

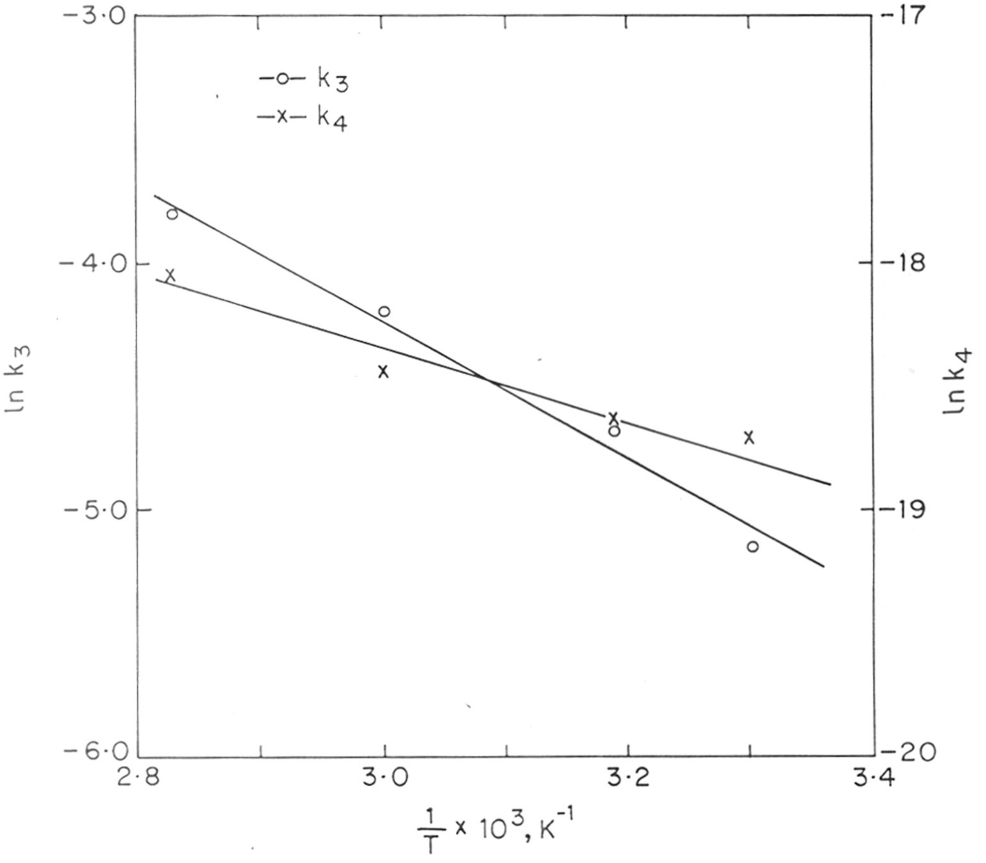


FIGURE 4.17: TEMPERATURE DEPENDENCE OF RATE PARAMETERS k_3 AND k_4

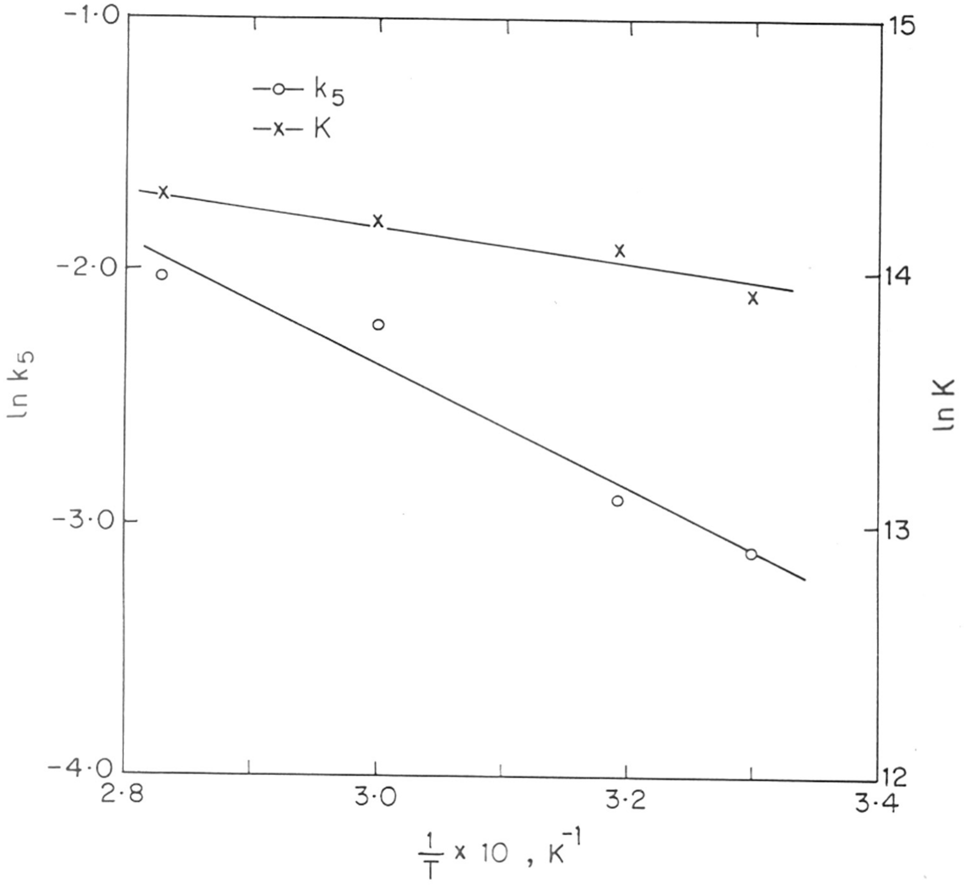


FIGURE 4·18 : TEMPERATURE DEPENDENCE OF RATE PARAMETERS k_5 AND K

TABLE - 4.7

ACTIVATION PARAMETERS

Activation energy, E_1,	:	34.40 kJ/mol
Activation energy, E_2,	:	24.10 kJ/mol
Activation energy, E_3	:	23.36 kJ/mol
Activation energy, E_4,	:	12.74 kJ/mol
Activation energy, E_5,	:	20.08 kJ/mol
Heat of absorptioin of butynediol, ΔH_β,	:	5.93 kJ/mol

could be indicative of diffusion control. However, in the present work, it was ensured that at the highest catalyst loading (12.0 kg/m^3) and highest temperature (353 K) studied, agitation speed had no effect at 15 Hz. Also the liquid-solid and intraparticle diffusion resistances were found to be negligible as already discussed. The lower activation energy appears to be an intrinsic characteristic of several liquid phase catalytic hydrogenation reactions as evidenced in earlier reports (Shutt and Winterbottom, 1971, Teresawa et al., (1979).

4.7 CONCLUSIONS

Hydrogenation of butynediol using 0.2% Pd/C catalyst was studied in a batch slurry reactor. While, in the initial region, only hydrogenation of butynediol to butenediol was dominant, in the latter region, several reactions leading to the formation of butanediol, γ-hydroxybutyraldehyde, n-butanol and acetal were found to occur. All these products were identified and characterised by GC, GCMS, IR, NMR, column chromatography and elemental analysis methods. The formation of these products, as a function of time was quantitatively observed with the aim of using these data for kinetic modelling. The initial rate data showed linear dependence of rates with respect to the catalyst loading and H_2 pressure, while with respect to butynediol, a substrate inhibited kinetics was observed. The concentration–time data at 303, 313, 333 and 353K were fitted using a set of rate equations and kinetic parameters were evaluated. The agreement between the experimental and predicted results was found to be excellent. The activation energies and heat of adsorption have also been evaluated.

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CHAPTER - 5

PERFORMANCE OF A CONTINUOUS BUBBLE COLUMN SLURRY REACTOR FOR HYDROGENATION OF BUTYNEDIOL

CHAPTER - 5

PERFORMANCE OF A CONTINUOUS BUBBLE COLUMN SLURRY REACTOR FOR HYDROGENATION OF BUTYNEDIOL

5.1 INTRODUCTION

Bubble column slurry reactors are extensively used in several industrial processes due to efficient heat and mass transfer. Also, very fine catalyst particles can be used in these reactors which eliminates intraparticle diffusional resistances, leading to more effective use of the catalyst. Generally, bubble columns can be operated in a semi batch or continuous mode. Some of the important industrial processes in bubble columns are, Fischer-Tropsch synthesis, hydrogenation of oils and several unsaturated organic compounds and polymerisation of ethylene.

The subject of mathematical modelling of slurry reactors has been reviewed by Chaudhari and Ramachandran (1980), Shah (1979), Shah et al.(1982) Ramachandran and Chaudhari (1983), and Deckwer (1985). Though the theoretical analysis of slurry reactors has considerably progressed, the information on modelling of continuous slurry reactors is rather limited.

Goto and Smith (1978) compared the performance of slurry, trickle bed and packed bed reactors for the oxidation of sulfurdioxide at 25°C and 1 atmosphere pressure, using activated carbon as a catalyst. They developed equations to predict the fractional conversion of the gaseous reactant.

Ramachandran and Chaudhari (1980) proposed a mixing cell model for continuous slurry reactors, which was used later by Brahme et al.(1984) to simulate pilot plant data on hydrogenation of glucose to sorbitol.

Deckwer et al. (1982) modelled the F-T synthesis in the slurry phase based on a first order rate expression for hydrogen consumption. They concluded, that under the process conditions, gas-liquid and liquid-solid mass transfer resistances and catalyst settling were negligible. Stern et al. (1980) also studied the effect of mass transfer, on the performance of slurry reactors used for F-T. synthesis.

Most of the literature reports deal with simple reaction kinetics and only a few attempts to analyse reactions with nonlinear L-H type kinetics have been made so far. The reliability of, mass transfer, kinetic and mixing parameters used in predicting the performance of these reactors is an important aspect. Several industrially important reactions follow non-linear kinetics, and also the system properties are such that the mass transfer parameters differ considerably from the ideal air-water system commonly used in most of the reported studies. This indicates a strong need for case studies on modelling of slurry reactors.

The objective of the present work was to develop a model for a continuous bubble column slurry reactor, and assess its applicability to hydrogenation of butynediol to butenediol using Pd-Zn-$CaCO_3$ catalyst. A mixing cell approach has been used in predicting the conversion of liquid phase reactant (i.e. butynediol). The effect of gas and liquid velocity, H_2 pressure, catalyst loading, butynediol concentration and temperature on the conversion of butynediol has been discussed based on theoretical predictions. The model predictions have also been compared with some experimental data obtained in a laboratory scale reactor and the applicability of the literature correlations for gas-liquid mass transfer coefficient has been critically discussed.

5.2 KINETICS

The kinetcs of selective hydrogenation of butynediol to butenediol, has been studied in detail by Chaudhari et al. (1985). Extensive experimental data were obtained in a batch slurry reactor in the temperature range of 303-343K. Analysing initial rate data, it was found that the rate was proportional to the square root of hydrogen pressure, while an increase in butynediol concentration decreased the rate of reaction indicating a substrate inhibition. The following type of L-H model has been proposed:

$$R_A = \frac{w\, k\, \sqrt{A_1}\ B_1}{(1 + K_B\, B_1)^2} \qquad (5.1)$$

which was found to represent the experimental data over a wide range of conditions satisfactorily. The details are discussed elsewhere (Parande, 1983).

Chaudhari et al. (1985) fitted the same rate data to different rate equations, some purely empirical and some corresponding to the L-H models. The list of equations considered, along with the best parameters obtained are presented in Table (5.1). A non-linear least square regression analysis was used with each equation in Table (5.1) to determine the best parameters for each model. The values of $\emptyset_{min}$, the minimised sums of square of difference between the observed and predicted rates are also listed in Table (5.1). It was found that only for equation (5.1), all the rate parameters values were positive for all temperatures. Also $\emptyset_{min}$ was lowest for equation (5.1) for all temperatures. This suggests that equation (5.1) is the best rate equation to represent the kinetics of butynediol hydrogenation, using Pd-Zn-$CaCO_3$ catalyst, within the experimental error of 5-7%.

5.3 DEVELOPMENT OF REACTOR MODEL

The stochiometric reaction of selective hydrogenation of butynediol to butenediol can be written as

$$HOH_2C-C \equiv C-CH_2OH + H_2 \xrightarrow{\text{Catalyst}} HOH_2C - CH = CH -CH_2OH$$

$$B\ (l) \qquad\qquad + A\ (g) \qquad\qquad\qquad (i)$$

with the intrinsic kinetics given by equation (5.1). In developing the mixing cell model, the following assumptions were made.

a) The catalyst is uniformly distributed in the reactor.

b) The liquid-solid and intraparticle mass transfer resistances

TABLE - 5.1

RATA EQUATIONS USED FOR FITTING THE KINETIC DATA AND PARAMETERS OBTAINED

S.No.	Rate Equation	Temp. K	k^+	K_A, $m^3/kmol$	K_B. $m^3/kmol$	Ø min, $(kmol/m^3/s)^2$
1.	2.	3.	4.	5.	6.	7.
1.	$\frac{wk\sqrt{P_{gA} \cdot H_A}\ B_1}{(1 + K_B\ B_1)^2}$	303	0.0116	-	0.267 x 10	0.758×10^{-10}
		313	0.0161	-	0.292 x 10	0.789×10^{-10}
		323	0.0263	-	0.322 x 10	0.142×10^{-8}
		343	0.0664	-	0.421 x 10	-
2.	$\frac{wk\ (P_{gA}\ H_A)\ B_1}{(1 + K_A(P_{gA}\ H_A))(1 + K_B\ B_1)^2}$	303	0.596	0.65×10^3	-0.595×10^2	0.444×10^{-7}
		313	0.438	-0.556×10^2	-0.798×10^3	0.580×10^{-7}
		323	0.409	0.603×10^2	0.321 x 10	0.148×10^{-8}
3.	$\frac{wk\ (P_{gA}\ H_A)\ B_1}{(1 + (K_A\ P_{gA}\ H_A) + K_B\ B_1)^2}$	303	0.590	0.652×10^3	-0.590×10^2	0.442×10^{-7}
		313	-0.430×10^2	-0.546×10^2	0.292 x 10	0.567×10^{-8}
		323	0.859	0.592×10^2	0.686 x 10	0.196×10^{-8}

1.	2.	3.	4.	5.	6.	7.
4.	$\frac{wk\ (P_{gA}\ H_A)\ B_1}{(1 + (K_A\ P_{gA}\ H_A) + K_B\ B_1)}$	303	0.241×10^{-2}	-0.125×10^{3}	0.164×10	0.483×10^{-7}
		313	0.661×10^{-1}	-0.155×10^{4}	0.534	0.907×10^{-7}
		323	0.322×10^{-3}	-0.124×10^{18}	0.230×10^{16}	0.315×10^{-6}
5.	$\frac{wk\ (P_{gA}\ H_A)\ B_1}{(1 + K_A \sqrt{P_{gA}\ H_A} + K_B B_1)^2}$	303	0.442×10	-0.151×10	0.181×10^{2}	0.213×10^{-8}
		313	0.205×10^{10}	0.115×10^{7}	-0.322×10^{7}	0.118×10^{-6}
		323	0.745	0.388×10^{2}	-0.662×10^{2}	0.289×10^{-6}
6.	$\frac{wk\ (P_{gA}\ H_A)\ B_1}{(1 + K_A \sqrt{P_{gA} H_A} + K_B\ B_1)^3}$	303	0.970×10^{-1}	0.296×10^{-1}	0.124×10	0.616×10^{-9}
		313	0.109×10	0.311	0.278×10	0.155×10^{-8}
		323	0.118	-0.720×10^{-2}	0.116×10	0.448×10^{-8}

+ Units of k are $(m^3/kg/s)\ (m^3/kmol)^{\frac{1}{2}}$ in model (1) and $(m^3/kg/s)(m^3/kmol)$ in models (2) to (6) are unimportant, and the primary resistance to mass transfer is at the gas-liquid interface.

c) Isothermal conditions prevail in the reactor.

d) Gas phase mixing as well as gas side mass transfer resistance is unimportant, as in the present case pure hydrogen gas was used.

In a mixing cell model, the three phase slurry reactor is visualised as a number of backmixed reactors (N cells) in series. The schematic of the model is presented in Figure (5.1). The mass balance equations for species A and B for a particular cell are given below.

$$Q_L\ (A_{li} - A_{lo}) + K_L\ a_B\ V_R\ (A^* - A_{lo}) = V_R\ \frac{wk\sqrt{A^*}\ B_{lo}}{(1 + K_B\ B_l)^2} \tag{5.2}$$

and

$$Q_L\ (B_{li} - B_{lo}) = V_R\ \frac{w\ k\sqrt{A^*}\ B_{lo}}{(1 + K_B\ B_l)^2} \tag{5.3}$$

where,

A_{li}, A_{lo} ,	concentration of species A and B entering and leaving a particular cell respectively, kmol/m^3.
Q_L ,	volumetric flow rate of liquid, m^3/s.
V_R ,	volume of the reactor, m^3.
B_{li}, B_{lo},	dissolved concentration of species B (Butynediol) entering and leaving a particular cell respectively kmol/m^3.
A^* ,	equilibrium concentration of A, in liquid phase, kmol/m^3.

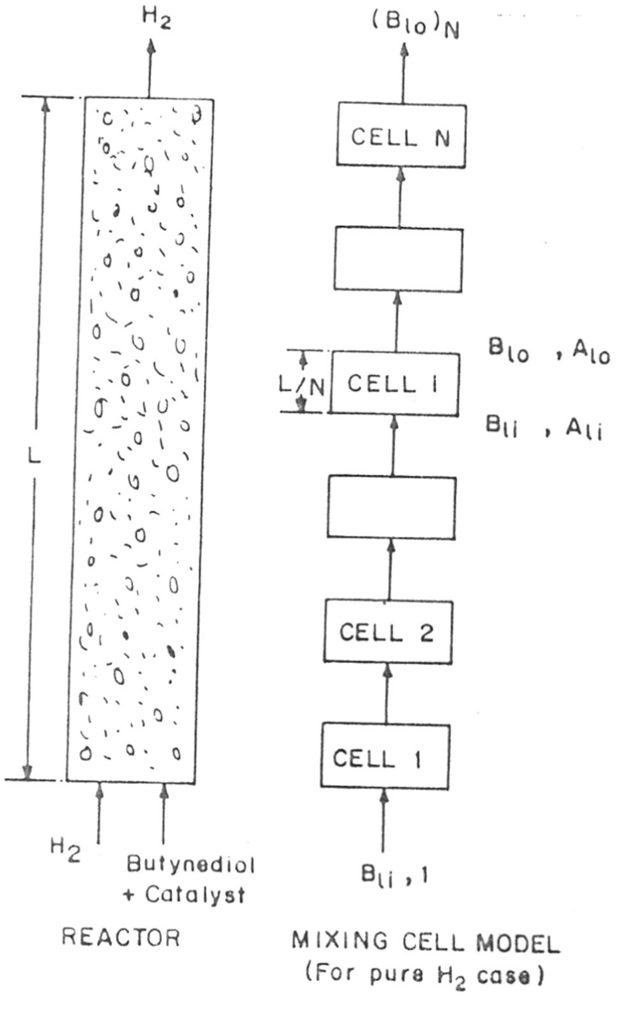


FIGURE 5·1: SCHEMATIC REPRESENTATION OF THE MIXING CELL MODEL

$K_L a_B$, Overall mass transfer coefficient, s^{-1}

Equations (5.2) and (5.3) can be written in a dimensionless form as

$$(a_{li} - a_{lo}) + \alpha_{gl} \, (1 - a_{lo}) = \frac{q \, \alpha_r \sqrt{a_{lo}} \; b_{lo}}{(1 + k_b \, b_{lo})^2} \qquad (5.4)$$

$$(b_{li} - b_{lo}) = \frac{\alpha_r \sqrt{a_{lo}} \; b_{lo}}{(1 + k_b \; b_{lo})^2} \qquad (5.5)$$

The dimensionless quantities are:

$$a_{li} = A_{li}/A^* \qquad (5.6)$$

$$a_{li} = A_{li}/A^* \qquad (5.7)$$

$$b_{li} = B_{li}/B_{li,1} \qquad (5.8)$$

$$b_{lo} = B_{lo}/B_{li,1} \qquad (5.9)$$

$$\alpha_{gl} = \frac{K_L \; a_B \; (L/N)}{u_l} \qquad (5.10)$$

$$\alpha_r = \frac{wk \quad A^* \quad (L/N)}{u_l} \qquad (5.11)$$

$$q = B_{li,1/A^*} \qquad (5.12)$$

$$k_b = K_B \; B_{li,1} \qquad (5.13)$$

where

L, length of the reactor, m

$B_{li,1}$ concentration of B entering first cell, kmol/m^3

Rearranging equation (5.4), we obtain the following relationship for a_{lo} and b_{lo}.

$$\sqrt{a_{lo}} = \frac{-m_2 + \sqrt{m_2^2 - 4\,m_1\,m_3}}{2\,m_1} \tag{5.14}$$

where,

$$m_1 = (1 + \alpha_{gl}) \tag{5.15}$$

$$m_2 = \frac{\alpha_r\ q\ b_{lo}}{(1 + k_b\ b_{lo})^2} \tag{5.16}$$

and

$$m_3 = -\ (\alpha_{gl} + a_{li}) \tag{5.17}$$

Substituting for $\sqrt{a_{lo}}$ in equation (5.5), the resulting equation can be solved for b_{lo} by a trial and error method. The procedure for calculation of the conversion of liquid reactant, B, in the entire reactor is as follows. For cell 1, $b_{li} = 1$, $a_{li} = 0$, if the feed liquid contains no dissolved hydrogen. Then using equations (5.14) and (5.5), a_{lo} and b_{lo} are evaluated for a given set of parameters. These are then used as a_{li} and b_{li} for the second cell. The calculations are continued for N cells and the conversion of B, (X_B), in the entire reactor is calculated as:

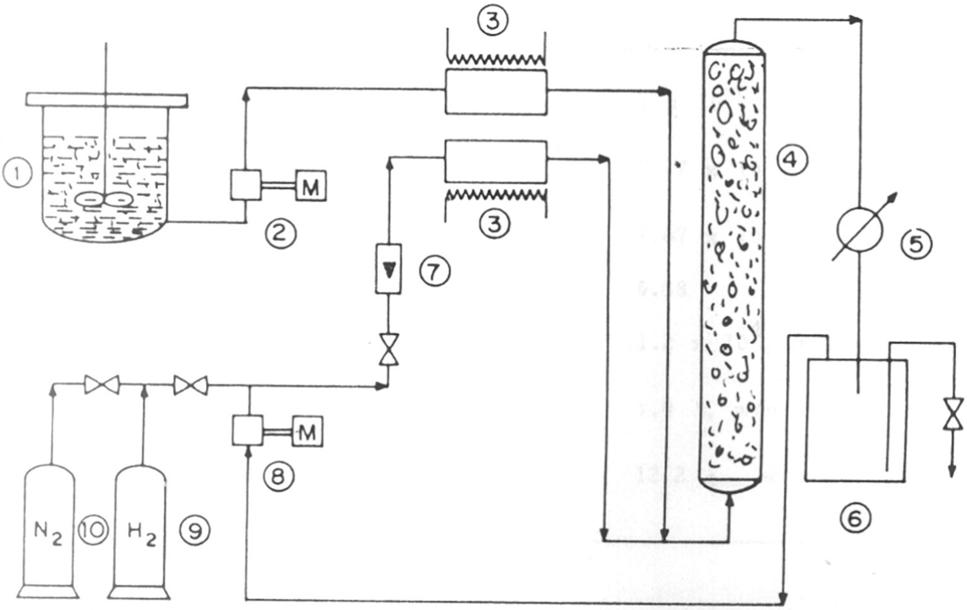
$$X_B = 1 - (b_{lo})_{Nth\ \ cell} \tag{5.18}$$

For the present case, X_B is a function of q, α_{gl}, k_b, N, a_{li} and b_{li}. In calculation of $\sqrt{a_{lo}}$ in equation (5.14), only positive values of the root were accepted. Using the procedure described above, the conversion, X_B was calculated for any given set of parameter values.

5.4 EXPERIMENTAL

The experiments were carried out using a continuous high pressure bubble column reactor. The reactor was 1,m, long and 4.2×10^{-2}, m, diameter. The set up was provided with a preheater for reactants, a gas - liquid separator, slurry feed and gas recycle pump. A schematic diagram of the set up is shown in Figure (5.2). The catalyst used was the same as that used by Parande (1983) in determining the kinetics. The specifications of the catalyst are given in Table (5.2).

An aqueous solution of butynediol prepared from a 35% (w/v) stock solution was mixed with the catalyst and the slurry was continuously stirred in the storage tank to keep the catalyst in uniform suspension. The system was flushed with nitrogen and then the slurry of aqueous butynediol and the catalyst along with hydrogen were introduced into the reactor in a co-current upflow mode at desired flow rates. The feeds were preheated before entering into the reactor. The reactor was maintained at a desired temperature and pressure. The temperature was recorded at three points. The reaction mixture coming out of the reactor was passed through a hydrogen-slurry separator. The hydrogen gas was recycled to the system after necessary make up to maintain uniform gas velocity and constant pressure in the reactor. The slurry samples



① BUTYNEDIOL+CATALYST-SLURRY
② METERING PUMP
③ PREHEATER
④ REACTOR
⑤ COOLER
⑥ GAS-LIQUID SEPARATOR
⑦ ROTAMETER
⑧ COMPRESSOR
⑨ H_2 CYLINDER
⑩ N_2 CYLINDER

FIGURE 5.2: A SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SET-UP

TABLE - 5.2

SPECIFICATION OF THE CATALYST

Pore size	:	4×10^{-6}, m
Particle density	:	2.17×10^{3}, kg/m^3
Pore volume	:	2.67×10^{-4}, m^3/kg
Porosity	:	0.58
Surface area	:	1.2×10^{4}, m^2/kg
Pd content	:	1.0 %, w/w
Zn content	:	12.2 % , w/w

were taken at different time intervals, filtered to remove the catalyst and analysed for concentrations of butynediol and butenediol. The analytical procedure is the same as described in Section (4.3). The experiment was carried out continuously and only the results under steady state conditions were considered in the present analysis. Effect of gas and liquid velocity, and temperature on the conversion of butynediol was observed following the above procedure. The reproducibility of the data was found to be within 5-8% error.

5.6 PARAMETER ESTIMATION

The use of model equations developed here requires a knowledge of various parameters such as, the physico-chemical properties, the intrinsic kinetic data, hydrodynamic and mass transfer parameters.

In the present work, the solubility data for H_2in aqueous butynediol solution at different temperatures were used from the work of Brahme et al. (1981). The relevant data used in this work are presented in Table (5.3) as Henry's constant. The intrinsic kinetic parameters were used from the work of Chaudhari et al.(1985). The values of the rate parameters are given in Table (5.4).

For effective utilization of the catalyst, it is necessary that the catalyst is uniformly suspended in the reactor. For the bubble column slurry reactor, there exists a certain minimum gas velocity, above which the catalyst particles are completely suspended. Roy et al(1964) have

TABLE - 5.3

SOLUBILITY OF H_2 IN AQUEOUS BUTYNEDIOL

Temperature K	Henry's constant, $H_A \times 10^6$, kmol/m^3/kPa
323	8.21
343	8.76
363	9.31

TABLE - 5.4

KINETIC PARAMETERS

Temperature, .K	k x 10^2, $(m^3/kg/s)(m^3/kmol)^{0.5}$	K_B, $m^3/kmol$
303	1.16	2.67
313	1.61	2.92
323	2.63	3.22
343	6.64	4.21
363	14.1	5.41

proposed a correlation for critical solid holdup, which is defined as the maximum amount of solid that can be kept in complete suspension for a given operating condition. This correlation is

$$\frac{w_{max}}{\rho_L} = 6.8 \times 10^{-4} \frac{C_{\mu} d_T \ u_g \ \rho_g}{\mu_g} \left[\frac{S_T \ \varepsilon_g}{u_g \ \mu_L}\right]^{-0.23} \left[\frac{\varepsilon_g \ u_{tp}}{u_g}\right]^{-0.18} \gamma'^{-3} \tag{5.19}$$

where u_{tp} is the terminal settling velocity of the particles. The equations for calculation of u_{tp} are as follows.

a) Stokes regime

$$u_{tp} = \frac{d_p^2 \, g \, [\rho_p - \rho_L]}{18 \mu_L} \quad \text{for } R_{eg} < 0.4 \tag{5.20}$$

b) Intermediate regime

$$u_{tp} = \left[0.0178 \frac{g^2 \ (\rho_p - \rho_L)^2}{\rho_L \ \mu_L}\right]^{1/3} d_p \quad \text{for } 0.4 < Re_g < 500 \tag{5.21}$$

c) Newton's regime

$$u_{tp} = \left[\frac{3.1 \ d_p \ g \ (\rho_p - \rho_L)}{\rho_L}\right]^{1/2} \quad \text{for } 500 < R_{eg} < 2 \times 10^5 \tag{5.22}$$

R_{eg} is the Reynolds number based on gas velocity defined as

$$R_{eg} = \frac{d_T \ u_g \ \rho_g}{\mu_g} \tag{5.23}$$

In equation (5.19), C_{μ} is a viscosity correction factor defined as

$$C_{\mu} = 2.32 \times 10^{-1} - 1.788 \times 10^{-1} \log \mu_L + 1.026 \times 10^{-1} (\log \mu_L)^2 \qquad (5.24)$$

where, μ_L is expressed in poise and γ' is the wettability factor which can be taken as unity for most catalysts (Roy et al 1964).

Using the above correlation, the minimum gas velocity required to suspend the particles at different catalyst loadings was calculated for the system under consideration and the data is presented in Figure (5.3). It can be seen that for the highest catalyst loading used (2.0 kg/m^3), the minimum gas velocity required is 1×10^{-3} m/s. The gas velocity used in the present work was greater than 2×10^{-3}, m/s in all cases thus indicating that for the present case the catalyst particles would be in the state of complete suspension.

The gas hold up ε_g, for use in equation (5.19) was calculated from the following correlation proposed by Mashelkar (1970):

$$\varepsilon_g = \frac{u_g \; (S_w / S_T \; / \rho_L)^{1/3}}{30 + 2\, u_g} \qquad (5.25)$$

The relevant physical properties of the gas, (H_2) and liquid (aqueous butynediol), like density, viscosity, surface tension and molecular diffusity which are required in the above correlations are given in Table (5.5). (Weast, R.C., 1973).

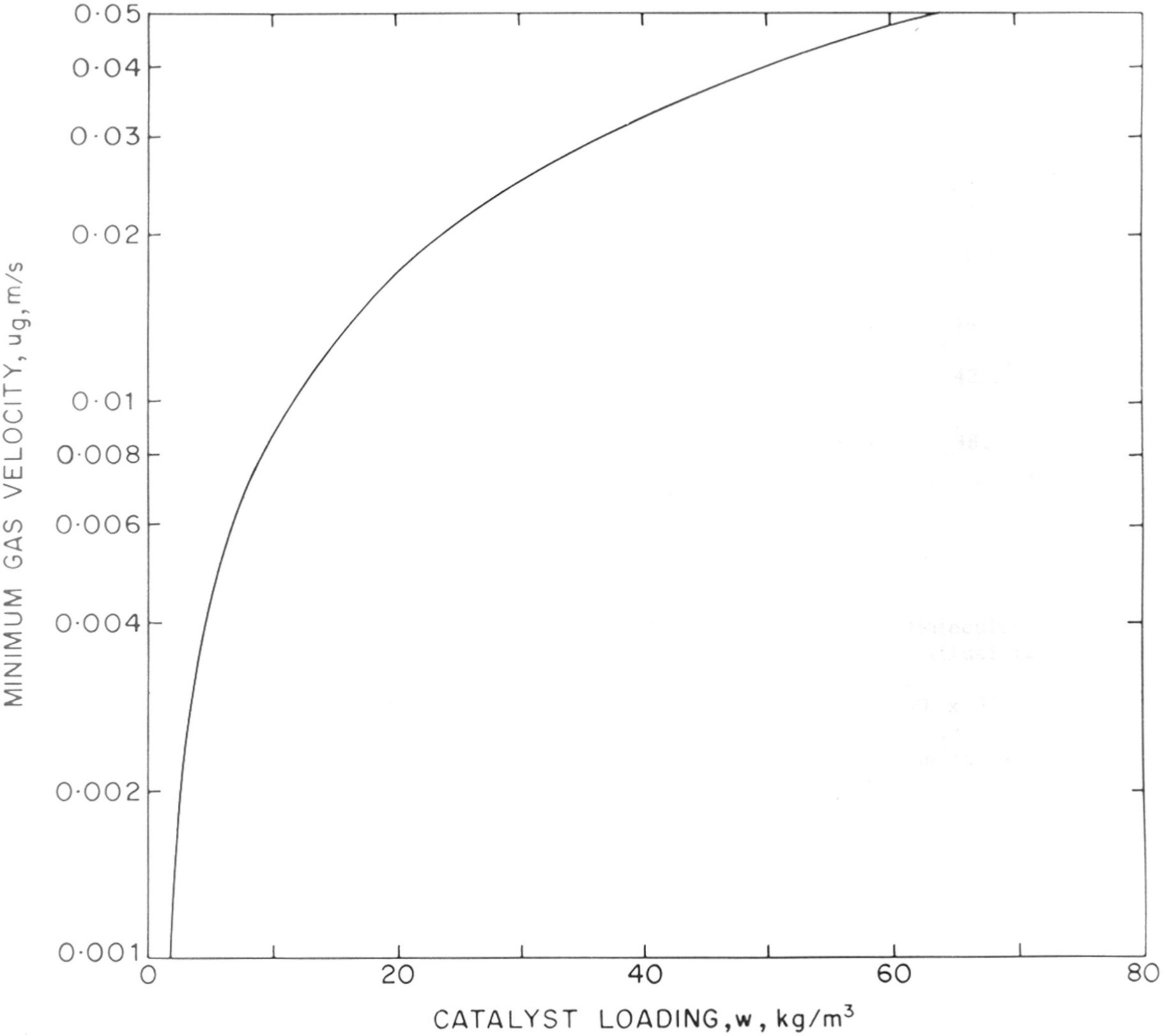


FIGURE 5·3: MINIMUM GAS VELOCITY REQUIRED FOR COMPLETE SUSPENSION OF CATALYST PARTICLES FOR PRESENT SYSTEM

TABLE - 5.5

PHYSICAL PROPERTIES OF LIQUID AND GAS

a) Physical properties of Liquid (15% Butynediol) :

Temperature	Density	Viscosity	Surface Tension
K	$\rho_L \times 10^{-3}$	$\mu_L \times 10^3$	$S_T \times 10^3$
	kg/m^3	kg/m/s	N/M
323	1.013	1.035	44.7
3343	1.009	0.735	42.2
363	1.002	0.604	38.5

b) Physical properties of Gas (H_2) :

Temperature	Density	Viscosity	Molecular diffusivity
	$\rho_g \times 10^2$	$\mu_g \times 10^7$	$D \times 10^9$
K	kg/m^3	kg/m/s	m^2/s
323	7.6	0.920	4.48
343	7.2	0.976	4.76
363	6.8	1.010	5.03

For evaluation of the mixing pattern in the bubble column reactor, liquid phase dispersion coefficient, D_{EL}, was estimated using the correlation proposed by Hikita and Kikukawa (1975). The variation in the predictions of D_{EL} using different correlations proposed in the literature has been discussed by Ramachandran and Chaudhari (1983). The correlations proposed by Kato and Nishiwaki (1972), Deckwer et al. (1974) and Hikita and Kikukawa (1975) predict D_{EL} values within a maximum error of about 20%. The correlation of Hikita and Kikukawa (1975) was used in the present work as it accounts for the influence of liquid properties, and is given below.

$$\frac{D_{EL}}{\sqrt{g\, d_T^3}} \left[\frac{\mu_L^4\, g}{\rho_L\, S_T^3} \right]^{0.3} = 0.037 + 0.188 \frac{u_g}{\sqrt{g\, d_T}} \tag{5.26}$$

Based on the D_{EL} values evaluated, Peclet number Pe_L was calculated as

$$Pe_L = \frac{u_l\, L}{D_{EL}} \tag{5.27}$$

For the range of u_g (2×10^{-3} to 3×10^{-2} m/s) and u_l (2×10^{-4} to 1×10^{-3} m/s) studied in this work, Pe_L values were found to be in a range of 0.8 to 1. This indicates almost complete backmixing (i.e. N = 1 for a mixing cell model) of the liquid phase in the present case.

The estimation of the overall gas-liquid mass transfer coefficient ($k_L a_B$) was most critical, since, the values of the k_La_B predicted by different correlations differ substantially (Ramachandran and Chaudhari, 1983). The correlations for k_La_B in a bubble column reactor have been proposed by Akita and Yoshida (1973), Kastanek (1977), Gestrich et al. (1978), and Hikita et al. (1981). These correlations are presented in Table (5.6). In order to assess the suitability of these correlations for the present system, the conversion of butynediol was predicted using k_La_B calculated by each of these correlations. The comparison of these results with experimental data is discussed in the next section. The mass transfer coefficients, k_La_B, axial dispersion coefficient D_{EL}, and gas hold up ε_g calculated from the correlations discussed above are given in Table (5.7).

5.6 RESULTS AND DISCUSSION

The mixing cell model presented above was used to predict the conversion of butynediol, X_B, under different conditions. The effect of liquid phase backmixing on X_B was studied by changing the parameter N (number of cells). The results are shown in Figure (5.4) for different catalyst loadings. Here, N=1 would be equivalent to a completely backmixed reactor, while N = 20 would approximately represent a plug flow of the liquid phase. It appears that at lower catalyst loadings (W = 0.5 and 1, kg/m^3), and lower liquid velocity, the effect of mixing is significant. Also, a higher conversion (X_B) is observed for N = 1 (backmixed flow) than for N = 20 (plug flow). This is

TABLE 5·6: CORRELATIONS FOR GAS-LIQUID MASS TRANSFER COEFFICIENT

1) AKITA AND YOSHIDA, (1973)

$$k_L a_B = 0.6\, D^{0.5} \left(\frac{\mu}{\rho_L}\right)^{-0.12} \left(\frac{S_T}{\rho_L}\right)^{-0.62} d_T^{-0.17}\, g^{0.93}\, \epsilon_g^{1.1}$$

2) KASTANEK, (1977)

$$k_L a_B = 2.875 \times 10^{-2}\, u_g^{0.65}\, \epsilon_g^{0.35}\, (1-\epsilon_g)^{0.65}$$

3) GESTRICH et.al., (1978)

$$k_L a_B = 0.0424\, u_g^{0.21} \left(\frac{L_o}{d_T}\right)^{-0.561} \left(\frac{\rho_L S_T^3}{g\, \mu_L^4}\right)^{0.116} \epsilon_g$$

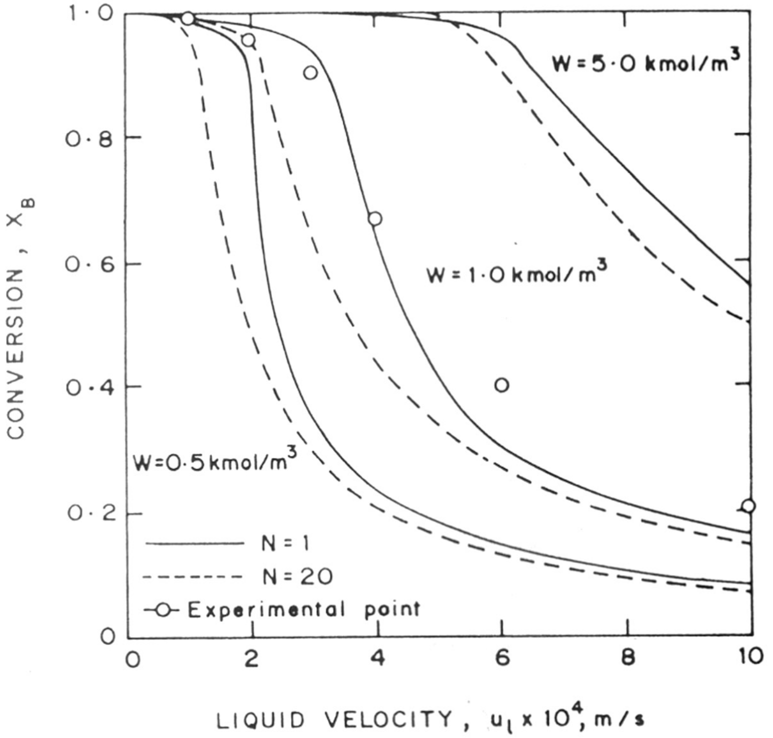
4) HIKITA et.al., (1978)

$$k_L a_B = \frac{14.98 g f}{u_g} \left(\frac{u_g\, \mu_L}{S_T}\right)^{1.76} \left(\frac{\mu_L^4\, g}{\rho_L\, \sigma^3}\right)^{-0.248} \left(\frac{\mu_g}{\mu_L}\right)^{0.243} \left(\frac{\mu_L}{\rho_L D}\right)^{-0.604}$$

TABLE - 5.7

VALUES OF ε_g, $k_L a_B$ AND D_{EL} FOR THE RANGE OF CONDITIONS STUDIED

Gas Velocity $u_g \times 10^2$ m/s	Gas holdup, $\varepsilon_g \times 10^2$	Gas-liquid mass transfer coefficient $k_L\ a_B \times 10^2$, s^{-1}				Axial dispersion coefficient, $D_{EL} \times 10^3$ m^2/s
		Akita and Yoshida, (1973)	Kastenak (1977)	Gestrich et al. (1978)	Hikita et al. (1978)	
0.2	0.77	0.32	0.18	0.06	0.81	2.146
0.5	1.88	0.84	0.45	0.18	1.60	2.295
1.0	3.64	1.75	0.88	0.40	2.70	2.495
2.0	6.85	3.64	1.68	0.87	4.60	2.824
4.0	12.30	6.65	3.12	1.81	7.90	3.366



TEMPERATURE : 343, K ,

H_2 PRESSURE : 5146, kPa ,

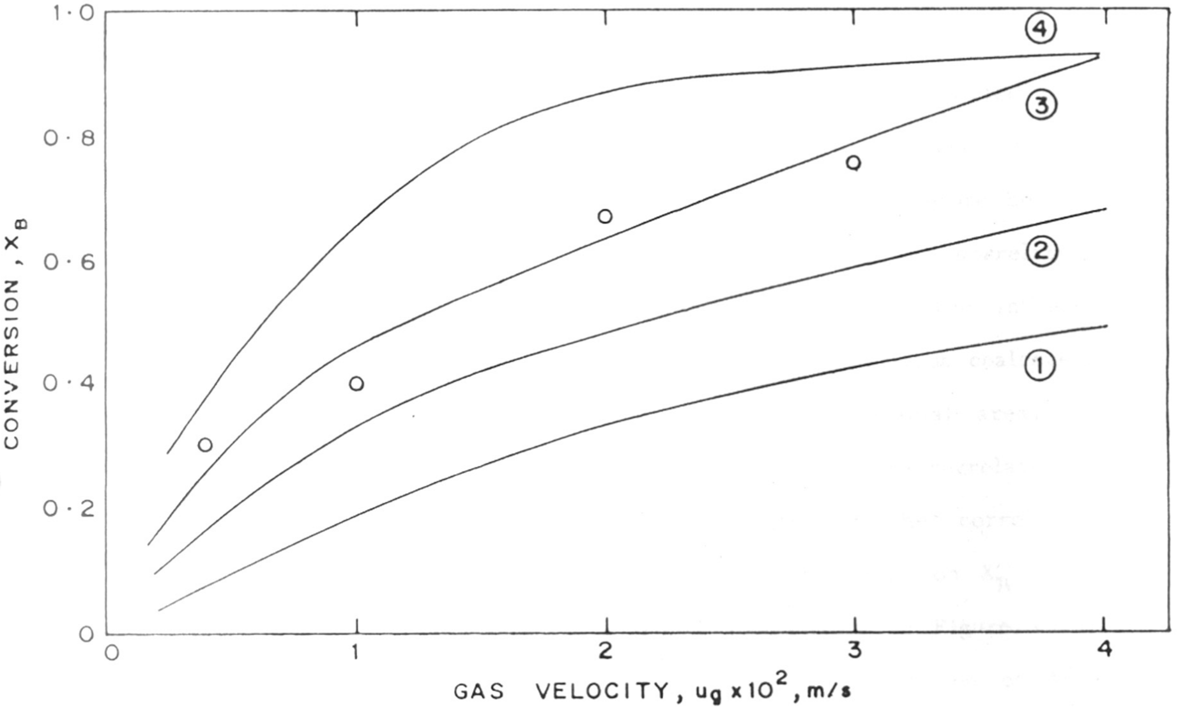
GAS VELOCITY: 2×10^{-2}, m/s

INITIAL BUTYNEDIOL CONCENTRATION: 2·0, kmol/m³

FIGURE 5·4 : EFFECT OF LIQUID PHASE MIXING ON CONVERSION due to the substrate inhibited kinetics (see equation (5.1) with respect to butynediol in the present case. At higher catalyst loading ($w = 5\ kg/m^3$), effect of N is not very significant, as under these conditions the contribution of gas-liquid mass transfer is expected to be more significant compared to the reaction kinetics. Here, the concentration of dissolved H_2 is not likely to change substantially with a change in N and also the conversion X_B will not be sensitive to variation in butynediol concentration, B_1, and hence a negligible effect of liquid phase mixing is observed.

As discussed earlier, for the conditions used in the present experimental study, the Pe_L values are in a range of 0.8 - 1 which is indicative of almost complete backmixing of the liquid phase. Therefore, in the following discussion, results with only N=1 have been presented. The above discussion of effect of mixing would however be pertinent for larger scale reactors wherein backmixing may be minimized.

The effect of H_2 gas velocity, u_g, on X_B is shown in Figure (5.5) for N=1. The gas velocity affects the gas holdup, and the overall gas to liquid mass transfer coefficient ($k_L a_B$) in the reactor and hence the conversion X_B , in cases where gas-liquid mass transfer contribution is significant. Since, the literature correlations for $k_L a_B$ predict values which are widely different, the conversion X_B, predicted using some of the correlations are compared in Figure (5.5). For the set of conditions chosen, increase



TEMPERATURE : 343, K ; H_2 PRESSURE : 5146, kPa ; LIQUID VELOCITY: 4×10^{-4}, m/s
INITIAL BUTYNEDIOL CONCENTRATION: 2·0, kmol/m^3; CATALYST LOADING: 1·0, kg / m^3

FIGURE 5·5 : EFFECT OF GAS VELOCITY ON CONVERSION

① GESTRICH AND CO-WORERS ② KASTANEK ③ AKITA AND YOSHIDA ④ HIKITA AND CO-WORKERS in u_g increases the conversion X_B mainly due to increase in k_La_B. This indicates that gas-liquid mass transfer contribution is significant for the present case. However, it is important to note that the conversions predicted using k_La_B values from different correlations, differ very widely. The question of reliability of k_La_B values therefore becomes important. As it is well known by now, the correlations predict widely different values of k_La_B, as the influence of changing physical properties of the systems(on coalescence of gas bubbles and hence gas-liquid interfacial area) has not been incorporated in most of the literature correlations.

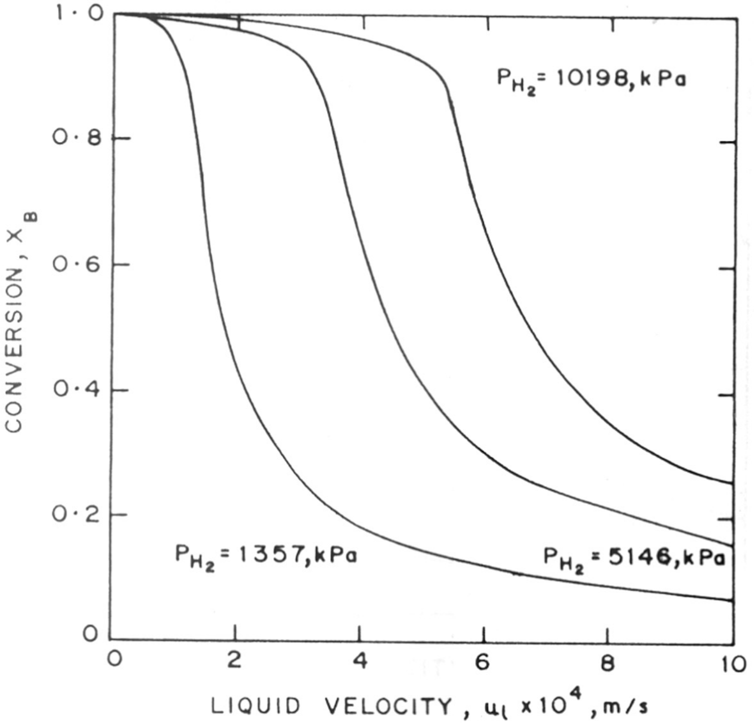
To assess the suitability of the correlations for the present case, the experimental data on X_B vs. u_g are also compared with model predictions in Figure (5.5). The results predicted using the k_La_B correlation of Akita and Yoshida (1973) agree with the experimental data, while those based on the other correlations differ very widely. This suggests that the correlation of Akita and Yoshida (1973) is more suitable for application to the present case. The physical properties of the liquid phase involved in hydrogenation of butynediol are also similar to that used in the work of Akita and Yoshida (1973) (wherein aqueous ethylene glycol was used as the liquid phase), unlike the other studies wherein mainly water has been used as the liquid phase. Therefore, for the discussion of the effect of other parameters, the k_La_B values predicted by the correlation of Akita and Yoshida (1973) were used.

Effect of liquid velocity u_1 on conversion, X_B, is shown in Figure (5.4). As expected, with increase in u_1, the conversion decreases. The experimental results of X_B vs u_1 at $w = 1$, kg/m^3, are also shown in Figure (5.4) which agree reasonably well with the model predictions for N=1. This further supports our conclusion of complete backmixing of liquid and suitability of Akita and Yoshida (1973) correlation of $k_L a_B$.

Effect of H_2 pressure, inlet concentration of butynediol, B_{li}, $_1$, and temperature on X_B are also shown in Figure (5.6) to (5.8). In general, increase in H_2 pressure increases conversion of butynediol, which is only expected. Increase in inlet concentration of butynediol led to a significant decrease in the conversion due to the substrate inhibited kinetics observed for the present case. The effect of temperature on X_B vs u_1 is shown in Figure (5.8) along with the experimental data for 323, 343 and 363 K. A change in the temperature results in not only an increase in the reaction rate and the solubility of H_2 but also a change in the contribution of gas-liquid mass transfer resistance and therefore, the results shown are a combined influence of all such changes with temperature. The model predictions were found to be in good agreement with the experimental data at 323, 343 and 363 K.

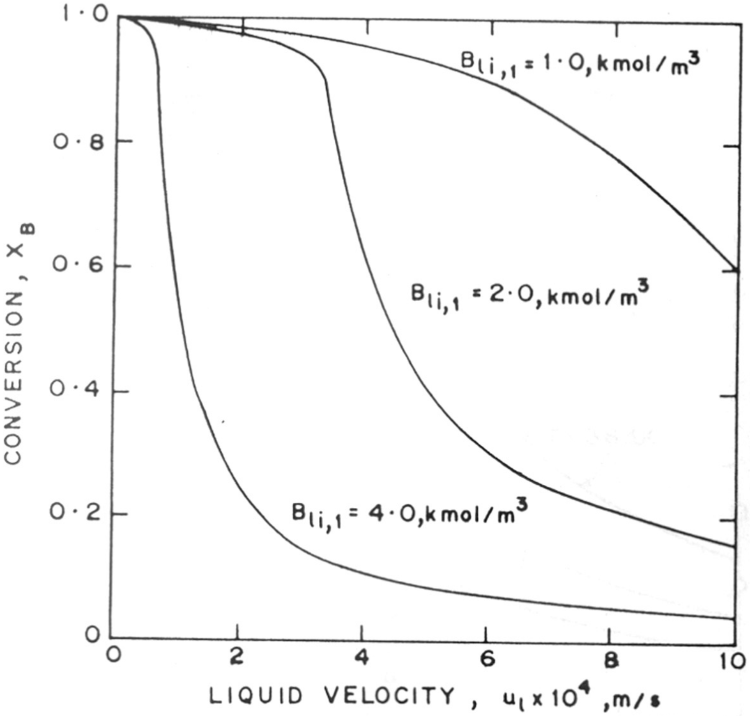
5.7 CONCLUSIONS

A mixing cell model for a continuous slurry reactor has been developed for application to hydrogenation of



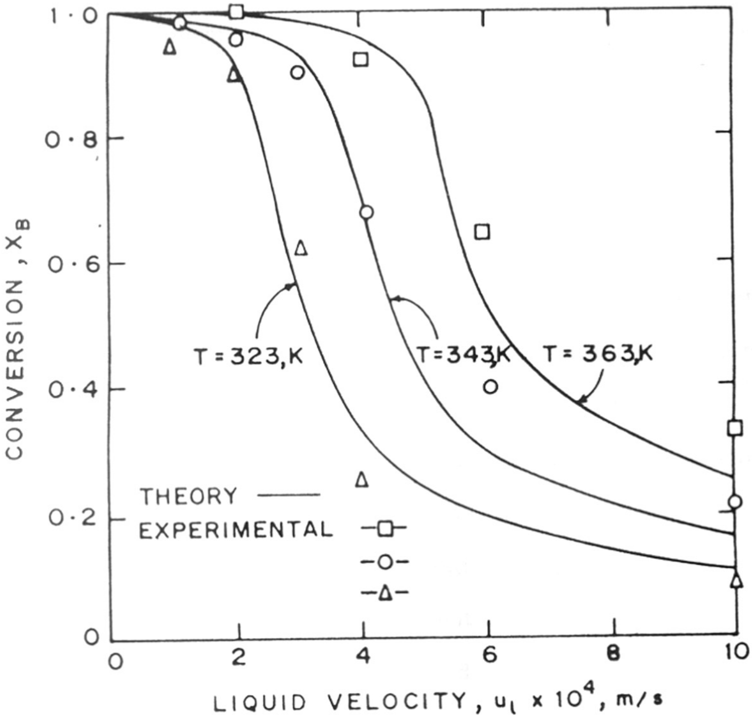
TEMPERATURE: 343, K
GAS VELOCITY: 2×10^{-2}, m/s
INITIAL BUTYNEDIOL CONCENTRATION: 2·0, $kmol/m^3$
CATALYST LOADING: 1·0, kg/m^3

FIGURE 5·6 EFFECT OF H_2 PRESSURE ON CONVERSION



TEMPERATURE : 343, K
GAS VELOCITY : 2×10^{-2}, m/s
H_2 PRESSURE : 5146 , kPa
CATALYST LOADING : 1·0, kg / m^3

FIGURE 5·7 : EFFECT OF INITIAL CONCENTRATION OF BUTYNEDIOL ON CONVERSION



GAS VELOCITY : 2×10^{-2}, m/s
H_2 PRESSURE : 5146, kPa
INITIAL BUTYNEDIOL
CONCENTRATION : 2·0, kmol/m^3
CATALYST LOADING : 1·0, kg/m^3

FIGURE 5·8 : EFFECT OF TEMPERATURE ON CONVERSION butynediol. The comparison of experimental data, obtained in a high pressure continuous reactor, with the model predictions showed a good agreement. All the data agreed with the assumption of complete backmixing of the liquid phase, which was also consistent with lower Pe_L values (0.8 - 1.0) for the present case. The conversion of butynediol predicted using different literature correlations for k_La_B (gas-liquid mass transfer coefficient) were found to vary widely indicating that no single k_La_B correlation can be reliably used without prior evaluation of the conditions under which k_La_B values were determined. The reactor performance predicted using the k_La_B correlation of Akita and Yoshida (1973) was however, found to agree well with the experimental data obtained in this work. The effect of H_2 pressure, inlet concentration of butynediol and temperature on X_B has also been discussed. The data at different temperatures was also found to agree with the model predictions within an average error of 10%.

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NOTATION

a_B	gas-liquid interfacial area per unit volume of reactor, m^2/m^3
a_l	dimensionless concentration of A in bulk liquid, $\frac{A_l}{A^*}$
a_{li}	dimensionless concentration of A in liquid phase entering a particular cell, A_{li}/A^*
a_{lo}	dimensionless concentration of A in liquid phase leaving a particular cell, A_{lo}/A^*
a_p	external area of particles per unit volume of reactor, m^2/m^3
A	species A, concentration of A, $kmol/m^3$
A^*	concentration of A in liquid in equilibrium with gas,
A_l	concentration of A in liquid phase, $kmol/m^3$
A_{li}	concentration of A in liquid phase entering a particular cell, $kmol/m^3$
A_{lo}	concentration of A in liquid phase leaving a particular cell, $kmol/m^3$
A_s	concentration of A at the catalyst surface, $kmol/m^3$
B_l	dimensionless concentratioin of B in bulk liquid, $B_l/B_{li,l}$
b_{li}	dimensionless concentration of B in bulk liquid entering a particular cell, $B_{li}/B_{li,l}$
b_{lo}	dimensionless concentration of B in bulk liquid leaving a particular cell, $B_{lo}/B_{li,l}$
B	species B, or concentration of B, $kmol/m^3$
B_l	butanediol or its concentration in liquid, $kmol/m^3$

B_2	butenediol or its concentration in liquid, kmol/m^3
B_3	butenediol or its concentration in liquid, kmol/m^3
B_l	concentration of B in bulk liquid, kmol/m^3
B_{li}	concentration of B in bulk liquid entering a particular cell, kmol/m^3
$B_{li,1}$	concentration of B in bulk liquid entering the first cell, kmol/m^3
B_{lo}	concentration of B in bulk liquid leaving a particular cell, kmol/m^3
C	species C, or concentration of C, kmol/m^3
C_1	γ-hydroxybutyraldehyde or its concentration in liquid, kmol/m^3
C_2	acetal or its concentration in liquid, kmol/m^3
C_3	butanol or its concentration in liquid, kmol/m^3
d_p	particle diameter, m
D	molecular diffusivity m^2/s
D_e	effective diffusivity, m^2/s
D_{EL}	axial liquid phase dispersion coefficient, m^2/s
D_T	diameter of reactor, m
e	energy supplied by agitator to the liquid per unit mass, m^2/s^3
[EB]	ethyl benzene or concentration of ethylbenzene, kmol/m^3
g	acceleration due to gravity, m/s^2
H_A	Henry's constant of solubility, kmol/m^3/kPa
[H]	Hydrogen or concentration of H_2 in liquid, kmol/m^3
k_b	dimensionless constant defined by equatioin (5.13)
k_i	reaction rate constant for the step i
k_La_B	volumetric gas-liquid mass transfer coefficient, s^{-1}

k_s	liquid-solid mass transfer coefficient, m/s
K_i	adsorption equilibrium constant for species i
L	length of the reactor, m
m_1	defined by equation (5.15)
m_2	defined by equation (5.16)
m_3	defined by equation (5.17)
N	agitation speed, Hz activity of the catalyst, mol/g.Pd/hr (in Chapter 2) number of cells (in Chapter 5)
P	pressure, kPa
Pe_L	liquid-phase Peclet number
[PH]	phenylacetylene or concentration of phenylacetylene, $kmol/m^3$
q	parameter defined by equation (5.12)
Q_l	volumetric flow rate of liquid, m^3/s
Q_g	volumetric flow rate of gas, m^3/s
R_A	rate of reaction of A, $kmol/m^3/s$
r_i	rate of reaction for step i, $kmol/m^3/s$
S	selectivity
S_T	surface tension of the liquid, kg/s^2
S_w	surface tension of water, kg/s^2
t	time, s
T	temperature, K
u_g	superficial gas velocity, m/s
u_l	superficial liquid velocity, m/s
V_L	volume of liquid, m^3

V_R	volume of the reactor, m^3
w	catalyst loading kg/m^3
X_B	conversion of, B

Greek Symbols

α_1	defined by equation (3.4)
α_2	defined by equation (3.5)
α_{gl}	defined by equation (5.10)
α_r	defined by equation (5.11)
γ	wettability factor in equation (5.19)
ΔH	heat of adsorption, kJ/mol
ϵ	porosity of the catalyst
ε_g	gas holdup
η	overall effectiveness factor
η_c	catalytic effectiveness factor
μ_g	viscosity of gas, kg/m/s
μ_L	viscosity of liquid, kg/m/s
ν	stochiometric coefficient
ρ_g	density of gas, kg/m^3
ρ_L	density of liquid, kg/m^3
ρ_p	density of solid particles, kg/m^3
ϕ	generalised Theile modulus defined by equation (1.8)
ψ	parameter defined by equations (3.8) and (3.9)
Ω	local rate of chemical reaction of species i, kmol/g/s/

APPENDIX - I

###

EXPERIMENTAL DATA ON HYDROGENATION OF PHENYLACETYLENE USING 0.1% Pd/C CATALYST

###

RUN NO. 171

Temperature : 318, K
H_2 pressure : 780, kPa
Catalyst loading : 4.0 kg/m^3
Initial PH concentration : 0.82, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$ PH	ST	EB
0	0.82	0.0 0.0	0.0
20	0.74	0.075	0.009
60	0.64	0.170	0.019
90	0.56	0.240	0.039
120	0.46	0.310	0.061
180	0.29	0.430	0.103
240	0.20	0.513	0.112
300	0.12	0.533	0.167
380	0.04	0.531	0.226
460	0.0	0.46	0.350
560	0.0	0.18	0.650
600	0.0	0.13	0.70

RUN NO. 172

Temperature : 318, K
H_2 pressure : 4906, kPa
Catalyst loading : 4.0 kg/m^3
Initial PH concentration : 0.82, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$ PH	ST	EB
0	0.82	0.0	0.0
10	0.62	0.19	0.02
21	0.43	0.36	0.03
30	0.32	0.46	0.05
40	0.20	0.51	0.11
60	0.07	0.55	0.20
90	0.0	0.36	0.44
120	0.0	0.13	0.70
180	0.0	0.01	0.79

RUN NO. 173

Temperature : 318, K

H_2 pressure : 3541, kPa

Catalyst loading : 4.0 kg/m^3

Initial PH concentration : 0.82, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.82	0.0	0.0
15	0.58	0.22	0.02
30	0.41	0.36	0.04
45	0.27	0.46	0.08
60	0.18	0.50	0.13
90	0.02	0.55	0.27
120	0.0	0.40	0.43
150	0.0	0.22	0.60
165	0.0	0.15	0.67

RUN NO. 174

Temperature : 318, K

H_2 pressure : 1470, kPa

Catalyst loading : 4.0, kg/m^3

Initial PH concentration : 0.82, $kmol/m^3$

Time, (Mins)	Concentrations, $kmol/m^3$		
	PH	ST	EB
0	0.82	0.0	0.0
20	0.67	0.11	0.03
30	0.50	0.18	0.04
60	0.46	0.31	0.05
105	0.31	0.46	0.06
140	0.19	0.53	0.10
160	0.11	0.59	0.13
200	0.05	0.55	0.22
280	0.0	0.36	0.46
360	0.0	0.16	0.67

RUN NO. 175

Temperature : 318, K
H_2 pressure : 2851, kPa
Catalyst loading : 4.0, kg/m^3
Initial PH concentration : 0.82, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.82	0.0	0.0
10	0.72	0.09 0.01	0.01
20	0.58	0.22	0.015
50	0.31	0.44	0.070
90	0.12	0.53	0.18
120	0.026	0.52	0.29
140	0.0	0.42	0.39
180	0.0	0.21	0.59
240	0.0	0.03	0.77

RUN NO. 176

Temperature : 318, K
H_2 pressure : 1470, kPa
Catalyst loading : 16.0 kg/m^3
Initial PH concentration : 0.82, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	DST	EB
0	0.82	0.0	0.0
5	0.67	0.10	0.01
10	0.55	0.23	0.02
15	0.45	0.32	0.03
30	0.21	0.52	0.09
60	0.0	0.47	0.34
75	0.0	0.29	0.52
90	0.0	0.17	0.65
105	0.0	0.08	0.70

RUN NO. 178

Temperature : 318, K

H_2 Pressure : 1470, kPa

Catalyst loading : 8.0, kg/m^3

Initial PH concentration : 0.82, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.82	0.0	0.0
10	0.70	0.11	0.01
20	0.56	0.23	0.03
30	0.45	0.32	0.06
50	0.28	0.45	0.07
90	0.08	0.53	0.17
120	0.02	0.46	0.34
160	0.0	0.28	0.51
200	0.0	0.11	0.72
240	0.0	0.03	0.77

RUN NO.180

Temperature : 318, K

H_2 pressure : 1470, kPa

Catalyst loading : 4.0, kg/m^3

Initial PH concentration : 0.165, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.165	0.0	0.0
3	0.14	0.02	0.006
6	0.11	0.04	0.010
9	0.10	0.05	0.02
15	0.07	0.08	0.02
20	0.05	0.10	0.023
30	0.02	0.11	0.036
50	0.0	0.09	0.07
60	0.0	0.07	0.10

RUN NO 181

Temperature : 318, K
H_2 pressure : 1470, kPa
Catalyst loading : 4.0, kg/m^3
Initial PH concentration : 0.42, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.42	0.0	0.0
5	0.38	0.029	0.001
10	0.35	0.057	0.002
25	0.25	0.16	0.008
45	0.14	0.24	0.030
75	0.05	0.28	0.090
105	0.0	0.25	0.17
150	0.0	0.16	0.26
180	0.0	0.07	0.37

RUN NO.182

Temperature : 318, K
H_2 pressure : 1470, kPa
Catalyst loading : 12.0, kg/m^3
Initial PH concentration : 0.82, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.82	0.0	0.0
10	0.62	0.19	0.009
20	0.46	0.32	0.04
30	0.34	0.43	0.05
50	0.15	0.52	0.14
75	0.02	0.48	0.28
105	0.0	0.30	0.49
135	0.0	0.08	0.72

RUN NO. 185

Temperature : 288, K
H_2 pressure : 3541, kPa
Catalyst loading : 12.0, kg/m^3
Initial PH concentration : 0.82, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.82	0.0	0.0
20	0.68	0.13	0.01
40	0.51	0.24	0.03
75	0.36	0.42	0.05
120	0.21	0.51	0.10
160	0.10	0.55	0.17
240	0.01	0.42	0.38
300	0.0	0.27	0.54
360	0.0	0.10	0.71

RUN NO. 186

Temperature : 288, K
H_2 pressure : 3541, kPa
Catalyst loading : 20.0, kg/m^3
Initial PH concentration : 0.82 $kmol,m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.82	0.0	0.0
10	0.70	0.11	0.02
20	0.56	0.22	0.037
40	0.41	0.36	0.058
75	0.19	0.51	0.11
105	0.09	0.53	0.19
150	0.01	0.45	0.36
180	0.0	0.34	0.48
240	0.0	0.12	0.70

RUN NO. 187

Temperature : 288, K
H_2 pressure : 3541, kPa
Catalyst loading : 8.0,kg/m^3
Initial PH concentration : 0.82, kmol/m^3

Time, (Mins)	Concentration, kmol/m^3		
	PH	ST	EB
0	0.82	0.0	0.0
15	0.73	0.08	0.005
30	0.65	0.15	0.008
60	0.56	0.25	0.02
120	0.35	0.42	0.05
240	0.12	0.54	0.16
360	0.004	0.43	0.39
460	0.0	0.25	0.57
540	0.0	0.09	0.72

RUN NO. 188.

Temperature : 288, K
H_2 pressure : 5255, kPa
Catalyst loading : 12.0, kg/m^3
Initial PH concentration : 0.82, kmol/m^3

Time, (Mins)	Concentration, kmol/m^3		
	PH	ST	EB
0	0.82	0.0	0.0
10	0.67	0.11	0.03
30	0.48	0.28	0.05
60	0.32	0.41	0.10
90	0.19	0.50	0.12
120	0.10	0.52	0.18
165	0.007	0.46	0.34
195	0.0	0.38	0.43
240	0.0	0.18	0.63
270	0.0	0.10	0.73

RUN NO. 189

Temperature : 288, K
H_2 pressure : 1812, kPa
Catalyst loading : 12.0, kg/m^3
Initial PH concentration : 0.82, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.82	0.0	0.0
15	0.73	0.09	0.0
30	0.69	0.10	0.02
80	0.56	0.23	0.03
160	0.33	0.43	0.06
240	0.20	0.51	0.10
330	0.09	0.53	0.19
410	0.0	0.50	0.32
500	0.0	0.41	0.41

RUN NO. 190

Temperature : 288, K
H_2 pressure : 6987, kPa
Catalyst loading : 12.0, kg/m^3
Initial PH concentration : 0.82, $kmol/m^3$

Time (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.82	0.0	0.0
5	0.70	0.10	0.01
10	0.66	0.12	0.047
30	0.44	0.33	0.07
50	0.29	0.47	0.08
75	0.13	0.55	0.13
105	0.02	0.50	0.28
135	0.0	0.39	0.41

RUN NO.191

Temperature : 288, K
H_2 pressure : 3541, kPa
Catalyst loading : 12.0, kg/m^3
Initial PH concentration : 0.153 $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$ PH	ST	EB
0	0.153	0.0	0.0
5	0.11	0.029	0.015
10	0.088	0.057	0.023
15	0.051	0.071	0.032
20	0.020	0.086	0.066
25	0.0	0.081	0.074
30	0.0	0.043	0.119

RUN NO. 192

Temperature : 288, K
H_2 pressure : 3541, kPa
Catalyst loading : 12.0, kPa
Initial PH concentration : 0.42 $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$ PH	ST	EB
0	0.42	0.0	0.0
5	0.36	0.047	0.012
10	0.31	0.081	0.022
20	0.24	0.130	0.039
40	0.14	0.226	0.063
60	0.082	0.266	0.081
75	0.021	0.270	0.128
105	0.0	0.231	0.174
120	0.0	0.200	0.202
140	0.0	0.17	0.22

RUN NO. 214

Temperature : 301, K
H_2 pressure : 2851, kPa
Catalyst loading : 4.0 kg/m^3
Initial PH concentration : 0.85

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.85	0.0	0.0
35	0.71	0.14	0.02
90	0.43	0.38	0.042
155	0.27	0.51	0.080
200	0.15	0.61	0.100
240	0.07	0.60	0.200
300	0.04	0.56	0.260
360	0.0	0.48	0.37
420	0.0	0.40	0.46

RUN NO. 215

Temperature : 301, K
H_2 pressure : 2851, kPa
Catalyst loading : 8.0, kg/m^3
Initial PH concentration : 0.85

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.85	0.0	0.0
20	0.64	0.20	0.01
40	0.47	0.36	0.03
60	0.35	0.46	0.04
100	0.15	0.59	0.11
160	0.01	0.51	0.30
200	0.0	0.44	0.41
260	0.0	0.25	0.58
320	0.0	0.09	0.76
350	0.0	0.04	0.81

RUN NO. 216

Temperature : 301,K
H_2 pressure : 2851, kPa
Catalyst loading : 12.0, kg/m^3
Initial PH concentration : 0.85 $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.85	0.0	0.0
10	0.68	0.17	0.002
20	0.55	0.28	0.020
40	0.33	0.48	0.064
60	0.16	0.55	0.145
90	0.04	0.59	0.230
120	0.0	0.48	0.39
160	0.0	0.28	0.56
200	0.0	0.13	0.71
230	0.0	0.06	0.79

RUN NO.217

Temperature : 301,K
H_2 Pressure : 4220,kPa
Catalyst loading : 4.0, kg/m^3
Initial PH concentration : 0.85 $kmol/m^3$

Time (Mins)	Concentration, $kmol/m^3$		
	PH	ST	EB
0	0.85	0.0	0.0
15	0.74	0.11	0.019
30	0.61	0.24	0.015
60	0.42	0.40	0.03
120	0.17	0.58	0.10
180	0.05	0.55	0.26
240	0.0	0.51	0.34
300	0.0	0.37	0.48
360	0.0	0.25	0.59
420	0.0	0.12	0.73

RUN NO. 218

Temperature : 301, K
H_2 pressure : 5535, kPa
Catalyst loading : 4.0, kg/m^3
Initial PH concentration : 0.85 kmol/m^3

Time, (Mins)	Concentration, kmol/m^3 PH	ST	EB
0	0.85	0.0	0.0
15	0.72	0.12	0.004
30	0.56	0.29	0.012
60	0.33	0.45	0.070
100	0.15	0.61	0.090
140	0.042	0.57	0.240
180	0.0	0.49	0.360
240	0.0	0.32	0.52
300	0.0	0.15	0.69
360	0.0	0.06	0.78

RUN NO. 219

Temperature : 301, K
H_2 pressure : 2851, kPa
Catalyst loading : 4.0, kg/m^3
Initial PH concentration : 1.582 kmol/m^3

Time, (Mins)	Concentration, kmol/m^3 PH	ST	EB
0	1.582	0.0	0.0
15	1.530	0.04	0.010
30	1.446	0.117	0.02
65	1.302	0.258	0.03
125	1.112	0.438	0.051
185	0.910	0.64	0.085
250	0.662	0.81	0.110
370	0.412	1.01	0.157
490	0.241	1.09	0.248
570	0.140	1.11	0.343
630	0.102	1.05	0.43

RUN NO. 6

Temperature : 333, K

H_2 pressure : 3541, kPa

Initial concentration of butynediol : 1.977, kmol/m^3

Catalyst loading : 4.0, kg/m^3

Agitation speed : 15, Hz

Time, (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.97	0.0	0.0	0.0	0.0	0.0
15	1.81	0.14	0.015	0.0	0.01	0.0055
30	1.67	0.29	0.02	0.0	0.02	0.0058
45	1.43	0.49	0.04	0.0	0.03	0.0062
60	1.21	0.72	0.06	0.0	0.04	0.0065
75	0.90	1.02	0.09	0.01	0.05	0.0106
90	0.41	1.28	0.11	0.02	0.05	0.0165
105	0.0	1.71	0.51	0.08	0.06	0.0252
130	0.0	1.11	0.67	0.12	0.07	0.0350
155	0.0	0.91	0.81	0.26	0.09	0.066
205	0.0	0.42	1.12	0.25	0.12	0.083
245	0.0	0.28	1.21	0.28	0.14	0.103

APPENDIX - II

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EXPERIMENTAL DATA ON HYDROGENATION OF BUTYNEDIOL USING 0.2% Pd/C CATALYST

##

RUN No.8

Temperature : 333, K Catalyst loading : 4.0,kg/m^3

H_2 pressure : 6987, kPa Agitation speed : 15, Hz

Initial concentration of butynediol : 1.977,kmol/m^3

Time, (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
15	1.63	0.29	0.0	0.0	0.0	0.005
25	1.41	0.44	0.02	0.0	0.0	0.018
30	1.17	0.64	0.04	0.02	0.01	0.018
40	0.43	1.28	0.13	0.04	0.04	0.036
60	0.0	1.41	0.45	0.06	0.05	0.064
90	0.0	0.73	0.81	0.08	0.07	0.094
145	0.0	0.96	1.43	0.10	0.11	0.013

RUN NO. 9

Temperature : 333, K Catalyst loading : 4.0,kg/m^3

H_2 pressure : 5264, kPa Agitation speed : 15, Hz

Initial concentration of butynediol : 1.97,kmol/m^3

Time; (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
10	1.78	0.12	0.01	0.0	0.0	0.003
20	1.63	0.31	0.02	0.0	0.01	0.004
30	1,40	0.48	0.02	0.0	0.02	0.005
39	1.10	0.71	0.03	0.0	0.02	0.009
49	0.83	0.88	0.07	0.0	0.03	0.016
62	0.41	1.27	0.13	0.02	0.03	0.037
100	0.0	0.88	0.83	0.11	0.04	0.063
115	0.0	0.74	0.99	0.14	0.06	0.08

RUN NO. 10

Temperature : 333,K
H_2 Pressure : 1473,kPa
Catalyst loading : 4.0, kg/m^3
Agitation speed : 15 Hz
Initial concentration of butynediol : 1.97 kmol/m^3

Time, (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.97	0.0	0.0	0.0	0.0	0.0
67	1.74	0.23	0.0	0.0	0.04	0.0
119	1.44	0.52	0.02	0.0	0.07	0.0
140	1.22	0.67	0.03	0.09	0.096	0.006
180	0.94	0.86	0.04	0.04	0.10	0.009
210	0.60	1.14	0.07	0.06	0.12	0.021
240	0.0	1.41	0.22	0.14	0.14	0.040

RUN NO. 11

Temperature : 333, K
H_2 pressure : 3541, kPa
Catalyst loading : 8.0, kg/m^3
Agitation speed : 15, Hz
Initial concentration of butenediol : 1.977, kmol/m^3

Time, (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.97	0.0	0.0	0.0	0.0	0.0
113	1.60	0.31	0.01	0.0	0.0	0.002
22	1.41	0.41	0.01	0.0	0.01	0.004
29	1.23	0.72	0.02	0.01	0.02	0.006
34	0.91	0.94	0.06	0.01	0.02	0.008
41	0.72	1.12	0.08	0.002	0.03	0.015
57	0.12	1.54	0.21	0.11	0.04	0.050
88	0.0	0.68	1.00	0.24	0.05	0.110
127	0.0	0.11	1.23	0.32	0.06	0.162

RUN NO. 11

Temperature : 333, K
Catalyst loading : 8.0, kg/m^3
H_2 pressure : 3541, kPa
Agitation speed : 15, Hz

Initial concentration of butynediol : 1.977, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.97	0.0	0.0	0.0	0.0	0.0
13	1.60	0.31	0.01	0.0	0.0	0.002
22	1.41	0.41	0.01	0.0	0.01	0.004
29	1.23	0.72	0.01	0.01	0.02	0.006
34	0.91	0.94	0.06	0.01	0.02	0.008
41	0.72	1.12	0.08	0.02	0.03	0.015
57	0.12	1.54	0.21	0.11	0.04	0.050
88	0.0	0.68	1.00	0.24	0.05	0.110
127	0.0	0.11	1.23	0.32	0.06	0.162

RUN NO. 12

Temperature : 333, K
Catalyst loading : 2.0, kg/m^3
H_2 pressure : 3541, kPa
Agitation speed : 15, Hz
Initial concentration :
of butynediol : 1.977, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.97	0.0	0.0	0.0	0.0	0.0
25	1.87	0.08	0.0	0.0	0.01	0.001
44	1.70	0.18	0.02	0.0	0.02	0.003
64	1.61	0.35	0.03	0.002	0.04	0.004
83	1.4	0.42	0.04	0.004	0.05	0.006
100	1.28	0.55	0.06	0.018	0.07	0.008
127	1.1	0.70	0.13	0.011	0.08	0.010
140	0.78	0.78	0.15	0.02	0.09	0.02

RUN NO. 13

Temperature : 333, K Catalyst loading : 4.0, kg/m^3
H_2 pressure : 3541, kPa Agitation speed : 15, Hz
Initial concentration :
of butynediol : 1.163, kmol/m^3

Time (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.163	0.0	0.0	0.0	0.0	0.004
15	0.82	0.32	0.01	0.0	0.0	0.004
26	0.24	0.81	0.04	0.0	0.01	0.006
35	0.15	0.94	0.08	0.01	0.02	0.008
45	0.0	0.84	0.29	0.06	0.04	0.012
72	0.0	0.70	0.38	0.08	0.05	0.041
103	0.0	0.47	0.54	0.11	0.06	0.051
115	0.0	0.31	0.58	0.12	0.07	0.069

RUN NO. 14

Temperature : 313, K Catalyst loading : 4.0, kg/m^3
H_2 pressure : 3543, kPa Agitation speed : 15, Hz
Initial concentration
of butynediol : 1.977, kmol/m^3

Time (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
35	1.83	0.14	0.0	0.0	0.01	0.0
65	1.66	0.30	0.0	0.0	0.03	0.004
89	1.42	0.47	0.0	0.0	0.04	0.006
110	1.31	0.55	0.01	0.0	0.05	0.008
127	1.08	0.63	0.02	0.002	0.06	0.01
154	0.85	0.96	0.04	0.002	0.08	0.01
220	0.0	1.24	0.40	0.11	0.1	0 .03
333	0.0	0.61	0.80	0.23	0.16	0.08
450	0.0	0.22	0.97	0.26	0.21	0.12

RUN NO. 15

Temperature : 313, K Catalyst loading : 12.0 kg/m^3

H_2 pressure : 3541, kPa Agitation speed : 15, Hz

Initial concentra- :
tion of butynediol: 1.977, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
27	1.61	0.34	0.016	0.0	0.0	0.001
42	1.23	0.66	0.054	0.0	0.0	0.004
52	0.80	1.03	0.091	0.0	0.0	0.007
60	0.36	1.31	0.145	0.03	0.0	0.012
67	0.08	1.62	0.218	0.104	0.0	0.018
85	0.0	1.21	0.601	0.195	0.01	0.042
98	0.0	0.76	0.860	0.29	0.03	0.063
116	0.0	0.55	1.03	0.31	0.035	0.081
150	0.0	0.23	1.12	0.38	0.042	0.123
180	0.0	0.18	1.21	0.38	0.05	0.138

RUN NO. 16

Temperature : 313, K Catalyst loading : 12.0 kg/m^3

H_2 pressure : 6987,kPa Agitation speed : 15, Hz

Initial concentra-
tion of butynediol: 1.977,$kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
15	1.46	0.48	0.01	0.0	0.0	0.0
23	1.15	0.70	0.02	0.012	0.0	0.003
27	0.80	1.10	0.04	0.035	0.0	0.006
31	0.38	1.36	0.18	0.04	0.01	0.01
35	0.0	1.72	0.25	0.062	0.01	0.02
43	0.0	1.35	0.43	0.139	0.03	0.04
61	0.0	0.85	0.75	0.20	0.04	0.07
85	0.0	0.53	0.91	0.31	0.05	0.127
100	0.0	0.48	0.93	0.33	0.06	0.132

RUN NO. 18

Temperature : 313, K   Catalyst loading : 12.0, kg/m^3

H_2 pressure : 1473, kPa   Agitation speed : 15, Hz

Initial concentration of butynediol: 1.977, kmol/m^3

Time, (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
75	1.45	0.46	0.0	0.0	0.03	0.0
105	1.10	0.70	0.02	0.02	0.05	0.01
130	0.96	0.84	0.06	0.06	0.06	0.01
153	0.37	1.21	0.12	0.14	0.07	0.02
186	0.0	1.15	0.27	0.34	0.08	0.03
233	0.0	0.71	0.52	0.58	0.10	0.06
292	0.0	0.29	0.64	0.71	0.15	0.08

RUN NO. 19

Temperature : 313 K   Catalyst loading : 4.0, kg/m^3

H_2 Pressure : 3541, kPa   Agitation speed : 15, Hz 15,

Initial concentration of butynediol : 2.85, kmol/m^3

Time, (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	2.85	0.0	0.0	0.0	0.0	0.0
30	2.75	0.06	0.0	0.0	0.01	0.0
60	2.68	0.15	0.001	0.0	0.003	0.002
90	2.61	0.23	0.002	0.0	0.043	0.003
120	2.51	0.31	0.002	0.0	0.06	0.004
180	2.40	0.45	0.003	0.0	0.08	0.007
240	2.00	0.68	0.004	0.0	0.11	0.009
300	1.75	0.92	0.006	0.0	0.14	0.013

RUN NO. 20

Temperature : 313, K Catalyst loading : 4.0, kg/m^3
H_2 pressure : 3541, kPa Agitation speed : 15, Hz
Initial concentration of butynediol : 1.197, $kmol/m^3$

Time (Mins)	Concentration, $kmol/m^3$					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.197	0.0	0.0	0.0	0.0	0.0
41	0.55	0.58	0.0	0.0	0.010	0.0
67	0.12	0.84	0.07	0.01	0.04	0.01
88	0.0	1.04	0.16	0.04	0.04	0.02
124	0.0	0.81	0.30	0.08	0.05	0.03
205	0.0	0.43	0.47	0.11	0.08	0.07
255	0.0	0.33	0.54	0.12	0.11	0.08
360	0.0	0.150	0.61	0.13	0.16	0.11
420	0.0	0.10	0.63	0.15	0.18	0.13

RUN NO. 22

Temperature : 303, K Catalyst loading : 12.0, kg/m^3
H_2 pressure : 6987, kPa Agitation speed : 15, Hz
Initial concentration of bvutynediol : 1.977, $kmol/m^3$

Time (Mins)	Concentration, $kmol/m^3$					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
32	1.40	0.54	0.02	0.0	0.01	0.01
46	0.93	0.92	0.08	0.0	0.02	0.02
56	0.20	1.40	0.25	0.02	0.02	0.03
64	0.0	1.61	0.31	0.03	0.03	0.04
73	0.0	1.73	0.58	0.09	0.03	0.06
90	0.0	1.15	0.80	0.10	0.04	0.10
120	0.0	0.65	1.12	0.15	0.05	0.13
165	0.0	0.31	1.34	0.21	0.06	0.17

RUN NO. 23

Temperature : 303, K

H_2 pressure : 3541, kPa

Initial concentrta-tion of butynediol : 1.977, kmol/m^3

Catalyst loading : 12.0,kg/m^3

Agitation speed : 15, Hz

Time, (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
55	1.55	0.41	0.03	0.008	0.0	0.004
81	1.07	0.75	0.04	0.01	0.0	0.006
98	0.67	1.12	0.09	0.04	0.0	0.011
116	0.13	1.50	0.24	0.04	0.0	0.015
139	0.0	1.38	0.45	0.12	0.02	0.043
171	0.0	0.89	0.74	0.18	0.04	0.072
200	0.0	0.57	0.92	0.26	0.05	0.112
285	0.0	0.24	1.05	0.35	0.10	0.166

RUN NO. 24

Temperature : 353, K

H_2 pressure : 3541, kPa

Initial concentra-tion of butynediol: 1.977, kmol/m^3

Catalyst loading: 12.0 kg,m^3

Agitation speed : 15, Hz

Time, (Mins)	Concentration, kmol/m^3					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
7	1.52	0.40	0.01	0.004	0.001	0.001
13	0.96	0.92	0.03	0.01	0.003	0.004
16	0.29	1.52	0.07	0.022	0.005	0.007
19	0.0	1.62	0.24	0.63	0.007	0.025
26	0.0	1.17	0.58	0.20	0.009	0.046
37	0.0	0.65	0.91	0.32	0.025	0.068
53	0.0	0.23	1.15	0.37	0.047	0.102
65	0.0	0.11	1.28	0.42	0.057	0.148

RUN NO. 25

Temperature : 353, K Catalyst loading : 4.0, kg/m^3

H_2 pressure : 3541, kPa Agitation speed : 15, Hz

Initial concentra-:
tion of butynediol: 1.977, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
12	1.81	0.17	0.0	0.0	0.008	0.001
23	1.58	0.36	0.02	0.01	0.010	0.005
32	1.34	0.60	0.03	0.036	0.03	0.007
40	0.97	0.91	0.04	0.041	0.04	0.009
50	0.31	1.44	0.11	0.052	0.04	0.014
76	0.0	1.31	0.60	0.18	0.07	0.042
105	0.0	0.74	0.87	0.26	0.08	0.071
155	0.0	0.30	1.15	0.28	0.09	0.100

RUN NO. 26

Temperature : 353, K Catalyst loading : 2.0 kg/m^3

H_2 pressure : 3541, kPa Agitation speed : 15, Hz

Initial concentra-
tion of butynediol: 1.977, $kmol/m^3$

Time, (Mins)	Concentration, $kmol/m^3$					
	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
17	1.84	0.12	0.0	0.0	0.01	0.001
33	1.62	0.30	0.02	0.002	0.03	0.002
49	1.48	0.46	0.03	0.003	0.04	0.006
66	1.20	0.66	0.04	0.004	0.06	0.007
83	0.97	0.93	0.06	0.004	0.07	0.013
143	0.0	1.36	0.42	0.12	0.10	0.046
208	0.0	0.72	0.80	0.21	0.17	0.079
270	0.0	0.39	1.02	0.22	0.20	0.097

RUN NO. 27

Temperature : 333, K

H_2Pressure : 3541, kPa

Initial concentration of butynedid : 1.977m kmol/m^3

Catalyst loading : 12.0, kg/ m^3

Agitation speed : 15, Hz

Time,	Concentration, kmol/m^3					
(Mins)	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
16	1.502	0.44	0.01	0.004	0.0	0.002
21	1.16	0.78	0.02	0.008	0.0	0.0035
26	0.70	1.10	0.10	0.012	0.0	0.005
31	0.22	1.50	0.19	0.034	0.0	0.011
36	0.0	1.52	0.33	0.080	0.007	0.033
48	0.0	1.02	0.71	0.200	0.024	0.059
66	0.0	0.46	1.12	0.270	0.040	0.114
90	0.0	0.15	0.410	0.064	0.178	

RUN NO. 28

Temperature : 353, K

H_2 pressure : 6987, kPa

Initial concentration: of butynediol : 1.977, kmol/m^3

Catalyst loading : 4.0, kg/m^3

Agitation speed : 15, Hz

Time,	Concentration, kmol/m^3					
(Mins)	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
6	1.81	0.16	0.0	0.0	0.004	0.003
12	1.45	0.47	0.03	0.0	0.006	0.04
17	1.20	0.75	0.05	0.005	0.012	0.0078
23	0.70	1.18	0.08	0.007	0.020	0.013
29	0.05	1.65	0.26	0.03	0.025	0.026
48	0.0	1.01	0.81	0.10	0.04	0.054
76	0.0	0.42	0.12	0.12	0.06	0.091
115	0.0	0.11	1.40	0.18	0.07	0.132

RUN NO. 29

Temperature : 303, K Catalyst loading : 4.0, kg/m^3

H_2 pressure : 3541, kPa Agitation speed : 15, Hz

Initial concentration of butynediol : 1.977, kmol/m^3

Time,	Concentration, kmol/m^3					
(Mins)	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
102	1.65	0.28	0.0	0.0	0.04	0.0
147	1.52	0.42	0.002	0.001	0.07	0.0022
182	1.41	0.52	0.004	0.002	0.08	0.0041
216	1.10	0.64	0.006	0.003	0.09	0.0084
280	0.92	0.87	0.020	0.005	0.11	0.016
375	0.02	1.47	0.24	0.070	0.13	0.045
420	0.0	0.92	0.49	0.16	0.14	0.055

RUN NO. 31

Temperature : 313, K Catalyst loading : 4.0, kg/m^3

H_2 Pressure : 3541, kPa Agitation speed : 15, Hz

Initial concentration of butynedion : 0.5, kmol/m^3

Time,	Concentration, kmol/m^3					
(Mins)	B_3	B_2	B_1	C_1	C_2	C_3
0	0.50	0.0	0.0	0.0	0.0	0.0
10	0.26	0.23	0.0	0.0	0.0	0.003
20	0.04	0.41	0.02	0.0	0.002	0.006
30	0.0	0.42	0.02	0.01	0.004	0.008
45	0.0	0.36	0.11	0.02	0.006	0.01

RUN NO. 32

Temperature : 333, K   Catalyst loading : 4.0, kg/m^3
H_2 pressure : 3541, kPa
Initial concentration of butynediol: 2.95, kmol/m^3

Time,	Concentration, kmol/m^3					
(Mins)	B_3	B_2	B_1	C_1	C_2	C_3
0	2.85	0.0	0.0	0.0	0.0	0.0
15	2.77	0.07	0.0	0.0	0.0	0.0
30	2.70	0.14	0.0	0.0	0.006	0.0
45	2.61	0.20	0.001	0.0	0.008	0.0
60	2.51	0.28	0.003	0.001	0.01	0.009
75	2.41	0.36	0.004	0.001	0.02	0.003
90	2.34	0.43	0.006	0.002	0.03	0.003

RUN NO.33

Temperature : 353, K   Catalyst loading : 8.0, kg/m^3
H_2 pressure : 3541, kPa   Agitation speed : 15, Hz
Initial concentration of butynediol : 1.977, kmol/m^3

Time,	Concentration, kmol/m^3					
(mins)	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
10	1.58	0.35	0.0	0.0	0.0	0.0
20	0.98	0.89	0.16	0.004	0.0	0.002
30	0.02	1.45	0.29	0.08	0.03	0.02
60	0.0	0.81	0.99	0.18	0.04	0.06
90	0.0	0.16	1.30	0.26	0.08	0.11
120	0.0	0.01	1.50	0.28	0.09	0.14

RUN NO. 34

Temperature : 353, K Catalyst loading : 4.0, kg/m^3

H_2 pressure : 1473, kPa Agitation speed : 15, Hz

Initial concentration of butynediol : 1.977 kmol/m^3

Time,	Concentration, kmol/m^3					
(Mins)	B_3	B_2	B_1	C_1	C_2	C_3
0	1.977	0.0	0.0	0.0	0.0	0.0
30	1.75	0.20	0.01	0.0	0.0	0.002
60	1.49	0.45	0.02	0.002	0.003	0.004
90	1.98	0.82	0.04	0.004	0.003	0.006
120	0.31	1.38	0.17	0.02	0.01	0.02
160	0.0	1.10	0.34	0.08	0.10	0.04
200	0.0	0.72	0.65	0.12	0.30	0.08