CHAPTER SIX

CONCLUSION, AND RECOMMENDATIONS FOR FUTURE WORK

6.1 CONCLUSION

- The addition of HCl increases the formation of CO and decreases the formation of NO_x in a fluidized bed. The increase in the concentration of CO is by up to 20 times, whereas the decrease in the concentration of NO_x is by up to 75%.
- Temperature has an impact on the effect of chlorine on the formation of CO. At higher temperature, the percentage increase in the concentration of CO is higher. However, temperature does not appear to have a significant influence on the effect of chlorine on the formation of NO_x. The concentrations of O_2 and pyridine do not have a significant impact on the effect of HCl.
- The effect of HCl on the formation of CO and NO_x is due to the suppression of O, OH and H radicals. The consumption of O, OH and H radicals by HCl inhibits the oxidation of CO to CO_2, and the formation of NO from HCN and NCO radicals.
- The addition of HCl increases the formation of N_2O at 825 and 900 °C, and decreases at 750 °C. The increase in the formation of N_2O at 825 and 900 °C is due to the inhibition of the decomposition of N_2O in the fluidized bed by HCl. The addition of HCl consumes OH radicals, and this results in a lack of OH radicals for the decomposition of N_2O. On the other hand, decrease in N_2O at 750 °C is due to the inhibition of pyridine combustion by HCl in the fluidized bed.

- The addition of CO in the fluidized bed increases the formation of N_2O. This is due to the consumption of OH radicals by CO to become CO_2. This prevents the decomposition reaction of N_2O with OH, and hence, there is an increase in the concentration of N_2O. This shows that the prominent decomposition reaction of N_2O in this particular combustion system is:

  $N_2O + OH \leftrightarrow N_2 + HO_2$

- The addition of $CaCl_2$ decreases the formation of NO_x. However, there is an increase in the concentration of NO_x subsequently due to the catalytic effect of calcium based compounds derived from the decomposition of $CaCl_2$.

- The addition of HCl in the presence of CaO in the fluidized bed decreases the formation of NO_x. However, the addition of HCl in the presence of residuals derived from the decomposition of $CaCl_2$ does not seem to affect the formation of NO_x.

6.2 RECOMMENDATIONS FOR FUTURE WORK

- Modeling the effect of HCl on the formation of NO_x and N_2O in a fluidized bed.

Since the study of chlorine effect is performed in a quartz sand bed by burning pyridine, the system can be assumed as homogeneous combustion. The homogeneous combustion of pyridine in a fluidized bed can be described using three increasingly complex reactor models which can be identified by their key features [Van der Vaart (1992)]:

1. two phases, bubble and emulsion with constant bubble size

2. three phases, bubble, cloud and emulsion with constant bubble size

3. three phases, bubble, cloud and emulsion with bubble growth

A simple plug flow model can be used to describe the freeboard region separately.

- Investigating the influence of coal and other waste materials on the effect of HCl on NO_x and N_2O.

In real life situation, burning of coal and other waste materials makes the fluidized bed combustion more complex, because the presence of solid particles promotes the heterogeneous reactions. There were few studies investigated the effect of chlorine, when coal was burned in the fluidized bed. However, the effect of chlorine on the formation of NO_x and N_2O is not yet clear. Since the industrial wastes contain quite amount of chlorine, the study of chlorine effect in the presence of different types industrial wastes would be more practical interest.

- The impact of the calcium based compounds on the effect of chlorine on NO and N_2O.

The calcium based compounds (e.g., CaO) enhance the formation of NO_x in a fluidized bed. However, as we have seen in this work, the effect of chlorine on the formation of NO_x is different in the presence of residual calcium based compounds derived from the decomposition of $CaCl_2$ from that of limestone. Thus, there is a necessity to study in detail the effect of different types of calcium based compounds on the effect of chlorine, since calcium based compounds present in practical fluidized beds to absorb SO_2. Uchida *et al.* (1979) and Weinell *et al.* (1992) investigated the reaction kinetics of HCl with limestone.

- Investigating the effect of other halogens, such as bromine and iodine, on the formation of NO_x and N_2O in a fluidized bed.

Considerable amount of the hlogenated industrial wastes contain bromine and iodine based compounds. Thus, it would be a practical interest to study the effect of bromine and iodine on the formation of NO_x and N_2O.

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APPENDIX 1
CALIBRATION DATA

Table A1.1: Calibration Curve Data for GC (Figure 3.3)

$[N_2O]$ ppmv	Area Count
1.14	8558
1.14	7536
1.14	7543
1.654	12597
1.654	12390
1.654	10371
7.075	41609
7.075	40326
7.075	41374
11.566	59876
11.566	54321
11.566	57390
19.328	86413
19.328	91242
19.328	89463
100	421812
100	413580
100	408773
100	421020
100	404101
100	353890
100	475272
100	430402
220	794179
220	790652
220	806916
220	816615
220	806429
321	1128880
321	1149422
321	1126172
321	1155618
321	1105993

Table A1.2: Calibration Curve Data for FTIR (Figure 3.5)

[HCl]	Wave #
ppmv	2651
0	0
41	0.011148
41	0.012073
41	0.012339
41	0.013699
135	0.030024
135	0.031795
135	0.031314
135	0.031529
304	0.051145
304	0.051907
304	0.053882
304	0.053394
382	0.059185
382	0.059704
382	0.059333
382	0.057215
503	0.064555
503	0.065157
503	0.065422
503	0.065231
637	0.083216
637	0.077216
637	0.075221
1103	0.10078
1103	0.10241
1103	0.098185
1344	0.11243
1344	0.11315
1344	0.1157
1344	0.11417

APPENDIX 2

EXPERIMENTAL RESULTS

Table A2.1: Experimental Data for Figures 4.2 and 4.5.

[Pyridine]	Temp	$[O_2]$	[HCl]	% Reduction in NO_x			% Increase in CO		
ppmv	°C	vol.%	ppmv	Meas-I	Meas-II	Mean	Meas-I	Meas-II	Mean
500	750	3.2	0	0	0	0	0	0	0
500	750	3.2	889	-45.572	-54.287	-50.104	337.663	326.008	331.705
500	750	3.2	2514	-67.324	-65.121	-66.178	360.221	329.597	344.565
500	750	3.2	4175	-70.509	-65.499	-67.904	360.52	333.993	346.959
500	750	3.2	5871	-72.21	-66.268	-69.12	302.223	290.928	296.448
500	900	3.2	0	0	0	0	0	0	0
500	900	3.2	889	-24.141	-24.691	-24.425	782.381	1177.36	948.231
500	900	3.2	2514	-19.99	-27.868	-24.054	1152.36	1689.87	1378.06
500	900	3.2	4175	-23.449	-22.785	-23.106	1218.73	1689.47	1416.39
500	900	3.2	5871	-16.325	-31.057	-23.924	1174.05	1611.95	1357.93
500	750	11.6	0	0	0	0	0	0	0
500	750	11.6	889	-4.8697	-15.287	-10.182	356.901	393.38	374.599
500	750	11.6	2514	-67.03	-61.068	-63.99	404.743	442.788	423.201
500	750	11.6	4175	-63.48	-71.052	-67.341	411.124	435.513	422.957
500	750	11.6	5871	-76.825	-72.196	-74.465	424.954	449.786	437.001

[Pyridine]	Temp	[O_2]	[HCl]	% Reduction in NO_x			% Increase in CO		
ppmv	°C	vol.%	ppmv	Meas-I	Meas-II	Mean	Meas-I	Meas-II	Mean
500	900	11.6	0	0	0	0	0	0	0
500	900	11.6	889	-13.608	-3.9339	-8.8556	487.812	748.831	598.462
500	900	11.6	2514	-36.925	-27.954	-32.518	1405.3	2002.82	1658.6
500	900	11.6	4175	-35.907	-36.215	-36.058	1443.66	2058.28	1704.21
500	900	11.6	5871	-45.821	-40.326	-43.121	1380.89	1979.47	1634.64
1500	750	3.2	0	0	0	0	0	0	0
1500	750	3.2	889	-60.149	-53.487	-56.884	524.992	503.467	514.059
1500	750	3.2	2514	-66.76	-63.313	-65.07	682.994	654.247	668.393
1500	750	3.2	4175	-64.508	-68.004	-66.221	706.922	683.085	694.815
1500	750	3.2	5871	-65.208	-68.845	-66.991	749.018	724.649	736.641
1500	900	3.2	0	0	0	0	0	0	0
1500	900	3.2	889	-57.603	-52.431	-55.058	295.628	348.161	320.738
1500	900	3.2	2514	-57.181	-58.08	-57.623	1269.84	1412.94	1338.24
1500	900	3.2	4175	-69.554	-65.617	-67.617	1913.06	2087.01	1996.21
1500	900	3.2	5871	-72.945	-74.708	-73.813	2037.03	2221.15	2125.04
1500	750	11.6	0	0	0	0	0	0	0
1500	750	11.6	889	-36.853	-30.995	-33.965	290.086	302.562	296.248
1500	750	11.6	2514	-62.555	-62.432	-62.494	424.47	438.567	431.433
1500	750	11.6	4175	-66.849	-61.703	-64.312	462.282	474.455	468.295
1500	750	11.6	5871	-66.1	-68.12	-67.096	494.111	505.268	499.622

[Pyridine]	Temp	$[O_2]$	[HCl]	% Reduction in NO_x			% Increase in CO		
ppmv	°C	vol.%	ppmv	Meas-I	Meas-II	Mean	Meas-I	Meas-II	Mean
1500	900	11.6	0	0	0	0	0	0	0
1500	900	11.6	889	-46.992	-48.813	-47.897	763.479	859.274	808.442
1500	900	11.6	2514	-55.111	-50.526	-52.831	1250.62	1414.52	1327.55
1500	900	11.6	4175	-61.393	-57.197	-59.307	1368.68	1569.22	1462.81
1500	900	11.6	5871	-64.169	-66.043	-65.101	1537.78	1742.69	1633.95

Table A2.2: Experimental Data for Figures 4.3, 4.4 and 4.6

Pyridine	Temp.	O_2	HCl	% Change in				
ppmv	°C	vol%	ppmv	NO_x	N_2O	CO	CO_2	CO_2+CO
2000	750	3.2	0	0	0	0	0	0
2000	750	3.2	250	-14.26	-11.57	502.93	-25.24	-8.82
2000	750	3.2	700	-28.58	-31.92	651.09	-50.58	-16.26
2000	750	3.2	1170	-39	-50.17	900	-59.24	-18.37
2000	750	3.2	1650	-58.77	-56.98	1160	-62.78	-19.64
2000	825	3.2	0	0	0	0	0	0
2000	825	3.2	250	-30.41	5.8	220.84	-0.25	4.97
2000	825	3.2	700	-49.62	5.96	585.25	-9.83	2.2
2000	825	3.2	1170	-59.38	18.33	753.08	-16.41	2.66
2000	825	3.2	1650	-69.79	10.13	1170	-39.04	-2.45
2000	900	3.2	0	0	0	0	0	0
2000	900	3.2	250	-7.01	5.63	59.38	1.91	2.56
2000	900	3.2	700	-18.835	6.965	195.885	1.19	4.34
2000	900	3.2	1170	-39.35	26.37	467.62	-4.44	1.18
2000	900	3.2	1650	-46.407	23.49	711.27	-10.53	-1.42
2000	750	11.6	0	0	0	0	0	0
2000	750	11.6	250	-11.55	-0.21	326.18	-16.71	-1.27
2000	750	11.6	700	-21.42	-18.02	577.01	-38.96	-7.89
2000	750	11.6	1170	-38.87	-28.14	625.74	-48.53	-7.52
2000	750	11.6	1650	-42.52	-32.02	772.84	-50.89	-5.51
2000	825	11.6	0	0	0	0	0	0
2000	825	11.6	250	-12.75	4.23	138.58	-7.51	0.33
2000	825	11.6	700	-21.42	1.32	586.49	-15.02	-0.45
2000	825	11.6	1170	-22.35	5.12	908.99	-19.29	0.13
2000	825	11.6	1650	-29.97	7.98	1232.25	-34.49	-1.98
2000	900	11.6	0	0	0	0	0	0
2000	900	11.6	250	-8.16	1.38	31.37	1.25	1.28
2000	900	11.6	700	-19.555	10.41	99.535	2.02	3.6
2000	900	11.6	1170	-28.59	13.97	140.16	1.42	3.48
2000	900	11.6	1650	-38.36	41.65	428.6	1.86	7.34

Table A2.3: Experimental Data for Figure 5.2.

[CO]	$[N_2O]$ in ppmv at		
ppmv	750 °C	825 °C	900 °C
0	0	0	0
630	22.65	10.24	13.14
1445	36.97	20.45	21.75
3300	45.44	39.41	

APPENDIX 3

EXPERIMENTAL DESIGN

Table A3.1: 2^4 Factorial Design with 2 replicate runs at each set of conditions

Factors	Lower	Higher
[Pyridine] - X1	500	1500
[HCl] - X2	0	5850
$[O_2]$ - X3	3.2	11.6
Temp. - X4	750	900
Code	-1	1

Run#	X1	X2	X3	X4	Meas: 1	Meas: 2	Mean	Std. Dev.
1	-1	-1	-1	-1	168.8	176.5	172.65	5.44472
2	1	-1	-1	-1	216.7	233.4	225.05	11.8087
3	-1	1	-1	-1	67.8	48.7	58.25	13.5057
4	1	1	-1	-1	119.2	96.6	107.9	15.9806
5	-1	-1	1	-1	177.5	165.7	171.6	8.34386
6	1	-1	1	-1	363.1	347.5	355.3	11.0309
7	-1	1	1	-1	40.6	55.3	47.95	10.3945
8	1	1	1	-1	96.5	107.2	101.85	7.56604
9	-1	-1	-1	1	181.5	194.8	188.15	9.40452
10	1	-1	-1	1	468.9	475.6	472.25	4.73762
11	-1	1	-1	1	129.4	147.2	138.3	12.5865
12	1	1	-1	1	181.5	185.2	183.35	2.6163
13	-1	-1	1	1	175.3	189.6	182.45	10.1116
14	1	-1	1	1	504.1	478.9	491.5	17.8191
15	-1	1	1	1	140.6	128.7	134.65	8.41457
16	1	1	1	1	187.4	200.6	194	9.33381

Mean =	201.58
Standard Deviation =	10.65
95% Confidence Interval =	+/- 17.38

Significant Effects:

Main Effects	Interaction Effects
X1	X1X2
X2	X1X3
X4	X1X4
	X1X2X4

VITA

Name: Ponnuthurai Gokulakrishnan

Place of birth: Jaffna, Sri Lanka

Education: Queen's University at Kingston, 1995 - 97; M.Sc.(Eng.)

University of Moratuwa, Sri Lanka, 1990 - 94; B.Sc.(Eng.)

The Chartered Institute of Management Accountants (CIMA), U.K., 1989 - 92; Passed Finalist

Experience: Research Assistant, Queen's University, Jan. 95 - present

Teaching Assistant, Queen's University, Jan. 95 - present

Technical Manager, Biotech Corporation Lanka Ltd., Sri Lanka, Nov. 94 - Jan. 95

Instructor, University of Moratuwa, Sri Lanka, May 94 - Nov. 94

Awards: Queen's Graduate Award (1996)

Queen's Dean's Award (1995)

Union Carbide Award for the Best Chemical Engineering Student (1994)

Publication: Gokulakrishnan, P. and Lawrence, A. D., (1997), "A Detailed Study of the Role of Halogens in the Inhibition of Nitrogen Oxide Formation in Fluidized Bed Incinerators", *Proceedings of the 14th International Conference on Fluidized Bed Combustion*, ASME, USA.