

WET AIR OXIDATION OF BENZENE

by

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and Research in Partial Fulfillment of the
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Doctorate of Philosophy



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This thesis is dedicated

to my parents,

my wife, Maram,

my daughter Jude,

&

my son Ahmed

whose true love and permanent support have enabled

me to achieve the goal I was after

ABSTRACT

Processing of petrochemical compounds produces a large amount of wastewater. This wastewater consists of toxic (hazardous) materials that can not be discharged to the environment without treatment. As restrictive environmental constraints increase, new technologies are needed to treat those toxic materials before discharging them to the environment. Wet Air Oxidation (WAO) is one of these new methods.

This study casts light on the effect of initial pH on the WAO of benzene at different temperatures and pressures. It was found that at pH 6, a temperature of 260°C and a partial pressure of oxygen of 1.38 MPa around 97% degradation was achieved in one hour. When the initial pH was lowered to 4 more than 90% degradation was achieved at 220°C and P_{O_2} of 1.38 MPa in only 15 minutes. It was concluded that the higher the temperature the better the benzene degradation, and the faster benzene degradation has been obtained with the increasing partial pressure of oxygen. The main intermediates were acetic acid and formic acid.

Furthermore, it was found that the degradation of benzene can be further enhanced in the presence of phenol. The main reason can be attributed to the effect of the free radicals generated from the fast phenol degradation. A simplified pathway for oxidation of benzene was proposed.

RÉSUMÉ

Le traitement de composants pétrochimiques produit une quantité importante d'eaux usées. Composées de matériaux toxiques, ces eaux usées ne peuvent être déversées dans la nature sans traitements additionnels. Au fur et à mesure que les contraintes environnementales augmentent, de nouvelles technologies sont indispensables afin de réduire ces matériaux dangereux; l'oxydation en phase aqueuse est l'une de ces techniques.

Cette étude s'intéresse à l'effet du pH initial sur l'oxydation en phase aqueuse du benzène à différentes températures et pressions. On note qu'à un pH de 6, une température de 260°C et une pression partielle d'oxygène P_{O_2} à 1.38 Mpa, environ 97% du benzène est oxydé en une heure. Lorsque le pH initial est diminué à 4, plus de 90% de la décomposition s'est produite en seulement 15 minutes à 220°C et à une pression partielle P_{O_2} de 1.38 Mpa. Ces résultats suggèrent que cette réaction se fait mieux à des températures plus élevées. De plus, une augmentation de la pression partielle de l'oxygène permet d'accélérer le processus. Les intermédiaires principaux de cette réaction sont l'acide acétique et l'acide formique.

En outre, on observe que la présence de phénol favorise la transformation du benzène; ceci peut être attribué aux radicaux libres générés par la décomposition rapide du phénol. Une approche simplifiée pour l'oxydation du benzène a été proposée.

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TABLE OF CONTENTS

ABSTRACT	i
RÉSUMÉ	ii
ACKNOWLEDGMENTS	iii
LIST OF FIGURES	viii
LIST OF TABLES	xiv

CHAPTER ONE

INTRODUCTION

1.1 Petrochemical Wastewater Effluent	2
1.1.1 Benzene	2
1.2 Objectives	3
1.3 Thesis Structure	4

CHAPTER TWO

LITERATURE REVIEW

2.1 WAO of Organic Compounds	5
2.1.1 WAO of Phenol	5
2.1.2 WAO of Formic Acid and Acetic Acid	6
2.2 Free Radical Mechanism	8
2.2.1 Induction Period	10
2.3 Effect of the Initial pH on the WAO	11
2.4 Wet Air Oxidation Enhancements	12

CHAPTER THREE

Experimental Setup and Procedure

3.1 Apparatus	15
3.2 Materials	17
3.3 Experimental Procedures	18
3.4 Analytical Methods	19
3.4.1 Gas Chromatography Analysis	19
3.4.1.1 Gas Chromatography Method	20
3.4.1.2 Calibration of the GC	21
3.4.2 Ion Chromatography	21
3.4.2.1 Ion Chromatography Method	22
3.4.2.2 Repeatability of the IC	22
3.4.3 Total Organic Compound Measurement	23
3.4.3.1 TOC Method	23

CHAPTER FOUR

RESULTS AND DISCUSSIONS

WET AIR OXIDATION OF BENZENE

4.1 Experiments with Benzene in the Absence of Oxygen	25
4.2 Chemical Oxygen Demand Measurements	26
4.3 Repeatability of the Results	26
4.4 Influence of pH on Benzene Degradation	28
4.4.1 Effect of Temperature on Degradation of Benzene at pH 6	32
4.4.2 Effect of Oxygen Pressure on Benzene Degradation at pH 6	36

4.4.3 Effect of Temperature on the Benzene Degradation at pH 5	38
4.4.4 Effect of the Oxygen Pressure on Benzene Degradation at pH 5	39
4.4.5 Effect of Temperature on Benzene Degradation at pH 4	40
4.4.6 Effect of the Oxygen Pressure on the Benzene Degradation at pH 4	42
4.4.7 The pH Fluctuation during the Experiments	45
4.4.8 Effect of Acidification Methods on the Degradation of Benzene	46
4.5 Effect of Initial Benzene Concentration on its Degradation	48
4.6 Kinetic Modeling	51

CHAPTER FIVE

RESULTS AND DISCUSSION

REACTION INTERMEDIATES

5.1 Total Organic Carbon Measurements	62
5.2 Effect of Temperature on the Production and Degradation of both Acetic Acid and Formic Acid	69
5.3 Effect of Oxygen Pressure on the Production and Degradation of both Acetic Acid and Formic Acid	72
5.4 Effect of pH on Acetic and Formic Acids	77
5.4.1 Effect of Acidification Methods on the Intermediates	81
5.5 Effect of Initial Benzene Concentration on Both Acetic and Formic Acids	83
5.6 Wet Air Oxidation of Both Acetic and Formic Acids	84
5.7 Repeatability of the Results	86

CHAPTER SIX
RESULTS AND DISCUSSIONS
WET AIR OXIDATION OF BENZENE ENHANCED BY
PHENOL

6.1 Wet Air Oxidation of Phenol in Absence of Benzene	91
6.2 Wet Air Oxidation of Benzene in Presence of Phenol	94
6.2.1 Effect of the Initial Phenol Concentration on Benzene Degradation	95
6.2.2 Effect of Temperature on the Benzene Degradation	97
6.2.3 Effect of Benzene on the Phenol Oxidation	99
6.3 Reaction Kinetics of Benzene Oxidation	101
6.4 Repeatability of the Experiments	103
6.5 Proposed Simplified Pathway for Oxidation of Benzene	104

CHAPTER SEVEN
CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions	106
7.2 Recommendations for future work	108
7.3 Contributions to Knowledge	109
REFERENCES	110

APPENDICES

Appendix A: Calculation of Oxygen Pressure Needed	119
Appendix B: Oxygen Solubility in Water	120
Appendix C: Calculation of Theoretical Amount of Carbon Dioxide Generated	121

LIST OF FIGURES

		Page
Figure 3.1	Schematic Diagram of the Experimental Setup	16
Figure 3.2	Schematic Diagram for the Reactor, ID = 8.2 cm, OD = 11.2 cm, L = 23.0 cm	17
Figure 3.3	Upper View for the Cap	17
Figure 4.1	Repeatability of Data from Two Experiments at 220°C, P _{O2} = 1.38 MPa, pH=4.	27
Figure 4.2	Repeatability of Data from Two Experiments at 240°C, P _{O2} = 1.38 MPa, pH=4.	27
Figure 4.3	Repeatability of Data from Two Experiments at 260°C, P _{O2} = 1.38 MPa, pH=4.	28
Figure 4.4	Effect of pH on Benzene Degradation at 190°C, P _{O2} = 1.38 MPa	29
Figure 4.5	Effect of pH on the Benzene Degradation at 220°C, P _{O2} = 1.38 MPa	30
Figure 4.6	Effect of pH on the Benzene Degradation at 240°C, P _{O2} = 1.38 MPa	31
Figure 4.7	Effect of pH on the Benzene Degradation at 260°C, P _{O2} = 1.38 MPa	31
Figure 4.8	Degradation of Benzene at Different Temperatures, P _{O2} = 1.38 MPa, pH= 6	33
Figure 4.9	Repeatability of Data from Two Experiments at 240°C, P _{O2} = 1.38 MPa, pH= 6	33
Figure 4.10	Degradation of Benzene at 200°C, P _{O2} = 1.38 MPa, pH= 6	34
Figure 4.11	Degradation of Benzene at 210°C, P _{O2} = 1.38 MPa, pH= 6.	34
Figure 4.12	Degradation of Benzene at Different Temperatures, P _{O2} = 1.38 MPa, pH=6	35
Figure 4.13	Degradation of Benzene at Different Oxygen Pressure, T= 260°C, pH=6	36

Figure 4.14	Effect of Oxygen Pressure on the Benzene Degradation at 260°C, pH=6	37
Figure 4.15	Effect of Temperature on the Benzene Degradation at pH 5, P _{O2} = 1.38 MPa	38
Figure 4.16	Effect of Oxygen Pressure on the Benzene Degradation at pH 5	39
Figure 4.17	Effect of Temperature on the Benzene Degradation at 1.03 MPa, pH= 4	41
Figure 4.18	Effect of Temperature on the Benzene Degradation at 1.38 MPa, pH= 4	41
Figure 4.19	Effect of Temperature on the Benzene Degradation at 1.72 MPa, pH= 4	42
Figure 4.20	Effect of Oxygen Pressure on the Benzene Degradation at 220°C, pH 4	44
Figure 4.21	Effect of Oxygen Pressure on the Benzene Degradation at 240°C, pH 4	44
Figure 4.22	Effect of Oxygen Pressure on the Benzene Degradation at 260°C, pH 4	45
Figure 4.23	Change of pH with Time during Experiment, P _{O2} = 1.38 MPa, Initial Benzene Concentration = 5.63 mmol/L	46
Figure 4.24	Degradation of Benzene with Sulfuric Acid at 220°C, P _{O2} = 1.38 MPa, pH=4	47
Figure 4.25	Degradation of Benzene at 240°C, P _{O2} = 1.38 MPa, pH=4	47
Figure 4.26	Degradation of Benzene at 260°C, P _{O2} = 2.07 MPa, pH= 6, Initial Benzene Concentration = 11.25 mmol/L	49
Figure 4.27	Degradation of Benzene at 260°C, P _{O2} = 2.07 MPa, pH= 6, Initial Benzene Concentration = 16.88 mmol/L	49
Figure 4.28	Effect of Temperature on Benzene Degradation, P _{O2} = 2.76 MPa, pH=4, Initial Benzene Concentration of 11.25 mmol/L	50
Figure 4.29	Change of pH with Time during Experiment, T= 220°C, P _{O2} = 2.76 MPa, Initial Benzene Concentration = 11.25 mmol/L	50
Figure 4.30	First Order Kinetic Model Fit of Benzene Degradation, T=220°C, P _{O2} =0.69 MPa, pH= 4	51
Figure 4.31	First Order Kinetic Model Fit of Benzene Degradation, T=220°C, P _{O2} =0.86 MPa, pH= 4	52

Figure 4.32	First Order Kinetic Model Fit of Benzene Degradation, $T=220^{\circ}\text{C}$, $P_{\text{O}_2}=1.03\text{ MPa}$, $\text{pH}=4$	52
Figure 4.33	First Order Kinetic Model Fit of Benzene Degradation, $T=220^{\circ}\text{C}$, $P_{\text{O}_2}=1.38\text{ MPa}$, $\text{pH}=4$	53
Figure 4.34	First Order Kinetic Model Fit of Benzene Degradation, $T=220^{\circ}\text{C}$, $P_{\text{O}_2}=1.72\text{ MPa}$, $\text{pH}=4$	53
Figure 4.35	First Order Kinetic Model Fit of Benzene Degradation, $T=240^{\circ}\text{C}$, $P_{\text{O}_2}=1.03\text{ MPa}$, $\text{pH}=4$	54
Figure 4.36	First Order Kinetic Model Fit of Benzene Degradation, $T=240^{\circ}\text{C}$, $P_{\text{O}_2}=1.38\text{ MPa}$, $\text{pH}=4$	55
Figure 4.37	First Order Kinetic Model Fit of Benzene Degradation, $T=240^{\circ}\text{C}$, $P_{\text{O}_2}=1.72\text{ MPa}$, $\text{pH}=4$	55
Figure 4.38	First Order Kinetic Model Fit of Benzene Degradation, $T=260^{\circ}\text{C}$, $P_{\text{O}_2}=1.03\text{ MPa}$, $\text{pH}=4$	56
Figure 4.39	First Order Kinetic Model Fit of Benzene Degradation, $T=260^{\circ}\text{C}$, $P_{\text{O}_2}=1.38\text{ MPa}$, $\text{pH}=4$	56
Figure 4.40	First Order Kinetic Model Fit of Benzene Degradation, $T=260^{\circ}\text{C}$, $P_{\text{O}_2}=1.72\text{ MPa}$, $\text{pH}=4$	57
Figure 4.41	k' vs. P_{O_2} , $T=220^{\circ}\text{C}$, $\text{pH}=4$	58
Figure 4.42	k' vs. P_{O_2} , $T=240^{\circ}\text{C}$, $\text{pH}=4$	59
Figure 4.43	k' vs. P_{O_2} , $T=260^{\circ}\text{C}$, $\text{pH}=4$	59
Figure 4.44	Arrhenius Plot for Oxidation of Benzene, $\text{pH}=4$	60
Figure 5.1	TOC Reduction with Time, $P_{\text{O}_2}=1.38\text{ MPa}$, $\text{pH}=6$	63
Figure 5.2	Detailed Change in Carbon Concentration with Time, $T=220^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{ MPa}$	64
Figure 5.3	Detailed Change in Carbon Concentration with Time, $T=240^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{ MPa}$	64
Figure 5.4	Detailed Change in Carbon Concentration with Time, $T=260^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{ MPa}$	65
Figure 5.5	Carbon Balance, $T=220^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{ MPa}$	65

Figure 5.6	Carbon Balance, T=240°C, pH=6, P _{O2} =1.38 MPa	66
Figure 5.7	Carbon Balance, T=260°C, pH=6, P _{O2} =1.38 MPa	66
Figure 5.8	Repeatability of Carbon Balance, T=220°C, pH=6, P _{O2} =1.38 MPa	67
Figure 5.9	Repeatability of Carbon Balance, T=240°C, pH=6, P _{O2} =1.38 MPa	67
Figure 5.10	Repeatability of Carbon Balance, T=260°C, pH=6, P _{O2} =1.38 MPa	68
Figure 5.11	Effect of Temperature on Acetic Acid, P _{O2} = 1.38 MPa, pH=6	70
Figure 5.12	Effect of Temperature on Acetic Acid, P _{O2} = 1.38 MPa, pH=4	70
Figure 5.13	Effect of Temperature on Formic Acid, P _{O2} = 1.38 MPa, pH=6	71
Figure 5.14	Effect of Temperature on Formic Acid, P _{O2} = 1.38 MPa, pH=4	72
Figure 5.15	Effect of Pressure on Acetic Acid T= 260°C, pH=6	73
Figure 5.16	Effect of Pressure on Formic Acid, T= 260°C, pH=6	73
Figure 5.17	Effect of Pressure on Acetic Acid, T= 220°C, pH=4	74
Figure 5.18	Effect of Pressure on Acetic Acid, T= 240°C, pH=4	74
Figure 5.19	Effect of Pressure on Acetic Acid, T= 260°C, pH=4	75
Figure 5.20	Effect of Pressure on Formic Acid, T= 220°C, pH=4	76
Figure 5.21	Effect of Pressure on Formic Acid, T= 240°C, pH=4	76
Figure 5.22	Effect of Pressure on Formic Acid, T= 260°C, pH=4	77
Figure 5.23	Effect of pH on Acetic Acid, T= 220°C, pH= 4, P _{O2} = 1.38 MPa	78

Figure 5.24	Effect of pH on Formic Acid, T= 220°C, pH= 4, P _{O2} = 1.38 MPa	79
Figure 5.25	Effect of pH on Acetic Acid, T= 240°C, pH= 4, P _{O2} = 1.38 MPa	79
Figure 5.26	Effect of pH on Formic Acid, T= 240°C, pH= 4, P _{O2} = 1.38 MPa	80
Figure 5.27	Effect of pH on Acetic Acid, T= 260°C, pH= 4, P _{O2} = 1.38 MPa	80
Figure 5.28	Effect of pH on Formic Acid, T= 260°C, pH= 4, P _{O2} = 1.38 MPa	81
Figure 5.29	Effect of Acidification Methods on Acetic Acid, T= 220°C, P _{O2} = 1.38 MPa, pH=4	82
Figure 5.30	Effect of Acidification Methods on Formic Acid, T= 220°C, P _{O2} = 1.38 MPa, pH=4	82
Figure 5.31	Effect of Temperature on Acetic Acid, P _{O2} = 2.76 MPa, pH=4, Initial Benzene Concentration = 11.3 mmol/L	83
Figure 5.32	Effect of Temperature on Formic Acid, P _{O2} = 2.76 MPa, pH=4	84
Figure 5.33	Degradation of Acetic Acid, T= 260°C, P _{O2} =2.07 MPa	85
Figure 5.34	Acetic acid profile for replicates, T=220°C, P _{O2} , 1.38 MPa, pH=4	87
Figure 5.35	Acetic acid profile for replicates, T=240°C, P _{O2} , 1.38 MPa, pH=4	87
Figure 5.36	Acetic acid profile for replicates, T=260°C, P _{O2} , 1.72 MPa, pH=4	88
Figure 5.37	Formic acid profile for replicates, T=220°C, P _{O2} , 1.38 MPa, pH=4	88
Figure 5.38	Formic acid profile for replicates, T=240°C, P _{O2} , 1.38 MPa, pH=4	89
Figure 5.39	Formic acid profile for replicates, T=260°C, P _{O2} , 1.72 MPa, pH=4	89
Figure 6.1	Acetic Acid and Formic Acid Profile, T= 220°C, P _{O2} =2.07 MPa, pH= 4. Initial Phenol Concentration= 500mg/L	92
Figure 6.2	Acetic Acid and Formic Acid Profile, T= 220°C, P _{O2} =1.38 MPa, pH= 6. Initial Phenol Concentration= 500mg/L	93

Figure 6.3	Acetic Acid and Formic Acid Profile, T= 220°C, P _{O2} =0.51 MPa, pH= 4. Initial Phenol Concentration= 200mg/L	93
Figure 6.4	Degradation of Benzene at 220°C, P _{O2} = 1.72 MPa	94
Figure 6.5	Degradation of Phenol at 220°C, P _{O2} = 1.72 MPa	95
Figure 6.6	Degradation of Benzene at Different Initial Phenol Concentrations, T=220°C, 100% Excess O ₂ , Initial pH= 6	96
Figure 6.7	Degradation of Benzene at Different Initial Phenol Concentrations, T=200°C, 100% Excess O ₂ , Initial pH= 6	97
Figure 6.8	Degradation of Benzene at Different Temperatures, 100% Excess O ₂ , Initial Phenol Concentration= 0.27 mmol/L, Initial pH= 6	98
Figure 6.9	Degradation of Benzene at Different Temperatures, 100% Excess O ₂ , Initial Phenol Concentration= 0.53 mmol/L, Initial pH= 6	99
Figure 6.10	Normalized concentration of Phenol with Time, 100% Excess O ₂ , Initial pH=6, Initial Phenol Concentration= 0.53 mmol/L	100
Figure 6.11	Normalized concentration of Phenol with Time, 100% Excess O ₂ , Initial pH=6, Initial Phenol Concentration= 0.27 mmol/L	101
Figure 6.12	Pseudo First Order Kinetic Plot for Benzene	102
Figure 6.13	Arrhenius Plot for Pseudo First Order Rate Constant Calculated from Benzene Removal Data	102
Figure 6.14	Repeatability of Benzene Result at 220°C, 100% Excess O ₂ , Initial pH= 6, Initial Phenol Concentration= 0.27 mmol/L	103
Figure 6.15	Repeatability of Phenol Result at 220°C, 100% Excess O ₂ , Initial pH= 6, Initial Phenol Concentration= 0.27 mmol/L	104
Figure 6.16	Simplified Pathway for Oxidation of Benzene	105

LIST OF TABLES

Page

Table 4.1	Solubility of Oxygen in Water at Different Temperatures	43
Table 4.2	k' Values at Different P_{O_2} for the Fast Step, $T=220^{\circ}\text{C}$	54
Table 4.3	k' Values at Different P_{O_2} for the Fast Step, $T=240^{\circ}\text{C}$	57
Table 4.4	k' Values at Different P_{O_2} for the Fast Step, $T=260^{\circ}\text{C}$	58
Table 4.5	Rate Constant Value at Different Temperatures	60
Table 5.1	Carbon Dioxide Measurement, $\text{pH}=6$, $P_{O_2}=1.38\text{ MPa}$	69
Table 5.2	Effect of Temperature on Formic Acid	86
Table 5.3	Concentration of Formic Acid at Different Temperatures	86
Table 6.1	Degradation of Phenol at 220°C	92

CHAPTER ONE

INTRODUCTION

Processing of organic compounds produces a large amount of wastewater, which consists of toxic (hazardous) materials that cannot be discharged to the environment without treatment. As restrictive environmental constraints increase, new technologies are needed to treat those toxic materials before discharging them to the environment. Wet Air Oxidation (WAO) is one of these methods. It is defined as the oxidation of soluble or suspended oxidizable components in an aqueous environment using either pure oxygen or air as an oxidizing agent at elevated temperature and pressure. It is a very attractive method for wastewater treatment, especially when the effluent is too dilute for incineration, and either too toxic or concentrated for biological treatment. Typically, WAO takes place at a temperature range of 125-320°C and at a pressure range of 0.5-30 MPa. The residence time ranges between 15 and 120 minutes. The need of the high pressure is to maintain the liquid phase at the elevated temperatures. The final products in this method are water, carbon dioxide and low molecular weight organics. The overall reaction for organic materials can be expressed as:



WAO has several advantages and disadvantages. Some of the advantages are as follows: It can treat more than one chemical compound at the same time; it is environmentally friendly since the destruction of the wastes is in the liquid phase and in comparison to incineration, no nitrogen oxides are generated. Finally, it does not need a dewatering step as a pretreatment. On the other hand, there are some disadvantages associated with the WAO. It is limited to wastes that contain oxidizable organic and

inorganic compounds. Also, it is costly since it involves both high temperatures and pressures.

1.1 Petrochemical Wastewater Effluent

The waste effluents from the petrochemical industries contain a large amount of various organic compounds which cannot be discharged to the environment without treatment. Among the many available methods, activated sludge treatment is the most widely used because of its simplicity and low cost [47]. However, it can not be used for highly concentrated wastes due to a low biodegradability and inhibitory effects of the organic compounds [50]. For the wastewaters containing phenol and phenolic compounds which are very common in petrochemical industries, solvent extraction is an economical method if the concentration of these compounds is high (i.e. over 1%) [12, 22]. If the concentration is low, biological treatment is the appropriate method. Finally, incineration can be an economically attractive alternative although it is limited only for concentrated wastes and it contributes to air pollution.

1.1.1 Benzene

Benzene (C_6H_6) is an aromatic hydrocarbon with a molecular weight of 78.1 g/mol. It is a clear, colorless liquid that is volatile and highly flammable. Its water solubility is about 1750 mg/L at 25°C [5]. It is known to be a carcinogenic compound [23] and is usually found in the wastewater effluents of the petrochemical industries. A strong association between leukemia and modest benzene exposure greater than 16 mg/L per year has been demonstrated [21]. Effluents that contain benzene can not be discharged to

the environment without further treatment in order to remove benzene, which is very harmful to the environment even at very low concentrations. While the exposure limit for drinking water to benzene is set to be 5 $\mu\text{g/L}$ in the United States, it is set to be 25 $\mu\text{g/L}$ in Canada [35]. Benzene is known to be a very refractory compound; that is very difficult to oxidize. While the aerobic benzene biodegradation has been observed since the 1950's, the anaerobic benzene degradation was only discovered on 1980 by Ward *et al.* [68] and since then much attention was given to it, especially when an extensive anaerobic zone was developed by soils and sediments contaminated with benzene [1,9,43]. Coates *et al.* [10] were the first group to report the isolation of two *Dechloromonas* strains that can completely degrade the benzene anaerobically under nitrate reducing conditions. There has been no single publication available that deals with the wet air oxidation of benzene.

1.2 Objectives

The objectives of this study were as follows:

- To study the effect of initial pH on the wet air oxidation of benzene at different temperatures and pressures, hence to find the optimum conditions at which the benzene will be degraded.
- To determine the main intermediates that resulted from benzene degradation.
- To study the kinetics of benzene degradation.
- To study the degradation of benzene in the presence of phenol which is known to be a common component in many of the wastewater streams.
- To study the kinetics of benzene degradation enhanced by phenol.

1.3 Thesis Structure

This thesis casts light on the wet air oxidation of benzene. The literature about the wet air oxidation of some of the organic components that exist in the wastewater from petrochemical industries will be reviewed in chapter 2.

Chapter 3 summarizes the experimental methods that were utilized in this study. A detailed description of the experimental setup, materials, procedures and analytical methods used for analysis is presented. In Chapter 4, the results for benzene degradation are presented. The influence of pH on benzene degradation at different temperatures and pressures is discussed. The kinetic modeling for benzene removal is presented.

Chapter 5 deals with the results that have been obtained regarding the reaction intermediates. Total Organic Carbon (TOC) measurements are presented. Effect of temperature, pressure and pH on both, production and degradation of intermediates, is discussed. WAO for acetic acid and formic acid is presented.

The WAO of benzene enhanced by phenol is presented in Chapter 6. The effect of the initial phenol concentration on benzene degradation is shown. The effect of temperature on the benzene degradation is discussed. The effect of benzene on the oxidation of phenol is presented. Reaction kinetics of benzene oxidation enhanced by phenol is presented. The simplified pathway for benzene oxidation is presented.

The general conclusions, recommendations for future work and contributions to knowledge are presented in Chapter 7.

CHAPTER TWO

LITERATURE REVIEW

During the last decades, WAO has been the subject of intensive studies in both chemical and environmental engineering literature. The most important applications are in municipal sewage sludge treatment, industrial wastewater treatment, carbon regeneration, and pulping spent liquors. Many of the studies that have been reported in the literature dealt with both phenol and carboxylic acids. [6,48]

2.1 WAO of Organic Compounds

Numerous studies have been done on the WAO of organic compounds. Phenol in particular was a subject of considerable interest since it is found in the wastewater of many industries such as the petrochemicals, plastics and pulp and paper industries. Also, numerous studies have been done on the wet air oxidation of the carboxylic acids since they are the main intermediates during the wet air oxidation of the other organic compounds, and they are usually difficult to oxidize.

2.1.1 WAO of Phenol

Phenol is considered to be one of the most common and important pollutants that can be found in the effluent streams of most chemical plants. It is highly toxic even at low concentrations and therefore wastewaters that contain phenol should be treated before they can be discharged to environment. WAO is an effective method for the treatment of effluents containing phenol. Some researchers studied the degradation of phenol while

the others were more concerned about the environment and therefore studied the COD reduction instead. Joglekar *et al.* [33] studied the WAO of phenol in the temperature range of 150-180°C and oxygen partial pressure from 0.3 to 1.5 MPa, and reported that more than 90% COD reduction was achieved, while Lin and Chuang [39] reached 100% COD reduction at an oxygen partial pressure of 10.3 MPa and 300°C. Kolaczowski *et al.* [36] showed that more than 95% phenol degradation was achieved in less than 30 minutes at 200°C and total pressure of 3.0 MPa. Portela Miguelez [52] studied the WAO of phenol and achieved around 100% degradation at 300°C and a total pressure of 10 MPa in less than 10 minutes. Imamura [24] studied the degradation of phenol at 220°C and oxygen partial pressure of 3MPa. The COD and TOC reduction achieved in two hours were 93% and 88%, respectively. Complete phenol degradation was achieved in 10 minutes at 220°C and 10.15MPa in the study that has been done by Vicente *et al.* [66]. Vaidya and Mahajani [64] reported more than 90% COD reduction in 30 minutes at 230°C and oxygen partial pressure of 0.69 MPa in their study of WAO of phenol.

In summary, the WAO of phenol was studied at a temperature range between 150 to 300°C and oxygen partial pressure range between 0.3 to 10.3 MPa. It was found that considerable phenol degradation can be achieved even at mild temperatures.

2.1.2 WAO of Formic Acid and Acetic Acid

Low molecular weight carboxylic acids, especially acetic acid, are resistant to oxidation [26,29,30,31]. They are either originally found in the waste or generated as intermediates during the WAO of various waste streams, and they accumulate at the latter stages of WAO [3,4,17,18,19,34,72], hence becoming a major limitation of the process.

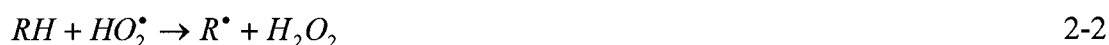
Many studies that deal with the oxidation of the mono-and dicarboxylic acids were carried out with the main aim being the determination of the kinetic parameters together with TOC and COD removal. Most of the studies were done using a temperature in the range of 230-290°C, and a pressure of 0.35-12.8 MPa [48]. Chowdary and Copa [8] achieved 98.3% reduction of formic acid at 300°C in 60 minutes. Shendi and Mahajani [59] studied the WAO of formic acid in the temperature range 150-240°C and partial oxygen pressure of 0.69 MPa. Their results showed 12.92% and 95% COD reduction at 150°C and 240°C, respectively. Shendi and Levec [58] studied the wet oxidation kinetic of some refractory low molecular mass carboxylic acids. While only 24% formic acid degradation was achieved in 2 hours at 240°C and 0.8 MPa of partial oxygen pressure, around 90 % degradation was achieved at 270°C.

For the acetic acid, 9% degradation was achieved at 300°C and partial oxygen pressure of 6 MPa while 20% degradation was achieved at 320°C and partial oxygen pressure of 3 MPa. The methyl group which is an electron donor to the carbon having =O and -OH group is the main cause for the high stability of acetic acid [58]. While Imamura *et al.* [25] showed only 24.9% TOC reduction at 150°C and an oxygen pressure of 1 MPa in 1 hour, 42.0% TOC removal was achieved for acetic acid when the temperature was increased to 247°C [28]. The wet air oxidation of acetic acid was studied by Merchant [46] and it was found that only 7% COD reduction was achieved at 275°C in 5 hours. The WAO of both formic acid and acetic acid were studied by Imamura [24] at 220°C and partial oxygen pressure of 3 MPa in 2 hours. 99% TOC reduction and 100% COD reduction was achieved for formic acid while only 4% TOC reduction and 10% COD reduction were achieved for acetic acid.

In summary, the wet air oxidation of acetic and formic acids was studied at a temperature range between 150 to 320°C and an oxygen pressure range between 0.35 to 12.8 MPa. It can be concluded that while the formic acid was easily degraded, the acetic acid was resistant to oxidation and in most cases stayed as a final product.

2.2 Free Radical Mechanism

The destruction of the organic compounds in the WAO method follows a free-radical mechanism [38]. The free radical mechanism has been proposed by many researchers [13,16,32,39,45,51,54,67]; however, only a few of them supported that by direct experimental evidence [6]. In the absence of initiators, free radicals are formed by the reaction of oxygen with the weakest C-H bonds of the oxidized organic compound as follows:



where R denotes the organic functional group. In the case of phenol, the reaction of oxygen with the O-H bond may also form free radicals. The hydrogen peroxide decomposes to generate hydroxyl radicals. The oxidation of the organic compound by hydroxyl radicals follows a hydrogen abstraction mechanism as shown in equation 2-4.



The organic radical R^\bullet then reacts with oxygen to form an organic peroxy radical (ROO^\bullet) which further abstracts hydrogen atom from the organic compound to produce an organic hydroperoxide ($ROOH$) and another organic radical.



The organic hydroperoxides, which are formed are relatively unstable and decompose to intermediates with lower carbon numbers. These reactions continue rapidly until the formation of the acetic and formic acid which will eventually be converted to carbon dioxide and water [38].

Robert *et al.* [56] is the only one who provided a direct experimental evidence of free radical intermediates under typical WO conditions when they studied the wet oxidation of cellulose. In their study, the (HO^\bullet) hydroxyl radical that is a free radical intermediate proposed by many researchers was identified. On the other hand, there are some indirect methods to determine the free radical reactions. The co-oxidation is one of these methods. In this method the free radicals that are produced from an easily oxidizable compound are used to initiate the oxidation of more refractory compounds [6]. In his study of WO of sodium malonate in highly alkaline solution, Tardio [61] used this method to determine the presence of free radical intermediates. Imamura also reported this method in his study of the wet oxidation of Polyethylene glycols (PEG's).

Some researchers used a free radical initiator to enhance the oxidation. Rivas *et al.* [55] showed that the addition of hydrogen peroxide not only significantly enhanced the wet air oxidation of phenol but also eliminated the induction time period experienced

during the conventional wet air oxidation at mild conditions. Rivas *et al.* [53] in their study about the wet air oxidation of landfill leachates tried both hydrogen peroxide and Oxone as free radical promoters. They showed that the additions of those promoters enhanced the COD reduction. Using free radical reaction inhibitors is another indirect method to determine free radical reactions. Vaidya and Mahajani [64] showed that by using t-butanol, which is known to be a free radical inhibitor, the degradation rate of phenol was decreased.

2.2.1 Induction Period

The induction period, which is typical of free radical reactions, is defined as the time needed for the free radicals to be generated in a sufficient concentration [69]. Willms *et al.* [70] studied the WAO of both m-xylene and phenol at a temperature range between 27 to 227°C and a total pressure range between 7-14 MPa. They found that the oxidation reactions of both compounds are characterized by an induction period during which no reaction was noticed. They reported that the induction time was inversely proportional to the dissolved oxygen concentration. The induction period was also observed for phenol by Joglekar *et al.* [33]. Their study was conducted in temperature range between 150-180°C and oxygen partial pressures range between 0.3 to 1.5 MPa and initial phenol concentration was 200 mg/L. Portela Miguelez *et al.* [52] studied the wet air oxidation of phenol in a batch reactor at temperatures between 150-300°C and pressures from 10 to 20 MPa, while the initial oxygen concentration was always above 800% excess. They found that the induction time was over 1 hour at 150°C and it decreased with the increase of the temperature until it almost disappeared at 300°C. Thomsen [62] in his study about the

degradation of quinoline by wet oxidation found that the temperature has a dramatic effect on the induction period. While the induction time was 45 minutes at 220°C, it was less than 10 minutes when the temperature was increased to 240°C. These studies showed the significant effect of the temperature on the induction period.

2.3 Effect of the Initial pH on the WAO

The initial pH has a significant effect on both the WAO reaction rate and pathway [36]. However, the operating pH, which is different than the initial pH, has a complex effect on reaction rate [36,64]. Only a few studies have been reported about the effect of pH on the wet oxidation of organic compounds [64]. The pH of the solution has an effect on the type of free radical reactions that occur during WAO and the stability of the free radical intermediates formed. The oxidizing strength of free radical intermediates decreases at alkaline conditions in most cases since in alkaline solution, carbonate, bicarbonate and hydroxide can scavenge hydroxyl radicals [6]



Kolaczowski *et al.* [36] studied the WAO of phenol at 200°C and pressure of 3.0 MPa with different initial pH and found that the initial pH has a significant effect on the WAO reaction rate. For pH less than or equal to 2 and between 7 and 10, no reaction took place. However, when no acid or base was added, i.e. when pH was approximately 4, significant phenol decomposition was achieved. Also, when the pH was adjusted to be above the pK_a of phenol, rapid oxidation was achieved with no induction period. This can

be attributed to the effect pH has on the chemical structure of the phenol, i.e. the phenolate ion is highly reactive [6,36]. The change of pH during the oxidation period has a noticeable effect on both the phenol decomposition and COD removal [39]. When buffer was added in order to stabilize the pH, the COD reduction decreased dramatically.

The WAO of carboxylic acids is also affected by the pH of the solution. While 90% TOC reduction was achieved for oxalic acid at a pH of 2.5 and 160°C within 20 minutes [27], less than 2% TOC conversion was achieved at pH greater than 14 within 2 h at 165°C [60,61]. In their study of the catalytic WAO of formic acid Imamura *et al.* [25] showed that the reactivity depends remarkably on pH. They achieved total TOC removal at 150°C, oxygen partial pressure of 1.0 MPa and at pH of 1.9, while only 7% degradation was achieved at pH of 5.6, which suggests that the reactivity of the formic acid is more than the formate ion since the pK_a of formic acid is 3.75. They showed also that the oxidation of acetic acid was also affected by the pH. While 44.5% TOC degradation was achieved at 200°C in 1 hour at pH of 2.7 in the oxidation catalyzed by Ru/Ce, only 19.4% was achieved at pH of 6.9. Those results show the strong influence of the pH on the WAO process for different organic compounds.

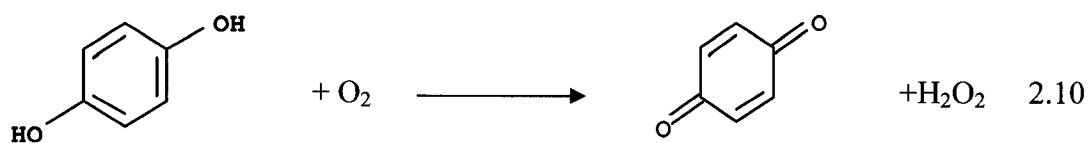
2.4 Wet Air Oxidation Enhancements

In the last section, it was shown how the pH can affect the WAO of many organic compounds. In addition, there are numerous other methods that have been reported in order to increase the effectiveness of the WAO. One of these is the catalytic wet air oxidation in which either homogenous or heterogeneous catalysts were used to enhance the degradation [11,25,40,44]. The wet oxidation method was also enhanced by using

ozone [3] or hydrogen peroxide [14,15,42] as an oxidizing agent. Supercritical oxidation [37] was also tried in order to improve the oxidation of some compounds.

The Co-oxidation method, which was discussed in section 2.3, was reported to be one of the promising methods that can be used to enhance the WAO. In 1987, Willims *et al.* [71] showed that the addition of phenol to a solution containing m-xylene enhanced the oxidation rate of m-xylene. Ingale *et al.* [32] reported that the degradation rate of acetic acid is faster when it is present with other compounds than when it is alone. Shendi and Levec [58] showed that at the same operating conditions, the conversion of formic acid was about 11% higher when an equal amount of acetic acid was added to the solution. Birchmeier *et al.* [7] reported that the oxidation of recalcitrant low molecular weight acids was enhanced by the addition of either phenol or cellobiose to the solution. The degradation of thiocyanate was significantly enhanced when simultaneously oxidized together with phenol, as shown by Vicente and Diaz [65]. Recently, Fu *et al.* [20] studied the wet air oxidation of nitrobenzene and they reported that the presence of phenol in the reaction media enhanced the removal of nitrobenzene.

As suggested in the literature, the first intermediate formed during the wet air oxidation of phenol is hydroquinone, which is unstable and breaks rapidly in the presence of excess oxygen forming other low molecular weight products and carbon dioxide [51]. It also forms hydrogen peroxide. The hydrogen peroxide then produces hydroxyl and perhydroxyl radicals [36]. Hydroxyl radicals have the second highest oxidation potential after fluorine, which makes them very reactive oxidants [64]. Because of the presence of these radicals the rate of the degradation reaction increases. The following reactions show the mechanism [64]:



Since the oxidation of phenol is very fast, the free radicals that will be produced from the phenol oxidation could also help to expedite the oxidation of benzene.

CHAPTER THREE

Experimental Setup and Procedure

3.1 Apparatus

A schematic diagram of the experimental setup is shown in Figure 3.1. The setup consists of 3 main parts: the high pressure reactor, the electrically heated autoclave shell and the rocking mechanism. For safety reasons, the setup is placed inside a metal protective cage during the experiment. Figure 3.2 shows that the reactor consists of the bomb, the cap and the lid. The bomb itself is made of a 316 stainless steel and has a volume of 1.24 L. The cap (Figure 3.3) contains 10 retention bolts and is fitted over the lid which is screwed tightly to the bomb. The lid that seals the bomb has 4 openings with a diameter of 5.50 mm to connect the gas inlet, the thermocouple, the pressure transducer and the sampling line. A micro sparger with a very fine opening is used to introduce the gas in the form of small bubbles. For heating purposes, the bomb is fitted inside the autoclave shell that contains a 1600 W heating coil and is rocked by a small motor through approximately thirty degrees to achieve a good mixing. The temperature is measured via a J type thermocouple, which sends the reading to the controller (Omega CN 8500). In turn, the controller sends a signal to the autoclave heater. The temperature within the reactor is controlled to an accuracy of ± 2 °C. The pressure transducer (Dynisco instruments Model PT-4626-5m) is designed for both high pressure and temperature and can be read from the digital pressure display. The capillary tubing is attached to the sampling line, which is well immersed in the reaction mixture. The unit is also equipped with the pressure safety valve.

There are some design limitations associated with the experimental setup. The rocking mechanism has to be stopped while the bomb is facing downward when a liquid sample is withdrawn. This limits the number of samples that can be collected. Also, the heating time to the operating temperature is considerably long and there is no cooling mechanism. In addition the sampling tube must be immersed in an ice bath in order to collect the sample in a liquid phase and to condense all the volatile compounds in the sample.

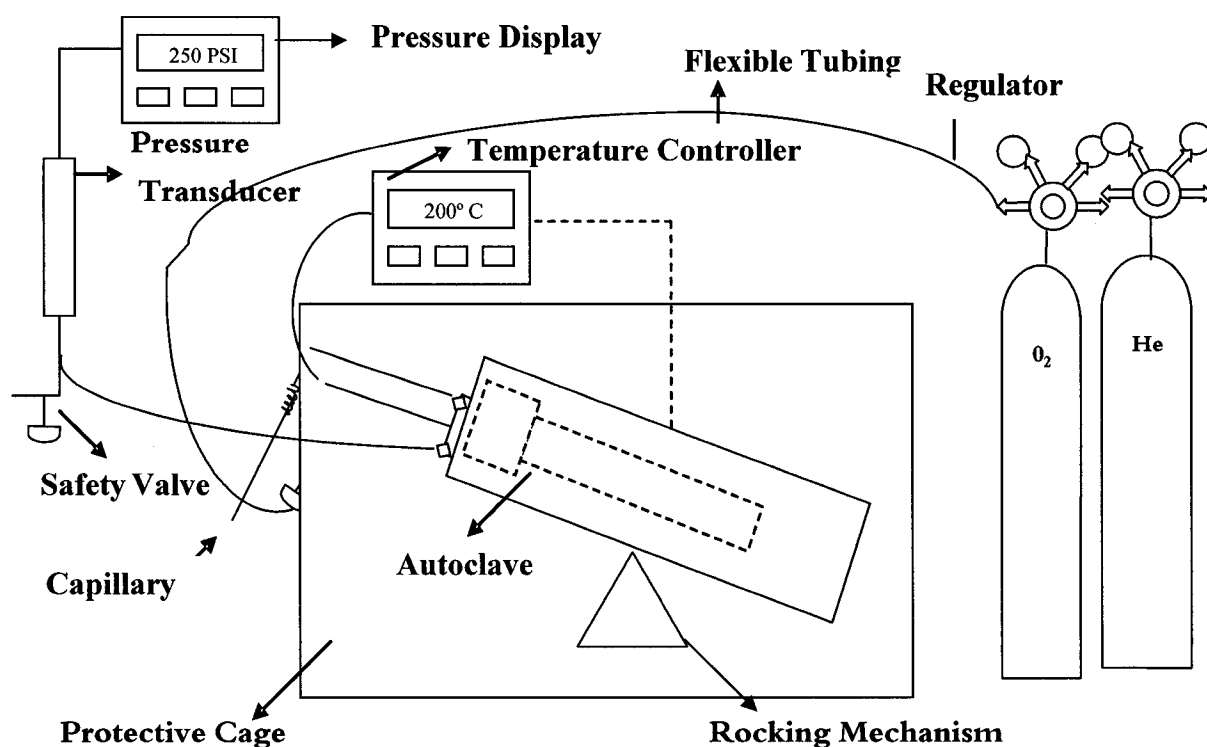


Figure 3.1: Schematic Diagram of the Experimental Setup.

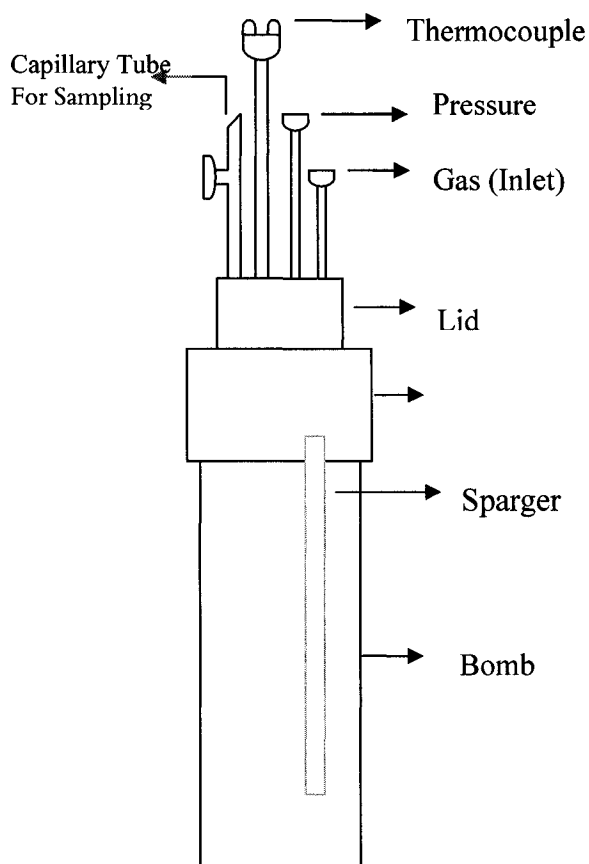


Figure 3.2: Schematic Diagram of the Reactor
ID = 8.2 cm, OD = 11.2 cm,
L = 23.0 cm.

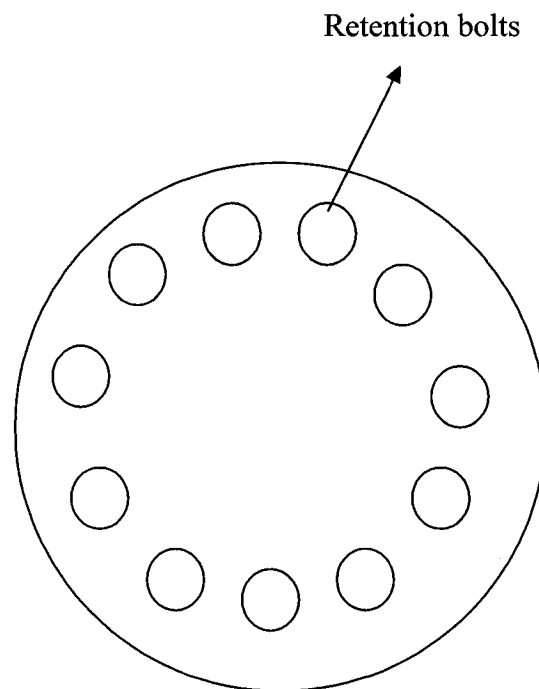


Figure 3.3: Upper View for the Cap

3.2 Materials

Benzene ACS grade was obtained from Fisher Scientific with a 99.9% purity and was used as received from the supplier. Toluene HPLC grade was obtained from American Chemicals LMD. Oxygen from a cylinder with a minimum purity of 99.6% was used as oxidant. Helium that is the inert gas used in the experiment was also used from a cylinder with a purity of 99%. Both oxygen and helium were obtained from BOC Gases in Montreal, Canada. Phenol (ACS grade) was obtained from J.T Baker and used without further purification. Sulfuric acid and nitric acid were ACS grade and obtained

Fisher Scientific. Formic acid (ACS grade) was obtained from American Chemicals LMD. Acetic acid (trace metal grade) was obtained from Fisher Scientific.

3.3 Experimental Procedures

Throughout the experiments, 500 μL of benzene was added to 1000 mL of water and stirred for 1 hour. Since the benzene is a very dangerous and carcinogenic material, this was done in the fume hood and gloves were worn. The initial pH of the solution was in the range of 4-6. Depending on the desired initial value, the pH was typically lowered with nitric acid, but sulfuric acid or acetic acid were also used to determine if the type of acid has any influence on the reaction. The solution was then transferred to the reactor, which was then sealed at once. All auxiliary components were connected and the reactor was purged with helium to remove any oxygen in the reactor. Helium was added to the system before heating to prevent the oxidation before the reaction temperature was reached and to keep the effluent in the liquid phase. After that, the reactor was placed inside the autoclave that was pre-heated for about 60-75 minutes to minimize the time needed to reach the operating temperature. Then, the system was heated to the predetermined operating temperature. The operating temperature was in the range of 190-260°C. When the operating temperature was reached, the reactor was pressurized with pure O_2 to the appropriate oxygen partial pressure. This was considered as time zero for the reaction. In all experiments the amount of oxygen was always in excess. Appendix A shows the calculation for the theoretical amount of oxygen needed. To collect a liquid sample from the reactor, the rocking mechanism was stopped, and with the bomb facing downward, the capillary tube was immersed in an ice bath. All collected samples were of

the same volume and they were weighed and stored in the refrigerator. Toluene was added to each sample as an internal standard for the GC analysis of the benzene and the phenol. The above mentioned procedure was repeated at different temperatures and pressures. Usually, experiments were done in duplicate.

In the second part of this study, phenol was used to enhance the degradation of the benzene. Experiments were done with different phenol concentrations in the range of 10 to 200 mg/L with 100% excess of oxygen. In those experiments, the concentration of benzene was kept constant at 5.63 mmol/L. The operating temperatures were in the range of 160-220°C. After the preparation of the solution, the experimental procedure was exactly as it was described before.

3.4 Analytical Methods

The main analytical method that was used to study the effectiveness of the WAO method was Gas Chromatography (GC). It was used to measure the degree of oxidation for both benzene and phenol. Also, in some experiments the Total Organic Carbon (TOC) analysis was used to determine the carbon degradation. Ion Chromatography (IC) was used to study the production and the degradation of organic acids.

3.4.1 Gas Chromatography Analysis

Gas Chromatography is one of the most important separation methods, which is based on components partitioning between a stationary phase that can be either liquid or solid, and a mobile phase, which is an inert carrier gas. The column used in this work was

bought from Chromatographic Specialties Inc. and it was a Stabilwax column 30 meter long with 0.32 mm ID and 0.25 μ m df. The GC apparatus was a Hewlett Packard 5890.

3.4.1.1 Gas Chromatography Method

The injector temperature was set to 215°C while the FID detector temperature was set at 275°C. The flow rates for the air, hydrogen, and helium were 300, 30, 30 mL/min, respectively. Before the analysis, the split ratio of helium was set to 10 mL/min and the column temperature was set at 215°C for about an hour, in order to flush the column. Then, the temperature was reduced to 80°C as the initial temperature. The initial time was set to 2 minutes, after which the temperature was increased to 200°C at a rate of 20°C/min. The sample volume was 0.3 μ L. Toluene was used as an internal standard because it has similar structure to benzene and has similar retention time. The use of internal standard is very important in order to minimize the error during the injection of the sample. When using an internal standard, the standard that contains known concentrations of both benzene and toluene was prepared. The standard was injected into the GC in order to calculate the k factor which is defined as

$$k = \frac{(\text{area} / \text{amount})_C}{(\text{area} / \text{amount})_I}$$

where,

[(area/amount)]_C: value of the compound

[(area/amount)]_I: Value of the internal standard

This k value is constant which is used to calculate the concentration of tested component.

3.4.1.2 Calibration of the GC

Three benzene standards that contain the same benzene and toluene concentrations were prepared. Five 0.3 μL samples from each standard were injected randomly in the GC. These 15 samples were used to calibrate the GC, which is done automatically by the instrument. After calibration, a sample from each standard was injected in order to check the calibration. The results that were obtained showed that the maximum deviation was 6.8%. There are many sources that can lead to this deviation, such as error that results from the preparation of the standards, error that can results from the addition of the internal standard and instrument's error. It should be mentioned that for two injections from the same sample, the reading was close to each other with a difference less than 4% in most cases. This difference decreased for highly concentrated samples and increased when the concentration of the sample was less than 0.1 mmol/L.

After the calibration of the GC apparatus, a repeatability of the standard was determined. A fresh standard with a known concentration was prepared and it was used to calibrate the GC. After calibration, two fresh standards that have the same concentration were prepared to check the repeatability of the results. It was found that the maximum deviation was 5.3%

3.4.2 Ion Chromatography

Ion Chromatography (IC), which is a form of liquid chromatography, is an analytical method used to separate atomic or molecular ions by the use of ion exchange resins, and this is based on their interaction with the resin. In this study, IC was used mainly to determine the concentration of the molecular ions for both the acetate and formate. The

IC used was the DX-100 which is manufactured by the Dionex Corporation. The column which was used is IonPac AS14 4mm while the eluent was 2.7 mmol Na₂CO₃/L + 0.3 mmol NaHCO₃/L. One limitation of this method was the poor separation between the acetic acid and the formic acid, due to the isocratic technique that was used. In this technique, the solvent composition remains constant throughout the analysis since no gradient pump was used to change the concentration of the eluent after certain time, which is important to achieve better separation. This problem was overcome by using a slow pump speed in order to get better separation.

3.4.2.1 Ion Chromatography Method

Standards with different concentrations for both acetic acid and formic acid were prepared. A calibration curve for each acid was produced and stored in the IC program. The pump speed was adjusted to 50 mL/min and the eluent nitrogen pressure was adjusted to 68.9 kPa. A blank was injected to check for any contaminants that may be present in the column. 1.0 mL of the sample was injected in the column after which the values of the acids were recorded.

3.4.2.2 Repeatability of the IC

Five different standards with five different concentrations of both acetic and formic acids were prepared for the IC calibration. After calibration, fresh standards of both acetic acid and formic acid were prepared and were injected to check the validity of the IC calibration. The results showed that the calibration was good and the error was less than 3%. To study the calibration of a mixture of both acetic and formic acids, a fresh

standard that contained a known concentration of both acids was prepared and injected in the IC. The results show that the calibration was good even for the mixtures. For example, when a standard that contain 60 mmol/L formic acid and 20 mmol/L acetic acid was prepared and injected in the IC after calibration, the results that were obtained were 59.4 mmol/L for formic acid and 19.6 for acetic acid. The same results were obtained even if only formic or acetic acid was injected.

3.4.3 Total Organic Compound Measurement

Total Organic Carbon analysis is a method that measures the carbon content of dissolved organic matter present in a solution and it is a common parameter that can describe the efficiency of the treatment process. TOC does not measure any organically bound elements other than carbon and it does not depend on the oxidation state of the organic matter. Also, TOC does not measure the inorganic compounds, which may contribute to the oxygen demand as measured by Chemical Oxygen Demand analysis (COD). For this study, the UV-Persulfate method was used. The organic compounds were oxidized to carbon dioxide by persulphate in the presence of a UV light source. A nondispersive infrared analyzer measured the CO₂ generated during the reaction. The apparatus that was used for the TOC measurement was the DC-80 Total Carbon Analyzer manufactured by Rose Mount Dohrmann.

3.4.3.1 TOC Method

Before the measurement, the TOC analyzer was calibrated with a 400 mg/L standard of Potassium Hydrogen Phthalate (KPH). After calibration, the sample was injected with

a 200 μL syringe into the apparatus. All samples were injected with both lamp on and lamp off. When the lamp was on, the results included both Total Organic Carbon and Total Inorganic Carbon, while with the lamp off, only the Total Inorganic Carbon was detected. Then, the TOC was calculated as the difference between the two values. This has been done in order to minimize any error that may occur because of the interference of the inorganic compounds. The repeatability of the TOC analysis was tested by 10 injections for the same sample and the standard deviation was found to be 2.95%.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

WET AIR OXIDATION OF BENZENE

The wet air oxidation of benzene was studied to determine the optimum conditions required to achieve benzene degradation. The effect of initial pH on the degradation of benzene has been studied at different temperatures and pressures. Results from experiments that have been performed in the absence of oxygen are presented. The repeatability of the results was tested. The pH fluctuation during the experiment was also shown. Both the effect of acidification method and the effect of the initial benzene concentration on its degradation were examined. Finally, a simple kinetic model was proposed.

4.1 Experiments with Benzene in the Absence of Oxygen

At the beginning of this study, two experiments were carried out without oxygen using only nitrogen to determine whether any pyrolysis of the benzene took place. These two experiments were done under 1.1 MPa nitrogen pressure with 11.3 mmol/L benzene solution at 20°C and 250°C. In the absence of oxygen, no degradation was observed. These experiments also showed that the sampling procedure did not have any effect on the liquid concentration and the benzene stayed in the liquid phase throughout the experiment.

4.2 Chemical Oxygen Demand Measurements

Chemical Oxygen Demand (COD) is one of the most widely used parameters to evaluate the degree of oxidation during the WAO. At the beginning of this study, the COD was one of the parameters used to study the extent of degradation of organic compound. However, the results showed that benzene was not completely oxidized under the conditions of the COD test. This observation is in agreement with the literature (2). For example, when the benzene concentration was 4.52 mmol/L, the equivalent COD concentration should have been 33.9 mmol O₂/L. In fact, the actual COD value measured was 26.6 mmol O₂/L. Therefore, in this thesis the results will be reported in terms of the concentrations of benzene, byproducts and the total organic carbon.

4.3 Repeatability of the Results

Repeatability of the experimental results has been tested by conducting duplicate experiments. The majority of the data points that will be shown in this chapter are averages of two experiments. Figures 4.1, 4.2 and 4.3 demonstrate the repeatability of the experimental points obtained at oxygen pressure of 1.38 MPa, pH 4 and temperatures of 220, 240 and 260°C, respectively. It is apparent that excellent repeatability has been achieved.

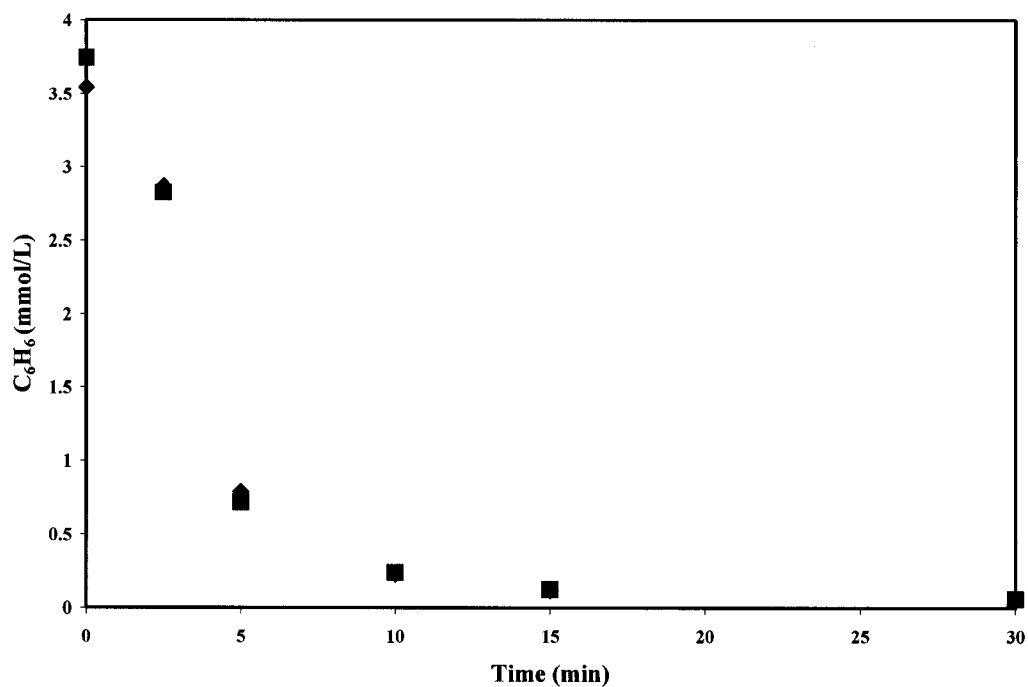


Figure 4.1: Repeatability of Data from Two Experiments at 220°C, $P_{O_2} = 1.38$ MPa, pH=4.

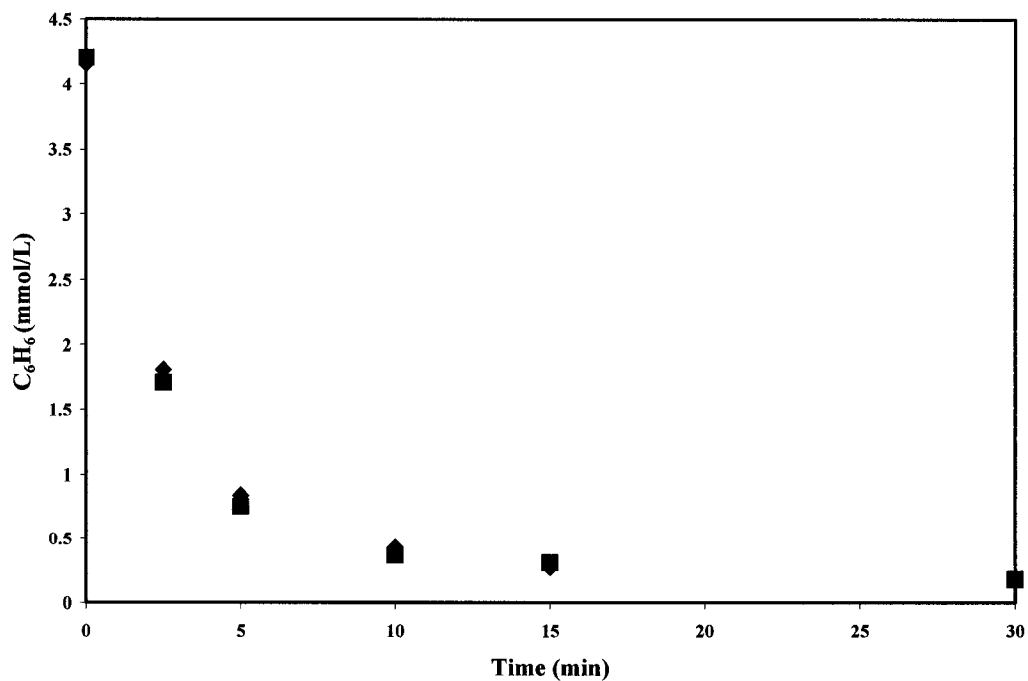


Figure 4.2: Repeatability of Data from Two Experiments at 240°C, $P_{O_2} = 1.38$ MPa, pH=4.

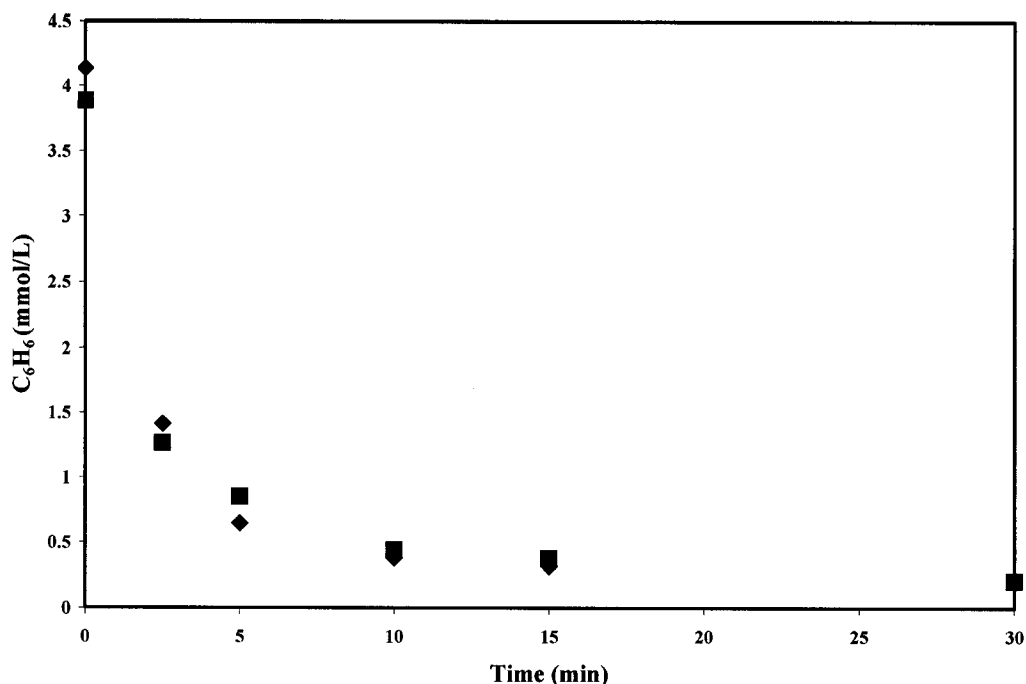


Figure 4.3: Repeatability of Data from Two Experiments at 260°C, P_{O_2} = 1.38MPa, pH=4.

4.4 Influence of Initial pH on Benzene Degradation

In this section, the effect of initial pH at four different temperature levels at 190°C, 220°C, 240°C and 260°C was studied. The oxygen pressure was kept constant at 1.38 MPa. Two experiments were conducted at 190°C. The initial pH was 4 and 6. Figure 4.4 demonstrates that when the initial pH was 6, almost no degradation took place even after 5 hours of oxidation time. However, when the initial pH was lowered to 4 about 98% degradation was achieved within 1 hour.

Figure 4.5 shows the effect of the initial pH on the benzene degradation at 220°C. When the initial pH was reduced from 6 to 5 the reaction became faster. However, when the initial pH was reduced from 5 to 4 the change in the reaction rate was only noticeable at the first 2.5 minutes and after that the results were similar. The induction time

decreased with pH from 50 minutes to 2.5 minutes when the pH was decreased from 6 to 5. At pH 4, the induction time disappeared suggesting that at lower pH there was much higher accumulation of the free radicals, which helped to initiate the oxidation even faster. During the course of the reaction and because of the intermediates that were produced, the pH of the reaction medium kept changing continuously. At the beginning of the reaction, due to the production of acetic and formic acid (See Chapter 5), the pH decreased to around 3. When the acids started to oxidize, the pH increased again (This change in pH will be presented in Section 4.4.7 in more detail). However, in almost all cases the final pH of the solution was about 4, mainly because of the acetic acid that remained as a final product as will be explained later.

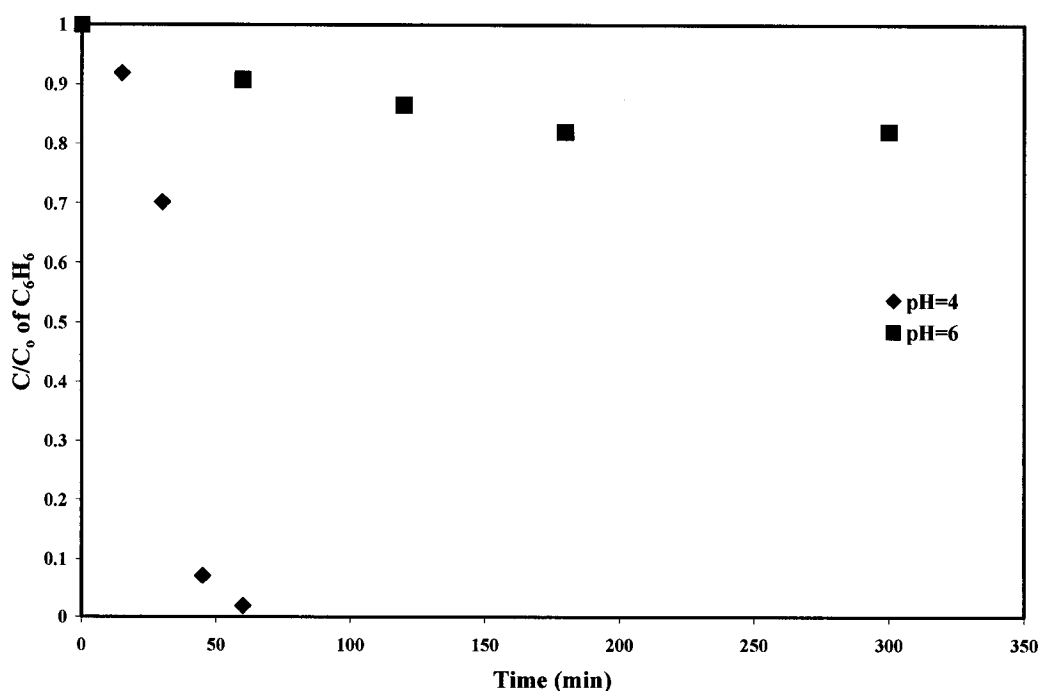


Figure 4.4: Effect of pH on Benzene Degradation at 190°C, P_{O2}= 1.38 MPa.

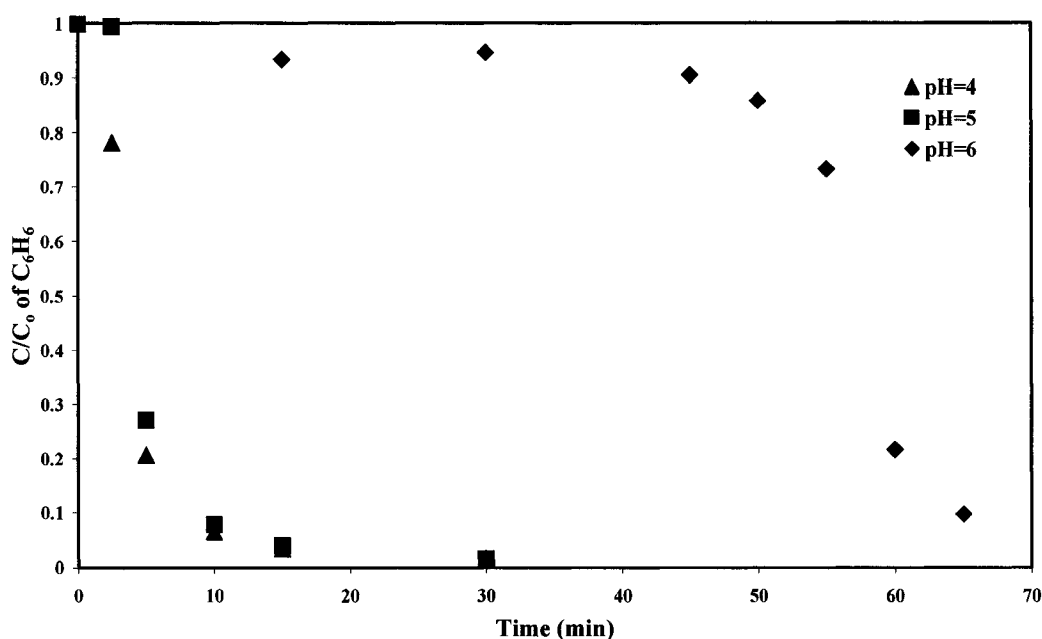


Figure 4.5: Effect of pH on the Benzene Degradation at 220°C, P_{O_2} = 1.38 MPa.

Similarly, at 240°C (Figure 4.6), reducing the pH from 6 to 5 had a large effect on the degradation of benzene. The induction time, which was about 15 minutes at pH 6, disappeared entirely at pH 5 and pH 4. Also, reducing the pH from 5 to 4 did not change the benzene degradation at this temperature, suggesting that at 240°C the accumulation of the free radicals at both pH 4 and pH 5 was comparable.

The effect of pH was further studied at 260°C where the oxidation was fast even in the first 5 minutes of the experiment. Figure 4.7 shows the degradation at 260°C at both pH 4 and pH 6. The degradation of benzene was enhanced dramatically especially at the beginning of the reaction. While only 48% degradation was achieved at pH 6 in the first 2.5 minutes, about 67% has been achieved at pH 4.

In summary, the initial pH of the reaction medium had a significant effect on the benzene oxidation; especially at lower oxidation temperatures, because the pH of the solution influences the type of free radical reactions that occur and also the stability of

the free radical intermediates formed (See Section 2.3). This confirms what was reported in the literature [6].

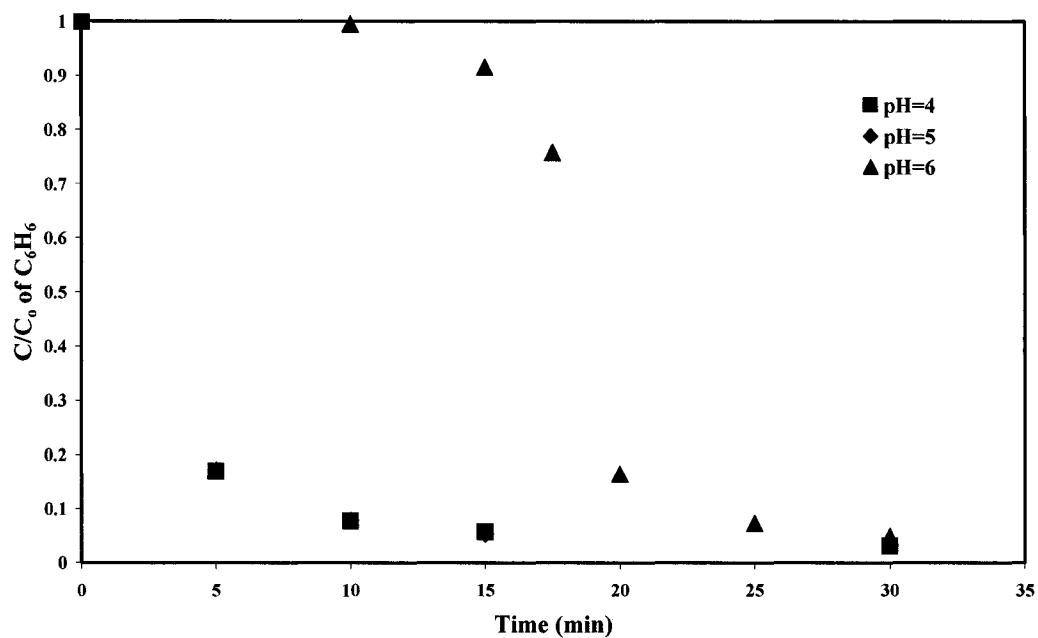


Figure 4.6: Effect of pH on the Benzene Degradation at 240°C, $P_{O_2} = 1.38$ MPa.

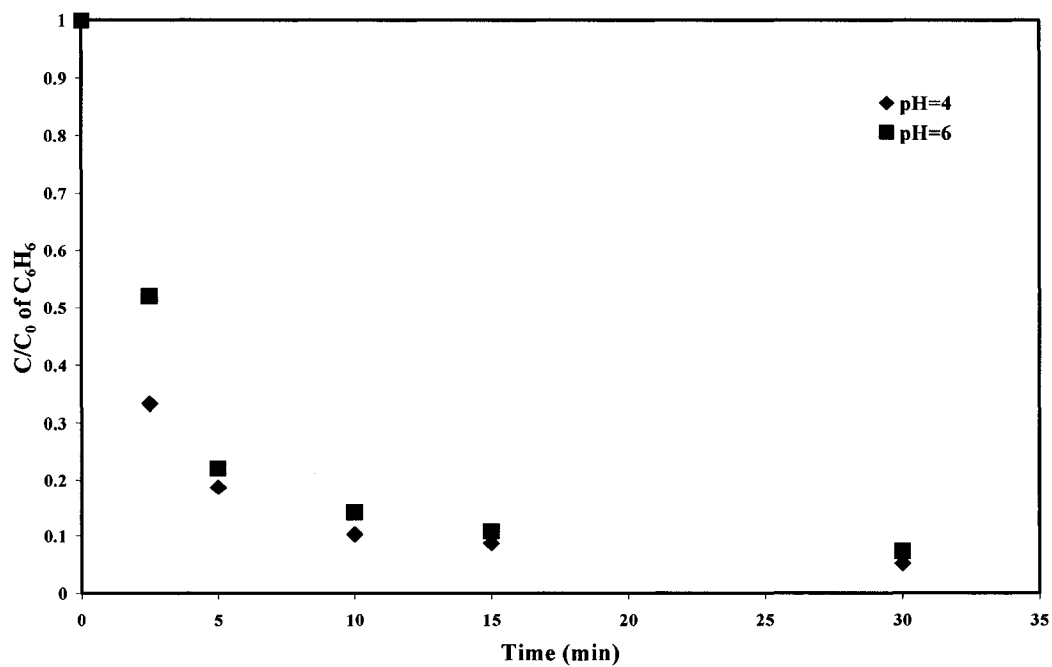


Figure 4.7: Effect of pH on the Benzene Degradation at 260°C, $P_{O_2} = 1.38$ MPa.

4.4.1 Effect of Temperature on Degradation of Benzene at pH 6

Based on the results of the previous section, further experiments were carried out at two different temperature ranges: (a) high temperatures (220°C, 240°C and 260°C) and (b) low temperatures (200°C and 210°C). The oxygen pressure was kept constant at 1.38 MPa at given temperature.

Figure 4.8 shows the normalized concentration of benzene at 220°C, 240°C and 260°C, respectively. The results shown in this figure are the averages of duplicate experiments. At 260°C, 92% degradation was achieved within 15 minutes, compared to 26% at 240°C in 15 minutes and only 12% at 220°C after 30 minutes. However, more than 97% degradation was achieved in one hour at all temperatures and degradation of about 99% was achieved after 3 hours (Figure 4.9). The experiments also show that taking a sample every 15 minutes was not sufficient to describe the decrease of benzene concentration. Therefore, in the next set of experiments samples were taken more frequently at the beginning of the experiments. Figure 4.9 shows an excellent repeatability of the experimental data at 240°C.

In two experiments at 260°C, a gas sample was collected at the end of the experiment after the bomb was cooled to room temperature. The purpose of this analysis was to ensure that there would not be a considerable amount of benzene in the gas phase. The gas sample was analyzed using the GC. The amount of benzene in the gas phase was found negligible, i.e. less than 0.03 mmol C₆H₆/L.

Eight experiments were done at 200°C and four experiments at 210°C. The results were very scattered (Figures 4.10 and 4.11). The only reason that can explain this is that

this may be near the border temperature at which the activation energy may be high and a small increase in the temperature may ignite the reaction.

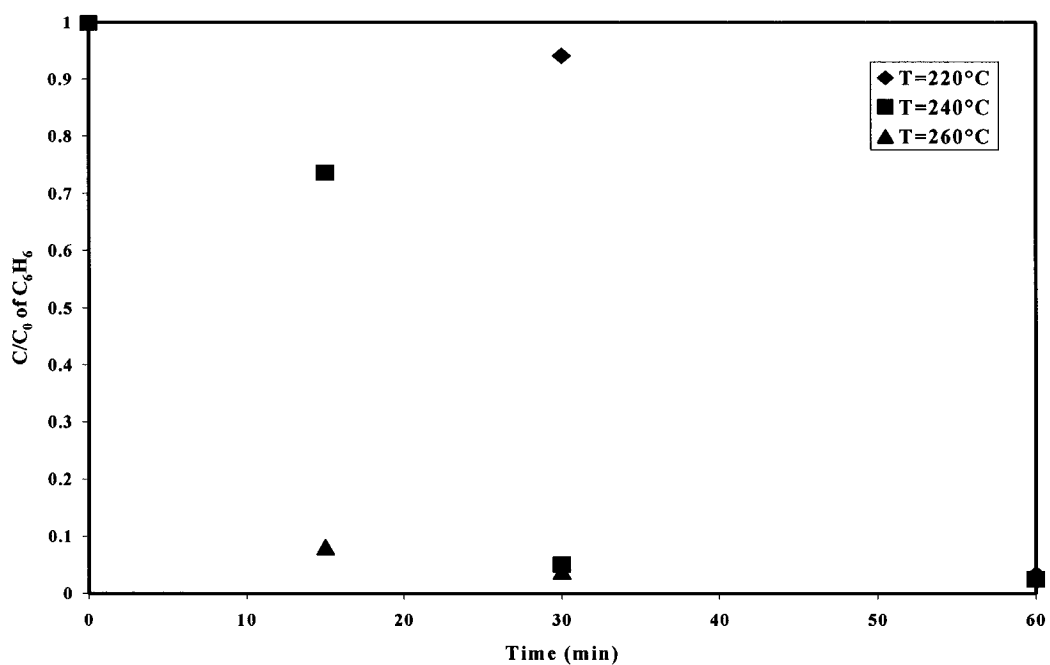


Figure 4.8: Degradation of Benzene at Different Temperatures, P_{O_2} = 1.38 MPa, pH= 6.

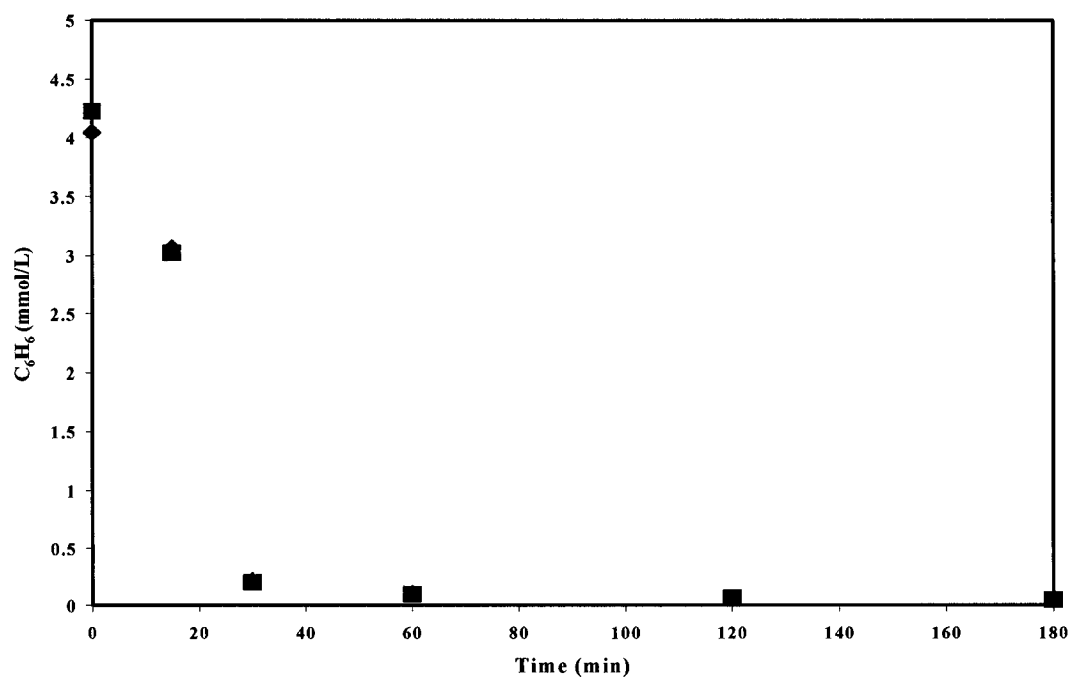


Figure 4.9: Repeatability of Data from Two Experiments at $240^\circ C$, P_{O_2} = 1.38 MPa, pH= 6.

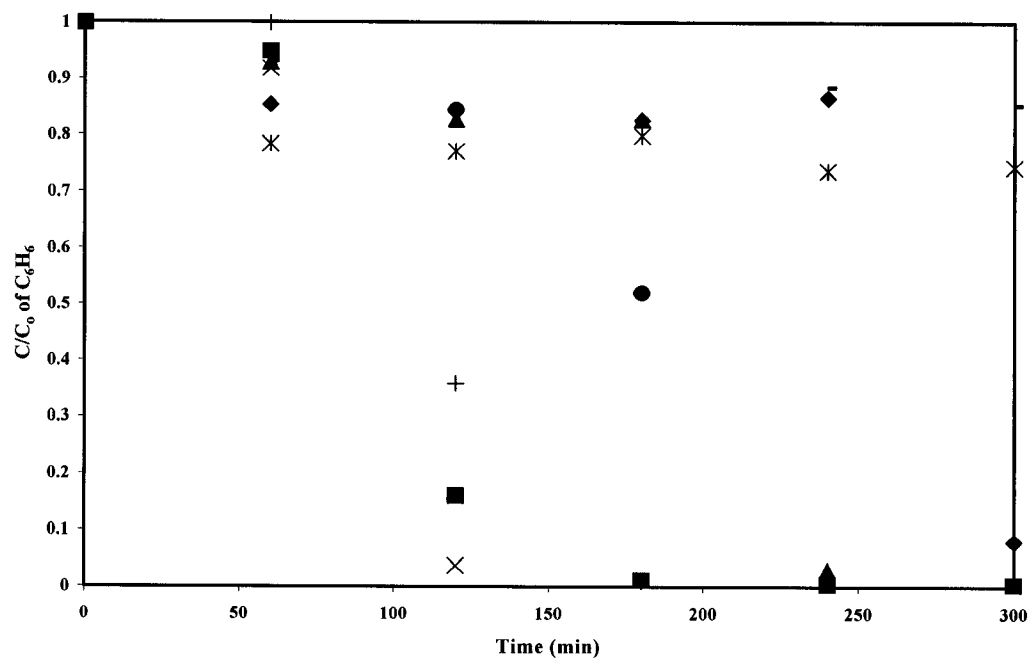


Figure 4.10: Degradation of Benzene at 200°C, $P_{O_2} = 1.38$ MPa, pH = 6.

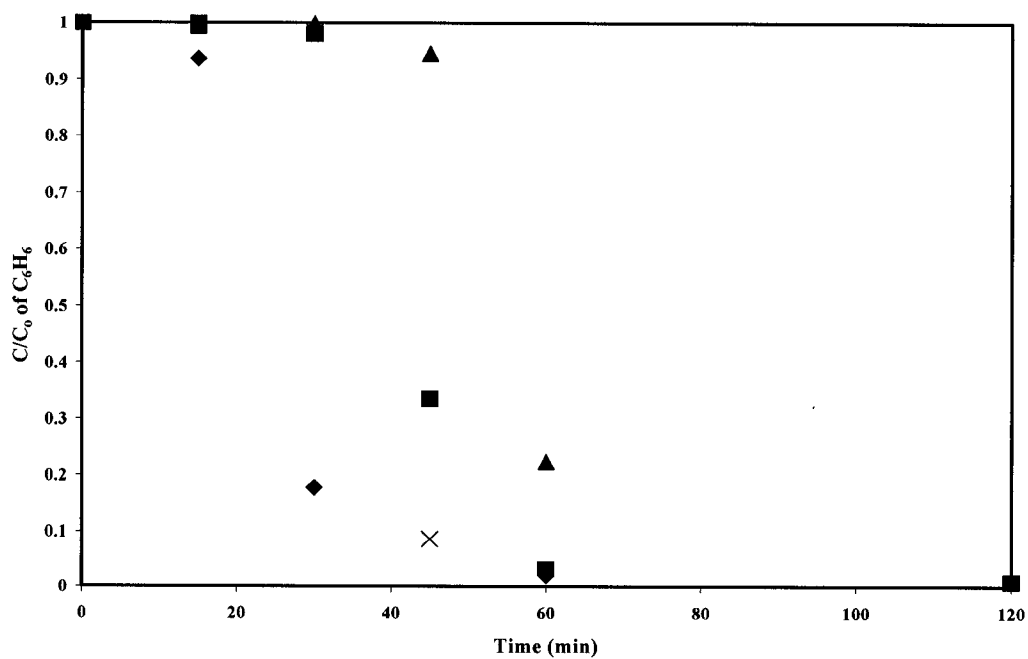


Figure 4.11: Degradation of Benzene at 210°C, $P_{O_2} = 1.38$ MPa, pH = 6.

The results that were obtained during the preliminary experiments led us to decide to work with the high temperatures range (from 220-260°C), at which more samples were collected at each run. In those experiments, the oxygen pressure was kept constant at 1.38 MPa at given temperature. The initial pH of the solution was 6. Figure 4.12 shows the degradation of benzene at 220°C, 230°C, 240°C, 250°C and 260°C, respectively. As expected the degradation of benzene became faster with the increasing temperature. The reaction consisted of three steps; induction, fast reaction, and the termination. This is a typical pattern of the reactions governed by the free radical mechanism (See Chapter 2). During the induction time there was an accumulation of the hydroxyl radicals and as soon as there was a sufficient amount of hydroxyl radicals, the reaction proceeded quickly until most of the reactant was oxidized [69]. Then the rate of reaction decreased until the oxidation was complete. As the temperature increased the induction time decreased until it almost disappeared at 250°C.

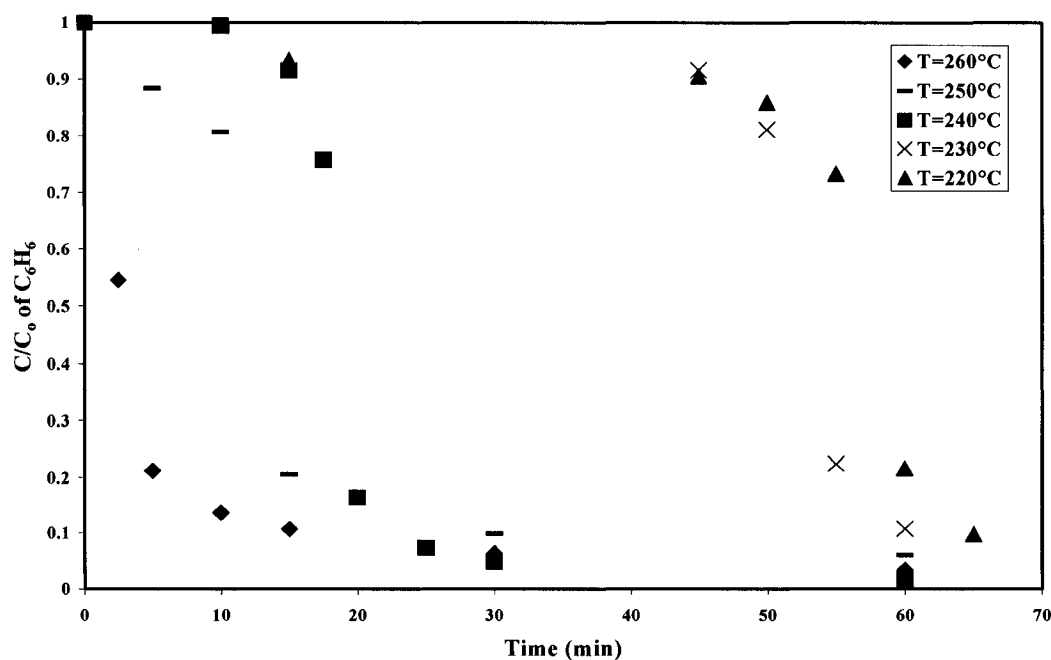


Figure 4.12: Degradation of Benzene at Different Temperatures, $P_{O_2} = 1.38$ MPa, pH=6.

4.4.2 Effect of Oxygen Pressure on Benzene Degradation at pH 6

The effect of pressure was studied at 260°C and the samples were collected periodically during the experiment and at the end of the experiment. Figure 4.13 shows the degradation of C_6H_6 at two different pressures. It was found that 99% degradation was achieved in just 15 minutes when the pressure was 5.52 MPa while only 86% was reached when the pressure was 1.38 MPa. However, the difference became negligible after 3 hours. The main reason is that at the higher oxygen pressure the solubility of the oxygen in the liquid phase increases.

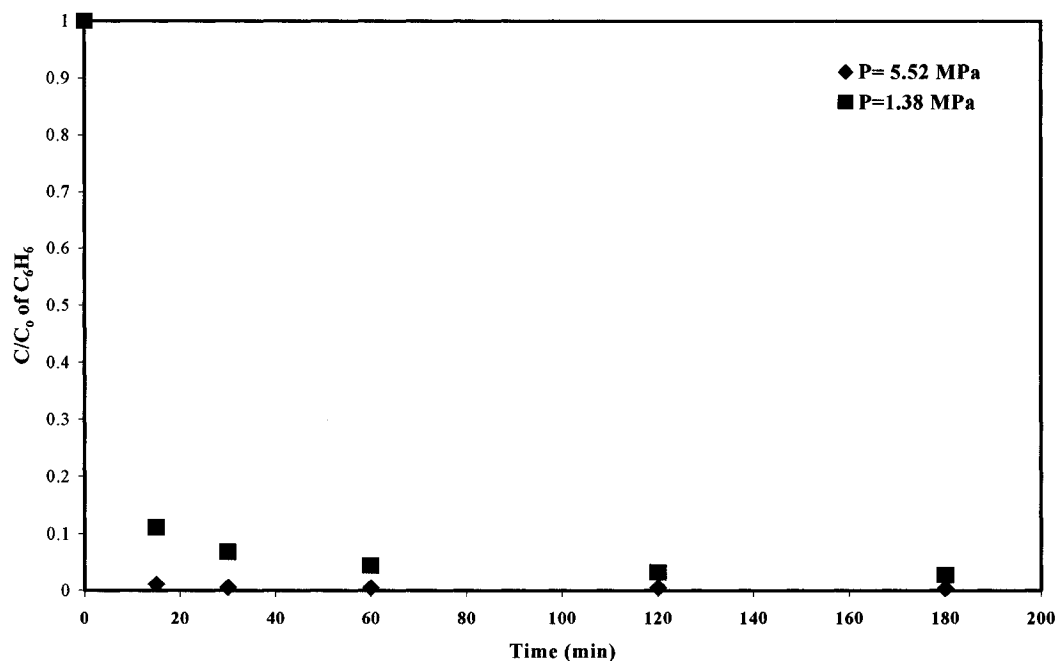


Figure 4.13: Degradation of Benzene at Different Oxygen Pressure, T= 260°C, pH=6.

Furthermore, the effect of the oxygen pressure on the benzene degradation was studied at 260°C and pH 6, at which more samples were collected. Figure 4.14 shows that

at 1.03 MPa the degradation of benzene was slow, and that in the first 2.5 minutes higher degradation was achieved with 2.07 MPa than 1.38 MPa. However, this effect diminished as the time proceeded. Also, comparable results were obtained for both 1.38 MPa and 1.72 MPa. This is attributed to the amount of dissolved oxygen in the liquid phase. More clearly, since at the beginning of the experiment more benzene was present in the solution, more oxygen was needed. However, after the oxidation proceeded less oxygen was needed, which made the results comparable at the later stages. A detailed discussion about the effect of P_{O_2} on the dissolved oxygen is discussed in Section 4.4.6.

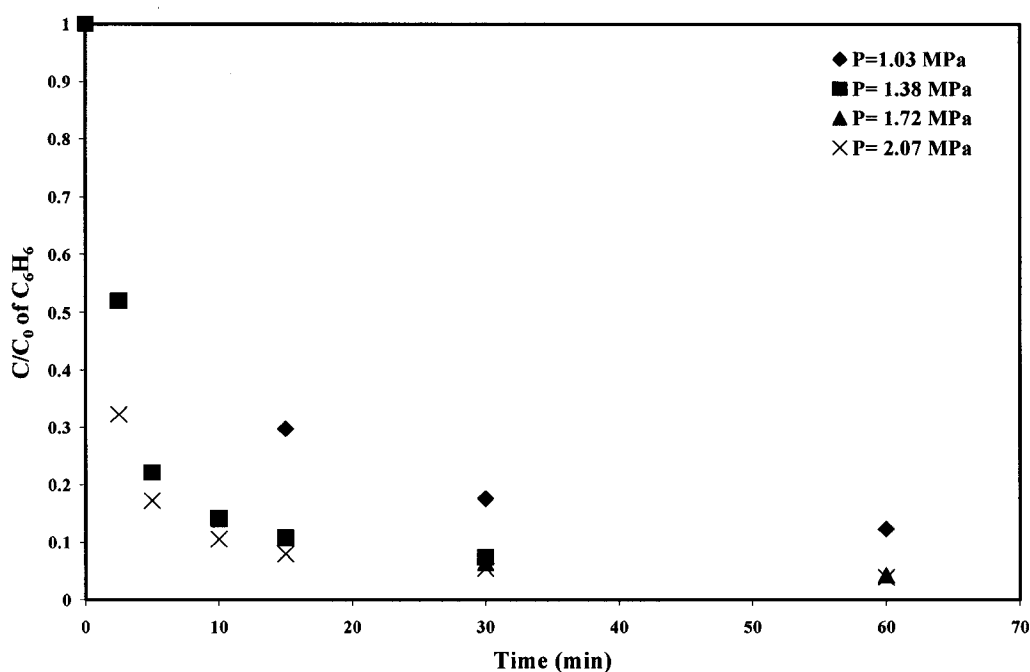


Figure 4.14: Effect of Oxygen Pressure on the Benzene Degradation at 260°C, pH=6.

4.4.3 Effect of Temperature on the Benzene Degradation at pH 5

As explained in the previous section, the major effect of temperature is in the high range; therefore experiments were done at pH 5 and two temperatures, 220°C and 240°C. As expected, the degradation was faster at 240°C; however, a slightly higher conversion was achieved after 15 minutes at the lower temperature (Figure 4.15). The main reason for this may be that at the lower temperature more of the carboxylic acids produced during the degradation of benzene stayed in the solution. This keeps the pH of the solution low hence resulting in higher conversion of benzene.

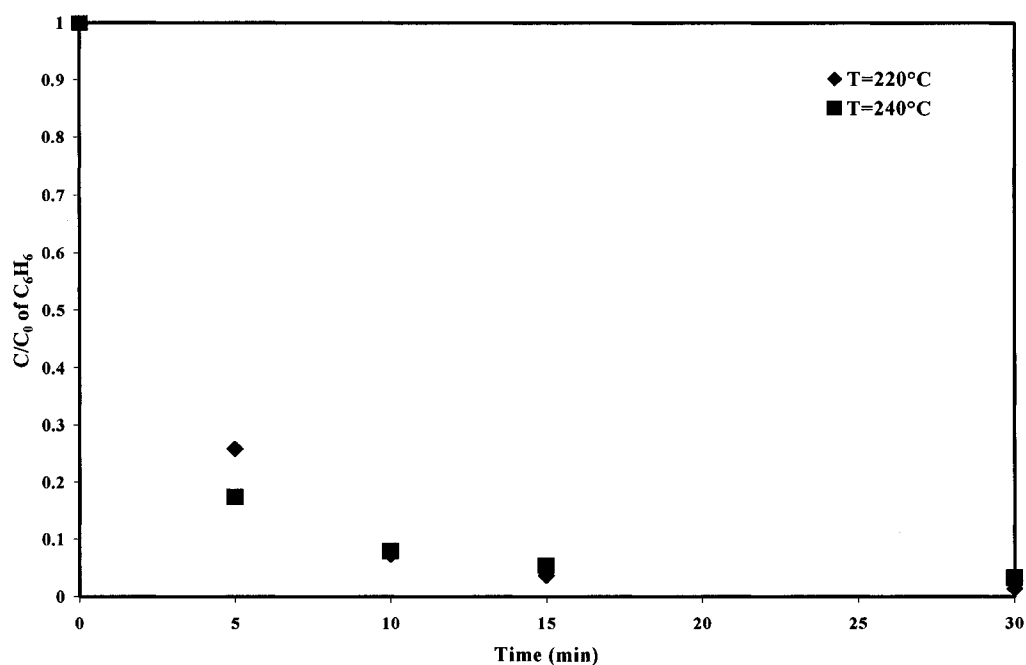


Figure 4.15: Effect of Temperature on the Benzene Degradation at pH 5, P_{O_2} = 1.38 MPa.

4.4.4 Effect of the Oxygen Pressure on Benzene Degradation at pH 5

Three different oxygen pressures were chosen (1.38, 1.72 and 2.07 MPa) to study the effect of oxygen pressure on the benzene degradation at 220°C and pH 5. Figure 4.16 shows the effect of oxygen pressure on the benzene degradation. It is apparent that the higher the oxygen pressure the higher the benzene degradation, especially at the beginning of the oxidation. This effect diminished as the oxidation proceeded. More details about the effect of P_{O_2} on the benzene degradation will be shown in Section 4.4.6

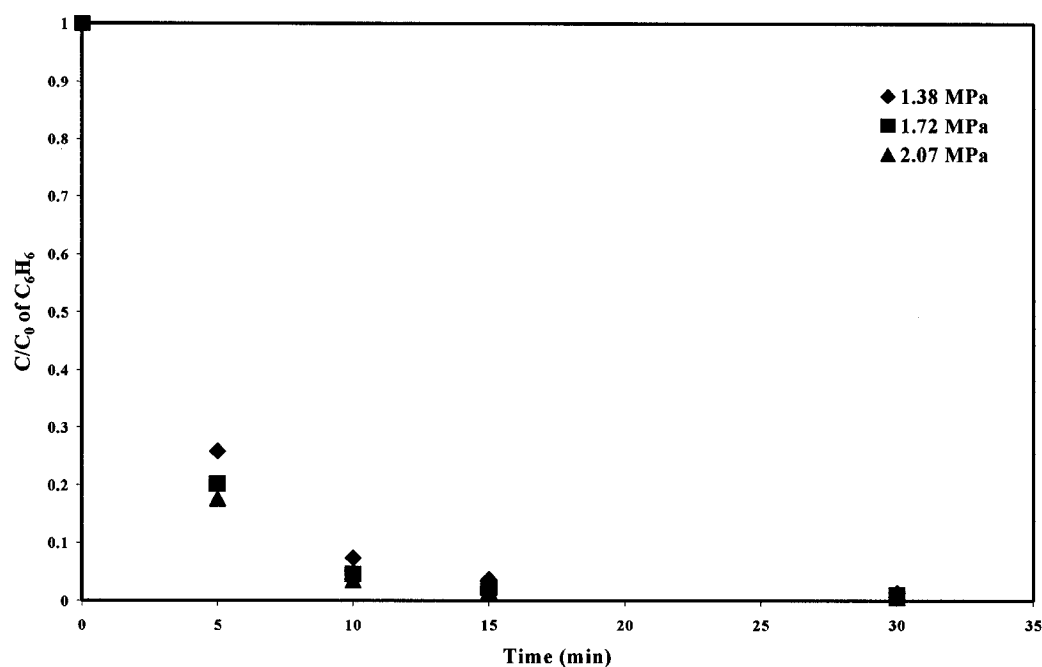


Figure 4.16: Effect of Oxygen Pressure on the Benzene Degradation at pH 5.

4.4.5 Effect of Temperature on Benzene Degradation at pH 4

The effect of temperature on the benzene degradation has been studied at different temperatures and pressures at pH 4. Figures 4.17, 4.18 and 4.19 show the effect of temperature on the degradation of benzene at pH 4 and at oxygen pressures of 1.03, 1.38 and 1.72 MPa, respectively. It can be seen that at lowest pressure almost same results have been obtained for the 240°C and 260°C, especially in the first 5 minutes. In this period the oxidation at those two temperatures was faster than that of 220°C. After 10 minutes of oxidation, the degradation was better at 220°C than those at 240°C and 260°C. At 1.38 MPa, higher benzene degradation has been achieved at 260°C at the beginning of the experiment. After 5 minutes of oxidation the results became comparable for all three temperatures and later, the higher benzene conversion has been achieved for the lowest temperature. When the pressure was increased to 1.72 MPa the similar pattern was observed. One possible reason for this is that at the beginning of the oxidation, the higher temperature resulted in higher degradation, hence more acids were produced. This lowered the pH of the reaction medium (Section 4.4.7). At higher temperatures (i.e. 260°C), these acids were oxidized faster (see Chapter 5), and because of that the pH of the medium increased. However, at lower temperature, produced acids were more stable which kept the pH lower than that achieved at higher temperature, thus resulting in higher degradation.

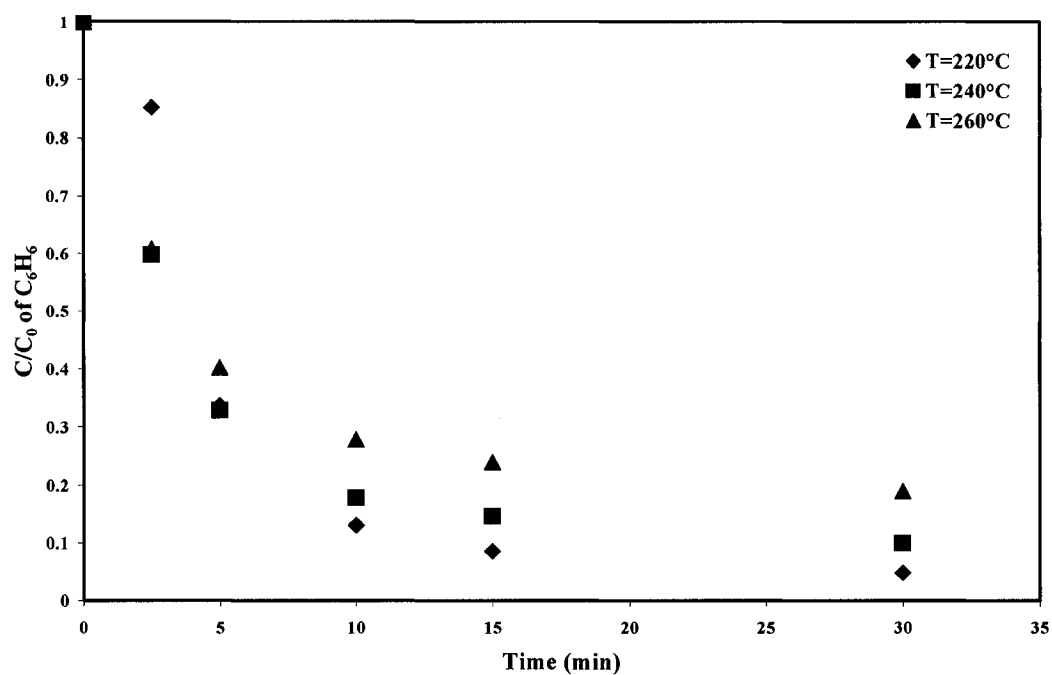


Figure 4.17: Effect of Temperature on the Benzene Degradation at 1.03 MPa, pH= 4.

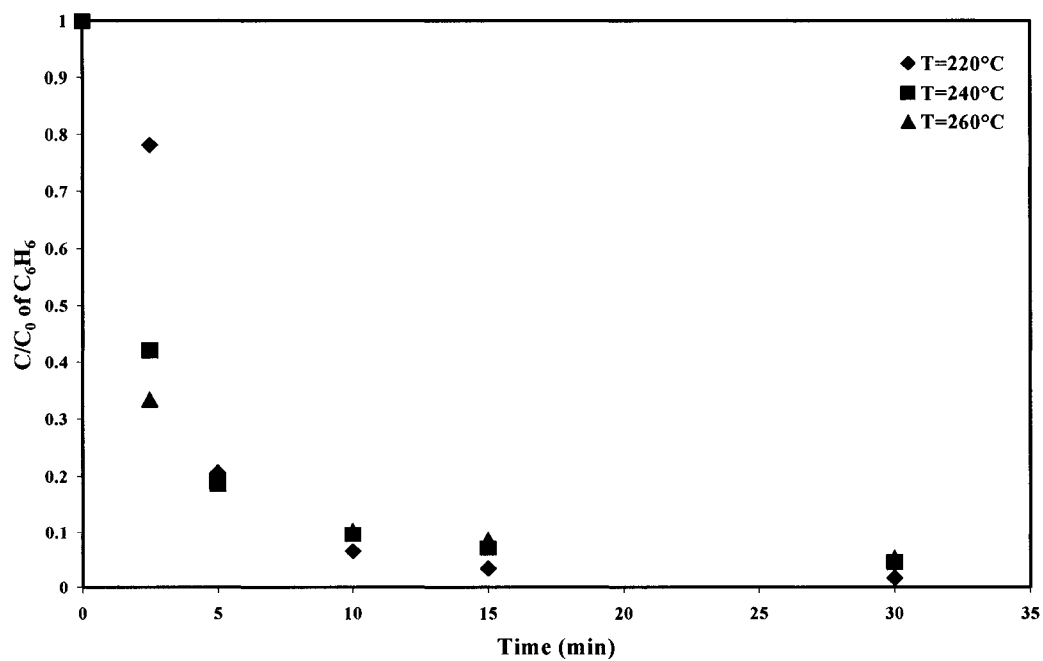


Figure 4.18: Effect of Temperature on the Benzene Degradation at 1.38 MPa, pH= 4.

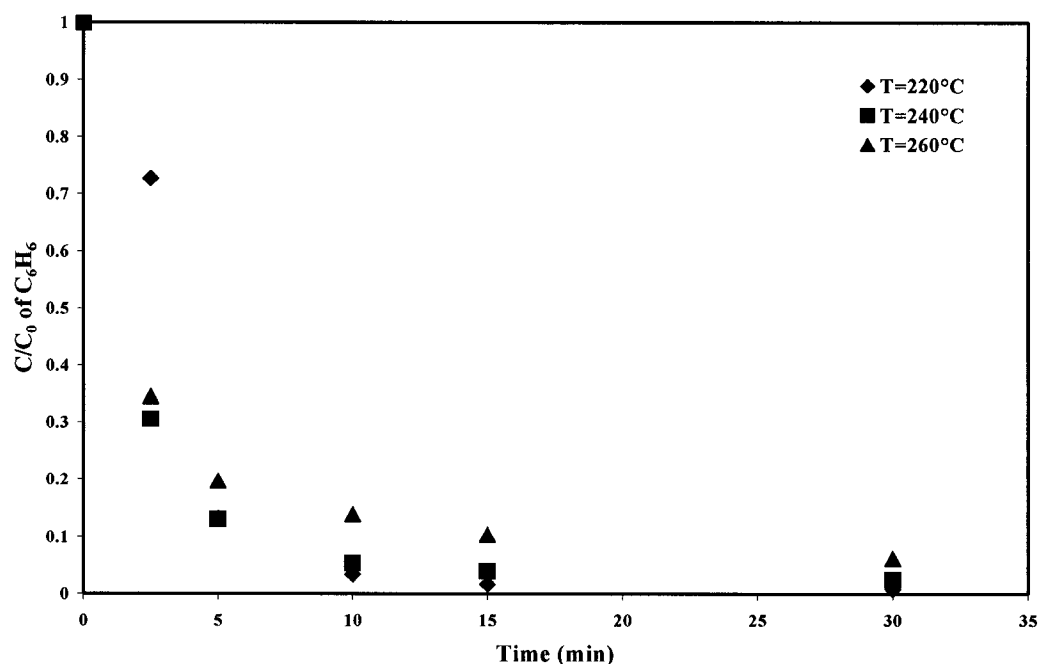


Figure 4.19: Effect of Temperature on the Benzene Degradation at 1.72 MPa, pH= 4.

4.4.6 Effect of the Oxygen Pressure on the Benzene Degradation at pH 4

The effect of oxygen partial pressure on the benzene degradation was further studied at 220, 240 and 260°C, respectively and at pH 4. At 220°C the degradation was studied at the range of 0.69 MPa to 1.72 MPa. Figure 4.20 demonstrates that the oxidation started slowly within the first 2.5 minutes followed by a fast oxidation step, during which most of the benzene was degraded. After that, the oxidation slowed down. It is apparent that the degradation in the first 2.5 minutes, in which the oxidation process was slow, was almost comparable for 0.69, 0.86 and 1.03 MPa, while it was slightly faster for both 1.38 and 1.72 MPa, respectively. This may be due to the accumulation of radicals at this low temperature and low P_{O_2} . After 5 minutes of oxidation, it was clear that the degradation of benzene increased with the increase of the oxygen partial pressure. At higher

temperatures, the effect of the oxygen pressure on the benzene degradation was more pronounced as it appears in Figures 4.21 and 4.22 at 240 and 260°C, respectively. While only 40% degradation was achieved at 240°C after 2.5 minutes with 1.03MPa, 58% and 70% have been achieved at 1.38 and 1.72MPa, respectively. It is apparent that the oxygen partial pressure has a significant effect on the benzene degradation. This is attributed to the amount of the oxygen dissolved in the liquid phase. Table 4.1 shows the solubility of oxygen (C_{aq}) in the water at different temperatures. The detailed calculation can be found in Appendix B.

Table 4.1: Solubility of Oxygen in Water at Different Temperatures.

P_{O_2} (MPa)	C_{aq} (mol/kg water)		
	T=220°C	T=240°C	T=260°C
0.69	0.012		
0.86	0.014		
1.03	0.017	0.021	0.027
1.38	0.023	0.028	0.035
1.72	0.029	0.035	0.044

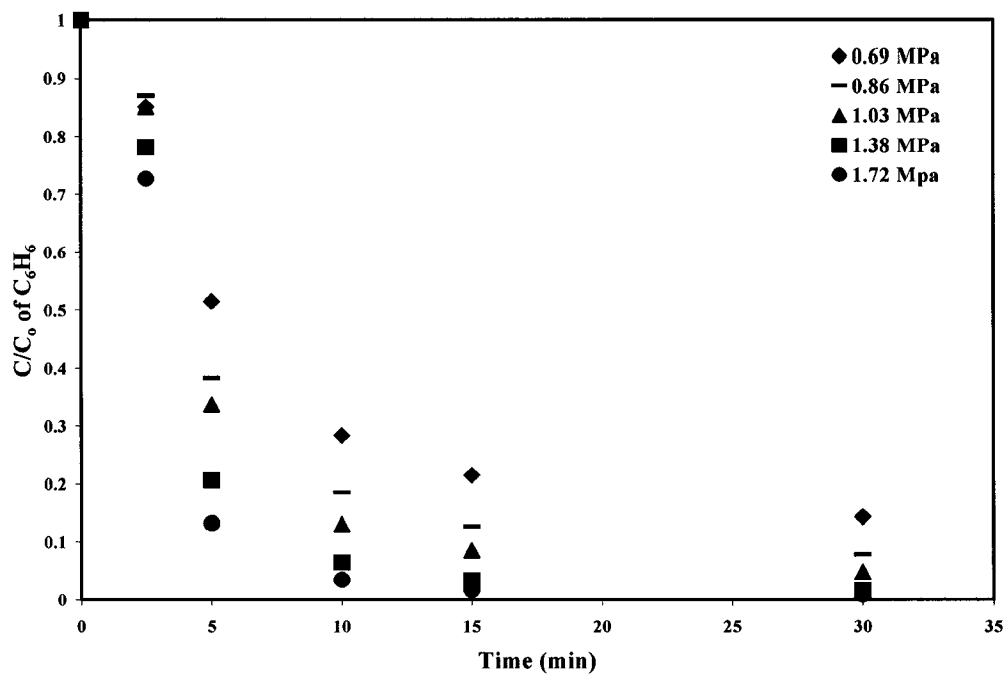


Figure 4.20: Effect of Oxygen Pressure on the Benzene Degradation at 220°C, pH 4.

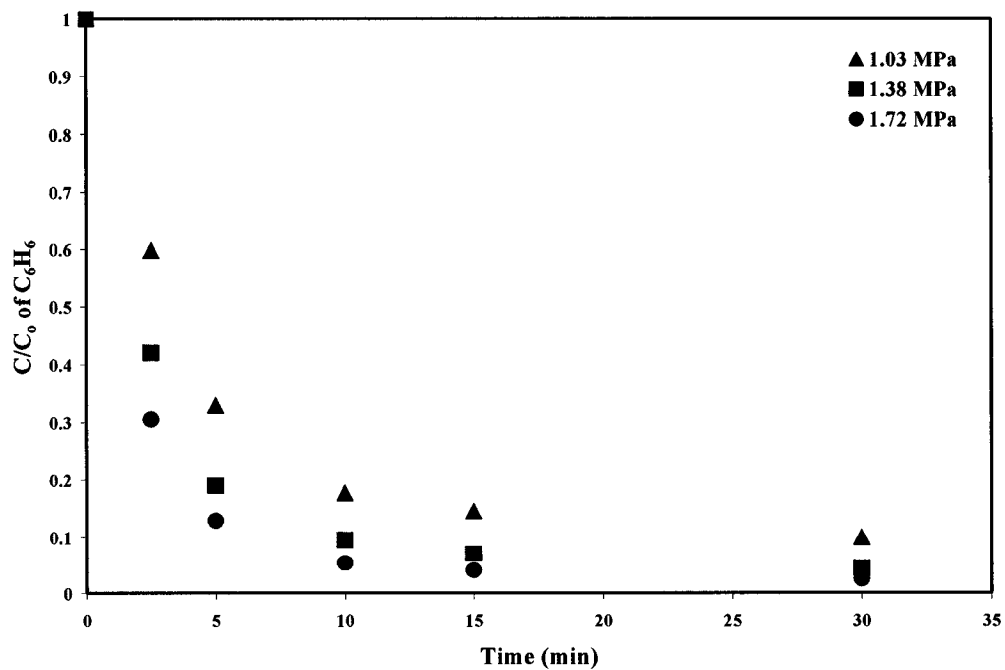


Figure 4.21: Effect of Oxygen Pressure on the Benzene Degradation at 240°C, pH 4.

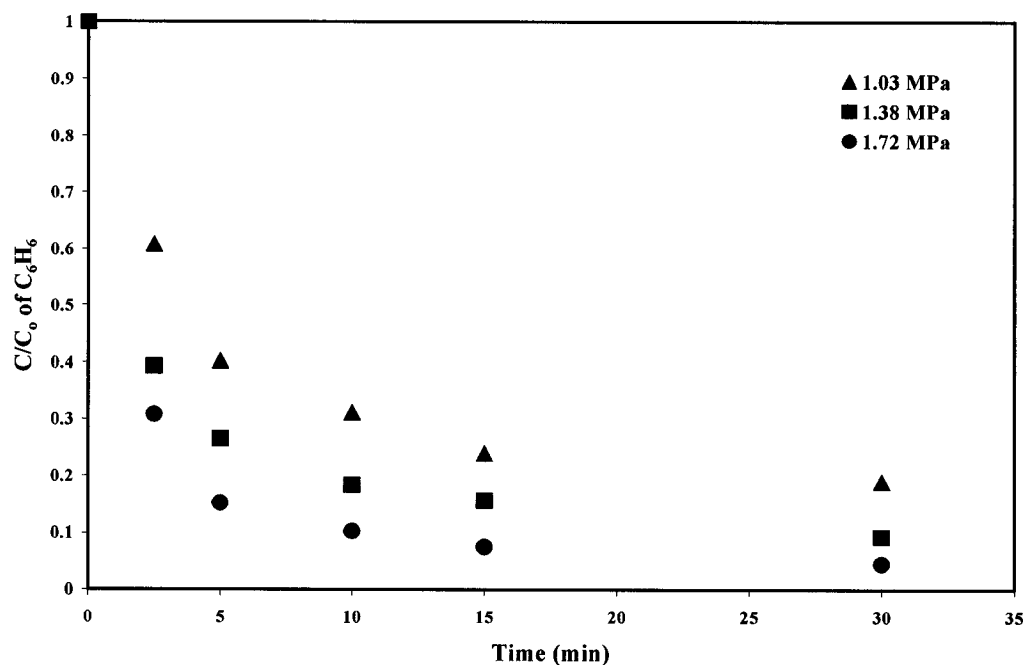


Figure 4.22: Effect of Oxygen Pressure on the Benzene Degradation at 260°C, pH 4.

4.4.7 The pH Fluctuation during the Experiments

As was mentioned before, during each experiment the pH of the solution fluctuated. At the beginning of the experiment, as benzene started to oxidize organic acids were produced and the pH of the solution decreased. As the experiment proceeded most of the produced organic acids oxidized, thus increasing the pH of the solution. As shown in Figure 4.23, the pH decreased faster at 240 and 260 than 220°C. Also, as will be seen in chapter 5, at higher temperatures lower amounts of acids were produced and degraded faster than at the lower temperature. This is reflected on the pH value with its initial steep decrease followed by the subsequent increase.

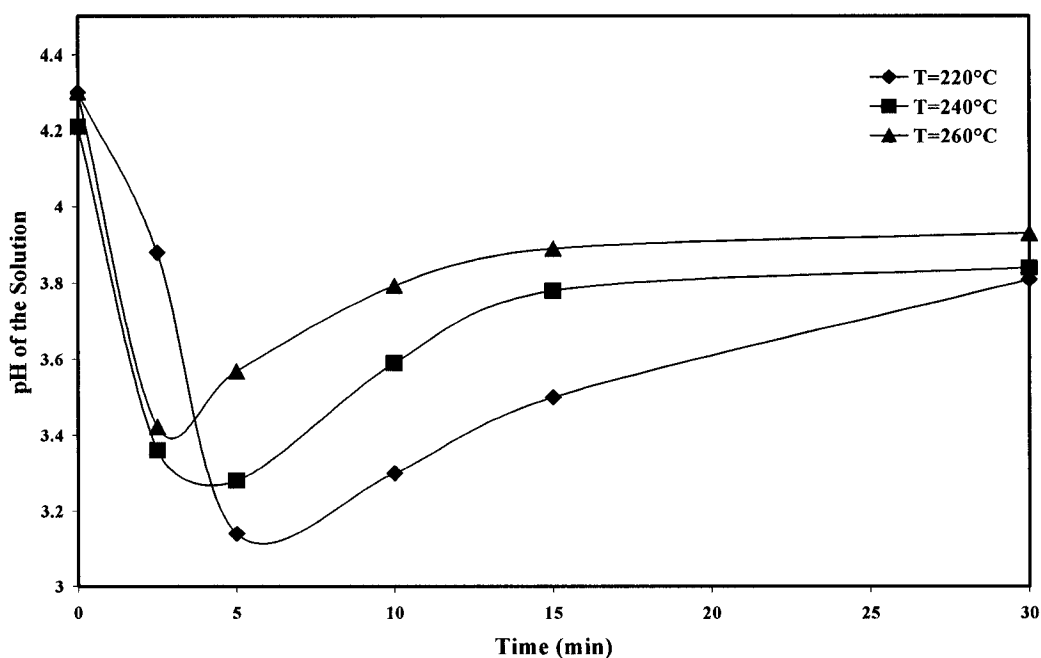


Figure 4.23: Change of pH with Time during Experiment, P_{O_2} = 1.38 MPa, Initial Benzene Concentration = 5.63 mmol/L.

4.4.8 Effect of Acidification Methods on the Degradation of Benzene

Nitric acid was commonly used to lower the pH of the reaction medium. However, sulfuric acid was also tried. From Figure 4.24, it is obvious that with the sulfuric acid also a good degradation was achieved at 220°C and 1.38 MPa. The initial pH of this experiment was 4. Furthermore, to determine whether the type of the additive has an effect on the quality of the oxidation, two experiments have been repeated at the same pH with two different additives, nitric and acetic acids. These experiments have been done at 240°C and oxygen pressure of 1.38 MPa. It can be seen from Figure 4.25 that the results were comparable, which suggests that the oxidation is independent on the type of acid, as long as the given pH is reached.

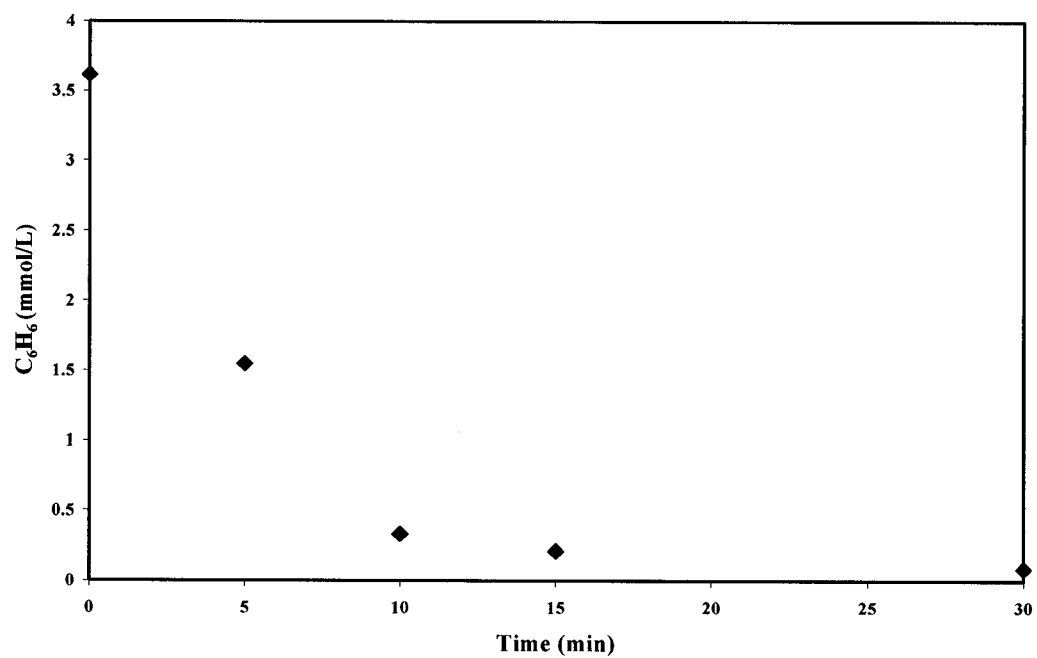


Figure 4.24: Degradation of Benzene with Sulfuric Acid at 220°C, P_{O_2} = 1.38 MPa, pH=4.

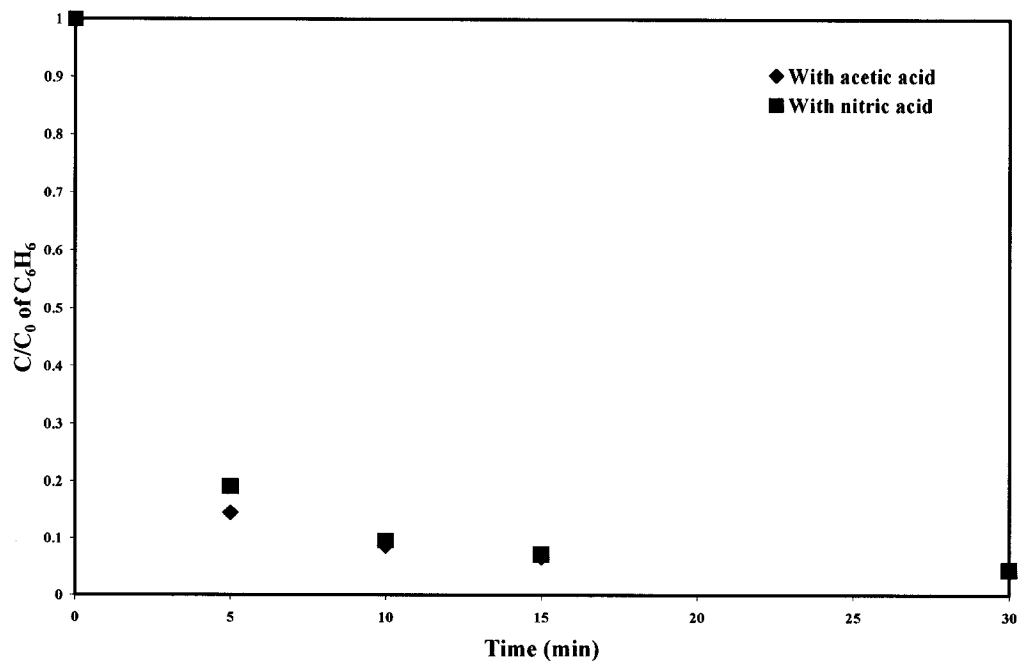


Figure 4.25: Degradation of Benzene at 240°C, P_{O_2} = 1.38MPa, pH=4.

4.5 Effect of Initial Benzene Concentration on its Degradation

In the results presented thus far, the initial benzene concentration was 5.63 mmol /L. In order to determine the effect of concentration, two experiments were done with initial benzene concentration of 11.25 mmol/L and 16.88 mmol/L. Experiments carried out in the high temperature region, i.e. 220, 240 and 260°C and at pH 6 and 4. There was always the excess amount of oxygen in these experiments.

Figures 4.26 and 4.27 show the benzene degradation at 260°C and pH 6. In both experiments, 95% degradation of benzene was achieved. In both of these experiments the amount of acids that have been produced was higher than what was produced with the lower initial benzene concentration, as expected, and that lowered the pH to less than 3. The effect of initial benzene concentrations was further studied at pH 4. Two experiments were done with initial benzene concentration of 11.25 mmol/L. These experiments were conducted at both 220 and 240°C, and the oxygen pressure of 2.76 MPa (Figure 4.28). It can be seen that at the first 2.5 minutes the degradation was much faster at 240°C and after that the results were comparable.

Figure 4.29 shows the pH profile of the solution when the initial benzene concentration was 11.25 mmol/L at 220°C and an initial oxygen pressure of 2.76 MPa. It is apparent that the pH reached below 3 after 5 minutes of oxidation. One of the important issues in these experiments was the safety concern raised from the high concentration of the organic acid produced due to the high initial benzene concentration when the pH of the solution dropped below 3. This low pH in combination with the high temperature and pressure may corrode the reactor walls thus weakening its structure.

Because of that, such experiments which resulted in pH lower than 3 could not be repeated often.

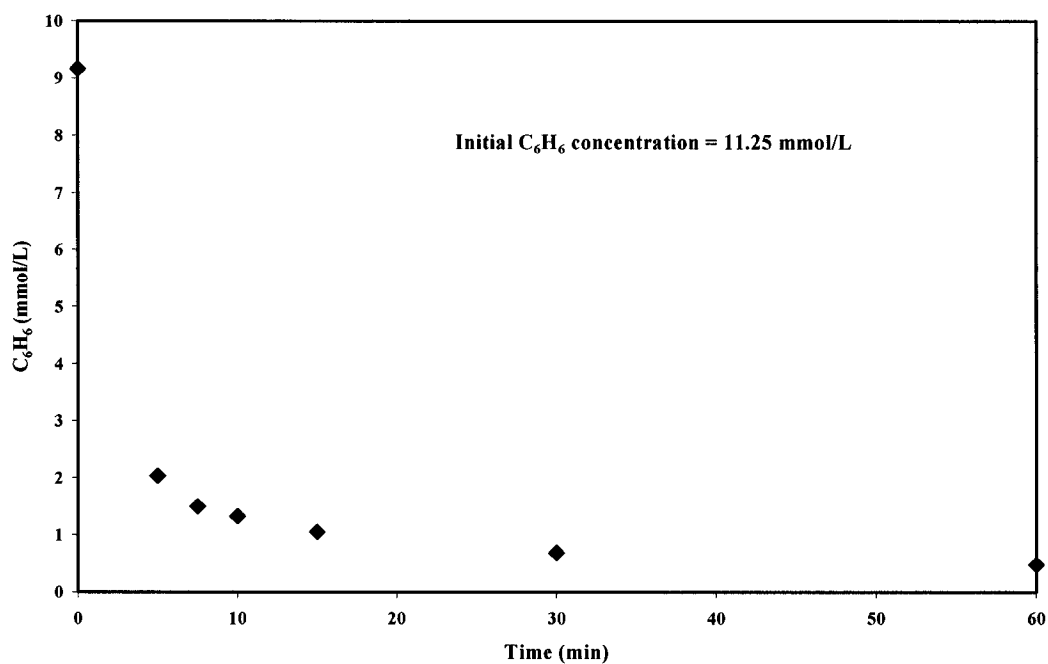


Figure 4.26: Degradation of Benzene at 260°C, P_{O_2} = 2.07 MPa, pH = 6.

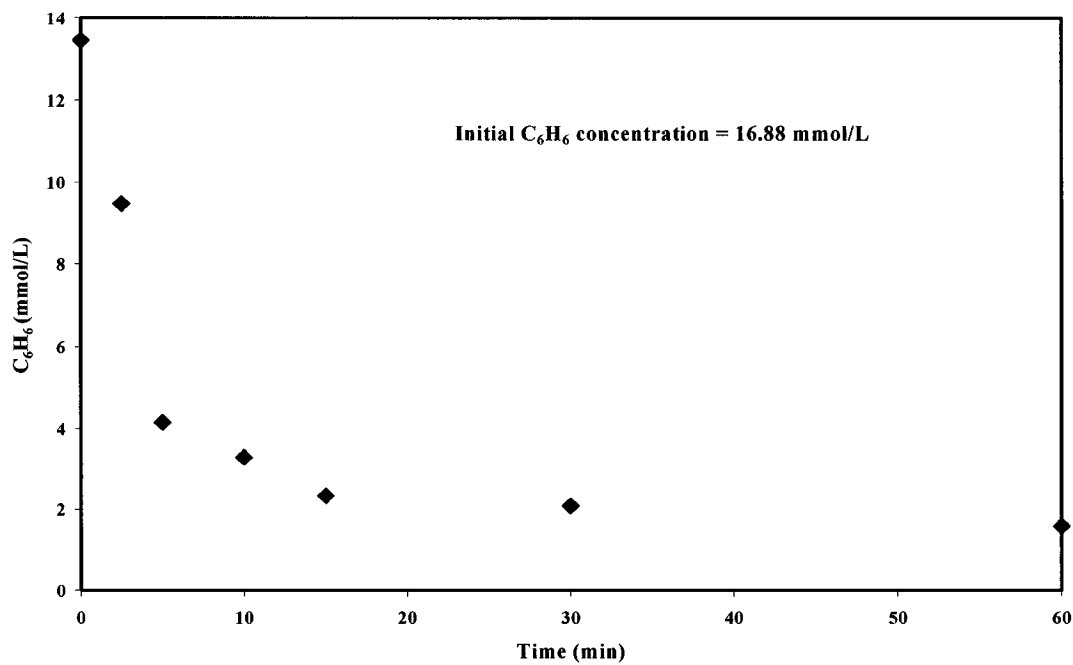


Figure 4.27: Degradation of Benzene at 260°C, P_{O_2} = 2.07 MPa, pH = 6.

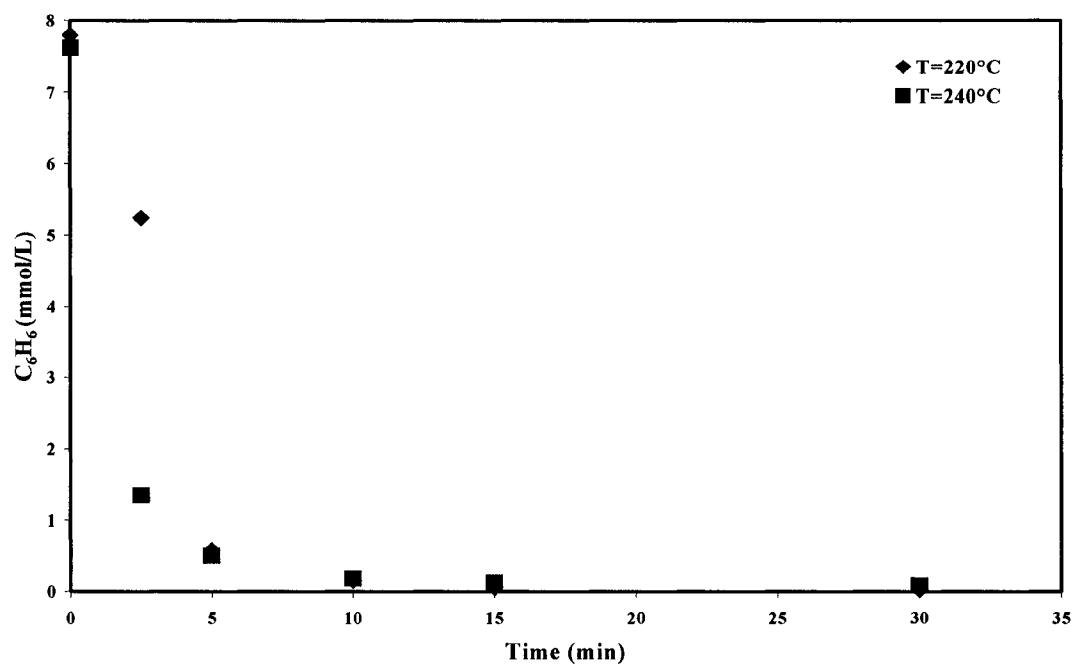


Figure 4.28: Effect of Temperature on Benzene Degradation, $P_{O_2}= 2.76$ MPa, pH=4. Initial Benzene Concentration of 11.25 mmol/L.

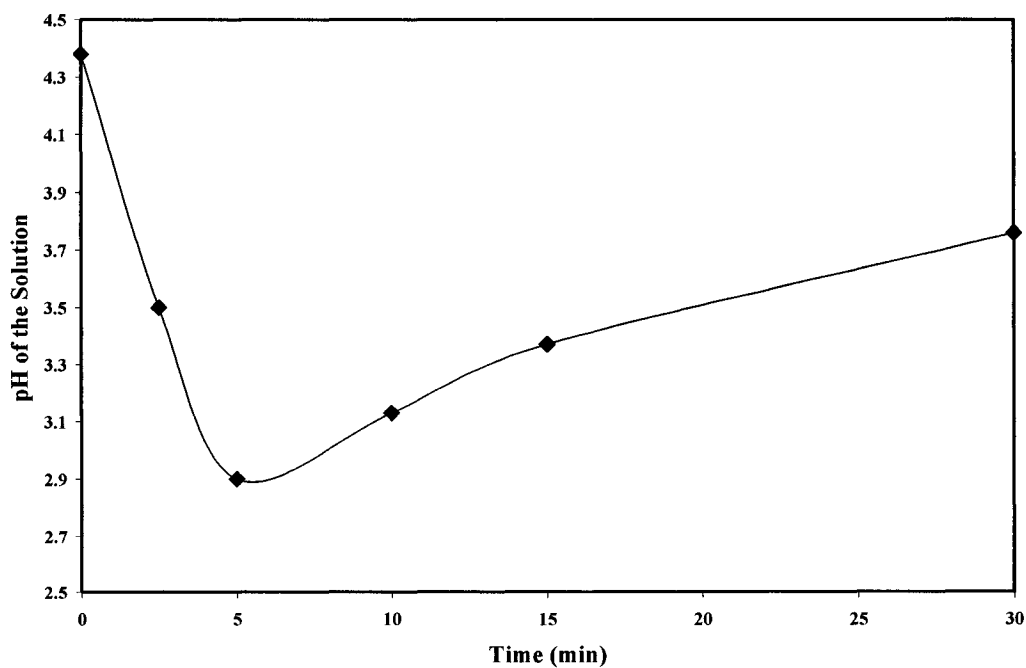


Figure 4.29: Change of pH with Time during Experiment, $T= 220^\circ C$ $P_{O_2}= 2.76$ MPa. Initial Benzene Concentration = 11.25 mmol/L.

4.6 Kinetic Modeling

The kinetics of benzene oxidation was studied at temperatures between 220-260°C with oxygen pressures from 0.69 MPa to 1.72 MPa, and at initial pH of 4. These conditions were chosen because they gave the best degradation results. Because of the experimental set-up limitation, the number of the samples collected during the experiments was limited especially at the beginning of the experiment when the oxidation was very fast. It has affected the quality of the model. Figures 4.30-4.34 show the results that were obtained at 220°C at different oxygen pressures. The oxidation reaction can be represented by two first order reaction kinetics, corresponding to the two steps of the degradation. At the beginning, the oxidation of benzene was fast and it was followed by the slow oxidation step. Most of the benzene was degraded during the first step.

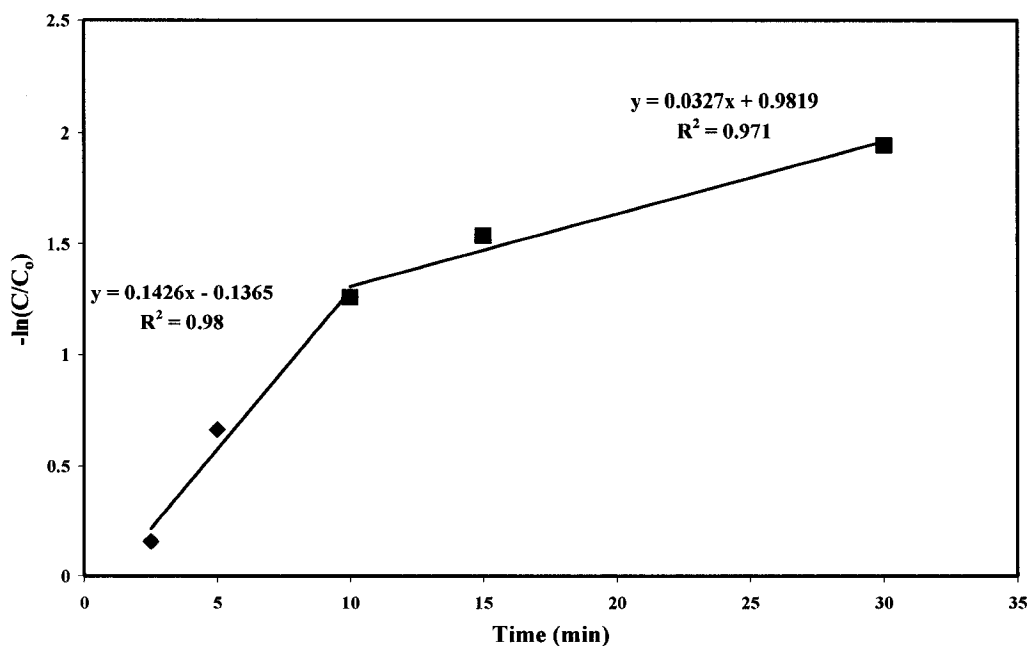


Figure 4.30: First Order Kinetic Model Fit of Benzene Degradation, T=220°C, P_{O2}=0.69MPa, pH= 4.

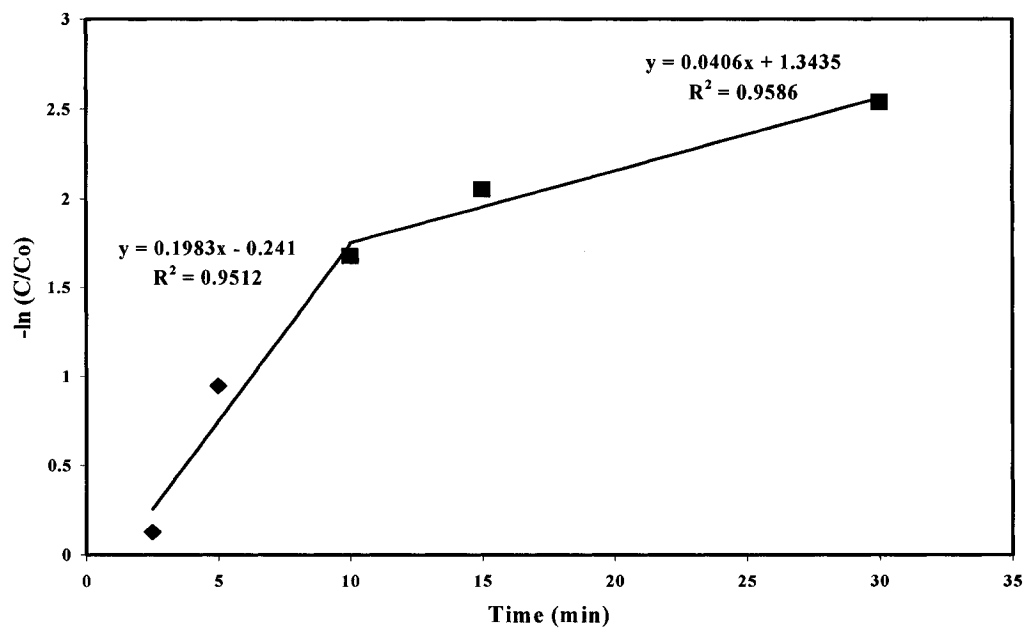


Figure 4.31: First Order Kinetic Model Fit of Benzene Degradation, $T=220^{\circ}\text{C}$, $P_{\text{O}_2}=0.86\text{ MPa}$, $\text{pH}=4$.

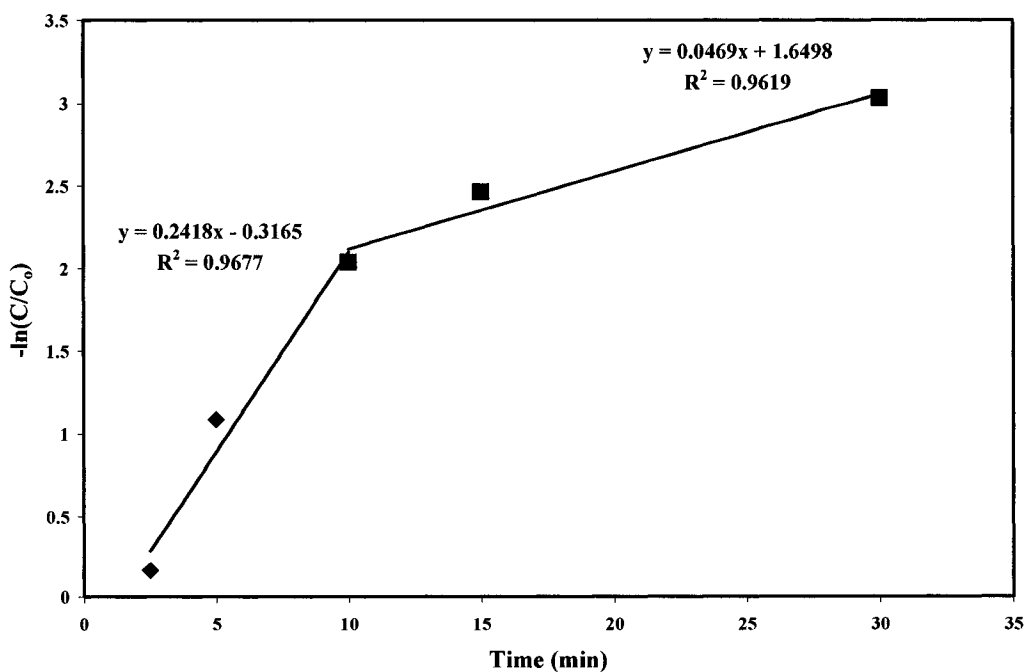


Figure 4.32: First Order Kinetic Model Fit of Benzene Degradation, $T=220^{\circ}\text{C}$, $P_{\text{O}_2}=1.03\text{ MPa}$, $\text{pH}=4$.

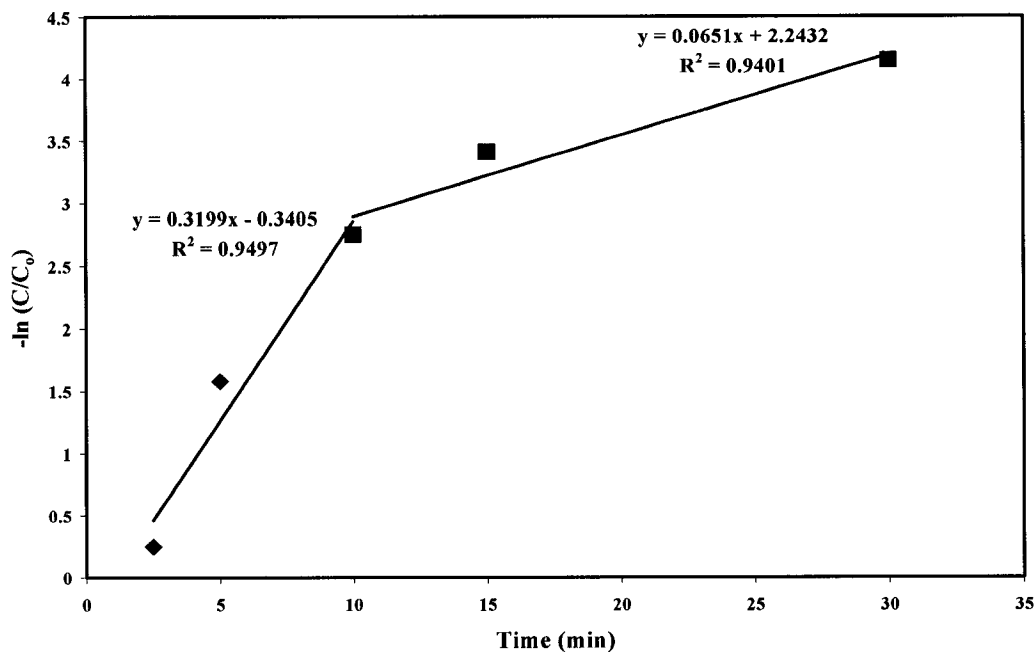


Figure 4.33: First Order Kinetic Model Fit of Benzene Degradation, $T=220^{\circ}\text{C}$, $P_{\text{O}_2}=1.38\text{ MPa}$, $\text{pH}=4$.

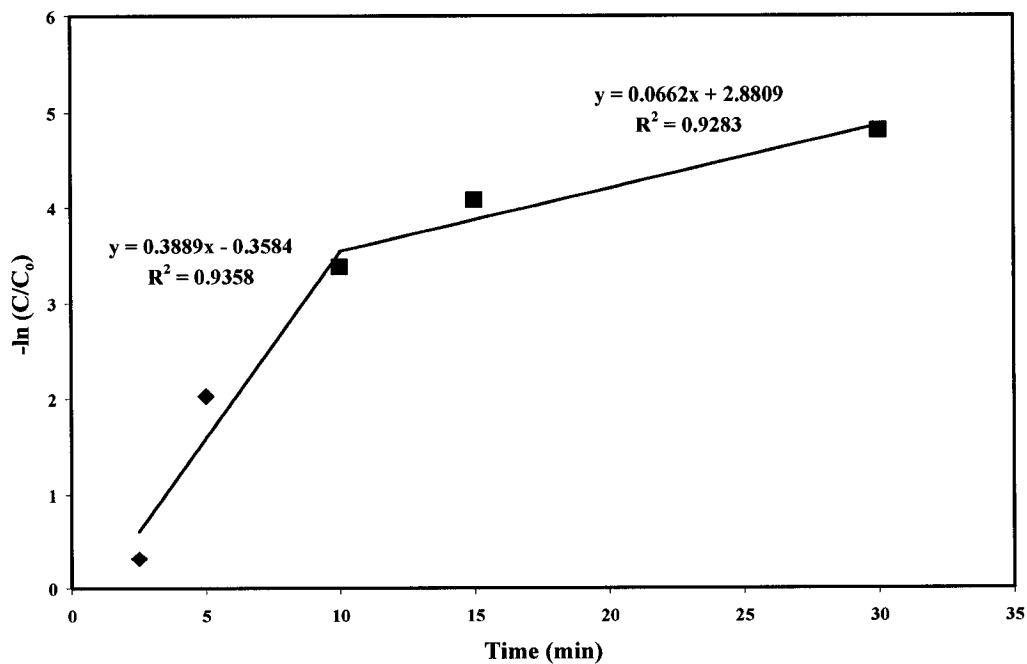


Figure 4.34: First Order Kinetic Model Fit of Benzene Degradation, $T=220^{\circ}\text{C}$, $P_{\text{O}_2}=1.72\text{ MPa}$, $\text{pH}=4$.

From those figures k' , which is equal to the reaction rate constant (k) multiplied by the oxygen pressure P_{O_2} , can be calculated and the values are summarized in Table 4.2.

Table 4.2: k' Values at Different P_{O_2} for the Fast Step, $T=220^\circ\text{C}$.

P_{O_2} (MPa)	k'
0.69	0.1426
0.86	0.1983
1.03	0.2418
1.38	0.3199
1.72	0.3889

The first order kinetic model fit for 240 and 260°C and different oxygen pressure can be found at figures 4.35-4.37 and figures 4.38-4.40, respectively.

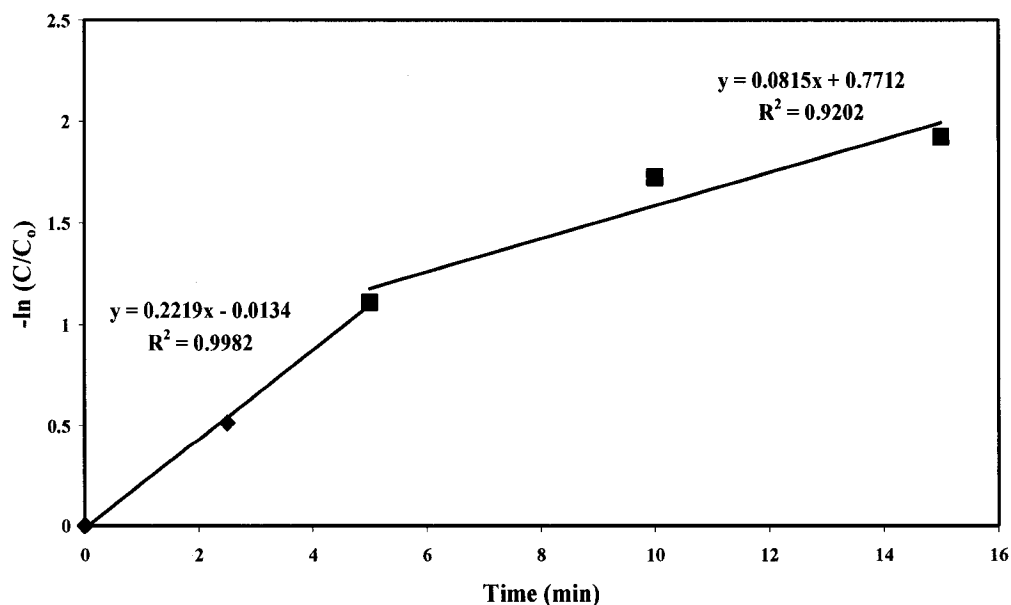


Figure 4.35: First Order Kinetic Model Fit of Benzene Degradation, $T=240^\circ\text{C}$, $P_{O_2}=1.03\text{MPa}$, $\text{pH}= 4$.

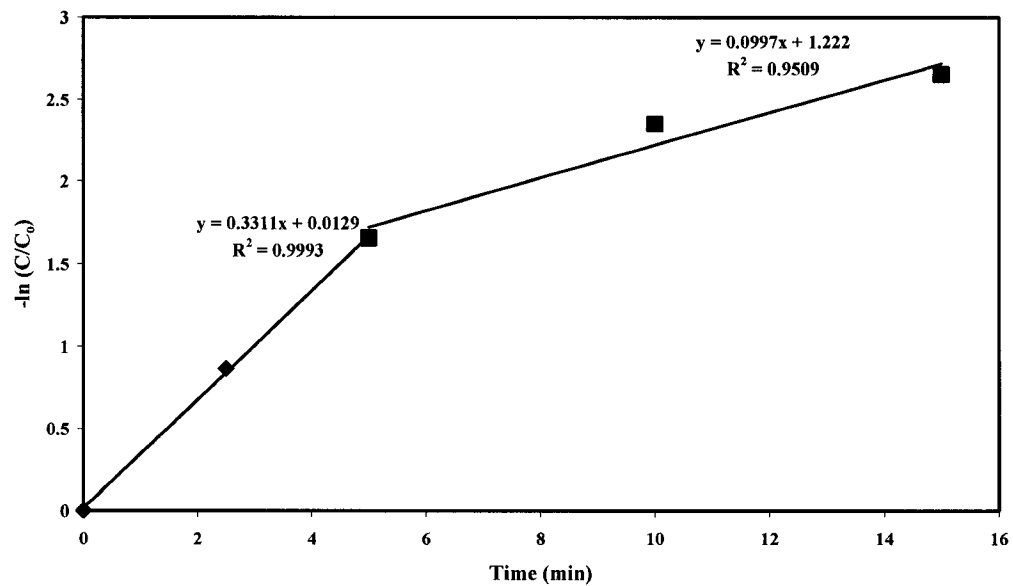


Figure 4.36: First Order Kinetic Model Fit of Benzene Degradation, T=240°C, P_{O2}=1.38MPa, pH= 4.

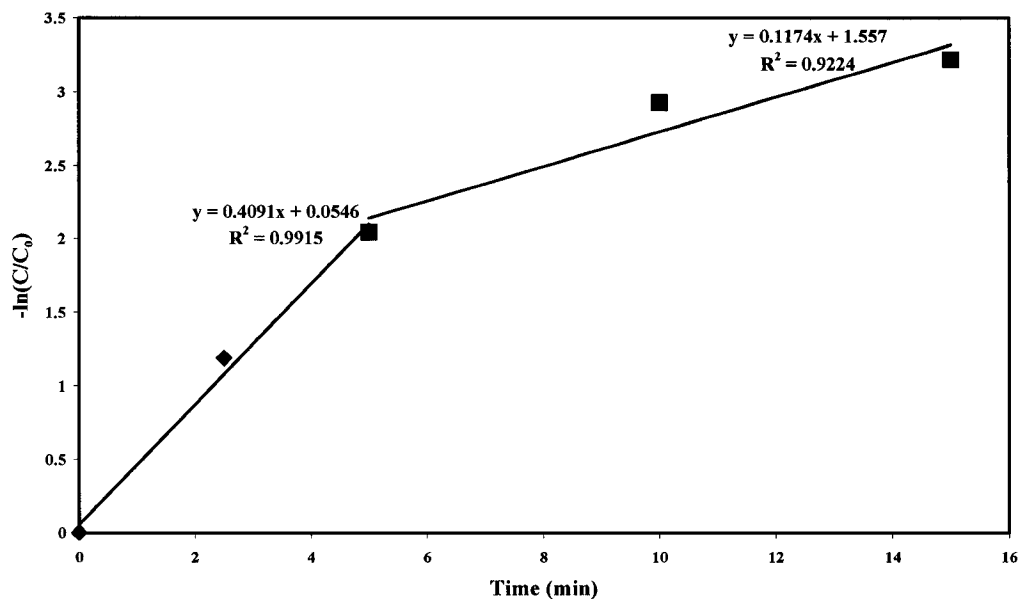


Figure 4.37: First Order Kinetic Model Fit of Benzene Degradation, T=240°C, P_{O2}=1.72MPa, pH= 4.

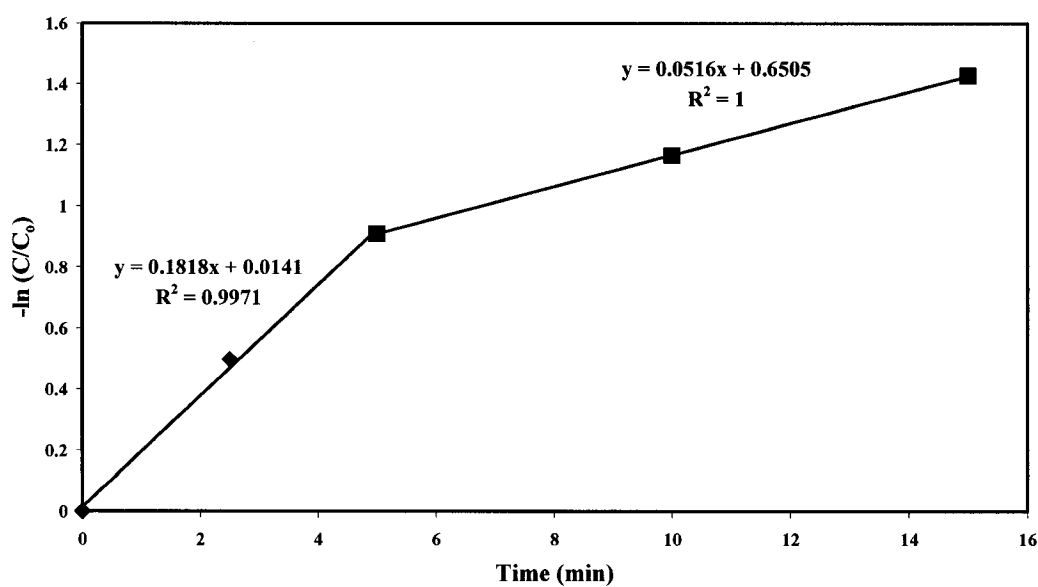


Figure 4.38: First Order Kinetic Model Fit of Benzene Degradation, $T=260^{\circ}\text{C}$, $P_{\text{O}_2}=1.03\text{MPa}$, $\text{pH}=4$.

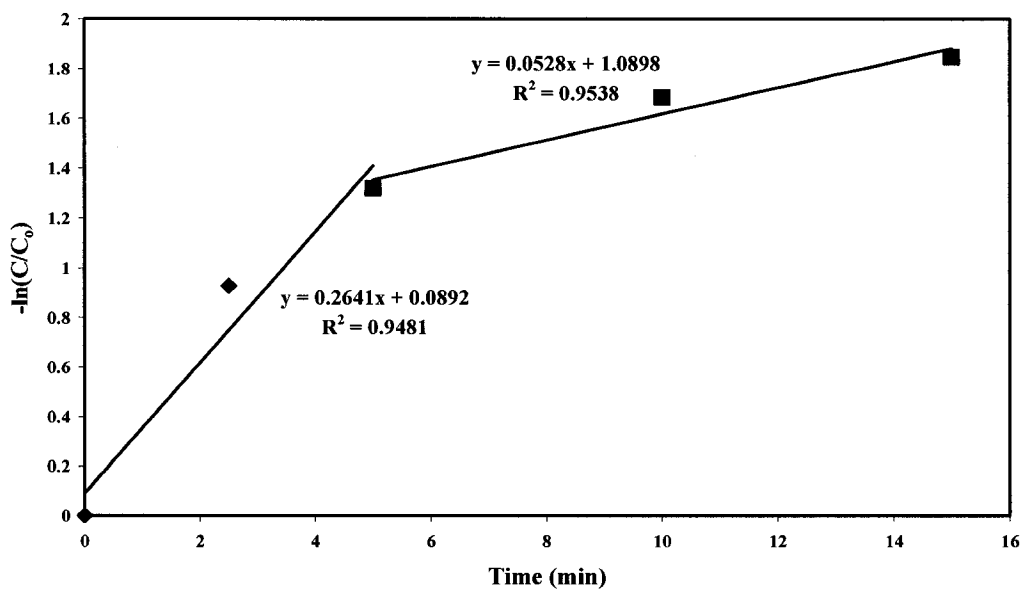


Figure 4.39: First Order Kinetic Model Fit of Benzene Degradation, $T=260^{\circ}\text{C}$, $P_{\text{O}_2}=1.38\text{MPa}$, $\text{pH}=4$.

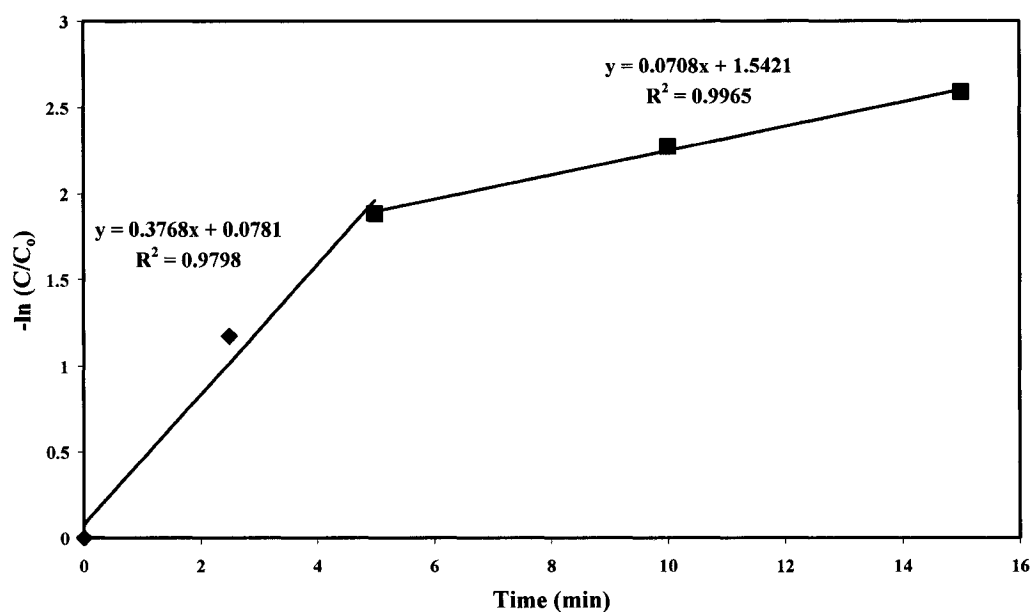


Figure 4.40: First Order Kinetic Model Fit of Benzene Degradation, T=260°C, P_{O2}=1.72MPa, pH= 4.

From the above figures k' can be calculated for both 240 and 260°C and the values are presented at Table 4.3 and 4.4, respectively.

Table 4.3: k' Values at Different P_{O2} for the Fast Step, T=240°C.

P _{O2} (MPa)	k'
1.03	0.2219
1.38	0.3311
1.72	0.4091

Table 4.4: k' Values at Different P_{O_2} for the Fast Step, $T=260^\circ\text{C}$.

P_{O_2} (MPa)	k'
1.03	0.1818
1.38	0.2641
1.72	0.3768

Figures 4.41-4.43 show plots of k' against P_{O_2} which are used to calculate the rate constant at 220, 240 and 260°C , respectively. Those figures also show that the reaction was first order with the oxygen pressure. The values for the rate constant can be found in Table 4.5.

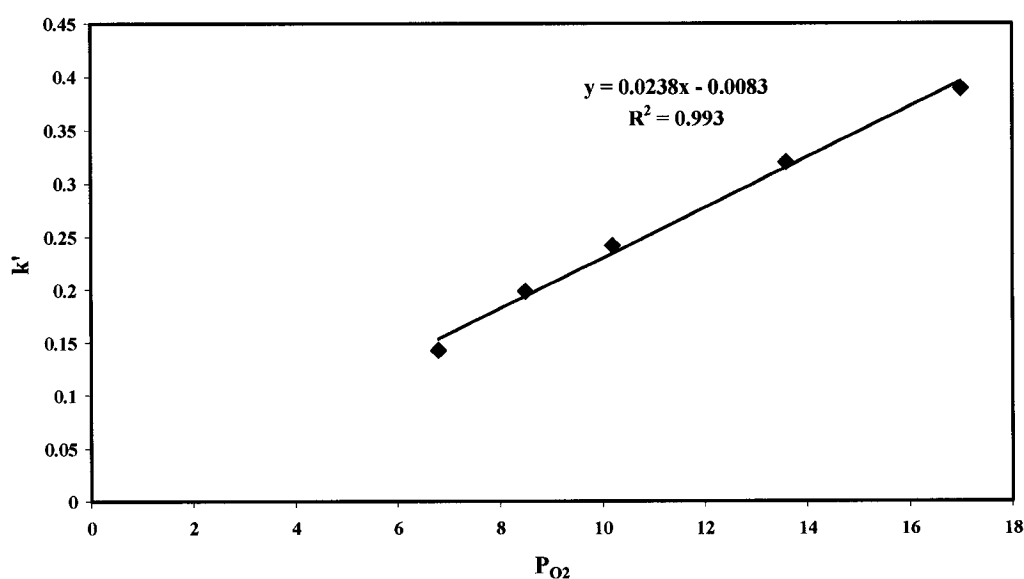


Figure 4.41: k' vs. P_{O_2} , $T=220^\circ\text{C}$, $\text{pH}=4$.

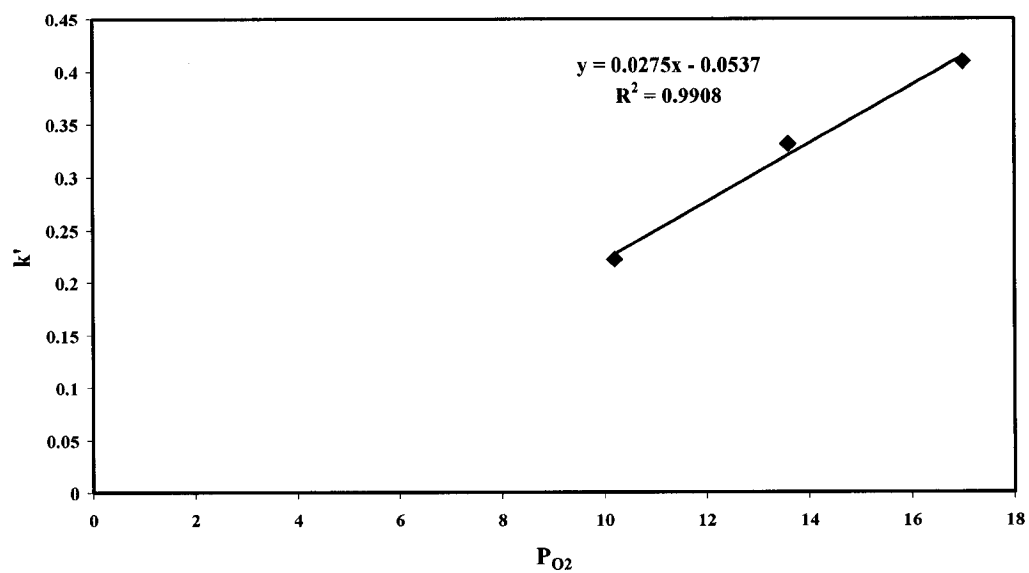


Figure 4.42: k' vs. P_{O_2} , $T=240^{\circ}\text{C}$, $\text{pH}=4$.

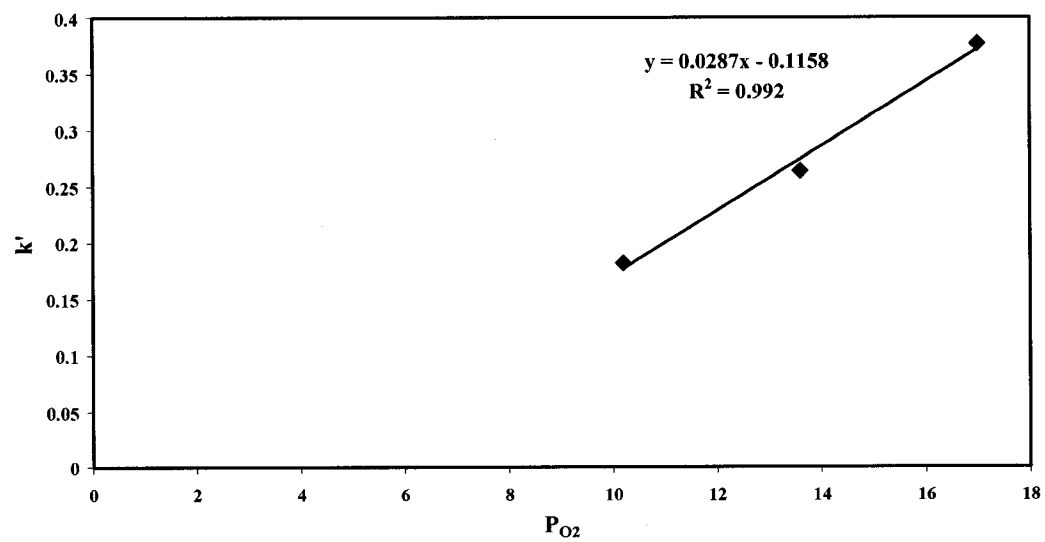


Figure 4.43: k' vs. P_{O_2} , $T=260^{\circ}\text{C}$, $\text{pH}=4$.

Table 4.5: Rate Constant Value at Different Temperatures.

T (°C)	k
220	0.0238
240	0.0275
260	0.0287

The Arrhenius plot is shown in Figure 4.44. The activation energy for the fast step of the benzene oxidation can then be calculated from the plot to be 10.3 kJ/mol.

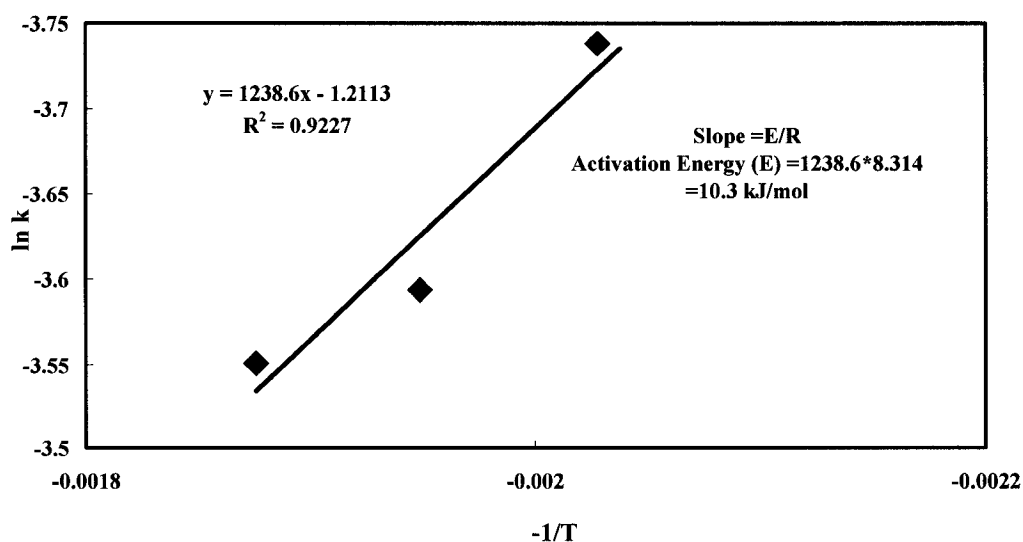


Figure 4.44: Arrhenius Plot for Oxidation of Benzene, pH=4.

In summary, it is apparent from the results obtained in this chapter that the wet air oxidation of benzene was affected by temperature, pressure and pH. Also, it was shown that the wet air oxidation of benzene exhibited a two-step reaction. The initial step was fast followed by a slow rate of reaction. The oxidation rate was found to be first order with oxygen. The order with respect to benzene was found to be one in both steps.

CHAPTER FIVE

RESULTS AND DISCUSSIONS

REACTION INTERMEDIATES

During the course of experiments, different reaction intermediates were produced. Most of those intermediates were oxidized further to the final products. Some of them were more stable during the oxidation under the experimental conditions and appeared as final products (e.g. the acetic acid). From an environmental point of view, it is important to know that the intermediates produced during waste treatment processes are not more harmful than the original materials in the waste effluent.

5.1 Total Organic Carbon Measurements

The Total Organic Carbon (TOC) measurements were performed in order to close the carbon balance, to demonstrate indirectly that the main reaction products were acetic acid and formic acid and that almost total degradation of benzene to CO_2 and H_2O was achieved. The effect of temperature on the formation of the intermediates was studied by measuring the TOC reduction during the experiment.

Figure 5.1 shows the TOC results obtained at oxygen pressure of 1.38 MPa, pH 6 and temperatures of 220, 240 and 260°C. The results suggest that the higher the temperature, the faster the TOC reduction, especially within the first 60 minutes, implying that at higher temperature, the reaction proceeded fast to the final products.

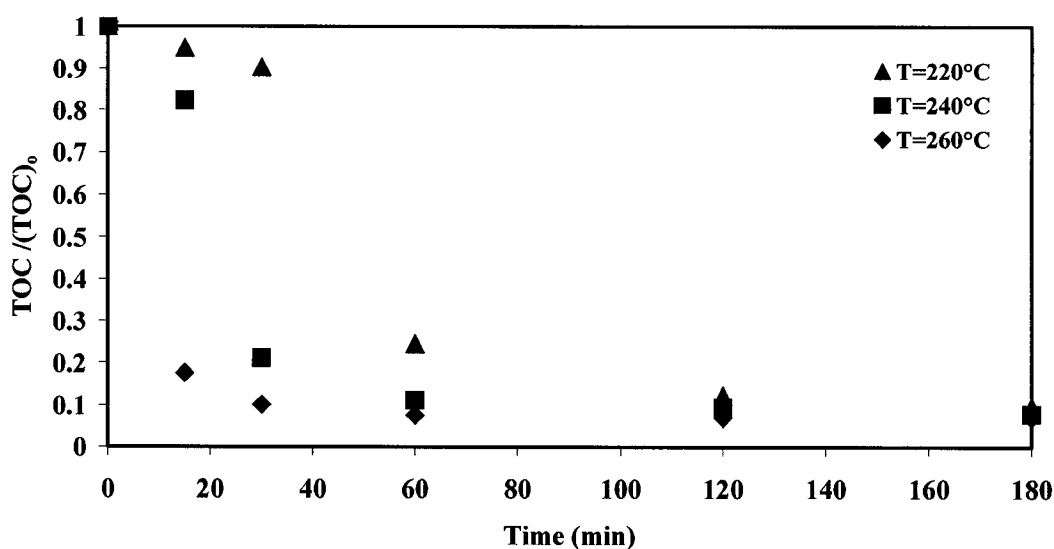


Figure 5.1: TOC Reduction with Time, $P_{O_2}=1.38$ MPa, pH=6.

Figures 5.2, 5.3 and 5.4 show the results from the TOC measurements together with the results that were calculated from the remaining benzene and the produced acids at 220, 240 and 260°C, respectively. The results show that the acetic acid was one of the final products and could not be degraded within the range of temperatures studied. The amount of TOC was compared to the total amount of carbon in the produced acetic acid, formic acid and in the remaining unreacted benzene during the experiment in order to verify the carbon balance. Figures 5.5, 5.6 and 5.7 show that the results obtained from the TOC measurement were comparable to the total amount of carbon that was calculated at 220, 240 and 260°C, respectively, confirming the carbon balance. It should be mentioned that negligible amounts of propanoic acid, glycolic acid and benzoquinone were detected during the oxidation at all conditions.

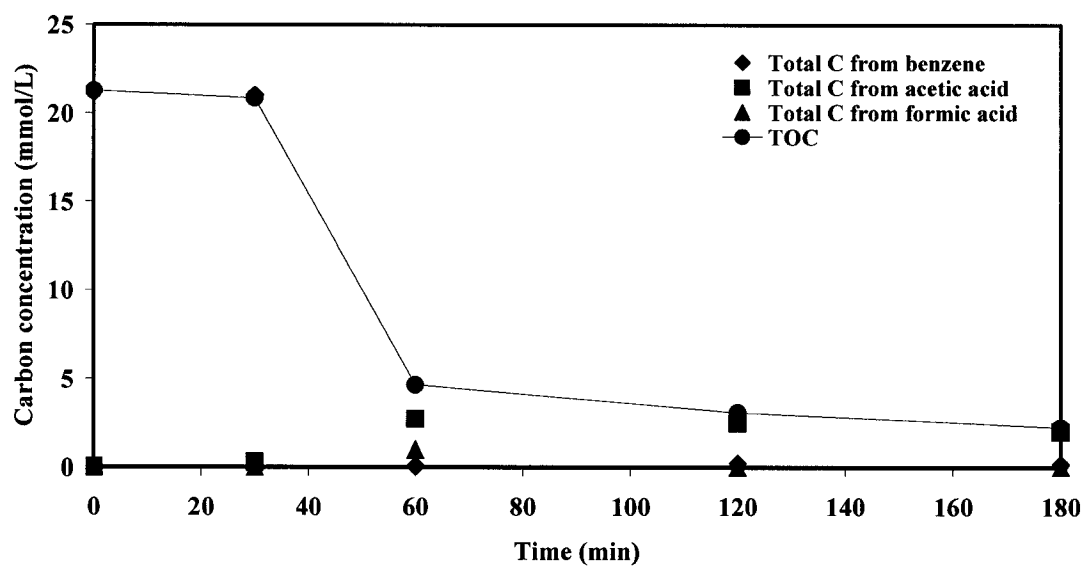


Figure 5.2: Detailed Change in Carbon Concentration with Time, $T=220^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{MPa}$.

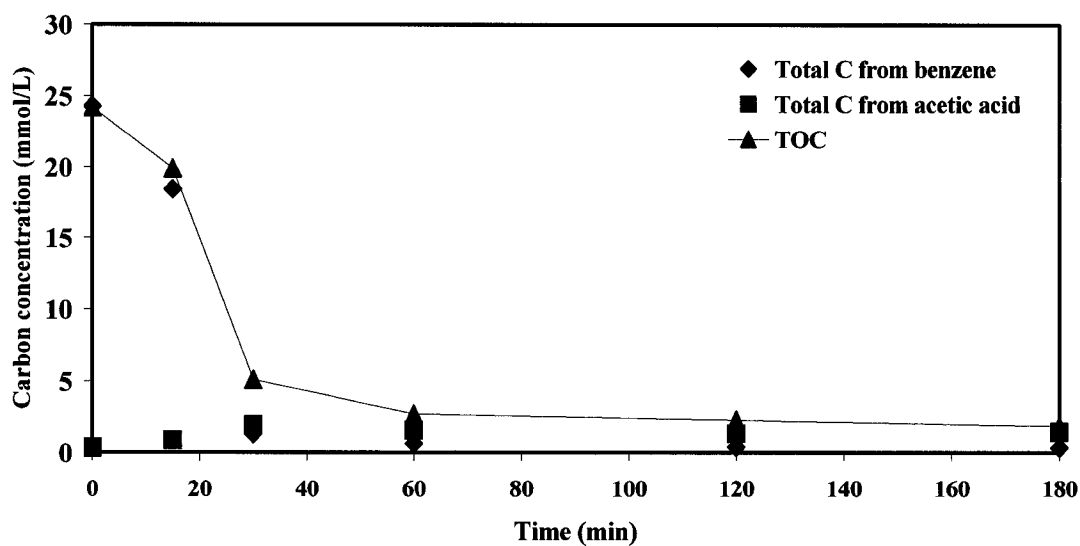


Figure 5.3: Detailed Change in Carbon Concentration with Time, $T=240^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{MPa}$.

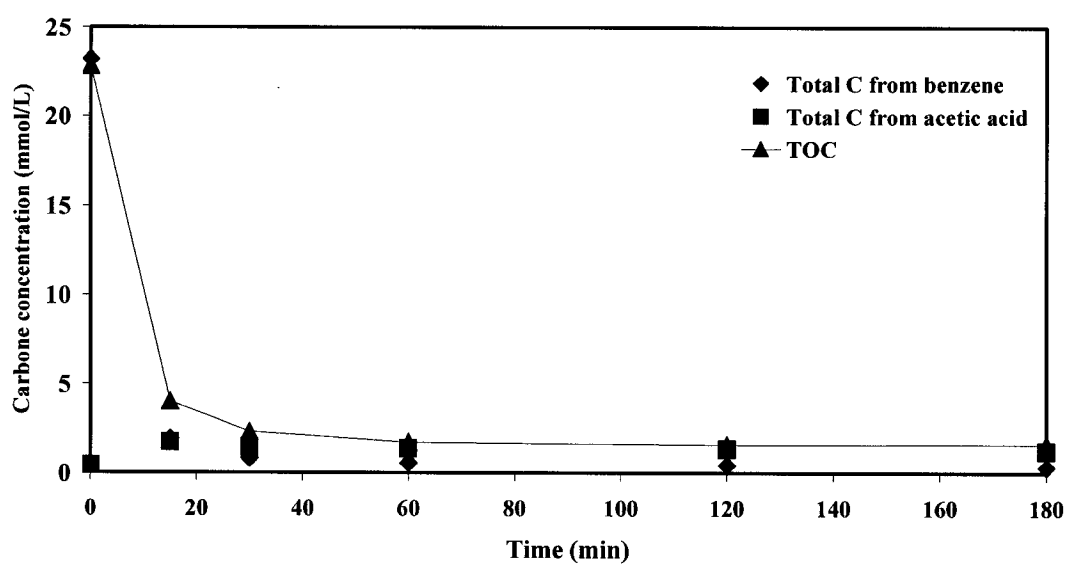


Figure 5.4: Detailed Change in Carbon Concentration with Time, $T=260^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{MPa}$.

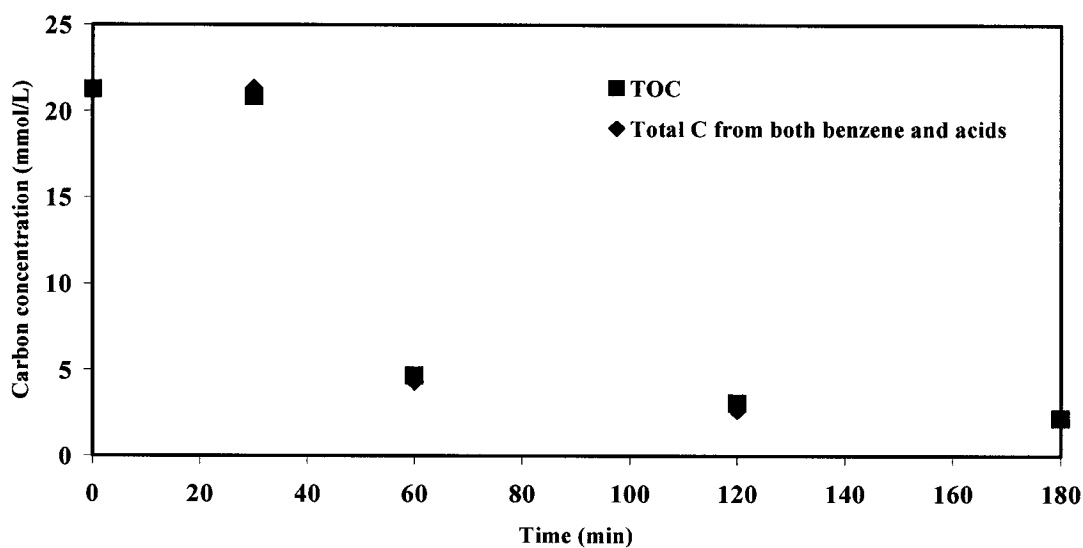


Figure 5.5: Carbon Balance, $T=220^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{MPa}$.

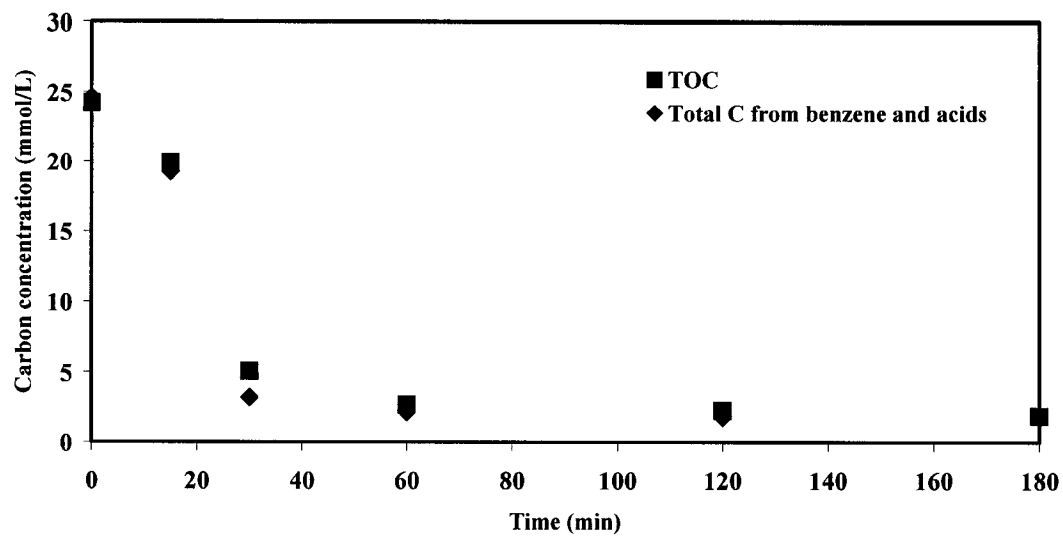


Figure 5.6: Carbon Balance, $T=240^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{MPa}$.

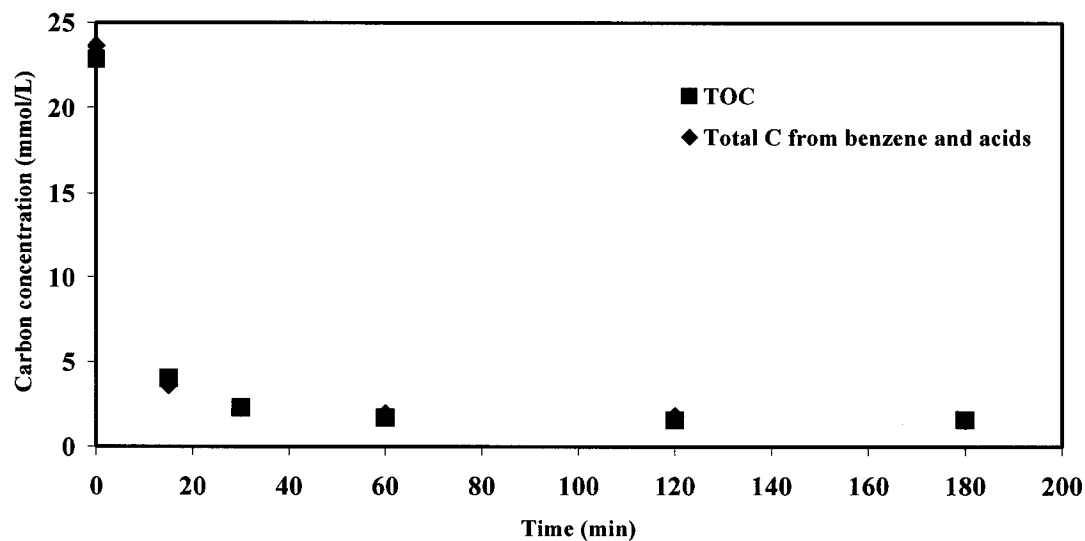


Figure 5.7: Carbon Balance, $T=260^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{MPa}$.

In order to test the repeatability of the results another set of experiments were done at 220°C, 240°C and 260°C, respectively. The experiment were performed at pH 6 and 1.38 MPa of oxygen pressure. Figures 5.8, 5.9 and 5.10 show that the results shown in figures 5.5, 5.6 and 5.7 were repeatable.

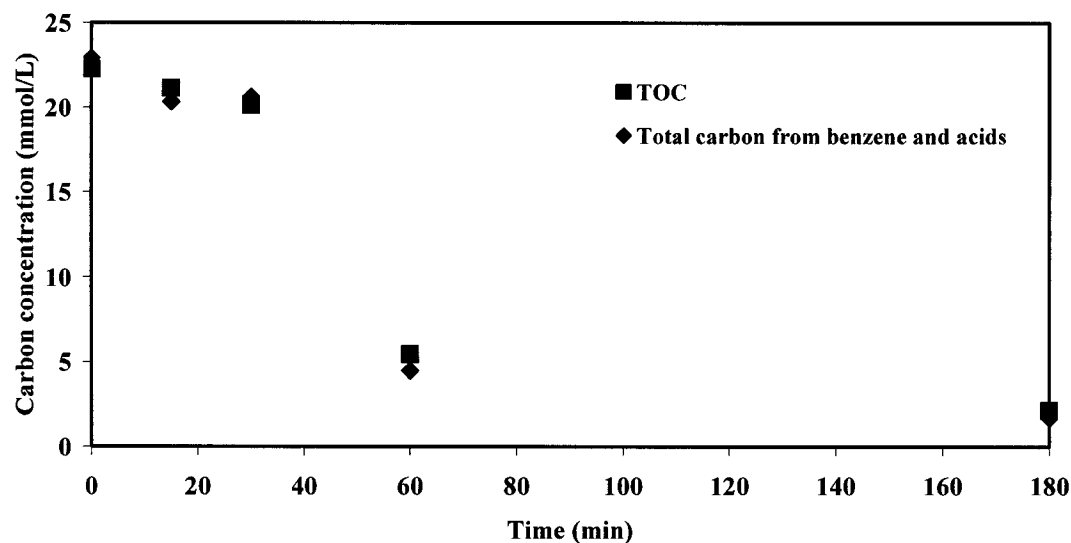


Figure 5.8: Repeatability of Carbon Balance, $T=220^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{MPa}$.

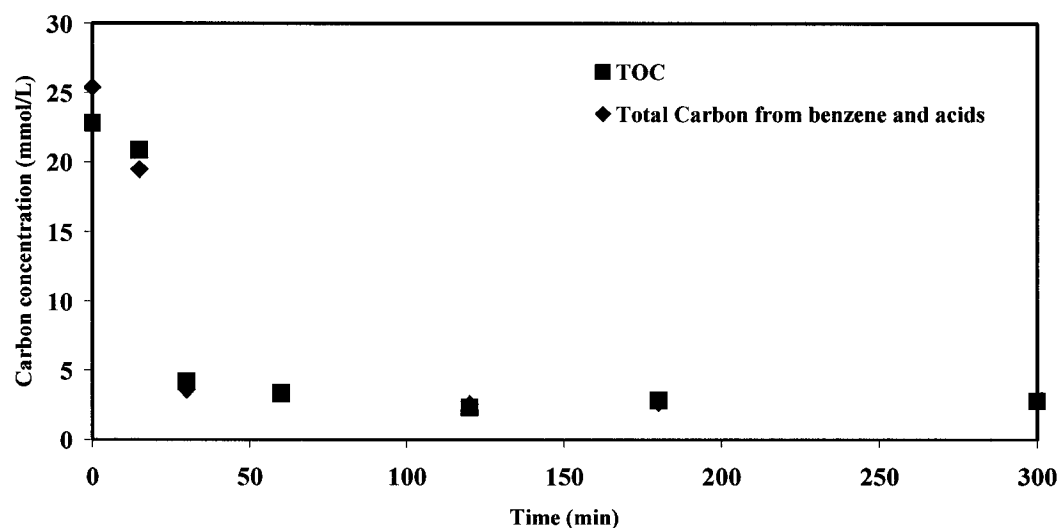


Figure 5.9: Repeatability of Carbon Balance, $T=240^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{MPa}$.

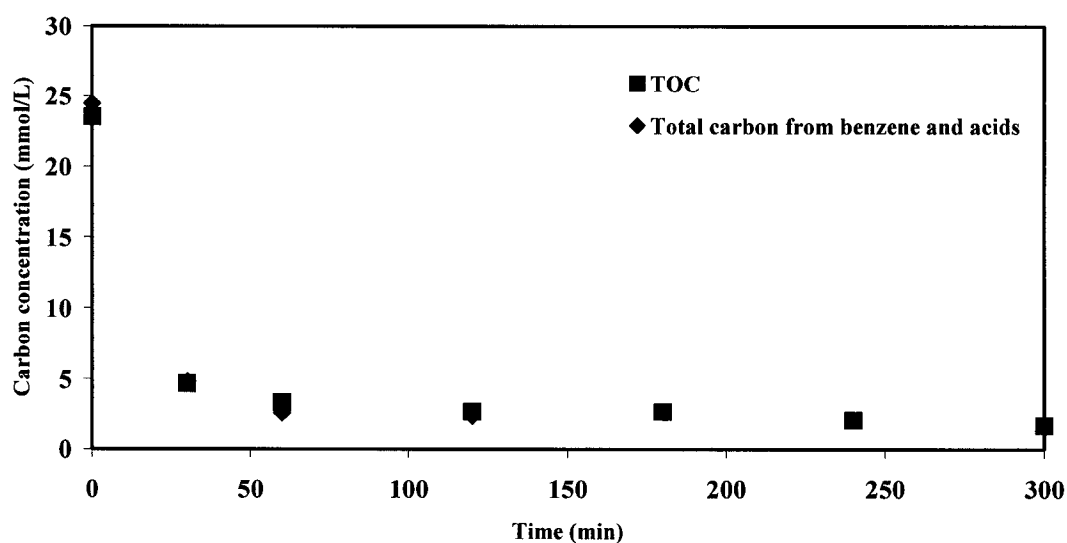


Figure 5.10: Repeatability of Carbon Balance, $T=260^{\circ}\text{C}$, $\text{pH}=6$, $P_{\text{O}_2}=1.38\text{MPa}$.

In some experiments, the amount of carbon dioxide that was produced during the oxidation was measured and compared with the theoretical amount that should be present at the end of the reaction if only the acetic acid and the remaining unreacted benzene existed as final products. The carbon dioxide in both the gas phase and the liquid phase was measured at the end of the experiment. The amount of the carbon dioxide in the gas phase was collected by passing the gas through a solution of a 2 M NaOH in order to convert the carbon dioxide to carbonate, which could then be analyzed in the TOC analyzer. Table 5.1 shows the results for an experiment that was conducted at 260°C , indicating a good agreement with those calculated theoretically. Detailed calculations can be found in the Appendix C.

Table 5.1: Carbon Dioxide Measurement, pH= 6, P_{O2}= 1.38 MPa.

Temperature (°C)	Theoretical CO ₂ (mmol)	Experimental CO ₂ (mmol)
260	21.4	20.8

5.2 Effect of Temperature on the Production and Degradation of both Acetic Acid and Formic Acid

In this section the results of the generation and degradation of acetic acid are shown at 220, 240 and 260°C and at different pH. In those experiments, the oxygen pressure was kept at 1.38 MPa. The results as shown in Figures 5.11 and 5.12 have been obtained at pH 6 and pH 4, respectively. In both cases the production of acetic acid reached a maximum followed by a partial degradation as the experiment proceeded. Also, it can be noted that at all temperatures some of the acetic acid produced during the process was further oxidized. However, since the reaction at pH 4 was faster, the production of acetic acid started earlier than at pH 6. At pH 4, at the higher temperature smaller amounts of acetic acid were produced suggesting that at higher temperature most of the benzene is converted directly to the final product, which is the carbon dioxide. Another explanation may be due to fast degradation of the acetic acid at the beginning of the reaction at higher temperature.

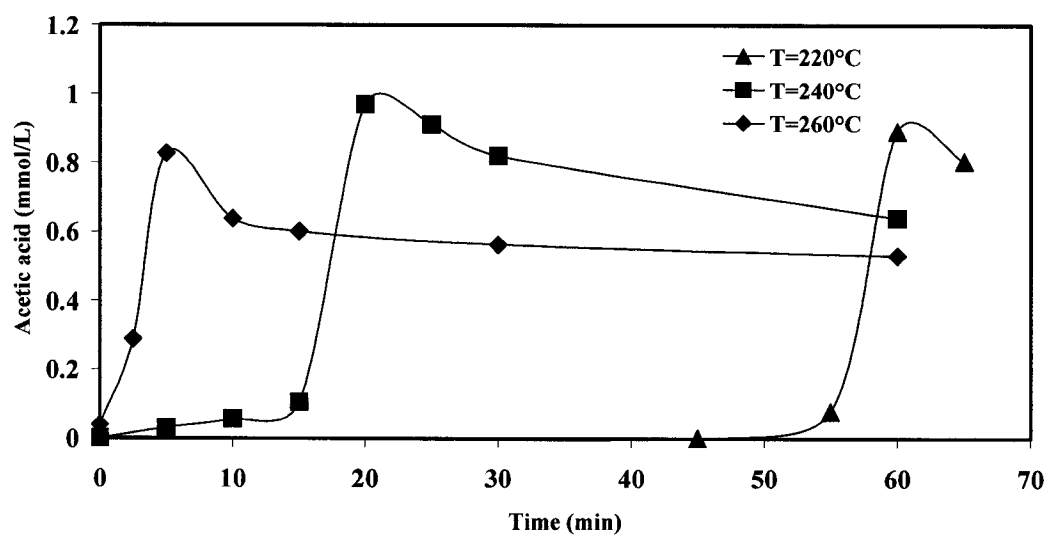


Figure 5.11: Effect of Temperature on Acetic Acid, $P_{O_2} = 1.38$ MPa, pH=6.

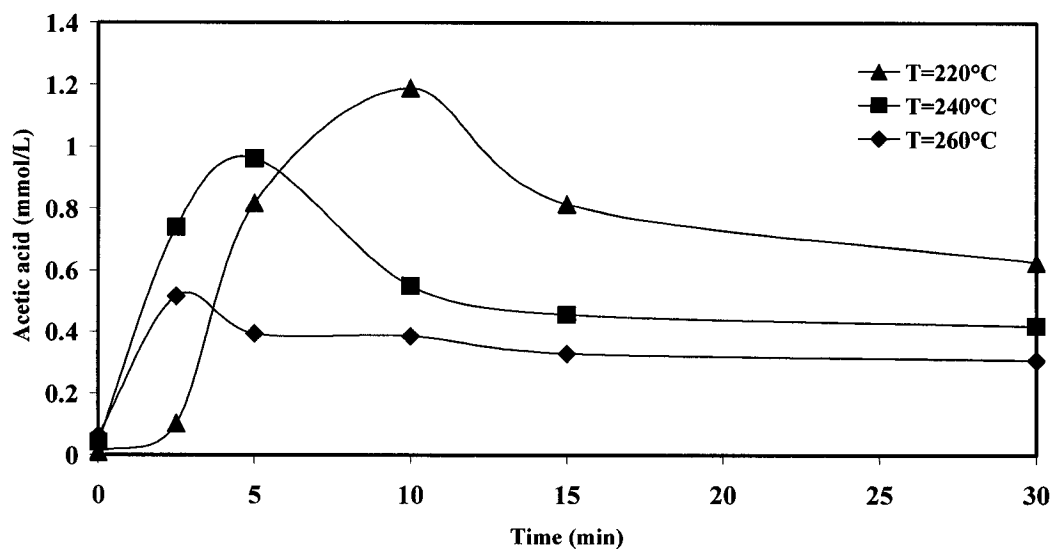


Figure 5.12: Effect of Temperature on Acetic Acid, $P_{O_2} = 1.38$ MPa, pH=4.

Unlike the acetic acid, the formic acid produced during the WAO was completely degraded to CO_2 and H_2O , especially at higher temperature. Figures 5.13 and 5.14 show the results obtained for formic acid at different temperatures for pH 6 and pH 4, respectively. At pH 6, all the formic acid produced at 260°C and most produced at 240°C , was degraded after 60 minutes of oxidation. However, at 220°C due to slow reaction, the production of formic acid started late and it did not get degraded during the course of the experiment. In contrast, at pH 4, as the temperature increased less formic acid was produced. Also, as the temperature increased the degradation of formic acid became faster, i.e. no formic acid was found after 15 minutes at 260°C . This will be further explored in section 5.6 where the WAO of acetic acid and formic acid is discussed.

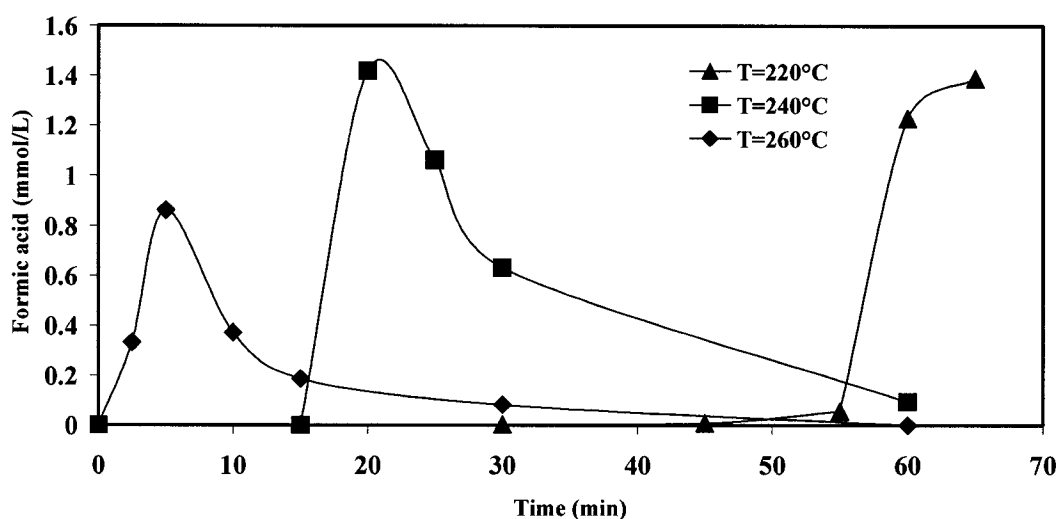


Figure 5.13: Effect of Temperature on Formic Acid, $P_{\text{O}_2} = 1.38 \text{ MPa}$, $\text{pH}=6$.

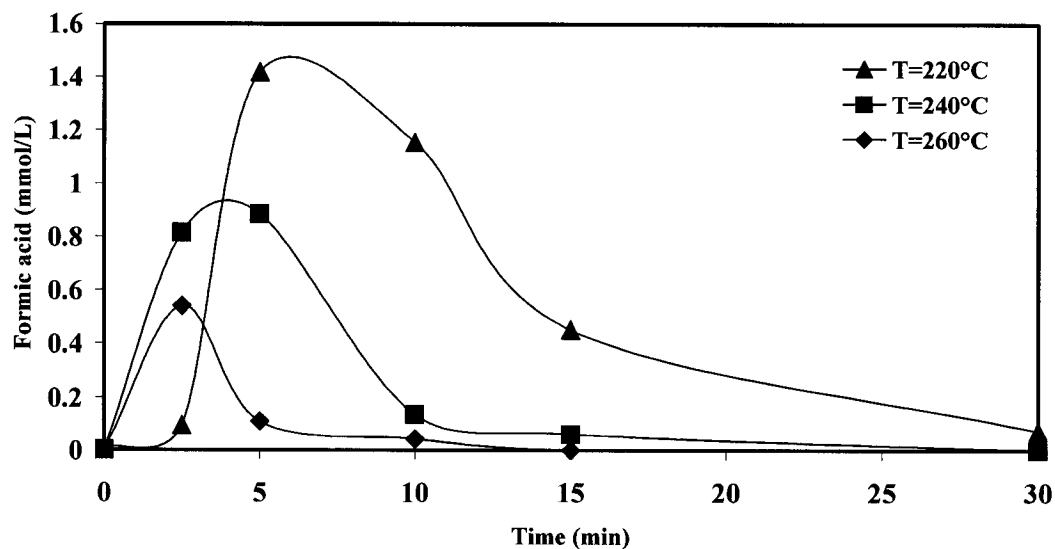


Figure 5.14: Effect of Temperature on Formic Acid, P_{O_2} = 1.38 MPa, pH=4.

5.3 Effect of Oxygen Pressure on the Production and Degradation of both Acetic Acid and Formic Acid

The effect of oxygen pressure was studied at different temperatures and different pH levels. Figures 5.15 and 5.16 show the effect of oxygen pressure on both the acetic and the formic acids, respectively, at 260°C and pH 6. At all pressures the same trend was observed for acetic acid, except that at lower pressure the acetic acid production was slower due to the slower benzene degradation. At all pressures, acetic acid remained as one of the final products while most of the formic acid produced was completely degraded to CO_2 and H_2O .

Figures 5.17, 5.18 and 5.19 show the effect of the oxygen pressure on the acetic acid at pH 4 and 220, 240 and 260°C, respectively. In all experiments, the same trend was observed, suggesting that acetic acid was produced at the beginning of the experiment,

and as the reaction proceeded some of the acetic acid was degraded. It can also be seen that more acetic acid was produced at the higher oxygen pressure because the higher oxygen pressure resulted in higher dissolution of oxygen in the liquid phase. This enhanced the benzene degradation and resulted in the higher production of acids (See section 4.4.6).

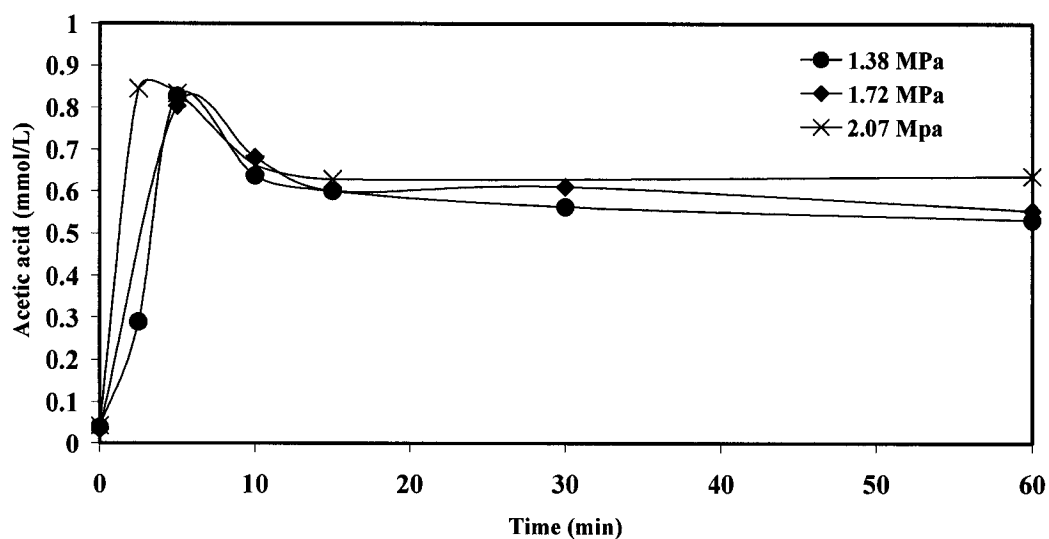


Figure 5.15: Effect of Pressure on Acetic Acid $T=260^{\circ}\text{C}$, $\text{pH}=6$.

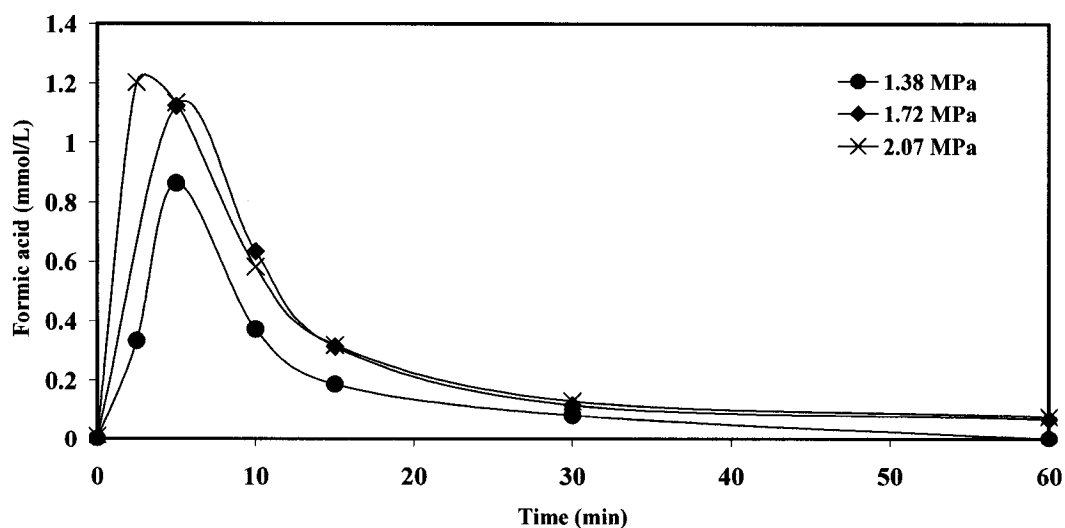


Figure 5.16: Effect of Pressure on Formic Acid, $T=260^{\circ}\text{C}$, $\text{pH}=6$.

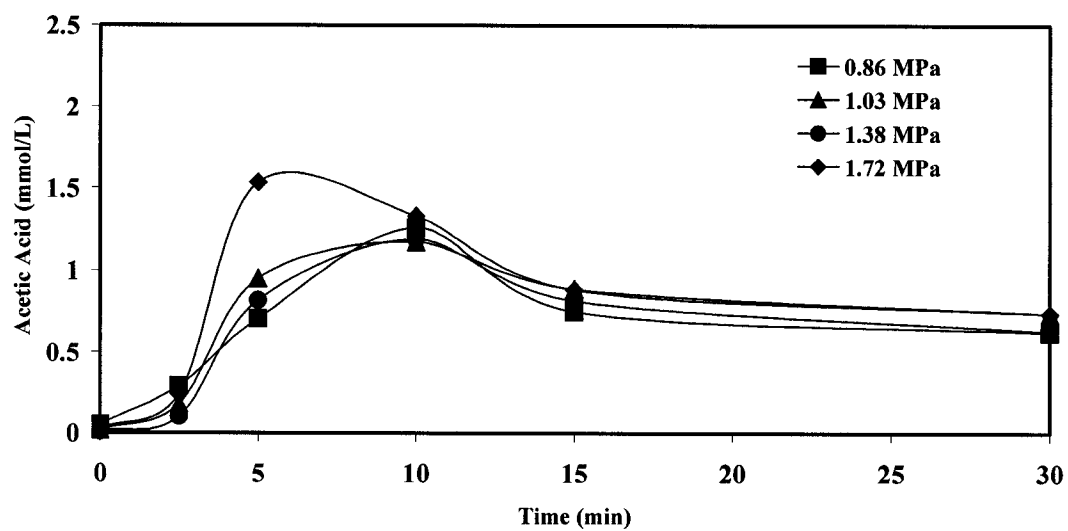


Figure 5.17: Effect of Pressure on Acetic Acid, $T = 220^{\circ}\text{C}$, $\text{pH} = 4$.

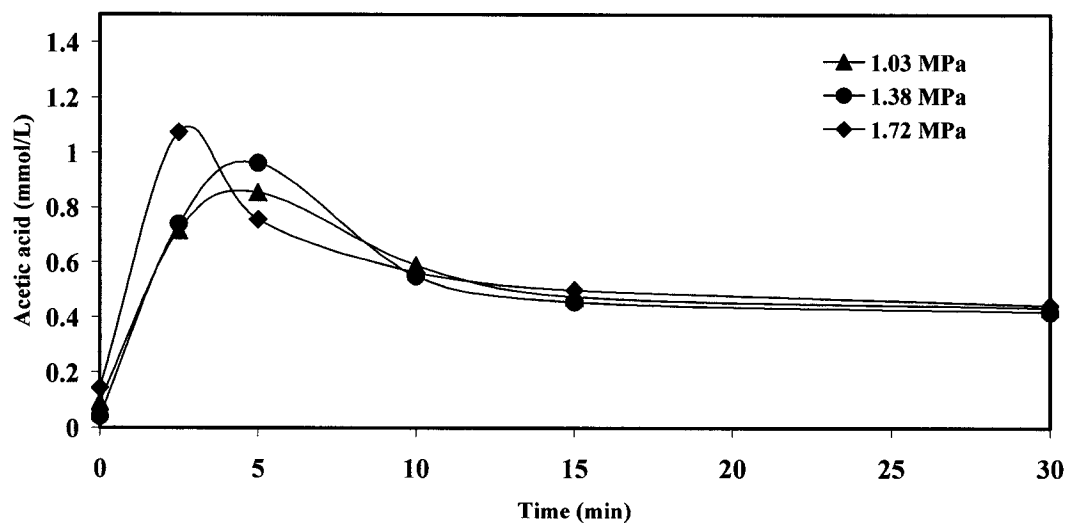


Figure 5.18: Effect of Pressure on Acetic Acid, $T = 240^{\circ}\text{C}$, $\text{pH} = 4$.

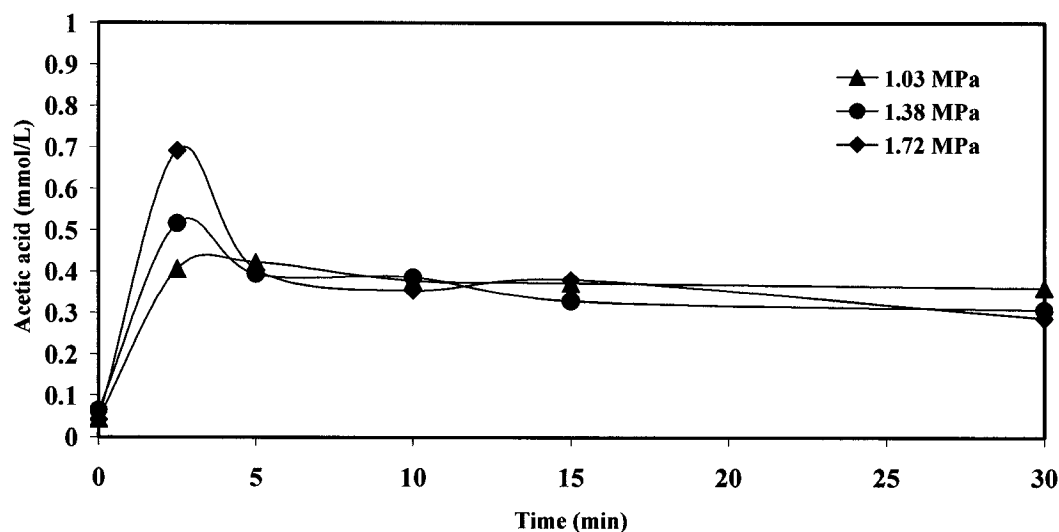


Figure 5.19: Effect of Pressure on Acetic Acid, $T = 260^{\circ}\text{C}$, $\text{pH} = 4$.

Figures 5.20, 5.21 and 5.22 show the effect of the oxygen pressure on the formic acid formation at pH 4 and 220, 240, and 260°C , respectively. As the oxygen pressure increased more formic acid was produced. The degradation of the formic acid was faster at the higher oxygen pressure. At 240°C , all of the formic acid produced during the reaction was degraded after 30 minutes, while at 260°C no formic acid was detected among the reaction products after 15 minutes at any given oxygen pressure. At 220°C , only a small amount of the formic acid was detected after 30 minutes.

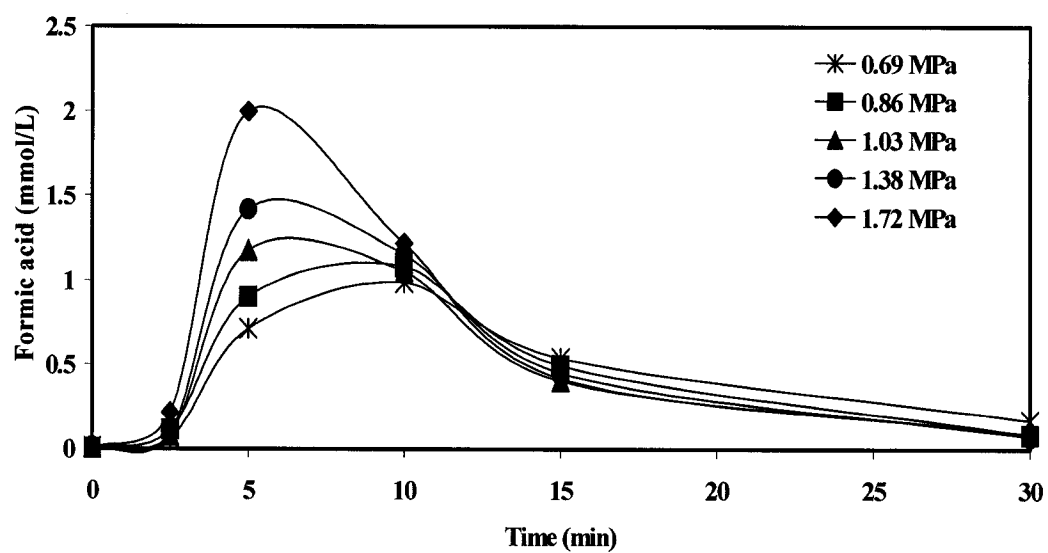


Figure 5.20: Effect of Pressure on Formic Acid, $T = 220^{\circ}\text{C}$, $\text{pH} = 4$.

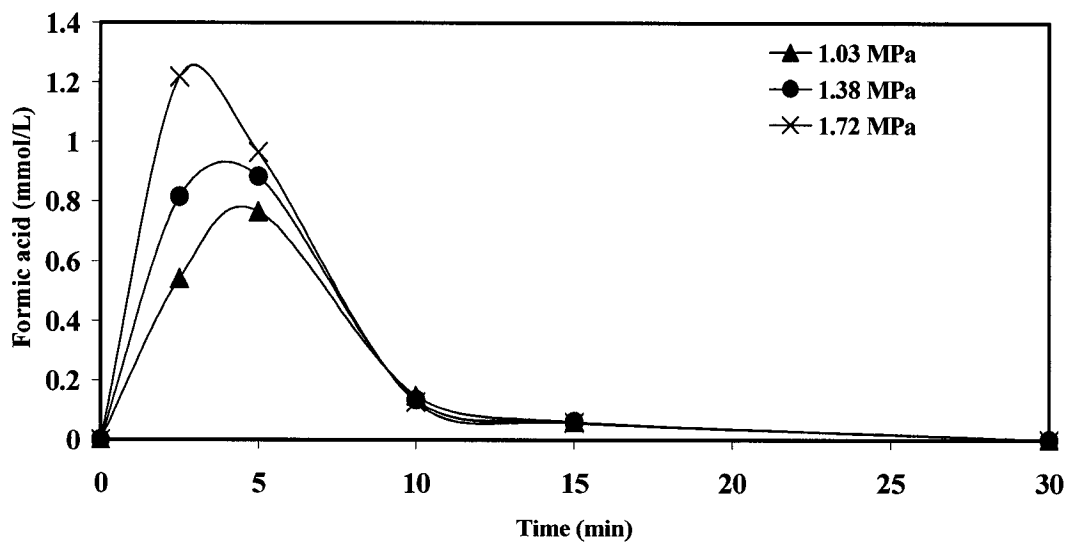


Figure 5.21: Effect of Pressure on Formic Acid, $T = 240^{\circ}\text{C}$, $\text{pH} = 4$.

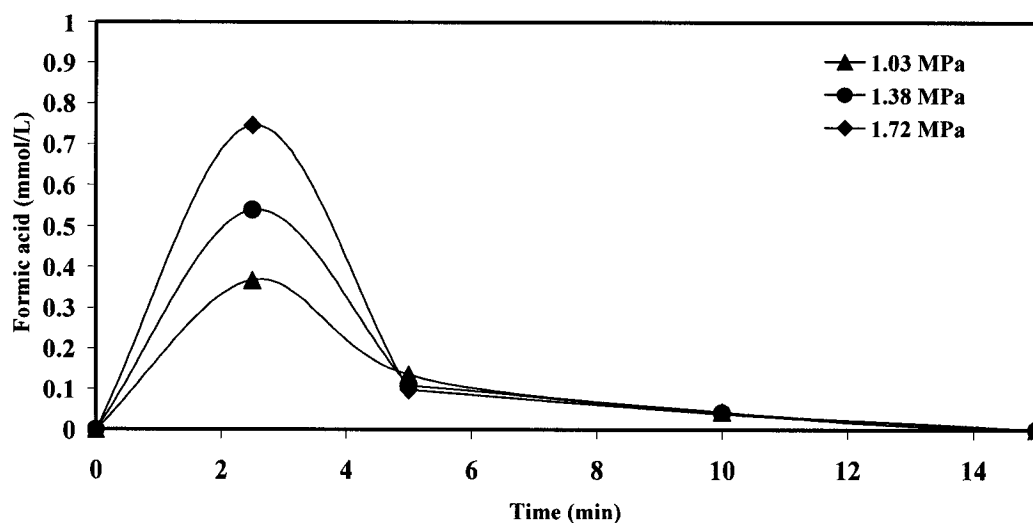


Figure 5.22: Effect of Pressure on Formic Acid, $T = 260^{\circ}\text{C}$, $\text{pH} = 4$.

5.4 Effect of pH on Acetic and Formic Acids

As mentioned before, the initial pH of the reaction medium has a significant effect on the benzene oxidation; it affects both the production as well as the degradation of both the acetic and the formic acids, as is evident in Figures 5.23 and 5.24, respectively. The experiments were done at 220°C and 1.38MPa . It should be mentioned that some of these results were obtained and reported before (Figures 5.11-5.14). At pH 6, the production of both acids started late because the oxidation of the benzene was slow. However, at lower pH, the production of both acids started early. Also, more acids were produced at pH 5 than that at pH 4. The main reason is that at the lower pH most of the benzene was oxidized to the final products (Section 4.4). Unlike pH 6, faster degradation was achieved at both pH 4 and pH 5. At 240°C , again higher concentrations of acids were produced at the lower pH and both the production and the degradation rates of the acids were faster at

lower pH, as seen in both Figures 5.25 and 5.26. Figures 5.27 and 5.28 show that lower pH produced faster rates than the higher pH at 260°C. As it appears in the figures, considerably lower concentrations of acids were produced at pH 4 than that at pH 6. The formic acid was degraded appreciably faster at pH 4. While no formic acid was noticed after 15 minutes at pH 4, it took more than 30 minutes at pH 6. The results show that higher temperatures and lower pH gave better results for both the production and the degradation of the acids. However, it should be noted that at the lower temperatures, slightly higher benzene oxidation was achieved after 30 minutes when larger amounts of acids were produced, thus further lowering the pH of the reaction medium (See Figures 4.17-4.19).

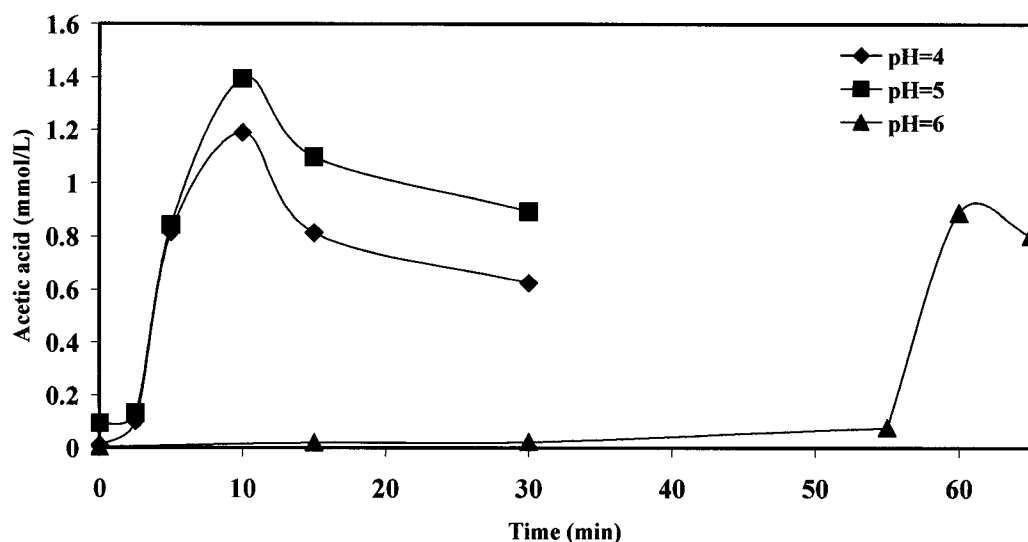


Figure 5.23: Effect of pH on Acetic Acid, $T = 220^{\circ}\text{C}$, $p\text{H} = 4$, $P_{\text{O}_2} = 1.38\text{MPa}$.

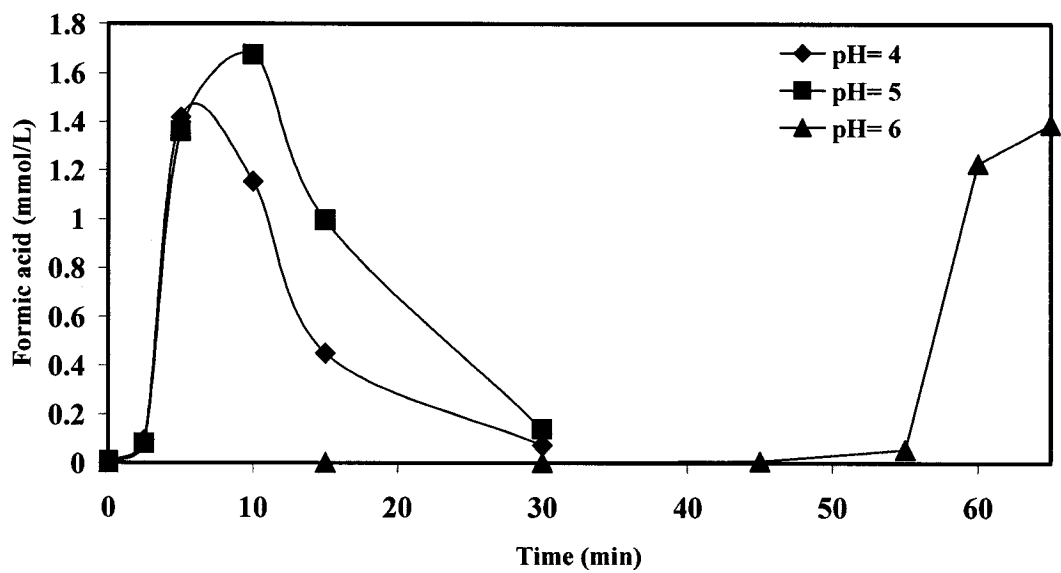


Figure 5.24: Effect of pH on Formic Acid, $T=220^{\circ}\text{C}$, $\text{pH}=4$, $P_{\text{O}_2}=1.38\text{MPa}$.

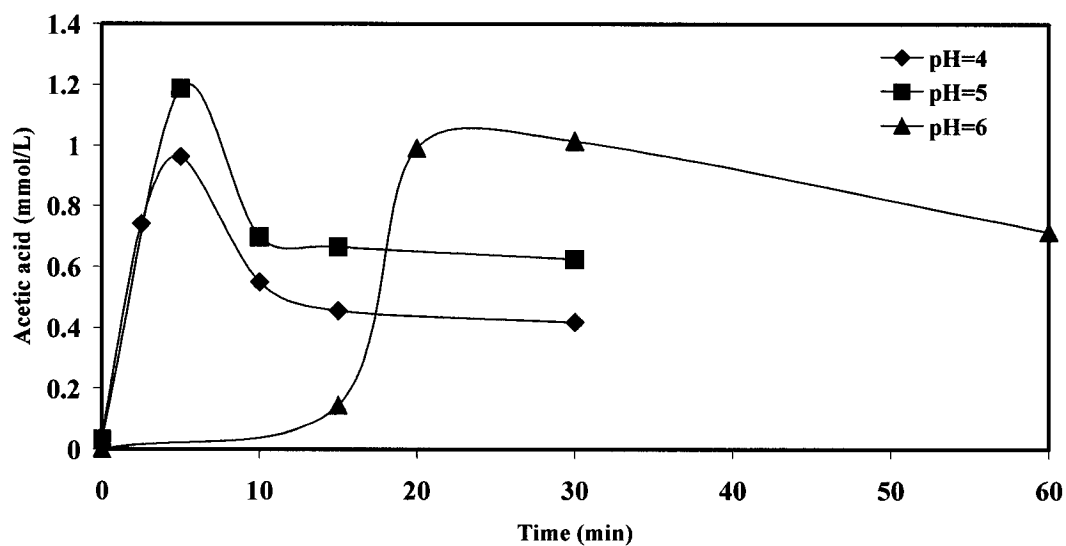


Figure 5.25: Effect of pH on Acetic Acid, $T=240^{\circ}\text{C}$, $\text{pH}=4$, $P_{\text{O}_2}=1.38\text{MPa}$.

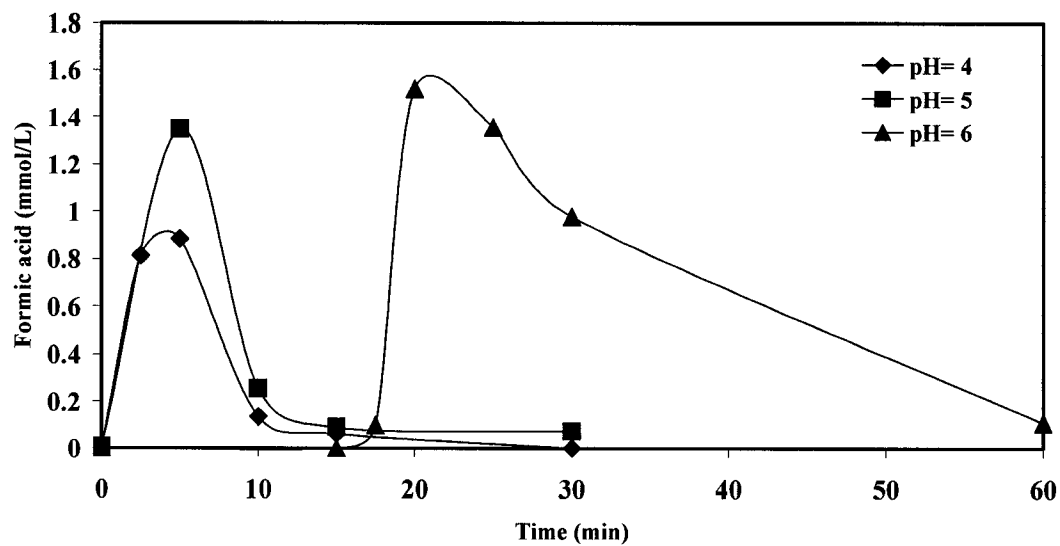


Figure 5.26: Effect of pH on Formic Acid, $T=240^{\circ}\text{C}$, $\text{pH}=4$, $P_{\text{O}_2}=1.38\text{MPa}$.

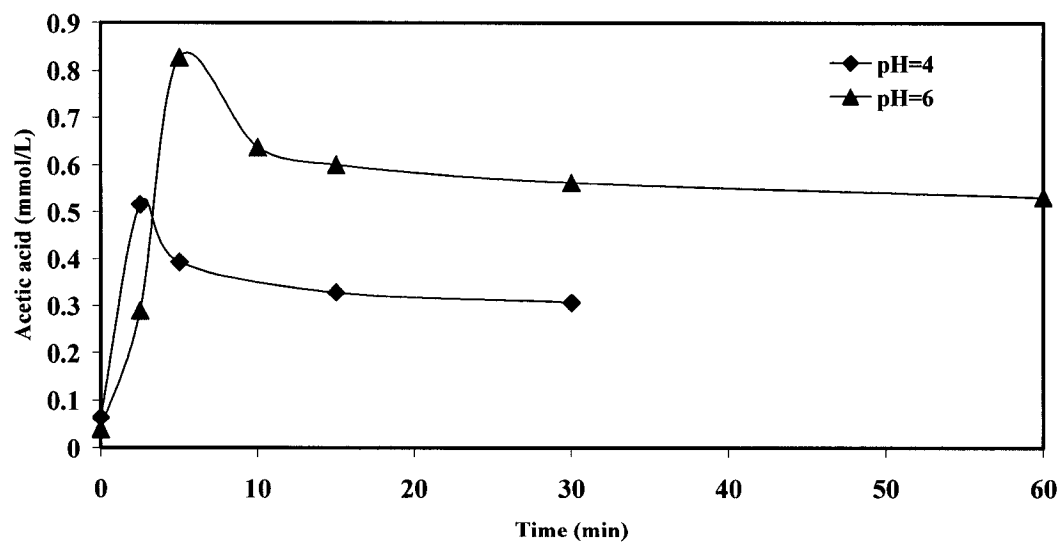


Figure 5.27: Effect of pH on Acetic Acid, $T=260^{\circ}\text{C}$, $\text{pH}=4$, $P_{\text{O}_2}=1.38\text{MPa}$.

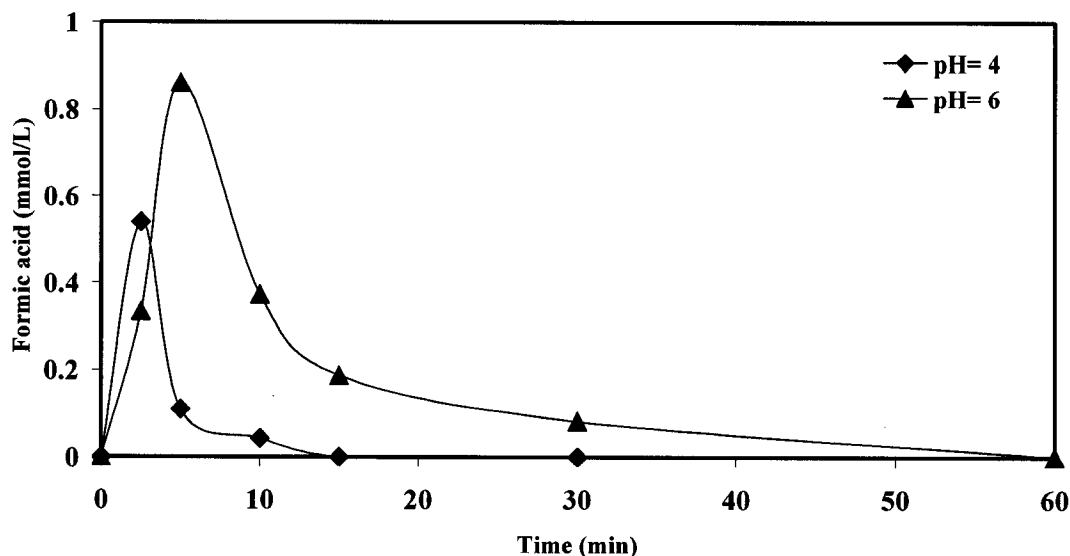


Figure 5.28: Effect of pH on Formic Acid, $T = 260^{\circ}\text{C}$, $\text{pH} = 4$, $P_{\text{O}_2} = 1.38\text{MPa}$.

5.4.1 Effect of Acidification Methods on the Intermediates

As mentioned before, nitric acid was usually used to lower the pH. However, sulfuric acid was also tried in order to find out whether the anion would have any effect on the process. The results shows that the same trend has been obtained for both acetic acid and formic acid, which means that the type of acid did not have any impact on the results, as long as the initial pH was similar (Figures 5.29 and 5.30). The difference in the amount of acids can be attributed to the slightly different initial amount of the benzene used in the experiments.

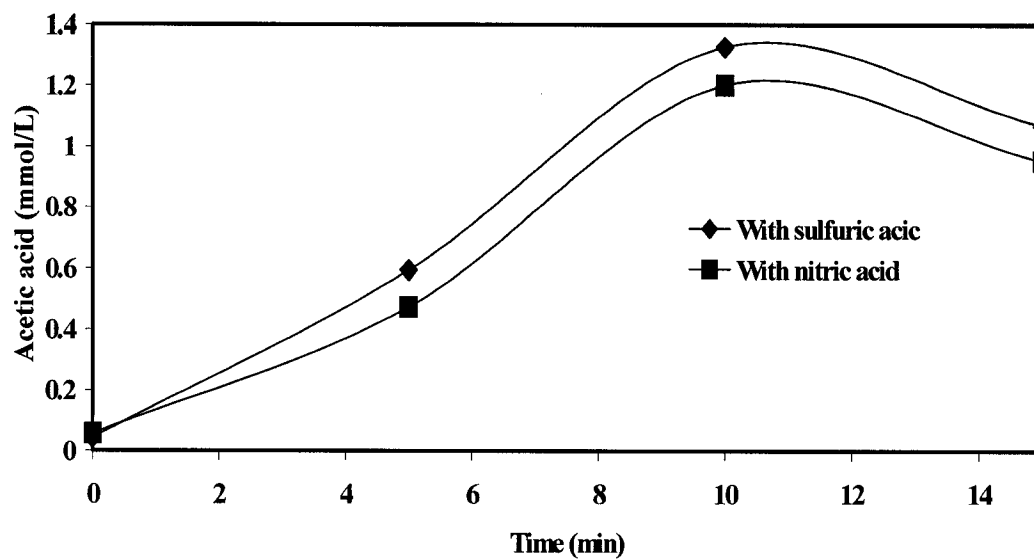


Figure 5.29: Effect of Acidification Methods on Acetic Acid, $T = 220^{\circ}\text{C}$, $P_{\text{O}_2} = 1.38\text{MPa}$, $\text{pH} = 4$.

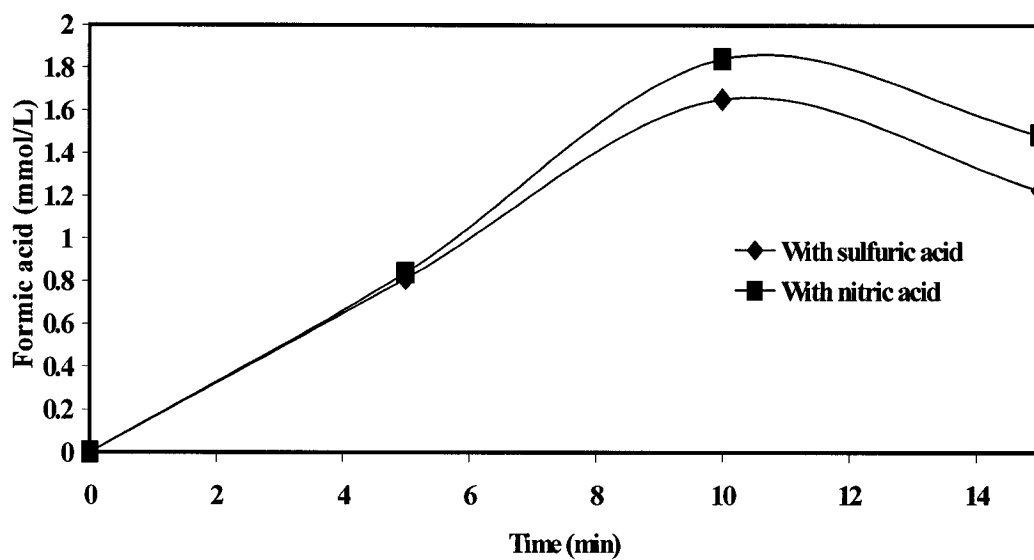


Figure 5.30: Effect of Acidification Methods on Formic Acid, $T = 220^{\circ}\text{C}$, $P_{\text{O}_2} = 1.38\text{MPa}$, $\text{pH} = 4$.

5.5 Effect of Initial Benzene Concentration on Both Acetic and Formic Acids

Two experiments were done at pH 4 with an initial benzene concentration of 11.25 mmol/L, which was double the amount that was typically used in this study (See section 4.5). The initial oxygen pressure was set to be 2.76 MPa. From the Figures 5.31 and 5.32 for acetic and formic acids, respectively, it is apparent that the higher amount of acids was produced when compared with results obtained from lower initial amount of benzene (See Figures 5.12 and 5.14). Since the oxidation of benzene was faster at 240°C the production of both acids started faster at this temperature. More acids were produced at 220°C than 240°C and no formic acid was noticed after 15 minutes at 240°C. At both temperatures, acetic acid was preserved as a final product.

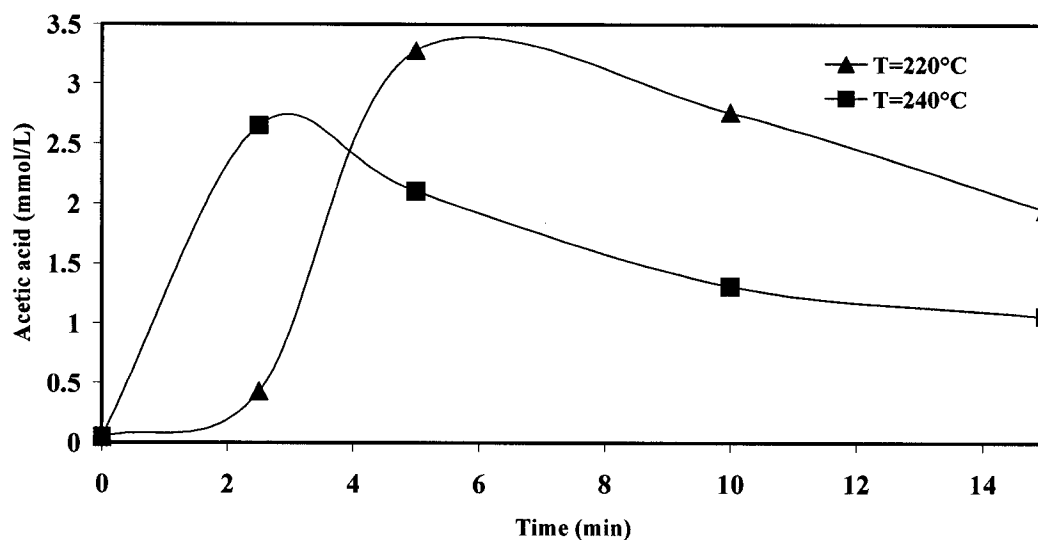


Figure 5.31: Effect of Temperature on Acetic Acid, P_{O_2} = 2.76 MPa, pH=4, Initial Benzene Concentration = 11.25 mmol/L.

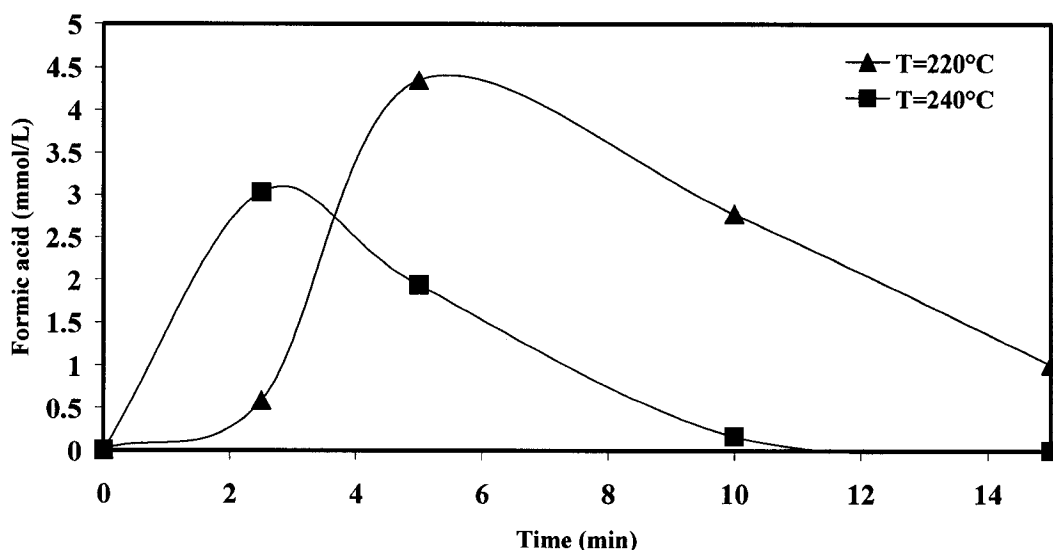


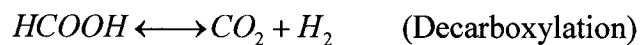
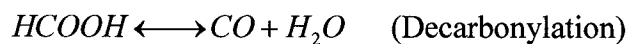
Figure 5.32: Effect of Temperature on Formic Acid, P_{O_2} = 2.76 MPa, pH=4. Initial Benzene Concentration = 11.25 mmol/L.

5.6 Wet Air Oxidation of Both Acetic and Formic Acids

The wet air oxidation of both the acetic and formic acids was studied in order to determine what will happen if they exist alone in the effluent. The wet air oxidation of acetic acid was studied at 260°C and oxygen pressure of 2.07 MPa, which were the extreme conditions used in this study. It was found that at these conditions no degradation was achieved (Figure 5.33). A comparison of this result with those shown in Figure 5.12 shows that the presence of other organic compounds (such as unreacted benzene and formic acid) enhanced the degradation of acetic acid. This phenomenon is widely observed in WAO and is the subject of the next chapter.

The wet air oxidation for formic acid was studied at both 260°C and oxygen pressure of 2.07 MPa and at 220°C and oxygen pressure of 1.38 MPa. In both experiments, almost all of the formic acid disappeared before the addition of the oxygen (Table 5.2), which

suggests that decomposition of the formic acid took place either by decarbonylation or decarboxylation [73].



Furthermore, an experiment was done with formic acid, in which samples were collected every 10 minutes in the heating up period. In this experiment no oxygen was added. The results (Table 5.3) show that the concentration of formic acid started to drop when the temperature reached around 193°C and after that it decreased even faster. At around 227°C, most of the formic acid disappeared. This suggests that at certain temperature and in the absence of oxygen the formic acid starts to decompose as mentioned above.

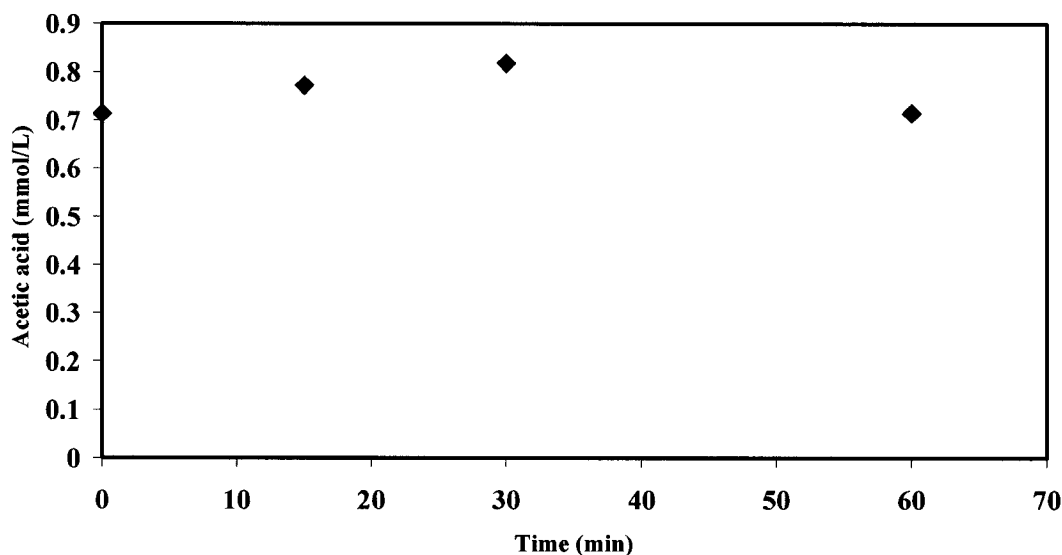


Figure 5.33: Degradation of Acetic Acid, $T = 260^\circ\text{C}$, $P_{\text{O}_2} = 2.07 \text{ MPa}$.

Table 5.2: Effect of Temperature on Formic Acid.

Time (min)	mmol Formic Acid (220°C, P _{O2} =1.38 MPa)	mmol Formic Acid (260°C, P _{O2} = 2.07 MPa)
Original Sample	2.1	2.1
0	0.1	0
15	0	0

Table 5.3: Concentration of Formic Acid at Different Temperatures.

Time (min)	Temperature(°C)	Total pressure (MPa)	mmol Formic acid/L
0	17	0.20	1.97
10	21	0.19	2.03
20	32	0.19	2.04
30	49	0.20	2.10
40	68	0.23	1.92
50	88	0.28	1.96
60	109	0.37	2.01
70	132	0.52	2.06
80	153	0.78	2.03
90	173	1.15	1.91
100	193	1.65	1.76
110	211	2.27	0.84
120	227	3.03	0.06
130	241	3.86	0.01
150	257	4.90	0.00

5.7 Repeatability of the Results

Since the initial benzene concentration was not exactly the same for the replicates it was expected not to have exactly the same results. The results that were obtained for replicates for acetic acid can be seen in figures 5.34, 5.35 and 5.36 while those for formic

acid can be seen in figures 5.37, 5.38 and 5.39 both at 220, 240 and 260°C, respectively.

These figures show that the trend in all experiment were comparable.

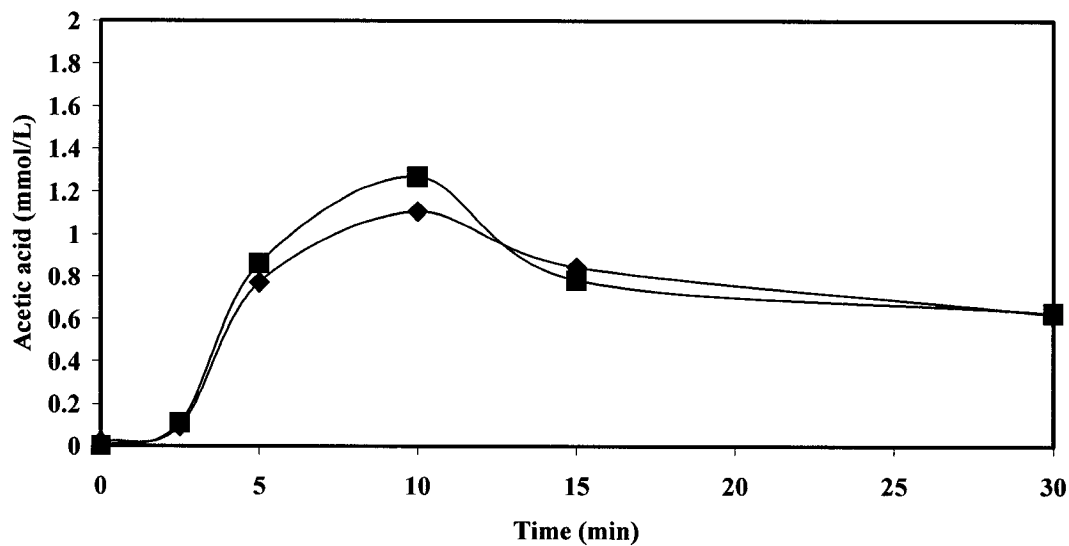


Figure 5.34: Acetic acid profile for replicates, $T=220^{\circ}\text{C}$, P_{O_2} , 1.38 MPa, $\text{pH}=4$.

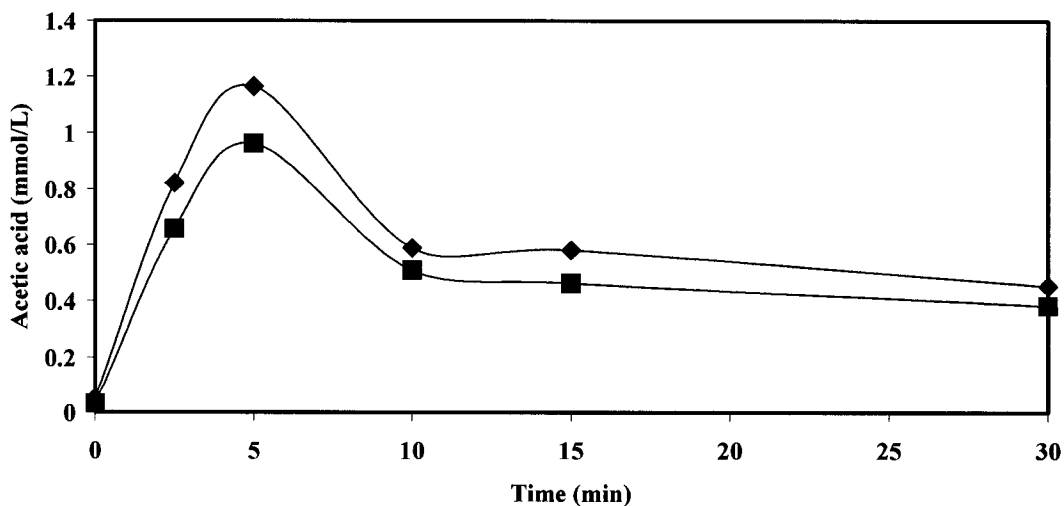


Figure 5.35: Acetic acid profile for replicates, $T=240^{\circ}\text{C}$, P_{O_2} , 1.38 MPa, $\text{pH}=4$.

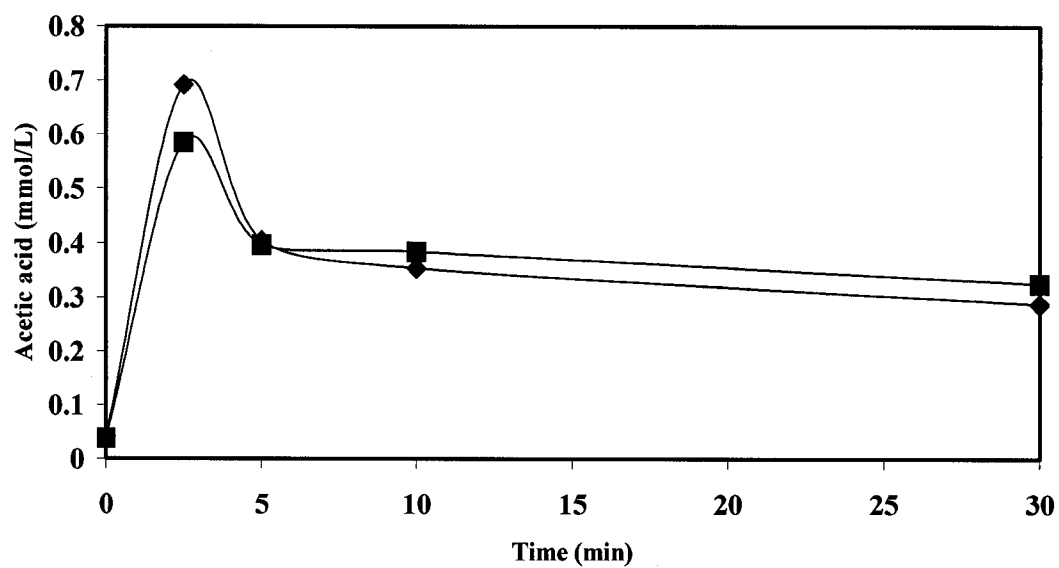


Figure 5.36: Acetic acid profile for replicates, $T=260^{\circ}\text{C}$, P_{O_2} , 1.72 MPa, $\text{pH}=4$.

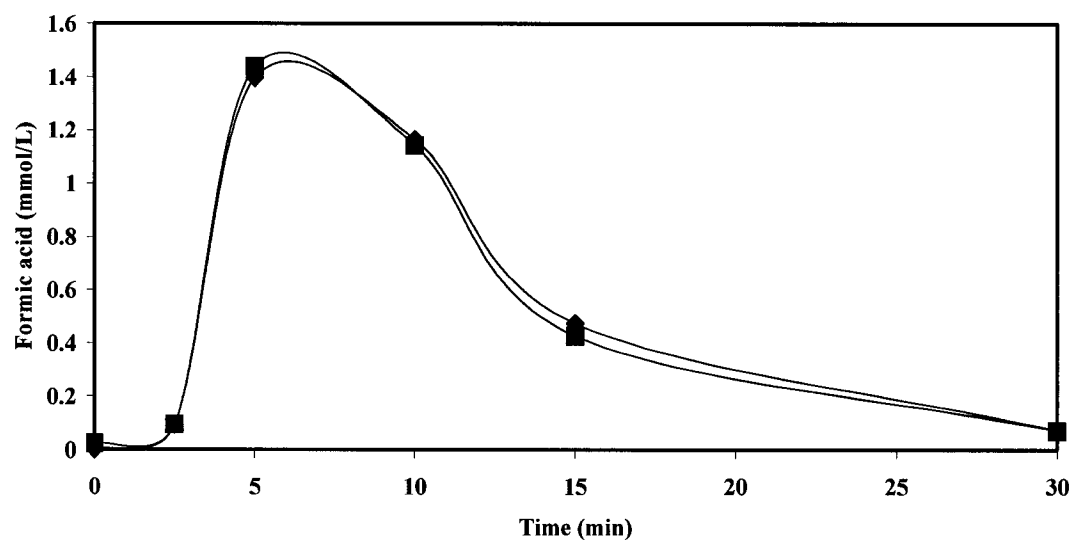


Figure 5.37: Formic acid profile for replicates, $T=220^{\circ}\text{C}$, P_{O_2} , 1.38 MPa, $\text{pH}=4$.

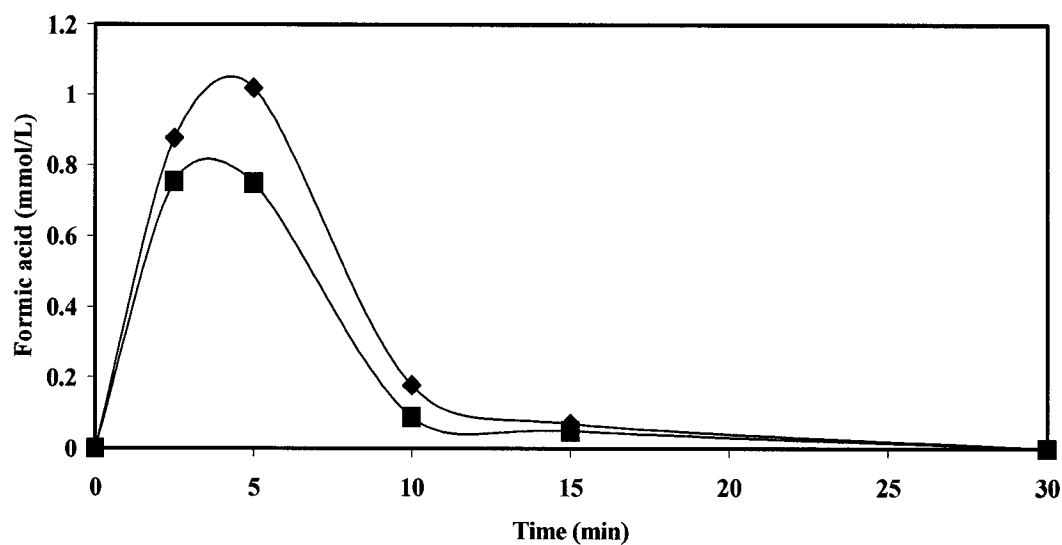


Figure 5.38: Formic acid profile for replicates, T=240°C, P_{O2}, 1.38 MPa, pH=4.

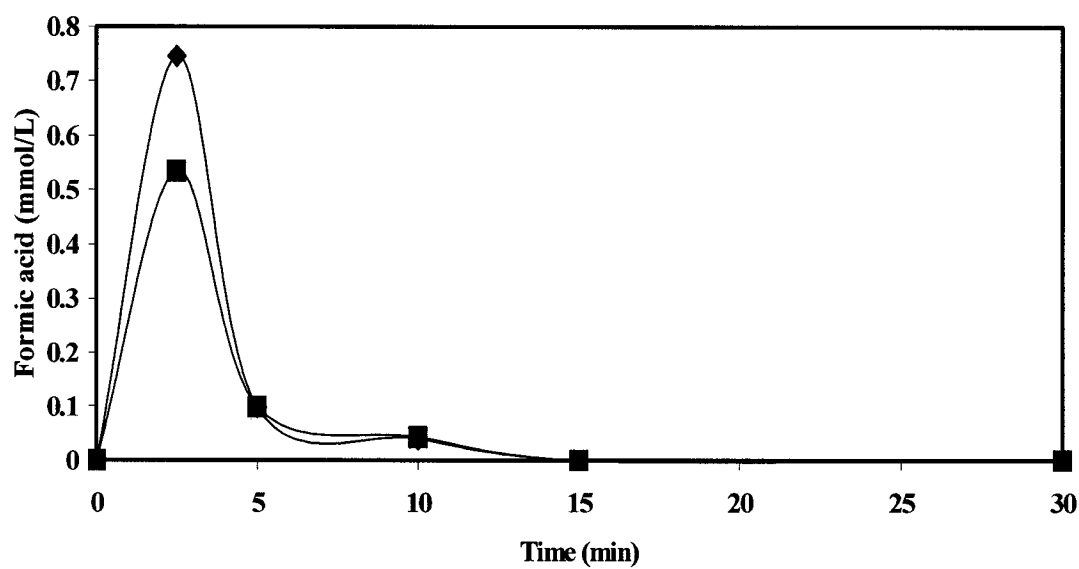


Figure 5.39: Formic acid profile for replicates, T=260°C, P_{O2}, 1.72 MPa, pH=4.

In summary, the results show that the main intermediates were found to be acetic acid and formic acid. Negligible amounts of both propanoic acid and glycolic acid were also detected. In addition, a negligible amount of benzoquinone was identified by the Gas Chromatography Mass Spectrometry (GCMS). Most of the intermediates were degraded to CO_2 and H_2O as the reaction proceeded. However, only some of the acetic acid produced during the oxidation was degraded and the remaining stayed as a final product.

CHAPTER SIX

RESULTS AND DISCUSSIONS

WET AIR OXIDATION OF BENZENE ENHANCED BY PHENOL

The co-oxidation method is used to enhance the wet air oxidation of many compounds (see Section 2.5). In this study, phenol was used to enhance the benzene degradation. Simultaneous benzene and phenol oxidation has been studied at a temperature range of 160-220°C. In most experiments the initial phenol concentration ranged from 0.11 to 2.13 mmol/L while the concentration of benzene was kept constant at 5.63 mmol/L. 100% excess of oxygen was used. However, at the beginning of this study, different conditions were applied, as described below.

6.1 Wet Air Oxidation of Phenol in Absence of Benzene

The wet air oxidation of phenol in the absence of benzene showed that 99.5% degradation can be achieved in 2.5 minutes at 220°C and oxygen pressure of 2.07 MPa. The initial phenol concentration was 5.31 mmol/L and the initial pH was set to be 4. This experiment was repeated at pH 6 with 1.38 MPa of oxygen pressure and again more than 99% degradation was achieved within 2.5 minutes. In contrast to benzene, this shows that the pH in the range of 4 to 6 does not have a significant influence on the phenol degradation. An experiment using 2.13 mmol/L as the initial concentration of phenol has been conducted at pH 6 with 100% excess of oxygen, which is the same as the excess that was used throughout this part of study. In this experiment, 95% degradation was achieved within 2.5 minutes and after 5 minutes no phenol was detected. Those experiments

showed that the degradation of phenol was very fast under the experimental conditions.

The above results are summarized in Table 6.1.

Table 6.1: Degradation of Phenol at 220°C.

Time (min)	C/C ₀ of Phenol		
	P _{O2} = 2.07 MPa pH=4	P _{O2} = 1.38 MPa pH=6	100 % excess of P _{O2} pH=6
0	1	1	1
2.5	0.005	0.006	0.05
5	0.002	0	0
10	0	0	0

Both acetic acid and formic acid were identified as intermediates during phenol degradation. While the formic acid was further degraded, the acetic acid stayed as a final product, as seen on Figures 6.1-6.3. Also, it can be noted that at higher oxygen pressure and lower initial pH the degradation of formic acid was faster and slightly less amount of acetic acid was produced.

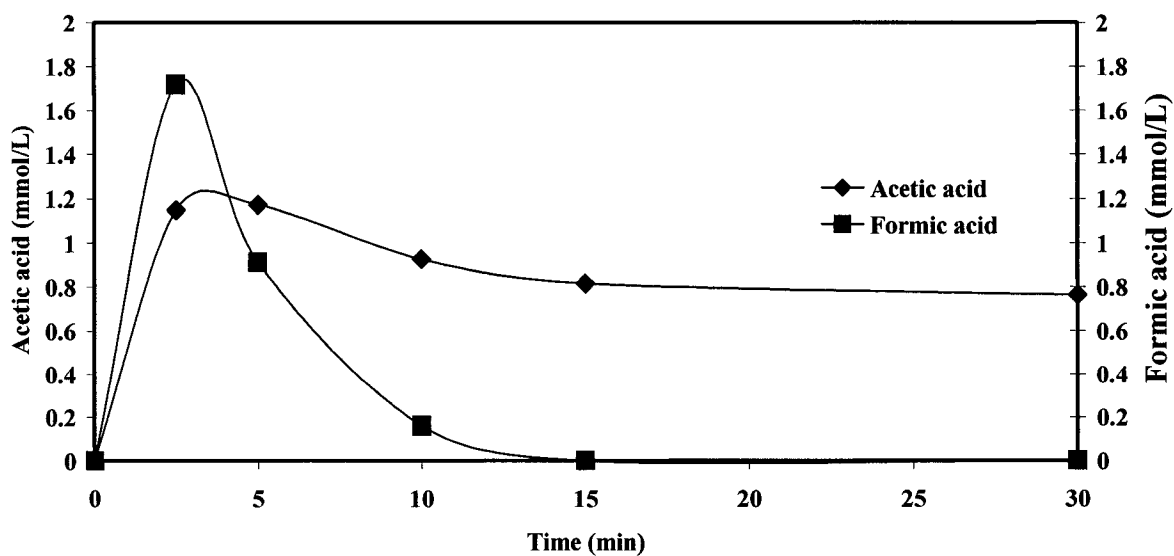


Figure 6.1: Acetic Acid and Formic Acid Profile, T= 220°C, P_{O2}=2.07 MPa, pH= 4. Initial Phenol Concentration= 5.31mmol/L.

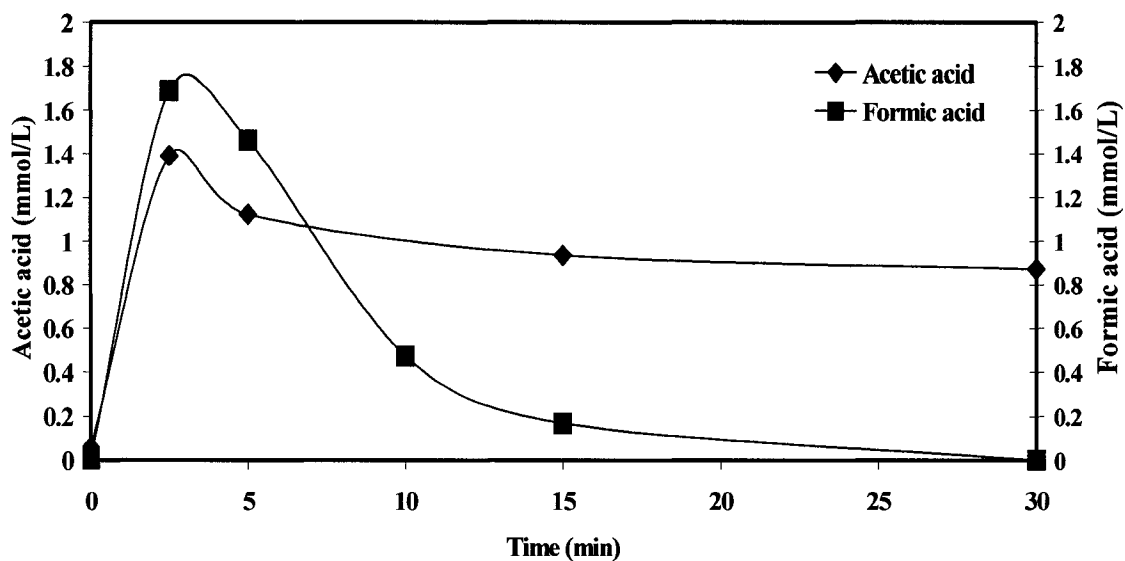


Figure 6.2: Acetic Acid and Formic Acid Profile, $T=220^{\circ}\text{C}$, $P_{\text{O}_2}=1.38\text{ MPa}$, $\text{pH}=6$. Initial Phenol Concentration= 5.31 mmol/L .

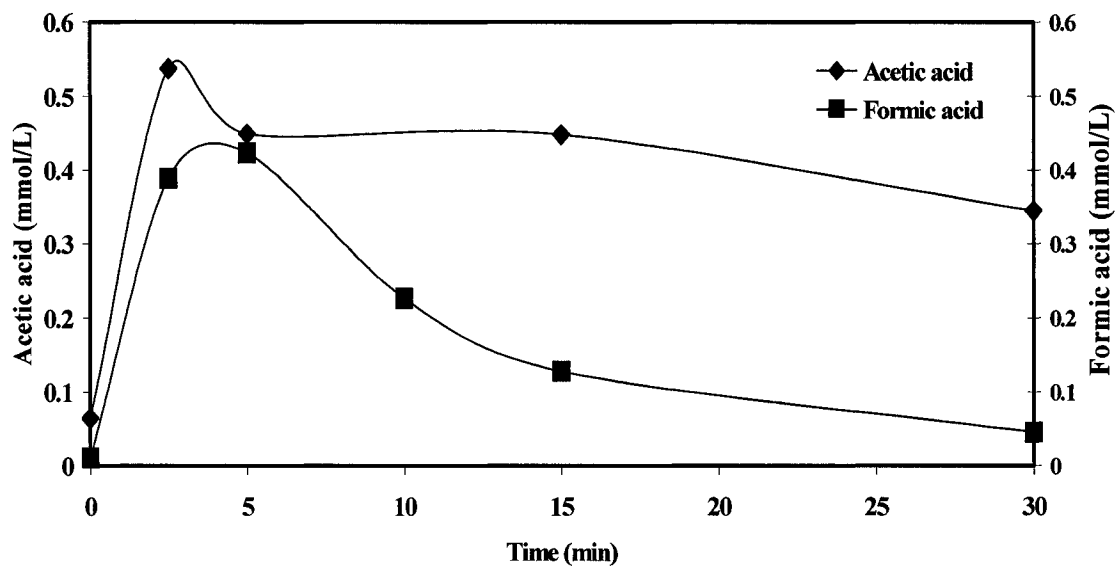


Figure 6.3: Acetic Acid and Formic Acid Profile, $T=220^{\circ}\text{C}$, $P_{\text{O}_2}=0.51\text{ MPa}$, $\text{pH}=4$. Initial Phenol Concentration= 2.13 mmol/L .

6.2 Wet Air Oxidation of Benzene in Presence of Phenol

Two experiments were done at 220°C and oxygen pressure of 1.72 MPa at both initial pH 4 and pH 6 in order to study the effect of phenol on the degradation of benzene. The initial phenol concentration was 5.31 mmol/L while the initial benzene concentration was chosen to be the same as the initial concentration that was used in chapter 4, i.e. 5.63 mmol/L. It can be seen from Figure 6.4, that the fast oxidation of benzene was achieved in the presence of phenol and the results were almost identical for both pH 4 and pH 6, which means that in the presence of phenol the effect of initial pH was not significant. Figure 6.5 shows an extremely fast degradation of phenol and it also suggests that the initial pH of the reaction did not have any effect on the phenol degradation.

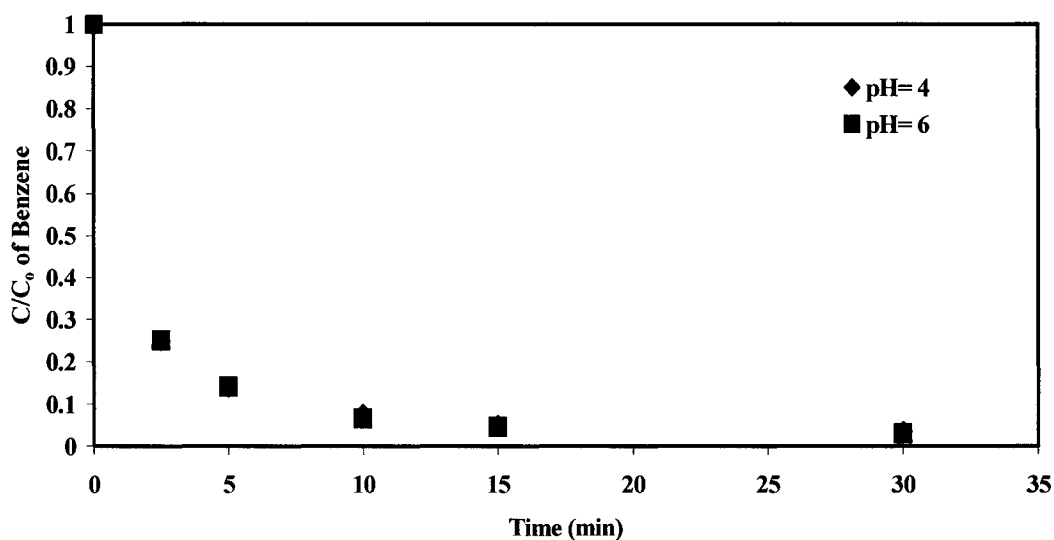


Figure 6.4: Degradation of Benzene at 220°C, P_{O_2} = 1.72 MPa.

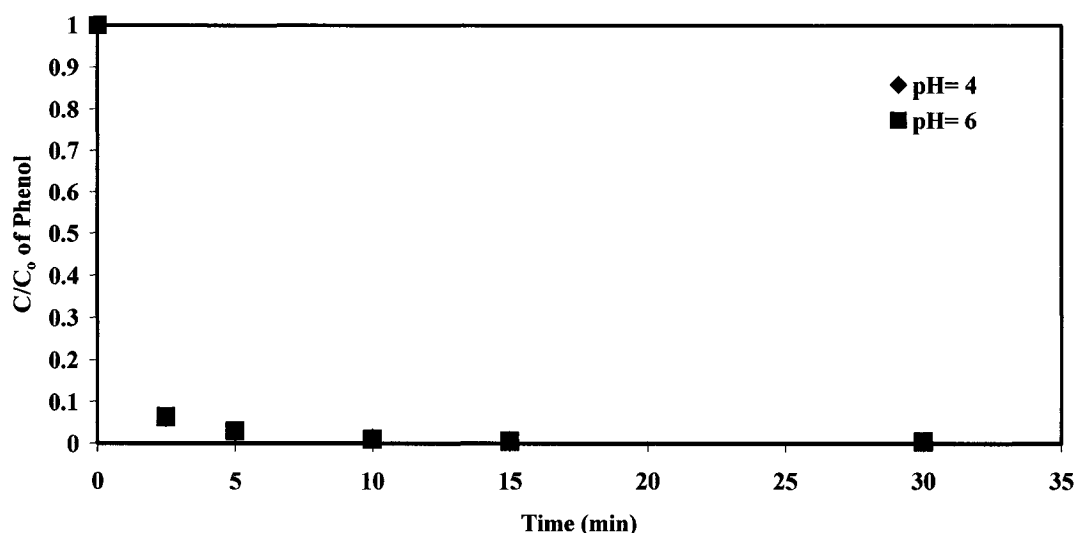


Figure 6.5: Degradation of Phenol at 220°C, P_{O_2} = 1.72 MPa.

6.2.1 Effect of the Initial Phenol Concentration on Benzene Degradation

Several experiments have been carried out with initial concentrations of phenol ranging from 0.11 to 2.13 mmol/L, in order to determine the effect of the initial phenol concentration on the wet air oxidation of benzene. The benzene concentration was kept constant at 5.63 mmol/L. These experiments were done at 220°C and 100% excess of O_2 . The initial pH of the solution was 6. From the Figure 6.6, it is apparent that the increased concentration of phenol enhanced the degradation of benzene dramatically, especially during the first 5 minutes. While no benzene degradation was achieved in 15 minutes in the absence of phenol, more than 95% degradation of benzene was achieved even with the smallest amount of phenol used in the experiment (0.11 mmol/L). After 15 minutes, the degradation rates were comparable. However, when the initial phenol concentration was increased from 1.59 to 2.13 mmol/L, no change in the degradation rate was detected.

As was mentioned earlier in Chapter 2, the effect of phenol can be attributed to the formation of free radicals and the active intermediates.

The effect of the initial phenol concentration at 200°C with 100% excess O₂ can be seen in Figure 6.7. The results show that at lower temperature the initial phenol concentration has more effect on the benzene degradation than at 220°C. While 89% benzene was degraded in 10 minutes with initial phenol concentration of 0.53 mmol/L, only 27% degradation was achieved when the initial phenol concentration was lowered to 0.27 mmol/L. However, after 30 minutes the results were comparable. The above results show that the presence of phenol, even at low concentration, enhanced the degradation of benzene dramatically. As was shown in Section 4.4, at this temperature the degradation of benzene was not reproducible, but in the presence of phenol, this was not observed. It appears that phenol acts as a catalyst by lowering the activation energy.

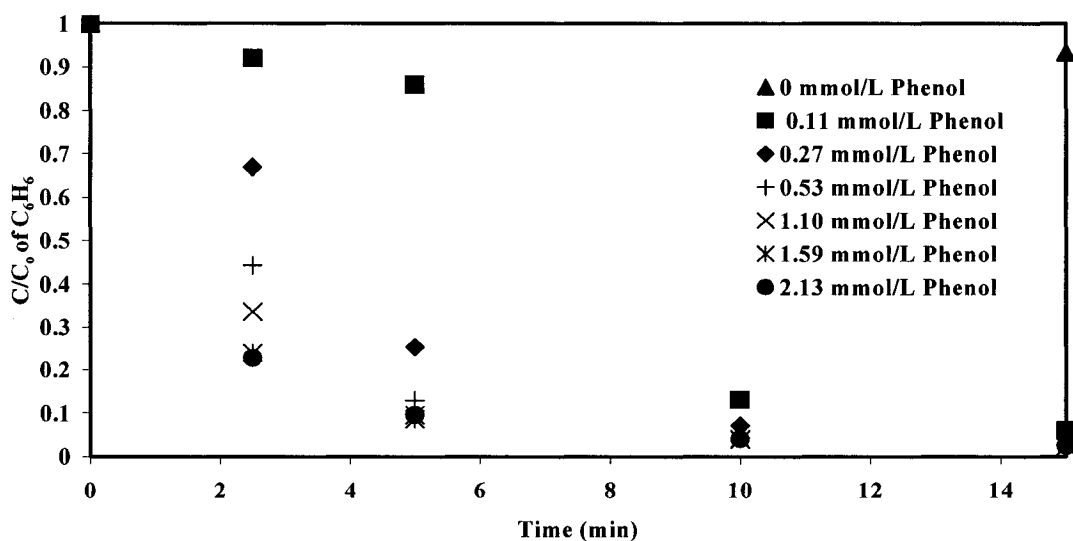


Figure 6.6: Degradation of Benzene at Different Initial Phenol Concentrations, T=220°C, 100% Excess O₂, Initial pH=6.

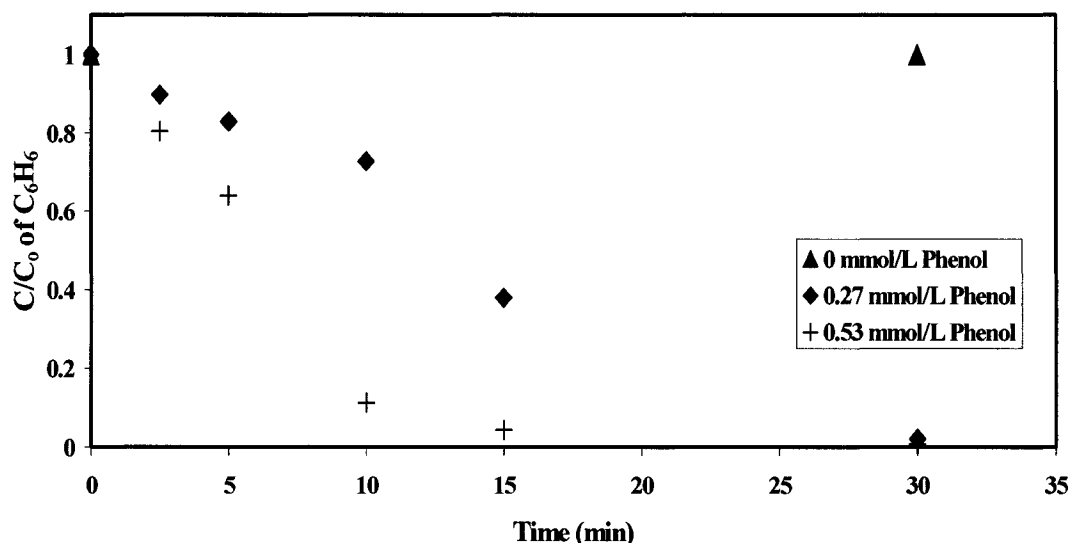


Figure 6.7: Degradation of Benzene at Different Initial Phenol Concentrations, $T=200^{\circ}\text{C}$, 100% Excess O_2 , Initial $\text{pH}=6$.

6.2.2 Effect of Temperature on Benzene Degradation in the Presence of Phenol

In the previous section, the effect of the initial phenol concentration on benzene degradation was studied at constant temperature. However, in this section the initial phenol concentration was kept constant and the temperature was varied to study the effect of the temperature on the benzene degradation at constant initial phenol concentration. Two different initial phenol concentrations were used. The initial selected phenol concentration was the lowest phenol concentration that gave good results at the lowest temperature used, i.e. 0.27 mmol/L, when the lowest temperature was 200°C and 0.53 mmol/L when the lowest temperature was 160°C . The oxygen concentration was kept at 100% excess and the initial pH was 6. Figure 6.8 shows the degradation of benzene at both 200 and 220°C . The initial phenol concentration was 0.27 mmol/L. It can be seen that when the temperature was increased from 200 to 220°C a considerably faster

degradation was achieved. The co-oxidation of benzene was further studied with the initial phenol concentration of 0.53 mmol/L at 4 different temperatures ranging from 160 to 220°C (Figure 6.9). The results show that the benzene degradation was rather slow at 160°C and only around 50% degradation was achieved within 60 minutes. However, with the increasing temperature, the degradation rate of benzene became faster and more degradation was achieved during the first 20 minutes. This implies that the higher the temperature, the faster phenol oxidation was achieved and this resulted in the rapid formation of the free radicals and the active intermediates. Also, as mentioned before higher temperatures lead to higher oxygen solubility in the liquid phase.

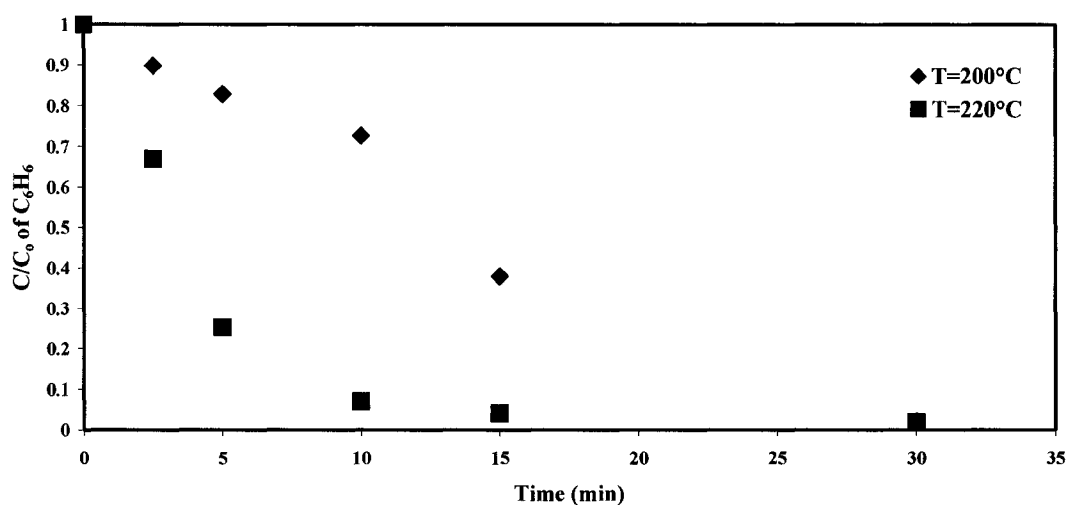


Figure 6.8: Degradation of Benzene at Different Temperatures, 100% Excess O₂, Initial Phenol Concentration= 0.27 mmol/L, Initial pH= 6.

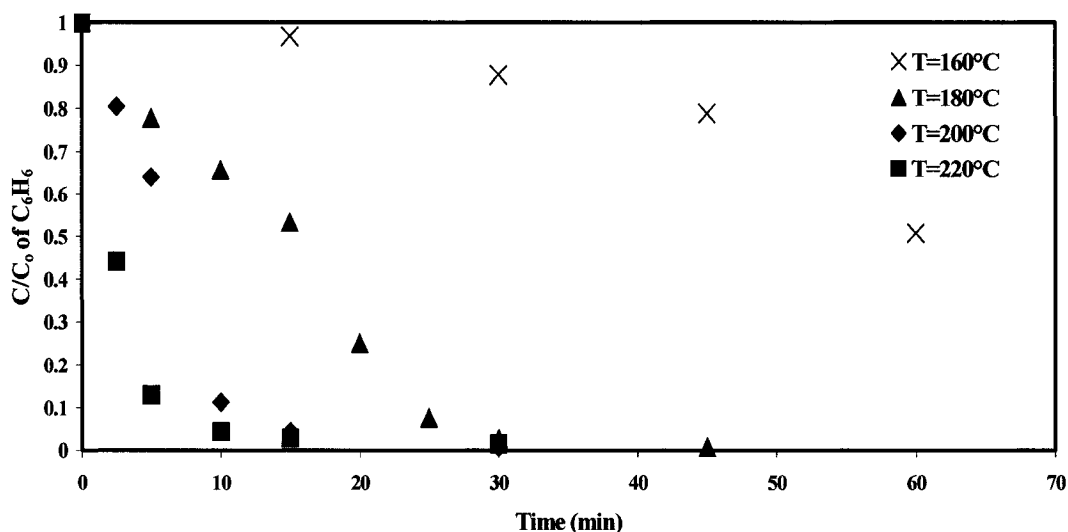


Figure 6.9: Degradation of Benzene at Different Temperatures, 100% Excess O₂, Initial Phenol Concentration= 0.53 mmol/L, Initial pH= 6.

6.2.3 Effect of Benzene on the Phenol Oxidation

Figure 6.10 shows the phenol profile at different temperatures when 0.53 mmol/L of phenol was used as initial concentration. It is apparent from the Figure that at 220°C the degradation of phenol was very fast. However, at 200°C the concentration of phenol decreased during the first 5 minutes of the oxidation, followed by the slight increase, and by final degradation of phenol. The same oxidation path can also be seen at 180°C. This suggests that, at the beginning of the oxidation, the small amount of phenol was degraded, and it was followed by the partial conversion of benzene to phenol which was then degraded. However, the peaks were shifted to the right as the oxidation temperatures decreased. At 160°C, the concentration of phenol increased with time, which implies that the rate of oxidation of benzene to phenol was faster than the rate of degradation of phenol during the duration of the experiment.

Figure 6.11 shows the effect of benzene on the phenol profile when the initial phenol concentration was 0.27 mmol/L. It can be seen that in first 2.5 minutes at 220°C the degradation of benzene was faster than the degradation of phenol which resulted in accumulation of phenol after which the phenol started to degrade. At 200°C, the degradation of phenol was faster than that of benzene in the first 5 minutes, and after that the oxidation of benzene became faster hence the concentration of phenol started to increase and it reached a peak after 15 minutes. After that the concentration of phenol started to decrease. After 30 minutes of oxidation almost the same degree of phenol oxidation has been obtained. These results show that both the rate of production and the rate of degradation of phenol are highly affected by the temperature. While the rate of the production of phenol was higher than the rate of degradation at lower temperatures, i.e. at 160°C, the opposite could be seen at higher temperatures i.e. at 220°C. These results also showed that the first stage in the wet air oxidation of benzene was the oxidation of benzene to phenol.

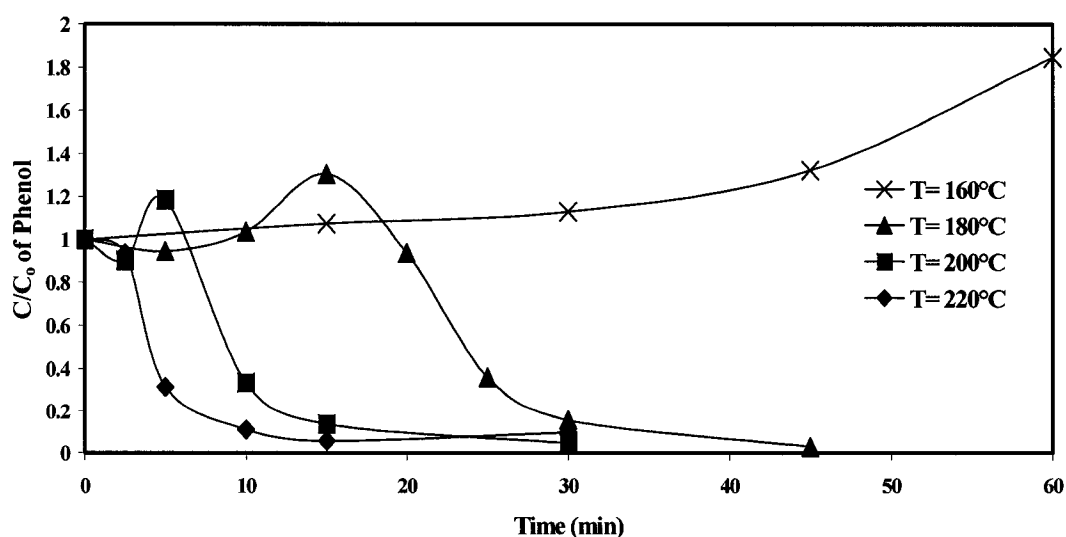


Figure 6.10: Normalized concentration of Phenol with Time, 100% Excess O₂, Initial pH=6, Initial Phenol Concentration= 0.53 mmol/L.

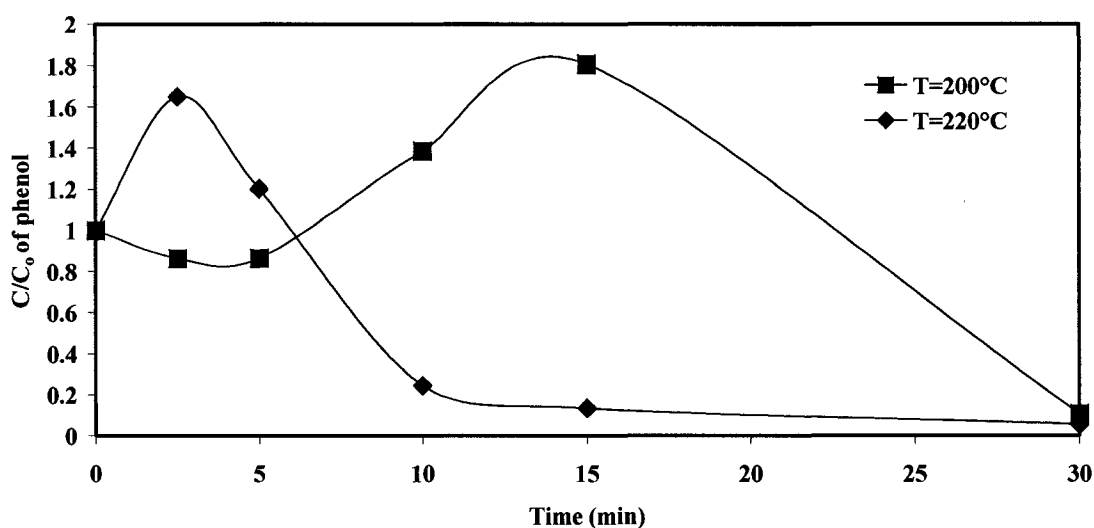


Figure 6.11: Normalized concentration of Phenol with Time, 100% Excess O_2 , Initial pH=6, Initial Phenol Concentration= 0.27 mmol/L.

6.3 Reaction Kinetics of Benzene Oxidation

The use of two first order reaction kinetics model represented well the WAO on many phenolic compounds [33, 39]. Lin *et al.* [41] also showed that this model worked in their study on the WAO of high concentration wastewater. It can be seen from figure 6.12 that this model fit our reaction well and it consists of 2 steps; namely the fast reaction step and the slow reaction step. While at 220°C only the fast step can be detected, at 160°C only the slow step exists. Figure 6.13 shows that the reaction follows the Arrhenius correlation and the activation energy was calculated to be 21.1 kJ/mol and 1.2×10^2 kJ/mol for the fast and slow step, respectively.

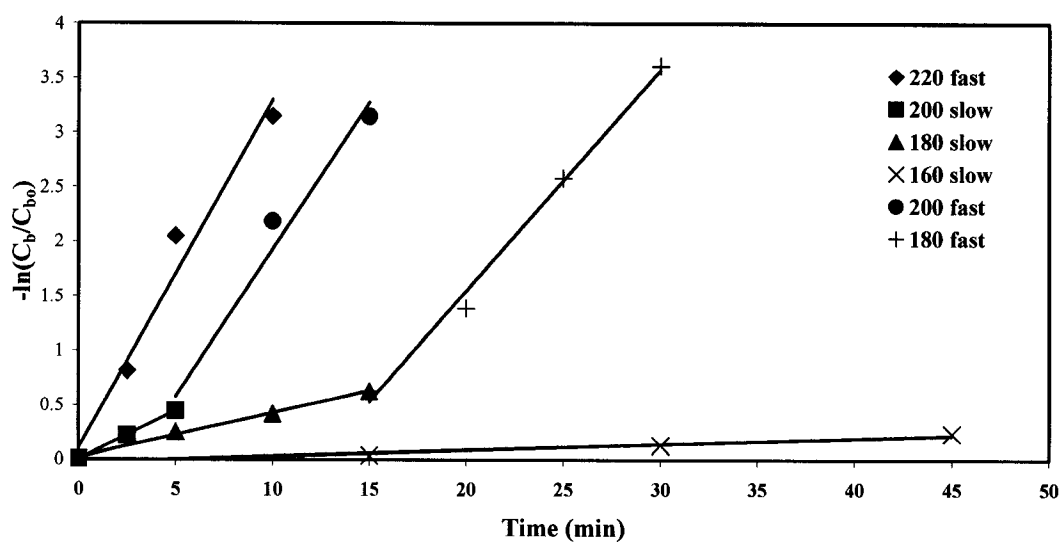


Figure 6.12: Pseudo First Order Kinetic Plot for Benzene.

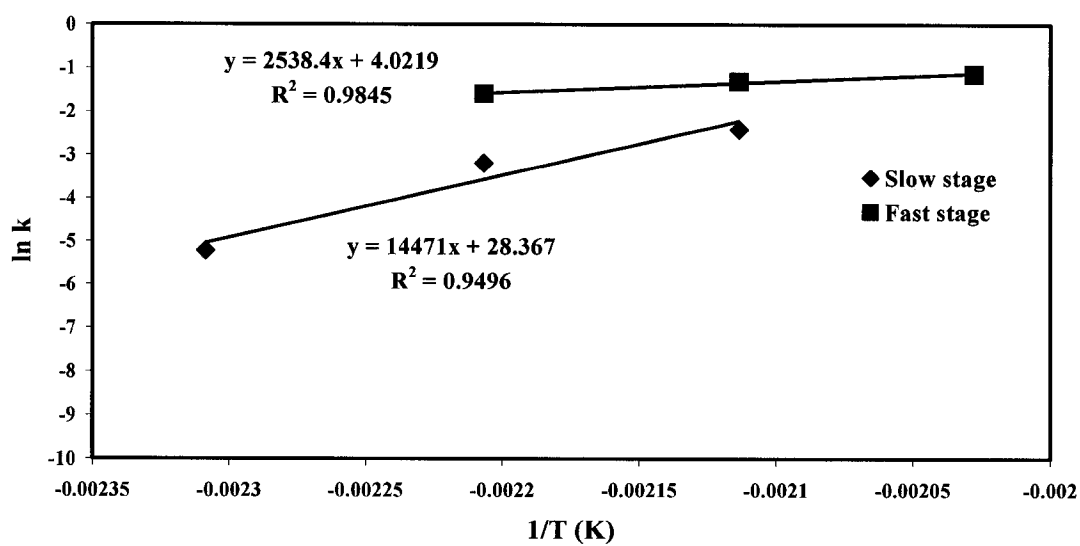


Figure 6.13: Arrhenius Plot for Pseudo First Order Rate Constant Calculated from Benzene Removal Data.

6.4 Repeatability of the Experiments

The repeatability of both benzene and phenol has been tested. Figure 6.14 shows the repeatability of benzene data at 220°C and 100% excess of oxygen pressure with an initial pH of 6. The initial phenol concentration was 0.27 mmol/L. It is apparent that the excellent repeatability was achieved. A good repeatability was also achieved for phenol as appears in Figure 6.15.

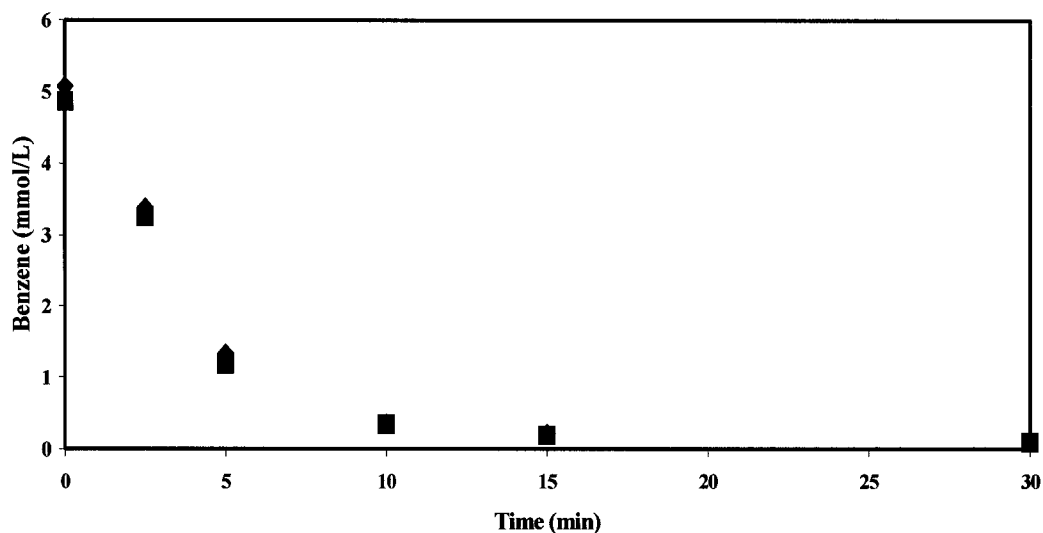


Figure 6.14: Repeatability of Benzene Result at 220°C, 100% Excess O₂, Initial pH= 6, Initial Phenol Concentration= 0.27 mmol/L.

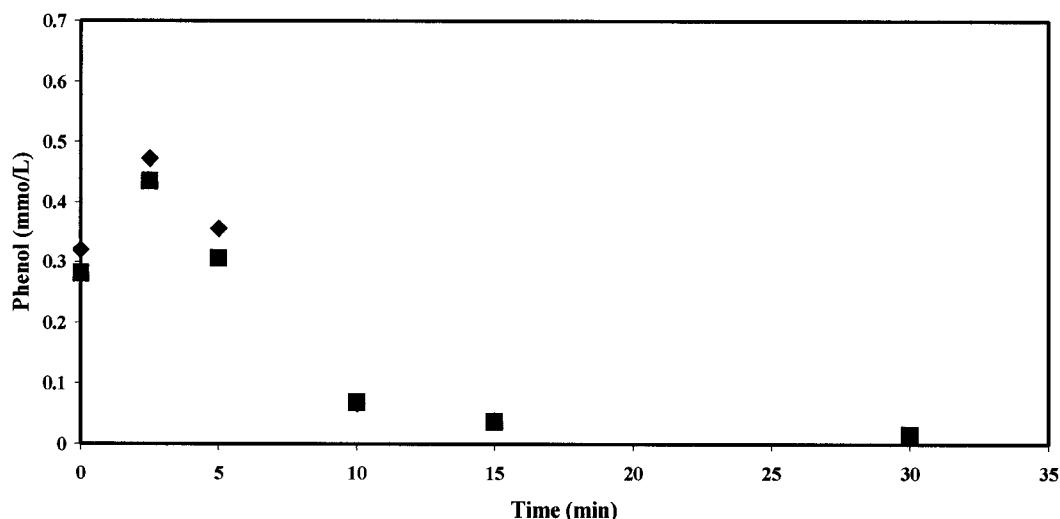


Figure 6.15: Repeatability of Phenol Result at 220°C, 100% Excess O₂, Initial pH= 6, Initial Phenol Concentration= 0.27 mmol/L.

6.5 Proposed Simplified Pathway for Oxidation of Benzene

From the results obtained in this chapter it was obvious that the benzene first oxidized to phenol and after that phenol further degraded. Also, as mentioned earlier, the benzoquinone has been identified by the GCMS. This means that the phenol was first degraded to either hydroquinone or catechol, or both of them, which was further degraded to the benzoquinone. The benzoquinone will further oxidized through many intermediates that have not been identified in this study. Later, those intermediates were degraded to low molecular weight organic acids. Some of these acids were identified in this study. Accordingly, the following pathway was proposed:

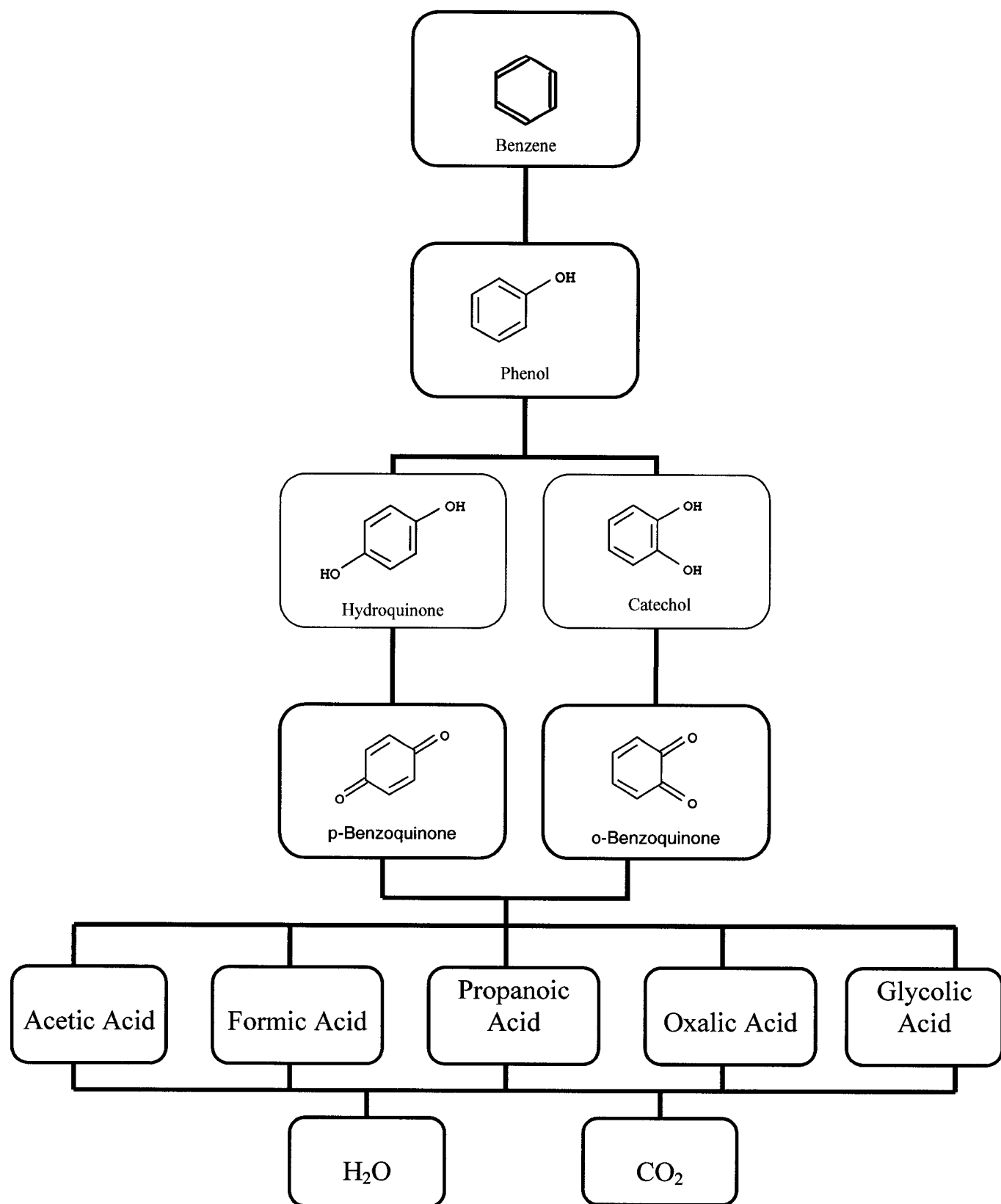


Figure 6.16: Simplified Pathway for Oxidation of Benzene.

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The following can be concluded from the work:

- The rate of benzene degradation depends on temperature, pressure, pH and the compositions of the reaction medium.
- At fixed temperature, the lower the pH the higher the rate of benzene degradation because of the accumulation of the free radicals at the lower pH. However, the major effect of pH was at lower oxidation temperatures.
- The pH of the solution kept changing throughout the reaction because of the production and degradation of the intermediates.
- Faster benzene degradation has been obtained with the increasing partial pressure of oxygen, especially at the first 5 minutes of the reaction time. The main reason is that the higher oxygen pressure resulted in the higher amount of oxygen dissolved in the liquid phase.
- The results showed that the reaction can be represented by two first order reaction with respect to benzene concentration and oxygen partial pressure. The reaction occurs in two steps, a fast step followed by a slow step. Most of the benzene was degraded during the fast step. When the initial pH was 4, the activation energy for the fast step was found to be 10.3 kJ/mol.

- Considerable TOC reduction was achieved and the degree of TOC reduction increased with temperature. This implies that the reaction tends to go to completion.
- Lower amounts of intermediates were produced at higher oxidation temperatures because at higher temperatures all reactions tend to go to completion.
- The main intermediates were found to be acetic acid and formic acid. Negligible amounts of both propanoic acid and glycolic acid were also detected. In addition, a negligible amount of benzoquinone was identified. Acetic acid was the most stable product.
- The optimum conditions for benzene degradation were found to be 220°C and oxygen partial pressure of 1.38 MPa in the pH range of 4-5. However at these conditions higher amounts of acids was produced.
- Addition of phenol to the system enhanced the benzene degradation because the free radicals that were produced during the phenol oxidation were used to initiate the oxidation of benzene.
- Since phenol is a common component that can be found in many of the wastewater streams and since it can enhance the degradation of benzene and some other component, this can have a significant economic impact.
- The higher the concentration of phenol, the higher the benzene degradation at a given temperature. However, the addition of 1.59 mmol/L of phenol was found to

be the optimum concentration. Above 1.59 mmol/L, the benzene degradation was not increased.

- The degradation of benzene enhanced with phenol proceeds in two stages and the activation energy was determined to be 21.1 kJ/mol and 1.2×10^2 kJ/mol for the fast and slow step, respectively
- A simplified pathway for the reaction suggested that the benzene first oxidized to phenol, followed by further phenol degradation.

7.2 Recommendations for future work

- Due to the present experimental setup, there was a limitation in the number of the samples that could have been collected during the experiments. It is recommended to modify the experimental setup so that more samples could be collected in order to test the kinetic model.
- It is recommended to use the High Pressure Liquid Chromatography (HPLC) to analyze the samples especially those that can be collected periodically when the oxidation is fast in order to identify if there are another intermediates produced in addition to those identified in this study.
- Different catalysts should be tried at different conditions to find out if they could enhance the benzene degradation.

- Since the metal wall can destroy the free radicals it is recommended to study the effect of Pyrex liner.
- It is recommended to try different additives, other than phenol, which might enhance the benzene degradation. An example of such an additive is hydroquinone, which is known to be a free radical initiator.
- Oxidizing agent other than oxygen such as ozone and hydrogen peroxide can be used for the reaction.
- Effect of impeller speed on the benzene degradation should be studied at different experimental conditions.

7.3 Contributions to Knowledge

As to our knowledge, this is the first study that deals with the wet air oxidation of benzene. The results that were obtained were very promising. The degradation of benzene was enhanced by lowering the initial pH of the reaction medium and enhanced further by the addition of phenol. From the results that were obtained, the optimum conditions were found, such as the optimum temperature, pressure, pH and the amount of the initial phenol. In addition, kinetic study was performed for the oxidation of benzene. Some of the oxidation intermediates were identified and a simplified pathway for benzene oxidation was proposed.

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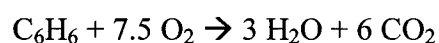
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Appendix A

Calculation of Oxygen Pressure Needed

The amount of oxygen needed at given condition was calculated using the ideal gas law as follows:



1 mole of C_6H_6 needs 7.5 mole of O_2

$$0.5\text{ml} \cdots \text{C}_6\text{H}_6 \left| \frac{0.879\text{g}}{\text{ml}} \right| \left| \frac{\text{mol}}{78.11\text{g}} \right| \left| \frac{1000\text{mmole}}{\text{mole}} \right| = 5.63 \text{ mmol C}_6\text{H}_6$$

So, 5.63 mmol C_6H_6 needs 42.23 mmol O_2

Using Ideal Gas Law,

$$PV = nRT$$

$$V = 0.24 \text{ L}$$

$$\text{Therefore, } P_{\text{O}_2} \text{ (at } 220^\circ\text{C)} = \frac{(0.0422) * (0.0821) * (493.15)}{0.24} = 7.12 \text{ atm} = 104.6 \text{ psi}$$

Appendix B

Oxygen Solubility in Water

In order to calculate the amount of oxygen dissolved in water the following equation that was developed by Tromans (63) was used:

$$c_{\text{aq}} = P_{\text{O}_2} \exp \left\{ \frac{0.046T^2 + 203.35T \ln(T/298) - (299.378 + 0.092T)(T - 298) - 20.591 \times 10^3}{(8.3144)T} \right\}$$

Where:

C_{aq} : Molal concentration of dissolved O_2 (mol/ kg H_2O).

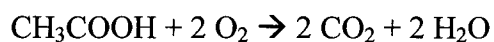
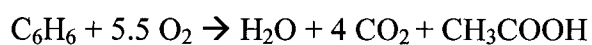
P_{O_2} : Oxygen partial pressure (atm).

T : Temperature ($^{\circ}\text{K}$)

Appendix C

Calculation of Theoretical Amount of Carbon Dioxide Generated

Since the benzene is not totally converted to H₂O and CO₂ and since acetic acid was determined in the final product, the following equations were used to calculate the total amount of carbon dioxide during the oxidation of benzene:



From the first equation it can be seen that

1 mole C₆H₆ produces 4 moles of CO₂

And 1 mole of C₆H₆ produces 1 mole of CH₃COOH

However, it can be seen from the second equation that

1 mole of CH₃COOH produces 2 moles of CO₂.

The following results were obtained at 260°C and 1.38 MPa of oxygen pressure

Time	mmol C ₆ H ₆ /L	mmol CH ₃ COOH
Original sample	3.83	0
Final product After 120 min	0.07	0.59

From the results,

Amount of benzene oxidized = $3.83 - 0.07 = 3.76$ mmol

$\therefore 3.76$ mmol C_6H_6 produces 15.04 mmol of CO_2 and 3.76 mmol of CH_3COOH

Also, the amount of CO_2 produces from the oxidation of CH_3COOH is

$$2 * (3.76 - 0.59) = 6.34 \text{ mmol } \text{CO}_2$$

\therefore Theoretical Amount of CO_2 produced = $15.04 + 6.34 = 21.38$ mmol