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**SIMULATION OF COAL AND CHAR NITROGEN
REACTIONS IN COMBUSTION**

Prepared for the

**U.S. Department of Energy
Office of Fossil Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236**

**Work Performed Under Contract No. DE-FG22-92MT92022
September 1992- August 1993**

**Rust College
Holly Springs, MS 38635**

October 1993

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LIST OF SYMBOLS

b	radius of the outer edge of boundary layer
C	total gas concentration
C_c	heat capacity of coal per unit mass
D_g	molecular diffusivity
d_c	particle diameter during burn out
ΔH_1	heat of combustion
k_1	carbon combustion rate $[=k_{10}T_c \exp(-E_1'/T_c)]$
k_g	thermal conductivity of gas
M_c	molecular weight of carbon
T_b	bed temperature
T_c	coal temperature during burn out
x_{3d}	mole fraction of oxygen in the gas phase
x_{3s}	mole fraction of oxygen at the coal (or char) surface
γ_c	mass fraction of carbon in coal (or char)
ϵ	particle emissivity
ρ_c	density of coal (or char)
σ	Stefan-Boltzman radiation constant

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Simulation of Coal and Char Nitrogen Reactions in Combustion

1.0 INTRODUCTION

Coal is a major contributor of the fossil fuel energy reserves. Though coal is surplus in availability and attractive in price, its combustion involves the production of pollutants. Therefore the utility of coal suffers a serious setback. One type of coal pollutant from coal combustion is NO_x (NO , NO_2 , N_2O), which is toxic and ozone depleting. High fuel nitrogen to NO_x conversion efficiency (40-60%), coupled with growing stringent regulations calls for advanced technologies.

The observed rate of increase of N_2O (0.18% to 0.26% annually) is a matter of increasing concern both because N_2O is a greenhouse gas and has a major and unfavorable influence on the ozone layer (Weiss, 1981). The combustion contribution to the overall nitrous oxide budget is difficult to assess; yet the emission of N_2O from fluidized bed combustion (FBC) has been identified in the past few years as significant (Amand and Anderson, 1989). It was concluded in the European workshop, 1988 that the emission level from a coal-fired fluidized bed boiler is 50-200 ppm but it is only 1-20 ppm in boilers equipped with other types of combustion devices (EPA, 1988). For this reason it is worthwhile to investigate the emissions from FBC more thoroughly. There is little knowledge on methods for controlling the nitrous oxide emissions at the current time.

Several studies, both experimental and analytical, have clarified some of the important aspects of formation and destruction of nitrous oxide in combustion of

gaseous fuels (Miller and Bowman, 1989), but the N_2O emissions under fluidized bed conditions is poorly understood. In fluidized bed combustion, N_2O can arise from homogeneous gas phase reactions involving amines and cyano species (Hiltunen et al, 1991) or it can be formed from heterogeneous reactions (eg. char oxidation). Removal of N_2O can be brought about by gas phase reactions or by catalytic or non-catalytic heterogeneous reduction on char/limestone.

This work was carried out with an objective of enhancing the fundamental understanding of coal and char nitrogen reaction pathways in fluidized bed combustion environment. The formation and destruction of HCN and N_2O under variety of influential parameters were investigated. This simulation contained a non-isothermal single particle combustion in a preheated reactor and a gas phase reaction zone with a plug flow reactor which are designed to stimulate the nitrogen chemistry in a circulating fluidized bed. The LSODE differential equation solver was used for single particle combustion and the CHEMKIN package, developed by Sandia National Laboratories, was applied for gas phase reactions. This computational work was done as an exploratory research program under the solicitation of the DOE fossil energy utilization.

2.0 BACKGROUND SURVEY AND RELEVANCE

The objective of this research is to enhance the fundamental understanding of coal and char nitrogen reaction pathways in combustion environments. The formation of HCN and its subsequent reaction paths to NO_x and N_2O in the fluidized bed combustion are the focal points of this study. The incentive of this research is promoted by recent developments in two major areas.

Recent literature has indicated that delayed evolution of HCN from coal and char could contribute to high emission of N_2O under relatively low temperature and short residence time conditions (Kramlich, et al., 1989). N_2O has been gaining increasing attention due to its role in the green house effect and ozone depletion (Tirpak, 1987; Hao, 1986). Recent research of this problem has resulted in several workshops in the United States (Lanier and Robinson, 1986; Kramlich, et al., 1988a) as well as in the Europe (1988, 1990). Fluidized bed combustion has been identified as a principal source of N_2O emissions (Amand and Andersson, 1989; Hiltunen et al., 1991). While the fluidized bed data reported by Amand and Andersson are qualitatively consistent with the N_2O formation mechanism proposed by Kramlich, et al. (1989), time resolved HCN evolution rate under various conditions becomes a missing link between these two findings. Specifically, the effects of solid fuel particle size, temperature history, fuel properties, and reacting gas composition have significant effects in the formation and destruction of HCN and N_2O .

The delayed evolution of HCN during char combustion plays an important role in the burnout stage of the reburning process. The char nitrogen chemistry in the

burnout stage is critical to the future development of NO_x reburning with coal. Literature has showed that NO_x emission in the burnout stage could be governed by temperature, residence time, fuel properties, stoichiometric ratio, and gas composition. Both homogeneous and heterogeneous phase reactions are involved, and either can be rate limiting.

The fate of fuel nitrogen during combustion has been the subject of a number of studies. Massachusetts Institute of Technology (Song, et al., 1982a) reported the effects of fuel/oxidant stoichiometry on the distribution of nitrogen species at two temperature levels: 1250 and 1750 K. Molecular nitrogen and NO_x were found to be the major products. Though HCN is a major product (6-8%) in the initial stage of the combustion, it undergoes fast decomposition to molecular nitrogen above 1250 K. Since pulverized coal combustion usually operates above this temperature, the MIT researchers did not concern the delayed HCN formation under 1250 K. In a subsequent paper, Song et al. (1982b) reported that evolutions of carbon and nitrogen from solid fuels have the same rate during lean combustion between 1250 and 1750 K.

The HCN reactivity in a flat flame burner was also observed at Rockwell International (Axworthy, et al., 1986). They reported that 65% of the doped HCN survived the luminous flame zone ($\phi=0.8$) which had a temperature in the range 1976- 2080 K and residence time about 0.5 ms. It, however, decomposes rapidly above the luminous zone. The decomposition rate also depends on the fuel/oxidant equivalence ratio. Both MIT and Rockwell's data indicated that HCN decomposition

is kinetically controlled in the flame condition, and the rate can be enhanced by high temperature, long residence time, and high stoichiometric ratio.

Energy and Environmental Research Corporation (S.L. Chen, et al., 1982a, 1982b; Kramlich, et al., 1988b) reported that the distribution of nitrogen products (HCN, NH_3 , and NO_x) strongly depend on the fuel type, particle size (even in the 40 to 80 μm range), and stoichiometric ratio. For all four of the bituminous coals, HCN yields exceeded NH_3 at all stoichiometries tested. However, the HCN/ NH_3 ratio decreases with decreasing rank. The authors claimed that it was due to the increased nitrogen bonding in the structure of the higher rank coals. This implies that nitrogen species may evolve at different time (or temperature) when a coal particle is suddenly brought into a hot zone. They also reported simulated yields of nitrogenous species derived from combustion of pulverized coal particle with a time varying temperature from 300 K in an environment at 1750 K. Similar to the work at MIT, their data were collected for fine particles at relatively high temperatures, and can be used to interpret pulverized coal combustion only. The nitrogen chemistry during combustion of large fuel particles at relatively low temperatures (such as those used in fluidized bed combustion) has not been the focal point of these studies.

The correlation between the delayed HCN evolution and N_2O formation is such a new subject that even the most recent fluidized bed combustion works contain little information on HCN or N_2O yield data. Some fluidized bed combustion work deal NO formation and destruction, with a few exceptions which include the

experimental or mathematical analysis of NH_3 . Examples of these research include those at MIT (Sarofim and Beer, 1979; Beer, et al., 1981), at Pyropower Corporation (Lee and Hiltunen, 1989; Lee and Hyppanen, 1989), at Babcock and Wilcox Company (Duqum, et al., 1989), at Tennessee Valley Authority (Manaker and Bass, 1989), and at the Technical University of Denmark (Johnsson, 1989; Hulgaard, 1991). However, in the past, a detailed fluidized bed combustion model of large carbon was developed at the University of Houston (Bukur and Amundson, 1981, 1982); general design principles of fluidized bed coal combustion were reviewed by LaNauze (1986) and some guidelines were provided for the fabrication of a model by Wen (1979). These efforts have provided at least the useful building blocks for the analysis of nitrogen chemistry in the fluidized bed combustion.

In order to predict the N_2O yield in the fluidized bed combustion, time resolved evolution profiles of nitrogen species are needed. Time resolved evolutions of major coal pyrolysis products (mostly hydrocarbons) under variable heating rate were conducted by Juntgen and van Heek (1968, 1969, 1970, 1979). A number of time resolved weight loss data have been conducted and they have been reviewed by Talwalkar (1983). But the nitrogen profiles in relating gas has not been studied.

The purpose of this work is to fill in the gap and develop a realistic model for the prediction of yields of nitrogen species in fluidized bed coal combustion. Upon an extensive literature study, a computation scheme was attempted as an exploratory research work by this historically black college. Detailed computation scheme is described in the following sections.

3.0 COMPUTER MODELING

This model contains two major elements: a non-isothermal single particle combustion in a preheated reactor and a gas phase reaction zone with a plug flow reactor. These elements are designed to stimulate the nitrogen chemistry in a circulating fluidized bed. Since majority of the time for this project was allotted for gas phase reactions, these reaction mechanisms and the results are discussed first. Very limited heat transfer analysis conducted on the single particle combustion is presented in Section 3.2.

3.1 Gas Phase Reactions And Findings

For the gas phase reactions, it is assumed that only homogeneous reactions occur and the gas phase reaction zone is treated as a plug flow reactor. The complex reaction pathways can be conducted based on Sandia's CHEMKIN package (Lutz, et al., 1987; Kee, et al., 1989). Initial concentrations of various species such as HCN, NH_3 and CO from the combustion of coal are assumed and the time history of various species, in particular the time history of nitrous oxide were obtained. The effect of fluidized bed temperature on these emissions was the focal issue in these gas phase reactions.

The major purpose of this work was to examine the homogeneous formation and destruction of N_2O from various nitrogen containing species under fluidized bed combustion conditions in a reactor. The nitrogen containing species, HCN and NH_3 were used since they have been found in the primary zone of a circulating fluidized

bed combustor (Amand and Leckner, 1990).

First of all, the kinetic calculations were performed with the reaction rate scheme shown in Table 1. This consisted of 53 gas phase reactions and 23 species applied to an ideal plug flow reactor. The CHEMKIN program (Kee et al, 1989) was used for the prediction of yields of nitrous oxide and other significant species. The thermodynamic properties were taken from the CHEMKIN thermodynamic data base (Kee et al, 1987).

The inlet mole fractions have been selected so as to compare our work with the trends observed by Hulgaard et al (1991). Figure 1, reproduced from their work indicates that even with over 400 ppm NO, little N_2O is seen. In order to ensure N_2O formation, 600 ppm of NO was chosen as the initial concentration for the first run. The three runs performed in this work have the following inlet mole fractions.

Run 1: 200 ppm HCN, 600 ppm NO, 10% O_2 , 5% H_2O and balance inert.

Run 2: 200 ppm HCN, 10% O_2 , 5% H_2O and balance inert.

Run 3: 200 ppm NH_3 , 10% O_2 , 5% H_2O and balance inert.

Figures 2 through 4 display the results for Run 1; Figures 5 and 6 display the results for Run 2 and Figure 7 presents the results for Run 3.

Presented in Figure 2 is the concentration of nitrous oxide versus residence time for various reaction temperatures for the case of HCN/NO oxidation (Run 1). It is apparent that HCN/NO reaction does not occur at lower temperatures such as 800 K. It is also noticeable that the reduction of NO by HCN to form N_2O is

Table 1. Elementary Reaction Scheme for the Modeling

REACTIONS	(k = A T**b exp(-E/RT))		
	A	b	E
1. CO+O+M=CO2+M	5.88E+15	0	4100
2. CO+OH=CO2+H	15000000	1.3	-770
3. CO+O2=CO2+O	2.51E+12	0	47690
4. HO2+CO=CO2+OH	5.75E+13	0	22930
5. OH+H2=H2O+H	2.2E+13	0	5150
6. H+O2=OH+O	2.3E+14	0	16800
7. O+H2=OH+H	1.8E+10	1	8890
8. H+O2+M=HO2+M	1.5E+15	0	-995
H2O Enhanced by 2.100E+01			
9. 2OH=O+H2O	6.3E+12	0	1090
10. H+HO2=2OH	2.5E+14	0	1900
11. OH+HO2=H2O+O2	5E+13	0	1000
12. O+HO2=O2+OH	4.8E+13	0	1000
13. NO+HO2=NO2+OH	3.4E+12	0	-260
14. HCN+OH=CN+H2O	1.5E+13	0	10929
15. OH+HCN=HNCO+H	4.8E+11	0	11000
16. HCN+O=NCO+H	14000	2.6	4980
17. CN+O2=NCO+O	5.6E+12	0	0
18. NO2+H=NO+OH	3.5E+14	0	1500
19. NO2+O=NO+O2	1E+13	0	600
20. NO2+M=NO+O+M	1.1E+16	0	66000
21. NCO+H=NH+CO	5E+13	0	0
22. NCO+O=NO+CO	5.6E+13	0	0
23. NCO+OH=NO+CO+H	1E+13	0	0
24. NCO+NO=N2O+CO	1E+13	0	-390
25. NCO+H2=HNCO+H	8.6E+12	0	9000
26. HNCO+H=NH2+CO	2E+13	0	3000
27. HNCO+OH=NCO+H2O	1E+11	0.5	6290
28. NH+O2=HNO+O	3E+13	0	3400
29. N2O+H=N2+OH	7.6E+13	0	15200
30. N2O+M=N2+O+M	1.6E+14	0	51600
31. N2O+O=N2+O2	1E+14	0	28200
32. N2O+O=2NO	1E+14	0	28200

33. $\text{NH}_2 + \text{O} = \text{NH} + \text{OH}$	$1.7\text{E}+13$	0	1000
34. $\text{NH}_2 + \text{OH} = \text{NH} + \text{H}_2\text{O}$	$5.5\text{E}+10$	0.7	1290
35. $\text{NH}_2 + \text{H} = \text{NH} + \text{H}_2$	$5\text{E}+11$	0.5	2000
36. $\text{NH}_2 + \text{NO} = \text{NNH} + \text{OH}$	$6.1\text{E}+19$	-2.5	1866
37. $\text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O}$	$9.1\text{E}+19$	-2.5	1866
38. $\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$	$3.3\text{E}+12$	0	2120
39. $\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$	$2.5\text{E}+13$	0	17100
40. $\text{NH}_3 + \text{O} = \text{NH}_2 + \text{OH}$	$1.5\text{E}+12$	0	6040
41. $\text{NNH} + \text{NO} = \text{N}_2 + \text{HNO}$	$9.1\text{E}+11$	0	0
42. $\text{NNH} + \text{OH} = \text{N}_2 + \text{H}_2\text{O}$	$3\text{E}+13$	0	0
43. $\text{NNH} + \text{NH}_2 = \text{N}_2 + \text{NH}_3$	$1\text{E}+13$	0	0
44. $\text{NCO} + \text{NH}_2 = \text{NH} + \text{HNCO}$	$1\text{E}+11$	0.5	5000
45. $\text{HNO} + \text{OH} = \text{NO} + \text{H}_2\text{O}$	$3.6\text{E}+13$	0	0
46. $\text{HNO} + \text{M} = \text{H} + \text{NO} + \text{M}$	$1.9\text{E}+16$	0	48680
47. $\text{HNO} + \text{NH}_2 = \text{NH}_3 + \text{NO}$	$1.8\text{E}+14$	0	1000
48. $\text{NH}_3 + \text{M} = \text{NH}_2 + \text{H} + \text{M}$	$4.8\text{E}+16$	0	93900
49. $\text{NNH} + \text{M} = \text{N}_2 + \text{H} + \text{M}$	$2\text{E}+14$	0	30000
50. $\text{O} + \text{O} + \text{M} = \text{O}_2 + \text{M}$	$1.4\text{E}+18$	-1	340
51. $\text{NH}_2 + \text{O}_2 = \text{HNO} + \text{OH}$	$5.1\text{E}+13$	0	30000
52. $\text{NH} + \text{NO} = \text{N}_2\text{O} + \text{H}$	$4.3\text{E}+10$	-0.5	0
53. $\text{NH}_2 + \text{NO} = \text{N}_2\text{O} + \text{H}_2$	$5\text{E}+10$	0	28500

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

II

Comparison of the experimental and theoretical concentrations of the major nitrogen-containing species in oxidation of HCN/NO. Residence time 52 ms at 1200 K. Inlet mole fractions: HCN = 303 ppm, NO = 441 ppm, N₂O = 3 ppm, O₂ = 2.28%, H₂O = 2.69%. The symbols represent experimental data (N₂O: $\square$, NO: Δ , HCN: $\circ$), while calculated profiles are shown as lines (N₂O: ---, NO and HCN: —).

Comparison of the experimental and theoretical concentrations of the major nitrogen-containing species in oxidation of HCN. Residence time 56 ms at 1200 K. Inlet mole fractions: HCN = 320 ppm, O₂ = 2.45%, H₂O = 3.01%. The symbols represent experimental data (N₂O: $\square$, NO: Δ , HCN: $\circ$), while calculated profiles are shown as lines (N₂O: ---, NO and HCN: —).

Comparison of the experimental and theoretical concentrations of NO and N₂O in oxidation of NH₃. Residence time 56 ms at 1200 K. Inlet mole fractions: NH₃ = 760 ppm, O₂ = 2.6%, H₂O = 1.0%. The symbols represent experimental data (N₂O: $\square$, NO: Δ), while calculated profiles are shown as lines (N₂O: ---, NO: —).

Fig. 1. Sample results taken from Hulgaard et al (1991).

Fig. 2. Concentration of N₂O in the oxidation of HCN/NO. Inlet mole fractions: 200 ppm HCN, 600 ppm NO, 10% O₂, 5% H₂O and balance inert.

favorable upto 1100-1200 K beyond which N_2O decomposes. So it is safe to say that in the narrow range of 1000-1200 K, i.e. under the fluidized bed combustion conditions, the reaction yields large amount of nitrous oxide (as high as 180 ppm at 1100 K and residence time of 0.4 s). It is worth mentioning that the temperature window for N_2O production is a sensitive function of the reaction time. At 1300 K, the production of N_2O is about 140 ppm at 0.05 s while it is only about 40 ppm at 0.5 s. The decomposition is favored at higher temperatures and higher residence times.

The observation of thermal decomposition (also seen in Figure 5 presented later on) of N_2O at long residence times (which is comparable to fluidized bed conditions) is in qualitative agreement with the observation of decreasing N_2O emission with increasing temperature in circulating FBCs (Amand and Anderson, 1989) and with the observation that increasing the temperature reduces N_2O yields (Gustavsson, 1990).

Figure 3 illustrates the effect of temperature on the concentrations of various nitrogen species, namely NH_3 , HCN , NCO , NO , NO_2 and N_2O in the oxidation of HCN/NO . It is clear that the major nitrogen containing species formed from this reaction is N_2O only. It can be seen that about 150-200 ppm of both HCN and NO are consumed in the process of N_2O formation in the like amount under fluidized bed conditions.

The dominating pathway to the formation of N_2O in the HCN oxidation is believed to involve the reaction $\text{NCO} + \text{NO} == \text{N}_2\text{O} + \text{CO}$ (R24). Hence the

Fig. 3. Effect of Temperature on the Concentrations of Various Nitrogen Containing Species in the oxidation of HCN/NO. Inlet mole fractions: 200 ppm HCN, 600 ppm NO, 10% O₂, 5% H₂O and balance inert.

presence of NO produced very high yields of N_2O than what the absence of NO yielded (see Fig. 5). The rate constants for this reaction are the same as given by Miller and Bowman (1989).

Figure 4 presents the concentrations of other significant species in the HCN/NO oxidation reaction for various reaction temperatures. Whatever HNCO radicals are formed intermediately, they would convert into NCO which upon reaction with NO produce N_2O . Since NO is present throughout the reaction there is ample opportunity for the cessation of HNCO radicals through reactions (R27) and (R24). Hence the ppm level of HNCO is lower in this case (Run 1) than for the case without NO (Run 2; compare Fig. 6).

Carbon dioxide is formed from carbon present in HCN in the already oxidizing environment. The yield is as high as 200 ppm which is expected since the initial concentration of HCN is also 200 ppm. At 1300 K, only CO_2 is present while the concentration of CO is nil. It is thus apparent that HCN oxidation is favored at high temperatures. The operation at 1300 K is safe since no CO and N_2O are formed.

Figure 5 depicts the concentration of nitrous oxide versus residence time for various reaction temperatures for the case of HCN oxidation. This is very similar to Fig. 2 except that NO is not present initially. Accordingly the N_2O yield is lower at all temperatures for HCN oxidation without the presence of NO. The reaction begins at somewhat higher temperature (1000 K onwards) than that in HCN/NO oxidation (900 K). Also, N_2O formation proceeds till 1200 K, peaking about 60 ppm. The lower levels of N_2O with HCN oxidation in the absence of NO substantiate the

Fig. 4. Concentrations of HNCO, CO₂ and CO in the oxidation of HCN/NO. Inlet mole fractions: 200 ppm HCN, 600 ppm NO, 10% O₂, 5% H₂O and balance inert. 16

Fig. 5. Concentration of N₂O in the oxidation of HCN. Inlet mole fractions: 200 ppm HCN, 10% O₂, 5% H₂O and balance inert.

fact that N_2O is formed primarily by reaction between NO and other nitrogen containing radicals such as NCO. The decomposition of N_2O at 1300 K is seen in this figure as well; irrespective of the presence of NO, the temperature dominates the reaction mechanism at 1300 K.

Presented in Figure 6 are the concentrations of significant species, namely HNCO, CO_2 and NO in the oxidation of HCN. It is apparent that there is a highly significant yield of HNCO in the FBC temperature zone (1000-1100 K). This is characterized by the absence of NO which would convert HNCO to N_2O via NCO. The reaction seems to proceed in the step $\text{HNCO} \rightarrow \text{NCO} \rightarrow \text{HNCO}$ (R27 and R25) rather than through the reaction of NCO with NO to produce N_2O (R24).

Increasing yield of CO_2 is seen due to the oxidation of carbon in the HCN radical. Similar trend of increasing concentrations of NO is expected due to the oxidizing environment aiding the decomposition of HCN. The irony is that there is not much NO at medium temperatures (10 ppm only at 1100 K) when HNCO could react via NCO to form nitrous oxide; and at higher temperatures, even though there is considerable NO (40 ppm at 1300 K), the nitrous oxide starts decomposing and HNCO radicals disappear. At 1300 K, the oxidation products (CO_2 and NO) peak as one expects. It can also be observed that there is a strong temperature dependence on the destruction of HNCO similar to the destruction of N_2O .

The results with NH_3 oxidation are presented in Figure 7. The reaction does not occur until about 1200 K. In fact the ammonia oxidation produced very much lower, rather insignificant yields of N_2O (only 0.02 ppm at 1300 K and 0.4 s). This

Fig. 6. Concentrations of HNCO, CO₂ and NO in the oxidation of HCN. Inlet mole fractions: 200 ppm HCN, 10% O₂, 5% H₂O and balance inert.

Fig. 7. Concentrations of N_2O and NO in the oxidation of NH_3 . Inlet mole fractions: 200 ppm NH_3 , 10% O_2 , 5% H_2O and balance inert.

suggests that at the temperatures prevailing in FBC, the homogeneous oxidation of NH_3 is only a minor source of N_2O . Comparison with Figure 5 indicates that HCN is more important than NH_3 as a precursor for N_2O under fluidized bed conditions. This observation is very well supported by the work done by Kilpinen et al (1991) and Hulgaard et al (1991).

The only significant yield of the ammonia oxidation is nitric oxide. A NO yield of 45 ppm is observed at 1300 K beyond the residence time of 0.2 s.

In order to include the effect of CO, a more detailed reaction mechanism was used for additional runs. This reaction mechanism which consists of 89 reactions and 35 species, is shown in Table 2. The inlet mole fractions were selected from Hulgaard et al (1991) in order to ensure realistic values for fluidized bed situation. The two runs contained HCN/NO oxidation and HCN/NO/CO oxidation with an emphasis on finding the effect of CO on nitrous oxide emissions for the temperature range of 900 K- 1300 K.

Run 4: 303 ppm HCN, 441 ppm NO, 3 ppm N_2O , 2.28% O_2 , 2.69% H_2O and balance inert.

Run 5: 298 ppm HCN, 434 ppm NO, 1618 ppm CO, 2.26% O_2 , 2.64% H_2O and balance inert.

A close look at these runs (Run 4 and Run 5) shows that except for a large initial concentration of CO in Run 5, the concentrations of all other species are almost the same. With a residence time of 51 ms, the yields are predicted for the entire temperature range (900 K - 1300 K) and are shown in Figures 8-11. It can be

Table 2. More detailed Reaction Scheme for the Modeling

REACTIONS	(k = A T**b exp(-E/RT))		
	A	b	E
CO+O+M = CO2+M	6.2E+14	0	3000
CO+OH = CO2+H	4400000	1.5	-740
CO+O2 = CO2+O	2.5E+12	0	48000
HO2+CO = CO2+OH	5.8E+13	0	23080
H2+O2 = 2OH	1.7E+13	0	48100
OH+H2 = H2O+H	1E+08	1.6	3320
O+OH = O2+H	4E+14	-0.5	0
O+H2 = OH+H	50600	2.67	6330
H+O2+M = HO2+M	6.9E+17	-0.8	0
OH+HO2 = H2O+O2	2.9E+13	0	500
H+HO2 = 2OH	1.7E+14	0	880
O+HO2 = O2+OH	3.2E+13	0	0
2OH=O+H2O	1.5E+09	1.14	100
2H+M = H2+M	1E+18	-1	0
2H+H2 = 2H2	9.2E+16	-0.6	0
2H+H2O = H2+H2O	6E+19	-1.25	0
2H+CO2 = H2+CO2	5.5E+20	-2	0
H+OH+M = H2O+M	2.2E+22	-2	0
2O+M = O2+M	1.9E+13	0	-1788
H+HO2 = H2+O2	4.3E+13	0	1420
H2CN+M = HCN+H+M	3E+14	0	22000
HCNO+H = HCN+OH	1E+14	0	12000
CO2+N = NO+CO	8.6E+11	0	2220
OH+HCN = HOCN+H	59000	2.4	12600
OH+HCN = HNCO+H	1980	4	1000
OH+HCN = NH2+CO	7800	4	4000
HOCN+H = HNCO+H	1E+13	0	0
HCN+O = NCO+H	13800	2.64	4980
HCN+O = NH+CO	3450	2.64	4980
HCN+O = CN+OH	2.7E+09	1.58	29400
CN+H2 = HCN+H	295000	2.45	2237
CN+O = CO+N	1.8E+13	0	0
CN+O2 = NCO+O	2.6E+14	-0.5	0
CN+CO2 = NCO+CO	4E+14	0	38400
CN+OH = NCO+H	6E+13	0	0
HO2+NO = NO2+OH	2.1E+12	0	-479

NO ₂ +H = NO+OH	3.5E+14	0	1500
NO ₂ +O = NO+O ₂	1E+13	0	600
NO ₂ +M = NO+O+M	1.1E+16	0	66400
NCO+H = NH+CO	5E+13	0	0
NCO+O = NO+CO	2E+13	0	0
NCO+N = N ₂ +CO	2E+13	0	0
NCO+OH = NO+CO+H	1E+13	0	0
NCO+M = N+CO+M	3.1E+16	-0.5	48000
NCO+NO = N ₂ O+CO	1E+13	0	-390
NCO+H ₂ = HNCO+H	8.6E+12	0	9000
HNCO+H = NH ₂ +CO	1.1E+14	0	12800
HNCO+O = NCO+OH	3.2E+12	0	10400
HNCO+OH = NCO+H ₂ O	2.6E+12	0	5600
NH+O ₂ = HNO+O	3.7E+13	0	18000
NH+O ₂ = NO+OH	7.6E+10	0	1530
NH+NO = N ₂ O+H	4.3E+14	-0.5	0
N ₂ O+OH = N ₂ +HO ₂	2E+12	0	10000
N ₂ O+H = N ₂ +OH	7.6E+13	0	15300
N ₂ O+M = N ₂ +O+M	1.6E+14	0	51940
N ₂ O+O = N ₂ +O ₂	1E+14	0	28400
N ₂ O+O = 2NO	1E+14	0	28400
N ₂ O+CO = CO ₂ +N ₂	2.5E+14	0	46300
NH+OH = HNO+H	2E+13	0	0
NH+OH = N+H ₂ O	5E+11	0.5	2000
NH+H = N+H ₂	3.2E+13	0	328
NH ₂ +O = HNO+H	6.6E+14	-0.5	0
NH ₂ +O = NH+OH	7E+12	0	0
NH ₂ +OH = NH+H ₂ O	4000000	2	1000
NH ₂ +H = NH+H ₂	4E+13	0	7300
NH ₂ +NO = NNH+OH	6.4E+15	-1.25	0
NH ₂ +NO = N ₂ +H ₂ O	6.2E+15	-1.25	0
NH ₃ +OH = NH ₂ +H ₂ O	4700000	1.9	500
NH ₃ +H = NH ₂ +H ₂	636000	2.39	10220
NH ₃ +O = NH ₂ +OH	1100000	2.1	5200
NNH = N ₂ +H	10000	0	0
NNH+NO = N ₂ +HNO	5E+13	0	0
NNH+H = N ₂ +H ₂	1E+14	0	0
NNH+OH = N ₂ +H ₂ O	5E+13	0	0
NNH+O = N ₂ O+H	1E+14	0	0
HNO+M = H+NO+M	1.5E+16	0	49000
HNO+OH = NO+H ₂ O	3.6E+13	0	0

$\text{HNO} + \text{H} = \text{H}_2 + \text{NO}$	$5\text{E}+12$	0	0
$\text{HNO} + \text{NH}_2 = \text{NH}_3 + \text{NO}$	$2.3\text{E}+13$	0	1000
$\text{N} + \text{NO} = \text{N}_2 + \text{O}$	$3.3\text{E}+12$	0.3	0
$\text{N} + \text{O}_2 = \text{NO} + \text{O}$	$6.4\text{E}+09$	1	6320
$\text{N} + \text{OH} = \text{NO} + \text{H}$	$3.8\text{E}+13$	0	0
$\text{NH}_3 + \text{M} = \text{NH}_2 + \text{H} + \text{M}$	$2.2\text{E}+16$	0	94080
$\text{NH}_2 + \text{O}_2 = \text{HNO} + \text{OH}$	$4.5\text{E}+12$	0	25200
$\text{NH} + \text{O} = \text{NO} + \text{H}$	$7.8\text{E}+13$	0	0
$\text{CN} + \text{H}_2\text{O} = \text{HCN} + \text{OH}$	$8\text{E}+12$	0	6500

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

noticed readily that the notation w/o CO in these figures refers to Run 4 whereas the notation w CO refers to Run 5.

Presented in Figure 8 is the concentration of nitrous oxide for various reaction temperatures for the above two runs, HCN/NO oxidation with and without CO. The presence of CO seems to help the reaction at lower temperatures, allowing the peak concentration to occur at 1100 K as opposed to 1200 K, the temperature at which peak occurs for HCN/NO oxidation. The decomposition of nitrous oxide, accordingly begins at 1100 K. The inclusion of CO not only yields a lower peak (about 170 ppm as opposed to 200 ppm) but also favors a greater reduction of N_2O at higher temperatures. The favorable nature of CO in terms of destruction of N_2O is seen from the fact that the N_2O concentration at 1300 K is only 80 ppm for HCN/NO/CO oxidation whereas it is 180 ppm for HCN/NO oxidation. Hence the absence of CO for 900 K- 1100 K operation and the presence of CO for 1100 K- 1300 K operation are recommended.

Figure 9 depicts the effect of CO on the concentration of NO for the two cases, namely Run 4 and Run 5. While the presence of CO disfavored the N_2O yield at higher temperatures, it favors the NO yield. In many ways the trend is exactly opposite; the NO yield decreases till 1100 K and increases thereafter while vice versa is true for nitrous oxide. The production of NO in the presence of CO is very significant- above 450 ppm at 1300 K. While NO is reduced for almost the entire temperature zone for the case of HCN/NO reaction, its formation can be noticed at higher temperatures (1100 K- 1300 K) in the case of HCN/NO/CO reaction.

Fig. 8. Effect of CO on the concentration of N_2O . Residence time 51 ms. Inlet mole fractions: (i) w/o CO: 303 ppm HCN, 441 ppm NO, 3 ppm N_2O , 2.28% O_2 , 2.69% H_2O and balance inert. (ii) w CO: 298 ppm HCN, 434 ppm NO, 1618 ppm CO, 2.26% O_2 , 2.64% H_2O and balance inert.

Fig. 9. Effect of CO on the concentration of NO. Residence time 51 ms. Inlet mole fractions: (i) w/o CO: 303 ppm HCN, 441 ppm NO, 3 ppm N_2O , 2.28% O_2 , 2.69% H_2O and balance inert. (ii) w CO: 298 ppm HCN, 434 ppm NO, 1618 ppm CO, 2.26% O_2 , 2.64% H_2O and balance inert.

Figure 10 presents the concentrations of other significant species, HCN and HNCO in the two reactions, HCN/NO oxidation and HCN/NO/CO oxidation. It can be easily noticed that HCN is consumed entirely through the reaction process for both cases. The formation and destruction of unstable intermediate, HNCO, that too in very small concentrations, is evident from this figure as well. The effect of CO thus is insignificant in the destruction of HCN as well as the formation and destruction of HNCO radical.

Figure 11 separates the two runs, Run 4 (HCN/NO oxidation) and Run 5 (HCN/NO/CO Oxidation). In the case of HCN/NO oxidation, CO is formed in the early temperatures but is destroyed at higher temperatures. In the case of HCN/NO/CO oxidation, the initially present CO participates in the reaction straightaway and its destruction is noticed throughout the temperature range. In both cases however, the concentration of CO₂ increases with increase in temperature. The apparent difference in the CO₂ yield is due to the fact that in the second case an initial concentration of 1618 ppm of CO gave rise to an equivalent amount of CO₂ during the reaction process.

On the whole, the presence of CO is found to be favorable in terms of lowering the N₂O peak and the peak occurring temperature. The key findings of the gas phase reactions addressed here, namely HCN oxidation, HCN/NO oxidation, NH₃ oxidation, HCN/NO/CO oxidation are summarized in Section 4.0. The subsequent section deals with the single particle combustion.

Fig. 10. Effect of CO on the concentrations of HCN and HNCO. Residence time 51 ms. Inlet mole fractions: (i) w/o CO: 303 ppm HCN, 441 ppm NO, 3 ppm N₂O, 2.28% O₂, 2.69% H₂O and balance inert. (ii) w CO: 298 ppm HCN, 434 ppm NO, 1618 ppm CO, 2.26% O₂, 2.64% H₂O and balance inert.

Fig. 11. Concentrations of CO and CO₂ in the oxidation of HCN/NO (i) with CO not present initially and (ii) with CO present initially. Residence time 51 ms. Inlet mole fractions: (i) w/o CO: 303 ppm HCN, 441 ppm NO, 3 ppm N₂O, 2.28% O₂, 2.69% H₂O and balance inert. (ii) w CO: 298 ppm HCN, 434 ppm NO, 1618 ppm CO, 2.26% O₂, 2.64% H₂O and balance inert.

3.2 Single Particle Coal Combustion And Results

It is assumed that the delayed nitrogen evolution is governed by rate of burning of carbon particles; i.e., the total nitrogen evolution is proportional to carbon evolution. This is based upon the finding of Song, et al. (1982b) under fuel lean conditions. NH_3 and HCN are the nitrogen decomposition products and their fraction yields are assumed to be fuel-dependent, adjustable constants in the model.

It is also assumed that the burning of carbon particles is controlled by mass transfer of oxygen to the particles surface, heat transfer to the particles initially at room temperature, and carbon oxidation rate. It was concluded by Mulcahy and Smith (1969) that the burning of particles larger than $100\text{ }\mu\text{m}$ are controlled by mass transfer. Bukur and Anderson (1981, 1982) later claimed that the rate of carbon burning could be comparable with mass transfer. Heat transfer is also considered to account for the non-isothermal reaction pathway. Although the complete time resolved coal combustion includes a series of reactions, such as drying, decomposition of individual species, and oxidation of carbon etc., the present model lumps the heat of all these physical/chemical changes (except sensible heat) in a single term: the heat of combustion. The coal or char is assumed to have uniform temperature inside the particles. Further, the radius of the outer edge of boundary layer, b , is assumed to be an adjustable constant. Bukur and Amundson (1981) found that the effect of boundary thickness on the combustor performance is not very significant provided that b is greater than the initial particle diameter, d_{0c} .

Following these assumptions and similar derivations of Bukur and Amundson

(1981, 1982), the particle diameter and temperature can be described by the following equations:

$$\frac{dr}{dt} = \frac{-B_1 x_{3d}}{r(1-\frac{r}{p}) + 2 \frac{D_s}{k_1 d_{oc}}} ; \quad r(0) = 1 \quad (1)$$

where

$$r = d_c/d_{oc}$$

$$p = 2b/d_{oc}$$

$$B_1 = 4CD_g M_c / (\rho_c \gamma_c d_{oc}^2)$$

and

$$\frac{dT_c}{dt} = \frac{6}{rd_{oc}\rho_c C_c} [\sigma \epsilon (T_b^4 - T_c^4) + (-\Delta H_1) k_1 C x_{3s} + \frac{k_s (T_b - T_c)}{rd_{oc}(1-\frac{r}{p})}] ; \quad T_c(0) = T_s^0 \quad (2)$$

The symbols are defined in the Nomenclature section. The values used in our simulation are listed in Table 3. Since the carbon oxidation rate is limited by both mass transfer of oxygen and reaction kinetics, the surface oxygen concentration is related to the dilute phase oxygen concentration by the relation:

$$x_{3s} = \frac{x_{3d}}{1 + \frac{k_1 d_c}{2 D_s} (1 - \frac{d_c}{2b})} \quad (3)$$

In the modeling of single particle combustion in an isothermal circulating bed,

Table 3. Parameter Values for Single Particle Combustion

$$b = 3 \text{ mm}$$

$$C = 1.06 \times 10^{-2} \text{ kgmol m}^{-3}$$

$$C_c = 1200 \text{ J kg}^{-1} \text{ }^{\circ}\text{K}^{-1} \text{ for coal}$$
$$= 1700 \text{ J kg}^{-1} \text{ }^{\circ}\text{K}^{-1} \text{ for char}$$

$$d_{oc} = .1 - .3 \text{ mm}$$

$$\Delta H_1 = -4.04 \times 10^8 \text{ J kg mol}^{-1}$$

$$k_1 = 535.3 \text{ (m/s)} T_c \exp(-17,976 \text{ }^{\circ}\text{K}/T_c)$$

$$k_g = 70 \text{ J s}^{-1} \text{ }^{\circ}\text{K}^{-1}$$

$$T_b = 1100 - 1200 \text{ }^{\circ}\text{K}$$

$$\gamma_c = 0.70$$

$$\epsilon = 0.7$$

$$\rho_c = 1330 \text{ kg m}^{-3} \text{ for coal}$$

$$\sigma = 5.69 \times 10^{-8} \text{ J s}^{-1} \text{ m}^{-2} \text{ }^{\circ}\text{K}^{-2}$$

$$D_g = 2.0 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$$

an assumed oxygen fraction, x_{3d} was used in the calculation of x_{3s} . With the values of all constants in equations (1) and (2) properly assigned, equations (1) and (2) were solved by a stiff differential equation solver, LSODE (Hindmarsh, 1979). After the equations were integrated to a predetermined time, the particle diameter was used to calculate oxygen consumption and the new x_{3d} was used in the new iteration until the two consecutive calculations give results within a reasonable tolerance. The particle size and temperature as a function of time are thus obtained in an iterative process.

The results of single particle coal combustion are presented in Figs. 12 through 15. Figures 12 and 13 portray the effect of initial particle size, d_{oc} and Figs. 14 and 15 present the influence of bed temperature, T_b on single particle combustion. In all the figures, non-dimensional coal particle size, r , $d_c(t)/d_{oc}$ and coal particle temperature, $T_c(t)$ are shown.

Presented in Figs. 12 and 13 are the predicted values of the coal particle size and its temperature for two cases of initial particle size, namely 1.0 mm and 3.0 mm. While Fig. 12 indicates the results for the bed temperature of 1100 K, Fig. 13 indicates the results for the bed temperature of 1200 K. An important observation is that the particle undergoes rapid heating in the region between $r=1.0$ and $r=0.98$ in either figure. It was to accurately predict this rapid heating phenomena, the LSODE stiff differential equation solver was needed and was fitly used. The particle temperature increases as the particle shrinks due to the combustion of the particle. Notice the effect of initial particle size from Fig. 12. While the 3.0 mm particle

Fig. 12. Effect of particle size on single particle coal combustion. Bed Temperature 1100K. Two values of initial particle size, d_{oc} tested: 1.0 mm, 3.0 mm.

Fig. 13. Effect of particle size on single particle coal combustion. Bed Temperature 1200K. Two values of initial particle size, d_{oc} tested: 1.0 mm, 3.0 mm.

shrinks only to about 95% of its size, the 1.0 mm particle shrinks to almost 35% for a residence time of 5 s. Similarly, while the temperature of the 3.0 mm coal particle reaches 1500 K, the temperature of the 1.0 mm coal particle reaches 2000 K for the residence time of 5 s. Figure 13 is very similar to Fig. 12 indicating the same trend explained above. Thus the smaller the initial particle size, the greater is its reduction (i.e combustion), and the higher is its temperature for a given residence time and a given bed temperature. This is expected since the oxidizing environment provided is the same for combustion of both particles.

The effect of bed temperature on the predicted values of the coal particle size and particle temperature obtained in this modeling is illustrated in Figs. 14 and 15. Figure 14 refers to the case where the initial particle size tested is 1.0 mm and Fig. 15 refers to the case of 3.0 mm initial particle size. It is apparent from both figures that combustion takes place very slowly at lower bed temperatures such as 1000 K. However, for bed temperatures beyond 1100 K, there is seen a rapid increase in the coal particle temperature at lower residence times and a levelling off of temperature as the particle resides further. The higher the bed temperature, the higher is the temperature of the coal particle. Also noticeable is the fact that the coal particle size decreases with increasing bed temperature at any given residence time. This clearly shows that combustion is taking place steadily in the favorable oxidizing environment. This also explains why the temperature of the coal particle is much higher than the bed temperature even as the particle shrinks. Unlike the temperature of the coal particle, its size steadily decreases with reaction time.

Fig. 14. Influence of bed temperature on single particle coal combustion. Initial particle size, d_{0c} 1.0 mm.

Fig. 15. Influence of bed temperature on single particle coal combustion. Initial particle size, d_{oc} , 3.0 mm.

Unfortunately, the single particle combustion model is limited in its scope since it purely addresses heat transfer modeling. The author wishes that there could be a bridge between the single particle combustion and the gas phase reactions through a much more detailed modeling. The one-year faculty exploration grant could only allow this much of work but yet the institution is very thankful that a good research collaboration has begun so as to meet the needs of our environment through working with the Department of Energy.

Presented in the following section are the summary and conclusions of the work performed under this project.

4.0 SUMMARY AND CONCLUSIONS

A computational model for the prediction of yields of nitrogen species in fluidized coal combustion was developed in this work. The two major elements that stimulated the nitrogen chemistry were a non-isothermal single particle combustion in a preheated reactor and a gas phase reaction zone with a plug flow reactor. The programs LSODE and CHEMKIN were appropriately applied for the numerical analysis. The effects of coal particle size and bed temperature on the single particle coal combustion were explored. The homogeneous reaction pathways involving nitrogen containing species such as HCN, NH_3 , N_2O were tested under varying bed temperatures and residence times. By and large, this work addressed the nitrous oxide emissions from fluidized bed combustion which is one of the primary environmental concerns of the present day.

Fluidized bed combustion produces substantial emissions of N_2O . The modeling calculations suggest that these emissions can be explained in terms of the reduction of NO by HCN. Some of the key findings are summarized below.

- i) The formation of nitrous oxide is favored at lower temperatures (900-1200 K) while the destruction of N_2O is favored at higher temperatures (1200-1300 K) of the FBC temperature zone.
- ii) The lower residence times (0-0.05 s) at higher temperatures (1300 K) favor N_2O formation while the higher residence times at such temperatures favor N_2O destruction.
- iii) The intermediate species, HNCO reacts with NO via NCO to form N_2O . Due

to this key reaction mechanism for HCN oxidation, one can see higher concentrations of N_2O and lower concentrations of HNCO in the presence of NO for temperatures up to 1200 K; vice versa is applicable for HCN oxidation without the presence of NO.

iv) The ammonia oxidation involves the species NH and NH_2 reacting with NO to form N_2O . The negligible N_2O yields in NH_3 oxidation confirm that HCN is a more important precursor of N_2O than NH_3 in FBC.

v) The presence of CO in HCN/NO oxidation is favorable for N_2O production at lower temperatures (900 K- 1100 K) and N_2O destruction at higher temperatures (1100 K-1300 K). The presence of CO lowers the N_2O concentration peak (by 30 ppm; see Fig. 8) as well as the temperature at which the peak occurs by 100 K.

With regard to the single particle combustion, the following results stood out.

i) The coal particle undergoes rapid heating in the region between $r=d_c/d_{oc}=1.0$ and $r=0.98$.

ii) The smaller the initial particle size (d_{oc}), the greater is its shrinking and the higher is its temperature (T_c) for a given residence time and a given bed temperature (T_b).

iii) The higher the bed temperature, the higher is the temperature of the coal particle at any given time of residence in the bed.

The present results are important in understanding the homogeneous nitrogen chemistry occurring in fluidized bed combustion. More experimental data and further improvement in modeling are needed to find adequate methods in controlling the nitrous oxide emissions.

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APPENDIX

This appendix contains the abstract published in the proceedings of the First Annual HBCU/PS/FE R&D Technology Transfer Symposium and the other details of that HBCU Fossil Research Presentation.

**The First Annual Historically Black Colleges and
Universities/Private Sector/Fossil Energy Research and
Development Technology Transfer Symposium**

Proceedings

**New Orleans, Louisiana
May 26-28, 1993**

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MODELING OF NITROUS OXIDE PRODUCTION UNDER FLUIDIZED BED COMBUSTION CONDITIONS

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ABSTRACT

The nitrous oxide emission from combustion systems has been a matter of increasing concern because N_2O contributes both to greenhouse effect and ozone depletion. This work employed a CHEMKIN package for the prediction of yields of nitrogen species in fluidized bed coal combustion which is identified hitherto as the principal source of nitrous oxide emissions.

In this paper computer modeling calculations are done for homogeneous formulation and destruction of nitrous oxide. This work focused primarily on oxidation of HCN and NO which are the predominant nitrogen containing species in fluidized conditions. The influence of temperature (900-1300 K) and the residence time (0-0.5 sec) on the formation of N_2O was investigated.

The results indicate that in the presence of NO, significant amounts of N_2O were produced from HCN oxidation. Peaking of N_2O was found at 1100 K. Also, the results affirm strong temperature dependence of N_2O destruction mechanisms.

Oxidation of HCN without the presence of NO produced low levels of N_2O indicating that N_2O is formed primarily by reaction between NO and other nitrogen containing radicals such as NCO. The results with NH_3 oxidation produced very much lower yields of N_2O , thus indicating that HCN is more important than NH_3 as a precursor of N_2O under fluidized bed conditions. Further improvement in modeling with additional reaction mechanisms is currently underway.

Key Findings

i) The formation of nitrous oxide is favored at lower temperatures (900-1200 K) while the destruction of N_2O is favored at higher temperatures (1200-1300 K) of the FBC temperature zone.

ii) The lower residence times (0-0.05 s) at higher temperatures (1300 K) favor N_2O formation while the higher residence times at such temperatures favor N_2O destruction.

iii) The intermediate species, HNCO reacts with NO via NCO to form N_2O . Due to this key reaction mechanism for HCN oxidation, one can see higher concentrations of N_2O and lower concentrations of HNCO in the presence of NO for temperatures up to 1200 K; vice versa is applicable for HCN oxidation without the presence of NO .

iv) The ammonia oxidation involves the species NH and NH_2 reacting with NO to form N_2O . The negligible N_2O yields in NH_3 oxidation confirm that HCN is a more important precursor of N_2O than NH_3 in FBC.

IMPORTANT REACTIONS

HCN Reactions

NH₃ Reactions

N₂O Destruction

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