

# CATALYTIC HYDROGENATION OF BENZOIC ACID TO BENZALDEHYDE

## A DISSERTATION

*Submitted in partial fulfilment of the  
requirements for the award of the degree*

*of*

MASTER OF TECHNOLOGY

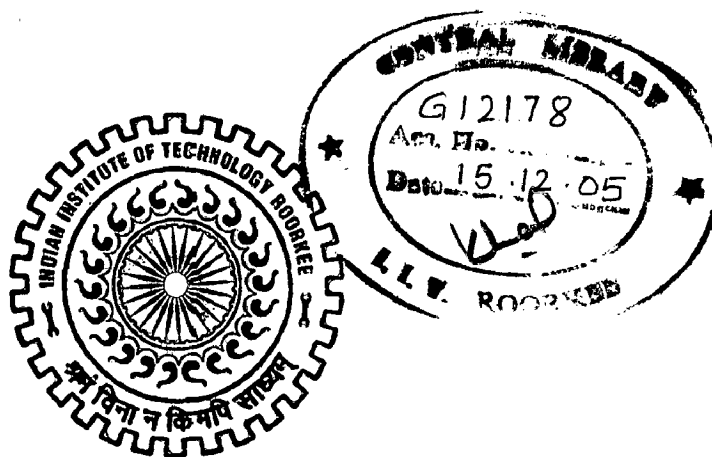
*in*

CHEMICAL ENGINEERING

(With Specialization in Computer Aided Process Plant Design)

*By*

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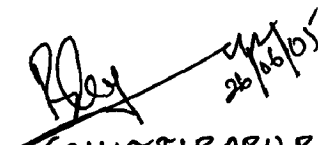
## CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the dissertation entitled " CATALYTIC HYDROGENATION OF BENZOIC ACID TO BENZALDEHYDE" in the partial fulfillment of the requirements for the award of the degree of Master of Technology in Chemical Engineering with specialization in Computer Aided Process Plant Design submitted in the department of CHEMICAL ENGINEERING, INDIAN INSTITUTE OF TECHNOLOGY ROORKEE is an authentic record of my own work carried out for the period from August 2004 to June 2005 under the guidance of Dr. V. K. Agarwal, Associate Professor, Department of Chemical Engineering, IIT Roorkee, Dr. S. K. sharma, Scientist, CBD, IIP Dehradun and Dr. S. C. Gupta, Professor, Department of Chemical Engineeirng, IIT Roorkee.

The Matter embodied in this dissertation has not been submitted by me for the award of any other degree.

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## CERTIFICATE

This is certified that above statement made by the candidate is correct to the best of my knowledge.

  
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## ABSTRACT

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The selective deoxygenation of aromatic acids to aldehydes is an example of “green” technology and an alternative to current aldehyde synthesis methods which are characterized by low yields and/or high amounts of waste formation.

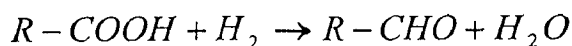
Aromatic aldehydes constitute an important group of fine chemicals that are used as intermediates in the production of pharmaceuticals such as analgetics, antipyretics and antispasmodics and in the production of agrochemicals, in particular pyrethroid-based insecticides.

Aromatic aldehydes can be produced in a variety of ways such as oxidation of alkylaromatics, halogenation of alkylaromatics followed by hydrolysis or halogenation of aromatic acids followed by hydrogenation, the so-called Rosenmund reduction.

There are, however, serious drawbacks to these technologies. The yield of aldehydes is often unsatisfactory. For example, in the case of toluene oxidation a mixture of benzaldehyde, benzoic acid and benzylalcohol is formed which has to be separated. Benzoic acid can be used to produce phenol but the added value of this process is rather small. Other processes require the use of corrosive reactants, which poses problems.

Moreover, the production of waste in stoichiometric amounts, as in the case of the Rosenmund reduction, is undesirable because of its impact on the environment.

An alternative method of preparing aromatic aldehydes is the selective deoxygenation of aromatic acids:



With a suitable catalyst high aldehyde yields can be achieved in a one-step process while the formation of environmentally damaging waste is minimised. Another advantage of this process is that aromatic acids are a cheap feedstock that is they are more easily produced by oxidation of alkylaromatics than the less oxygenated aldehyde. For this reason the selective deoxygenation of benzoic acid has received much attention in industry as an alternative method for preparing aldehydes, as can be inferred from the large volume of patents (primarily on metal oxides) that has appeared over the last 20 years.

Group III metals are found to present good behavior as hydrogenation catalysts when supported on highly porous materials such as alumina. Nevertheless, derived from the fact of working simultaneously with 3 phases—a solid catalyst, liquid reactants, and solvents, and gaseous hydrogen—several problems mainly of diffusional nature arise with respect hydrogen access to the liquid phase. Studying these problems in which their effects are negligible are essential before going any further. Hydrogen partial pressure is an important factor. Too fast hydrogenation induced by high hydrogen partial pressure may lead to mass transfer limitations that would result in decrease of the selectivity.

Therefore a low hydrogen pressure is used and the space velocity (LHSV) is selected accordingly in order to get required conversion level. Hydrogenation reactions are a class of reactions that are valuable in the pharmaceutical and speciality chemical industry. Studies on catalytic hydrogenation reactions have been carried out in the gas phase or in the liquid phase. Nowadays attention is being led toward some liquid-phase processes of increasing importance in the chemical industry.

Carrying out the reaction in the liquid phase, in a slurry reactor, presents important advantages with respect to the gas phase. In liquid phase reactions, better temperature control due to higher heat capacity of the liquids, thus increasing the catalyst life and quality and uniformity of the reaction products, saving the devices and energy, higher rate of reaction per unit weight of catalyst because of the use of smaller particles, and higher conversions and selectivity attained. Hydrogenation is performed in liquid phase to save vaporization and condensation energy and at relatively low temperature. It has also been found out that for the same conversions reactions are more selective in liquid phase than the gas phase.

In contrast relatively few studies exist in open literature on “vapour phase catalytic hydrogenation of benzoic acid to benzaldehyde” and no literature is available on liquid phase catalytic hydrogenation of benzoic acid. Moreover, those relevant publications provide conflicting views on the mechanism of this reaction.

The present work has been carried out to invent a process for catalytic hydrogenation of benzoic acid to benzaldehyde in liquid phase.

## ACKNOWLEDGEMENTS

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I wish to take this opportunity to pay my regards and a deep sense of gratitude to *Dr.V.K.Agarwal*, Associate Professor, Department of Chemical Engineering, IIT Roorkee, *Dr.S.K.Sharma, Scientist, CBD, IIP Dehradun* and *Dr.S.C.Gupta*, Professor, Department of Chemical Engineering, IIT Roorkee, with whom I had the privilege to complete this dissertation. It is my pleasure and deep sense of indebtedness. I wish to express my sincere thanks to them.

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Above all, I would like to acknowledge that the greatest role has been of my parents, family members, who have helped me to cultivate the system of values and instincts that shall always enlighten my path all these living years.

  
(CHITTIBABU B.)

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C H A P T E R - 1

# INTRODUCTION

## 1.1 BENZALDEHYDE

Benzaldehyde( $C_6H_5CHO$ ) is the simplest and the most industrially useful member of the family of aromatic aldehydes. Benzaldehyde exists in nature, primarily in combined form such as glycoside in Almond, apricot, cherry and peach seeds. The characteristic benzaldehyde odour of oil of bitter almond occurs because of trace amounts of free benzaldehyde formed by hydrolysis of the glycoside amygdalin. Amygdalin was first isolated in 1830 from the seed of the bitter almond sometime later Liebermann and Wohler found that when amygdalin was hydrolyzed with water and emulsion, Benzaldehyde hydrogen cyanide and D Glucose were formed.

Now a days benzaldehyde is produced by many process like - Chlorination of Toluene (liquid phase) - Oxidation of Toluene (liquid phase) & (vapour phase). The hydrolysis of benzalchloride, which is produced by side chain chlorination of toluene, is older of the two processes. Other process includes - Oxidation of benzyl alcohol - Reduction of benzoyl chloride - reaction of carbon monoxide and benzene have also been used in the past, but they no longer have any industrial application.

There is considerable demand for the chlorine free benzaldehyde as it is used in pharmaceutical industry. As multinational are coming up the competition is been developing and major challenge faced by the industry is purity of product (free from chlorine). Electroplating industry has great demand for benzaldehyde. Hence, benzaldehyde industry is an important raw material for many industries. Benzaldehyde is found in nature in many foods. It helps give coffee and cocoa their characteristically pleasant aromas.

Less known is the fact that benzaldehyde has shown significant cancer-fighting abilities. In the 1970s, Japanese scientists used a distillate of ordinary figs to successfully treat cancer in mice. They eventually found that the active ingredient in this distillate was ordinary benzaldehyde, present in mere one ppm concentrations.

Building on this finding, in 1985, Dr. M. Kochi and colleagues reported in the US National Cancer Institutes own cancer treatment reports that a “gluconated” form of benzaldehyde (called BG) causes an “overall objective response rate” of 55%. Seven patients achieved complete response, 29 achieved partial response, 24 remained stable, and 5 showed progressive disease.

In 1990, Dr. Tatsumura and colleagues at Toyama University reported similar results (41.7% response). In all cases, the treatment was free of toxicity. It is thus documented, safe and inexpensive. The leading manufacture of Benzaldehyde in India is, Indian Organic Chemicals Ltd, Khopoli (Maharashtra state). Estimated requirement of Benzaldehyde in India is as below:

YEAR	QUANTITY(Tons)
1976 – 77	6000
1984 – 85	8000
1989 – 90	10000
1994 – 95	12000
1999 – 2000	14000
2004 - 2005	16000

## 1.2 BENZALDEHYDE APPLICATIONS

1. The technical grade benzaldehyde is a versatile chemical intermediate in the manufacture of pharmaceuticals, dyes, perfumes and flavoring chemicals, mainly cinnamaldehyde, amyl cinnamaldehyde, hexyl cinnamaldehyde and cinnamyl alcohol.
2. Intermediate for numerous derivatives, i.e. chemical intermediate for aromatic alcohol, used in the manufacture of benzoic acid, photographic chemicals, in the manufacture of cinnamic and mandelic acids.
3. Solvent for oils, resins, some cellulose ethers, cellulose acetate and nitrate.
4. Benzaldehyde is also used as starting material for pharmaceuticals(Ampicillin) and pesticides(Dibenzoquat).
5. Phenol benzaldehyde resins have been utilized to prepare fireproof structural foam, ferrocene polymers are also prepared from benzaldehyde.
6. Used in the production of Triphenylmethane green, which is obtained by benzaldehyde with dimethylaniline.
7. It is also used in extractive separation of isomeric amines.
8. It is FDA sanctioned synthetic flavoring substance generally recognized as safe for foods.
9. The most important use of Benzaldehyde is in organic synthesis where it is a raw material for a large number of products.

## 1.3 Commercial Processes for Benzaldehyde Production

### 1.3.1 Liquid phase oxidation route

This route involves oxidation of liquid toluene to benzaldehyde in the presence of homogenous catalyst.  $\text{MnO}_2$  with  $\text{H}_2\text{SO}_4$  has been used as the most suitable catalyst. A 14% yield of Benzaldehyde has been reported. When the Cobalt is used as a catalyst at 3atm pressure, the total conversion of benzoic acid and Benzaldehyde was found to be 40%. Benzaldehyde is separated by fractional distillation.

### 1.3.2 Vapour phase oxidation route

Vapour phase oxidation provides chlorine free benzaldehyde with the minimum amount of byproduct formation. Toluene is directly oxidized by air in the vapour phase at atmospheric pressure in the presence of a catalyst maintained at above  $400^\circ\text{C}$ . In this route extensive work has been carried out using different catalysts. The most selective catalyst appears to be  $\text{V}_2\text{O}_5$  promoted with Potassium Sulphate and promoted Uranium Oxide catalyst. Both catalysts gives approximately 60% yields of benzaldehyde based upon toluene. There is a varying amount of byproduct formation during oxidation. The principle byproducts are Benzoic Acid,  $\text{CO}_2$ , Anthraquinone, CO and  $\text{H}_2\text{O}$ .

### 1.3.3 Electrochemical route

There are two approaches for getting benzaldehyde by electrochemical route. In a single stage process an emulsion of toluene in 60%  $\text{H}_2\text{SO}_4$  is oxidized electrically to Benzaldehyde with electrodes.  $\text{Mn}_2(\text{SO}_4)_4 \cdot 5\text{H}_2\text{O}$  is used as the oxygen carrier with  $\text{CaSO}_4$

as the promoter. Unreacted toluene and the electrolytes are recycled. In a two-stage process, the first stage involves electrolytic oxidation of Manganous Sulphate to Manganic Sulphate paste. In the second stage, Manganic Sulphate is reacted with toluene in the reactor to form Benzaldehyde. The Manganous Sulphate formed is regenerated electrolytically.

#### **1.3.4 Chlorination of toluene**

In this process chlorine is reacted with toluene in the presence of light to give Benzalchloride as intermediate which is hydrolysed to give Benzaldehyde. The chlorination method is cheapest and gives Benzaldehyde in good yield, but the presence of chlorine in the product is not ruled out and more over large quantity of byproducts are also formed.

The electrochemical route is also expensive as it uses electricity and catalyst in large amount. There is another process i.e Chlorination of Toluene using catalyst. The catalyst used is  $\text{PCl}_3$  handling and storage of this catalyst creates problems and therefore the process is not considered.

Considering the different processes and studying it for manufacture of Benzaldehyde this does not give high percentage of yield and unwanted materials are produced in a large amount.

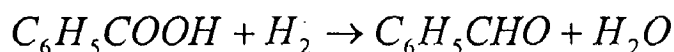


## 1.4 DEOXYGENATION OF BENZOIC ACID

There are two pathways in the Selective Deoxygenation of Benzoic acid to Benzaldehyde:

1. A Selective pathway in which benzaldehyde is formed. This reaction proceeds via Reverse type of Mars-Van Krevelen Mechanism.
2. A Non Selective pathway in which benzene and benzophenone are formed preferentially. These products are via the slow decomposition of strongly bound benzoates.

### 1.4.1 SELECTIVE PATH-WAY

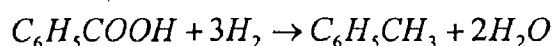


### 1.4.2 NON SELECTIVE PATH-WAY

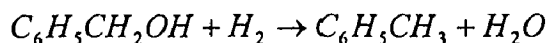
#### 1. Toluene Formation

There are three potential reaction pathways for the formation of toluene:

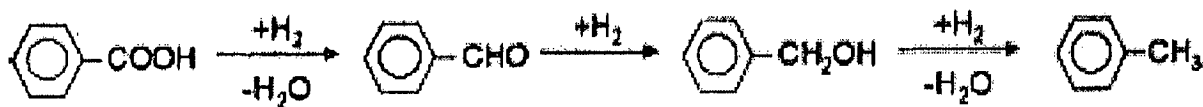
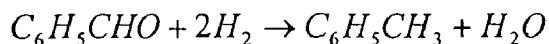
##### A. Direct Reduction of Benzoic Acid



##### B. Hydrogenation/ Hydrolysis of Benzyl Alcohol



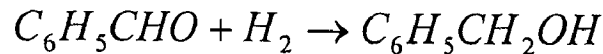
##### C. Hydrogenation(Deoxygenation) of Benzaldehyde



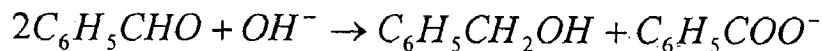
### 3. Benzylalcohol Formation

There are two probable routes from Benzaldehyde to Benzylalcohol.

#### A. Hydrogenation of Benzaldehyde



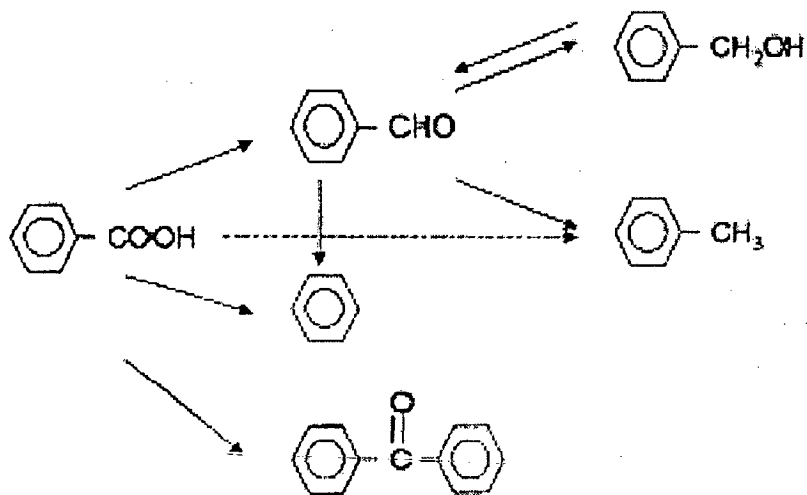
#### B. Cannizzaro Mechanism



### 4. Formation of Benzene & Benzophenone

- Benzene and Benzophenone are formed in significant amounts only when hydrogen is not present in the feed. Apparently decarboxylation of benzoic acid is a much slower process than deoxygenation to benzaldehyde or toluene. Decarboxylation of metal benzoates to benzene probably proceeds via a radical mechanism:
  - A benzyloxyradical is formed via homolytic cleavage of the  $RCO_2-M$ .
  - The benzyloxyradical rapidly decarboxylates to a benzyl radical and the radical chain is terminated by reaction with a H-atom.
- For the Ketonisation of aromatic acids on oxidic catalysts different reaction mechanisms have been proposed. Kwart and King suggested a concerted reaction between two carboxylate groups bound to one metal cation. Lee and Spinks proposed a polar mechanism involving acylium ( $R-C^+=O$ ) species. Given the relative stability of the benzylradical (due to resonance) the radical-chain mechanism put forward by Bell and Reed might also be a valid mechanism. Ketonisation is absent in steady state reactions.

## 1.5 OVERALL REACTION MODEL



- At  $430^\circ\text{C}$  and at a high partial pressure of hydrogen, conditions for surface reduction are favorable. So the concentration of oxygen vacancies is high and first benzoic acid is deoxygenated to benzaldehyde and subsequently benzaldehyde is deoxygenated to toluene, or benzoic acid reacts through to toluene directly.
- If the hydrogen partial pressure is decreased the concentration of oxygen vacancies drops which means that neighboring oxygen vacancies are rare and, moreover, that benzaldehyde cannot readsorb on a direct site. So the selectivity to toluene drops and to benzaldehyde increases.
- If hydrogen is completely excluded from the feed, benzoic acid will oxidize the surface and eventually no oxygen vacancies will be available for its adsorption. Under these conditions no deoxygenation can take place and, thus the slower parallel running reactions to benzene and benzophenone can takeover.
- Upon re-introduction of hydrogen the original situation leading to benzaldehyde is restored.

It was determined that the deoxygenation proceeds in two steps involving lattice oxygen, i.e. a type of Mars–Van Krevelen mechanism operates. In the first step, hydrogen removes a lattice oxygen atom, in the second step benzoic acid is deoxygenated to benzaldehyde by replenishing the oxygen vacancy. The main byproducts are benzene, toluene and benzylalcohol. Formation of benzene and toluene is undesirable, but a mixture of benzaldehyde and benzylalcohol can be of commercial interest. It is not clear how these compounds are produced and how the selectivity can be manipulated by changing the reaction conditions.

Due to the increasing demand for aromatic aldehydes (used as fragrances and, for example, the synthesis of pyrethroid insecticides), there is also increasing interest in information on the selective production of aldehydes from aromatic carboxylic acids. The direct hydrogenation of carboxylic acids by using suitable catalysts is a very convenient method for synthesis of aldehydes. By this method, aldehydes would be synthesized effectively without producing undesirable by-products that can pollute the environment.

Therefore, much attention has been paid to exploring new catalysts with high activities and a selectivity to aldehydes, suitable for industrial processes. A long list of available patents documents show the growing interest in practical applications, but an inspection of scientific and patent literature reveals that only very little is known about the fundamentals of the reactions and the function of the catalysts. It is, for example, still impossible to predict which catalysts should be suitable for which substrate (aliphatic vs aromatic acid; benzoic vs substituted acids) and why.

A glance at the patent literature would reveal that a large portion of the elements of the periodic table has already been suggested for use in their oxidic form as catalysts (or catalysts component) for selective deoxygenation. Among them are alkaliearth, transition metal, and rare earth oxides.

**C H A P T E R - 2**

**LITERATURE  
REVIEW**

## 2.1 Journals Review

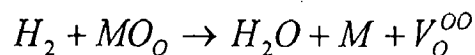
*M.W.de Lange, et al.*<sup>1</sup> studied selective deoxygenation of benzoic acid to benzaldehyde on ZnO and ZrO<sub>2</sub>. The results show conclusively that the reaction proceeds as a reverse type of Mars and van Krevelen mechanism consisting of two steps: hydrogen activates the oxide by reduction resulting in the formation of oxygen vacancies. Subsequent re-oxidation of these vacancy sites by benzoic acid yields benzaldehyde. Inhibition of the deoxygenation reaction can be achieved by addition of suitable polar compounds with a high affinity for the oxygen vacancy sites such as carbon dioxide or water. Differences in the catalytic activity and selectivity of ZnO and ZrO<sub>2</sub> can be attributed to differences in hydrogen activation, redox properties and extent of benzoic acid coverage.

Benzaldehyde was only found after a reductive pretreatment and not after a pretreatment in nitrogen. Benzaldehyde is produced in very high yields (>95%) on both the ZnO and ZrO<sub>2</sub> catalysts under steady-state conditions with a high partial pressure of hydrogen.

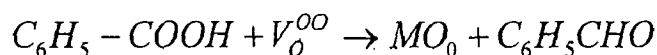
Active site for deoxygenation has been created during pretreatment in hydrogen. The benzoic acid adsorbed at this site will desorb as benzaldehyde upon heating.

### **The mechanism consisted of two steps:**

#### **1. Activation of the catalyst by hydrogen:**



#### **2. Re-oxidation of the catalyst by benzoic acid yielding benzaldehyde:**



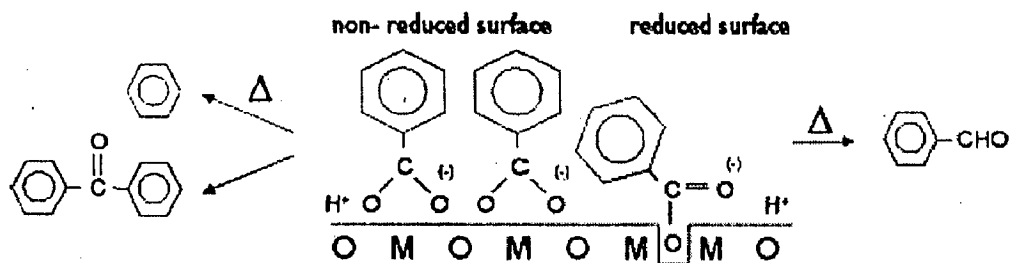


Fig. 8. Reaction model of benzoic acid adsorbed on a catalyst pretreated in hydrogen.

The fact that during the steady-state experiments the selectivity to benzaldehyde is much higher than after a reductive pretreatment when decomposition products prevail is clarified as follows. During steady-state reactions hydrogen is constantly supplied and oxygen vacancies are continuously created. The benzoic acid reacts much more readily with the oxygen vacancies than that the benzoates decompose into benzene and benzophenone.

*Activation of hydrogen is related to the rate-determining step and this was confirmed by some elementary kinetic experiments. It was found that the reaction orders varied between 0.6 and 0.9 with respect to hydrogen and between 0.0 and 0.1 with respect to benzoic acid.*

*M.W.de Lange, et al.<sup>2</sup> studied selective deoxygenation of benzoic acid to benzaldehyde on ZnO and ZrO<sub>2</sub> and the pathways to the byproducts are discussed and a complete overview of the reaction network is presented. Benzene and benzophenone are products of the decomposition of the strongly adsorbed benzoic acid at elevated temperature. Toluene is formed by the deoxygenation of benzaldehyde at oxygen vacancy sites. Direct hydrogenation of benzaldehyde yields benzylalcohol. Selectivity to byproducts is not only determined by the reaction temperature, but also by the degree of surface reduction and the difference in adsorption strength between reactant and product.*



At temperatures less than 360° benzoic acid forms a strongly benzoate layer which is stable and prevents readsorption of benzaldehyde. Reduction of the catalyst by hydrogen leads to a small number of oxygen vacancy sites which deoxygenate benzoic acid to benzaldehyde and as a result selectivity to benzaldehyde is very high (>95%). Higher temperatures induce decomposition of the benzoate layer into benzene and more importantly enhance the degree of reduction of the catalyst, which results in the formation of toluene from benzaldehyde.

*Y. Sakata, et al.*<sup>3</sup> studied selectivity problems in catalytic deoxygenation of benzoic acid on oxides of Mg, Pb, Cr, La, Pr, Yb, Mn, Fe, Co, Zn, Zr, and Ce in the temperature range 523–723°K. All experiments were performed in a continuous flow apparatus, at a total pressure of about one bar, with hydrogen as the reductant. The oxides studied could be subdivided into several groups according to their product pattern. The groups indicate the prevailing mechanism. The two basic mechanisms are: (i) Mars and van Krevelen (selective to benzaldehyde) and (ii) radical-like decomposition of benzoate. The highest yield of benzaldehyde can be obtained with oxides of high metal–oxygen bond strength.

*T. Yokoyama, et al.*<sup>4</sup> presented a novel process for synthesizing aromatic aldehydes by a direct hydrogenation reaction of the corresponding carboxylic acids was established. The catalyst used was modified zirconia which showed satisfactory performance for commercial production. The optimization of the catalyst, application to various carboxylic acids, and mechanistic considerations using reaction kinetics and FT-IR spectroscopy are reported.

*Y. Sakat and V. Ponc*<sup>5</sup> studied catalytic behaviour of CeO<sub>2</sub> in the reduction of benzoic acid has been studied in the temperature range 523–723°K. Two types of catalytic behaviour are observed in this the whole temperature range. One type is observed from 523 up to 648°K.

In this range, the selectivity to benzaldehyde can be higher than 95% and the reaction proceeds by the redox (Mars and van Krevelen) mechanism, with the oxygen vacancy as the active site. The activity is controlled by the steady-state concentration of oxygen vacancies under reaction conditions. The second type behaviour is observed above 648°K. Under these conditions the conversion of benzoic acid achieved is nearly 100%, but the selectivity to benzaldehyde decreases, while that to toluene and benzene increases. In this range of temperatures, the reaction proceeds too far, due to a very high concentration of vacancies. Besides the redox mechanism decarboxylation (hydrogenolysis) of the relative stable adsorbed benzoic acid takes place. The results observed with the reaction of adsorbed benzoic acid, under a flow of H<sub>2</sub> reflects the two types of reaction. The potential promotion effects by Al, Cr, Mn, Fe, Ga, Zr, In and Pb oxides added to CeO<sub>2</sub> were investigated. The catalytic behaviour of CeO<sub>2</sub> changes by the addition of the metal oxides, positive effects are observed after adding Mn, Zr, In and Pb oxides.

*F. Dury, et al.*<sup>6</sup> investigated the potentiality of the deoxygenation of benzoic acid in the presence of hydrogen as a probe of the reduction state of molybdenum oxide in catalytic processes. On one hand, a complicated hysteresis phenomenon is observed when measuring the conversion of benzoic acid and selectivities to benzene, toluene and benzaldehyde of Mo<sub>8</sub>O<sub>23</sub> along a cycle of temperatures between 628 and 723°K. On the other hand, Mo<sub>8</sub>O<sub>23</sub> undergoes a reduction to Mo<sub>4</sub>O<sub>11</sub> and MoO<sub>2</sub> throughout the catalytic reaction. These results, together with the performances of Mo<sub>4</sub>O<sub>11</sub> and MoO<sub>2</sub> under the same conditions, allow to understand the reduction pathway of Mo<sub>8</sub>O<sub>23</sub>. The proposed pathway fits with that suggested in the literature, thus confirming the deoxygenation of benzoic acid as a promising probe reaction of the behavior of molybdenum based oxides at work.

## 2.2 Patents Review

*Feinstein, et al.*<sup>8</sup> reported a process for converting an aromatic methyl ester (methyl benzoate) to a corresponding aromatic aldehyde (benzaldehyde) by subjecting the ester to temperatures of 400°C to 500°C and one atmosphere pressure for 3 to 100 seconds in the presence of a solid alumina catalyst.

Other known catalysts for benzoic acid hydrogenation by gaseous hydrogen include a copper/chromium-containing substance made by co-precipitating copper, chromium and manganese salts and pelletizing the resulting product with diatomaceous earth and CrO<sub>3</sub> (Japan Kokai 75 111,034). Studies of alkali metal oxides and zinc oxide catalysts have also been carried out. The alumina-containing catalysts was treated at elevated temperatures i.e 1000°C in order to improve their selectivity towards production of aldehyde product.

At a reaction temperature of 450°C and a contact time of 17 sec (WHSV - 0.33 based on methyl benzoate), 39% conversion of benzoic acid and 37mol% of benzaldehyde selectivity was reported.

*Strojny*<sup>9</sup> invented an improved vapor phase process for producing aldehydes from corresponding carboxylic acids and esters of said carboxylic acids by contacting the acid or ester at temperatures from about 300°C to about 500°C. with hydrogen, in the presence of a catalyst selected from certain metal oxides.

*Wattimena, et al.*<sup>10</sup> prepared aldehydes by hydrogenating a compound of general formula R'COOR, wherein R represents a hydrogen atom, an alkyl or an acyl group, or a metal, and R' represents an optionally substituted hydrocarbyl group having at most two alpha-hydrogen atoms, provided it has at most one beta-hydrogen atom, in case it has two alpha-hydrogen atoms, in the presence of a catalyst comprising at least one metal selected from rare earth metals and iron on an alumina-based carrier.

*Gelbein, et al.*<sup>11</sup> described a process for selectively forming aldehydes which comprises hydrogenating a carboxylic acid or a carboxylic acid ester in the presence of a manganese catalyst supported on an activated alumina.

*Holy, et al.*<sup>12</sup> reported a process for selectively forming aldehydes which comprises hydrogenating a carboxylic acid or a carboxylic acid ester in the presence of an yttrium catalyst activated with copper.

At a reaction temperature of 430°C and with a feed of 2.0 mol% benzoic acid, 88% of benzoic conversion and 94mol% of benzaldehyde selectivity was reported.

*John*<sup>13</sup> showed that an aldehyde is prepared by passing an aromatic carboxylic compound or an aliphatic carboxylic compound having at most one alpha-hydrogen atom in the acyl group, in the presence of hydrogen at elevated temperature over a catalyst comprising at least 25% w of iron oxide expressed as Fe<sub>2</sub>O<sub>3</sub>, calculated on the total catalyst.

*Maki, et al.*<sup>14</sup> invented an improved process for catalytic hydrogenation of aromatic carboxylic acids to produce aromatic aldehydes is described, using a catalyst comprising zirconium oxide containing as an essential component at least one element selected from the group consisting of chromium, manganese, iron, cobalt, zinc, bismuth, lead, rhenium and the elements of Group III of periods 3 to 6 of the periodic table; the process results in improved catalyst activity and produces the desired aromatic aldehydes in high yield.

*Hargis*<sup>15</sup> showed that Monocarboxylic acids or esters thereof are reduced to aldehydes using hydrogen and a vanadium catalyst. For example, meta-phenoxybenzoic acid can be effectively converted to m-phenoxybenzaldehyde in a vapor phase process using hydrogen as the carrier gas/reductant and a catalyst composed at least initially of vanadium pentoxide, either supported or unsupported.

*Van Geem, et al.*<sup>16</sup> reported a process for the preparation of a benzaldehyde by hydrogenation of a corresponding benzoic acid in the gas phase in the presence of a manganese containing catalyst on an acid carrier. The invention is characterized in that use is made of a catalyst prepared by: (a) coprecipitation, at a pH between 7 and 10, of a manganese salt and a salt from which an acid carrier is formed (b) subsequent calcination at a temperature between 300°C and 700°C (c) followed by reduction with a hydrogen containing gas mixture. Preferably the catalyst contains oxides of aluminum, zirconium, titanium, hafnium and/or niobium.

*Joentgen, et al.*<sup>17</sup> showed that aromatic and aliphatic aldehydes can be prepared from the corresponding aromatic or aliphatic carboxylic acids or the esters, anhydrides or halides thereof at elevated temperature by catalytic gas phase hydrogenation using hydrogen if use is made of a catalyst system composed of oxides of titanium and/or vanadium and of one or more co-metals, the co-metals being selected from the group consisting of chromium, molybdenum, cobalt, nickel, zinc, cadmium and copper.

*Yokohama, et al.*<sup>18</sup> invented a method for producing an aldehyde, which comprises hydrogenating a carboxylic acid or its alkyl ester with molecular hydrogen in the presence of a catalyst, wherein (1) chromium oxide of high purity having a specific surface area of at least 10 m<sup>2</sup> /g and a total content of sodium, potassium, magnesium and calcium of not more than 0.4 wt %, is used as the catalyst, and (2) the hydrogenation reaction is conducted while maintaining the carboxylic acid or its alkyl ester at a concentration of not more than 10 vol %.

*Ferrero, et al.*<sup>19</sup> invented a process for the preparation of aldehydes by hydrogen reduction of carboxylic acids, esters or anhydrides, characterized in that the reduction is conducted in the vapour phase, in the presence of a bimetallic catalyst of the ruthenium/tin type.

*Weiguny, et al.*<sup>20</sup> reported a process for the preparation of aldehydes by catalytic gas phase hydrogenation of carboxylic acid or their derivatives with the aid of a tin catalyst. The invention relates to a process for the preparation of aldehydes by catalytic gas phase hydrogenation of carboxylic acids or carboxylic acid derivatives at elevated temperature, which comprises employing a tin catalyst supplied to an oxidic support material.

*Van Geem, et al.*<sup>21</sup> invented a process for the conversion of benzoic acid into the corresponding benzaldehyde. The catalyst can be obtained via coprecipitation of a manganese salt, a salt from which an acid support is formed, a zinc salt and optionally a copper salt at a pH between 4 and 10, calcination, after precipitation, of the coprecipitate at a temperature of between 300 and 700°C and then, optionally, reduction of the calcined coprecipitate with the aid of a hydrogen-containing gas mixture. Using such a catalyst the hydrogenation of benzoic acid was carried out at lower temperature resulting in energy-savings and, hence, cost-savings. The typical results obtained are as follows:

Catalyst	Temperature, °C	Selectivity to Benzaldehyde	Conversion of Benzoic acid
MnO <sub>2</sub> /CuO	330	88.3	98.9
MnO <sub>2</sub> /ZnAl <sub>2</sub> O <sub>4</sub>	350	95.2	85.7
MnO <sub>2</sub> /ZnAl <sub>2</sub> O <sub>4</sub>	380	78.2	100
MnO <sub>2</sub> /ZnO ZnAl <sub>2</sub> O <sub>4</sub>	350	91.0	48.4
MnO <sub>2</sub> /ZnO ZnAl <sub>2</sub> O <sub>4</sub>	380	83.8	100
MnO <sub>2</sub> /ZnO ZnAl <sub>2</sub> O <sub>4</sub>	350	95.0	53.2
MnO <sub>2</sub> /ZnO ZnAl <sub>2</sub> O <sub>4</sub>	380	74.3	100
MnO <sub>2</sub> /ZnO ZnAl <sub>2</sub> O <sub>4</sub>	350	96.4	70.0
MnO <sub>2</sub> /ZnO ZnAl <sub>2</sub> O <sub>4</sub>	380	79.7	100
MnO <sub>2</sub> /Al <sub>2</sub> O <sub>4</sub>	414	84.0	89.0
MnO <sub>2</sub> /Al <sub>2</sub> O <sub>4</sub>	435	81.0	100

C H A P T E R - 3

**EXPERIMENTAL**

### 3.1 Materials Used:

#### *BENZOIC ACID*

*S. D. Fine-Chem Ltd,*

*BOISAR 401 506*

Minimum assay	99.5%
Mp	121-122.5
Max. limits of impurities:	
Sulphated Ash	0.05%
Total Chlorine	0.1%
Lead (Pb)	0.0005%

#### *COPPER CHROMITE (Cu 1920p)*

*Harshaw (Lot No:4)*

#### *COPPER CHROMITE*

Cu	-	33
Cr	-	27
Ba	-	11
Mn	-	05



## **M-XYLENE**

### **FLUKA CHEMIKA**

Assay > 98%(GC)

Bp 136 - 138

## **IPA (2-Proponal)**

*E. Merck (India) Ltd.*

*Mumbai-400 018*

Assay  $\geq 99\%$

Density 0.784 - 0.786

Water  $\leq 0.2$

## **Zn O**

**MAY & BAKER LTD.**

*Dagenham, England.*

Assay  $\geq 99\%$

Iron (Fe)  $\leq 0.01$

Mn  $\leq 0.001\%$

## 3.2 Experimental Set-Up

The experimental set-up used for the hydrogenation is shown below:

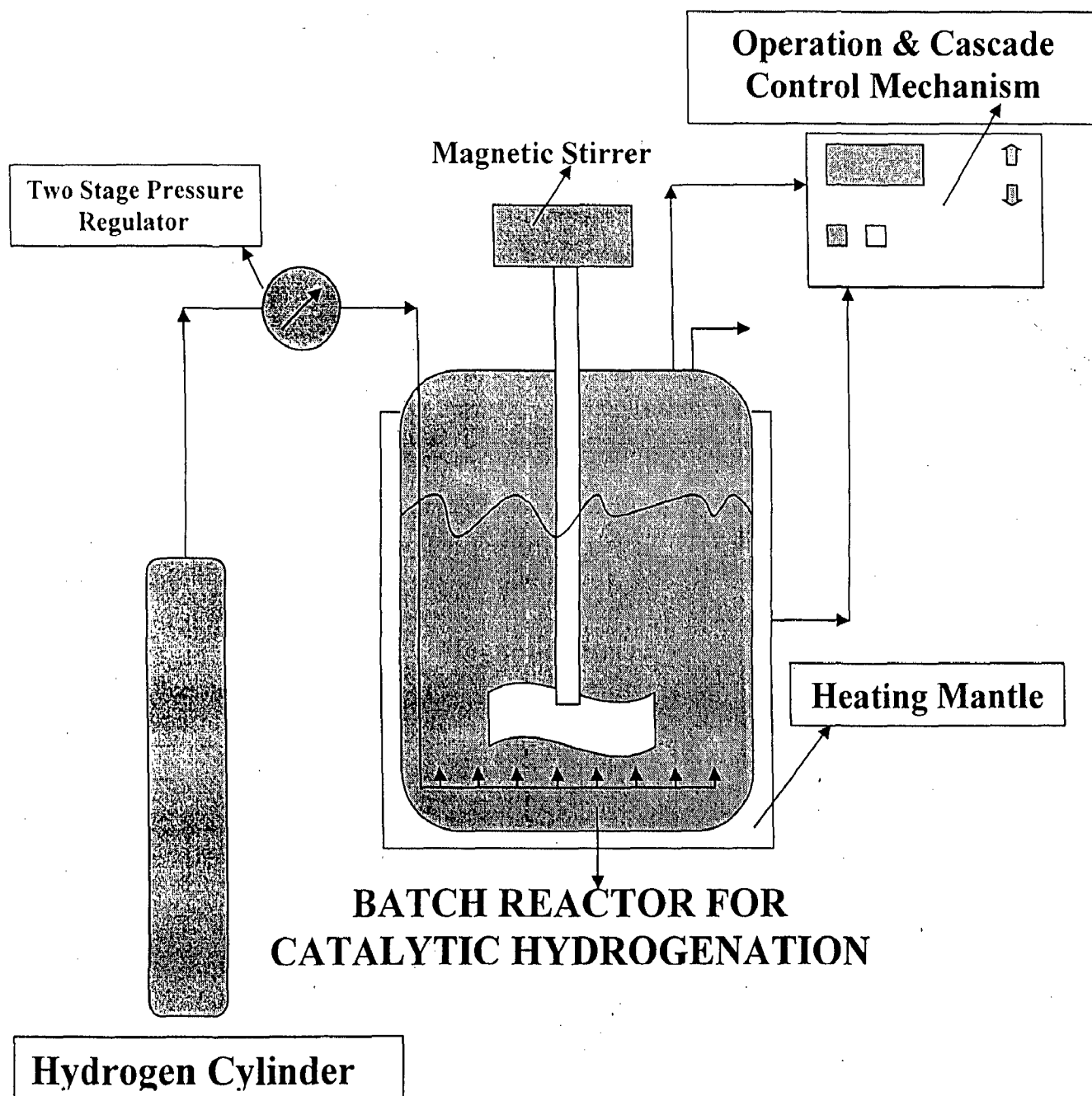


Fig. 3.1 Schematic Diagram of Experimental Set-Up

### 3.2.1 STANDARD REACTOR FITTINGS

All the Parr stirred reactors are equipped with convenient valves and fittings for handling the various functions listed below.

**Pressure gage** with a stainless steel Bourdon tube and stainless steel movement, usually having a range from 0 to 2000 psi for use at working pressures up to 1400 psig. A 4<sup>1/2</sup>" diameter gage is standard on all reactors except the "Mini" series which uses a 3<sup>1/2</sup>" diameter gage.

**A Safety Rupture Disc** made of Inconel, with a burst rating to match the range of the pressure gage is installed in each reactor.

**A Gas Inlet Valve** for charging gas in to the reactor. Connections to this valve are made with a Type A coned pressure fitting which is provided on the A495HC pressure furnished with each reactor.

**A Liquid Sampling Valve** for withdrawing samples from the reactor under pressure. This valve and the gas inlet valve are both connected to the dip tube described below.

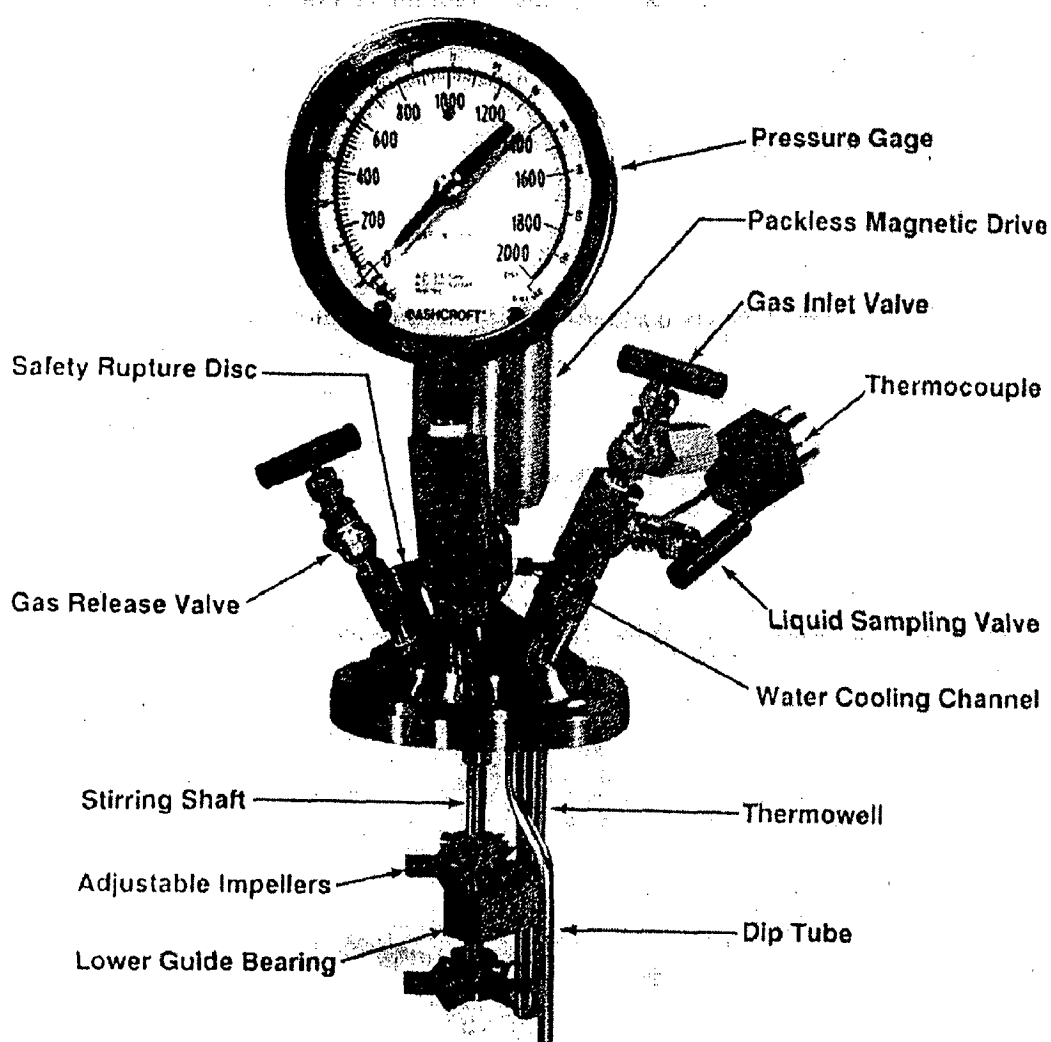
**A Gas Release Valve** for withdrawing gas samples or for releasing pressure from the reactor.

**A Stirrer Drive System** with ball and needle bearings to absorb the thrust and rotational loads. The select either a packless magnetic drive or Parr self-sealing packing gland to maintain a gas-tight seal on the rotating shaft.

**A Leak Detector Nipple** is installed on units equipped with a packing gland to monitor the performance of the gland.

A *Water Cooling Channel* is included on all reactors to prolong the life of the sealing elements in a gland-type seal or to protect the fixed seals in a magnetic drive, when working at elevated temperatures.

A *Thermocouple* is furnished with each reactor for temperature measurements. On one liter and larger units, the thermocouple is inserted in to a thermowell extending to a point near the bottom of the reactor cavity. On Parr "Mini" reactors the thermowell is omitted, and a sheathed thermocouple is inserted directly into the reactor cavity through a sealed fitting in the head.



**Fig. 3.2 Standard Reactor-Head Fittings**

A *Dip Tube* extending to the bottom of the reactor, connected to both the gas inlet and liquid sampling valves described above. With this arrangement, incoming gas is always introduced below the surface of the liquid; and the operator is provided with a means for clearing the dip tube to be sure that any sample taken during a run will be representative of the charge. This can be done by opening the gas inlet valve momentarily to force any liquid in the tube back in to the reactor before withdrawing a sample. Dip tubes are either screwed into the head or attached to fittings from which they can be released easily.

A *Stirring Shaft* with one turbine type impeller is used in the smallest "Mini" reactors. A universal coupling is provided on the upper end of the shaft on all one liter and larger reactors to compensate for any slight misalignment in the stirring system.

A *Lower Guide Bearing* with an easily replaced reinforced Teflon insert is provided on all one liter and larger reactors to stabilize the rotating shaft.

### 3.2.2 REACTOR SPECIFICATIONS

**Bomb** : 452HC2 TITAN 4010400 16636

Size : 450ml

Capacity : 300ml

Maximum allowable pressure: 1350 psi @ 300°C

**Head** : 6746 TITANIUM

Controller : 4844

Manufacturer : Parr Instrument Co., Moline, USA – 61265

Rupture Disk : 600 psi

Quartz fabric heating mantle

Thermo couple in steel sheath

Thermocouple : Iron – Constantan ( -100°C to 760°C); Resolution – 0.25°C

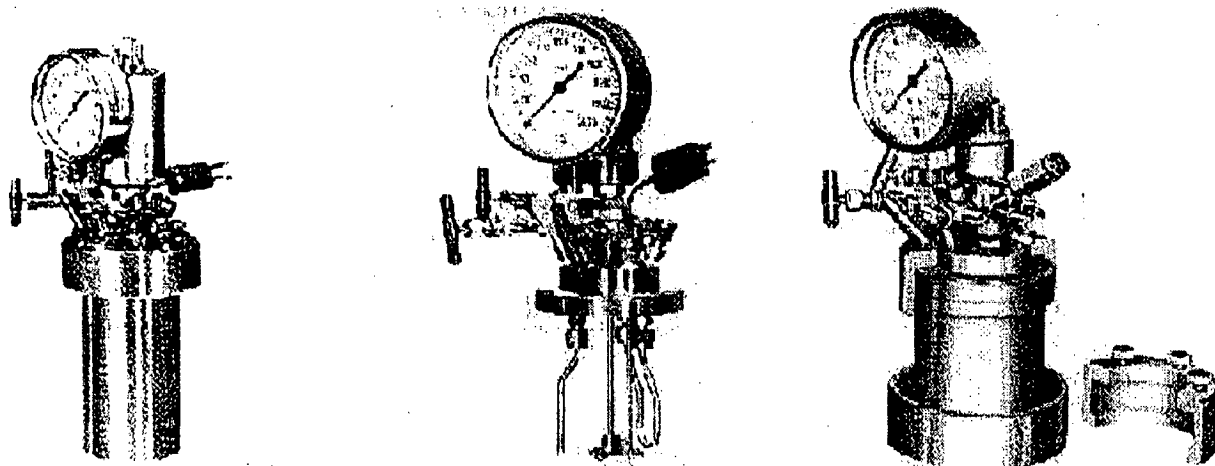


Fig. 3.3 Parr Reactor (Bomb: 452HC2 Titan 4010400 16636; Head: 6746 Titanium)

### 3.2.3 MODEL 4844 PROGRAMMABLE CONTROLLER

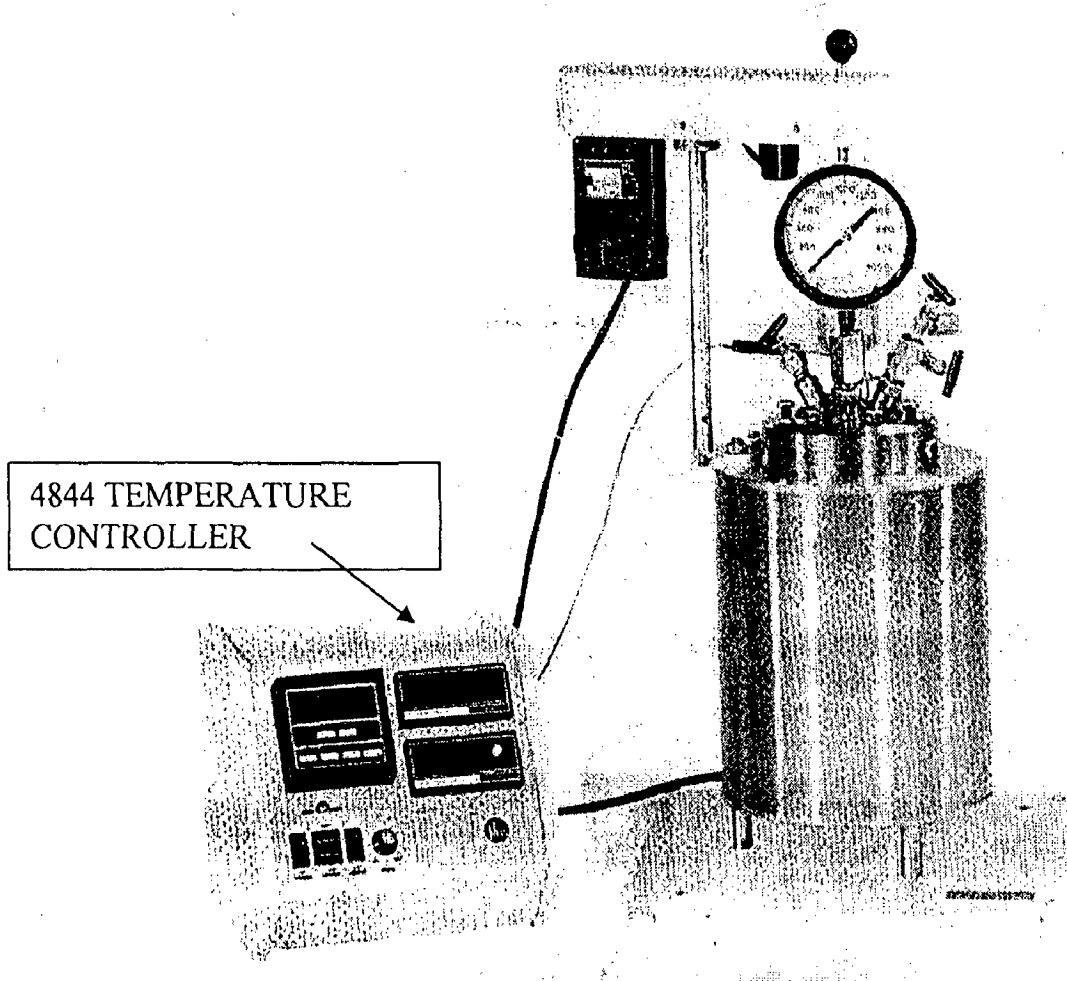


Fig. 3.4 4844 Temperature Controller

### Specifications

Input thermocouple	:	Iron –Constantan
Operating Range	:	0°C to 600°C
Readout resolution	:	1°C
Setpoint resolution	:	1°C
System accuracy	:	+/-2°C
Control action	:	Three term PID control with programmable ramp and soak temperatures, plus limit control
Operating voltages	:	115v and 230 v. a. c
Maximum switching load	:	15 amp

### 3.3 Experimental Procedure

1. The autoclave was charged with the desired quantity of benzoic acid, solvent and catalyst, its weight is noted.
2. Autoclave was pressurized with Hydrogen to 5 bar stirring is continued for 10 minutes at slow speed 500 rpm.
3. Release the Hydrogen slowly while stirring at much low speed.
4. Repeat the purging once again as described above.
5. Close the Gas out let valve before all the gas leaves the reactor and is replaced by air.
6. The contents were heated to the desired temperature while stirring.
7. After the set point temperature is reached, note down the reaction starting time and the operating pressure.
8. Samples were withdrawn at the desired time intervals and GC was done to know the progress of the reaction.
9. After the reaction was over, the autoclave was cooled to the ambient temperature by removing the heating mantle, while stirring at low speed.
10. Put off the stirring and pressure is released slowly.
11. The reactor was then weighed for any change in weights.





### 3.4 Analytical Technique (Gas Chromatography)

A Gas chromatograph or Gas liquid chromatograph is a chemical analysis instrument for separating and identifying various components in a sample. It is based on the principle of adsorption technology, in which liquid is a still media on which moving gas having different component is adsorbed. Heart of the gas chromatograph system is the separation column. The function of the column is to separate and concentrate different components in order to maximize the detection signal.

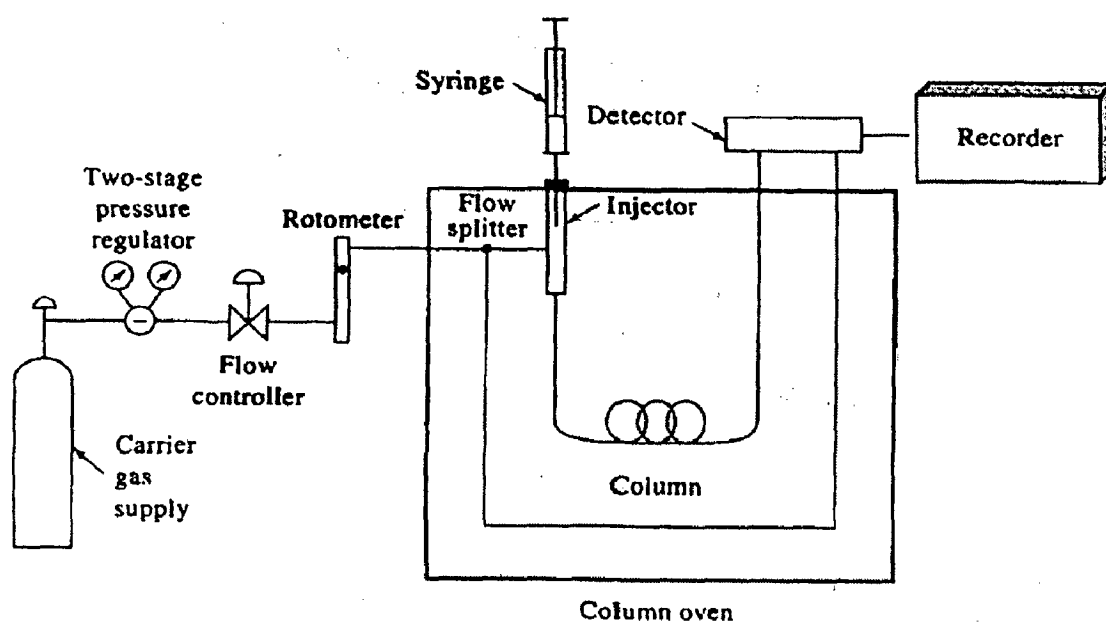
**Gas chromatograph has the following components:**

1. Carrier gas
2. A column
3. Injection port and a system for the introduction of the sample into the column (Micro syringe).
4. Column oven
5. Detector
6. A recorder

Chemoti 8510 gas chromatograph with data processor was used under the following conditions:

- |              |   |   |
|--------------|---|---|
| A. Detector  | : | FID                                     |
| B. Column    | : | OV-17(Length = 1m)                      |
| C. Programme | : | 60°C - 2 min - 10°C/min - 250°C - 5 min |

- D. Detector Temperature : 250°C
- E. Injection Temperature : 250°C
- F. Carrier gas : Nitrogen
- G. Detector current : 200mA



**Fig. 3.5 Gas chromatograph**

In order to identify the components comparison was done with the pure samples. Samples of the organic acids were esterified with Diazomethane and were analyzed as esters in the GC column. Preparation of Diazomethane and Nitrosomethyl urea is given as under.

### **3.5 Preparation of Nitrosomethyl urea:**

49 grams of acetyl methyl urea is added to 50 mL. of concentrated HCl and heated on a steam bath until no more solid is dissolving, continue for 3 - 4 minutes. Total time of heating must be 8-12 minutes. The resulting mixture is diluted with 50 mL. of distilled water and cool below 10°C in an ice bath. 38 grams of saturated solution of A. R. Sodium Nitrate is added to 55mL. of distilled water. Run in slowly and with stirring a cold saturated solution of A. R. Sodium Nitrate in water, below the level of liquid. Keep the mixture in ice bath for 5 - 10 minutes, filter, wash with 8-10 mL. of ice water and then dry in air. The resulting compound after drying is NMU.

### **3.6 Preparation of Diazomethane:**

60mL. of 50% Aq. KOH solution is taken in a 500 mL. round bottom flask and 50mL. of diethyl ether is added and cool to 5°C. 20.6grams of NMU is added to the reaction mixture while shaking. Equip the flask with a condenser set for distillation, attach to the lower end of the condenser an adapter passing through a two holed rubber stopper and dipping below the surface of 40mL. Pure ether contained in a 300mL. conical flask and immersed in an ice-salt mixture.

Pass the exit gases through a second 40mL. portion of ether in a 300mL. wash bottle cooled below 0°C. Place the reaction flask on a water bath at 50°C and bring it to the boiling point of ether, shake occasionally. Distill 2/3<sup>rd</sup> of ether and as the reaction mixture passes colourless(not all ether should be distilled). The combined ether solutions in the receivers contain 5.4-5.9 grams DAM. This is sufficiently dry for most purposes. If a really dry solution is required the ether solution may be allowed to stand for 2-3 hours over pellets of A.R KOH. The anhydrous ethereal solution may be kept for a day or two.

### 3.7 Quantitative Analysis

The volume of different compounds present in an injected sample is proportional to area percentage in the resulting chromatogram(excluding unknowns peak areas) and different peaks are identified by injecting a standard sample and comparing the retention times.

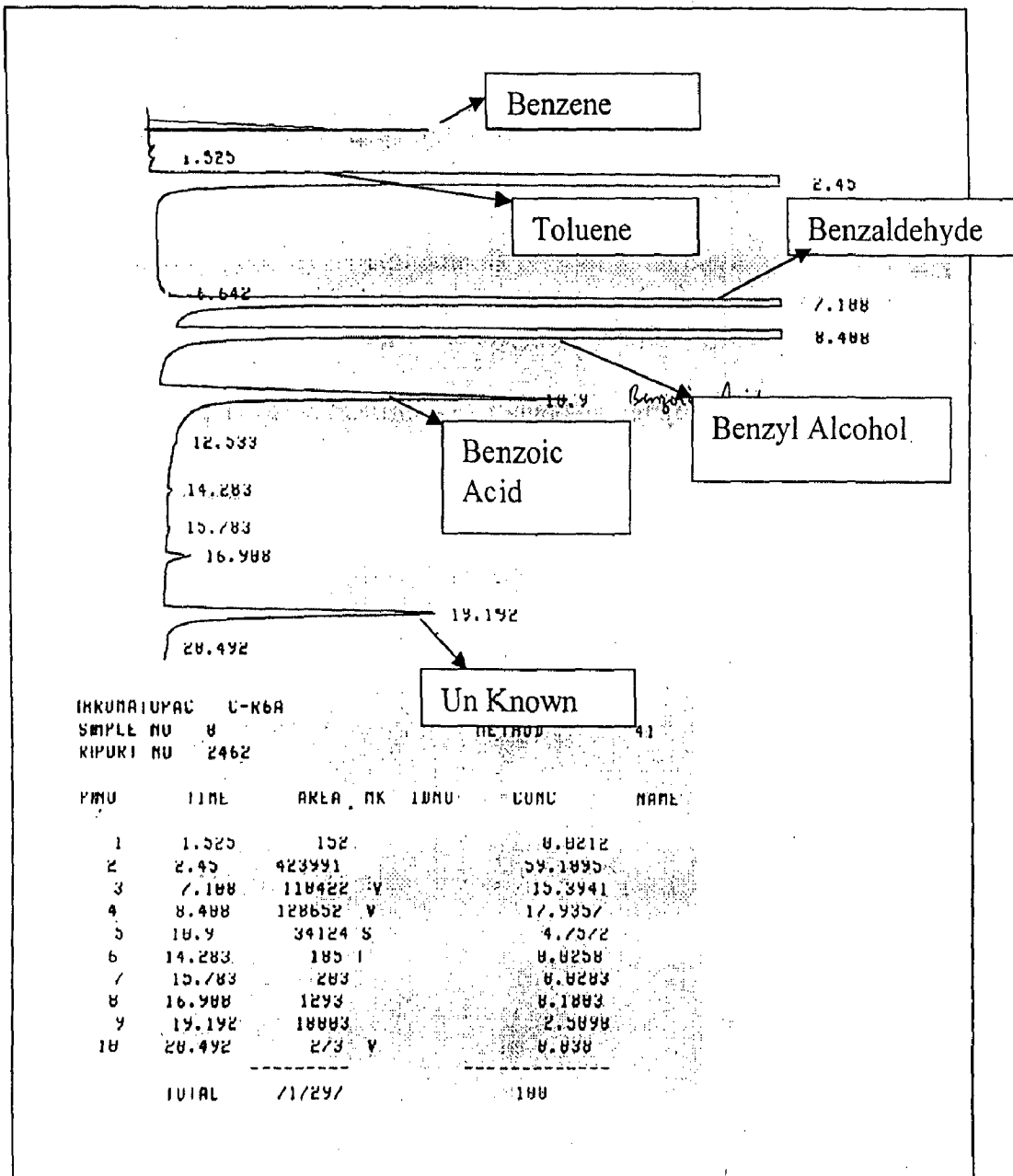


Fig. 3.6 A Typical Chromatogram

### 3.8 RETENTION TIMES

CHEMICAL NAME	TIME, min
ETHER	0.4 - 0.6
IPA	1.5 - 2.0
M-XYLENE	5.5 - 6.0
BENZENE	1.5 - 2.0
TOLUENE	3.2 - 3.7
BENZALDEHYDE	8.5 - 9.0
BENZYL ALCOHOL	10.2 - 10.7
METHYL ESTER OF BENZOIC ACID	10.3 - 13.3
ISOPROPYL BENZOATE	11.6 - 12.1
BENZOIC ACID	12.7 - 13.2

**C H A P T E R - 4**

**RESULTS**

**&**

**DISCUSSION**

#### 4.1 ALL EXPERIMENTS AT A GLANCE

EXPT. NO.	REACTANTS USED				OPERATING CONDITIONS				OBSERVATION
	REACTANT	SOLVENT	CATALYST	CATALYST/ SUBSTRATE (Molar Ratio)	H <sub>2</sub> PRESSURE	DURATION (HOURS)	AGITATION (RPM)	T °C	
1	BENZOIC ACID - 12.2gr (0.1 mole)	HEPTANE- 150ml	ZnO- 0.336gr	0.041	12	4	1200	150	No Reaction
2	BENZOIC ACID - 12.2gr (0.1 mole)	IPA	ZnO- 0.336gr	0.041	14	4	1200	150	Formation of Iso Propyl Benzoate was Observed
3	BENZOIC ACID - 12.2gr (0.1 mole)	IPA	ZnO-0.17gr	0.021	13	4	1200	150	Formation of Iso Propyl Benzoate
4	BENZOIC ACID - 12.2gr (0.1 mole)	IPA	ZnO-0.17gr	0.021	26	4	1200	200	Formation of Iso Propyl Benzoate
5	BENZOIC ACID - 12.2gr (0.1 mole)	IPA	-	-	-	2	1200	200	To see Formation of Iso Propyl Benzoate (16.17%)

6	BENZOIC ACID - 12.2gr (0.1 mole)	m-Xylene	ZnO- 0.336gr	0.041	12	4	1200	200	No Reaction
7	BENZOIC ACID - 12.2gr (0.1 mole)	m-Xylene	ZnO- 0.504gr	0.061	20	4	1200	250	No Reaction Catalyst & Temp. increased
8	BENZOIC ACID - 12.2gr (0.1 mole)	m-Xylene	Cu. Chromite- 1.55gr	0.05	20	4	1200	200	Harsha Cu. Chromite Toluene-33.28 Benzene-4.323
9	BENZOIC ACID - 12.2gr (0.1 mole)	m-Xylene	Cu. Chromite- 1.55gr	0.05	20	4	1200	150	Reaction Observed
10	BENZOIC ACID - 12.2gr (0.1 mole)	m-Xylene	Cu. Chromite- 1.55gr	0.05	20	4	1200	175	Reaction Observed
11	BENZOIC ACID - 12.2gr (0.1 mole)	m-Xylene	Cu. Chromite- 1.55gr (Pellets)	0.05	25	4	1200	250	Reaction Observed
12	BENZOIC ACID - 12.2gr (0.1 mole)	m-Xylene	Cu. Chromite- 1.55gr (Pellets)	0.05	32	4	1200	150	Reaction Observed



13	BENZOIC ACID - 12.2gr (0.1 mole)	m-Xylene	Platinum on Alumina 0.366gr	3%on B.A.	13	4	1200	200	No Reaction
14	BENZOIC ACID - 12.2gr	m-Xylene	ZnO 0.504gr.	0.06	20	4	1200	200	Reduction-2 hrs followed by Re-oxidation-2 hrs. No Reaction
15	BENZOIC ACID - 12.2gr	m-Xylene	ZrO <sub>2</sub> 1gr.	1%on B.A.	16	4	1200	200	No Reaction

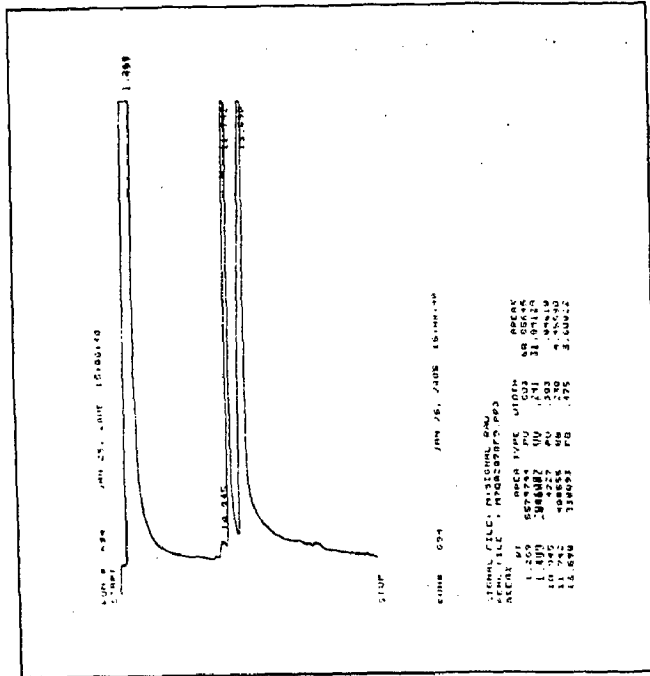
## 4.2 EXPERIMENTAL RESULTS

### EXPERIMENT NO : 1

#### REACTION CONDITIONS:

Benzoic Acid : 12.2gr.  
 Reducing Agent : H<sub>2</sub>  
 Catalyst : ZnO  
 Solvent : IPA  
 Agitation : 1200 RPM  
 Temperature : 150°C  
 Operating Pressure : 12 bars

Fig 4.1 Chromatogram - Experiment No. 1



REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)						
	Ester(IPB)	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	1.2	-	-	-	-	93.2	5.6
1.0	6.7	-	-	-	-	87.0	6.3
2.0	18.3	-	-	-	-	81.0	0.7
3.0	32.3	-	-	-	-	64.0	3.7
4.0	49.7	-	-	-	-	36.1	14.2

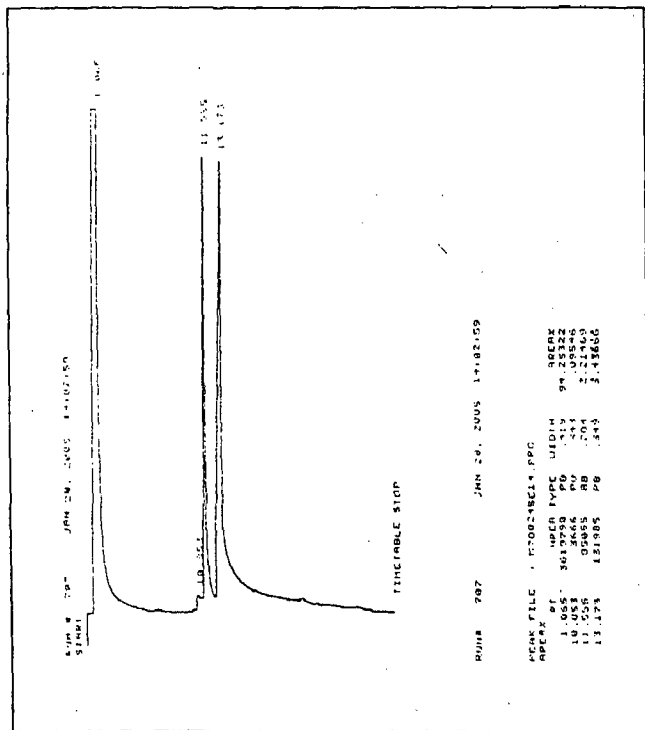
Table 4.1 Results of Experiment No. 1

Fig 4.2 Chromatogram - Experiment No. 2

**EXPERIMENT NO: 2**

**REACTION CONDITIONS:**

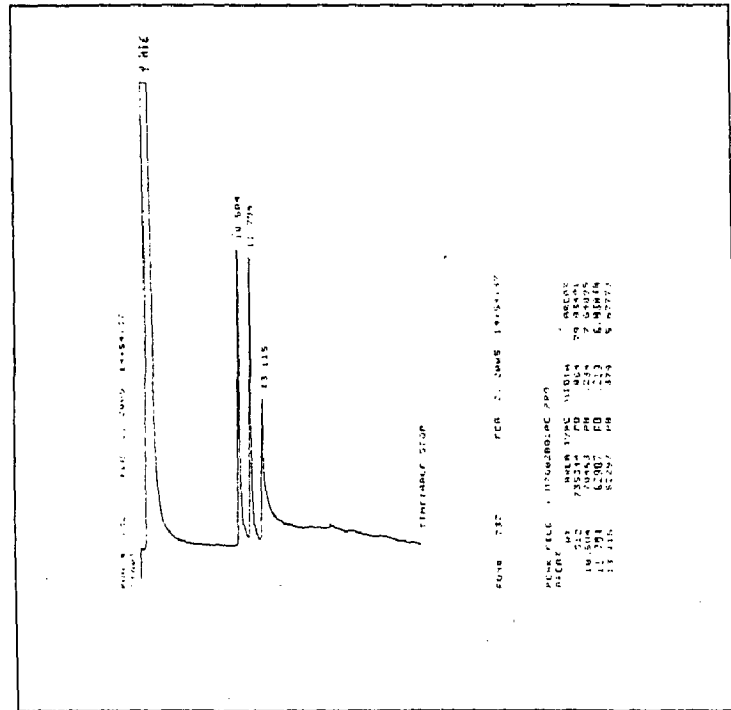
Benzoic Acid : 12.2gr.  
 Reducing Agent : H<sub>2</sub>  
 Catalyst : ZnO  
 Solvent : IPA (150ml)  
 Agitation : 1200 RPM  
 Temperature : 150°C  
 Operating Pressure : 14 bars



REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)						
	Ester(IPB)	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	-	-	-	-	-	-	-
1.0	18.5	-	-	-	-	81.4	-
2.0	33.9	-	-	-	-	66.1	-
3.0	46.0	-	-	-	-	54.0	-
4.0	55.0	-	-	-	-	45.0	-

Table 4.2 Results of Experiment No. 2

Fig 4.3 Chromatogram - Experiment No. 3



**EXPERIMENT NO: 3**

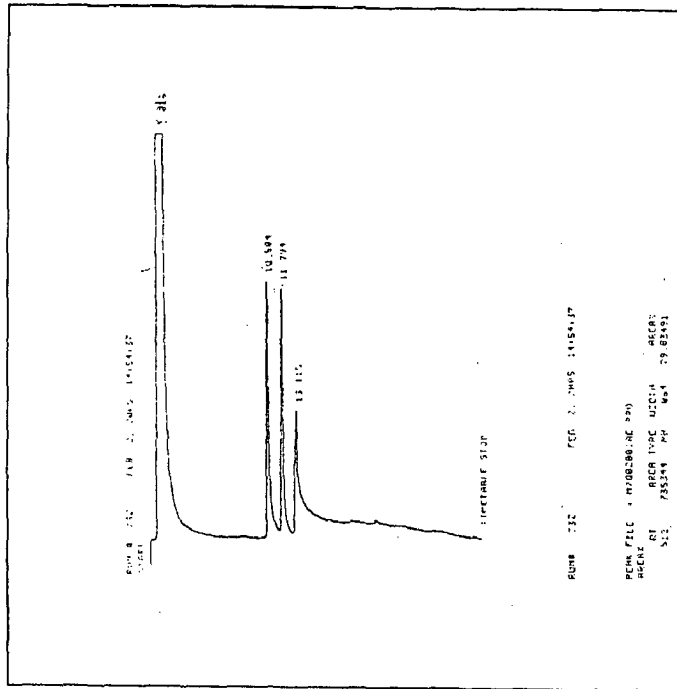
**REACTION CONDITIONS:**

Benzoic Acid : 12.2gr.  
 Reducing Agent : H<sub>2</sub>  
 Catalyst : ZnO  
 Solvent : IPA(150ml)  
 Agitation : 1200 RPM  
 Temperature : 150°C  
 Operating Pressure : 13 bars

REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)						
	Ester(IPB)	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	1.2	-	-	-	-	93.2	4.0
1.0	6.7	-	-	-	-	87.4	5.0
2.0	17.3	-	-	-	-	81.3	1.4
3.0	31.3	-	-	-	-	65.6	0.2
4.0	48.7	-	-	-	-	37.1	13.0

Table 4.3 Results of Experiment No. 3

**Fig 4.4 Chromatogram - Experiment No. 4**



**EXPERIMENT NO: 4**

**REACTION CONDITIONS:**

- Benzoic Acid : 12.2gr.
- Reducing Agent : H<sub>2</sub>
- Catalyst : ZnO
- Solvent : IPA
- Agitation : 1200 RPM
- Temperature : 200°C
- Operating Pressure : 26 bars

REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)						
	Ester(IPB)	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	25.4	-	-	-	-	74.5	-
1.0	49.5	-	-	-	-	50.5	-
2.0	84	-	-	-	-	16	-
3.0	90	-	-	-	-	10	-
4.0	98.9	-	-	-	-	1.1	-

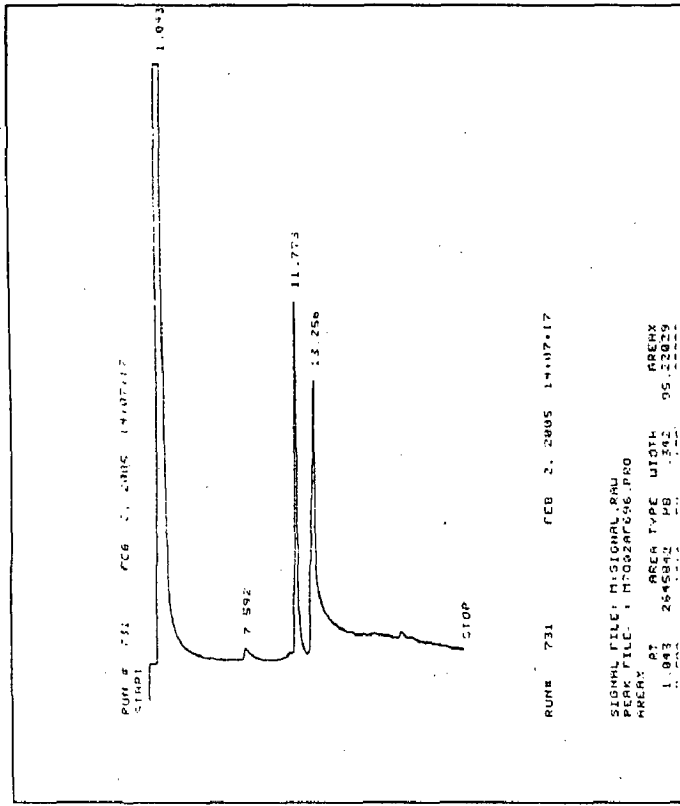
**Table 4.4 Results of Experiment No. 4**

**EXPERIMENT NO: 5**

**REACTION CONDITIONS:**

Benzoic Acid : 12.2gr.  
 Reducing Agent : H<sub>2</sub>  
 Catalyst : ZnO  
 Solvent : IPA  
 Agitation : 1200 RPM  
 Temperature : 200°C  
 Operating Pressure : atm.

**Fig 4.5 Chromatogram - Experiment No. 5**



REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)						
	Ester(IPB)	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	10.4	-	-	-	-	89.5	-
1.0	21.9	-	-	-	-	78.0	-
2.0	48	-	-	-	-	52	-
3.0	78.1	-	-	-	-	21.8	-
4.0	87.6	-	-	-	-	12.4	-

**Table 4.5 Results of Experiment No. 5**

Fig 4.7A Chromatogram - Experiment No. 7

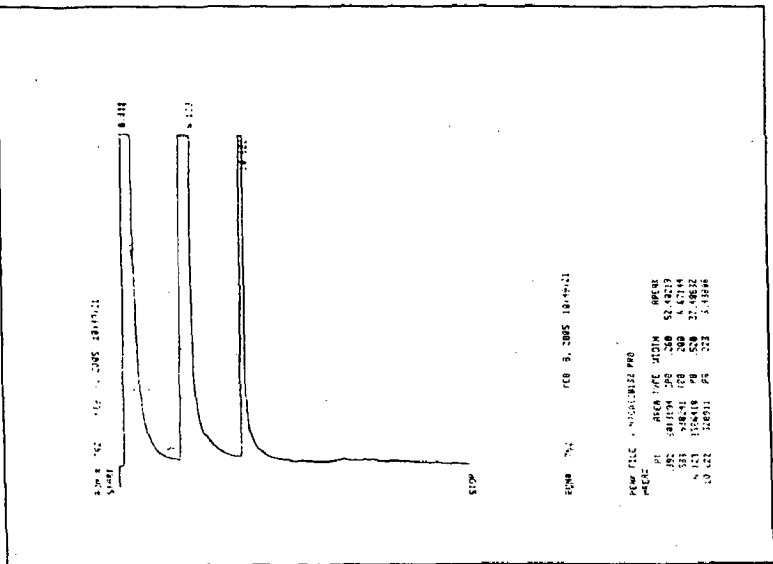
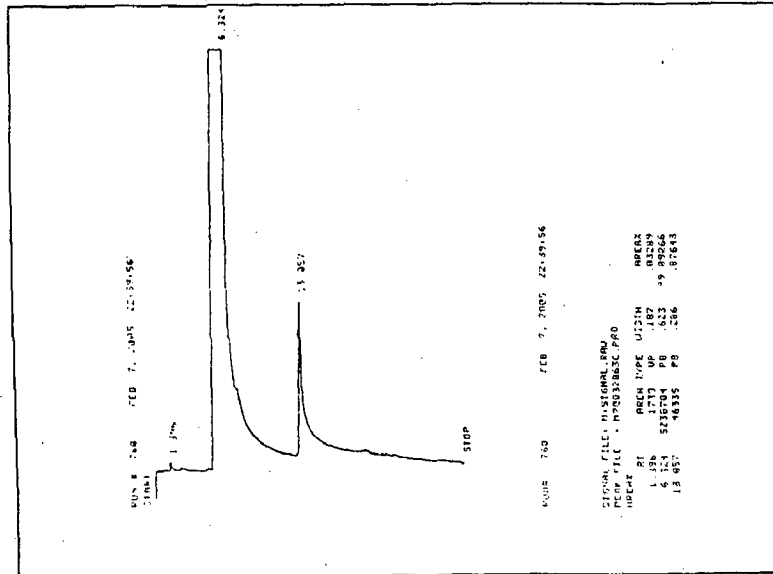


Fig 4.7B Chromatogram - Experiment No. 7



**EXPERIMENT NO: 7**

**REACTION CONDITIONS:**

- Benzoic Acid : 12.2gr.
- Reducing Agent : H<sub>2</sub>
- Catalyst : ZnO
- Solvent : m-Xylene
- Agitation : 1200 RPM
- Temperature : 250°C
- Operating Pressure : 20 bars

REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)					
	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	-	-	-	-	99.0	1.0
1.0	-	-	-	-	98.5	1.5
2.0	-	-	-	-	97.3	2.7
3.0	-	-	-	-	97.0	3.0
4.0	-	-	-	-	96.4	3.6

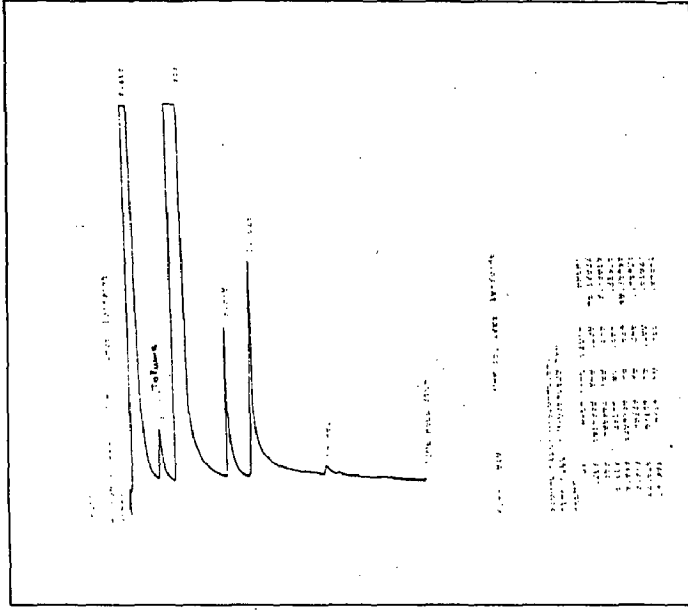
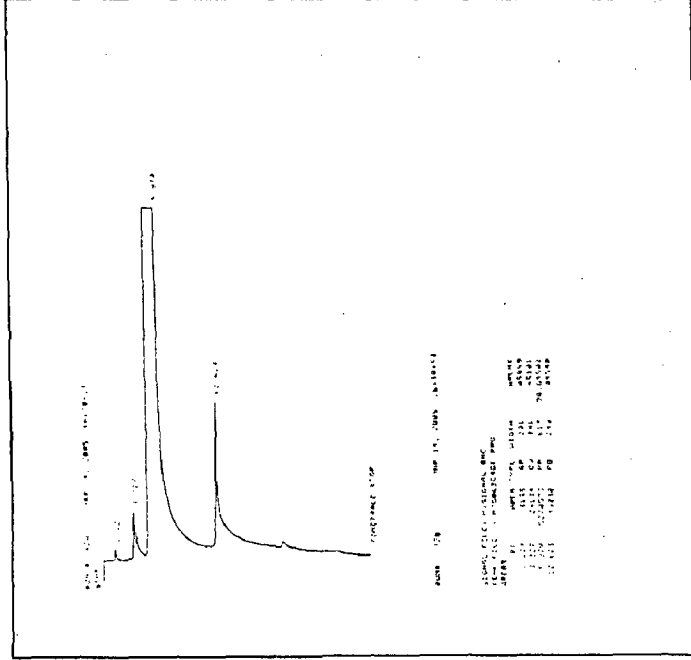
Table 4.7 Results of Experiment No. 7

Fig 4.8A Chromatogram - Experiment No. 8      Fig 4.8B Chromatogram - Experiment No. 8

**EXPERIMENT NO: 8**

**REACTION CONDITIONS:**

- Benzoic Acid : 12.2gr.
- Reducing Agent: H<sub>2</sub>
- Catalyst: Cu. Chromite
- Solvent: m-Xylene
- Agitation: 1200 RPM
- Temperature: 200°C
- Operating Pressure: 20 bars

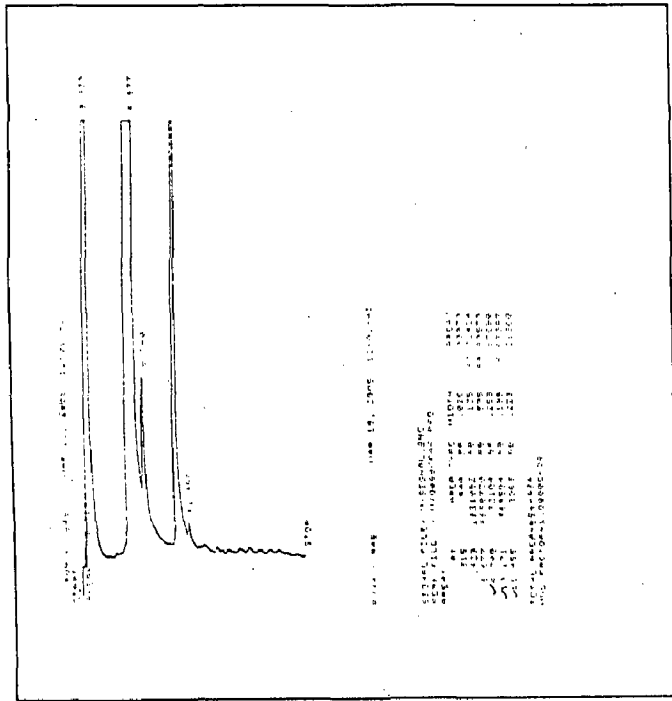


REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)					
	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	-	-	-	-	99.5	0.5
1.0	-	-	-	-	99.0	1.0
2.0	-	-	-	-	98.3	1.7
3.0	0.6	7.2	-	-	89.1	3.1
4.0	4.3	33.2	-	-	56.4	6.1

Table 4.8 Results of Experiment No. 8



Fig 4.9 Chromatogram - Experiment No. 9



**EXPERIMENT NO: 9**

**REACTION CONDITIONS:**

Benzoic Acid : 12.2gr.  
 Reducing Agent : H<sub>2</sub>  
 Catalyst : Cu. Chromite  
 Solvent : m-Xylene  
 Agitation : 1200 RPM  
 Temperature : 150°C  
 Operating Pressure : 20 bars

REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)					
	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	-	-	-	-	97.6	2.4
1.0	-	-	-	-	95.3	4.7
2.0	-	-	-	-	91.3	8.7
3.0	-	-	-	-	86.5	13.5
4.0	-	-	4.5	-	83.2	12.2

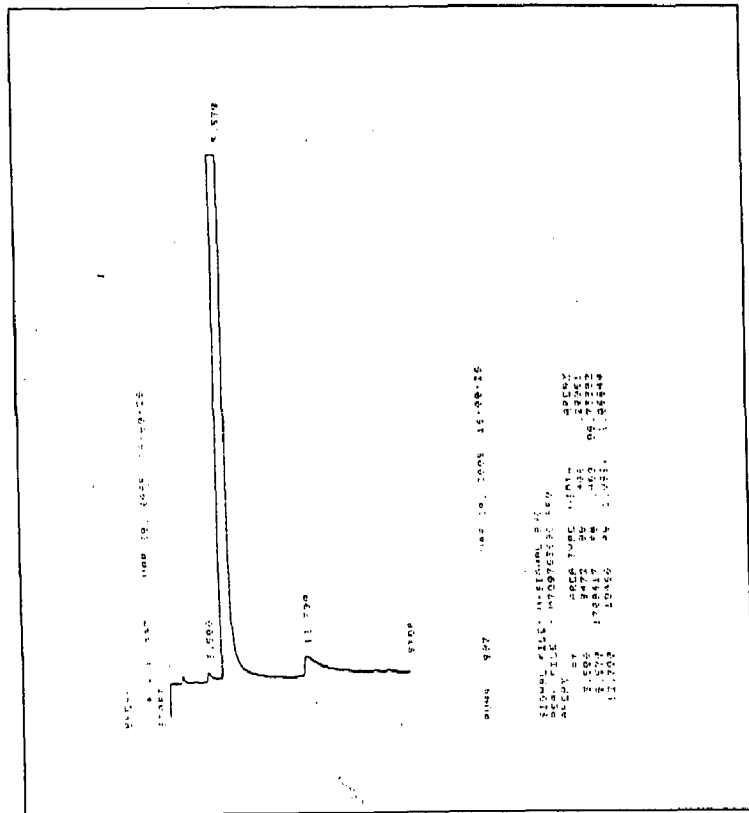
Table 4.9 Results of Experiment No. 9

Fig 4.10 Chromatogram - Experiment No. 10

**EXPERIMENT NO: 10**

**REACTION CONDITIONS:**

Benzoic Acid : 12.2gr.  
 Reducing Agent : H<sub>2</sub>  
 Catalyst : Cu. Chromite  
 Solvent : m-Xylene  
 Agitation : 1200 RPM  
 Temperature : 175°C  
 Operating Pressure : 20 bars



REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)					
	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	-	-	-	-	98.2	1.8
1.0	47.3	14.4	-	-	38.3	-
2.0	-	-	-	-	38.0	-
3.0	-	-	-	-	37.5	0.5
4.0	-	15.8	-	-	21.6	-

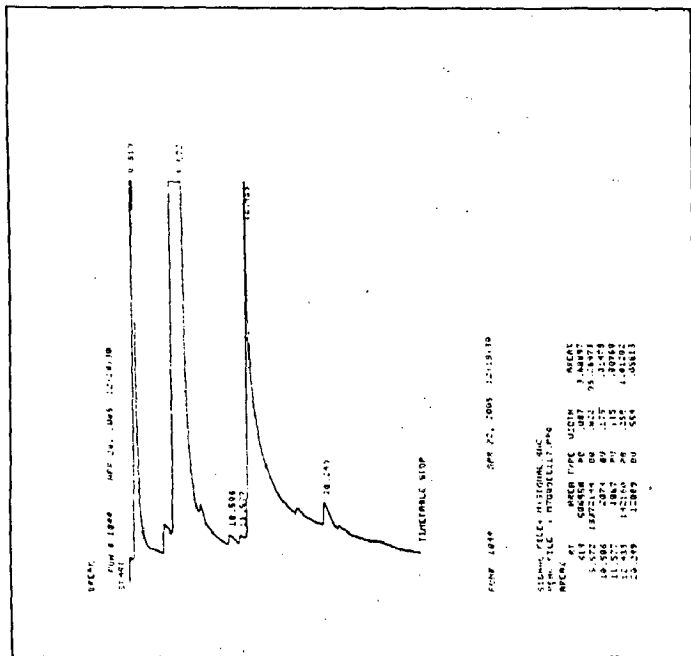
Table 4.10 Results of Experiment No. 10

Fig 4.11 Chromatogram - Experiment No. 11

**EXPERIMENT NO: 11**

**REACTION CONDITIONS:**

Benzoic Acid : 12.2gr.  
 Reducing Agent : H<sub>2</sub>  
 Catalyst : Cu. Chromite(Pellets)  
 Solvent : m-Xylene  
 Agitation : 1200 RPM  
 Temperature : 250°C  
 Operating Pressure : 25 bars



REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)					
	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol*	Benzoic Acid	Un Identified
0.5	-	-	-	1.3	90.3	2.0
1.0	-	7.7	-	1.2	86.6	1.3
2.0	-	15.0	-	0.6	80.0	4.5
3.0	-	4.6	-	0.3	72.0	23.1
4.0	-	7.3	-	-	63.5	29.2

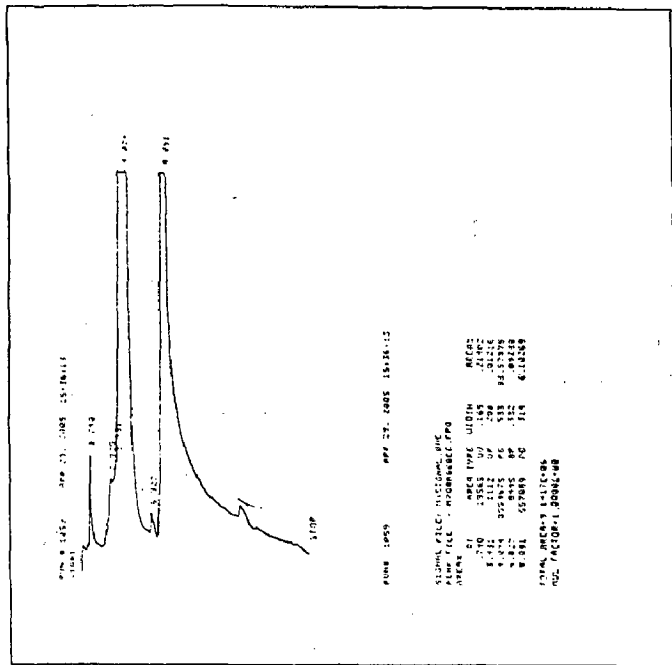
\*To be conformed by authentic sample

**Table 4.11 Results of Experiment No. 11**

Fig 4.12 Chromatogram - Experiment No. 12

**EXPERIMENT NO: 12**  
**REACTION CONDITIONS:**

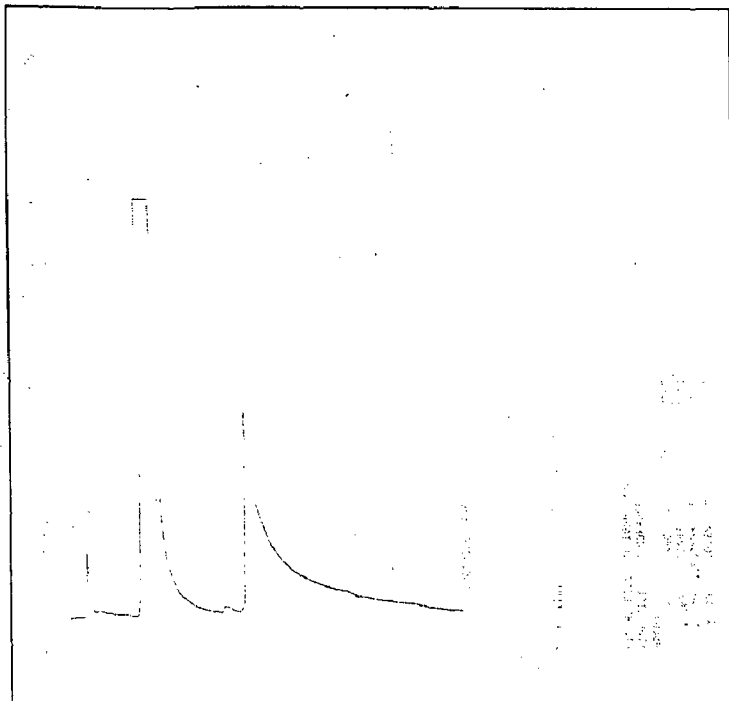
Benzoic Acid : 12.2gr.  
 Reducing Agent : H<sub>2</sub>  
 Catalyst : Cu. Chromite (Pellets)  
 Solvent : m-Xylene  
 Agitation : 1200 RPM  
 Temperature : 150°C  
 Operating Pressure : 32 bars



REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)					
	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	-	-	-	-	84.1	15.9
1.0	47.3	14.4	-	-	38.3	-
2.0	-	-	-	-	38.0	-
3.0	-	-	-	-	37.0	-
4.0	-	15.8	-	-	21.2	-

Table 4.12 Results of Experiment No. 12

Fig 4.15 Chromatogram - Experiment No. 15



**EXPERIMENT NO: 15**  
**REACTION CONDITIONS:**

Benzoic Acid : 12.2gr.  
 Reducing Agent : H<sub>2</sub>  
 Catalyst : ZrO<sub>2</sub>  
 Solvent : m-Xylene  
 Agitation : 1200 RPM  
 Temperature : 200°C  
 Operating Pressure : 16 bars

REACTION DURATION (Hours)	COMPOSITION OF REACTION MIXTURE (%)					
	Benzene	Toluene	Benzaldehyde	Benzyl Alcohol	Benzoic Acid	Un Identified
0.5	-	-	-	-	90.3	0.7
1.0	-	-	-	-	86.6	13.4
2.0	-	-	-	-	80.0	20.0
3.0	-	-	-	-	72.0	28
4.0	-	-	-	-	63.5	36.5

Table 4.13 Results of Experiment No. 15

## CONCLUSIONS

Conversion of a carboxylic acid to an aldehyde by direct reduction is not easy to achieve because acids are generally difficult to reduce, whereas aldehydes are easily reduced. Thus the problem is to keep the reaction from going too far.

The formation of Toluene in my experiment suggests that selectivity to Toluene is much higher on ZnO catalyst because oxygen vacancies are more easily created. The activity in benzaldehyde deoxygenation resolves the activity in benzoic acid deoxygenation. The main difference between the two reactions is that the latter reaction requires a slightly higher temperature. This is probably related to the fact that in benzaldehyde C=O bond must be broken whereas in benzoic acid the C-O bond order is firmly like 1.5 and in the transition state even lower 1 and 1.5.

Though Catalytic Hydrogenation of Benzoic Acid to Benzaldehyde is possible in vapour phase, with high selectivity (>95%) to benzaldehyde using catalysts ZnO and ZrO<sub>2</sub>, the reaction is highly unfavorable in the liquid phase and a detailed thermodynamic analysis is required to clarify the reasons and to suggest possible solutions for this problem.

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