N2O-Emissions from Fluidized Bed Combustion

Proceedings of IEA AFBC Technical Meting held in November 1988 in Amsterdam, The Netherlands

Citation for the published paper:
Andersson, S. ; Åmand, L. ; Leckner, B. (1988) "N2O-Emissions from Fluidized Bed Combustion". Proceedings of IEA AFBC Technical Meting held in November 1988 in Amsterdam, The Netherlands

Chalmers
University of
Technology
Department of Energy Conversion

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Sven Andersson
Lars-Erik Åmand
Bo Leckner

Presented at the IEA AFBC Technical Meeting,
Amsterdam, November 1988

Postal address:
Department of Energy Conversion
Chalmers University of Technology
S-412 96 Göteborg, Sweden

Visiting address:
Hörsalsvägen 7

Phone: +46-31 72 10 00

Telex: 54-2369 CHALBIB S
Telefax: +46-31 72 11 92

N_2O EMISSIONS FROM FLUIDIZED BED COMBUSTION

INTRODUCTION

Nitrous oxide, N_2O, was until recently regarded harmless. It is now known as a gas which contributes to the greenhouse effect as well as to the ozone layer depletion. In order to increase the knowledge about N_2O and its role in the atmosphere, and about the chemistry of its formation and destruction in combustion processes, three workshops have been held (1, 2, 3).

The results presented in the two first workshops indicated that low–NO_x techniques would also give low N_2O emissions. However, this conclusion was based on erroneous measurements and most values were too high. Figure 1 shows the "old" correlation as well as the "new" values (here called "European" since the sampling technique in Europe was probably correct, whereas most American values were wrong). This was revealed by two US delegates (Kramlich and Muzio) during the last workshop. Hence, one of the major conclusions of this workshop was that sampling and analysis of N_2O must be thoroughly examined and improved.

In spite of this, it was possible to conclude that N_2O emissions from flame combustion are very low, 1–20 ppm, and that they are considerably higher from fluidized bed combustion.

EXPERIMENTS

A survey made by Götaverken Energy during the spring of 1988 on a number of CFBs shows that the combustion of coal gives high values, peat both high and low, and wood and municipal waste result in low values (Table 1). This is in accordance with other measurements made in both Sweden and Finland regarding stationary and circulating beds burning all kinds of fuels. The N_2O emission from a fluidized bed boiler is usually between 50 and 200 ppm.

N_2O was measured in an 8–MW Götaverken Energy CFB boiler, as a part of a NO_x–emission study by the Department of Energy Conversion at Chalmers University of Technology (4). The results show that the N_2O emission in a CFB

- decreases when the temperature increases, Figure 2,
- increases when the excess air ratio increases, Figure 3,
- increases when the nitrogen content of the fuel increases, Figure 2 and Table 2.

The explanation of the results is not straightforward, since the chemistry of formation and destruction of N_2O is not well known. Also, the results of Figures 2 and 3 reflect what leaves a system in which the conditions vary. For instance, it is possible that the dependence of oxygen concentration shown in Figure 3 is partially a temperature dependence. The bottom bed temperature is kept constant whereas the top temperature drops when the excess air ratio increases.

PRELIMINARY MODEL

Three formation mechanisms for N_2O have been proposed. They are

- homogeneous oxidation of volatile compounds containing nitrogen,
- heterogeneous oxidation of char nitrogen,
- heterogeneous reduction of NO on particle surfaces,

and two destruction mechanisms

- homogeneous reduction to N_2,
- heterogeneous reduction of N_2O on particle surfaces.

Volatile nitrogen

During devolatilization some of the fuel nitrogen is released, but not all. For instance the experiments of Freihaut and Seery (5) show that coal heated up at an intermediate rate up to 900° C releases approximately half of its nitrogen and the rest remains in the char (Figure 4).

A major source of N_2O is HCN, see for instance Kramlich et al. (6). At temperatures of interest for fluidized bed combustion only a small fraction of the volatile nitrogen forms HCN. Figure 4 shows that around 20% of the fuel nitrogen will appear as HCN under these temperature conditions. This situation is different from that in a flame, where much more HCN is released.

It is not fully known if other devolatilization products like NH_3 also form N_2O. However, numerical calculations for post–flame conditions by Kramlich et al. (6) and experiments in a CFB by Åmand and Andersson (4) indicate that no N_2O is produced from NH_3.

Hence, a first assumption is that only HCN produces N_2O.

Calculations with a homogeneous reaction model (7) show that the conversion of 3000 ppm HCN in 5% O_2, 7% H_2O, 11% CO_2 and 77% N_2 in a well mixed reactor at constant temperatures ranging from 1050 K to 1300 K gives an almost constant maximum yield of N_2O of around 50%.

Char nitrogen

The result of the heterogeneous reactions is much harder to estimate. The approach of Kramlich et al. (6), where he assumes that all char nitrogen forms N_2O and that all NO reduction results in N_2O, did not give any N_2O out of his reactor, but that could well be because of the high temperature of the system.

Experiments by de Soete (8) show that N_2O is formed when NO is reduced and also during combustion of char particles. Both NO and N_2O are reduced on the surface of a particle, NO partly producing N_2O and N_2O producing N_2. If the reduction of NO is faster than that of N_2O, the N_2O concentration increases.

De Soete showed that the reduction of N_2O on the surface of a particle is faster than the reduction of NO when the CO concentration is low. However, the NO reduction rate is much more sensitive to the concentration of CO than the rate of N_2O reduction. When the CO concentration increases, the N_2O reduction rate does not change, whereas the NO reduction rate increases (Figure 5). The experiments by de Soete were carried out on Pt–catalyst surfaces, not on sand or char surfaces. Still, a shift like the one shown in

Figure 5 can be expected also for such surfaces. In the bottom of the combustors the CO concentration is very high, sometimes several percent. This is a consequence of the staged combustion, the devolatilization and the low temperature of a fluidized bed combustor. The NO reduction can therefore be expected to be much faster than the N_2O reduction, and the N_2O concentration will increase.

Another finding of de Soete's is that a small part of the char nitrogen produces N_2O during combustion (≈ 5%), whereas ≈ 50% of the char nitrogen produces NO (Figure 6). However, this is not only the result of direct oxidation of nitrogen to NO and N_2O, but of the output from the porous reactor that a char particle is. Nitrogen oxidized to NO is reduced to N_2O (and N_2) during the transport out through the pores of the char particle.

N_2O reduction

Heterogeneous reduction is slow compared to the NO reduction but it will decrease the output of N_2O.

A calculation with a homogeneous reaction scheme, Grimsberg (7), gives the destruction rate of N_2O according to gas–phase chemistry. In Figure 7 it can be seen how much of the maximum yield of N_2O that is reduced to N_2 in two seconds. Although the results of this calculation are only qualitative, the conclusion is evident: the influence of temperature is dramatic. At fluidized bed combustion temperatures the reduction of N_2O is small compared to the case of flame combustion temperatures. This could explain the temperature effect seen in Figures 2 and 3, and also the difference between fluidized bed combustion and flame combustion.

ESTIMATION

Using these data it is possible to form a rough estimation of the N_2O concentration in the CFB furnace. Assume that a coal with 2% fuel nitrogen is used, comparable to the bituminous coal of the experiments of Figures 2 and 3. This can give 3200 ppm NO or 1600 ppm N_2O if all is converted to either NO or N_2O.

See Figure 8!

The source of N_2O formed from volatile nitrogen is assumed to be HCN. The fraction of nitrogen found in HCN compared to the total amount of fuel nitrogen is $\approx 20\%$. According to the kinetic model of Grimsberg, half of this amount produces N_2O. This gives a maximum concentration of volatile–nitrogen of 160 ppm N_2O (10% of 1600).

In a similar way the contribution from char nitrogen can be calculated. Half of the fuel nitrogen remains in the char and 5% of the char nitrogen produces N_2O giving 40 ppm (2.5% of 1600). At the same time 50% of the char nitrogen is converted into NO, which gives 800 ppm (25% of 3200).

These two formation mechanisms, from HCN and from char nitrogen, most probably take place at different locations in the combustion chamber. The N_2O formed from char nitrogen may appear where a major part of the combustion takes place, i.e. in the bottom bed. N_2O formed from HCN, on the other hand, should be formed up along the combustion chamber since HCN released during devolatilization is transported upwards at a high velocity. Also, the reactions are quite slow at the temperature conditions of a CFB.

The third formation mechanism of N_2O, NO reduced to N_2O, takes place throughout the combustion chamber, mainly above the bottom bed. Starting at 800 ppm NO this mechanism could, if efficient, produce large amounts of N_2O. In order to investigate this, NO was added to the combustion air of the 8–MW Götaverken Energy CFB boiler. The NO injected behaves like the NO released during combustion. As is seen in Figure 9, approximately 90% of the NO injected disappeared, but 10% was emitted as N_2O. This would result in 40 ppm N_2O from 800 ppm NO.

Hence it can be expected that the N_2O concentration in the bottom bed is around 40 ppm. The N_2O concentration should then increase up through the furnace, depending on the relative importance of the formation from HCN, the formation during the reduction of NO, and the destruction reactions. The maximum value that could be achieved in this case is $40 + 160 + 40 = 240$ ppm N_2O.

One test run was carried out to investigate the gas composition with gas analysis at different locations in the combustion chamber. The result is shown in Figure 10. It is seen that the NO concentration decreases greatly up through the combustion chamber, whereas the N_2O concentration seems to be almost constant. However, the values presented in Figure 10 are the measured values not corrected for the different air flows at different heights. To make these values comparable, the lower ones (below 2 m) should be multiplied by 0.6, the relative amount of primary air. This changes the gradient along the furnace, and N_2O actually increases up through the bed. The values in the bottom are different from those predicted. The NO concentration is much lower, 240 ppm instead of 800 ppm, and the N_2O concentration is higher, 60 ppm instead of 40 ppm. This can be explained by assuming a better NO reduction in the pores of the char particles than estimated above, which would reduce the NO concentration while increasing the N_2O concentration.

With the results from Figure 9, it is possible to estimate the N_2O produced through NO reduction. Starting with 240 ppm in the bottom bed, a calculation[1] gives that only 12 ppm N_2O is formed this way.

The sum of these two contributions, 60 ppm from the char nitrogen during combustion and 12 ppm from the NO reduction, is 72 ppm N_2O. This is only half the measured value in the outlet. The other half should come from volatile nitrogen. Hence, this rough calculation shows that the same amount of N_2O is produced from volatile nitrogen as from char nitrogen.

CONCLUSIONS

Nitrous oxide, N_2O, is formed during combustion. In flames the N_2O is removed because of the fast destruction at high temperatures. At the temperatures of fluidized bed combustion the destruction is much slower and N_2O will leave the system, normally at a concentration of 50–200 ppm when burning coal. Using the results of the preliminary model in a CFB, it can be assumed that

- N_2O is formed from char nitrogen in the bottom bed because of reactions in the pores of the particle.
- Only some N_2O is formed when NO is reduced during its journey up through the combustion chamber.
- N_2O is formed from HCN. This is a slow process (taking seconds) and it therefore takes place principally above the bottom bed.

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[1] 240 ppm NO can give 120 ppm N_2O. 10% of that is 12 ppm N_2O.

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Table 1 Survey of N_2O emissions from CFBBs during normal operation

Boiler type (design load)	**Load**	**Fuel**	**N_2O**	**Remarks**
CFB (20 MW)	18 MW	RDF (Municipal waste)	12 ppm 10	$O_2 \approx 6\%$ $NO_x \approx 240$ ppm Limestone
CFB (50 MW)	51 MW	Wood waste	19 ppm 14	$O_2 = 4–5\%$ $NO_x = 45$ ppm
CFB (20 MW)	–	Peat	10 ppm 6	$O_2 = 5.5\%$
CFB (40 MW)	26 MW	Peat	75 ppm 76	$O_2 = 4.5\%$ $NO_x \approx 100$ ppm $SO_2 = 80$ ppm Limestone
	33 MW	Coal	56 ppm 49	$O_2 = 5.7\%$ $NO_x \approx 160$ ppm
	34 MW	Coal + 8% peat	69 ppm 62	$O_2 = 4.0\%$ $SO_2 = 146$ ppm Limestone

Table 2 The Fuels

Type	Brown coal	Bituminous coal	Petroleum coke
Size, mass mean, mm	*	9	10
% smaller than 1 mm	0	0	0
Volatiles % maf	57	35	14
Proximate analysis, %			
Combustibles	80	87	91
Ash	5	7	2
Moisture	15	6	7
Ultimate analysis, % maf**			
C	70	85	92
H	5	6	4
O	23	6	0
S	0.8	1.6	1.8
N	1.3	2.1	1.7

* The brown coal was supplied as uniform cylinders, diameter 60 mm, length 35 mm.

** Preliminary values

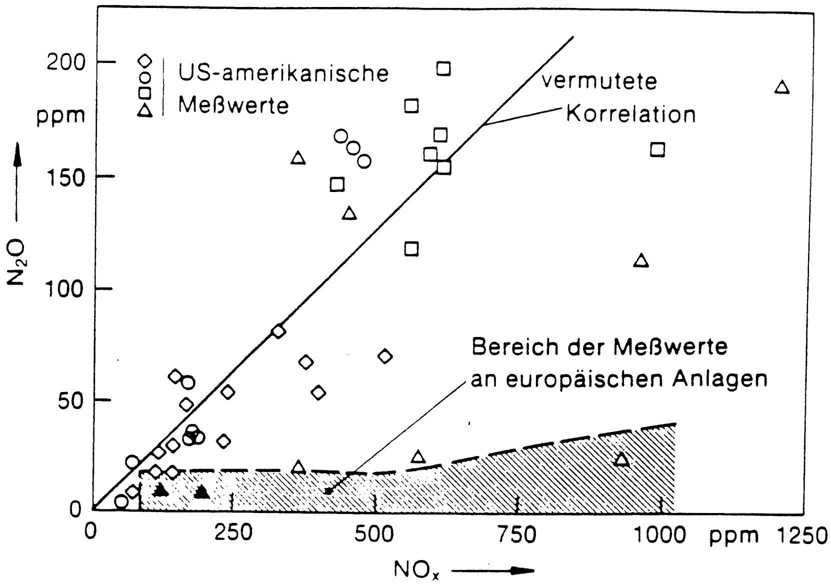

Figure 1 Measurements of N_2O from research plants, as well as from commercial plants in the USA and Europe. From (10).

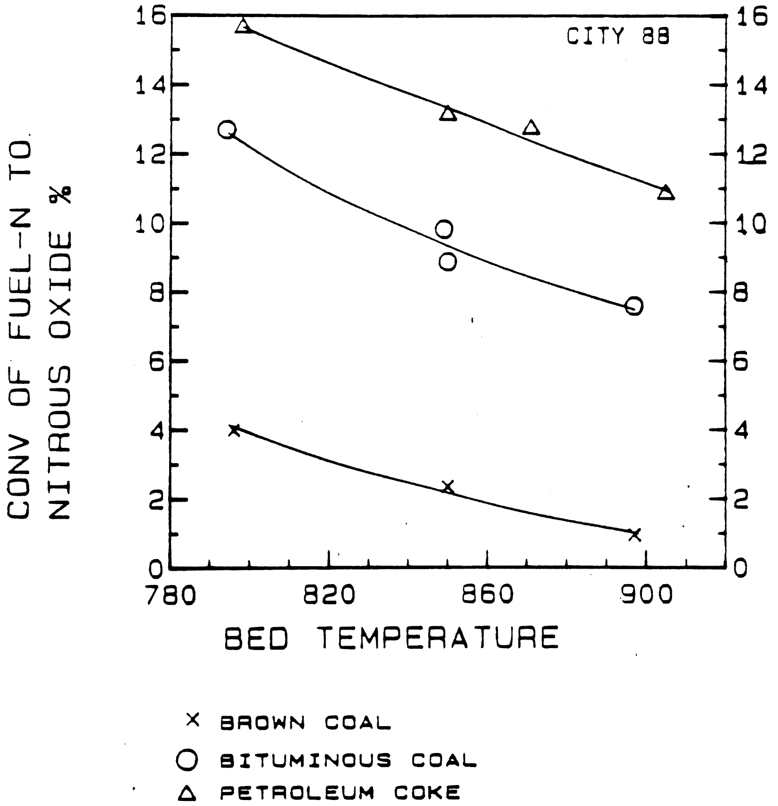

Figure 2 Conversion of fuel nitrogen to N_2O versus bottom bed temperature in the CFBB. From (4). Based on a preliminary ultimate analysis.

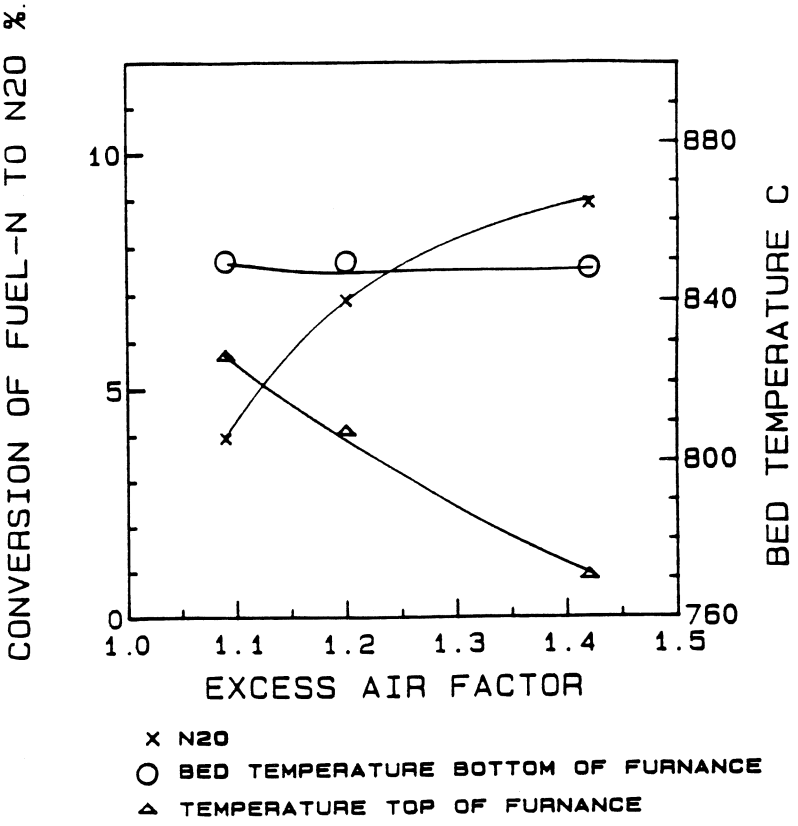

Figure 3 Conversion of fuel nitrogen to N_2O versus excess air factor in the CFBB. Bottom and top bed temperatures are also shown. From (4). Based on a preliminare ultimate analysis.

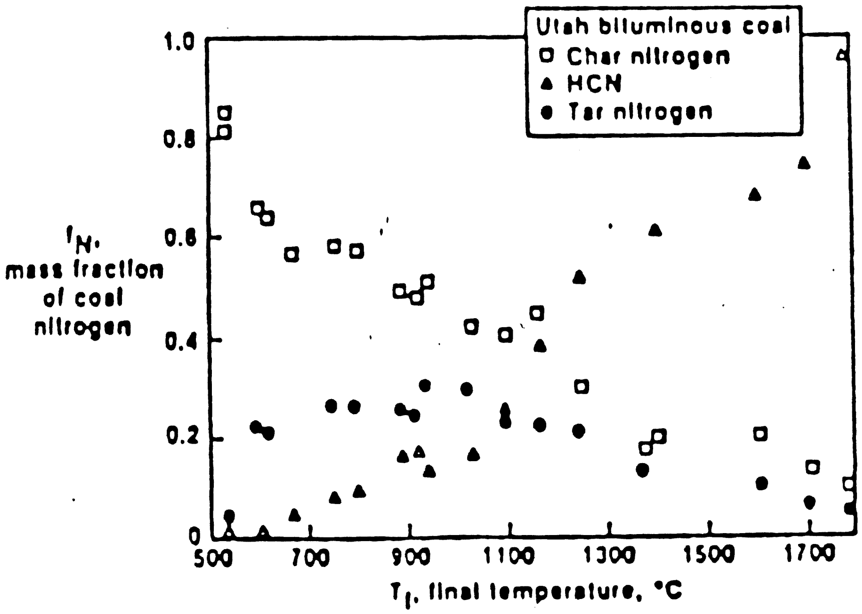

Figure 4 Nitrogen distribution from a sub–bituminous coal heated up to different final temperatures. From (5).

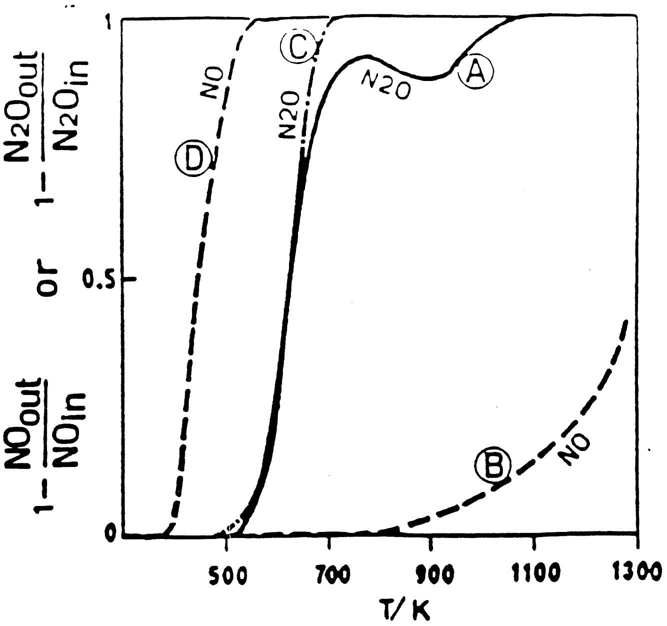

Figure 5 Reduction of NO and N_2O on a Pt.Rh catalyst. From (8).

Curves A and B: without reducing gases

Curves C and D: with 0.15% CO present

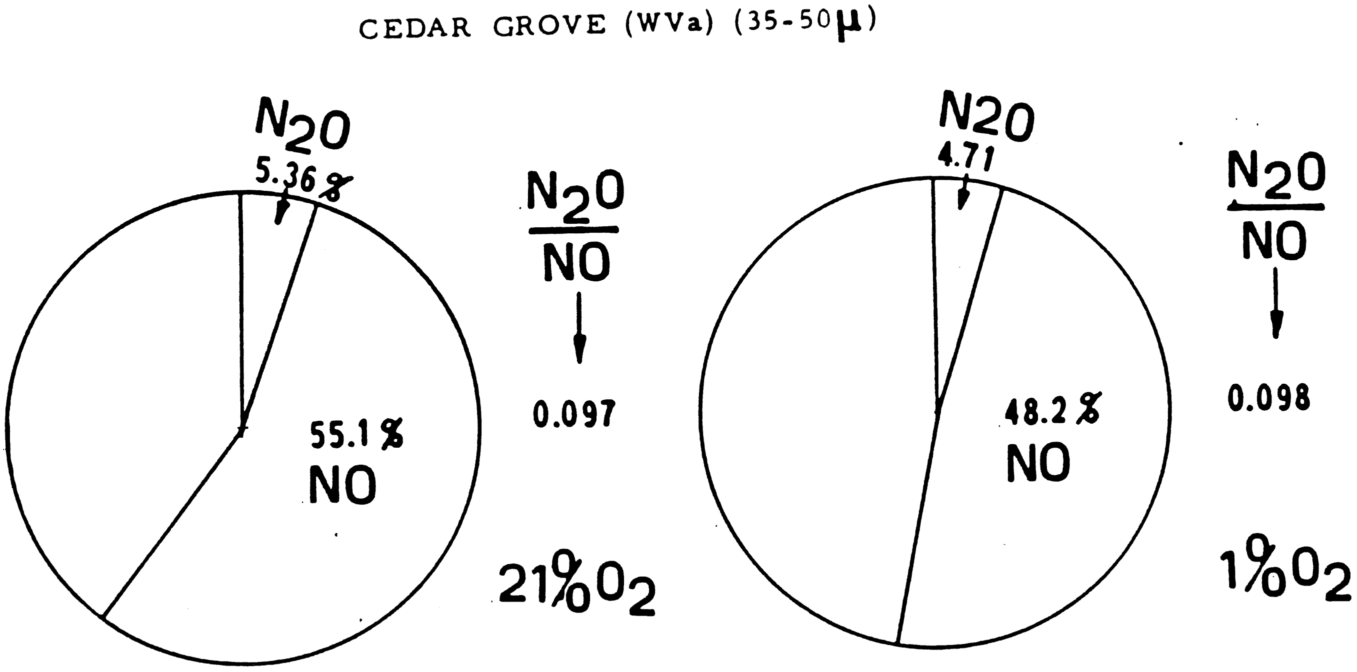

Figure 6 Fractions of char nitrogen transformed into NO and N_2O during char combustion at two oxygen concentration levels. From (8).

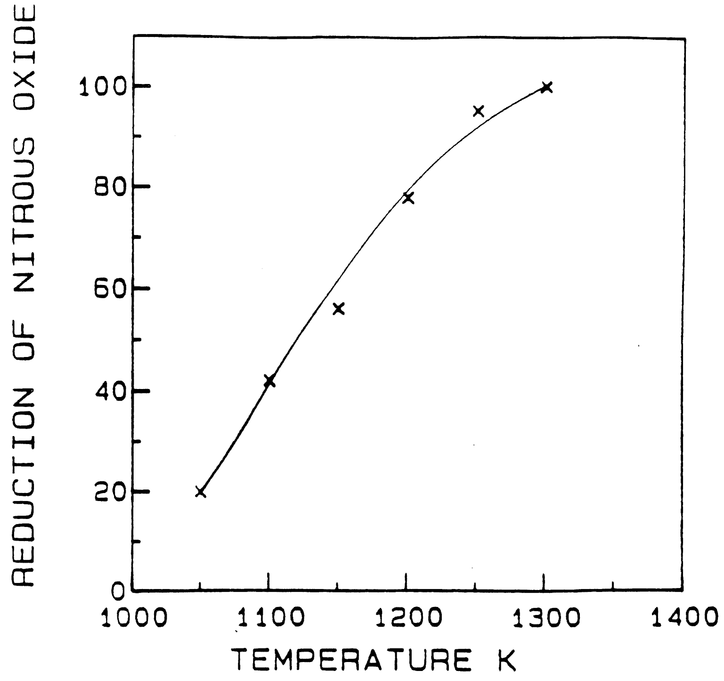

Figure 7 Reduction of N_2O as a result of the homogeneous reaction scheme for different temperatures. From (7).

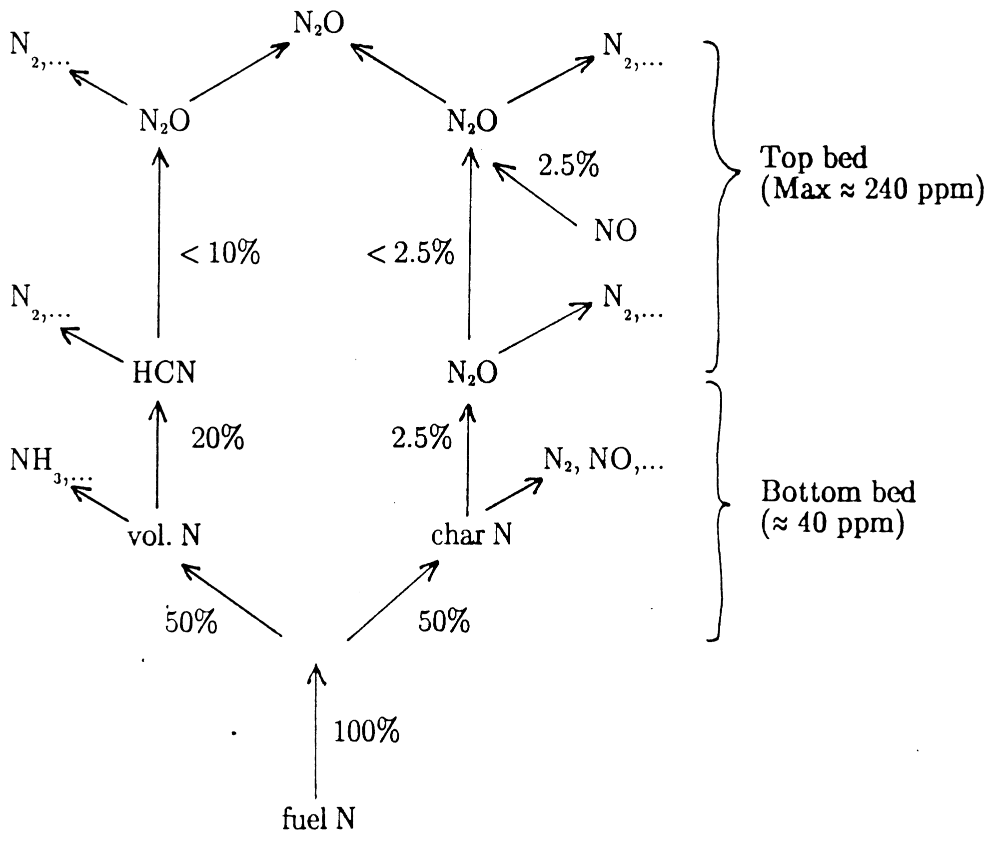

Figure 8 An estimation of N_2O formation along the gas path of a CFBB combustion chamber.

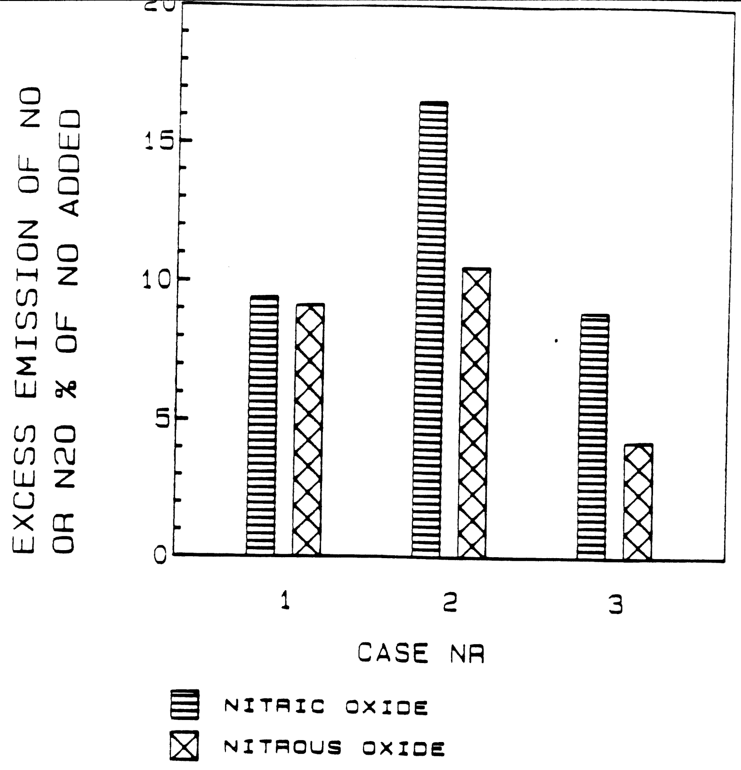

Figure 9 The fate of NO injected into the primary air duct of the CFBB. From (4).

1. Petroleum coke, 1200 ppm NO related to total air
2. Petroleum coke, 2200 ppm NO related to total air
3. Bituminous coal, 2200 ppm NO related to total air

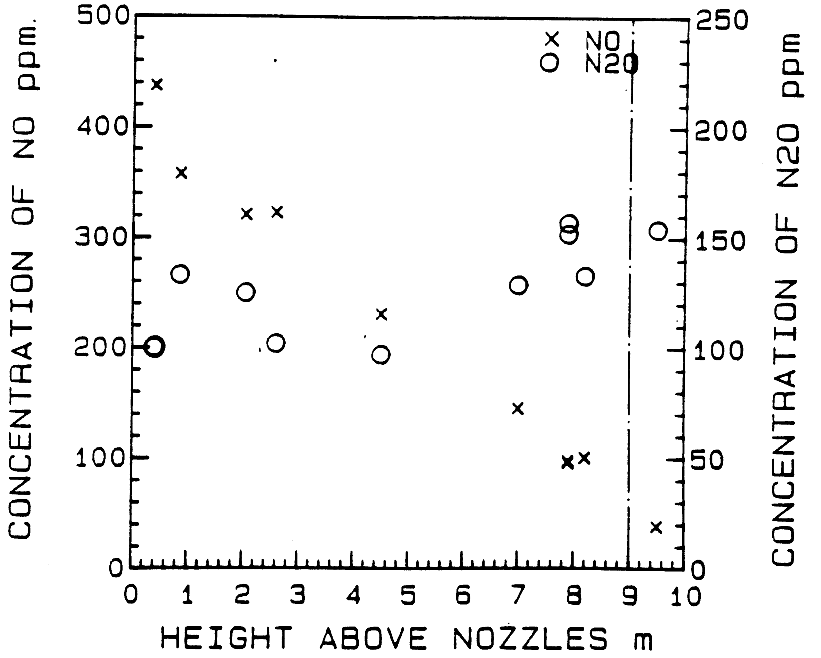

Figure 10 Concentrations of NO and N_2O along the gas path through the furnace of the CFBB. The entrance of the cyclone is indicated at 9 m. From (4).

Fuel: Bituminous coal.