

# CATALYTIC WET AIR OXIDATION OF CARBOXYLIC ACID

## 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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**JUNE, 2005**

## CANDIDATE'S DECLARATION

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I hereby certify that the work which is being presented in this dissertation entitled "CATALYTIC WET AIR OXIDATION OF CARBOXYLIC ACID" in 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 during the period from June 2004 to June 2005 under the guidance of Dr. Shri Chand, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

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

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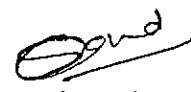
  
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## CERTIFICATE

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

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## ACKNOWLEDGEMENT

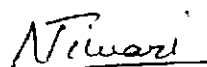
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(NIVESH TIWARI)

## ABSTRACT

Today, the survival of process industries is increasingly dependent upon the environmental sustainability of their technologies. There is growing concern about the problems of waste minimization. Waste streams from various industries constitute high BOD, COD, pH, temperature, color, obnoxious odors. Rising concern about environment, strict implementation of environmental norms and the need to survive in competitive green pollution free market are slowly forcing the industries to upgrade and improve the waste minimization and treatment techniques.

Among the various types of processes which can be used for treating aqueous wastes polluted with organic matter, wet air oxidation (WAO) is very attractive. The basic idea of the process is to enhance contact between molecular oxygen and organic matter to be oxidized. High temperature conditions convert the organic matter to carbon dioxide and water. The liquid phase is maintained by high pressure which also increases the concentration of dissolved oxygen and thus the oxidation rate. In this process insoluble organic matter is converted to simpler soluble organic compounds which in turn oxidized to carbon dioxide and water without emissions of NO<sub>x</sub>, SO<sub>2</sub>, HCl, dioxins, furans, fly ash etc. The last residual organic compounds are fatty acids, especially acetic acid.

In the present work, CWAO of carboxylic acid (butyric acid) was carried out in a pressurized reactor at a partial pressure of air 4 kg/cm<sup>2</sup> and temperature from 140°C to 180°C to reduce the COD of butyric acid. The catalysts tested in CWAO of butyric acid include both homogeneous (CuSO<sub>4</sub> and FeSO<sub>4</sub>) and heterogeneous [Co:Bi (5:1) and Mn:Ce (1:1)] catalysts. The characterization of catalysts by SEM and XRD proves that heterogeneous catalysts are far better than homogeneous catalysts.

The percent COD reduction of the butyric acid was found to be a function of initial pH of the solution and temperature. It has been found that it works more effectively at a certain pH for a given individual catalyst. The percent COD reduction was found to increase with temperature in the range 140°C to 180°C. An increase in the temperature from 140°C to 180°C increases the % COD reduction from 40.0% to 83 % with Mn : Ce (1: 1) after 4 hour reaction time. Maximum COD reduction of 83% was obtained with catalyst Mn : Ce (1: 1) at 180°C and 14 kg/cm<sup>2</sup> pressure after a reaction time of four hours.

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## NOMENCLATURE

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A	Pre exponential factor
COD	Chemical oxygen demand
CWAO	Catalytic wet air oxidation
E	Energy of activation based on COD reduction
m	Order with respect to oxygen
n	Order with respect to substrate concentration
$p_{air}$	Air partial pressure
T	Temperature
WAO	Wet air oxidation
$T_P$	Total pressure



# CHAPTER 1

## INTRODUCTION

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### 1.1 HISTORY

More than 60 years ago, Zimmermann,[Debellefontaine et al.(2000)] was looking for an alternative method to treat special black liquors from paper mills. Because of their very high silica content, the usual evaporation and combustion method (Kraft process) was unsuitable. Zimmermann found he could burn pulp mill liquors and described a method using air at high pressure leading to the combustion of organic compounds dissolved or suspended in liquid water, at relatively low temperatures, as long as oxygen was present. Wet air oxidation (WAO) was beginning to take off. Zimmermann added that this new method was quite similar to incineration as the organic residues were mainly burned up to Carbon dioxide, to nitrogen (ammonia) and to ashes, together with a limited amount of volatile fatty acids (acetic) and traces of carbon monoxide. When the temperature was about 300°C the organic matter removal efficiency exceeded 95% and enabled the mineral fraction of the oxidized liquor to be recycled. Because of the vapor pressure of water (86 bar at 300°C) and because of nitrogen from the air, the total pressure figure came to 175 bar or so and the energy aspect of WAO was obviously an important feature to consider.

By the early 1970s, wet air oxidation was regenerating spent powdered activated carbon from wastewater treatment processes and from chemical industries. The process had been used on sewage sludge since 1960, with different results achieved through changes in the operating temperatures and pressures. But the process was rediscovered during the 1980s, it enjoyed renewed popularity as a means of detoxifying liquids prohibited from land disposal by restrictions related to new regulations decreed worldwide for environment protection. The first patent of WAO was put forward by Strehlenert in 1911. After the 60s ,with the study and application of WAO to the reclaim of paper pulp and sludge oxidation in wastewater factory ,it was developed as technology for wastewater treatment .From 70s to present , the

research and application range of WAO quickly spreads from recycle of materials and energy to treatment of toxic wastewater and materials, especially the treatment of deleterious regents containing hydroxybenzene, cyanogens , etc.

## **1.2. WET AIR OXIDATION: WHY?**

Fresh and unfrozen water of earth constitutes only 1 % of that in the hydrosphere, the bulk of which (99%) is ground water and only 1 % is surface water in lakes, rivers, soil, and atmosphere. During consumption the water becomes contaminated with various kinds of substances. We have to focus our attention on contamination of water due to its use in industrial processing.

The industrial effluents are as varied as industries themselves, in terms of nature of contaminants, their concentrations, treatment, and disposal methods required. Even the effluent characteristics from a single manufacturing unit vary with time and are quiet unpredictable. The contents of effluent may vary from totally inorganic components to highly toxic organochemicals.

The industrial waste water can be divided in three categories: cooling water blowdown, boiler blowdown, and process waste water. It is the process waste water that is of interest to the present work. These wastewaters need to be treated to meet local discharge standards. The choice of method for treatment of a particular effluent stream is governed by various factors such as the constituents, their concentrations, volume to be treated, and toxicity to microbes.

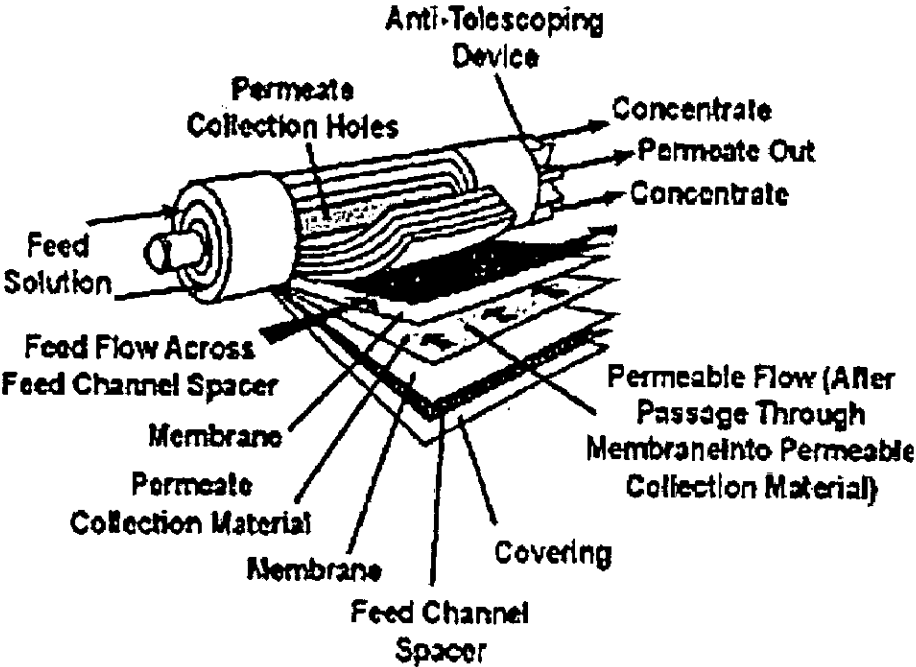
The various treatment methods available are chemical treatment, physical treatment (adsorption, reverse osmosis, etc), biological treatment, wet air oxidation, incineration etc. more often combination of the above methods is used to get better results.

Chemical treatment is used for pH adjustment, coagulation of colloidal impurities (using alum,  $\text{FeSO}_4$ , polyelectrolytes, etc.), precipitation of dissolved pollutants (metal removal as hydroxides, carbonates, etc.) and reduction, and sludge conditioning. However, chemical treatment is usually prohibitively costly if large volumes are to be treated particularly if the waste is predominantly organic in nature. In view of this chemical treatment is usually used as pretreatment step for pH

adjustment, color removal, and removal of toxic compounds so that other treatment methods such as biological treatment can be used.

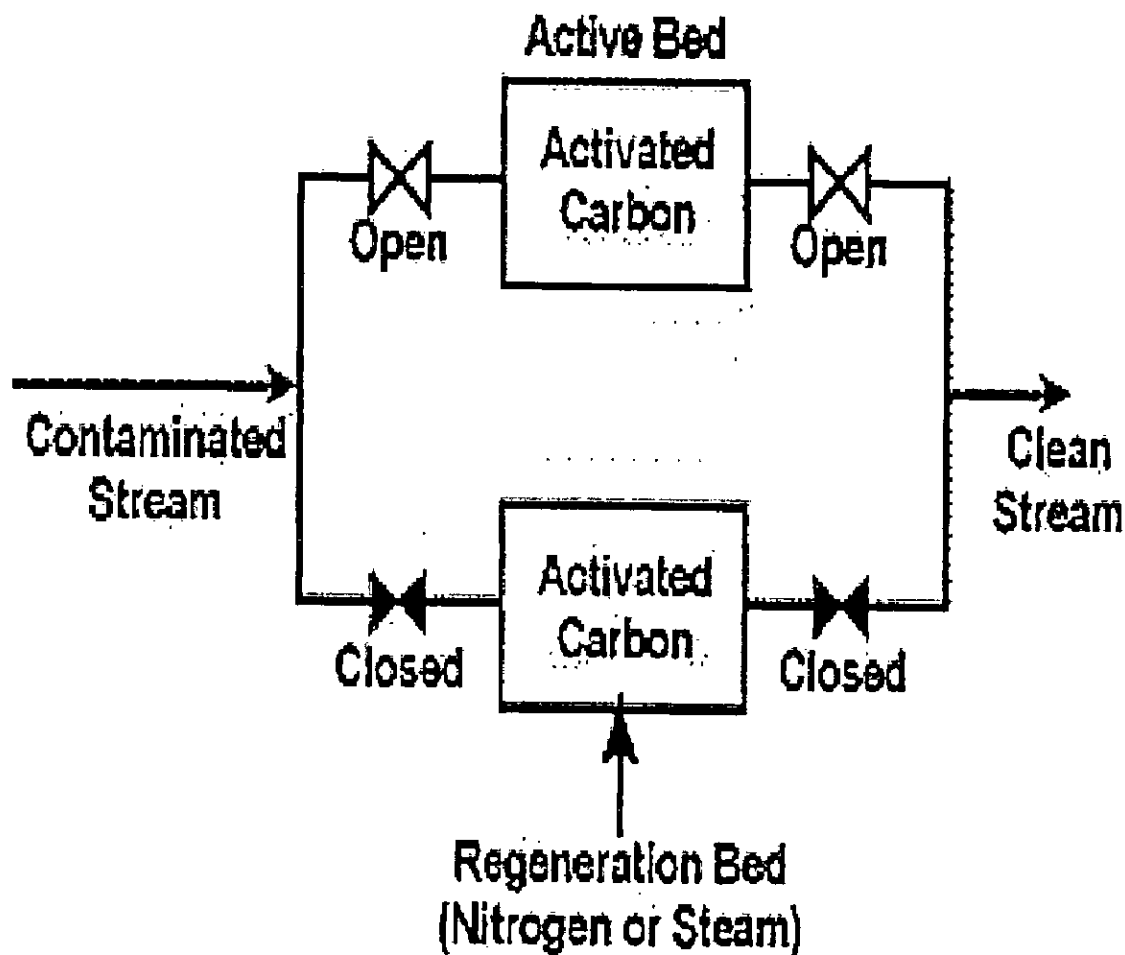
Biological treatment is a method suitable for nearly all applications. However, it is necessary for the resulting sludge to be disposed off by either land filling or burning with a corresponding expenditure of energy following elaborate thickening and dewatering procedures. In spite of this, it is the most popular treatment method. It is popular to extent that the wastewaters that are not suitable for biotreatment due to toxicity or high organic load are treated by other means to make the final effluent suitable for biotreatment. Biological treatment requires a large area of land, which is costly and may not be always available. Further, biological treatment processes react unfavorably to shock loads.

Reverse osmosis is a membrane process used for desalinating of brackish water and removing dissolved solids from certain industrial wastewaters. A concentrated and much smaller waste stream are produced, presumably making disposal simpler. However, the technique is not frequently used primarily due to high membrane replacement costs.



Reverse Osmosis

Activated carbon and some synthetic resins are used frequently to treat waste water by adsorptive process. High molecular weight organics particularly those having low solubility in water are adsorbed preferentially on carbon surface. Carbon treatment becomes attractive if the spent carbon can be regenerated by biotreatment, solvent extraction, WAO, etc.



### Activated Carbon Adsorption & Adsorption

Wet air oxidation is a well-established technique of importance for wastewaters particularly toxic and highly organic wastewaters. Wet air oxidation involves the liquid phase oxidation of organics or oxidizable inorganic components at elevated temperatures (125- 320°C) and pressures (0.5- 20 M Pa) using a gaseous source of oxygen (usually air). Enhanced solubility of oxygen in aqueous solutions at

elevated temperatures and pressures provides a strong driving force for oxidation. The elevated pressures are required to keep water in liquid state. Water also acts as a moderant by providing a medium for heat transfer and removing excess heat by evaporation. WAO has been demonstrated to oxidize organic compounds to CO<sub>2</sub> and other innocuous end products. An advantage of wet air oxidation is that the majority of contaminants remain in the aqueous phase. Elemental sulphur is converted to sulphate, halogens to halides and phosphorous to phosphate, they all, therefore, remain in the aqueous phase forming inorganic salts and acids. The production of acids results in a decrease in the pH of the aqueous phase (Kolaczowski et al. 1999).

The higher the temperature the higher is the extent of oxidation achieved, and the effluent contains mainly low molecular weight oxygenated compounds, predominantly carboxylic acids. The degree of oxidation is mainly a function of temperature, oxygen partial pressure, residence time, and the oxidizability of the pollutants under considerations. The oxidation conditions depend on the treatment objective. For low molecular weight carboxylic acids for achieving low COD reductions also high temperature and partial pressures are required as compared to paper and pulp and sewage or distillery wastewaters. Sometimes preheating may be necessary to raise the temperature of wastewater. The feed temperature is adjusted such that the exothermic heat of reaction raises the mixture temperature to the operating temperature. Preheating can be done using treated effluent. The reactor effluent can be cooled by cooling water or the waste water-air mixture.

Wet air oxidation requires much less fuel than other thermal oxidation process such as incineration. This is because, for WAO, the only energy required is difference in enthalpy between the incoming and outgoing streams. However, for incineration, not only the sensible enthalpy (combustion products and excess air to be heated to the combustion temperature of about 1000°C) is to be provided but also it is required to supply heat for the complete evaporation of water. The capital cost of a WAO system is higher and depends on the flow, oxygen demand of effluent, severity of the oxidation conditions, and the material of construction required.

WAO becomes self sustaining with no auxiliary fuel requirement when the COD is above 2000mg/l (Joshi et al 1995). In fact energy recovery is possible when feed COD is sufficiently high. Incineration becomes self sustaining when the COD is

in the range of 30000-40000mg/l (Joshi et al 1995). In most applications, WAO is not used as a complete treatment method ,but only as a pretreatment step where the waste water is rendered nontoxic and the COD is reduced sufficiently, so that biological treatment becomes applicable for the final treatment .This strategy means that extreme oxidation conditions are no longer necessary. But however WAO increased the biodegradability of landfill leach ate substantially. It also makes possible the recovery of inorganic chemicals.

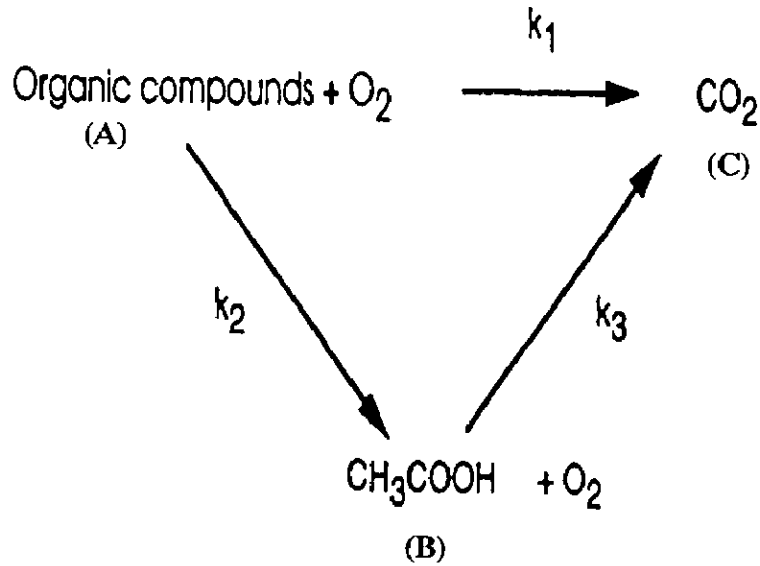
A better understanding of the reactions taking place during WAO (reaction mechanism and kinetics)is important as it leads to reliable design of oxidation reactors and also to cost reduction by optimization of the operating conditions .WAO has been fond very promising for desulphurization of coal(Joshi et al 1995). The organic material is not normally completely destroyed ,but converted via a free radical mechanism to intermediate end products with a significant reduction in toxicity and chemical oxygen demand (Kolaczowski et al .1999).

The development of WAO technology is based on the use of a cheap oxidant gas like air or oxygen. However, compared to ozone or hydrogen peroxide, dioxygen presents low reactivity in water, which requires severe operating conditions (200-350°C, 50-150 bar) if thermal processes are used. This is in line with the standard reduction potential of the three oxidant molecules:  $E^\circ (\text{O}_3)$ , 2.08 V >  $E^\circ (\text{H}_2\text{O}_2)$ , 1.78V >  $E^\circ (\text{O}_2)$ , 1.23V and with the ability of ozone and hydrogen peroxide to form  $\text{OH}^\bullet$  radicals which are powerful oxygen-reactive species (Duprez et al. 2000). Catalytic wet air oxidation (CWAO) allows processing under less severe conditions.

### 1.3 WAO REACTION CONCEPTS

During WAO, the longer molecules are oxidized to various intermediate products, Most of the initial intermediates formed are unstable and are further oxidized to oxidation end products or low molecule carboxylic acids. The low molecular weight carboxylic acids are quite resistant to further oxidation as mentioned earlier. It is well known that acetic acid is one of the most resistant chemicals to oxidation because of the difficulty to oxidize the methyl group in  $\alpha$ -position of the carboxylic group. Thus, in the oxidation scheme of phenol proposed by P. Gallezot (1997), the route conducting to acetic acid is a dead-end. Thus, the

organics in the effluent from a WAO system can be divided into three groups molecules (Joshi et al 1995):all initial and relatively unstable intermediates except acetic acid (group A), refractory intermediates like acetic, acrylic acids(group B) and oxidation end products (groupC) as shown below.



$$\frac{[\text{O.C.} + \text{CH}_3\text{COOH}]}{[\text{O.C.} + \text{CH}_3\text{COOH}]_0} = \frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{k_1 \cdot k_3}{k_1 + k_2 - k_3} e^{-(k_1 + k_2)t}$$

Fig. 5. Simplified kinetic model of sludge oxidation.

Fig. 1 shows a basic flow diagram of a WO plant, which consists mainly of a high-pressure pump, an air or oxygen compressor, a heat-exchanger as well as a reactor with a relief valve and a downstream separator. The waste is retained in the reactor for a sufficient period of time to achieve the desired chemical oxidation (30-120 min). The simplest reactor design is usually a cocurrent vertical bubble column with a height-to-diameter ratio in the range of 5-20.

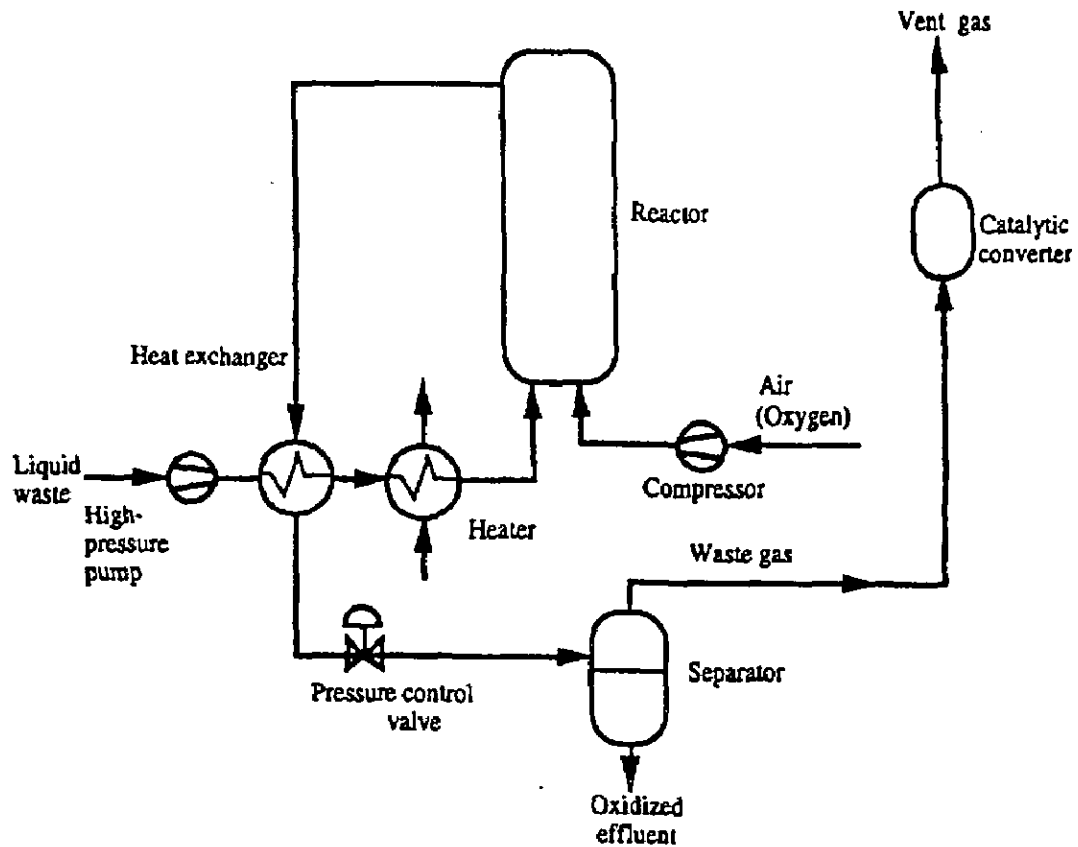


Fig. 1. Flow diagram of a WO process.

## 1.4 WAO DESIGN AND SAFETY

We should consider our environment as being borrowed for future generations and refrain from leaving a legacy of problems we are not able to solve. There is growing concern about the problem of waste elimination. Among the various types of processes which can be used for treating aqueous wastes polluted with organic matter, wet air oxidation (WAO) is very attractive. The basic idea of the process is to enhance contact between molecular oxygen and the organic matter to be oxidized. High temperature conditions convert the organic matter to carbon dioxide and water. The liquid phase is maintained by a high pressure which also increases the concentration of dissolved oxygen (Debellefontaine et al .2000) and thus the oxidation rate. The process can treat any kind of organic aqueous waste, even toxic, produced by various branches of industrial activity, or it can be coupled with a biological treatment facility to eliminate the sludge. WAO is one of the few processes that does not turn pollution from one form to another, but really make it disappear. This process has been used



under mild conditions that alter molecular structures and improve biodegradability in spite of a limited COD reduction, but, usually, it is run under conditions that give almost entire oxidation of the organic matter and that can allow mechanical power generation because the reaction releases energy.

The wet air oxidation reactor contains a heterogeneous system, which necessitates consideration to be given to mass transfer and the kinetics and mechanism of the chemical reaction. An understanding of how these steps are influenced by reactor configuration and selected operating conditions is therefore the key to the optimization of the process. It follows that a better understanding of system performance would be attained if the mechanisms behind the processes occurring in the reactor could be elucidated and the complex nature of their interdependence identified.

High initial capital investment coupled with safety concerns of combined high pressure and high temperature operation can be a barrier to the proliferation of the technology. To rectify these limitations wet air oxidation research should primarily concentrated on ways of reducing the prohibitive capital costs of the process, whilst still maintaining acceptable mass transfer and reaction kinetics. To achieve this goal technique for enhancing reaction kinetics and oxygen mass transfer should be investigated. In the area of reactor design this leads to investigate into design factors such as degree of reactant mixing (i.e. mixed or plug flow), reactant contacting, and hydrodynamic flow regime and catalyst incorporation. In the design of the process as a whole, further consideration should be given to heat recovery, scaling problems, effective utilization of space and safe operation when dealing with the pressures temperatures and hazardous waste associated with the system.

The capital costs for wet air oxidation depend on the material of construction selected for the main process items, which must be suitable for the severe operating conditions (high temperature and high pressure) and the corrosion problems resulting from the waste. Although industrial experience in the treatment of domestic sewage sludge has shown austenitic stainless steel (American designation AISI 316) to be resistant to chloride ion concentration of up to 300 mg/l at temperatures of 450K to 560K, with wastes containing higher chloride ion concentrations, stress corrosion cracking and pitting have been experienced. This leads to the use of alternative

materials such as titanium inconel and hastelloy, all of which are more expensive ,but have the advantage of an increased resistance to chloride ions. For very high chloride ion concentrations (>1000 mg/L) titanium has the best corrosion resistance. However, as titanium is capable of spontaneous combustion in the presence of oxygen and water at elevated pressures, it is unsuitable for operation in pure oxygen or oxygen enriched systems .The high capital cost of the main process item may render wet air oxidation technology uneconomic. A reduction in the severity of the operating conditions would allow saving in the capital cost to be made, due to thinner equipment wall thicknesses, diminished corrosion problems and smaller design duties for the compressor, feed pump and heat exchangers.

Depending on the composition of the waste feed, the build-up of scale on the walls of equipment and piping can be a problem as its leads to a decrease in the efficiency of the heat exchangers and an increase in system pressure drop. The scale is predominantly hard anhydrite scale, comprised of calcium sulphate aluminium-phosphates, which tend to deposit heavily in the hottest sections of the system. This is due to the decrease in solubility with increasing temperatures of calcium and other scale materials at wet air oxidation conditions If scaling of equipment surfaces is a serious problem then it has to be removed periodically by acid washing. Alternatively, in an attempt to prevent scale formation, reagents such as  $\text{Na}_2\text{HPO}_4$  can be added to the waste stream to bind the  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  ions. In addition to organic scale, fouling problems can be experienced due to the formation of polymeric reaction intermediates which can adhere to equipment surfaces. Operational experience in treating steam cracker spent caustic in a low pressure wet air oxidation unit at Grange mouth, Scotland, has shown problems due to fouling of the sparger by insoluble inorganic carbonates and polymerized organic material. This problem was overcome by using a 100-mesh screen in a simplified sparger arrangement and by supplying a small quantity of preheat stem via the air supply to ensure that the nozzle remained hot enough to prevent solidification of organic polymer (Kolaczowski et al .1999).

## **1.5 CATALYTIC WET AIR OXIDATION**

In view of slow rates of oxidation the use of homogeneous and heterogeneous catalysts has received a great attention. Another reason for going to catalytic WAO is

to reduce the severity of the process conditions. The oxidation of dilute aqueous solutions of refractory organic pollutants using air or oxygen as oxidizing agent over a catalyst, so called catalytic wet air oxidation (CWAO), has largely demonstrated its effectiveness in removing toxic compounds. Via the CWAO method, the organic compounds are completely converted to CO<sub>2</sub> and H<sub>2</sub>O or partly oxidized to less toxic intermediates. (S S Lin et al, 2003)

### 1.5.1. Homogeneous Vs Heterogeneous Catalysis

In view of the slow rates of oxidation, the use of homogeneous and heterogeneous catalysts has received a great attention. Homogeneous catalysts, which usually consist of transition metal ions of the first row dissolved in the reaction medium, are efficient to destroy organic effluents under less drastic conditions, but the dissolved species must be recovered from the treated waters. Most of the heterogeneous catalysts employed so far were not stable enough in strongly corrosive reaction media, so that a treatment is required to recover the mineral species leached from supports and/or active phases. It is important to use catalyst systems which are stable and do not get leached away in the solution by reacting with acids present. The most promising processes involving heterogeneous catalysts, which do not dissolve readily in the reaction medium are based on precious metals (Pt, Pd, Ru) on acid-resistant supports (Gellezot et al 1997). The homogeneous catalysts are, in general more effective oxidation catalysts, but their use necessitates a precipitation step to recover/remove the toxic catalyst from final effluent. In view of this, heterogeneous catalyst systems are preferable. It is important to use catalyst systems which are stable and do not get leached away in the solution by reacting with acids present.

The use of homogeneous transition metal catalysts (especially, cupric salts) has been shown to significantly enhance the reaction rate in wet air oxidation systems. The presence of the homogeneous catalyst, in the same liquid phase as the reactants, simplifies reactor operation (compared to heterogeneous catalysts) as it avoids the need for an additional third phase. However, the catalyst may itself be a pollutant and may need to be recovered from the treated effluent. This is clearly a major disadvantage in the use of homogeneous catalysts. Heterogeneous catalysts have been the subject of numerous previous studies as they avoid the requirement of an

additional metal recovery step (J. Revas et al, 1999). However, the use of heterogeneous catalysts can be limited due to rapid deactivation of the catalyst. For example, the hot acidic wet air oxidation environment can result in the dissolution of the active component into the aqueous phase. This is specifically the case when using the supported oxides of transition metals like copper oxide, manganese oxide, etc. This problem can be overcome by the use of noble metal catalysts such as platinum. In addition, catalyst deactivation can occur due to poisoning of active sites or fouling of the catalyst surface following the deposition of reaction intermediates.

Copper sulfate and copper nitrate have been used as homogeneous catalysts for the oxidation of carboxylic acids. The heterogeneous catalysts used include transition as well as noble metals. The various heterogeneous catalysts that have been used are Cu, Pd, CoO/ZnO, Cu : Mn : La oxides (4 : 2 : 1) supported on spinal support (ZnO and Al<sub>2</sub>O<sub>3</sub>, 48.5 and 51.5, respectively), copper chromite, iron oxide, Co : Bi (5 : 1) complex oxides, Ru: Ce, and Mn/Ce. Of these catalysts Co : Bi, Cu : Co, Cu : Co : Bi and Ru/Ce were more effective catalysts (except Mn/Ce). Activity of Co: Bi (5 : 1) was one of the most effective, because of the basic sites on the catalyst surface on which acetic acid is adsorbed. This is followed by a redox reaction between catalyst and adsorbed acetic acid to induce its decomposition. Use of Mn/Ce (1 : 1) catalyst resulted in complete removal of acetic acid at 200°C. Activity of Mn/Ce catalyst can be further improved by using Ru as a promoter.

## **1.6. WET AIR OXIDATION OF CARBOXYLIC ACIDS**

Carboxylic acids are very valuable commercial products as they find their use in a large number of synthetic organic products. Several dicarboxylic acids are also of commercial importance because of their use in synthetic polymers. Many acids find their use in preparation of pharmaceuticals, dyes, flavoring ingredients; perfumery esters etc. During manufacture and during their use in synthetic process, carboxylic acids find their way into the waste streams. Caprolactam plant waste stream, petrochemical waste stream, and pharmaceutical plant waste stream contain appreciable quantities of carboxylic acids. The understanding of the wet air oxidation of low molecular weight acids is important for yet another reason. During the WAO

of a variety of waste streams, the pollutant molecules are broken down mainly to low molecular weight carboxylic acids. These acids may be further oxidized to carbon dioxide and water if oxidation conditions are sufficiently severe.

The low molecular weight carboxylic acids in general and acrylic acid, propionic acid, acidic acids in particular are resistant to oxidation and hence accumulate at the later stages of wet air oxidation (Joshi et al. 1995). The slow rate low molecular weight carboxylic acids is a major limitation of the WAO technique. With this realization, the WAO of low molecular weight acids has received fairly good attention in the published literature. Oxidation of various mono- and dicarboxylic acids ( $C_1-C_6$ ) has been studied in great detail. The mono carboxylic acids which have been focused are formic, acetic, propionic, butyric, valeric, and caproic acids. Dicarboxylic acids that have been focused are oxalic, adipic, succinic, and gluteric acids. Kinetic parameters, TOC, COD reduction and oxidation mechanisms of some low molecular weight carboxylic acids have been studied in detail. The temperatures varied in the range of 112-300°C and pressure varied from 0.35 to 12.8 MPa.

WAO is well suited to treat effluents where the concentrations of organic pollutants are too low to incinerate and too high to biological treatment where it becomes ineffective, e.g. in the case of toxic effluents. The typical range of COD in which WAO is considered to be effective is 2 - 50 gm/L (O Duprez et al. 2000). The recrudescence interest for WAO is accompanied by the need for a rational approach to establish reaction mechanisms and propose reliable kinetic models. Downstream real wastes are normally very rich in diversity, and therefore, difficult to characterize completely. In order to reduce complexity and improve the impact of treatment, good model systems should be chosen, either by mimicking upstream effluents with a mixture of a few representative components, or by studying the individual components. Low molecular weight carboxylic acids proved to be good model systems in non-catalytic wet air oxidation (J. L. Faria et al. 2000).

High temperature and pressure leads to very high investment costs, because reinforced materials are needed to support the strong pressures, and special metal alloys, which are much more expensive than commonly used stainless steel alloys, must be employed to avoid corrosion which is highly favored under these conditions.

In spite of this, there has been a strong effort on the research and development of catalysts in order to bring down pressure and temperature to milder values catalytic wet air oxidation (J. L. Faria et al, 2002). WAO is a process that can speed the reaction, lower the reaction temperature and pressure with catalyst. It is an available method used in disposing high concentration effluents, as well as poisonous, detrimental and hardly degradable wastewater. For the practical treatment of wastewaters discharged from petrochemical industries WAO is very suitable method (W Zhu et al 2002).

WAO is usually an expensive process to install and operate because of the severe conditions required. High capital and operating costs are associated with the elevated pressures and temperatures employed, long residence times and use of construction materials which should be resistant to the high corrosion rates occurring under severe operating conditions (Mantzavinos et al 2002). The investigation of the oxidation of waste waters is generally complicated by the presence of a large variety of organic molecules having a different reactivity. Therefore, individual organic compounds are used in the first screening of catalysts (Galvagno et al.2002) and therefore, there is a necessity to investigate WAO of carboxylic acids.

A high temperature is required to attain a rapid rate of reaction and a high solubility of oxygen in water. Any increase in temperature will also increase the saturated water vapor pressure, which means that a high pressure is required to maintain an aqueous phase. An increase in oxygen partial pressure will also have a beneficial effect on oxygen solubility. Wet air oxidation, therefore, provides a suitable environment to remove oxidizable organic and inorganic material. In the process, the organic waste is oxidized to carbon dioxide, water and intermediate oxidation products that are predominantly low molecular weight compounds including carboxylic and dicarboxylic acids, ketones and alcohols. Although the degree of oxidation in the process depends upon the process conditions, retention time and feed composition, in most operations, some low molecular weight compounds (i.e. acetic acid) will accumulate as they tend to be refractory to further oxidation.

### 1.6.1. Sources of Some Carboxylic Acids

Among mono carboxylic acids, formic acid is used as disinfectant, as a preservative, to make formates and cellulose esters and in the textiles and leather industries. Acetic acid is an important solvent in organic processes apart from its major use in cellulose acetates. Other acids also find their use in preparation of pharmaceuticals, dyes, flavoring ingredients, perfumery esters, etc. during manufacture and during their way into the waste streams. Sometimes these acids are formed as byproducts in a process and a part invariably find their way in the waste streams. For example, the caprolactant plant waste stream, petrochemical waste stream and pharmaceutical plant waste stream contain appreciable quantities of carboxylic acids.

PCA belongs to a range of phenolic components such as gallic, caffeic and vanillic acids which strongly inhibit biological treatment of agricultural waste waters. It is a representative of biorecalcitrant phenolic compounds found in the olive oil processing wastewater.

H-acid (1-amino-8-naphthol-3, 6-disulfonic acid) is an important dye intermediate. It is widely used in chemical industry for the synthesis of direct, acidic, reactive and azoic dye, as well as in the pharmaceutical industry. Under certain conditions, naphthalene, as a raw material, is used to manufacture the H-acid through a series of chemical processes such as sulfonation, nitration, neutralization, reduction, alkaline dissolving, acid precipitation and so on. Since the production process of H-acid is complicated and the utilization ratio of raw materials is low, the wastewater from the manufacturing processes is rich in various substituted derivatives of naphthalene compound and is of dark color and strong acidity. Organic substances in dye intermediate wastewater are often aromatic compounds substituted by some groups, such as  $-NH_2$ ,  $-NO_2$ ,  $-SO_3^-$ ; etc. They are extremely toxic to organisms. The biological processes cannot effectively degrade these substances and decolorize the H-acid wastewater. As aromatic ring with  $-SO_3H$  is easily dissolved in water, the general chemical and physical method is very inefficient (W Zhu et al 2002).

Lin et al. (2002) reported that maleic, fumaric and acrylic acids were major constituents of waste streams from a petrochemical industry manufacturing methyl tetra butyl ether, methyl-ethyl-ketone and *sec*-butyl alcohol.

Maleic acid is an important raw material used in the manufacture of phthalic-type alkyl and polyester resins, surface coatings, lubricant additives, copolymers, etc. Besides being observed as intermediates during wet oxidation of many organic pollutants, 3-hydroxypropionic and propionic acids have also a wide range of applications in the industrial sector. 3-HPA ( $\text{OHCH}_2\text{CH}_2\text{CO}_2\text{H}$ ) is used as cross linking agent for polymer coatings, metal lubricants, antistatic agents for textiles, and so on, where as propionic acid is largely used for the production of cellulose esters and plastic dispersions. Petrochemical industry manufacturing methyl tetra butyl ether (MTBE), methyl ethyl ketone (MEK) and sec- butyl alcohol (SBA) produces waste waters, which usually contain acids with  $\text{C}=\text{C}$  groups ( e.g., maleic, fumaric and acrylic). Fumaric acid is a trans isomer of maleic acid and can also be produced during oxidation of aromatic pollutant such as phenol. Wet oxidation of an aqueous stream of aromatic compounds produces several intermediates, among them are unsaturated carboxylic acids, such as acrylic, maleic, fumaric and muconic acids.



## CHAPTER 2

### LITERATURE REVIEW

Investigator	Substrate	Catalyst	Treatment Conditions	Observations
Foussard (1983)	Oxalic acid (0.1 – 0.2 gm/L)	No catalyst	T = 227-288°C P <sub>T</sub> = 2-20 MPa	n = 1, E = 133.8 kJ/mol, A = 6.83 x 10 <sup>8</sup>
Chowdhury and Copa (1986)	25000 mg/L	No catalyst	T = 300°C	98.3% reduction in 60 min
Imamura et al. (1986)	Acetic acid (5000 mg/L)	Cu(NO <sub>3</sub> ) <sub>2</sub> and Mn/Ce Co : Bi (5 : 1) (20 mM total metal ion concentration used)	T = 247°C P <sub>O<sub>2</sub></sub> = 1 MPa t = 1 hr	42% TOC removal w/o catalyst, 87.1% TOC removal for Cu(NO <sub>3</sub> ) <sub>2</sub> and 99.5% removal for Mn/Ce (7 : 3)
Imamura et al. (1988)	Acetic acid (TOC = 2000 mg/L)	Ru/Ce; Cu(NO <sub>3</sub> ) <sub>2</sub> and Mn/Ce (12 mM total metal ion	T = 200°C P <sub>O<sub>2</sub></sub> = 1 MPa	With Ru/Ce (5 wt% on Ce) 44.5 and 19.4% TOC removal at pH 2.7 and 6.9 respectively; with

		concentration used)	t = 1 hr	Cu(NO <sub>3</sub> ) <sub>2</sub> at pH 2.5, 32.6% TOC removed; with Mn : Ce (1 : 1) complete removal of acetic acid is achieved.
Imamura et al. (1988)	Formic acid (TOC = 2000 mg/L)	Ru/Ce; Cu(NO <sub>3</sub> ) <sub>2</sub> and Mn/Ce (total catalyst concentration = 12 mM)	T = 150°C P <sub>O<sub>2</sub></sub> = 1 MPa t = 1 hr	Reactivity highly dependent on pH; 24.9% TOC reduction w/o catalyst; at pH 1.964.7% TOC removal using Cu(NO <sub>3</sub> ) <sub>2</sub> using Ru/Ce (5 wt% on Ce) 100% TOC removal at pH 1.9 compared to 7% at pH = 5.6.
Foussard (1989)	Acetic acid (about 30 gm/L) Formic acid (24-43 gm/L)	No catalyst	T = 270-320°C P <sub>T</sub> = 2-20 MPa T = 190-313°C P <sub>T</sub> = 2-20 MPa	n = 1, E = 167.7 kJ/mol, A = 5.6 x 10 <sup>10</sup> n̄ = 1.33, E = 143.5 kJ/mol, A = 3.1 x 10 <sup>9</sup>
Mahajani et al. (1994)	Glyoxalic acid	No catalyst  CuSO <sub>4</sub>	T = 150-200°C P <sub>O<sub>2</sub></sub> = 0.345-1.173 MPa	1 <sup>st</sup> order w.r.t. COD reduction; 46% COD reduction in 5 hrs at 150°C and 0.69 MPa and 93% reduction in 1.5 hr at 200°C and 0.69 MPa; two step reduction 1 <sup>st</sup> step E = 12.8 kcal/gmol(fast); m = 0.926; 2 <sup>nd</sup> step E = 27.9 kcal/gmol; m = 0.207; oxalic acid as intermediate. A <sub>1</sub> = 1.453 x 10 <sup>5</sup> ; A <sub>2</sub> = 2.871 x 10 <sup>9</sup>

				<p>T = 135-165°C</p> <p>P<sub>O2</sub>=0.345-1.173MPa</p>	<p>1<sup>st</sup> order w.r.t. COD reduction; oxalic acid as intermediate; 93% COD reduction at 160°C, 0.69 MPa in 5 hr; 1<sup>st</sup> step E = 22.7 kcal/gmol; 2<sup>nd</sup> step E = 28.2 kcal/gmol; m = 0; A<sub>1</sub> = 6.646 x 10<sup>11</sup>; A<sub>2</sub> = 7.534 x 10<sup>12</sup></p> <p>n = 1; m = 0.321; 30% COD reduction in 5 hr at 245°C; E = 30.9 kcal/gmol; A = 1.256 x 10<sup>9</sup></p> <p>COD reduction is not significant above catl loading 6.2687 x 10<sup>-3</sup> kmol/m<sup>3</sup> at 140°C; 96% COD reduction in 1 hr at 150°C and 0.69 MPa; m = 0.146; m = 0.283; E = 19.1 kcal/gmol; A = 7.169 x 10<sup>6</sup></p>
	Oxalic acid		<p>No catalyst</p> <p>CuSO<sub>4</sub> (3.1506 x 10<sup>-3</sup> - 6.2687 x 10<sup>-3</sup> kmol/mol<sup>3</sup>)</p>		
P. Gallezot (1996)	<p>Formic acid(5gm/L)</p> <p>Oxalic acid (5 gm/L)</p> <p>Maleic acid 5 gm/L)</p>	<p>Carbon-supported platinum;</p> <p>homogeneous dispersion (1-2 nm metal particles)</p>	<p>T = 293-463K</p> <p>P<sub>air</sub> = 1-15 bar</p>	<p>100% conv in 140 min at 293K with sub/Pt of 2470 or at 326K with ratio of 11645</p> <p>100% conv at 326K, n = 0</p> <p>100% conv at 405K and 15 bar, formic acid as intermediate</p>	
P. Gallezot (1997)	<p>Acetic acid (5-20 gm/L)</p>	Carbon supported Ruthenium	<p>T = 448-473K,</p> <p>P<sub>air</sub> = 10 MPa</p>	<p>Total conversion in 2 hr, E = 1000.5 kJ/mol</p> <p>A = 1.8 x 10<sup>10</sup>; n = 0, m = 0.65</p>	

V. V. Mahajani et al. (1997)	Formic acid	No catalyst  CuSO <sub>4</sub> (6.888 x 10 <sup>-4</sup> kmol/m <sup>3</sup> )	T = 150-240°C P <sub>O2</sub> = 0.345-1.38MPa T = 150-180°C P <sub>O2</sub> =0.345-1.035MPa	12.92% COD reduction at 150°C and 0.69MPa, 95% COD reduction at 240°C; m = 1, n = 0.68, E = 28.48kJ/gmol, A = 4.712 x 10 <sup>10</sup> sec <sup>-1</sup> 97% COD reduction at 180°C in 1.5 hr; m = 1.5, n = 1, E = 22.5 kcal/gmol, A = 1.752 x 10 <sup>12</sup> sec <sup>-1</sup> 80% COD reduction in 5 hrs at 235°C, E = 22.77 kcal/gmol, m = 1, n = 0.92, A = 8.479 x 10 <sup>9</sup> sec <sup>-1</sup>
B.F.M. Kuster et al. (1997)	Acetic acid	CuSO <sub>4</sub> (6.262 x 10 <sup>-4</sup> - 6.262 x 10 <sup>-3</sup> kmol/m <sup>3</sup> )	T = 250-235°C P <sub>O2</sub> =0.3452-1.04MPa	Steady state disappearance rate of formic acid as a function of formic acid, temperature and pH
J. Levec et al. (1998)	Formic acid (30-4000 mol/m <sup>3</sup> )  Propionic acid (< 5 mg/L) 3-hydroxy Propionic acid (9.75-2.7 mg/l)	Carbon supported platinum (1% Pt/C); L <sub>1</sub> = 0.022 mol.kg <sub>cat</sub>  No catalyst	T = 282-293K P <sub>T</sub> = 0.6 MPa pH = 1.1-13.0  T = 280-310°C P <sub>O2</sub> = 10-45 bar	At 290°C, 44% and at 310°C 88% conversion achieved, A = 2.65 x 10 <sup>10</sup> min <sup>-1</sup> , m = 1, n = 0.5, E = 142.4 kJ/mol
J. Rivas et al. (1999)	Maleic acid (0.03 M)	No catalyst	T = 413-478K, P <sub>T</sub> = 3-4.5 MPa	No COD changed. 18% yield of conversion of maleic acid to formic acid; lower yield (12%) at highest temperature (478); n = 1; m = 0; E <sub>N2</sub> = 66.7 kJ/mol; E <sub>air</sub> = 66.7 kJ/mol (apparent); A = 1

			Platinum			<p><math>\times 10^4</math>.</p> <p>30% yield of conv of maleic acid to formic acid</p> <p>70% COD reduction at low temperature 431K; m = 0</p>
M. Besson et al. (1999)	Succinic acid (30-4000 mol/m <sup>3</sup> )	TiO <sub>2</sub> -supported Ruthenium (2.8% Ru/TiO <sub>2</sub> ); surface area = 50 m <sup>2</sup> /g	T = 180-200°C P <sub>O2</sub> = 0.3 - 1.8MPa pH = 1.1-13.0	m = 0.4, n = 0, E = 125 kJ/mol; acetic acid, acrylic acid as intermediates; total conv in 150 min; TOC reduction = 97.6% in 4 hr; oxidation of acetic acid severely affected by inorganic salts such as NaCl; TOC reduction = 99% in 6 hr		
S. Perathoner et al. (2000)	Formic acid  Acetic acid; Propionic acid (TOC = 30 mgC/L)	Fe/ZSM-5 (Fenton honeycomb model catalyst)	T = 25-70°C H <sub>2</sub> O <sub>2</sub> as oxidising agent	80% conversion in 2 hr, acetic acid and formic acid as intermediates at pH = 4, Fe/ZSM5 = 0.1g, H <sub>2</sub> O <sub>2</sub> /substrate = 1.5. 60% conversion of formic acid; 20% of conversion of acetic acid at pH = 4, Fe/ZSM5 = 0.1 g. H <sub>2</sub> O <sub>2</sub> /substrate = 1.5		
Levec et al. (2000)	Acrylic acid	No catalyst	T = 180-280°C P <sub>O2</sub> = 10-55	Three half order dependence with acrylic acid concentration; at 290°C and 45 bar p.p. of oxygen		

	Maleic acid and Fumaric acid			<p>order increase to 1.7; <math>E = 94.3 \text{ kJ/mol}</math>; <math>m = 0.54</math>;  <math>A = 1.077 \times 10^6</math>; <math>n = 1.5</math>; acetic acid formic acid,  3-hydroxypropionic acid, <math>\alpha</math>- or <math>\beta</math>- oxo propionic  acid, tartonic acid are intermediates formed; TOC  reduction at <math>260^\circ\text{C}</math> and 30 bar is 30% and at  <math>290^\circ\text{C}</math> is 78% in 2 hr; order w.r.t. to TOC is 1; <math>E</math>  <math>= 102 \text{ kJ/mol}</math>; <math>A = 7.06 \times 10^6</math>  At <math>280^\circ\text{C}</math> complete conv into formic acid and  oxalic acid; 1<sup>st</sup> order kinetics followed; <math>E_{\text{MA}} =</math>  <math>56.6 \text{ kJ/mol}</math>; <math>E_{\text{FA}} = 71 \text{ kJ/mol}</math>; <math>A_{\text{MA}} = 2.68 \times 10^2</math>;  <math>A_{\text{FA}} = 8.909 \times 10^5</math>; thermal degradation shown 1<sup>st</sup>  order kinetics, but higher kinetic order shows that  oxidation takes simultaneously; <math>m = 0.12</math>; <math>n =</math>  0.54</p>
D. Duprez et	Acrylic acid	Carbon-supported	T = $160^\circ\text{C}$	<p>45.2% TOC reduction at <math>240^\circ\text{C}</math> and 20 bar p.p. of  <math>\text{O}_2</math>; 72.7% reduction at <math>260^\circ\text{C}</math> in 2 hr; 1<sup>st</sup> order  kinetics; <math>m = 0.75</math></p> <p>Carbon-supported catalysts were very active for</p>

al. (2000)	(30-4000 mol/m <sup>3</sup> )	Ruthenium-Ceria oxide d <sub>p</sub> = 4.8nm Carbon supported Ruthenium, d <sub>p</sub> = 2.4nm	P <sub>O2</sub> = 20 bar	the CWAO of phenol but not for acrylic acid; although high conversions were obtained, phenol was not totally mineralized after 3 h; it was shown that acrylic acid was more strongly adsorbed than phenol; hydroxyl propionic acid, oxo-propionic acid, formic acid and acetic acids found as intermediates.
J. L. Faria et al. (2000)	Acetic acid (83 mmol/dm <sup>3</sup> ) Propionic acid (68 mmol/dm <sup>3</sup> ) Butyric acid (57 mmol/dm <sup>3</sup> )	Carbon supported Ruthenium	T = 200°C P <sub>O2</sub> = 6.9 bar	60.2% conversion in 2 hr; 93.3% COD reduction in 8 hr; 1 <sup>st</sup> order kinetics; k = 1.79 x 10 <sup>-4</sup> /sec; selectivity = 100% apparent 1 <sup>st</sup> order kinetics; k = 1.98 x 10 <sup>-4</sup> /sec; 75% conversion in 2 hr; 96.3% COD reduction in 8 hr; selectivity = 98.7% 59.4% conversion in 2 hr; 79.1% COD reduction in 8 hr; apparent 1 <sup>st</sup> order kinetics; k = 1.23 x 10 <sup>-4</sup> /sec; selectivity = 98.7%.
D-K Lee et al. (2001)	Maleic acid (3 g/L)	Pt/Al <sub>2</sub> O <sub>3</sub> (pore volume : 0.2 cm <sup>3</sup> /g) Pt (d <sub>p</sub> = 20Å)	T = 373-453K P <sub>O2</sub> = 160 psi	Formic acid, oxalic acid, fumaric acid found as intermediates; non-catalytic thermal oxidation ; 50% conversion in 40 min; catalyzed oxidation

	Oxalic acid; Formic acid		T = 353K; Atmospheric pressure	total conversion in 40 min. 90% conversion of oxalic acid in 20 min; total conversion of formic acid in 10 min
D. Mantzavinos et al. (2001)	Maleic acid	5 wt% Ru/CeO <sub>2</sub> surface area = 125 m <sup>2</sup> /g	T = 200°C P <sub>O<sub>2</sub></sub> = 20 bar	m = 0.4, n = 0, E = 125 kJ/mol; acetic acid, acrylic acid as intermediates; total conversion in 150 min; TOC reduction = 97.6% in 4 hr; oxidation of acetic acid severely affected by inorganic salts such as NaCl TOC reduction = 99% in 6 hr
W. Zhu et al. (2002)	H-acid (1-amino-8-naphthol-3,6-disulfonic acid (10 g/L))	Ce:Cu(3:1) (0.2 g/300 ml) (best catalyst) (Cu:Zn(2:1), Cd:Ce:Cu(2:1:1))	T = 200°C P <sub>O<sub>2</sub></sub> = 3 MPa pH = 12	85% and 91.3% COD reduction in 10 and 30 min respectively (catalyst selection) 75.6%, 92%, 92.9% COD reduction in 30 min at 180°C, 200°C, and 220°C (temp. effect) 53.5%, 90.7% and 92% COD reduction in 30 min at 0, 0.1 and 0.2 g/L of catalyst (catal dosage effect) 81.8%, 71.7% and 68.3% COD reduction at pH 8, 10 and 12 respectively (pH effect) All the H-acid is decomposed in 5 min and is



				oxidized into $\text{NH}_4^+$ , $\text{SO}_4^{2-}$ , formic acid, acetic acid and other end products. CWAO process not only can get a high reaction rate, but also can oxidize the short-chain organic acid.
J. L. Faria et al. (2002).	Butyric acid (57 mmol/dm <sup>3</sup> )	Carbon supported iridium (0.4-1.2 gm)	T = 453-493K P <sub>O2</sub> = 0.69-1.39 MPa	63% conversion in 8 hr, with 75% selectivity of CO <sub>2</sub> ; propionic acid, acetic acid, acetone, oxalic acid, formic acid are possible intermediates; E = 59 kJ/mol; A = 1.8 x 10 <sup>6</sup> ; m = 0.68; n = 1; order w.r.t. Ir = -0.35.
J. L. Faria et al. (2002).	Butyric acid (57 mmol/dm <sup>3</sup> )	Carbon supported iridium (0.2-0.8 gm)	T = 180-220°C P <sub>O2</sub> = 6.9-13.9 bar	72.2% conversion in 8 hr, with 74.2% selectivity of CO <sub>2</sub> ; propionic acid, acetic acid, acetone, oxalic acid, formic acid are possible intermediates; E = 57.9 kJ/mol; A = 3.2 x 10 <sup>5</sup> ; m = 0.61; n = 1; order w.r.t. Ir = -0.63.
S. Galvagno et al. (2002)	p-coumaric acid (4.5 mM)	Fe- promoted ceria Zn- promoted ceria	T = 353-493K, 0 P <sub>air</sub> = 2 MPa	90% conversion in 1 hr with ceria catalyst Main reaction intermediates : (a) chain side oxidation products : catechol, p-hydroxybenzaldehyde, p-hydroxybenzoic acid

					<p>(b) Ring cleavage products : oxalic, oxalacetic acid and formic acid</p> <p>(c) Hydroxylation of the aromatic ring with and 3,4-dihydroxybenzoic acid has been also observed.</p> <p>90% TOC removal at 403K</p>
M. Besson et al. (2003)	Succinic acid (5 g/l), Acrylic acid (5 g/l), Acetic acid (5 g/l)	Ru/TiO <sub>2</sub> (500 mg/l) Au/TiO <sub>2</sub> (500 mg/l)	T = 190°C P <sub>air</sub> = 50 bar		<p>Gold catalysts are efficient for the degradation of this organic acid</p> <p>High dispersion of gold resulted in good reaction rates.</p>
J. Oneto et al. (2004)	Caprylic acid (1 g/l) Oleic acid (1 g/l)	No catalyst	T = 473-573K P <sub>T</sub> = 15 MPa		<p>13% COD reduction after 80 min; 70% conversion of both CA and OA in less than 20 min at 523K; at 573K, 90% conversion of both OA and CA in 10 min; at 473K, 90% conversion of both OA and CA in 70 min; pseudo first order kinetics was proposed</p> <p><math>E_{OA} = 53.8 \text{ kJ/mol}</math>; <math>E_{CA} = 55.5 \text{ kJ/mol}</math>; <math>A_{OA} = 3.52 \times 10^5/\text{min}</math>; <math>A_{CA} = 2.12 \times 10^5/\text{min}</math></p>

## 2.1 Objective of Thesis

From the scrutiny of the past literature it is found that less work is there on butyric acid (BA) compared to the other carboxylic acids. Besides butyric acid being commercially important, it is found in many industrial effluents. Butyric acid, also called *butanoic acid*, viscous, foul-smelling, liquid carboxylic acid; . It is miscible with water, ethanol, and ether. It is a low molecular weight fatty acid that is present in butter as an ester of glycerol; the odor of rancid butter is due largely to the presence of free butyric acid. Butyric acid, is also found in some fruits and is produced synthetically to be used as a flavoring agent in various food products. Butyric acid is used in the manufacture of plastics. Butyric acid is known to oxidize at a significant rate under very severe conditions of pressure, temperature and residence times in the traditional non-catalytic wet air oxidation (non-CWAO). These demanding conditions prompted us to develop heterogeneous catalysts, more efficient at milder conditions. Butyric acid is found in pharmaceuticals plant effluent streams, food and beverage waste streams, plastic industry, cosmetic industrial waste streams and effluent streams from plants in which butyric acid is being used.

Most of the investigators have found that heterogeneous catalyst is a better catalyst rather than homogeneous catalyst, and  $\text{CuSO}_4$  is a better catalyst among the other homogeneous catalysts. Joshi et al (1985) have shown that Mn:Ce (1:1) completely converted acetic acid at  $200^\circ\text{C}$ . Co:Bi (5:1) is also one of the active catalysts found in literature. Ferrous ions are also found to be good oxidative capacity (Sperathoner 2000).

The present study deals with WAO of butyric acid using  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ , Co:Bi, Mn:Ce catalyst. The catalysts were also characterized for determining internal structure by SEM and X-ray diffraction. The effect of pH and temperature on % COD reduction of butyric acid was studied in details. Kinetic parameters of WAO of butyric acid are also studied.

## Chapter - 3

# EXPERIMENTAL SETUP AND PROCEDURE

### 3.1 ESTIMATION OF PARAMETERS

#### 3.1.1 Chemical Oxygen Demand (COD)

##### Theory of Test

Chemical Oxygen Demand. (COD) is also referred to as the Dichromate Oxygen consumed. The COD test is a quick method of estimating the approximate amount of organic matter in sewage and industrial wastes. In COD determination, the organic matter is oxidized by the presence of sulphuric acid. A catalyst such as silver sulphate is used to help the oxidation of the organic matter. The excess of dichromate is titrated by ferrous ammonium sulphate solution.

The test is carried out on an average waste to determine the extent of readily oxidizable organic matter, which is of two types:

- i. that, which is biologically oxidized and called biologically active
- ii. that which can not be oxidized biologically and called biologically inactive.

COD gives the oxygen required for the complete oxidation of both biodegradable and non-biodegradable matter.

##### COD Test

##### *Apparatus*

Reflux apparatus consisting of flat bottom 250 or 500 ml capacity flask with ground glass joint, a condenser, and a heater, and a temperature regulator.

##### *Reagents*

Standard potassium dichromate solution (0.25N)

Sulfuric acid

Standard ferrous ammonium sulfate (0.1N)

Ferroun indicator

Mercuric sulphate

Silver sulfate

Flask with glass beads was rinsed cleanly with distilled water. A pinch or mercuric sulphate was dropped into it. Diluted sample was made up to 20 ml with distilled water and poured into flask. 10 ml of potassium dichromate solution was added to the contents of flask. 30 ml H<sub>2</sub>SO<sub>4</sub> containing silver sulphate was then added slowly to the contents of the flask. The slow addition along with swirling prevents fatty acids to escape out from the flask. One flask without sample is prepared for blank solution. After thorough mixing, the flask was connected to the condenser and refluxed for 2 hours. After being cooled for 10-15 min, the condenser interior was washed with distilled water. The sample in the condenser was diluted to 250 ml, cooled and then excess K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was titrated with 0.1 N ferrous ammonium sulphate using ferroun indicator.

#### *Calculations*

$$\text{mg/L of COD} = \frac{(X - Y) \times \text{Normality of FAS} \times 8000 \times 0.25}{\text{ml of sample}}$$

X = ml of ferrous ammonium sulphate for blank

Y = ml of ferrous ammonium sulphate for sample

FAS = ferrous ammonium sulphate

The above calculations were carried out to determine COD of the solution before and after experimental runs.

*Note* : When silver sulphate is not used, the chloride content of the sample has to be determined and a correction applied as follows:

$$\text{Chloride correction} = \text{mg/L Chloride} \times 0.23$$

## **3.2 PREPARATION OF CATALYSTS**

### **3.2.1 Preparation of Co:Bi (5:1)**

Nitrate salts of cobalt [Co (NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O] and bismuth [Bi (NO<sub>3</sub>)<sub>3</sub> 5H<sub>2</sub>O] were weighed in 5:1 mass ratio. Bismuth nitrate was diluted with minimum amount of concentrated nitric acid in a cleanly rinsed beaker. Then cobalt nitrate was added to the

beaker and diluted with water. Ammonia solution was added to the beaker content slowly by stirring the whole content. Ammonia was added to the catalyst to get maximum amount of precipitation. pH was approximately maintained at 8, where the maximum amount of precipitate was formed. Then beaker was kept on a stirring plate and stirred for 30min, for getting good mixing and for attaining same composition through out. The contents of the beaker were kept for settling and water was removed without losing any amount precipitate. Then the catalyst was washed with water. The procedure of washing out the catalyst was repeated 3-4 times. After that the catalyst was dried overnight in an oven at 110°C. The dried catalyst was calcined in a silica crucible from 200-600°C for 6 hours. Stepwise calcination was started from 200°C and kept constantly for 30 min. The temperature was raised about 50°C in a step and kept constant for 30 min. The procedure was repeated up to 600°C. At 600°C it was heated for 2 hours. Due to the stepwise calcination uniform structure of catalyst was obtained.

### **3.2.2 Preparation of Mn: Ce (1 : 1)**

Chloride salt of manganese  $[\text{Mn} (\text{Cl}_2) 4\text{H}_2\text{O}]$  and nitrate salt of ceria  $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$  were weighted in 1 : 1 mass ratio. The salts were mixed in a cleanly rinsed beaker and diluted with distilled water and pH was maintained at 8. The beaker - was kept for stirring and then the precipitate was washed 3-4 times. The catalyst was dried overnight in an oven at 110°C. It was then calcined stepwise from 200-600°C for 6 hours as it was done for Co: Bi to get the uniform structure and more active sites of the catalyst.

## **3.3 EXPERIMENTAL PROCEDURE**

### **3.3.1 Wet oxidation at atmospheric pressure**

The wet oxidation reaction of synthetic sample butyric acid (5g/L) was carried out in a three necked conical flask of 250 ml capacity fitted with a magnetic stirrer. The central mouth of the flask was fitted with a total reflux condenser and the remaining two ports with thermocoupled temperature indicator and an air inlet respectively. Care was taken to ensure that the pressure of the compressed air inside the compressor was raised

to at least  $5 \text{ kg/cm}^2$  before starting the experiment to get smooth and uniform flow of air. Temperature was maintained constant with an accuracy of  $\pm 2^\circ\text{C}$ . Concentration of the catalyst was maintained  $5\text{g/L}$ , except for Co : Bi (5 : 1). Each experiment was conducted at atmospheric pressure and  $95^\circ\text{C}$  with a feed of 200 ml.

### 3.3.2 Wet Oxidation in a Pressurized Reactor

The thermal pretreatment were conducted in a 250 ml glass reactor to see that the reactant is fed to the actual reactor at the desired temperature. 200 ml of wastewater was taken in each run. The temperature was maintained at the desired value by a P.I.D. temperature controller. A vertical water-cooled condenser was attached to the middle neck of the reaction flask to prevent any loss of vapor.

The experimental assembly for WO consists of a stainless steel pressure reactor of 2 liter capacity. The reactor was equipped with magnetic stirring and heating arrangement, a port each for water entry into the reactor, and another for oxygen supply and also a liquid sampling port. PID temperature controller and digital pressure indicator were installed for measuring the temperature and pressure, respectively. The schematic diagram of the reactor is shown in Fig. 2.

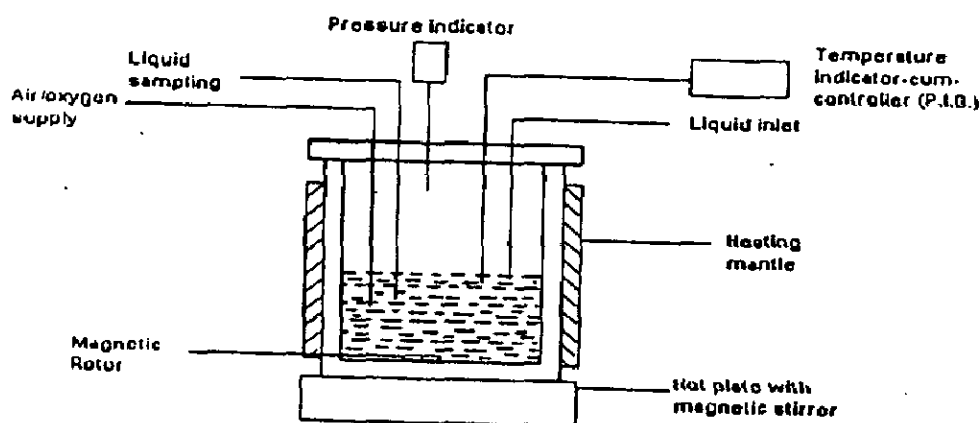


Fig. 3.2 : Schematic diagram of high pressure reactor

## Chapter - 4

# RESULTS AND DISCUSSION

## 4.1 CATALYST CHARACTERIZATION

### 4.1.1 Scanning Electron Micrographic Studies

The SEM (Scanning Electron Micrographic) analysis of the different catalysts are shown in the plates from SEM 4.1 to SEM 4.4. It may be observed that the structure of homogeneous catalysts ( $\text{CuSO}_4$  and  $\text{FeSO}_4$ ) were quite different from the structure of the heterogeneous catalysts [ $\text{Co} : \text{Bi} (5 : 1)$  and  $\text{Mn} : \text{Ce} (1 : 1)$ ]. Among the four catalysts  $\text{Mn} : \text{Ce} (1:1)$  [SEM 4.4] has a very good organized structure and it is also having high surface area and more active sites. The shapes of the particles were somewhat like cubical. In the literature it was mentioned that ceria doped catalysts were very effective and will have high surface area and active sites available on them for reaction occurrence. SEM 4 represents the  $\text{Mn} : \text{Ce} (1 : 1)$  structure at a magnification of 101 X.  $\text{Co} : \text{Bi} (5: 1)$  [SEM 4.3] also has the similar structure like  $\text{Mn} : \text{Ce} (1 : 1)$ . The shape of the particles was something like cuboids. The available surface area available was high as compared to the other homogeneous catalysts, but less than that of  $\text{Mn} : \text{Ce} (1 : 1)$ . This result also coincides with the literature (Joshi et al. 1995). SEM 3 represents the  $\text{Co} : \text{Bi} (5 : 1)$  structure at a magnification of 235 X.

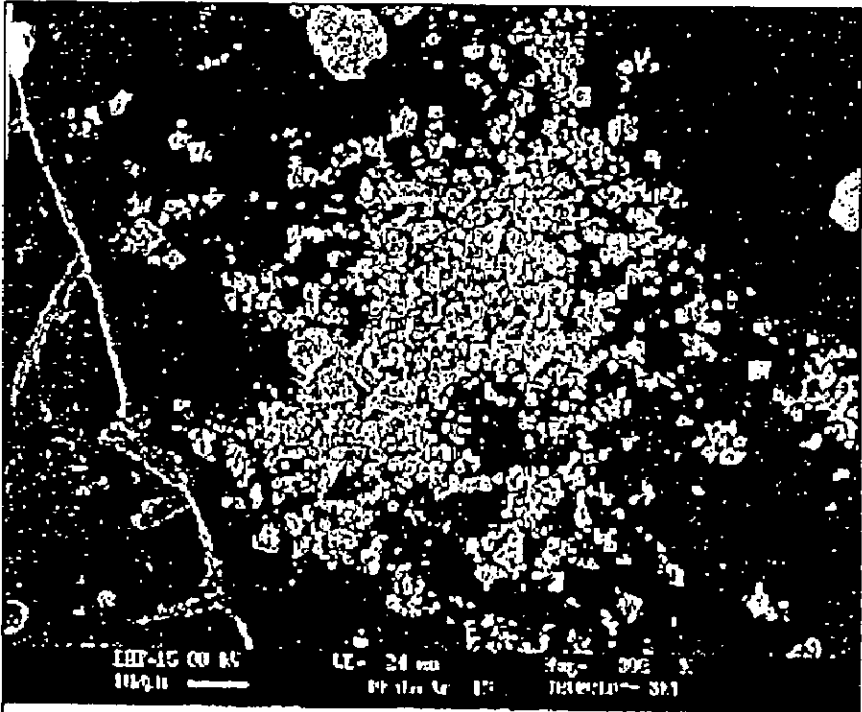
The structures of the homogeneous catalysts are shown in the SEM 4.1 and SEM 4.2. The particles in the both the figures were observed to be closely packed. Even the size of the particles was very small in comparison with the heterogeneous catalysts. The shape of the catalyst was seen something like spike. The surface area available was very less in comparison with the heterogeneous catalysts. SEM 4.1 represents the  $\text{CuSO}_4$  structure at a magnification of 300 X. SEM 4.2 represent the  $\text{FeSO}_4$  structure at a magnification of 300 X.

From SEM 4.5 to SEM 4.8 also it was clearly observed that the heterogeneous catalysts have more surface area compared to homogeneous catalysts. The intrinsic active

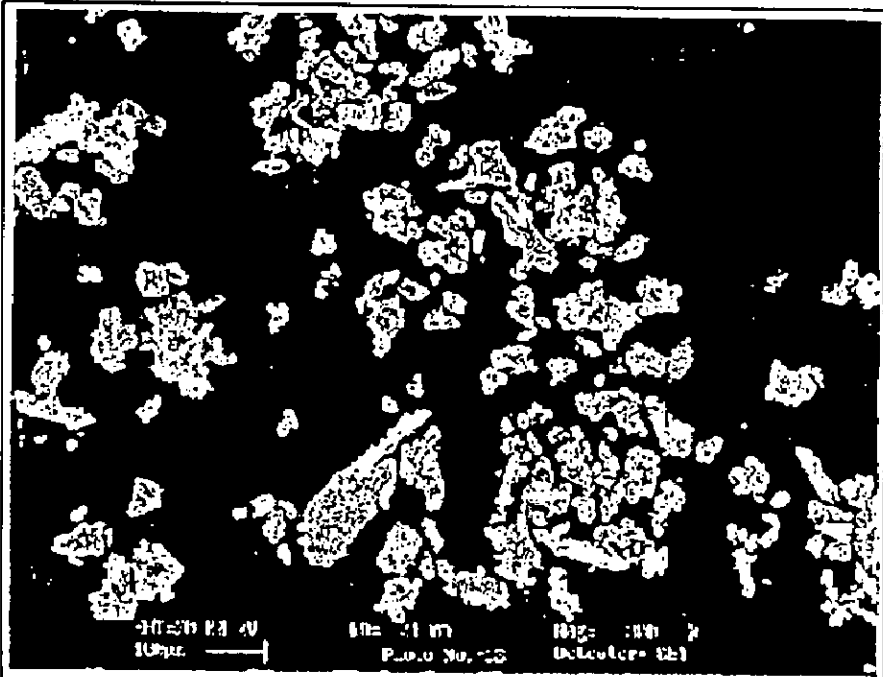


sites were clearly seen at higher magnification. The active reaction sites on heterogeneous catalysts were more compared to homogeneous catalysts.

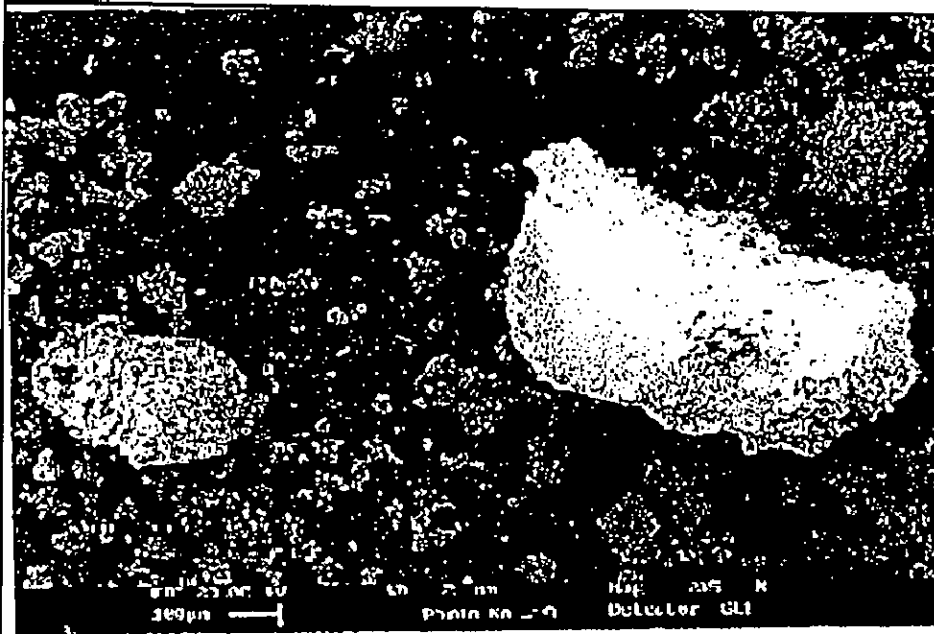
So, it is clear that the use of heterogeneous catalysts will obviously gives the better results compared with homogeneous catalysts.



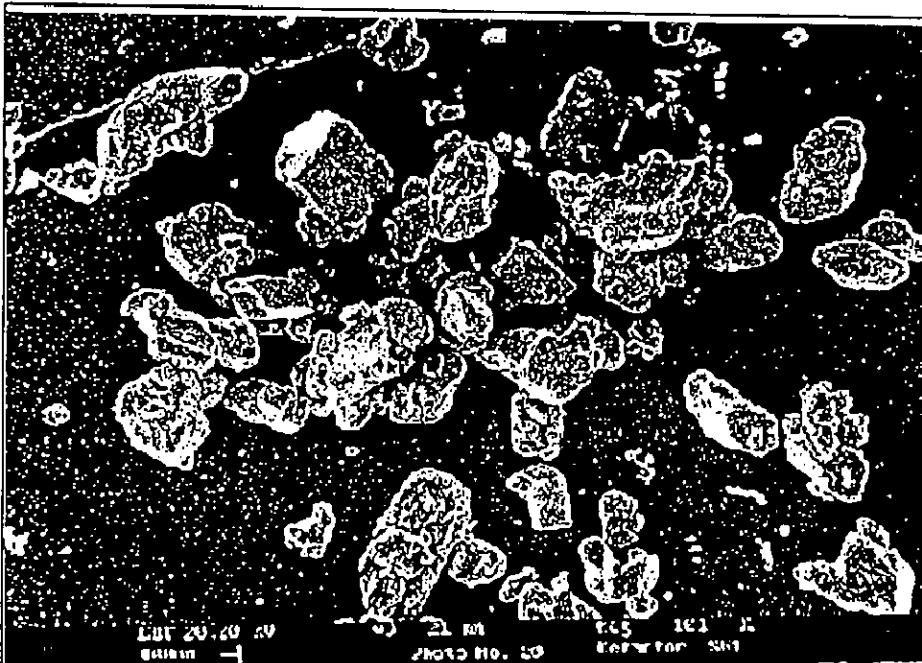
SEM 4.1 CuSO<sub>4</sub> Catalyst at Mag 300 X



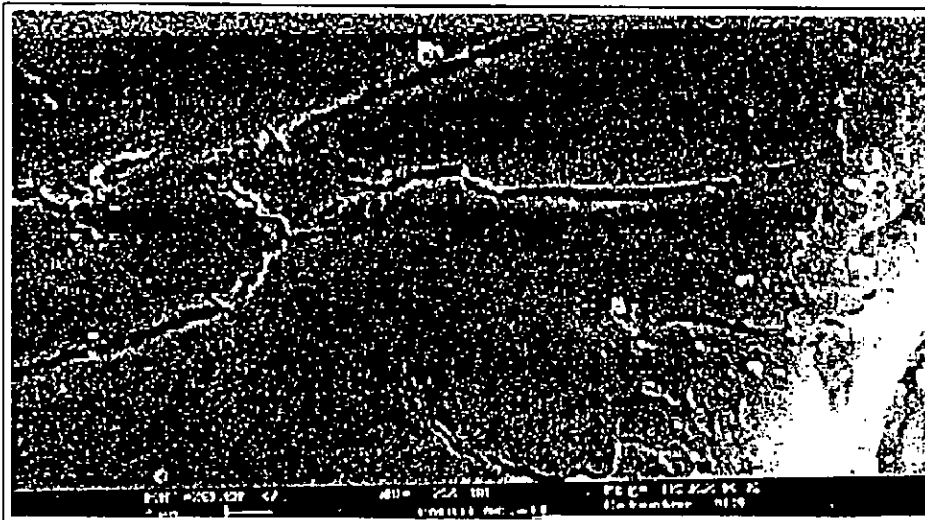
SEM 4.2 FeSO<sub>4</sub> Catalyst at Mag 300 X



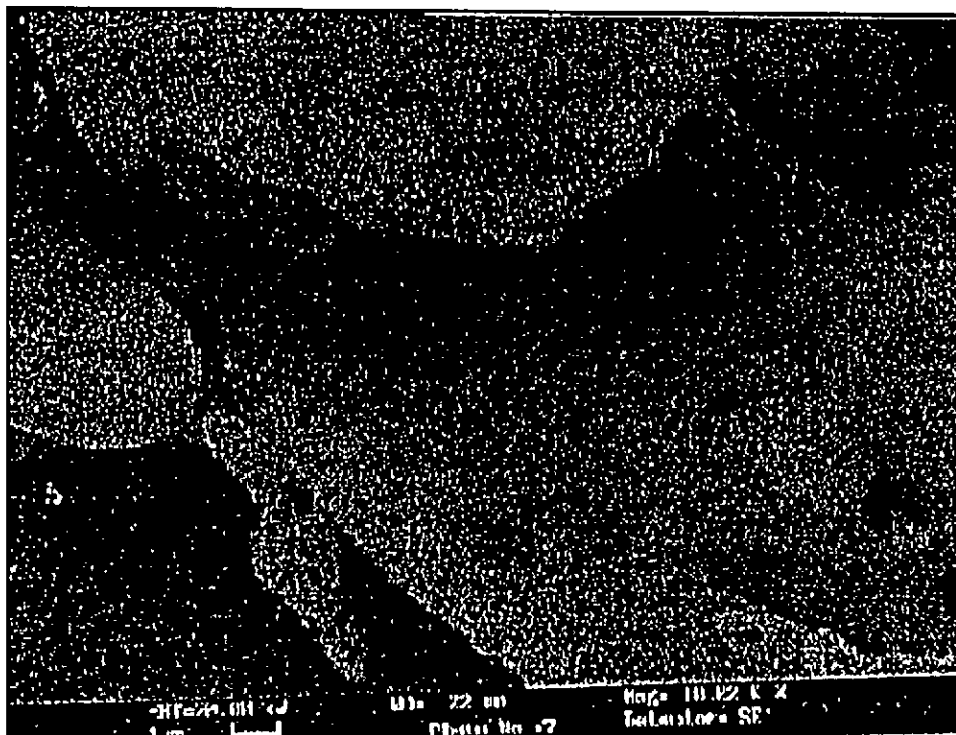
SEM 4.3 Co: Bi (5:1) Catalyst at Mag 235 X



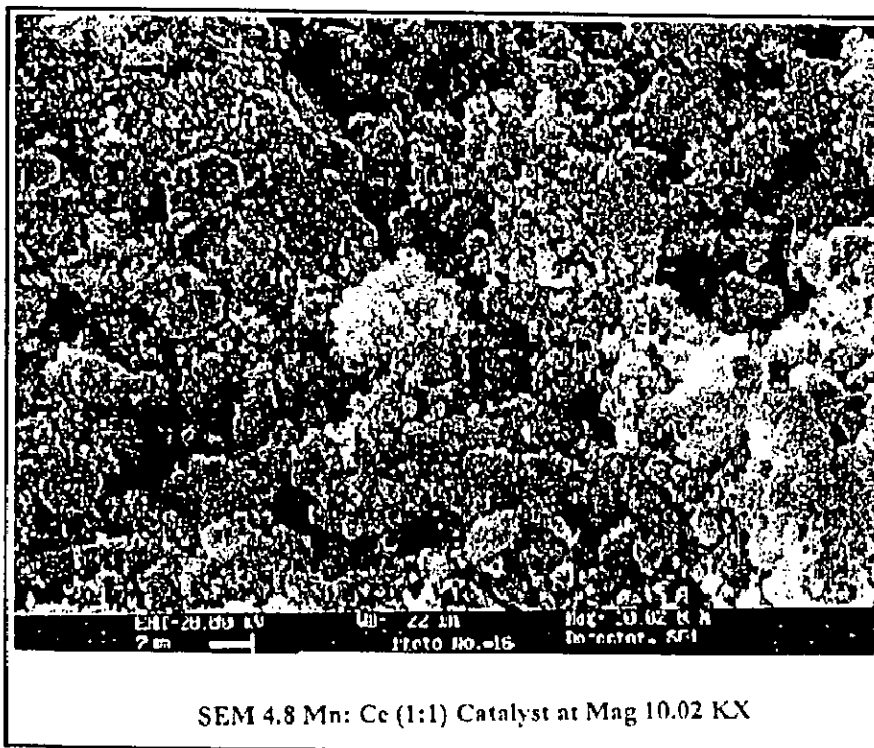
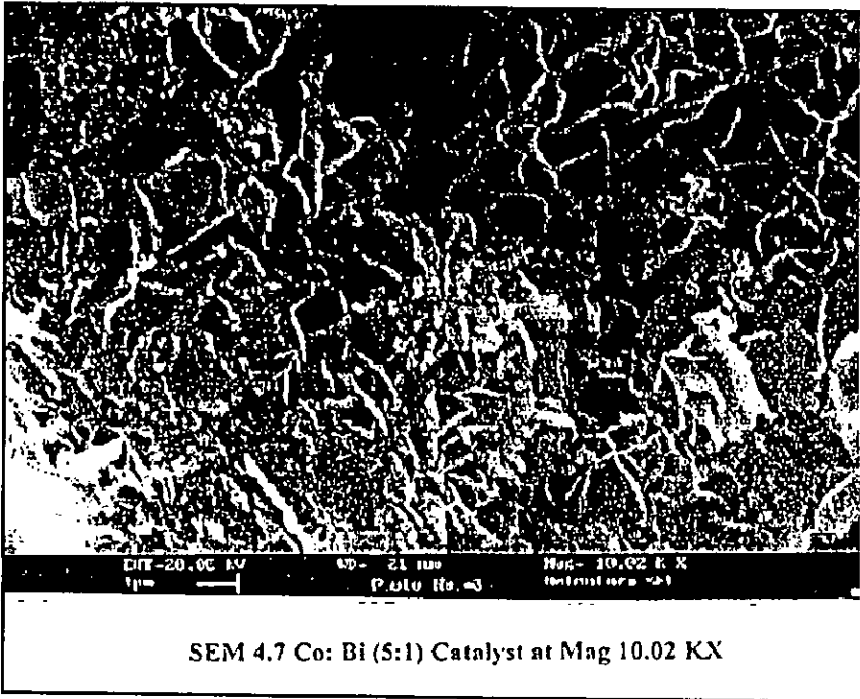
SEM 4.4 Mn: Ce (1:1) Catalyst at Mag 101 X



SEM 4.5 CuSO<sub>4</sub> Catalyst at Mag 10.02 KX



SEM 4.6 FeSO<sub>4</sub> Catalyst at Mag 10.02 KX

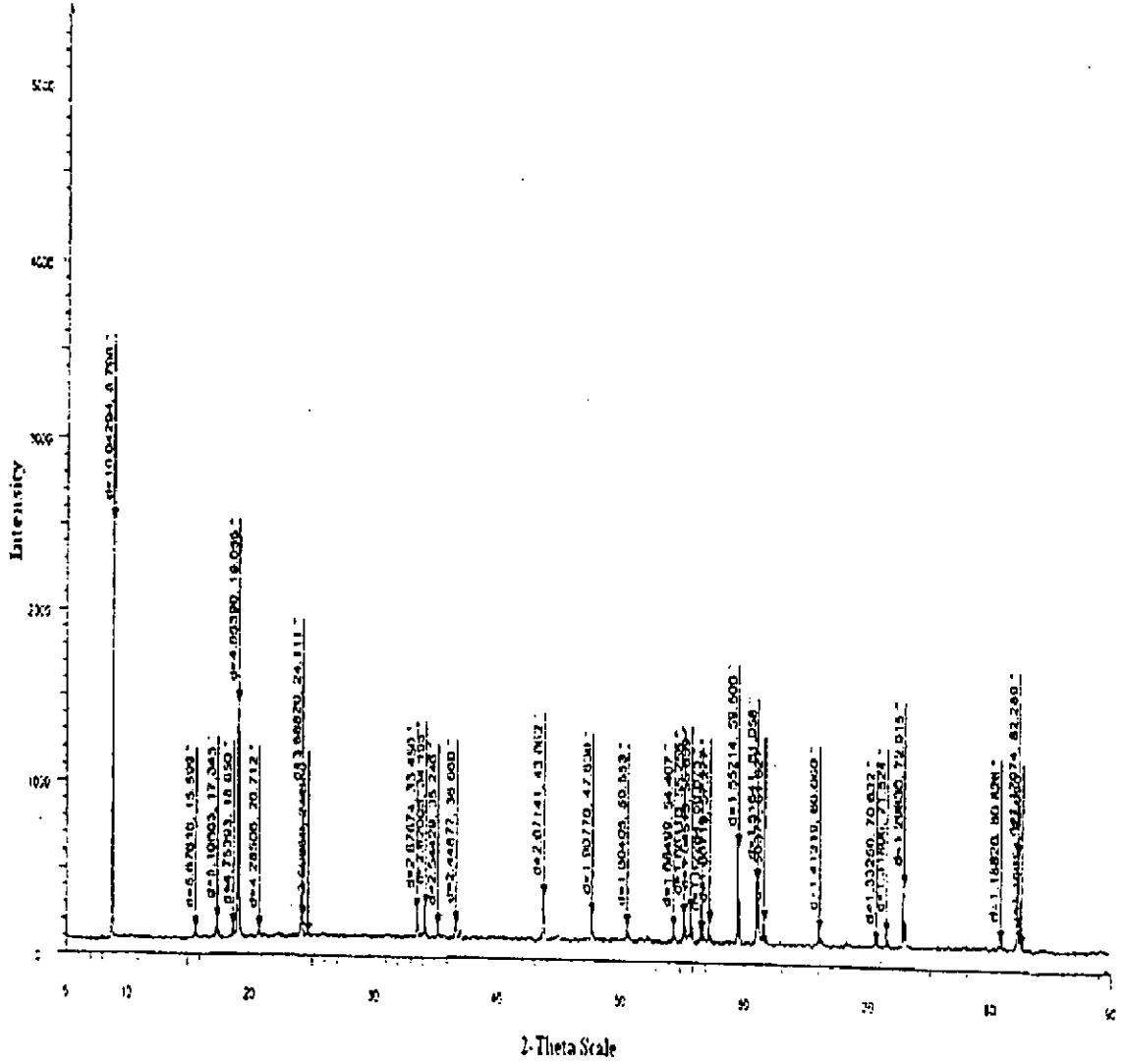


#### 4.1.2 X-Ray Diffraction Analysis

The determination of structure of catalysts was carried out by X-ray diffractometer in Institute Instrumentation Centre. Copper was used as a target through out the characterization. Goniometer speed was kept at  $1^\circ/\text{min}$ . The chart speed was  $1\text{ cm}/\text{min}$ . The range of scanning scale ( $2\theta$ ) was kept between  $5$  to  $90^\circ$ . For analysis the goniometer was scanned over angular range and plot of  $2\theta$  against intensity was obtained. The intensity peaks indicate values of  $2\theta$  where Bragg's law ( $n\lambda = 2d\sin\theta$ ) is fulfilled. Since  $\lambda$  values for copper target was constant ( $1.5418$ ) the  $2d$  values were known from JCPDS files. The  $2\theta$  (in degrees) setting of each peak which corresponds to certain wavelength was determined and matched with the  $2\theta$  values obtained from the samples. The X-ray diffractogram of the catalysts  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Co} : \text{Bi}$  ( $5 : 1$ ) and  $\text{Mn} : \text{Ce}$  ( $1 : 1$ ) are shown in XRD-4.1, XRD-4.2, XRD-4.3 and XRD-4.4 respectively. In XRD-4.1, major intensity peaks for  $\text{CuSO}_4$  were found at  $2\theta = 8.798, 19.055, 24.111, 43.662, 59.509, 72.915$  and  $82.289$ . In XRD-4.2 major intensity peaks for  $\text{FeSO}_4$  were found at  $2\theta = 16.32, 19.857, 22.331, 27.67, 30.044, 34.801$  and  $53.085$ . In XRD-4.3 major intensity peaks for  $\text{CuSO}_4$  for  $\text{Co} : \text{Bi}$  ( $5 : 1$ ) were found at  $2\theta = 28.105, 30.120, 36.884, 44.96, 59.075$  and  $65.478$ . In XRD-4.4, major intensity peaks for  $\text{Mn} : \text{Ce}$  ( $1 : 1$ ) were found at  $2\theta = 28.78, 32.965, 47.646, 55.2, 56.459$  and  $65.823$ .

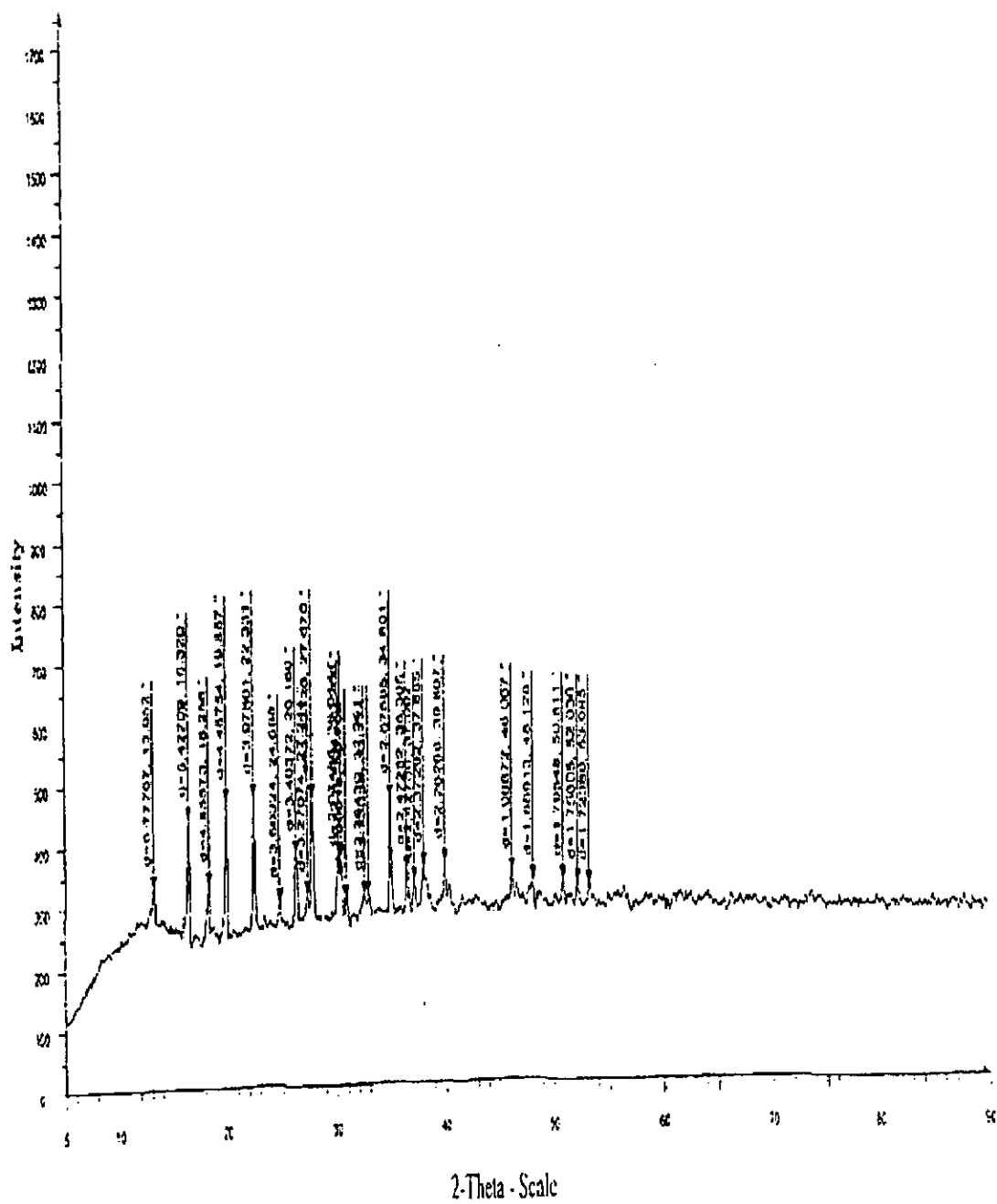
From XRD-4.1 through XRD-4.4, it is clearly observed that the range of intensity peaks are broad in case of  $\text{Mn} : \text{Ce}$  ( $1 : 1$ ), narrow in case of  $\text{CuSO}_4$ ,  $\text{Co} : \text{Bi}$  ( $5 : 1$ ) is found to have broad range peaks after  $\text{Mn} : \text{Ce}$  ( $1 : 1$ ).  $\text{CuSO}_4$  and  $\text{FeSO}_4$  are found to be have very narrow compared to  $\text{Co} : \text{Bi}$  ( $5 : 1$ ) and  $\text{Mn} : \text{Ce}$  ( $1 : 1$ ). From this we can say that the heterogeneous catalysts are far better than homogeneous catalysts. The surface area available is more for heterogeneous catalysts compared to homogeneous catalysts.

CuSO<sub>4</sub> (Catalyst)



XRD-4.1 CuSO<sub>4</sub> Catalyst on 2θ-Scale (5° -90°)

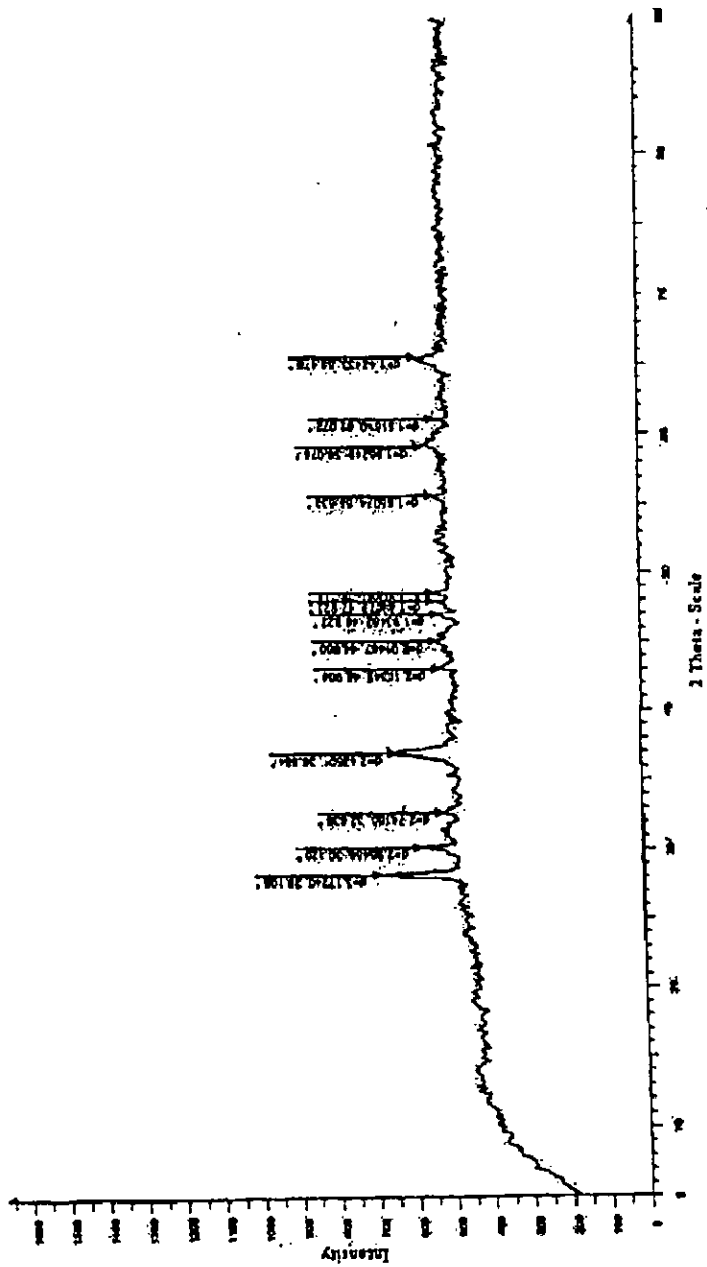
FeSO4 Catalyst



XRD-4.2 FeSO4 Catalyst on 2θ -Scale (5° -90°)

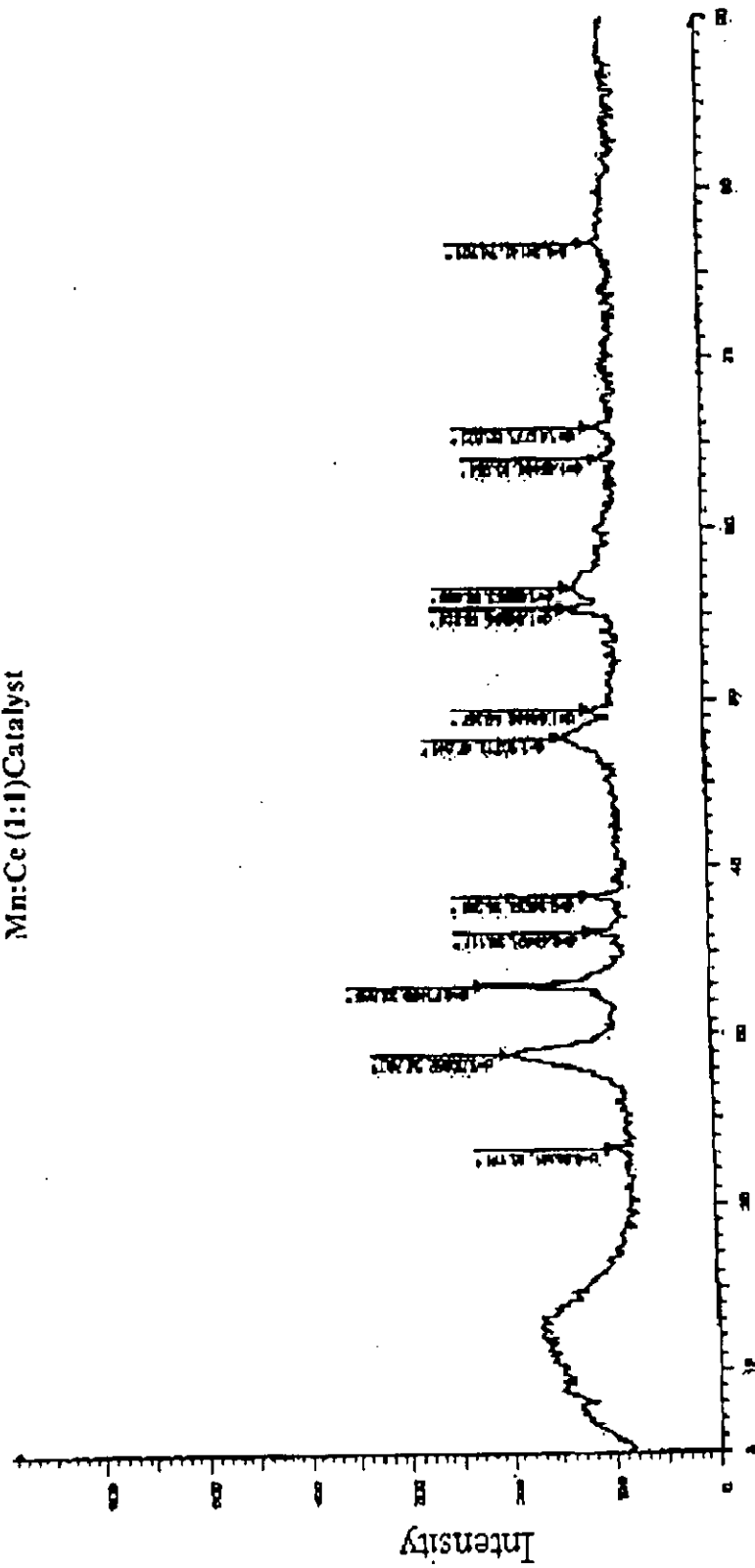


Co : Bi (5:1) Catalyst



XRD-43 Co:Bi (5:1) Catalyst on 20-Scale (5° -90°)

Mn:Ce (1:1) Catalyst



2 Theta - Scale

XRD-4.4 Mn: Ce (1:1) Catalyst on 20 -Scale (5° -90°)

## 4.2 RESULTS OF CATALYTIC WET AIR OXIDATION

Butyric acid synthetic solution was prepared by dissolving it in distilled water with a concentration of 5g/L. Its pH was 2.7 and initial COD 7000 mg/L. Several investigators studied WAO of carboxylic acids. Some of them devoted their work to butyric acid. J.L.Faria. (2002), D. Duprez et. al. (2000) studied the conversion of butyric acid, the kinetic parameters, intermediates formed, and reaction mechanism with and without catalyst. Their studies involved reaction temperatures in the range of 160-280°C and oxygen partial pressure 10-55 bar. The main aim of their work was the conversion or complete reduction of butyric acid. For this, they used several catalysts like Ru/Ce, Ru/C, and Ru/Ce over carbon support. They achieved satisfactory conversions. J.L.Faria. (2002) proposed a first order reaction kinetics with respect to TOC removal of butyric acid.

From the result of J.L.Faria (2002) heterogeneous catalysts are more effective than homogeneous catalysts. They also mentioned that Mn : Ce (1: 1) was very effective among the other heterogeneous catalysts for WAO of carboxylic acids. Use of Mn : Ce (1 : 1) resulted in complete removal of acetic acid at 200°C. Its activity can be further improved by using Ru as a promoter. Ceria support was found very effective in the removal of carboxylic acids. Co: Bi (5: 1) was found to be the very effective catalyst among heterogeneous after Mn : Ce (1: 1). From the literature copper sulfate was found to be the very effective homogeneous catalyst. S. Perathoner et al. (2000) prepared a very effective honey comb model Fenton (Fe/ZSM-5) catalyst which gave 60-80% conversion of formic, acetic and propionic acid even at a temperature of 25 -70 °C in presence of H<sub>2</sub>O<sub>2</sub>. But H<sub>2</sub>O<sub>2</sub> can not be used at high temperatures, since it gets completely converted at 120°C within 5 min (S. Imamura, 1999).

From the literature we found that presence of noble metals will obviously give higher conversion rates even at low temperature and pressures. So we have to make a wise balance between cost and conversion and then select the catalyst. The non-noble metals were chosen for the present work on the account of their low cost and ease in

availability. The experimental results include the effects of reaction variables such as pH, temperature, and kinetic parameter determination. The catalysts were characterized using XRD and SEM analysis.

#### 4.2.1 Effect of pH

pH was optimized for four different catalysts, individually at 140°C and air partial pressure 4 kg/cm<sup>2</sup>. The catalyst concentration was 5 gm/L in all the cases. Total pressure was maintained at 8 kg/cm<sup>2</sup>. The pH values selected for optimization tests of pH were 3, 5, 7 and 9. The catalysts used include CuSO<sub>4</sub>, FeSO<sub>4</sub>, Co: Bi (5 : 1) and Mn : Ce (1 : 1). Figures 4.1 through 4.4 represent the effect of pH on COD removal of butyric acid with initial concentration of 7000 mg/L for the catalysts CuSO<sub>4</sub>, FeSO<sub>4</sub>, Co : Bi (5 : 1) and Mn : Ce (1: 1) respectively.

From Fig. 4.1, it is concluded that using CuSO<sub>4</sub> as catalyst maximum reduction is obtained at pH 5. Maximum COD reduction obtained using this catalyst was 32% at pH 5 after 6 hrs reaction time. At pH 3, pH 7 and pH 9, the % COD reductions were 29%, 25% and 18.7% respectively. From Fig. 4.2, it is concluded that using FeSO<sub>4</sub> as catalyst maximum reduction is obtained at pH 5. Maximum COD reduction obtained using this catalyst was 36.4% at pH 5 after 6 hrs reaction time. At pH 3, pH 7 and pH 9 the % COD reductions were 32.3%, 34.5% and 22.1 % respectively.

From Fig. 4.3, it is concluded that using Co: Bi (5: 1) as catalyst maximum reduction is obtained at pH 7. Maximum COD reduction obtained using this catalyst was 38.6% at pH 7 after 6 hrs reaction time. At pH 3, pH 5 and pH 9 the %COD reduction were 30.3%, 34.7% and 26.2% respectively.

From Fig. 4.4, it is concluded that using Mn : Ce (1: 1) as catalyst maximum reduction is obtained at pH 3. Maximum COD reduction obtained using this catalyst was 41.54% at pH 3 after 6 hrs reaction time. At pH 5, pH 7 and pH 9 the %COD reduction were 33.33%, 38.66% and 10.0% respectively.

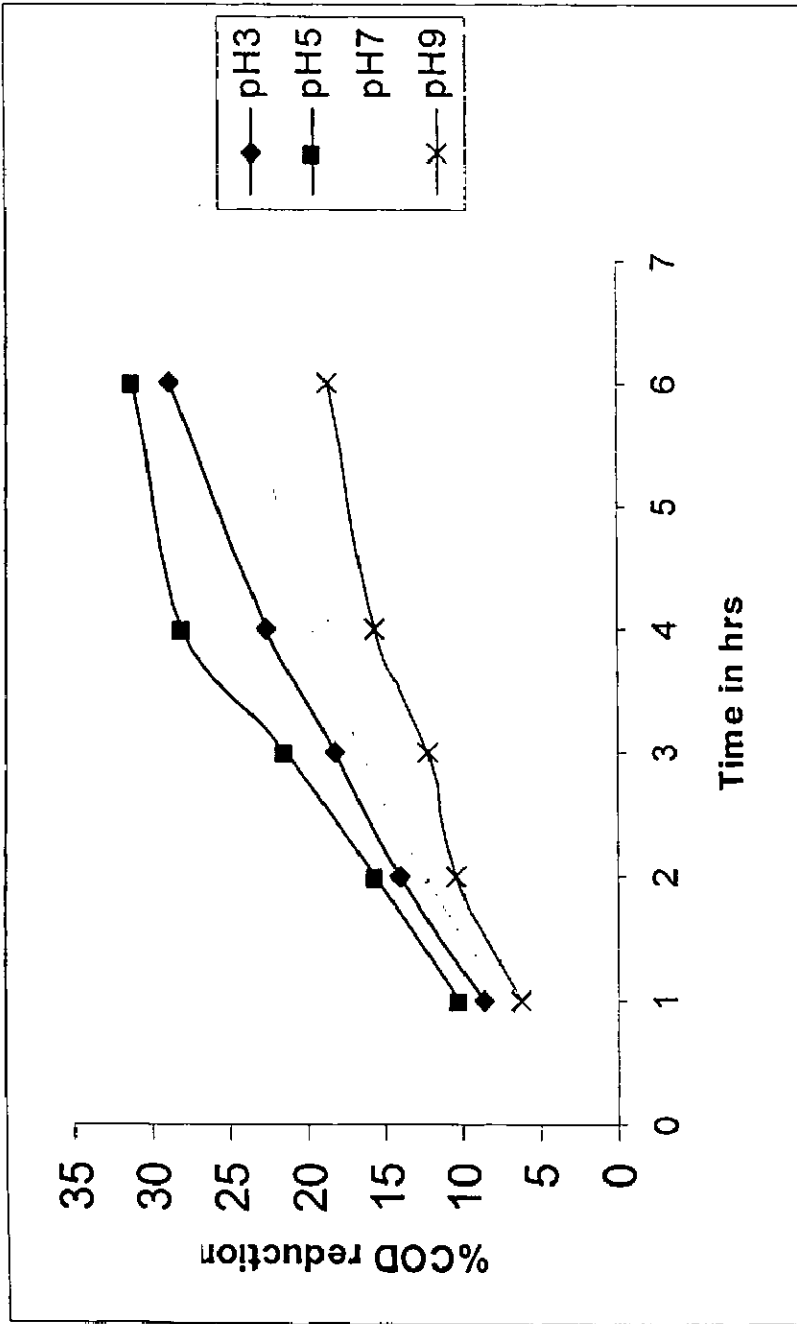


Figure 4.1 Effect of pH on %COD reduction of butyric acid;  
 Initial COD=7000mg/L, Temperature=140°C, P<sub>air</sub>=4kg/cm<sup>2</sup>  
 Catalyst : CuSO<sub>4</sub>(5 gm/L)

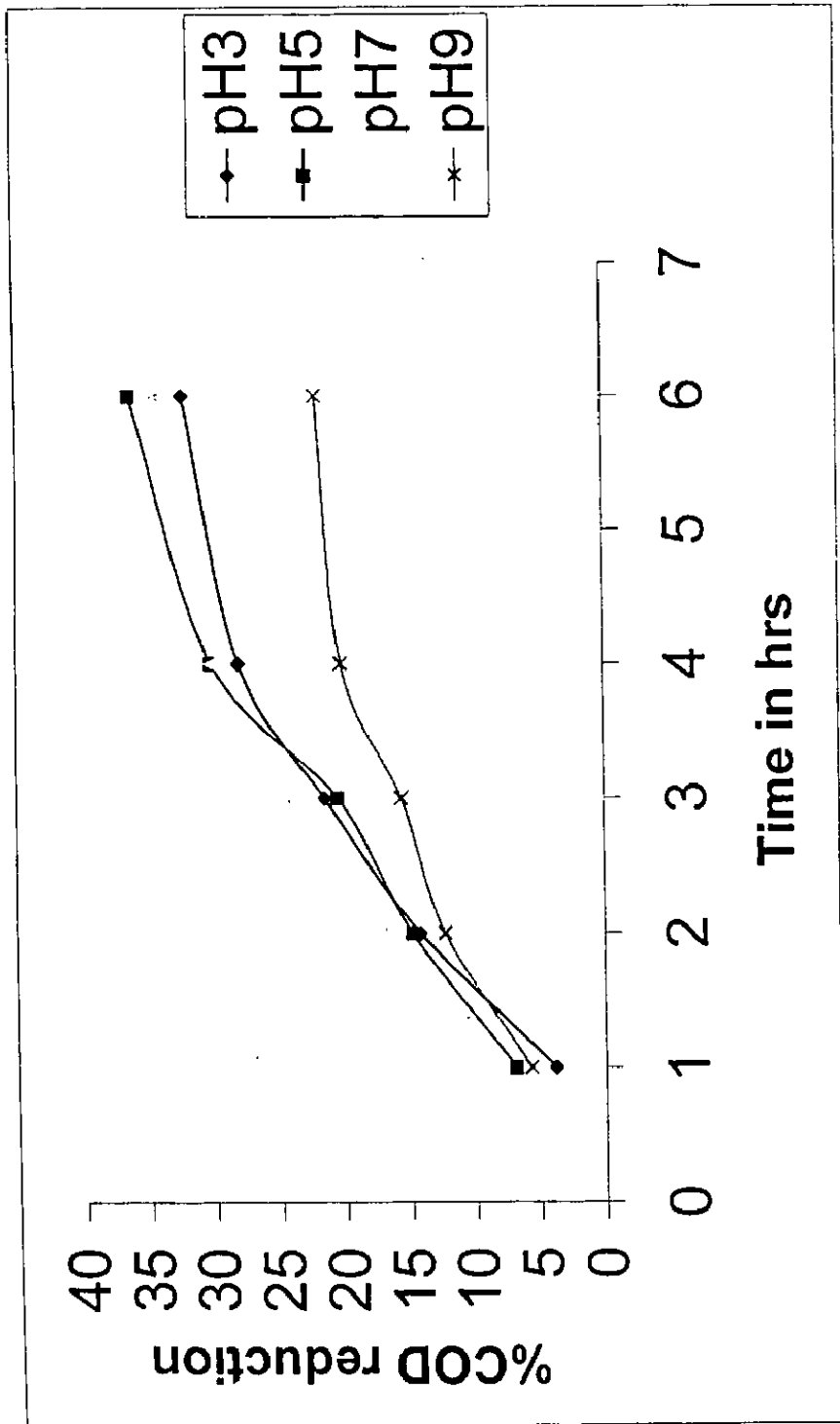


Figure 4.2 Effect of pH on %COD reduction of butyric acid;  
 Initial COD=7000mg/L, Temperature=140°C,  $p_{air}$ =4kg/cm<sup>2</sup>  
 Catalyst : FeSO<sub>4</sub>(5 gm/L)

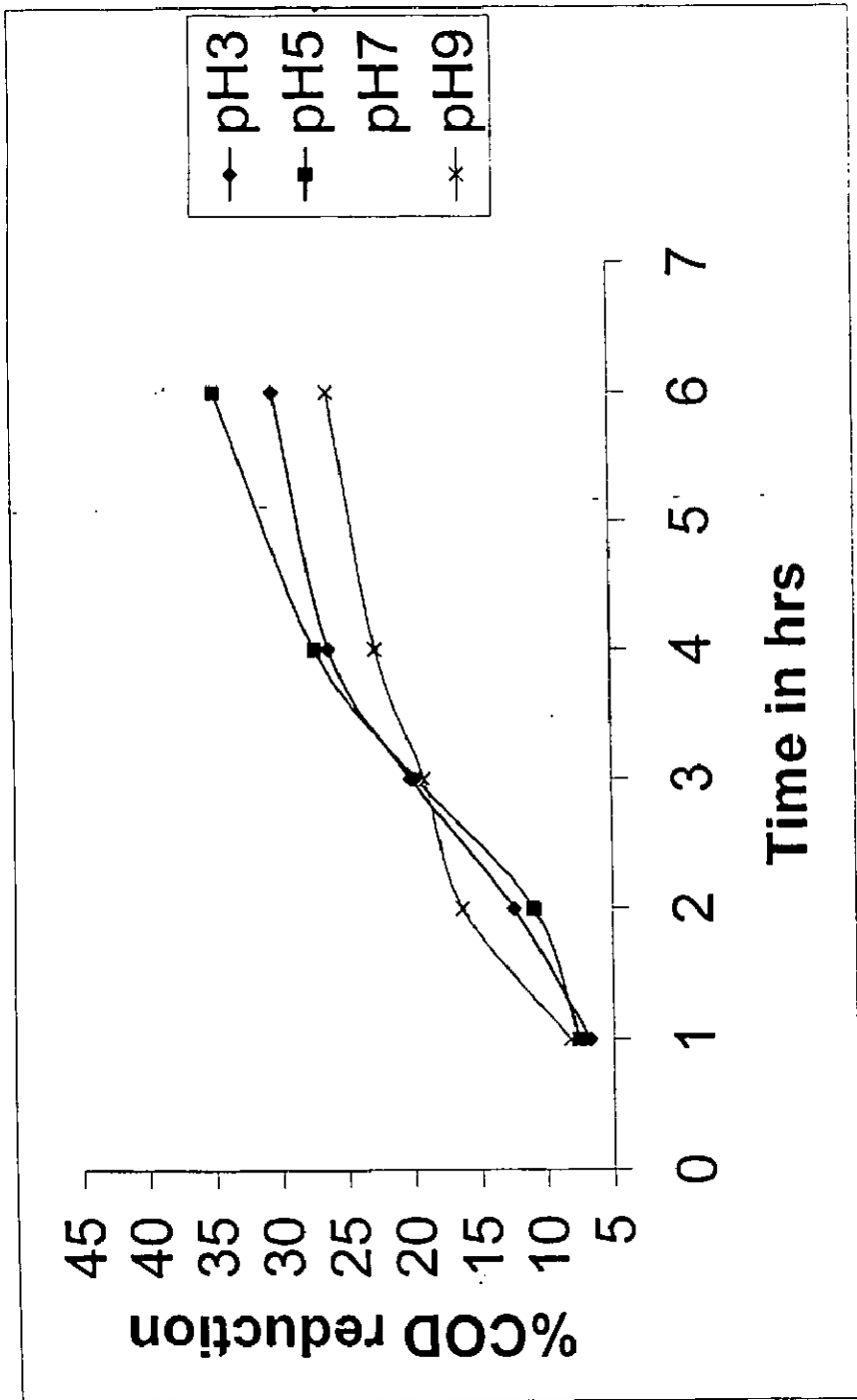


Figure 4.3 Effect of pH on %COD reduction of butyric acid;  
 Initial COD=7000mg/L, Temperature=140°C,  $p_{air}=4\text{kg/cm}^2$   
 Catalyst : Co:Bi(5 gm/L)



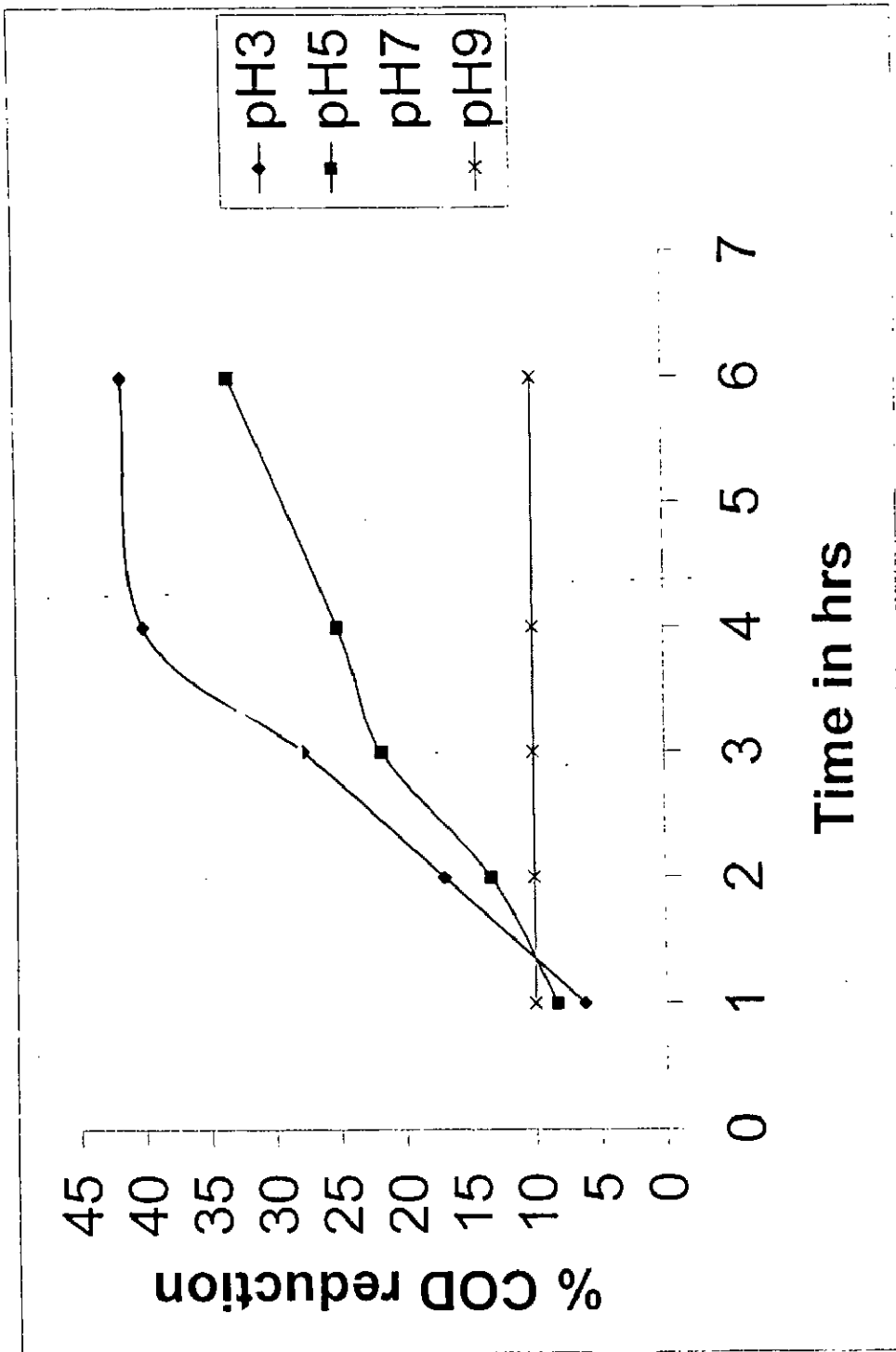


Figure 4.4 Effect of pH on %COD reduction of butyric acid;  
 Initial COD=7000mg/L, Temperature=140°C,  $p_{air}=4\text{kg/cm}^2$   
 Catalyst :Mn:Ce(5 gm/L)

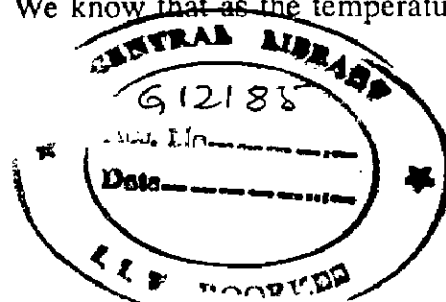
#### 4.2.2 Effect of Temperature

Effect of temperature on COD reduction of butyric acid was studied for various catalysts at their respective optimized pH. Four catalysts  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Co} : \text{Bi} (5 : 1)$  and  $\text{Mn} : \text{Ce} (1 : 1)$  were tested. The catalyst concentration was 5 gm/L in all the cases. Three different temperatures  $140^\circ\text{C}$ ,  $160^\circ\text{C}$  and  $180^\circ\text{C}$  were used. The partial pressure of air in the reactor was  $4 \text{ kg/cm}^2$  in all the cases. But the total pressure of the reactor was varied as the temperature was raised. The total pressure in the reactor at  $140^\circ\text{C}$ ,  $160^\circ\text{C}$ , and  $180^\circ\text{C}$  were  $8 \text{ kg/cm}^2$ ,  $10 \text{ kg/cm}^2$  and  $14 \text{ kg/cm}^2$ , respectively.

Figures 4.5 through 4.8 represent the effect of temperature on COD removal of ac butyric acid with initial concentration of 7000 mg/L for the catalysts  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Co} : \text{Bi} (5 : 1)$  and  $\text{Mn} : \text{Ce}$  respectively. In Fig 4.5, a graph is plotted %COD reduction Vs reaction time in hrs. From this graph, we can observe that using  $\text{CuSO}_4$ , maximum COD reduction that was obtained at  $180^\circ\text{C}$  was 52.39 in 6 hrs reaction time. It is observed that as the temperature is raised, the COD removal would also increase. At the temperatures  $140^\circ\text{C}$ ,  $160^\circ\text{C}$  and  $180^\circ\text{C}$ , the %COD reductions were 33.1 %, 44.81 % and 52.39 % respectively in 6 hrs reaction time. In fig 4.6, a graph is plotted %COD reduction Vs reaction time in hrs. From this graph it is observed that using  $\text{FeSO}_4$  maximum COD reduction that was obtained at  $180^\circ\text{C}$  was 56.85 in 6 hrs reaction time. We know that as the temperature is raised the COD removal would also increase. At the temperatures  $140^\circ\text{C}$ ,  $160^\circ\text{C}$  and  $180^\circ\text{C}$ , the %COD reductions were 36.4%, 49.56% and 56.85% respectively in 6 hrs reaction time.

In fig 4.7 a graph is plotted %COD reduction Vs reaction time in hrs. From this graph we can observe that using  $\text{Co} : \text{Bi} (5 : 1)$  Maximum COD reduction that was obtained at  $180^\circ\text{C}$  was 62.67 in 6 hrs reaction time. We know that as the temperature is raised the COD removal would also be increased. At the temperature  $140^\circ\text{C}$ ,  $160^\circ\text{C}$  and  $180^\circ\text{C}$  the %COD reduction was 38.6%, 58.32% and 62.67% respectively in 6 hrs reaction time.

In fig 4.8, a graph is plotted %COD reduction Vs reaction time in hrs, from this graph we can observe that using  $\text{Mn} : \text{Ce} (1 : 1)$  maximum COD reduction that was obtained at  $180^\circ\text{C}$  was 81.57 in 4 hrs reaction time. We know that as the temperature is



raised the COD removal would also be increased. At the temperatures 140°C, 160°C and 180°C the %COD reductions were 40.0%, 68.33% and 82.57% respectively in 4 hrs reaction time.

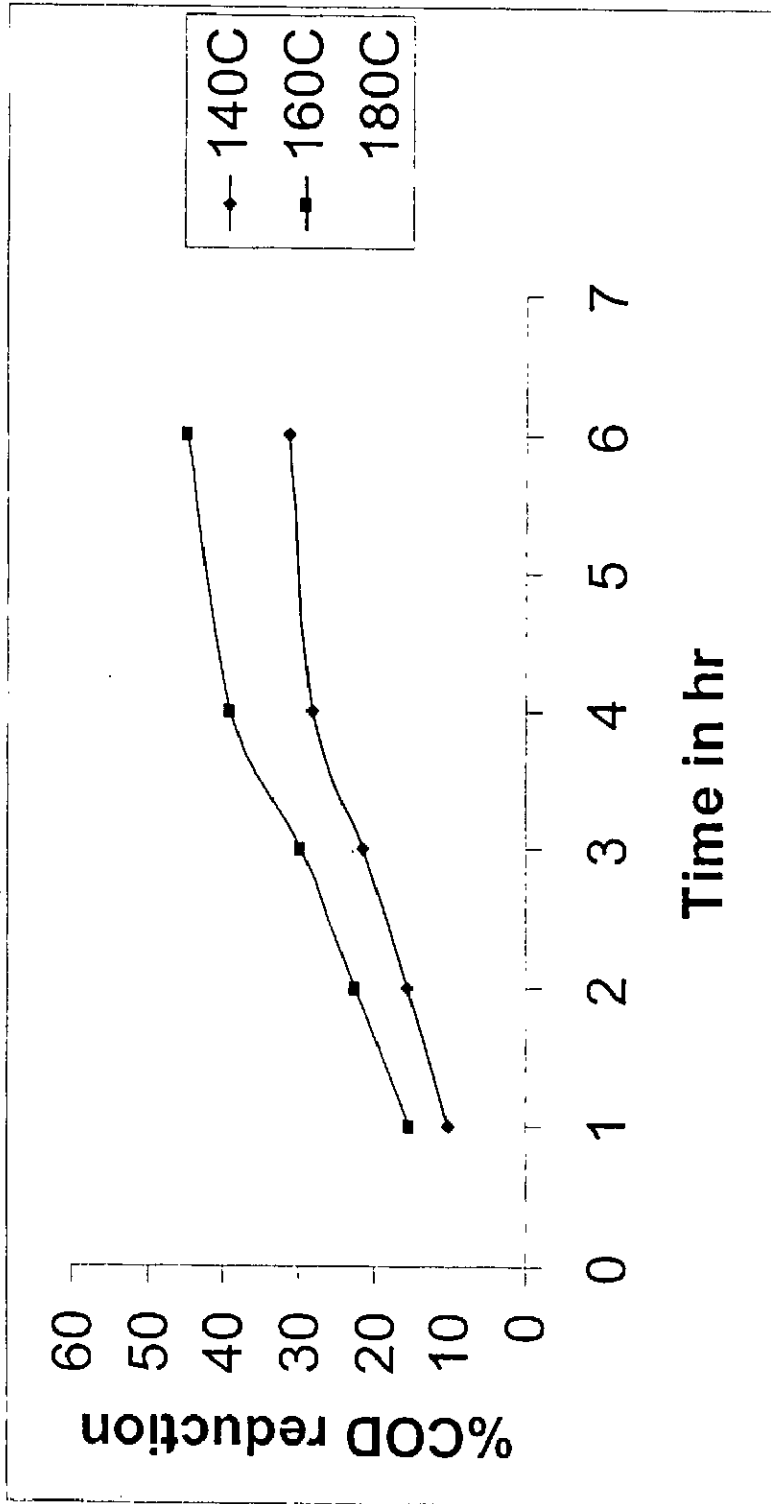


Figure 4.5 Effect of Temperature on %COD reduction of butyric acid;  
 Initial COD=7000 mg/L, pH=5,  $p_{air}=4\text{kg/cm}^2$   
 Catalyst :  $\text{CuSO}_4$  (5 gm/L)

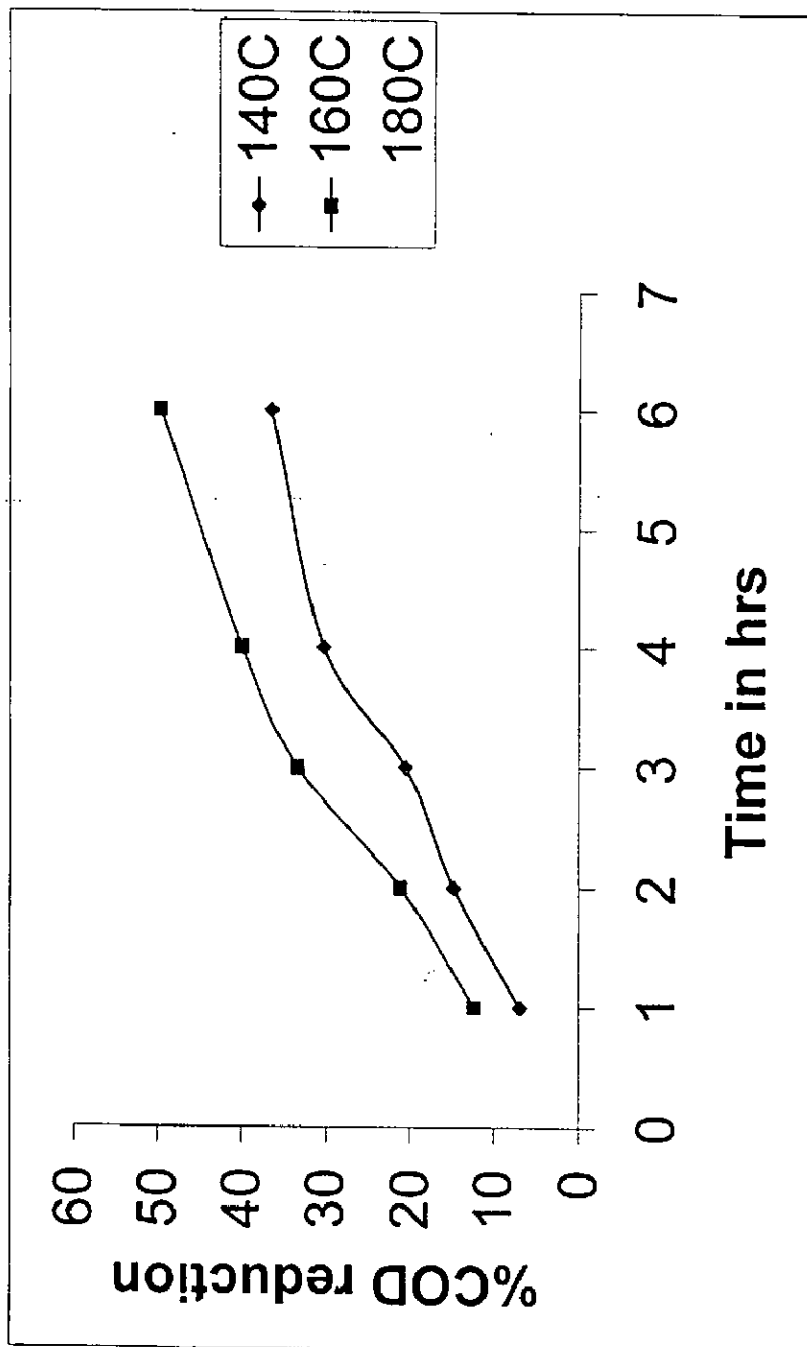


Figure 4.6 Effect of Temperature on % COD reduction of butyric acid;  
 Initial COD=7000mg/L,pH=5 , $p_{air}=4\text{kg/cm}^2$   
 Catalyst :  $\text{FeSO}_4(5 \text{ gm/L})$

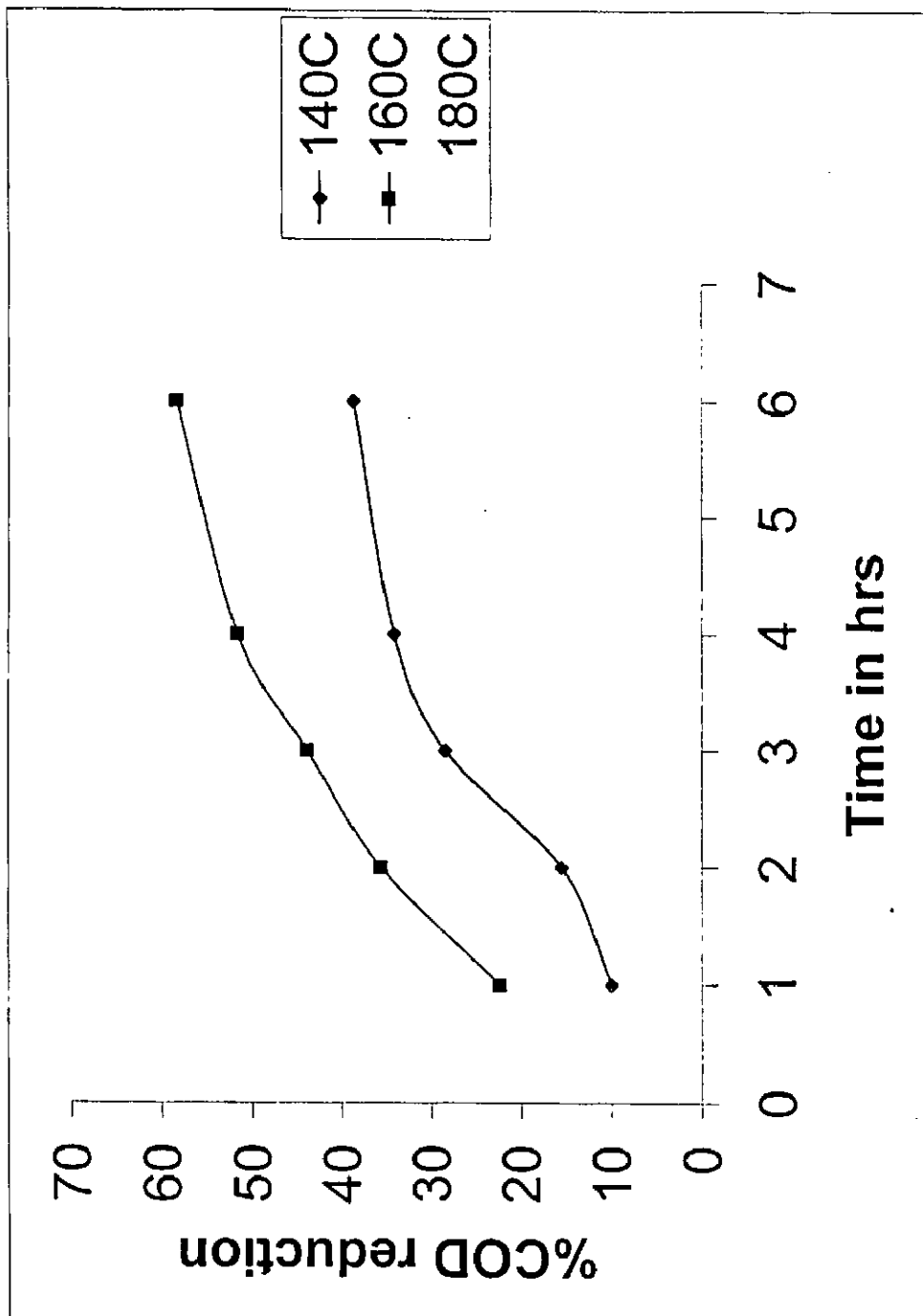


Figure 4.7 Effect of Temperature on % COD reduction of butyric acid;  
 Initial COD=7000mg/L,pH=7 , $p_{air}=4\text{kg/cm}^2$   
 Catalyst :Co:Bi(5:1)(5 gm/L)

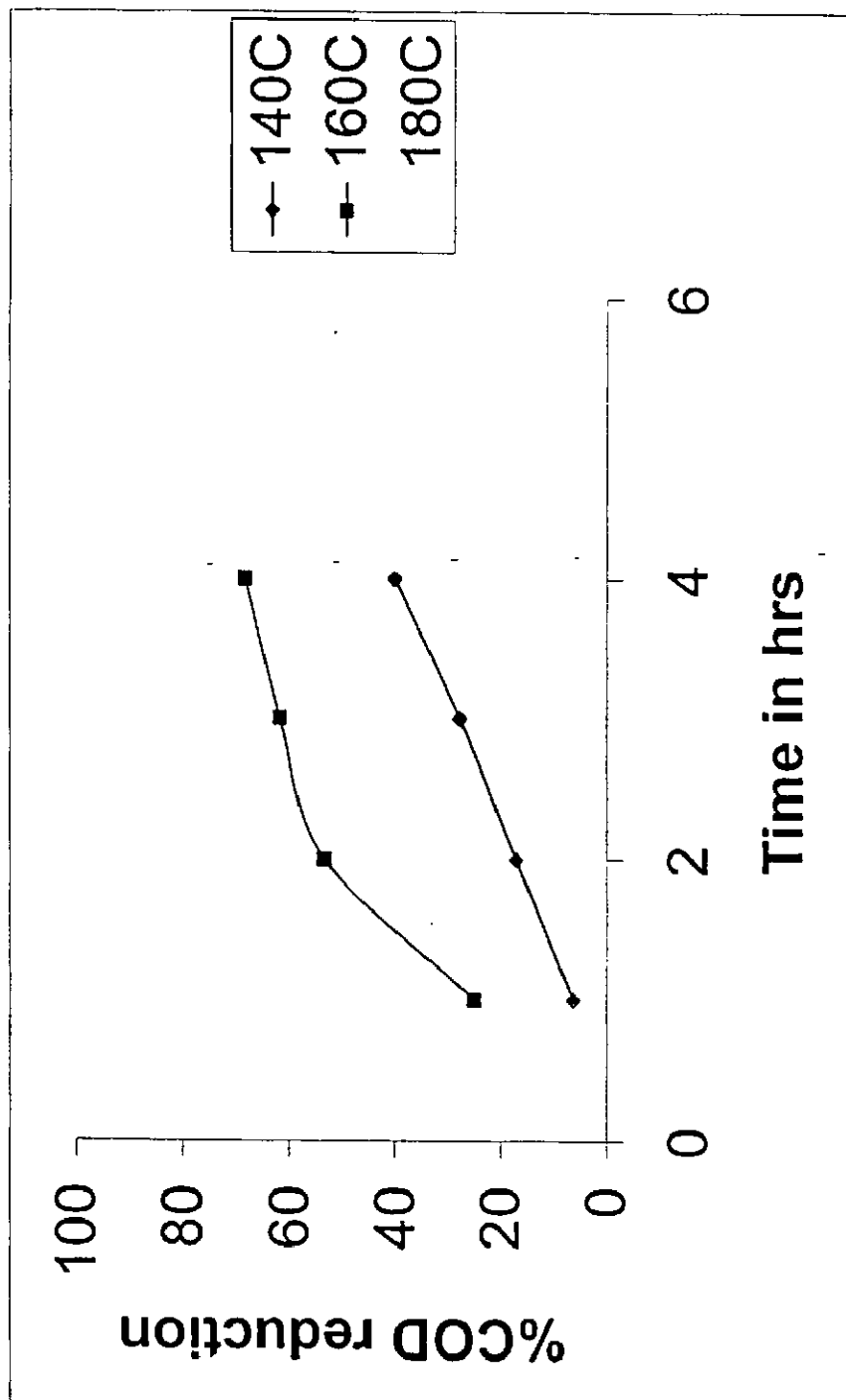


Figure 4.8 Effect of Temperature on % COD reduction of butyric acid;  
 Initial COD=7000mg/L, pH=3,  $p_{air}=4\text{kg/cm}^2$   
 Catalyst :Mn:Ce(1:1)(5 gm/L)

#### 4.2.4 Kinetic Parameter Studies

The rate equation for the COD reduction was assumed to be a function of the concentration of organic substrate as well as oxygen partial pressure. Since, in all the runs air (oxygen) partial pressure was ( $4 \text{ kg/cm}^2$ ) kept constant, the rate of the reaction would invariably be a function of organic concentration. Levee et. al. (2000) proposed 1<sup>st</sup> order kinetics with respect to TOC removal of butyric acid. We consider the rate to follow a first order reaction kinetics and try to show through the experiment data whether it is applicable.

For a first order reaction, we can write:

$$-r_A = -\frac{dC_A}{dt} = k C_A$$

Where,  $C_A$  = Concentration of organic substance, (COD)

Since,  $C_A = C_{A0} (1 - X_A)$

$$-C_{A0} \frac{d(1 - X_A)}{dt} = k C_{A0} (1 - X_A)$$

$$-k dt = -\frac{1}{(1 - X_A)} d X_A$$

$$kt = -\ln (1 - X_A)$$

For determining rate constant of the reaction of a 1<sup>st</sup> order equation a plot of  $[-\ln (1 - X_A)]$  Vs reaction time in hrs is plotted. Rate constants were found individually for each catalyst at three different temperatures. The catalysts were  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ , Co: Bi (5 : 1), Mn : Ce (1: 1). The catalyst concentration was 5 gm/L in all the cases. Temperature was varied from 140 to 180°C. Three different temperatures were selected in this range are 140°C, 160°C and 180°C. The partial pressure of air if the reactor was  $4 \text{ kg/cm}^2$  in all the cases. The total pressure of the reactor, however, varied as the temperature was raised. The total pressure in the reactor at 140°C, 160°C, 180°C were  $8 \text{ kg/cm}^2$ ,  $10 \text{ kg/cm}^2$  and  $14 \text{ kg/cm}^2$  respectively. pH value was maintained at optimized value for each individual catalyst.

Figures 4.9 through 4.12 gives the values of rate constants of COD reduction of butyric acid using various catalysts. Figs 4.9, 4.10 and 4.12 give the rate constant of butyric acid using  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ , Co: Bi (5 : 1), Mn : Ce (1 : 1) at three different



temperature 140°C, 160°C and 180°C. In figure 4.9, depicts a plot of  $[-\ln(1 - X_A)]$  Vs reaction time in hrs. From this plot it is observed that the value of rate constant with respect to COD removal of butyric acid using  $\text{CuSO}_4$ . The data exactly fit a straight line, showing the validity of the first order rate expression. Values of reaction rate constants using  $\text{CuSO}_4$  at three different temperatures 140°C, 160°C and 180°C were tabulated in Table 4.1.

In Fig. 4.10 present a plot of  $[-\ln(1 - X_A)]$  Vs reaction time in hrs. From this plot, we get the value of rate constant with respect to COD removal of butyric acid using Co : Bi (5 : 1). The data exactly fit to a straight line, showing the validity of the first order rate expression. However, little variations from the straight line were shown in the plot with acceptable correlation factor of 0.9. Values of reaction rate constants using  $\text{FeSO}_4$  at three different temperatures 140°C, 160°C and 180°C were shown in Table 4.1.

In Fig. 4.11, a graph is plotted  $[-\ln(1 - X_A)]$  Vs reaction time in hrs. From this plot we get the value of rate constant with respect to COD removal of butyric acid using Co: Bi (5: 1). The data exactly fit to a straight line, showing the validity of the first order rate expression. However little variations from the straight line were shown in the plot with acceptable correlation factor of 0.9. Values of reaction rate constants using Co: Bi (5 : 1) at three different temperatures 140°C, 160°C and 180°C were tabulated in Table 4.1.

In Fig. 4.12, a graph is plotted  $[-\ln(1 - X_A)]$  Vs reaction time in hrs. From this plot, we get the value of rate constant with respect to COD removal of butyric acid using Mn : Ce (1 : 1). The data exactly fit to a straight line, showing the validity of the first order rate expression. However little variations from the straight line were shown in the plot with acceptable correlation factor of 0.9. Values of reaction rate constants using Mn : Ce (1: 1) at three different temperatures 140°C, 160°C and 180°C were tabulated in Table 4.1.

**Table 4.1 Values of Rate Constants**

S No	Temperature (°C)	Rate Constants, $\text{hr}^{-1}$			
		$\text{CuSO}_4$	$\text{FeSO}_4$	Co : Bi (5 : 1)	Mn : Ce (1: 1)
1	140	0.0696	0.0961	0.10 13	0.1477
2	160	0.1095	0.1375	0.1528	0.2783
3	180	0.1369	0.1552	0.1693	0.4344

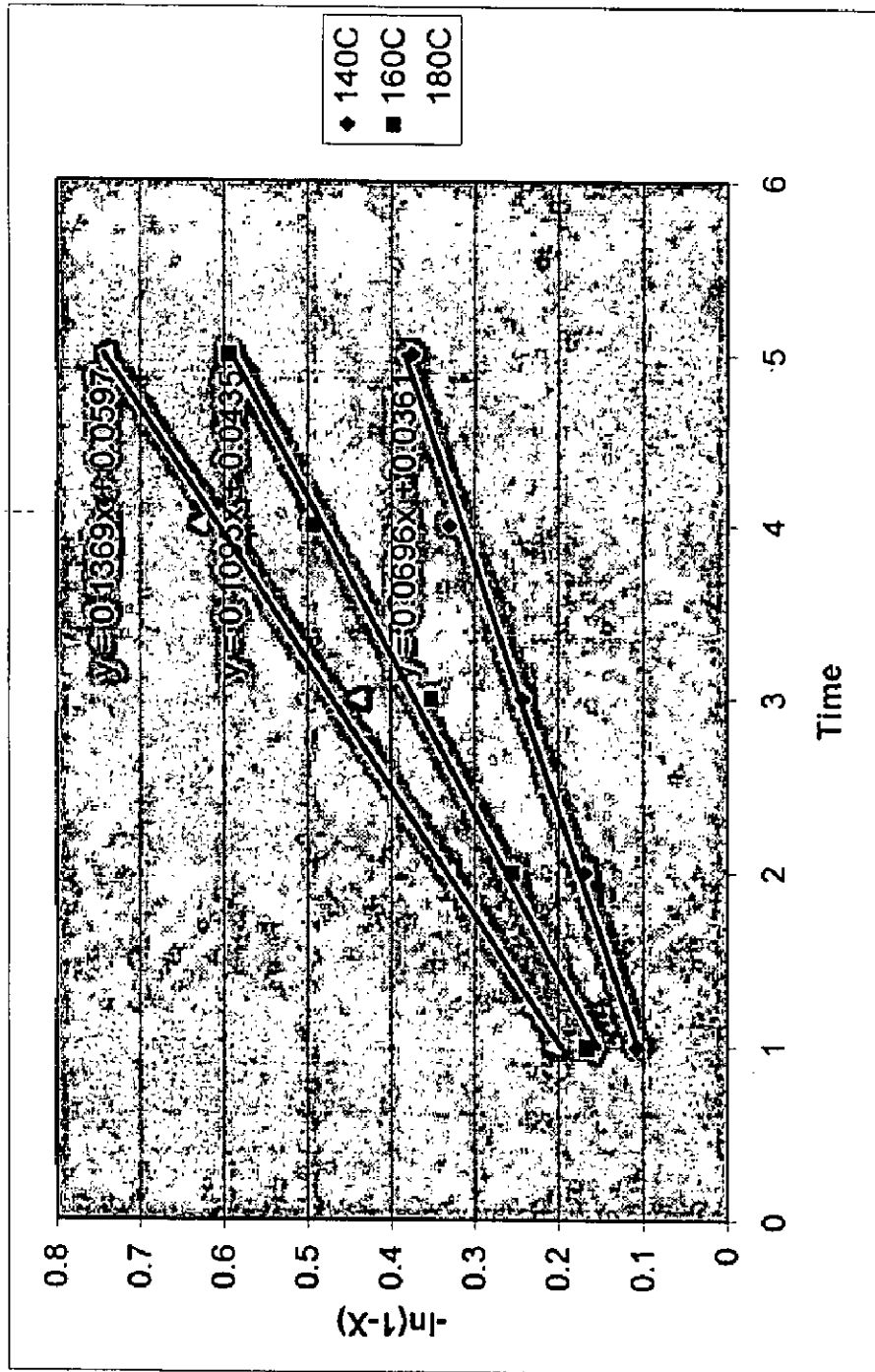


Figure 4.9 Kinetic plot of  $-\ln(1-X)$  Vs Time  
 Initial COD = 7000 mg/L, pH = 5,  $P_{air} = 4 \text{ kg/cm}^2$   
 Catalyst :  $\text{CuSO}_4$  (5 gm/L)

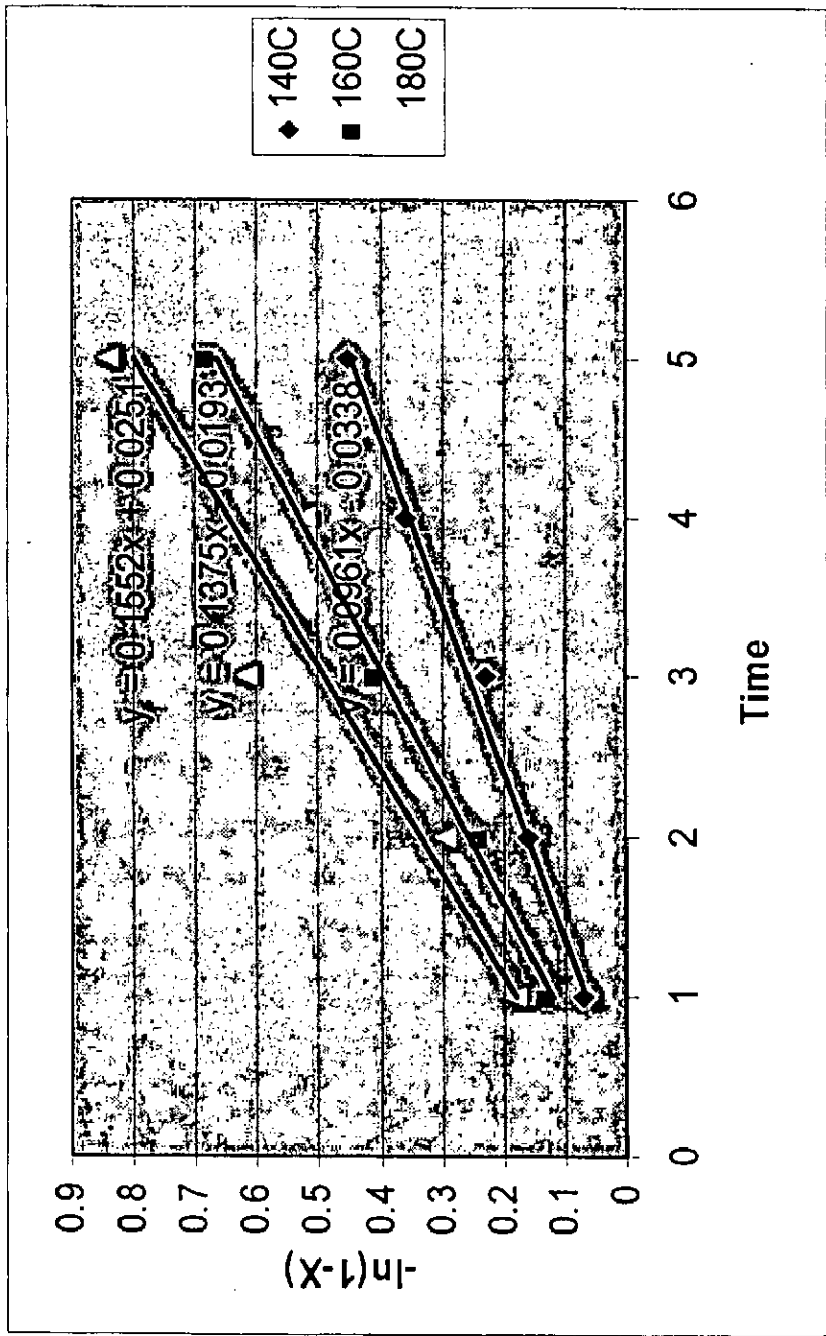


Figure 4.10 Kinetic plot of  $-\ln(1-X)$  Vs Time  
 Initial COD = 7000 mg/L, pH = 5,  $P_{air} = 4 \text{ kg/cm}^2$   
 Catalyst : FeSO<sub>4</sub> (5 gm/L)

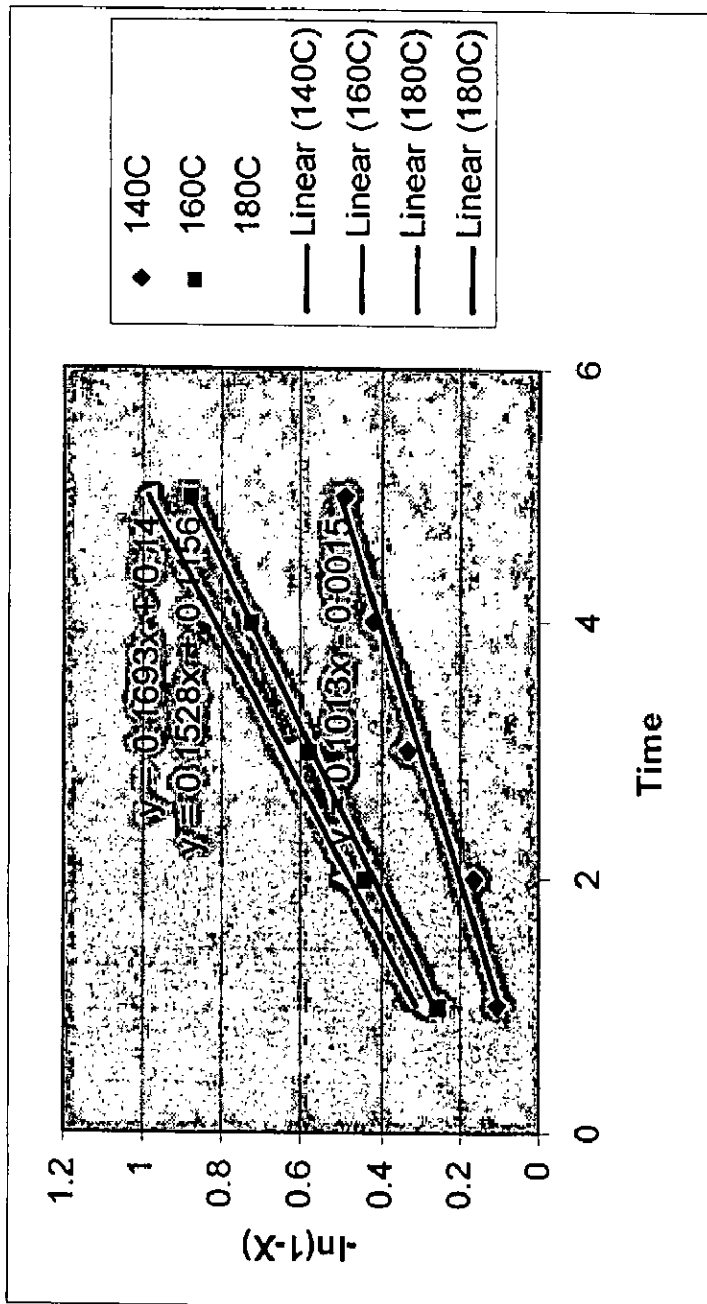


Figure 4.11 Kinetic plot of  $-\ln(1-X)$  Vs Time  
 Initial COD = 7000 mg/L, pH = 7,  $P_{air} = 4 \text{ kg/cm}^2$   
 Catalyst : Co:Bi (5 gm/L)

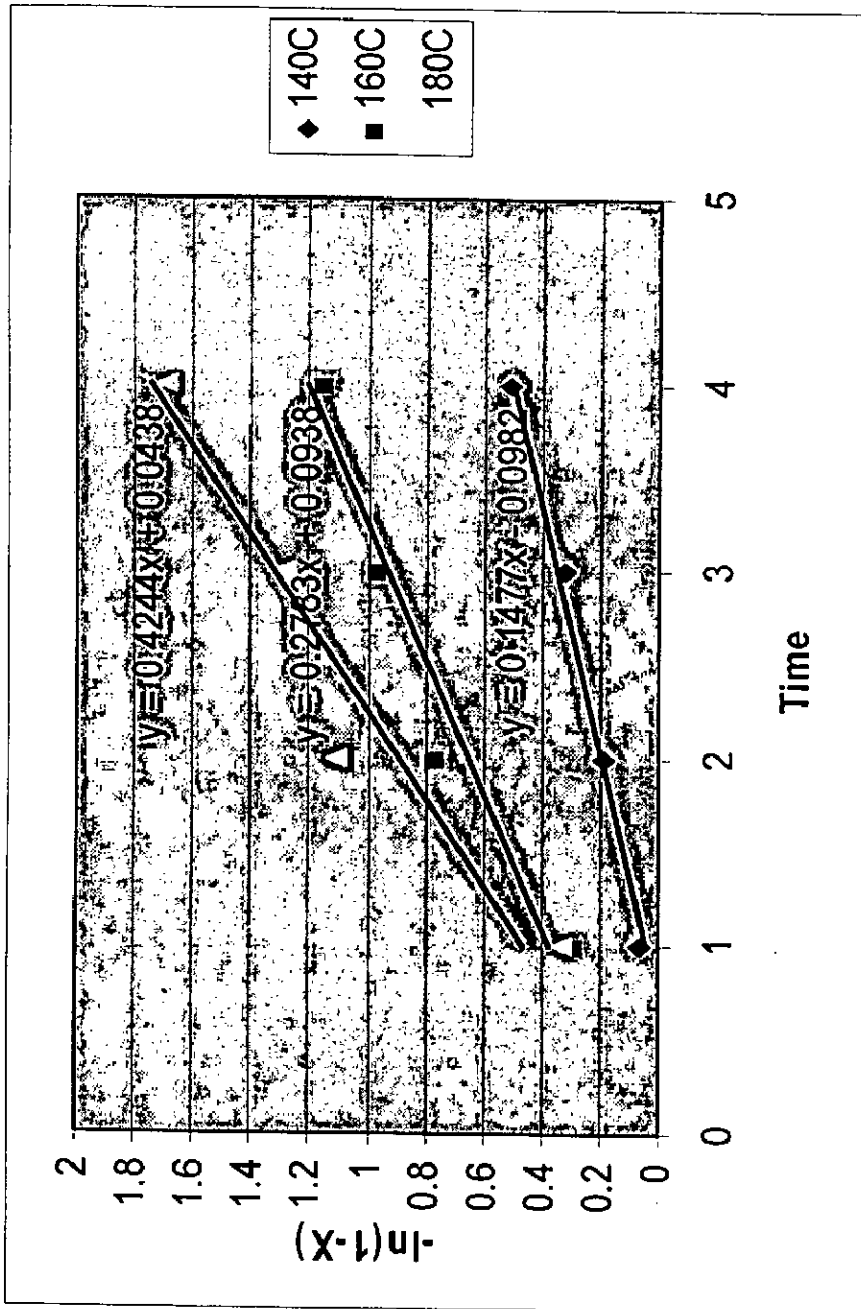


Figure 4.12 Kinetic plot of  $-\ln(1-X)$  Vs Time  
 Initial COD=7000mg/L, pH=3,  $p_{air} = 4\text{kg/cm}^2$   
 Catalyst :Mn:Ce (5 gm/L)

#### 4.2.5 Arrhenius Plot

The dependency of equilibrium rate constant with temperature is related by Arrhenius equation as  $k = A e^{-E/RT}$ .

The values of activation energies and pre-exponential factors of the first order reaction were calculated by plotting  $\ln k$  Vs  $1/T$ . Figures 4.13 through 4.16 represent corresponding plots for different catalysts  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ , Co: Bi (5 : 1), Mn : Ce (1: 1) respectively. The values of activation energy and pre-exponential factors are tabulated for each catalyst separately in Table 4.2.

**Table 4.2 Values of Activation energy and pre-exponential factor**

S. No.	Catalyst	Activation Energy, E J/mol	Pre-exponential factor, $h^{-1}$
1	$\text{CuSO}_4$	25912	141
2	$\text{FeSO}_4$	23956	81
3	Co : Bi (5 : 1)	24595	134
4	Mn : Ce (1 : 1)	50378	312123

Some experimental runs were also performed at atmospheric pressure and temperature of 98°C with air as oxidizing agent. Hydrogen peroxide was also used as an oxidizing agent at atmospheric pressure and temperature of 98°C. Reactions at atmospheric conditions were performed for very long time periods of 30 hrs continuously. Runs were taken using various catalysts  $\text{CuSO}_4$ ,  $\text{FeSO}_4$  and Co: Bi (5 : 1). The catalyst concentration was 5gm/L in all the cases. However, the results obtained at atmospheric conditions were not encouraging. So, it is advisable to treat the studies which were carried out at atmospheric conditions are not effective. After long runs of 30 hrs the COD reduction was at the most 16% using Co: Bi (5: 1) catalyst.

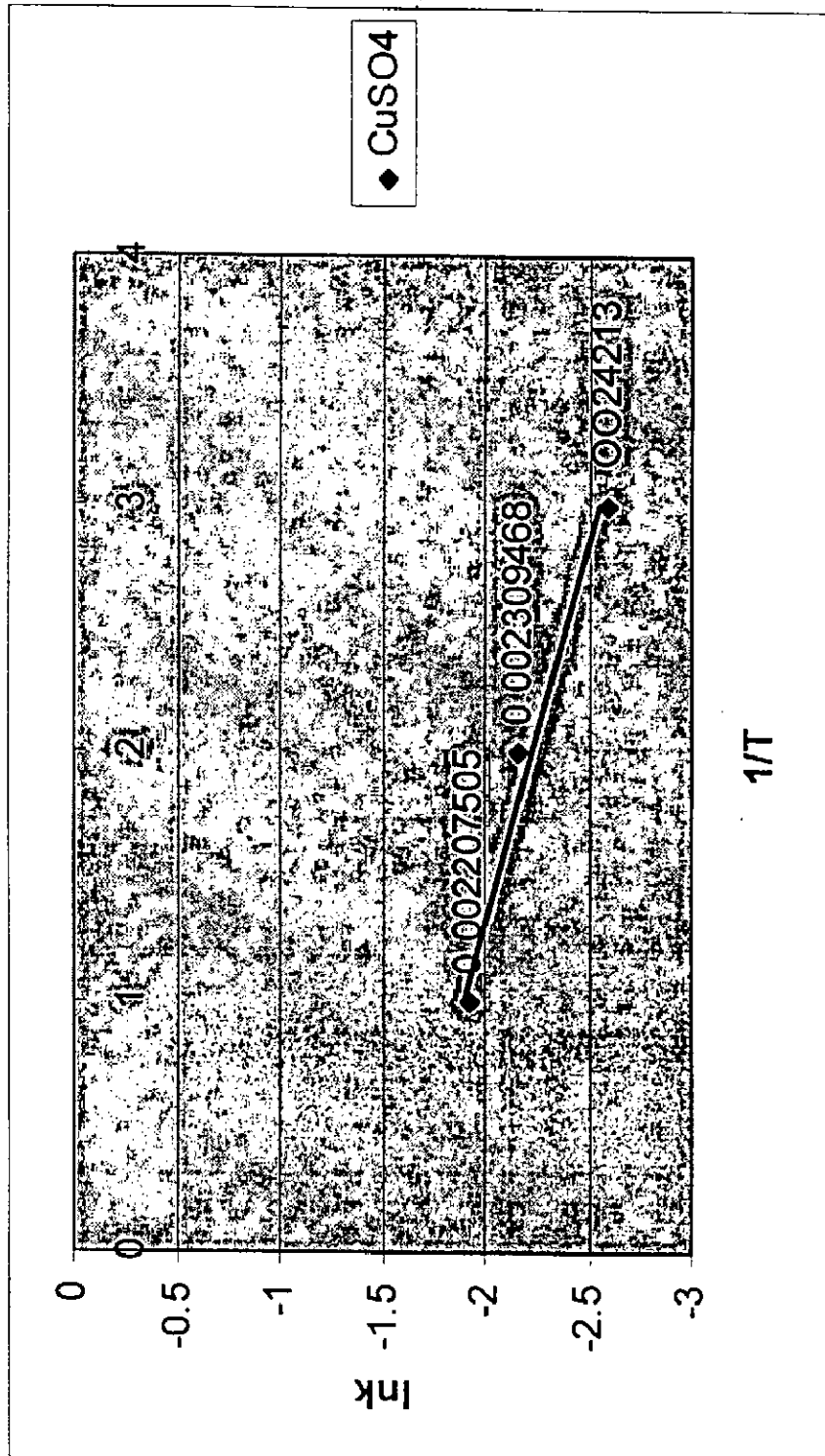


Figure 4.13 Arrhenius plot of  $\ln k$  Vs  $1/T$   
 Initial COD = 7000 mg/L, pH = 5, Pair = 4 kg/cm<sup>2</sup>  
 Catalyst : CuSO<sub>4</sub> (5 gm/L)

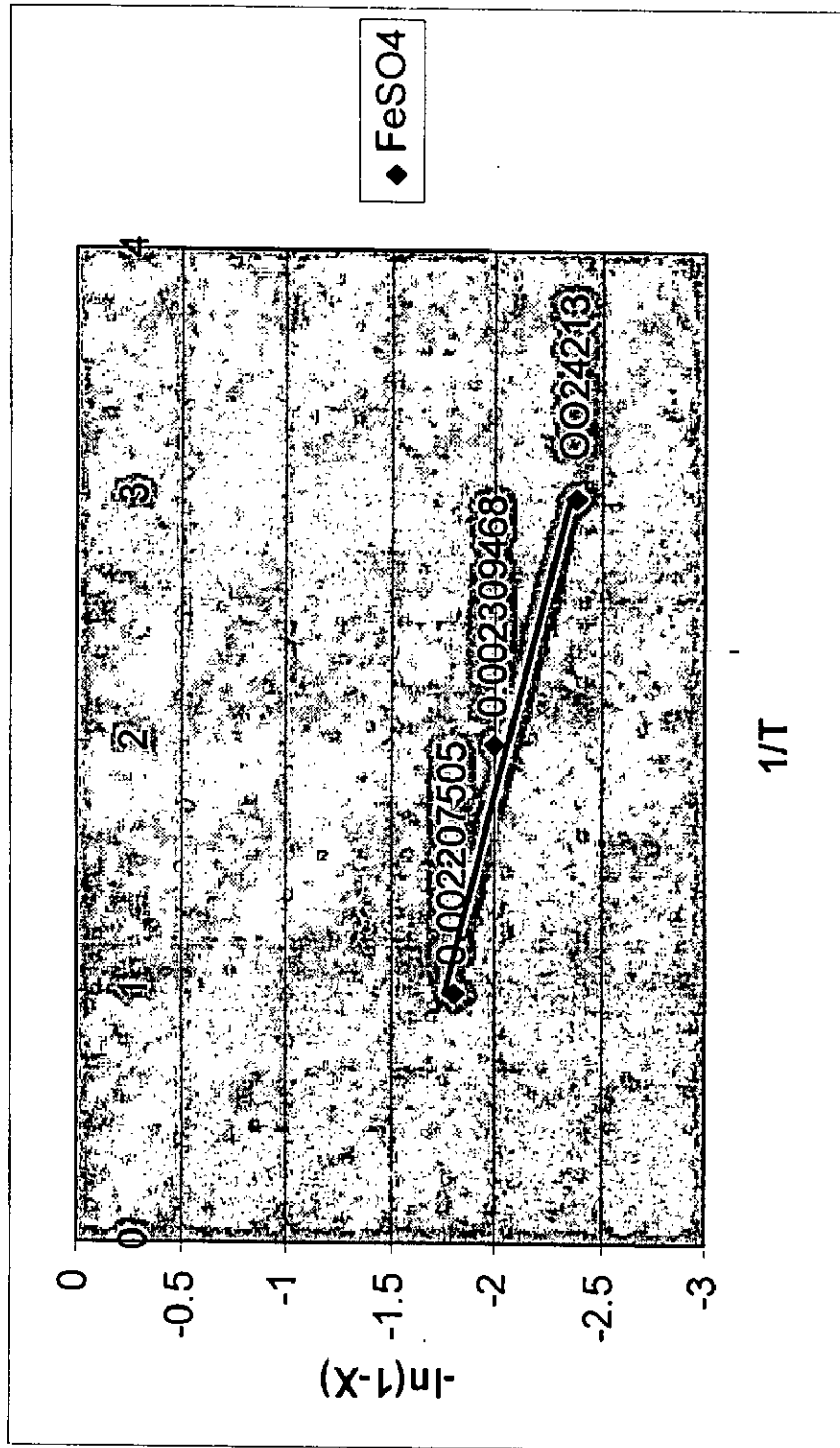


Figure 4.14 Arrhenius plot of  $\ln kVs 1/T$   
 Initial COD=7000mg/L, pH=5,  $P_{air} = 4kg/cm^2$   
 Catalyst : FeSO<sub>4</sub> (5 gm/L)



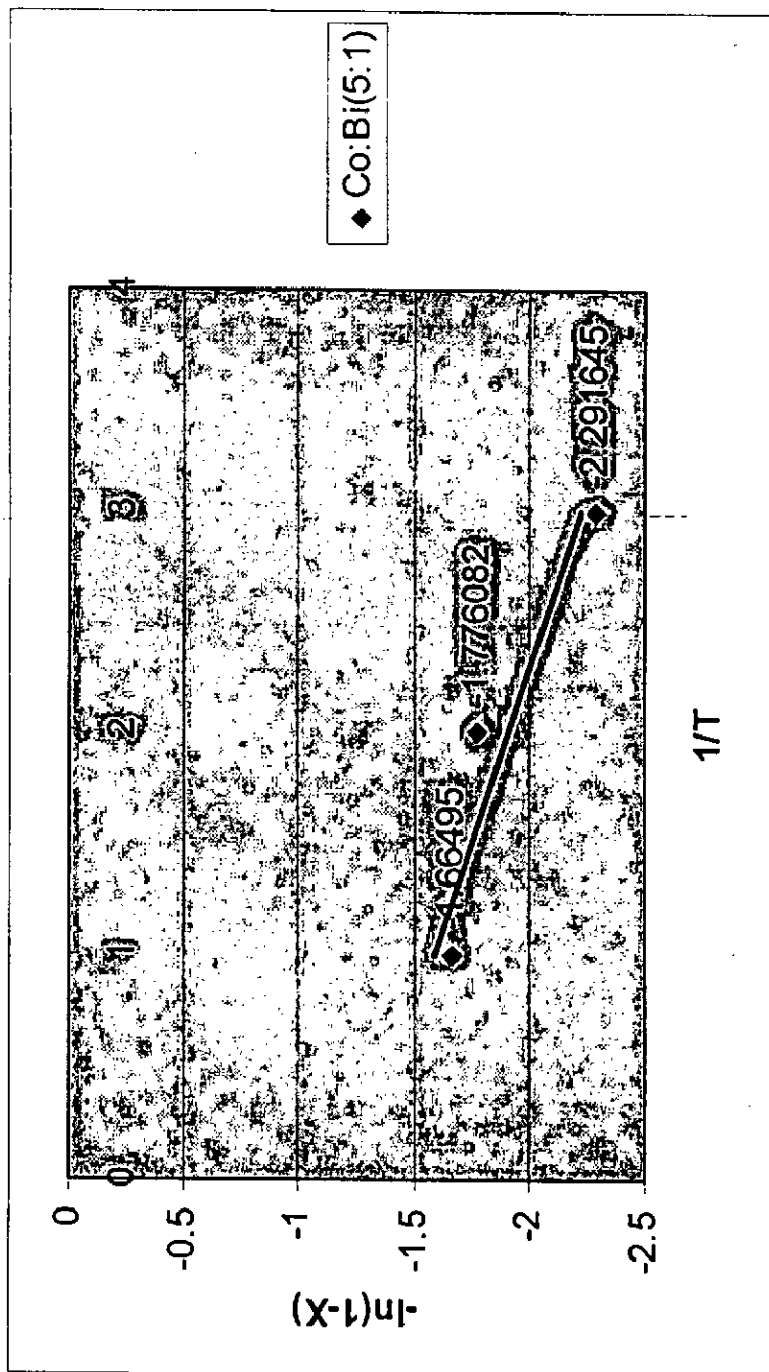


Figure 4.15 Arrhenius plot of lnVs 1/T  
 Initial COD=7000mg/L,pH=5 , P<sub>air</sub> =4kg/cm<sup>2</sup>  
 Catalyst :Co:Bi (5 gmV/L)

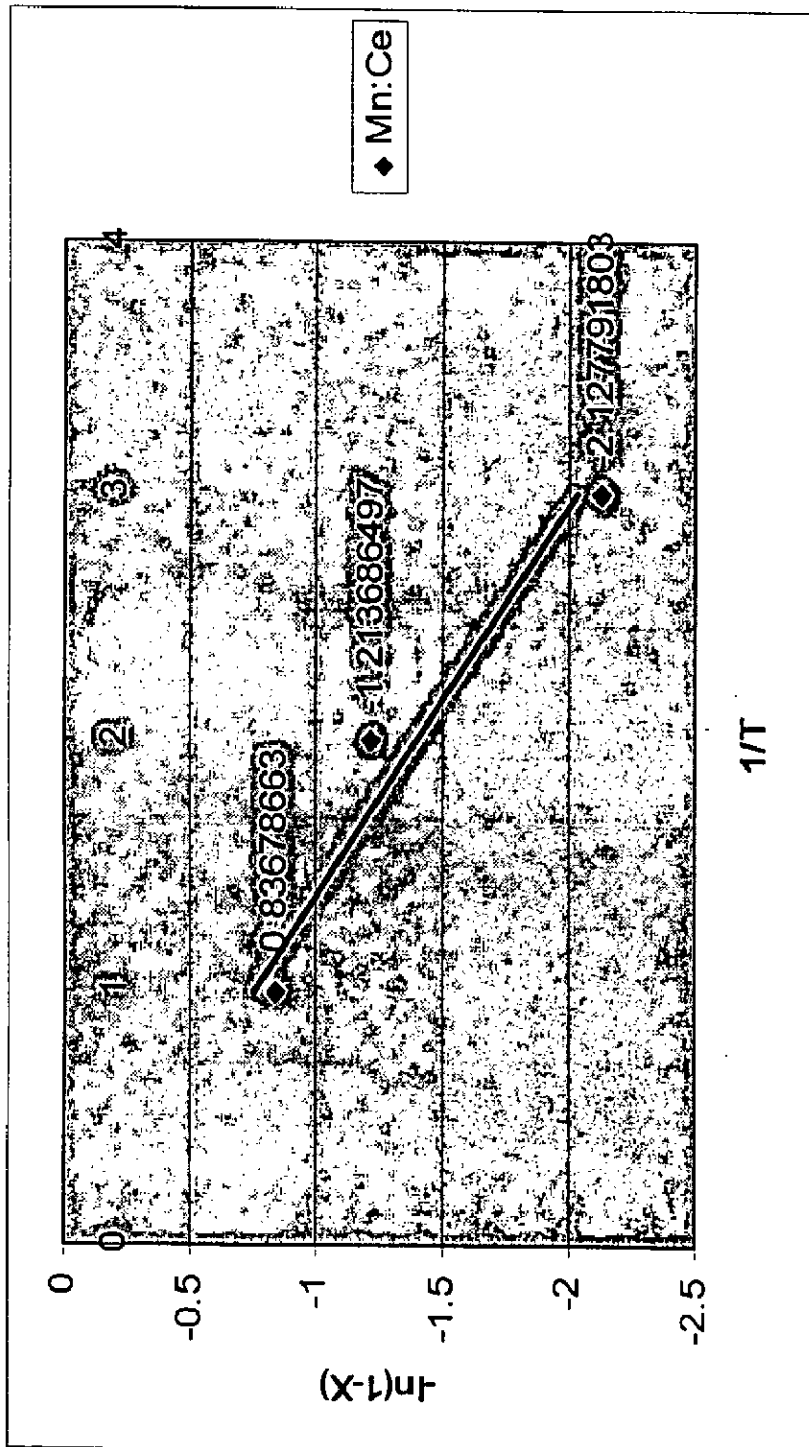


Figure 4.16 Arhenious plot of lnkVs 1/T  
 Initial COD=7000mg/L, pH=3,  $P_{air}$  =4kg/cm<sup>2</sup>  
 Catalyst : Co:Bi (5 gm/L)

## Chapter - 5

### CONCLUSIONS

The following conclusions are drawn from the present work :

- The percent COD reduction of the butyric acid was found to be a function of initial pH of the solution and temperature. It has been found that it works more effectively at a certain pH for a given individual catalyst.
- Heterogeneous catalysts were found to be more active as compared to the homogeneous catalysts. The complete solubility of homogeneous catalysts is another problem and it needs an additional step for the recovery/removal of the catalyst.
- The experimental results that were obtained at atmospheric pressure and temperature of 100°C with a reaction time of 30 hours were not encouraging (maximum 16 % removal).
- As mentioned in the literature ceria doped or based catalysts were very active. Among all the four catalysts tested ceria based catalyst [Mn: Ce (1: 1)] gave the best result.
- Maximum COD reduction of 83% was obtained with catalyst Mn : Ce (1: 1) at 180°C and 14 kg/cm<sup>2</sup> pressure after a reaction time of four hours.
- The percent COD reduction was found to increase with temperature in the range 140°C to 180°C. An increase in the temperature from 140°C to 180°C increases the % COD reduction from 40.0% to 83 % with Mn : Ce (1: 1) after 4 hour reaction time.
- The COD reduction of butyric acid followed first order kinetics . The values of activation energies, pre- exponential factors and rate constants for Mn : Ce (1 : 1) are  $k_{180} = 0.433 \text{ h}^{-1}$ ,  $E = 50378 \text{ kJ/kmol}$  and  $A = 312123$ .

## RECOMMENDATIONS FOR FUTURE WORK

1. Ceria based catalyst found to have a very good oxidative capacity . Its activity can be further improved using noble metal support . Noble metals such as Ru, Pt and Pd may be added to the best catalysts and tested
2. Fenton (Fe/ZSM-5 honeycomb model) catalyst can be tried .It worked effectively even at atmospheric conditions and low temperatures. The catalysts may be prepared by ion exchange method.
3. Effluent after WAO constitutes additional color due to catalysts . It indicates that some amount of catalyst will remain in the effluent. There is a greater necessity in treating that effluent using coagulation.
4. Ceria based catalysts are very active for WAO .This catalyst system can be tested with other carboxylic acids, which are industrially important.
5. Wet air oxidation of mixtures of several carboxylic acids such as acrylic acid, acetic acid, fumaric acid, maleic acid, caprylic acid, oleic acid etc.should be studied. Because most of the industrial effluents contains mixtures of several acids, but not found with single acid.

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