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**Computational Modeling and Experimental Studies on NO_x Reduction
Under Pulverized Coal Combustion Conditions**

Technical Progress Report
Second Quarter

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Technical Progress Report
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1. Introduction

Presented in this second quarterly report are the computational results of NO reburning with (a) a combination of methane and acetylene- (i) with the reaction mechanism listed in the first quarterly report and (ii) with the updated reaction mechanism (Table 1 of this report); and (b) a combination of methane and ammonia. The impact of the updated reaction scheme was not significant on the results of NO reburning with methane/ acetylene; however, the reaction scheme needed changes to improve the accuracy of some reactions of crucial intermediates in methane/ ammonia reburning. An extensive literature survey was made in order to update the mechanism.

Also, some efforts were made to receive quotations on various pieces of equipment for our experimental facility during this quarter. The experimental plan for the Year 1 was submitted to Dr. Lori D. Gould, the Contracting Officer's Technical Representative and is currently under review. The experimental work will begin upon the approval.

In terms of conference presentations, the Overview of this project "Computational Modeling and Experimental Studies on NO_x Reduction Under Pulverized Coal Combustion Conditions" was presented by the PI at the Third Annual Historically Black Colleges and Universities/Private Sector Energy Research and Development Technology Transfer Symposium in Atlanta, Georgia (April 27-29, 1995).

2. NO Reburning with CH₄/C₂H₂

During the month of April, computer simulation studies were performed on NO reburning with a combination of methane and acetylene. The reaction mechanism employed was the same as reported in the first quarterly report. The results of these studies are as portrayed in Figures 1 through 3. The legends describe the reburn fuel composition between methane and acetylene. A typical CH₄/C₂H₂ : 90/10 combination at SR2=0.9 would represent the initial concentrations of flue gas as 1.88% CH₄, 0.21% C₂H₂, 16.47% CO₂, 1.89% O₂, 1000 ppm NO and 79.45% N₂/He. With varying SR2 conditions, the program is run for a fixed reburn fuel composition for a residence time of 0.2 s at the reactor temperature of 1373 K. The final concentrations of various nitrogen containing species are obtained from these tests. Then another reburn fuel composition (say, 70/30) is chosen, the initial concentrations of various species at different SR2 values (0.7 through 1.05) are calculated based on stoichiometry analysis and fed to the CHEMKIN to solve for the exit concentrations of nitrogen containing species at this reburn fuel composition. Likewise, the tests are repeated for various combinations of methane and acetylene. The three nitrogen containing species that are significant are NO, HCN and NH₃. The concentrations of NO₂ and N₂O were found to be negligible as in the case of methane reburning. The following Figures 1 through 3 are the result of 48 computer runs (6 reburn fuel compositions X 8 SR2 conditions) on the CHEMKIN. These figures display the effect of the composition of CH₄/C₂H₂ on exit concentrations of NO, HCN and NH₃ respectively in NO reburning.

The addition of acetylene to methane as reburn fuel seems to favor the reduction of NO appreciably, as seen in Fig. 1. The best achievable NO concentration for 100/0 combination of $\text{CH}_4/\text{C}_2\text{H}_2$ is 46 ppm from the initially fed 1000 ppm, as the equilibrium comes to completion. But with 10% acetylene, that is, 90/10 combination of $\text{CH}_4/\text{C}_2\text{H}_2$, we are able to obtain the much needed further reduction by shifting the equilibrium. For the 90% CH_4 and 10% C_2H_2 the concentration of NO is reduced from 1000 ppm to 7 ppm. This is very significant and contributes greatly toward meeting the regulations on NO_x reduction. From Fig. 2, it can be seen that HCN concentration is increased only slightly for 90% CH_4 and 10% C_2H_2 reaction (864 ppm) in comparison with the 100% CH_4 reaction (833 ppm). This HCN is highly unstable at high temperatures and its recovery is reported to be 30% at 1100 C for a residence time of 1 s (Song et al, 1982).

For all the reburn fuel combinations between CH_4 and C_2H_2 the variation of exit concentrations with SR2 values shows trends that are similar. At $\text{SR2} < 0.9$ the HCN formation is more from NO (70 - 90%). But above SR2 of 0.9, the $\text{NO} \rightarrow \text{HCN}$ mechanism is greatly affected, that is, at $\text{SR2} > 0.9$ the NO concentration increases and HCN concentration decreases. Both HCN and NH_3 show similar trend with SR2. It appears from Figures 2 and 3 that a fragmental portion of HCN is always converted to NH_3 by some reaction. The NO reduction could go through a series reaction $\text{NO} \rightarrow \text{HCN} \rightarrow \text{NH}_3$.

The computer simulation of NO reburning with a combination of $\text{CH}_4/\text{C}_2\text{H}_2$ shows promising results in terms of NO_x reduction. The findings will be verified when the reburning experiments are conducted in the near future.

Figure 1. Effect of the composition of methane/ acetylene on NO exit concentration in NO reburning (Input NO Concentration: 1000 ppm; Reactor Temperature: 1373 K; Residence Time: 0.2 s)

Figure 2. Effect of the composition of methane/ acetylene on HCN exit concentration in NO reburning (Input NO Concentration: 1000 ppm; Reactor Temperature: 1373 K; Residence Time: 0.2 s)

Figure 3. Effect of the composition of methane/ acetylene on NH_3 exit concentration in NO reburning (Input NO Concentration: 1000 ppm; Reactor Temperature: 1373 K; Residence Time: 0.2 s)

3. Updated Reaction Mechanism

During this quarter constant efforts were made to update the reaction scheme based on the most recent literature. As many as 25 new reactions were added to the mechanism employed previously (218 reactions as reported in the first quarterly report). Also, some of the reaction constants data was updated to improve the kinetics accuracy for the existing scheme. Listed in Table 1 is the updated version of the reaction mechanism.

Glarborg et al (1994) have carried out an experimental and theoretical study of isocyanic acid (HNCO) oxidation in an isothermal quartz flow reactor at 1 atm pressure in the temperature range 1025-1425 K. Due to its role as an important intermediate in fuel nitrogen oxidation, HNCO chemistry is important in our work as well. Reactions 223 through 243 listed in Table 1 are taken from the work of Glarborg et al (1994). These include HNCO paths (Miller and Bowman, 1991 and Miller and Melius, 1992), NCO paths (Tsang, 1992) and HONO paths (Tsang, 1991). Efforts were made to include the most recent reaction constants data for reactions pertaining to NH_3 oxidation and the formation/destruction of NO and N_2O . Reactions 182 through 186 include the recent reaction constants, taken from Davidson (1991) and Glarborg (1994). The new reaction constants data for R146 is from East (1993) and for R179 and R194 is from Linstedt (1994).

The reaction mechanism given in Table 1 is more comprehensive in terms of predicting the ammonia and isocyanic acid oxidation chemistry. However, this was employed to check the existing $\text{CH}_4/\text{C}_2\text{H}_2$ reburning results before CH_4/NH_3 reburning studies are simulated.

Table 1. Updated Reaction Mechanism

REACTIONS CONSIDERED	(k = A T**b exp(-E/RT))		
	A	b	E
1. C2H6+M=2CH3+M	5.80E+13	0	75000
2. CH4+M=CH3+H+M	4.17E+17	0	92300
H2O Enhanced by 5			
3. CH4+O2=CH3+HO2	4.00E+13	0	56910
4. CH4+H=CH3+H2	2.02E+04	3	8750
5. CH4+OH=CH3+H2O	1.90E+05	2.4	2110
6. CH4+O=CH3+OH	1.02E+09	1.5	8604
7. CH4+HO2=CH3+H2O2	1.80E+11	0	18700
8. CH4+CH2=CH3+CH3	4.30E+13	0	10030
9. CH3+CH2O=CH4+HCO	5.50E+03	2.8	5860
10. CH3+HCO=CH4+CO	1.20E+14	0	0
11. CH3+M=CH2+H+M	1.90E+16	0	91600
12. CH3+HO2=CH3O+OH	2.00E+13	0	0
13. CH3+O2=CH3O+O	2.05E+19	-1.6	29229
14. CH3+O=CH2O+H	8.40E+13	0	0
15. CH3+OH=CH2+H2O	7.50E+06	2	5000
16. CH3+H=CH2+H2	9.00E+13	0	15100
17. CH3O+M=CH2O+H+M	1.00E+14	0	25000
18. CH2OH+M=CH2O+H+M	1.00E+14	0	25000
19. CH3O+H=CH2O+H2	2.00E+13	0	0
20. CH2OH+H=CH2O+H2	3.00E+13	0	0
21. CH3O+OH=CH2O+H2O	1.00E+13	0	0
22. CH2OH+OH=CH2O+H2O	1.00E+13	0	0
23. CH3O+O=CH2O+OH	1.00E+13	0	0
24. CH2OH+O=CH2O+OH	1.00E+13	0	0
25. CH3O+O2=CH2O+HO2	6.30E+10	0	2600
26. CH2OH+O2=CH2O+HO2	1.48E+13	0	1500
27. CH2+HCO=CH3+CO	2.00E+13	0	0
28. CH2+H=CH+H2	1.00E+17	-1.2	0
29. CH2+OH=CH+H2O	1.13E+07	2	3000
30. CH2+OH=CH2O+H	3.00E+13	0	0
31. CH+O2=HCO+O	3.30E+13	0	0
32. CH+O=CO+H	1.00E+13	0.3	0
33. CH+OH=HCO+H	5.00E+13	0	0
34. CH+CO2=HCO+CO	3.40E+12	0	690

35. CH+H=C+H2	1.50E+14	0	0
36. CH+H2O=CH2O+H	5.70E+12	0	-755
37. CH+CH2O=CH2CO+H	9.46E+13	0	-515
38. CH+C2H2=C3H2+H	8.40E+13	0	0
39. CH+CH2=C2H2+H	4.00E+13	0	0
40. CH+CH3=C2H3+H	3.00E+13	0	0
41. CH+CH4=C2H4+H	6.00E+13	0	0
42. C+O2=CO+O	2.00E+13	0	0
43. C+OH=CO+H	5.00E+13	0	0
44. C+CH3=C2H2+H	5.00E+13	0	0
45. C+CH2=C2H+H	5.00E+13	0	0
46. CH2+CO2=CH2O+CO	1.10E+11	0	1000
47. CH2+O=CO+2H	1.70E+13	0.2	0
48. CH2+O=CO+H2	9.00E+12	0.2	0
49. CH2+O2=CO2+2H	1.60E+12	0	1000
50. CH2+O2=CH2O+O	5.00E+13	0	9000
51. CH2+O2=CO2+H2	6.90E+11	0	500
52. CH2+O2=CO+H2O	1.90E+10	0	-1000
53. CH2+O2=CO+OH+H	8.60E+10	0	-500
54. CH2+O2=HCO+OH	4.30E+10	0	-500
55. CH2O+M=CO+H2+M	8.30E+15	0	69550
56. CH2O+O=CO2+2H	3.50E+05	2.4	1360
57. CH2O+OH=HCO+H2O	3.43E+09	1.2	-447
58. CH2O+H=HCO+H2	2.19E+08	1.8	3000
59. CH2O+M=HCO+H+M	1.00E+16	0	80270
60. CH2O+O=HCO+OH	1.70E+16	2.3	3080
61. HCO+OH=H2O+CO	1.00E+14	0	0
62. HCO+H=CO+H2	1.19E+13	0.3	0
63. HCO+O=CO+OH	3.00E+13	0	0
64. HCO+O=CO2+H	3.00E+13	0	0
65. HCO+O2=HO2+CO	3.30E+13	-0.4	0
66. CO+O+M=CO2+M	6.17E+14	0	3000
67. CO+OH=CO2+H	1.51E+07	1.3	-758
68. CO+O2=CO2+O	2.50E+12	0	47700
69. HO2+CO=CO2+OH	5.80E+13	0	22934
70. C2H6+CH3=C2H5+CH4	5.50E-01	4	8300
71. C2H6+H=C2H5+H2	5.40E+02	3.5	5210
72. C2H6+O=C2H5+OH	1.20E+12	0.6	7310
73. C2H6+OH=C2H5+H2O	8.70E+09	1	1810
74. C2H4+OH=CH2O+CH3	5.60E+12	0	1500

75. $\text{C}_2\text{H}_4 + \text{CH}_3 = \text{C}_2\text{H}_3 + \text{CH}_4$	6.60E+00	3.7	9500
76. $\text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_3 + \text{H}_2$	1.30E+06	2.5	12240
77. $\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	9.00E+13	0	6860
78. $\text{CH}_2 + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{H}$	4.20E+13	0	0
79. $\text{C}_2\text{H}_5 + \text{M} = \text{C}_2\text{H}_4 + \text{H} + \text{M}$	1.00E+17	0	31000
80. $\text{C}_2\text{H}_5 + \text{H} = 2\text{CH}_3$	2.30E+12	0.5	0
81. $\text{C}_2\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_4 + \text{HO}_2$	8.43E+11	0	3875
82. $\text{C}_2\text{H}_2 + \text{O} = \text{CH}_2 + \text{CO}$	1.70E+08	1.6	2210
83. $\text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H}$	2.50E+08	1.6	2210
84. $\text{H}_2 + \text{C}_2\text{H} = \text{C}_2\text{H}_2 + \text{H}$	4.09E+05	2.4	864
85. $\text{C}_2\text{H}_3 + \text{M} = \text{C}_2\text{H}_2 + \text{H} + \text{M}$	8.00E+14	0	31550
86. $\text{C}_2\text{H}_3 + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$	4.00E+13	0	0
87. $\text{C}_2\text{H}_3 + \text{O} = \text{CH}_2\text{CO} + \text{H}$	3.30E+13	0	0
88. $\text{C}_2\text{H}_3 + \text{O}_2 = \text{C}_2\text{H}_2 + \text{HO}_2$	4.00E+12	0	-250
89. $\text{C}_2\text{H}_3 + \text{OH} = \text{C}_2\text{H}_2 + \text{H}_2\text{O}$	5.00E+12	0	0
90. $\text{OH} + \text{C}_2\text{H}_2 = \text{C}_2\text{H} + \text{H}_2\text{O}$	3.37E+07	2	14000
91. $\text{OH} + \text{C}_2\text{H}_2 = \text{CH}_2\text{CO} + \text{H}$	2.18E-04	4.5	-1000
92. $\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$	1.13E+13	0	3428
93. $\text{CH}_2\text{CO} + \text{H} = \text{HCCO} + \text{H}_2$	5.00E+13	0	8000
94. $\text{CH}_2\text{CO} + \text{O} = \text{HCCO} + \text{OH}$	1.00E+13	0	8000
95. $\text{CH}_2\text{CO} + \text{O} = \text{CH}_2\text{O} + \text{CO}$	1.50E+12	0	1350
96. $\text{CH}_2\text{CO} + \text{OH} = \text{HCCO} + \text{H}_2\text{O}$	7.50E+12	0	3000
97. $\text{CH}_2\text{CO} + \text{M} = \text{CH}_2 + \text{CO} + \text{M}$	1.50E+15	0	57600
98. $\text{C}_2\text{H} + \text{O}_2 = \text{CO} + \text{HCO}$	5.00E+13	0	1500
99. $\text{C}_2\text{H} + \text{C}_2\text{H}_2 = \text{C}_4\text{H}_2 + \text{H}$	4.00E+13	0	0
100. $\text{O} + \text{HCCO} = \text{H} + 2\text{CO}$	1.00E+14	0	0
101. $\text{HCCO} + \text{O}_2 = 2\text{CO} + \text{OH}$	1.60E+12	0	854
102. $\text{CH} + \text{HCCO} = \text{C}_2\text{H}_2 + \text{CO}$	5.00E+13	0	0
103. $2\text{HCCO} = \text{C}_2\text{H}_2 + 2\text{CO}$	1.00E+13	0	0
104. $\text{C}_2\text{H} + \text{O} = \text{CH} + \text{CO}$	5.00E+13	0	0
105. $\text{C}_2\text{H} + \text{OH} = \text{HCCO} + \text{H}$	2.00E+13	0	0
106. $2\text{CH}_2 = \text{C}_2\text{H}_2 + 2\text{H}$	1.00E+12	0.6	0
107. $\text{CH}_2 + \text{HCCO} = \text{C}_2\text{H}_3 + \text{CO}$	3.00E+13	0	0
108. $\text{C}_4\text{H}_2 + \text{OH} = \text{C}_3\text{H}_2 + \text{HCO}$	3.00E+13	0	0
109. $\text{C}_3\text{H}_2 + \text{O}_2 = \text{HCO} + \text{HCCO}$	1.00E+13	0	0
110. $\text{C}_4\text{H}_2 + \text{O} = \text{C}_3\text{H}_2 + \text{CO}$	2.70E+13	0	1700
111. $\text{C}_2\text{H}_2 + \text{M} = \text{C}_2\text{H} + \text{H} + \text{M}$	4.20E+16	0	107000
112. $\text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_2 + \text{H}_2 + \text{M}$	1.50E+15	0	55440
113. $\text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_3 + \text{H} + \text{M}$	1.40E+16	0	81280
114. $\text{H}_2 + \text{O}_2 = 2\text{OH}$	1.70E+13	0	47780

115. $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$	6.40E+06	2	2961
116. $\text{O} + \text{OH} = \text{O}_2 + \text{H}$	4.50E+14	-0.5	600
117. $\text{O} + \text{H}_2 = \text{OH} + \text{H}$	5.06E+04	2.7	6290
118. $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	7.00E+17	-0.8	0
H2O Enhanced by 18.6			
CO2 Enhanced by 4.2			
H2 Enhanced by 2.86			
CO Enhanced by 2.11			
N2 Enhanced by 1.26			
119. $\text{H} + \text{HO}_2 = 2\text{OH}$	2.50E+14	0	1900
120. $\text{O} + \text{HO}_2 = \text{OH} + \text{O}_2$	4.80E+13	0	1000
121. $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$	5.00E+13	0	1000
122. $2\text{OH} = \text{O} + \text{H}_2\text{O}$	2.10E+08	1.4	-400
123. $2\text{H} + \text{M} = \text{H}_2 + \text{M}$	1.00E+18	-1	0
H2 Enhanced by 0			
H2O Enhanced by 0			
CO2 Enhanced by 0			
124. $2\text{H} + \text{H}_2 = 2\text{H}_2$	9.20E+16	-0.6	0
125. $2\text{H} + \text{H}_2\text{O} = \text{H}_2 + \text{H}_2\text{O}$	6.00E+19	-1.3	0
126. $2\text{H} + \text{CO}_2 = \text{H}_2 + \text{CO}_2$	5.49E+20	-2	0
127. $\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	7.50E+23	-2.6	0
H2O Enhanced by 5			
128. $2\text{O} + \text{M} = \text{O}_2 + \text{M}$	1.89E+13	0	-1788
129. $\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$	2.50E+13	0	700
130. $2\text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$	2.00E+12	0	0
131. $\text{H}_2\text{O}_2 + \text{M} = 2\text{OH} + \text{M}$	1.20E+17	0	45500
132. $\text{H}_2\text{O}_2 + \text{H} = \text{HO}_2 + \text{H}_2$	1.70E+12	0	3750
133. $\text{H}_2\text{O}_2 + \text{O} = \text{HO}_2 + \text{OH}$	9.60E+06	2	3974
134. $\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$	1.00E+13	0	1800
135. $\text{CH} + \text{N}_2 = \text{HCN} + \text{N}$	3.00E+11	0	13600
136. $\text{CN} + \text{N} = \text{C} + \text{N}_2$	1.90E+15	-0.6	0
137. $\text{CH}_2 + \text{N}_2 = \text{HCN} + \text{NH}$	1.00E+13	0	74000
138. $\text{H}_2\text{CN} + \text{M} = \text{HCN} + \text{H} + \text{M}$	3.00E+14	0	22000
139. $\text{C} + \text{NO} = \text{CN} + \text{O}$	3.70E+13	0	0
140. $\text{CH} + \text{NO} = \text{HCN} + \text{O}$	1.10E+14	0	0
141. $\text{CH}_2 + \text{NO} = \text{HCNO} + \text{H}$	1.39E+12	0	-1100
142. $\text{CH}_3 + \text{NO} = \text{HCN} + \text{H}_2\text{O}$	5.30E+11	0	15000
143. $\text{CH}_3 + \text{NO} = \text{H}_2\text{CN} + \text{OH}$	5.30E+11	0	15000
144. $\text{HCCO} + \text{NO} = \text{HCNO} + \text{CO}$	2.00E+13	0	0
145. $\text{HCNO} + \text{H} = \text{HCN} + \text{OH}$	1.00E+14	0	12000

146. HNCO+O=NCO+OH	2.00E+06	2.1	11415
147. HNCO+OH=NCO+H2O	6.40E+05	2	2560
148. CH2+N=HCN+H	5.00E+13	0	0
149. CH+N=CN+H	1.30E+13	0	0
150. CO2+N=NO+CO	1.90E+11	0	3400
151. HCCO+N=HCN+CO	5.00E+13	0	0
152. CH3+N=H2CN+H	3.00E+13	0	0
153. C2H3+N=HCN+CH2	2.00E+13	0	0
154. HCN+OH=CN+H2O	1.45E+13	0	10929
155. OH+HCN=HOCN+H	5.85E+04	2.4	12500
156. OH+HCN=HNCO+H	1.98E-03	4	1000
157. OH+HCN=NH2+CO	7.83E-03	4	4000
158. HOCN+H=HNCO+H	1.00E+13	0	0
159. HCN+O=NCO+H	1.38E+04	2.6	4980
160. HCN+O=NH+CO	3.45E+03	2.6	4980
161. HCN+O=CN+OH	2.70E+09	1.6	29200
162. CN+H2=HCN+H	2.95E+05	2.5	2237
163. CN+O=CO+N	1.80E+13	0	0
164. CN+O2=NCO+O	7.50E+12	0	-389
165. CN+OH=NCO+H	6.00E+13	0	0
166. HO2+NO=NO2+OH	2.11E+12	0	-479
167. NO2+H=NO+OH	3.50E+14	0	1500
168. NO2+O=NO+O2	1.00E+13	0	600
169. NO2+M=NO+O+M	7.30E+14	0	53000
170. NCO+H=NH+CO	5.00E+13	0	0
171. NCO+O=NO+CO	4.70E+13	0	0
172. NCO+N=N2+CO	2.00E+13	0	0
173. NCO+OH=NO+CO+H	1.00E+13	0	0
174. NCO+M=N+CO+M	3.10E+16	-0.5	47700
175. NCO+NO=N2O+CO	6.20E+17	-1.7	763
176. NCO+H2=HNCO+H	7.60E+02	3	4000
177. HNCO+H=NH2+CO	2.20E+07	1.7	3800
178. NH+O2=HNO+O	1.00E+13	0	12000
179. NH+O2=NO+OH	1.00E+10	-0.2	4800
180. NH+O=NO+H	7.00E+10	0	0
181. NH+NO=N2O+H	2.90E+14	-0.4	0
182. N2O+OH=N2+HO2	2.00E+12	0	40000
183. N2O+H=N2+OH	3.30E+10	0	4729
184. N2O+M=N2+O+M	4.00E+14	0	56100
185. N2O+O=N2+O2	1.40E+12	0	10800

186. $\text{N}_2\text{O} + \text{O} = 2\text{NO}$	2.90E+13	0	23150
187. $\text{NH} + \text{OH} = \text{HNO} + \text{H}$	2.00E+13	0	0
188. $\text{NH} + \text{OH} = \text{N} + \text{H}_2\text{O}$	5.00E+11	0.5	2000
189. $\text{NH} + \text{H} = \text{N} + \text{H}_2$	1.00E+14	0	0
190. $\text{NH}_2 + \text{O} = \text{HNO} + \text{H}$	7.90E+14	-0.5	0
191. $\text{NH}_2 + \text{O} = \text{NH} + \text{OH}$	7.00E+12	0	0
192. $\text{NH}_2 + \text{OH} = \text{NH} + \text{H}_2\text{O}$	4.00E+06	2	1000
193. $\text{NH}_2 + \text{H} = \text{NH} + \text{H}_2$	6.92E+13	0	3650
194. $\text{NH}_2 + \text{NO} = \text{NNH} + \text{OH}$	1.39E+09	0	0
195. $\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$	2.04E+06	2	566
196. $\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$	6.36E+02	2.4	10171
197. $\text{NH}_3 + \text{M} = \text{NH}_2 + \text{H} + \text{M}$	1.40E+16	0	90600
198. $\text{NNH} = \text{N}_2 + \text{H}$	1.00E+04	0	0
199. $\text{NNH} + \text{NO} = \text{N}_2 + \text{HNO}$	5.00E+13	0	0
200. $\text{NNH} + \text{H} = \text{N}_2 + \text{H}_2$	1.00E+14	0	0
201. $\text{NNH} + \text{OH} = \text{N}_2 + \text{H}_2\text{O}$	5.00E+13	0	0
202. $\text{NNH} + \text{O} = \text{N}_2\text{O} + \text{H}$	1.00E+14	0	0
203. $\text{HNO} + \text{M} = \text{H} + \text{NO} + \text{M}$	1.50E+16	0	48680
H2O Enhanced by 10			
O2 Enhanced by 2			
N2 Enhanced by 2			
H2 Enhanced by 2			
204. $\text{HNO} + \text{OH} = \text{NO} + \text{H}_2\text{O}$	3.60E+13	0	0
205. $\text{HNO} + \text{H} = \text{H}_2 + \text{NO}$	5.00E+12	0	0
206. $\text{N} + \text{NO} = \text{N}_2 + \text{O}$	3.27E+12	0.3	0
207. $\text{N} + \text{O}_2 = \text{NO} + \text{O}$	6.40E+09	1	6280
208. $\text{N} + \text{OH} = \text{NO} + \text{H}$	3.80E+13	0	0
209. $\text{NO} + \text{NH}_2 = \text{N}_2\text{O} + \text{H}_2$	5.00E+13	0	24640
210. $\text{NO} + \text{N}_2\text{H}_2 = \text{N}_2\text{O} + \text{NH}_2$	3.00E+12	0	0
211. $\text{NO}_2 + \text{NH}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$	1.90E+20	-3	0
212. $\text{HNO} + \text{NO} = \text{N}_2\text{O} + \text{OH}$	2.00E+12	0	26000
213. $\text{HNO} + \text{HNO} = \text{N}_2\text{O} + \text{H}_2\text{O}$	4.00E+12	0	5000
214. $\text{N}_2\text{O} + \text{CO} = \text{N}_2 + \text{CO}_2$	5.00E+13	0	44000
215. $\text{HCCO} + \text{OH} = \text{HCO} + \text{CO} + \text{H}$	1.00E+13	0	0
216. $\text{HCO} + \text{M} = \text{CO} + \text{H} + \text{M}$	2.50E+14	0	16802
217. $\text{NH}_3 + \text{O} = \text{NH}_2 + \text{OH}$	2.10E+13	0	9000
218. $\text{NO} + \text{NH}_2 = \text{N}_2 + \text{H}_2\text{O}$	2.00E+20	-2.6	925
219. $\text{NCO} + \text{O}_2 = \text{NO} + \text{CO}_2$	2.00E+12	0	20000
220. $\text{NH} + \text{OH} = \text{NO} + \text{H}_2$	2.00E+13	0	0
221. $\text{NH} + \text{NO} = \text{N}_2 + \text{OH}$	1.20E+15	-0.8	0

222. $\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	4.70E+18	-1	0
223. $\text{HNCO} + \text{M} = \text{NH} + \text{CO} + \text{M}$	1.10E+16	0	86000
224. $\text{HNCO} + \text{O} = \text{NH} + \text{CO}_2$	9.60E+07	1.4	8520
225. $\text{HNCO} + \text{O} = \text{HNO} + \text{CO}$	1.50E+08	1.6	44012
226. $\text{HNCO} + \text{HO}_2 = \text{NCO} + \text{H}_2\text{O}_2$	3.00E+11	0	29000
227. $\text{HNCO} + \text{O}_2 = \text{HNO} + \text{CO}_2$	1.00E+12	0	35000
228. $\text{HNCO} + \text{NH}_2 = \text{NCO} + \text{NH}_3$	5.00E+12	0	6200
229. $\text{HNCO} + \text{NH} = \text{NCO} + \text{NH}_2$	3.00E+13	0	23700
230. $\text{NCO} + \text{OH} = \text{HCO} + \text{NO}$	5.00E+12	0	15000
231. $\text{NCO} + \text{HCO} = \text{HNCO} + \text{CO}$	3.60E+13	0	0
232. $\text{NCO} + \text{NO}_2 = \text{CO} + 2\text{NO}$	1.30E+13	0	0
233. $\text{NCO} + \text{NO}_2 = \text{CO}_2 + \text{N}_2\text{O}$	5.40E+12	0	0
234. $\text{NCO} + \text{HNO} = \text{HNCO} + \text{NO}$	1.80E+13	0	0
235. $\text{NCO} + \text{HONO} = \text{HNCO} + \text{NO}_2$	3.60E+12	0	0
236. $\text{NCO} + \text{NCO} = 2\text{CO} + \text{N}_2$	1.80E+13	0	0
237. $\text{NO}_2 + \text{NO}_2 = \text{NO} + \text{NO} + \text{O}_2$	1.60E+12	0	26123
238. $\text{NO}_2 + \text{CO} = \text{CO}_2 + \text{NO}$	9.00E+13	0	33800
239. $\text{NO}_2 + \text{HCO} = \text{CO} + \text{HONO}$	2.10E+00	3.3	2350
240. $\text{NO}_2 + \text{HCO} = \text{H} + \text{CO}_2 + \text{NO}$	8.40E+15	-0.8	1930
241. $\text{HONO} + \text{H} = \text{NO}_2 + \text{H}_2$	1.20E+13	0	7350
242. $\text{HONO} + \text{O} = \text{NO}_2 + \text{OH}$	1.20E+13	0	6000
243. $\text{HONO} + \text{OH} = \text{NO}_2 + \text{H}_2\text{O}$	1.30E+10	1	135

NOTE: A units mole-cm-sec-K, E units cal/mole

Figures 4 through 6 compare the exit concentrations of NO, HCN and NH₃ at various reburning stoichiometric ratios for one reburn fuel composition, namely methane: 90% and acetylene: 10%. The impact is not significant. The highest NO_x reduction occurs at SR2=0.9.

Hereafter this updated reaction mechanism (Table 1) will be employed in the subsequent modeling studies.

4. NO Reburning with CH₄/NH₃

Computer modeling was carried on NO reburning with a combination of methane and ammonia during the month of June, the results of which are displayed in Figures 7 through 10. The updated reaction scheme was employed to run the CKINTERP program. Using the binary file created by executing the above program and the input SR2 conditions, the CHEMKIN package predicts the exit concentrations of various species involved in NO reburning. As in the case of methane/acetylene, the legends in Figures 7 through 10 describe the reburn fuel composition between methane and ammonia. A typical CH₄/NH₃: 96/4 combination at SR2=0.9 would represent the initial concentrations of the flue gas as 2.11% CH₄, 0.0877% NH₃, 16.45% CO₂, 1.89% O₂, 1000 ppm NO and 79.366% N₂/He. The program is run for varying SR2 conditions for a fixed reburn composition and the entire process is repeated for various reburn fuel compositions. Unlike in the case of CH₄/C₂H₂, NO reburning with CH₄/NH₃ resulted in some N₂O formation. Figures 7 through 10 depict the exit concentrations of significant nitrogen containing species, namely NO, HCN, NH₃, N₂O for SR2 range of 0.7 to 1.05 and for various combinations of methane/ammonia. The

Figure 4. Comparison of the influence of the updated reaction mechanism over the previous reaction scheme on NO exit concentration in NO reburning with methane/ acetylene as reburn fuel (90/10 composition)

Figure 5. Comparison of the influence of the updated reaction mechanism over the previous reaction scheme on HCN exit concentration in NO reburning with methane/ acetylene as reburn fuel (90/10 composition)

Figure 6. Comparison of the influence of the updated reaction mechanism over the previous reaction scheme on NH₃ exit concentration in NO reburning with methane/ acetylene as reburn fuel (90/10 composition)

Figure 7. Effect of the composition of methane/ ammonia on NO exit concentration in NO reburning (Input NO Concentration: 1000 ppm; Reactor Temperature: 1373 K; Residence Time: 0.2 s)

Figure 8. Effect of the composition of methane/ ammonia on HCN exit concentration in NO reburning (Input NO Concentration: 1000 ppm; Reactor Temperature: 1373 K; Residence Time: 0.2 s)

Figure 9. Effect of the composition of methane/ ammonia on NH_3 exit concentration in NO reburning (Input NO Concentration: 1000 ppm; Reactor Temperature: 1373 K; Residence Time: 0.2 s)

Figure 10. Effect of the composition of methane/ ammonia on N_2O exit concentration in NO reburning (Input NO Concentration: 1000 ppm; Reactor Temperature: 1373 K; Residence Time: 0.2 s)

residence time is 0.2 s and the reactor temperature is 1373 K for these runs.

From Fig. 7, it can be observed that the NO concentration has decreased considerably for 96/4 composition of CH_4/NH_3 . This result looks very promising. The NO exit concentration for 100% methane reburning ranges 46-250 ppm while the composition with 4% ammonia brings the concentration to 6-25 ppm. This can be a very significant reduction strategy.

Figure 8 shows that the HCN concentration drops considerably from 690-830 ppm range to 340-570 ppm range for SR2 values 0.7 to 0.9 with the introduction of 4% ammonia as reburn fuel. As mentioned before, HCN is highly unstable at high temperatures and its recovery is reported to be 30% at 1100 C for a residence time of 1 s (Song et al, 1982). From Fig. 9, we can observe an increase in ammonia concentration for the above SR2 range; the NH_3 concentration at SR2=0.9 is 157 ppm for CH_4/NH_3 : 96/4 while it is 39 ppm for 100% CH_4 reburning. This level of exiting ammonia can be easily handled in the burnout zone where $\text{NH}_3 + \text{O}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$. There is very little increase of N_2O at SR2=0.9 due to addition of ammonia in the reburn fuel, as seen in Fig. 10.

5. Conclusions

On the whole for 96% methane and 4% ammonia, the best operating point will be SR2=0.9. Comparing its effect with 100% methane as reburn fuel, the NO concentration reduced from 46 ppm to 6 ppm out of the initially fed 1000 ppm. While HCN concentration reduced from 830 ppm to 570 ppm, ammonia concentration increased from 40 ppm to 160 ppm. This trend could be due to trace amounts of unreacted ammonia slippage through the

reburning zone. Also, the reduction seen in HCN could have reflected on ammonia increase through the series reaction $\text{NO} \rightarrow \text{HCN} \rightarrow \text{NH}_3$. The increase in N_2O is negligible (0.24 ppm to 1.33 ppm) and is well within the state and federal limits.

On the whole for 90% methane and 10% acetylene the best operating point will be $\text{SR}_2=0.9$ as well. Comparing with the results of 100% methane reburning, the NO concentration has decreased from 46 ppm to 7 ppm from the initially fed 1000 ppm; the HCN concentration increased slightly from 833 ppm to 864 ppm and the NH_3 increased from 33 ppm to 47 ppm. Considering the high instability at high temperatures and the burnout zone reactions the HCN could be easily handled. Likewise, ammonia will be converted to nitrogen and water in the burnout zone and hence would not be a problem. The N_2O level is practically insignificant for both cases, either 100 % methane or 90% methane/ 10% acetylene.

The above observations would point to the fact that the presence of ammonia almost brings $\text{NO} \rightarrow \text{HCN}$ to completion and at the same time greatly favors $\text{HCN} \rightarrow \text{NH}_3$. That is why we see a little more ammonia formation and less HCN concentration. The presence of 10% acetylene greatly favors the completion of $\text{NO} \rightarrow \text{HCN}$ but favors the $\text{HCN} \rightarrow \text{NH}_3$ very little. That is why we observe increased HCN concentration and insignificant increase in ammonia concentration.

The above findings will be verified when the experimental facility is ready and reburning experiments are conducted.

6. References

1. Song et al., Comb. Sci. And Tech., 28: 731 (1982).
2. Glarborg, P., Kristensen, P.G., Jensen, S.H. and Johansen, K.D., *Combustion and Flame*, 98:241-258 (1994).
3. Miller, J.A. and Bowman, C.T., *Int. J. Chem. Kinetics*, 23: 289 (1991).
4. Miller, J.A. and Melius, C.F., *Int. J. Chem. Kinetics*, 24:421 (1992).
5. Tsang, W., *Phys. Chem. Ref. Data*, 21:753 (1992).
6. Tsang, W., and Herron, *Phys. Chem. Ref. Data*, 20:609 (1991).
7. Davidson, D.F., DiRosa, M.D., Chang, A.Y. and Hanson, R.K., *Eighteenth International Symposium on Shock Waves*, Springer Verlag, Vol. 2, p. 813 (1991).
8. East, A.L.L. and Allen, W.D., *J. Chem. Phys.*, 99:4638 (1993).
9. Lindstedt, R.P., Lockwood, F.C. and Selim, M.A., *Combust. Sci. And Tech.*, 99:253-276 (1994).