



**N₂O: A GREENHOUSE GAS RELEASED FROM THE COMBUSTION
OF COALS IN FLUIDISED BEDS**

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Abstract

This paper discusses the results of the experimental work investigating the formation of N₂O and NO during fluidized bed combustion of coals, and of chars and volatiles produced from the pyrolysis of these coals. Ammonia (NH₃) and hydrogen cyanide (HCN) are shown to play important roles as gas-phase precursors of both NO and N₂O. The conversion of fuel-N through NH₃ and HCN to N₂O and NO was studied using a fluidized bed combustor in the temperature range between 973 K and 1273 K, for two different coals. The results suggest that the principal contribution to N₂O emission originated from volatile-N, however, char-N could also have an important role, depending upon the temperature.

1. INTRODUCTION

The emissions of nitrogen oxides have been identified as one of major environmental problems originating from the combustion of coals in fluidized bed systems. Nitric oxide (NO) and nitrogen dioxide (NO₂) contribute to the acid rain problem and photochemical smog formation. Nitrous oxide (N₂O) is a greenhouse gas and also acts indirectly in the depletion of stratospheric ozone [1,2].

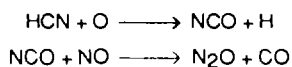
Nitrogen is present in coal mainly in the form of relatively stable aromatic structures [3] and its release is delayed until ring structures occurs. Simultaneously, other volatiles are driven off as a result of the breakup of side chains and aliphatic links. The formation of nitrogen oxides from coal-N during combustion in a fluidized bed occurs in a complex process involving coal devolatilization, homogeneous gas-phase reactions and heterogeneous oxidation of char. During devolatilization, nitrogen in coal is divided between char-N and volatile-N compounds which are mainly released in tars and as NH₃ and HCN. During combustion, the char-N is oxidized to NO and N₂O whilst simultaneously partly reduced to N₂, however, small amounts of NH₃ and HCN may also be formed [4].

The division of nitrogen between char and volatiles and the type of volatile nitrogen compounds formed during devolatilization are very important for the eventual fate of coal-N in FBC, because the

extent of subsequent reactions involving the oxidation of char-N and volatiles-N are dependent on this division and on the different volatile nitrogen species. The speciation of volatile nitrogen compounds is very important for the formation of NO and N₂O, because of the different reactions pathways for NH₃ and HCN. The amounts of NH₃ and HCN released during pyrolysis depend on a number of factors, most importantly coal type, heating rate, final temperature and residence time. A wide variety of experimental techniques have been used and this may be why the data in literature do not provide conclusive evidence about the influence of coal type on the formation of NH₃ and HCN during pyrolysis [5].

Calculations, using comprehensive kinetic models, show that the relative amounts of NO and N₂O depend strongly on the relative concentrations of NH₃ and HCN [6,7,8]. The formation of N₂O through HCN was strong at 1000 K, and weak at 1200 K, when NO was the major product. NH₃ was not observed to be an intermediate causing significant amounts of N₂O production. NO was the main product from NH₃ at 1000 K, together with some N₂.

There is a general agreement [6,7,8,9] that HCN is a very important precursor for N₂O formation in the range of temperatures used in FBC of coals. The most important reactions were found to be



over the combustion temperature range in FBC.

This was experimentally shown by Kramlich *et al.* [9] by injecting NH₃, HCN and acetonitrile into the post-flame gases. The results clearly demonstrated that N₂O was preferentially formed from cyano species, whereas very little N₂O was released during NH₃ injection.

Recently Hulgaard [10] made extensive plug flow reactor studies on NH₃ and HCN oxidation at temperatures between 900 and 1350 K. His data suggest that HCN produced approximately one order of magnitude more N₂O than NH₃, under similar oxidation conditions.

2. EXPERIMENTAL

Samples

The two coals studied, Cimpor coal and South African coal, were crushed and sieved to a particle size 0.50 -1.00 mm. Chars were produced in a FBC from coals at three temperatures (1073 K, 1173 K and 1273 K) and at a heating rate in the order of 10⁴ K/s. The characterization of the samples are given in Tables I and II.

Combustion of chars and coal

The combustion of coals and chars were carried out in an electrically heated fluidised bed combustor with 80 mm of ID and 500 mm height, as shown in Fig.1. The combustion temperature of coals and chars was varied in the range of 1000 -1200 K.

Both chars and coals were supplied using a screw-feeder located at the top of the combustor. The particles were injected through a pipe immersed in the bed which was water- cooled to prevent any devolatilization during feeding. The combustion gases leaving the combustor having been filtered and dried were constantly analyzed for NO, N₂O, CO, CO₂ and O₂ by specific analyzers .

Analyses of Volatiles

The analyses of hydrogen cyanide (HCN) and ammonia (NH₃) in the gases released during the pyrolysis of coals were carried out. The samples were collected by passing the gas sample through a wash bottle with a 0.01M NaOH as absorption solution.

The determination of HCN and NH₃ were performed with ion-selective electrodes supplied by ORION. The ammonia electrode (model 95-12) is a gas sensing electrode and the cyanide electrode (model 94-06) is a solid state electrode. The measures were done with the direct method and assuming that the efficiency of absorption was 100% and the gases behave as ideal gases.

Combustion of Volatiles

The gases released during the pyrolysis of coals at different temperatures were burned in a second reactor, at the same temperature that chars preparation was performed. The tube that makes the connection to the second reactor was isolated with kaolwool to prevent the deposition of tars. The gases released were constantly analyzed for NO, N₂O, CO, CO₂ and O₂ by specific analyzers and HCN and NH₃ with ion-selective electrodes, Fig.1.

3. RESULTS AND DISCUSSION

NO and N₂O from coal and char combustion

The results were interpreted based on the assumption that coal-N was divided between the volatiles (volatile-N) and char (char-N) and they were subsequently converted into NO, N₂O and N₂. Table 3 provides the distribution of fuel-N in both volatiles and char for the two coals studied and calculations for the mass balance confirmed the split of fuel-N between volatiles and char. It should be noted that with temperature, the amount of volatile-N was found to increase which could be due to higher heating rates which encouraged the greater rate of release of volatiles from coal particles. The conversion of both volatile-N and char-N to the products were assumed to be through relatively independent processes although some reduction of both N₂O and NO, once formed, on the char

surface were expected to occur. Conversions of coal-N and char-N to N_2O and NO in percentage by weight, at different temperatures, are presented in Tables IV and V. The data showed that the conversion of nitrogen in coal and char to NO and N_2O followed the same pattern in which amounts of N_2O and NO formed varied inversely with temperature, which have previously been observed as well [11,12].

The conversion of coal-N to NO, for both coals, are somewhat similar to those observed with char-N. These results suggest that the contribution of char-N is primarily responsible for total NO formed. Regarding coal-N and char-N conversions to N_2O the observation is different, and it is apparent that N_2O levels were found to be greater with the higher nitrogen amounts in the parent coal and the temperature of devolatilisation which was observed to determine the amount of volatiles remained in chars. It could be seen that for combustion temperatures higher than 1100 K the char-N conversion to NO became much greater than the conversion to N_2O .

HCN and NH_3 in Volatiles

During pyrolysis and combustion of solid fuels, NH_3 and HCN are the major nitrogen-containing precursors [10]. The results of this work demonstrated that the yields of NH_3 and HCN for the two coals responded in a similar way as the temperature of pyrolysis increased. At higher temperatures, the yield of NH_3 was observed to decrease, as given in Tables VI and VII.

HCN and NH_3 were not in significant quantities at temperatures below 1073 K, but the sum of the yields of HCN and NH_3 is similar in both Cimpor coal and in South African coal. Also, it could be seen that the yields of HCN and NH_3 in the gases that leaving the second reactor, following the combustion of volatiles, decreased and no NH_3 was found at temperatures higher than 1173 K. It is interesting to note that, while the yield of HCN released with the volatiles increased with temperature, the amount of HCN measured in combustion gases decreased with the temperature of pyrolysis increased. This suggests that HCN became increasingly more prevailing intermediate for the formation of NO above 1173 K.

N_2O and NO from the combustion of volatiles

Conversions of the volatile-N in percentage by weight to N_2O and NO, corresponding to the temperatures at which chars were prepared are presented in Table VIII. The data show that much higher conversion to N_2O than to NO took place. It is the opinion of the authors that the volatile-N had a dominating contribution to N_2O . With the increase in the char preparation temperature the amount of NO formed went up whilst the contribution of the volatile-N to N_2O decreased.

Upon correlating these results with the yields of HCN and NH_3 observed, it could be concluded that at temperatures less than 1173 K, HCN was primarily responsible for the formation of N_2O .

4. CONCLUSIONS

The distribution of fuel-N between HCN and NH₃ species in the pyrolysis is an important factor in determining the amounts of N₂O and NO formed. It is believed that there is a significant contribution to the N₂O emission that originates from volatile-N but also the char-N has an important share, particularly at lower devolatilisation temperatures. Char-N is the principal source of NO formed. It is the opinion of the authors that the determination of HCN and NH₃ species in the gases released in the pyrolysis of coal could help to have a better understanding of the chemical states of nitrogen in coals.

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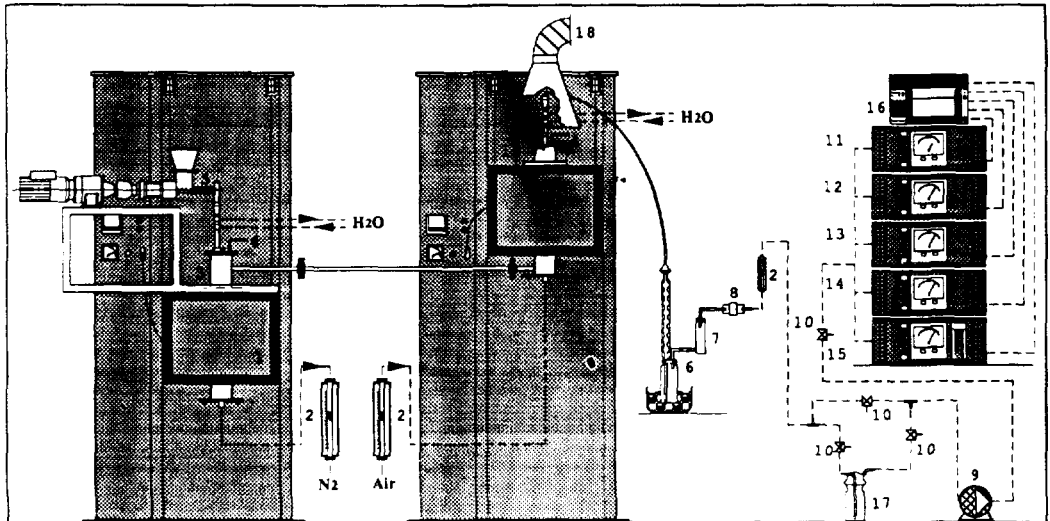


Figure 1 - Schematic illustration of the experimental set-up

1. Electric Furnace; 2. Rotameter; 3. Fluidized Bed Combustor; 4. Termocouple; 5. Continuous Screw-Feeder;
6. Collector; 7. Glasswool Filter; 8. Paper Filter; 9. Pump; 10. Valve; 11. CO Analyser; 12. O₂ Analyser;
13. CO Analyser; 14. N₂O Analyser; 15. NO Analyser; 16. Recorder; 17. Wash Bottle; 18. To the atmosphere;
19. Volatiles Combustor

TABLE I: CHARACTERIZATION DATA FOR CIMPOR COAL AND CHARs

Proximate and Elemental analysis (wt%, db)	Cimpor	Char	Char	Char
	Coal	(1073K)	(1173K)	(1273K)
Ash	16.49	17.45	18.68	18.72
Volatile matter	23.24	4.02	2.18	2.06
Fixed Carbon	60.27	78.53	79.14	79.22
C	68.57	76.71	65.62	83.27
H	3.84	0.55	0.89	0.86
N	1.68	1.78	1.64	1.55
N/C	0.025	0.023	0.024	0.019

TABLE II: CHARACTERIZATION DATA FOR SOUTH AFRICAN COAL AND CHAR

Proximate and Elemental analysis (wt%, db)	South	Char	Char	Char
	African Coal	(1073K)	(1173K)	(1273K)
Ash	14.44	16.13	16.33	17.40
Volatile matter	29.81	4.42	3.53	2.16
Fixed carbon	55.75	79.45	80.14	80.44
C	69.00	78.14	82.22	82.52
H	4.47	1.06	0.60	0.49
N	1.74	2.03	1.90	1.87
N/C	0.025	0.026	0.023	0.022

TABLE III: SPLIT OF NITROGEN (%) BETWEEN CHAR AND VOLATILES

Temp. (K)	Cimpor	Cimpor	S.African	S African
	chars	volatiles	chars	volatiles
1073	1.78	0.26	2.03	0.25
1173	1.64	0.39	1.90	0.36
1273	1.55	0.47	1.87	0.40

TABLE IV: YIELDS (%N IN COAL) OF HCN AND NH₃ AS FUNCTION OF TEMPERATURE OF PYROLYSIS OF COALS AND TEMPERATURE OF COMBUSTION OF VOLATILES OF

Temperature (K)	CIMPOR COAL			
	in volatiles		after combustion of volatiles	
	HCN yield	NH ₃ yield	HCN yield	NH ₃ yield
1073	13.9	6.8	1.8	0.7
1173	20.7	7.8	1.7	0.0
1273	24.6	7.7	0.9	0.0

TABLE V: YIELDS (%N IN COAL) OF HCN AND NH₃ AS FUNCTION OF TEMPERATURE OF PYROLYSIS OF COALS AND TEMPERATURE OF COMBUSTION OF VOLATILES OF

Temperature (K)	SOUTH AFRICAN COAL			
	in volatiles		after combustion of volatiles	
	HCN yield	NH ₃ yield	HCN yield	NH ₃ yield
1073	17.8	4.6	2.5	1.0
1173	24.2	4.1	2.1	0.0
1273	28.0	2.0	1.4	0.0

TABLE VI: CONVERSIONS TO N₂O AND NO IN THE COMBUSTION OF CIMPOR COAL AND CHAR (% BY WEIGHT).

Temp (K)	Cimpor coal		Char (1073 K)		Char (1173 K)		Char (1273 K)	
	f(N ₂ O)	f(NO)	f(N ₂ O)	f(NO)	f(N ₂ O)	f(NO)	f(N ₂ O)	f(NO)
1000	7.56	11.03	27.55	10.81	25.45	13.43	24.94	15.41
1050	8.72	11.95	18.81	13.09	17.42	15.56	16.62	17.61
1100	8.87	16.83	15.94	17.12	12.65	16.06	12.54	17.23
1150	6.77	18.96	14.30	19.75	13.10	18.45	14.05	19.05
1200	5.39	19.08	12.71	21.90	12.56	20.08	12.23	20.82

TABLE VII: CONVERSIONS TO N₂O AND NO IN THE COMBUSTION OF SOUTH AFRICAN COAL AND CHAR (% BY WEIGHT)

Temp. (K)	South African coal		Char (1073 K)		Char (1173 K)		Char (1273 K)	
	f(N ₂ O)	f(NO)	f(N ₂ O)	f(NO)	f(N ₂ O)	f(NO)	f(N ₂ O)	f(NO)
1000	5.23	7.93	18.53	10.25	16.76	10.43	21.21	10.74
1050	5.82	9.91	17.05	15.16	15.13	15.81	16.67	16.25
1100	5.41	11.20	10.01	12.29	11.90	17.40	14.34	20.01
1150	4.86	12.53	13.78	16.90	11.26	19.81	13.39	20.90
1200	3.70	12.42	10.38	20.68	10.31	21.20	10.21	20.23

TABLE VIII: FRACTIONAL CONVERSIONS TO NO AND N₂O IN THE COMBUSTION OF VOLATILES AT THE SAME TEMPERATURE OF PYROLYSIS

	Cimpor Coal		S.African Coal	
	f(NO)	f(N ₂ O)	f(NO)	f(N ₂ O)
Volatiles(1073 K)	0.53	10.48	0.38	6.62
Volatiles(1173 K)	0.83	7.66	0.55	3.64
Volatiles(1273 K)	0.96	4.62	0.86	3.32