

LB/20N

# THE EFFECT OF CHLORINE ON THE FORMATION OF NITROGEN OXIDES IN A FLUIDIZED BED COMBUSTOR

by

**PONNUTHURAI GOKULAKRISHNAN**

පුස්තකාලය  
මාලුව විශ්ව විද්‍යාලය, ශ්‍රී ලංකාව  
මොරටුව.

A thesis submitted to the Department of Chemical Engineering  
in conformity with the requirements for the degree of  
Master of Science (Engineering).

72117  
66 "97"  
662.612.2

Department of Chemical Engineering  
Queen's University at Kingston  
Kingston, Ontario  
Canada, K7L 3N6.  
March 1997

copyright © Ponnuthurai Gokulakrishnan, 1997

TH

72117

## ABSTRACT

The effect of chlorine on  $\text{NO}_x$  and  $\text{N}_2\text{O}$  emissions has been studied in an electrically heated bed of fluidized sand. Pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) was burnt as a model compound in a mixture of  $\text{O}_2$  and  $\text{N}_2$  to produce  $\text{NO}$  and  $\text{N}_2\text{O}$ . The experiments were done at temperatures 750, 825 or 900 °C. The concentrations of  $\text{O}_2$  and pyridine in the fluidizing gas were maintained at 3.2 or 11.6%, and 500, 1500 or 2000 ppmv, respectively. When pyridine was burnt in the fluidized bed, the concentrations of  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{CO}$  were measured continuously in the freeboard. Chlorine was introduced to the fluidized bed as  $\text{HCl}$  at concentrations up to 6000 ppmv. The effect of  $\text{CaCl}_2$  on the formation of  $\text{NO}_x$ ,  $\text{N}_2\text{O}$  and  $\text{CO}$  was also studied.

The addition of  $\text{HCl}$  to the fluidizing gas mixture decreased the concentration of  $\text{NO}_x$ , and increased the concentration of  $\text{CO}$ . However, the addition of  $\text{HCl}$  caused the concentration of  $\text{N}_2\text{O}$  to decrease or to increase, depending on the temperature. At 750 °C, the addition of  $\text{HCl}$  reduced the concentration of  $\text{N}_2\text{O}$ , while it increased the concentration at 825 and 900 °C. Temperature has a significant impact on the effect caused by the addition of  $\text{HCl}$  on the formation of  $\text{NO}_x$ ,  $\text{N}_2\text{O}$  and  $\text{CO}$ . On the other hand, the concentrations of pyridine and  $\text{O}_2$  do not have a significant effect on the percentage decrease or increase in the concentrations of  $\text{NO}_x$  and  $\text{CO}$ . The addition of  $\text{CaCl}_2$  also seems to decrease the concentration of  $\text{NO}_x$ , while it increases the concentration of  $\text{CO}$ . However, the presence of calcium based compounds in the fluidized bed also tends to catalyze the formation of  $\text{NO}_x$ .

The increase in the concentration of  $\text{CO}$  caused by  $\text{HCl}$  is due to the suppression of  $\text{OH}$  radicals, which are the main precursor for the formation of  $\text{CO}_2$  from  $\text{CO}$ . During pyridine combustion, the radical pool of  $\text{O}$ ,  $\text{H}$  and  $\text{OH}$  plays a major role in converting  $\text{HCN}$  and  $\text{NCO}$  to  $\text{NO}_x$ . Thus, the decrease in  $\text{NO}_x$  caused by  $\text{HCl}$  is due to the suppression of  $\text{O}$ ,  $\text{H}$  and  $\text{OH}$  radicals. Again the increase in the concentration of  $\text{N}_2\text{O}$  at 825 and 900 °C is due to the suppression of  $\text{OH}$  radical by  $\text{HCl}$ . However, the decrease in  $\text{N}_2\text{O}$  at 750 °C is probably due to the inhibition of pyridine combustion by  $\text{HCl}$ .

## ACKNOWLEDGMENTS

I would like to thank my research supervisor, Dr. David Lawrence for his guidance and continuous encouragement throughout this work, and also, for inspiring my interest in the area of Combustion Science. I would like to thank Mr. Peter Gogolek for devoting his invaluable time for useful discussions related to this work. Thanks must also go to Dr. Henry Becker for lending the FTIR analyzer.

My sincere gratitude goes to members of the support staff in the Department of Chemical Engineering for their assistance to my experimental work, and especially, to Mr. Steve Hodgson who was a tremendous help in setting up and in troubleshooting my experimental system.

I would like to express my great appreciation to Queen's University and the National Sciences and Engineering Council of Canada for providing me with financial support throughout my stay at Queen's University.

# CONTENTS

Abstract	i
Acknowledgments	ii
List of Tables	vi
List of Figures	vii
<b>Chapter One: Introduction</b>	
1.1 Coal Combustion	1
1.2 Waste Incineration	3
1.3 Statement of Purpose	5
<b>Chapter Two: A Review of the Combustion Chemistry of Nitrogen and Chlorine</b>	
2.1 Introduction	7
2.2 Nitrogen Chemistry in Combustion	9
2.2.1 The Formation of Nitric Oxide	9
2.2.2 The Formation of Nitrous Oxide	12
2.2.3 The Formation of Nitrogen Oxides during Fluidized Bed Combustion	13
2.3 Chlorine Chemistry in Combustion	16
2.3.1 The Effect of Chlorine on the Formation of PAH	16
2.3.2 The Effect of Chlorine on the Formation of Soot	17
2.3.3 The Effect of Chlorine on the Formation of CO	20
2.3.4 The Effect of Chlorine on the Formation of Nitrogen Oxides	24
2.4 Summary	27

### **Chapter Three: Experimental Procedure**

3.1	Introduction	28
3.2	Fluidized Bed	28
3.3	Analytical Systems and Instrumentation	32
3.3.1	Nitrous Oxide Measurement	33
3.3.2	Nitric Oxide and NO <sub>x</sub> Measurements	37
3.3.3	Carbon Dioxide and Carbon Monoxide Measurements	39
3.3.4	Hydrogen Chloride Measurement	39
3.3.5	Data Acquisition System	41

### **Chapter Four: Experimental Results**

4.1	Introduction	42
4.2	Carbon Dioxide and Carbon Monoxide	44
4.3	Nitric Oxide	47
4.4	Nitrous Oxide	49
4.5	The Effect of Calcium Chloride	50
4.6	Summary	56

### **Chapter Five: Discussion**

5.1	Introduction	58
5.2	The Combustion of Pyridine without Chlorine	58
5.2.1	Formation of Nitrogen Oxides	59
5.2.2	The Effect of NO on Pyridine Combustion	62
5.2.3	The Effect of CO on Pyridine Combustion	64

5.3	The Combustion of Pyridine in the Presence of Chlorine	66
5.3.1	Carbon Monoxide	66
5.3.2	Nitric Oxide	69
5.3.3	Nitrous Oxide	74
5.4	Summary	78
<b>Chapter Six: Conclusion, and Recommendations for Future Work</b>		
6.1	Conclusion	80
6.2	Recommendations for Future Work	81
<b>References</b>		84
<b>Appendix 1: Calibration Data</b>		96
<b>Appendix 2: Experimental Results</b>		98
<b>Appendix 3: Experimental Design</b>		103
<b>Vita</b>		104



## LIST OF TABLES

3.1	Instrumentation for gas analysis	33
3.2	The operating conditions of the ECD/GC	35
A1.1	Calibration curve data for GC	96
A1.2	Calibration curve data for FTIR	97
A2.1	Experimental data for Figures 4.2 and 4.5	98
A2.2	Experimental data for Figures 4.3, 4.4 and 4.6	101
A2.3	Experimental data for Figure 5.2	102
A3.1	2 <sup>4</sup> factorial design with 2 replicate runs at each set of conditions	103



## LIST OF FIGURES

3.1	Schematic diagram of the fluidized bed	29
3.2	A sample of Chromatogram generated by the ECD/GC	36
3.3	The calibration curve for the measurement of N <sub>2</sub> O using ECD/GC	36
3.4	The measurement of NO and NO <sub>x</sub> using the NO/NO <sub>x</sub> analyzer	38
3.5	Calibration curve for the FTIR to measure the concentration of HCl	40
4.1a	Typical experimental measurements of [CO <sub>2</sub> ] and [CO]	43
4.1b	Typical experimental measurements of [NO <sub>x</sub> ] and [N <sub>2</sub> O]	43
4.2	The percentage increase in [CO] caused by HCl	45
4.3	The percentage change in [CO <sub>2</sub> ] caused by HCl	46
4.4	The percentage change in [CO <sub>2</sub> ] + [CO] caused by HCl	46
4.5	The percentage reduction in [NO <sub>x</sub> ] caused by HCl	48
4.6	The percentage change in [N <sub>2</sub> O] caused by HCl	50
4.7	The effect of CaCl <sub>2</sub> on the formation of NO <sub>x</sub> and CO at 825 °C	51
4.8	The effect of CaCl <sub>2</sub> on the formation of NO <sub>x</sub> and CO at 900 °C	52
4.9	The effect of HCl and CaCl <sub>2</sub> on the formation of NO <sub>x</sub> and CO at 825 °C	53
4.10	The effect of limestone on the formation of NO <sub>x</sub> at 825 °C	54
4.11	The effect of HCl on the formation of NO <sub>x</sub> and CO in the presence of CaO	55
5.1	Main pathways for the oxidation of pyridine	59
5.2	The percentage increase in [N <sub>2</sub> O] caused by CO	66
5.3	The correlation between the percentage change in [N <sub>2</sub> O] and in the total carbon measured in the freeboard: (a) at 750 °C; (b) at 900 °C	76