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Proccedings of International Workshop on Nitrous Oxide Emissions held in June 7-9, 1994 in Turku, Finland

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Homogeneous and Heterogeneous Reactions for Formation and Destruction of N_2O - Results from the 12 MW CFB-Boiler at Chalmers

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ABSTRACT

Influence of homogeneous and/or heterogeneous reactions for formation and destruction of N_2O under fluidized-bed combustion conditions has been subject of discussion during the two previous workshops on N_2O (Lisbon, Tsukuba). The research program on N_2O emissions from combustion at the Chalmers circulating fluidized bed (CFB) boiler has been focused on projects that further elucidate the various reaction paths connected with N_2O. These projects include tests where NH_3, CH_3CN, NO and N_2O were injected into three locations in the combustion chamber when burning fuels of different volatile content. Apart from this, measurements of local concentrations of nitrogen species including NH_3 and HCN in the entire combustion chamber have been carried out with bituminous coal as fuel. The present paper summarizes the results from these tests. It is concluded that both homogeneous and heterogeneous reactions are important for the formation and destruction of N_2O. Furthermore, the various regions (bottom, top) of the CFB play different roles for the effective formation of the N_2O emitted.

INTRODUCTION

During the previous two N_2O-Workshops [1], [2] there were discusions on the significance of homogeneous and heterogeneous reactions for the emissions of N_2O from fluidized-bed combustion. It is the purpose of the present paper to illustrate the influence of homogeneous and heterogeneous reactions for the formation and reduction of N_2O in a circulating fluidized bed (CFB) combustor using measurement results from the 12 MW CFB boiler at Chalmers University of Technology

EXPERIMENTAL

Research equipment. The boiler and the measurement equipment have been described in several publications [3], [4], [5] and here only a few complementary remarks are given. Figure 1 shows the location of the measurement holes and measurement positions. Only results from the "CC" position (Figure 1) will be used below.

For the determination of NH_3, HCN and HNCO a Fourier transform infra-red (FTIR) analyser was used, a Bomem M110-D11 with a 500 cm^3 heated quartz glass cell in which an optical pathlength of 3.6 meter is achieved. The instrument is equipped with a MCT detector and the resolution was 4 cm^{-1}. Spectra were evaluated by spectral subtraction. The following wavelengths were used: NH3: 930 and 965 cm^{-1}; HCN: the dubble peak between 3200-3375 cm^{-1}; HNCO: absorption between 760-860 cm^{-1}. The determination of HCN and especially HNCO are very uncertain due to severe problems with spectral interferences from water and carbon dioxide, which could not be eliminated with the present equipment. The uncertainty is estimated, but care should be taken nevertheless when the absolute levels of HCN are discussed. For HNCO the concentration level is only an indication of the presence of HNCO. Further details about the determination of NH_3, HCN and HNCO can be found in [6].

The Tests. The present paper summarizes results from the following three projects:

1. Supply of CH_3CN, NH_3, NO and N_2O to three locations in the combuston chamber during operation with three different fuels.
2. Measurement of gas-concentration profiles along the height of the combustion chamber.
3. Recirculation of flyash from the secondary cyclone to the combustion chamber.

The Fuels. Several fuels were used in the projects. Two bituminous coals with very similiar fuel analysis served as reference fuel. In addition, high-volatile wood chips and low-volatile coke were used for comparison. The fuel analyses can be found in Table 1.

The operating conditions. A reference case with standard operating conditions was run during all tests in order to make interpretation easy. This reference case is characterized by the following operating conditions:

Bottom-bed temperature=850 °C; excess-air ratio=1.20 to 1.25;quotation of primary to secondary air corresponding to a calculated primary-air stoichiometry = 0.70 to 0.75; load=8 MW giving a fluidisation velocity of 5 to 6 m/s at the top of the combustion chamber with the air ratio chosen.

Since calcined lime is known to influence the formation of N_2O as well as to catalyze the decomposition, the tests were carried out without lime addition in order to avoid this furher complication. The bed consisted of commercial silica sand mixed with some fuel ash and char from the combustion of the various fuels.

RESULTS AND DISCUSSION

FORMATION OF N_2O

The increase of N_2O as function of height, Figure 2, is similiar to that obtained previously [3]. However, the present N_2O profile shows a more pronounced formation in the lower part of the combustion chamber than the previously measured one.
This formation may be caused by several processes:

1. Oxidation of volatile nitrogen species, such as NH_3, HCN and HNCO, which are present in the lower part of the combustion chamber (Figure 3-5) together with volatiles such as total hydrocarbons and hydrogen, Figure 6.
2. Simultaineous reduction of NO, especially in the bottom bed region, Figure 2.
3. Combustion of the char, in the bottom below the 2 meter level where most of the char is located and burns, Figure 7.

In order to study the significance of these processes a series of tests have been carried out, the results of which will be discussed in the following.

Formation of N_2O from Volatile Nitrogen. When CH_3CN was injected to the bottom of the combustion chamber during combustion of bituminous coal, 35% of the CH_3CN added was oxidized to N_2O, Figure 8. This value was calculated by measuring the excess emission of N_2O in the stack caused by the CH_3CN injection considering the N_2O reduction along the height of the combustion chamber as obtained from separate N_2O injection tests presented in [17], Figure 9. In a similiar test with NH_3 injection only about 5-10% of the NH_3 was oxidized to N_2O, Figure 10.These tests prove that volatile nitrogen in the form of HCN and NH_3 can explain some of the increase of N_2O in the lower part of the combustion chamber as caused by homogeneous conversion in spite of the high concentration of solids. A larger fraction of HCN than of NH_3 is oxidized to N_2O, but since the concentration of NH_3 is about four times higher than that of HCN (Figures 3 and 4) the N_2O formation from NH_3 oxidation cannot be neglected. The larger tendency of HCN to form N_2O compared to NH_3 is in agreement with calculations with kinetic models using homogeneous reactions, [7] to [9], and with laboratory investigations, [8] and [9].

Formation of N_2O when NO is Reduced. Injection of NO to the bottom of the combustion chamber during combustion of bituminous coal showed that 45% of the NO reduced was found as N_2O, Figure 11. This proves that part of the NO reduced at the bottom of the combustion chamber (Figure 2) is transformed into N_2O.The mechanism is however unclear. Is it a pure homogeneous step where, according to calculations [9],

[7], NO reacts with NCO radicals to form N_2O or is char involved? In order to investigate this, NO was also injected when coke was used as a fuel and the influence of volatile nitrogen was minimized. In this case 35% of the NO reduced was converted to N_2O (Figure 11). On the other hand, in the case with almost no char present (and probably less HCN also), the wood chips case, the lowerst conversion of added NO was obtained. These tests prove that the char-related NO reduction is important for the formation of N_2O as well. The mechanism is however unclear. If the char-related N_2O formation is a purly heterogeneous step, which was suggested by Tullin & Sarofim [10] or if a homogeneous step is also involved, according to the disussion in [5], remains to be investigated.

Formation of N_2O from Oxidation of Char Nitrogen. Combustion of coke without any injection of chemicals leads to the highest conversion of fuel nitrogen to N_2O of all investigated fuels. This is shown in Figure 12 together with results from other investigations carried out in CFB combustors of various sizes. (A key to Figure 12 is found in Table 2.) All investigations yield a higher conversion of fuel nitrogen to N_2O for fuels with a lower volatile content. The same result was also obtained in an investigation of emissions from a bubbling fluidized bed [14].
During the test with coke as fuel in the Chalmers boiler most of the fuel nitrogen was bound to the char fraction of the fuel and formation of N_2O during char combustion is therefore the most plausible reason for the high overall fuel nitrogen conversion to N_2O. On the other hand, primary formation of NO during char oxidation and secondary formation of N_2O when NO is reduced on char (see above) cannot be exluded. In other words, it is difficult to distinguish between indirect formation from NO reduction on char surfaces and direct formation from char nitrogen oxidation to N_2O. The flyash-recirculation experiment discussed below is a further effort to understand the role of char.

Recirculation of Flyash to the Combustion Chamber. Figure 13 shows the result from a 4.5 hours test with flyash recirculation from the secondary cyclone to the combustion chamber. The test can be divided into five separate periods. Period I and V correspond to the reference conditions without flyash recirculation. Period II is a case with flyash recirculation. The primary fuel feed rate was kept constant and this resulted in a lower overall excess-air ratio during this period. During period III flyash recirculation substituted the primary fuel and the same excess-air level was maintained as during period I (reference conditions). Finally, during period IV the flyash recirculation was stopped, but the primary fuel feed rate was kept constant for another 30 minutes leading to an increase of the overall excess-air ratio before the reference conditions were attained again, period V. Substitution of the primary coarse fuel with fine devolatilized char particles contained in the recirculated flyash led to an increase of the combustion in the cyclone. This is demonstrated by the difference in behaviour between oxygen concentration measured 4.8 meters from the bottom of the combustion chamber and the concentration measured in the stack as seen in Figure 13. The oxygen concentration at 4.8 meters did not change when the flyash recirculation was started or stopped. Also, the oxygen concentration in the inlet of the primary cyclone was higher during period III (compared to period I and V) than the oxygen concentration in the stack, and this is another proof of the combustion of fines in the cyclone. Finally the CO concentration increased followed by an increase of the temperature after the cyclone, and this is also an indication of cyclone combustion. Interpretation of the N_2O (and NO) data is far more complicated because of the simultaineous change of local oxygen concentration and temperature in the cyclone, parameters which are known to influence both N_2O and NO [11],[4]. For this reason the various differences between the periods are summarized in a qualitative way in Table 3. It is most important to point out the difference between period I and III. Period III where more combustion of devolatilized char particles took place, led to a much higher concentration of N_2O in the stack, than during period I, despite the higher temperature in the cyclone. This is taken as a poof of N_2O formation from oxidation of char nitrogen. The imediate change of the NO reduction performance when the flyash recirculation was started or stopped (period I to period II; period III to period IV) did not give any corresponding change of the N_2O emission, probably because of the simultaineous change of both temperature and excess-air ratio.

REDUCTION OF N_2O

The N_2O injection tests, Figure 9 show that injected N_2O was more effectivly reduced during combustion of the high-volatile wood chips than in the case when the boiler was run on the low-volatile coke. This means that the volatiles in the wood chips promote a radical-induced reduction of N_2O in agreement with the homogeneous gas phase reaction schemes. This reaction seems to be far more important for the reduction of N_2O than the large amounts of char present in the combustion chamber when coke was burned, char which could be expected to favour the char-catalyzed N_2O reduction according to the investigations carried out by de Soete [15] and Suzuki et al. [16].
In [17] an estimation was carried out of N_2O reduction in the combustion chamber during combustion of bituminous coal. The calculation was based on mass flows and content of char and solids taken from the measurements during the actual injection test. The boiler was treated as a plug flow reactor and simple first order kinetics evaluated by Johnsson [18] were adopted. The results of the calculations are shown in Figure 14. With the actual concentrations of solids and char and the calculated residence times, both heterogeneous reduction on char and on bed material are shown to be important parallel to the thermal decomposition in the gas phase. The importance of the char found is probablly an overestimation due to the simple kinetic expression used. The

influence of radicals could not be included at this stage of calculation. Finally, both measurements and calculations show that the reduction potential is extremly high when N_2O was injected to the bottom of the combustion chamber. This means that, if the N_2O emission should be substantially decreased by increasing the reduction potential, this should be done by further increasing the N_2O reduction capacity in the upper parts of the combustion chamber and/or in the cyclone.

CONCLUSIONS

Formation of N_2O. N_2O is formed from both volatile and char nitrogen, and when NO is reduced both homogeneously and with char surfaces present. All these three reaction paths contribute to the N_2O formation seen in Figure2. The relative importance of the various reaction paths cannot be evaluated at present.

Reduction of N_2O. Both homogeneous and heterogeneous reactions are important for the total N_2O reduction potential achieved in a full-scale CFB combustor. The relative importance of the various reduction paths cannot be evaluated at present. Efforts in increasing the N_2O reduction should be focused on the upper parts of the combustion chamber and the cyclone.

ACKNOWLEDGEMENT

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Table 1 Fuel Characteristics

Type	Wood-chips	Bituminous coal[a]	Bituminous coal[b]	Coke
Size, mass mean (mm)	9.6	6.0	not analysed	2.5
% smaller than 1 mm	0.0	28.5	not analysed	54.5
Volatiles, % m.a.f.	78.0	39.9	28.2	3.4
Proximate analysis, % as delivered:				
Combustibles	71.1	78.6	88.6	79.5
Ash	0.2	6.6	6.7	9.8
Moisture	28.7	14.8	4.7	10.7
Ultimate analysis, % m.a.f.:				
C	50.6	79.8	86.9	96.1
H	6.2	5.3	5.2	0.7
O	43.0	12.6	5.6	1.2
S	0.02	0.7	0.8	0.7
N	0.14	1.6	1.5	1.3

a The bituminous coal used in 12—MW CFB boiler.

b The bituminous coal used for the production of coke in a cokery.

Table 2 **Key to Figure 12**

	This work A o—o—o	Åmand[11] B *...*...*	Mann[12] C + – – +	Moritomi[13] D ●—●—●
Bed temp., °C	850	850	830–875	850
Excess air ratio	1.2–1.25	1.2–1.25	unknown	1.4–1.5
Prim. air stoichiometry	0.7–0.75	0.7–0.75	unknown	unknown
Bed area, m^2	2.9	1.8	0.20	0.008
Height of furnace, m	13.5	8.5	12.8	5.0
Ca/S	0	0	0	0
Fuels used (% volatiles, maf)	Coke (2.5)	Pet. coke (14.4)	Bitum.coal (39.5)	Idemitsu–B coal (30.9)
	Bitum.coal (35.7)	Bitum.coal (35.5)	Subbit.coal (42.0)	Datong coal (33.1)
	Bitum.coal (39.9)	Bitum.coal (35.5)	Lignite (50.7)	Taiheiyo coal (54.8)
	Wood-chips (78.0)	Brown coal (53.1)		

Table 3 Flyash recirculation Test in Figure 13

	Change between subsequent periods			
Effect on	I→II	II→III	III→IV	IV→V
Flyash–recirc.	↗	→	↘	→
Coarse fuel flow	→	↘	→	↗
Excess air ratio	↘	↗	↗	↘
Temp. after cyclone	↗	→	↘	→
Emission of CO	↗	→	↘	→
Emission of N_2O	↘	↗	→	↘
Emission of NO	↘	↗	↗	↘

unchanged = → increased = ↗ decreased = ↘

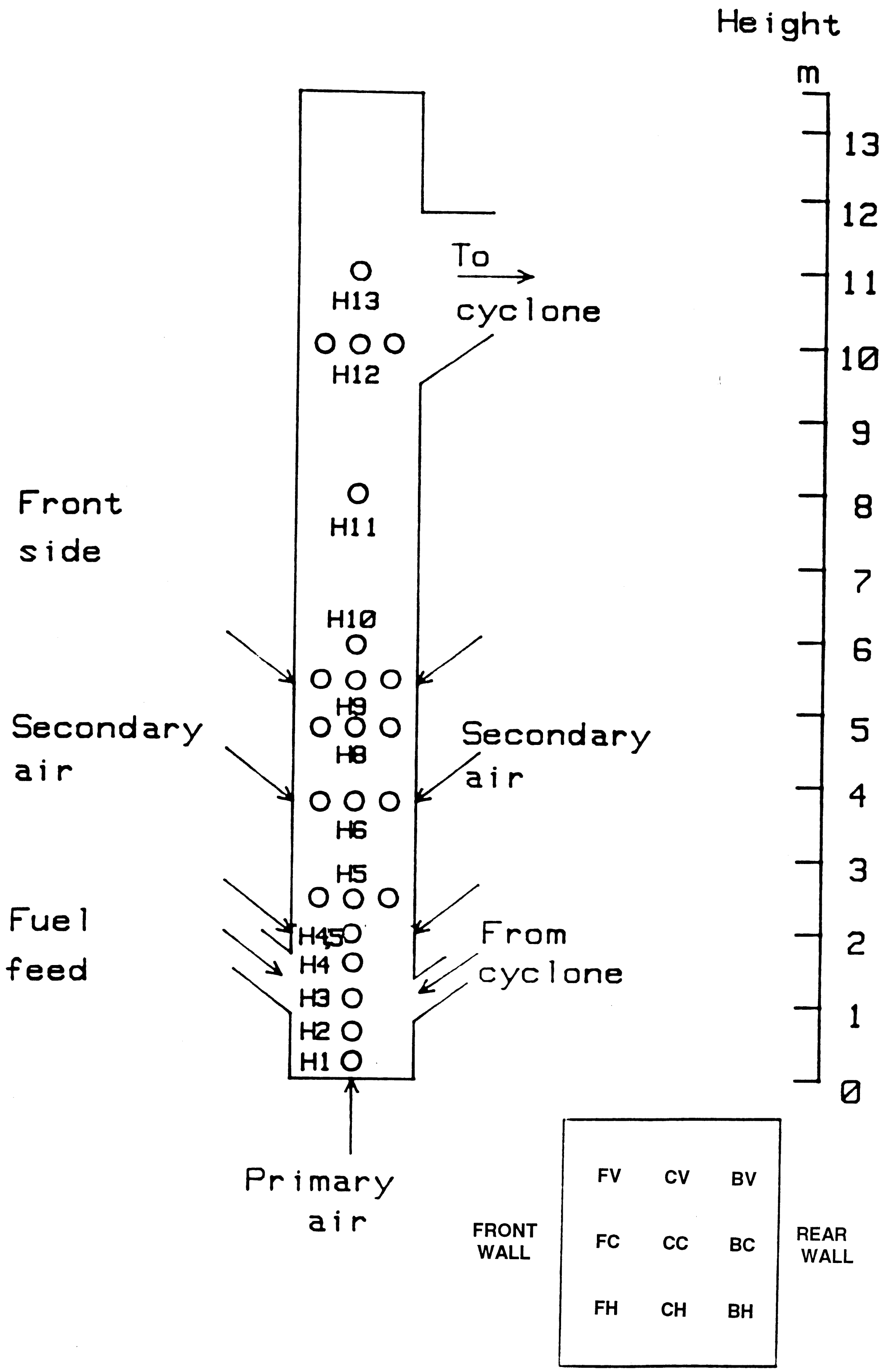

Figure 1. The 12 MW CFB-boiler at Chalmers with measurment holes (H1-H13) indicated. FH, FC, FV, CH, CC, CV, BH, BC and BV in the small figure are measurement positions in the cross-section of the combustion chamber.

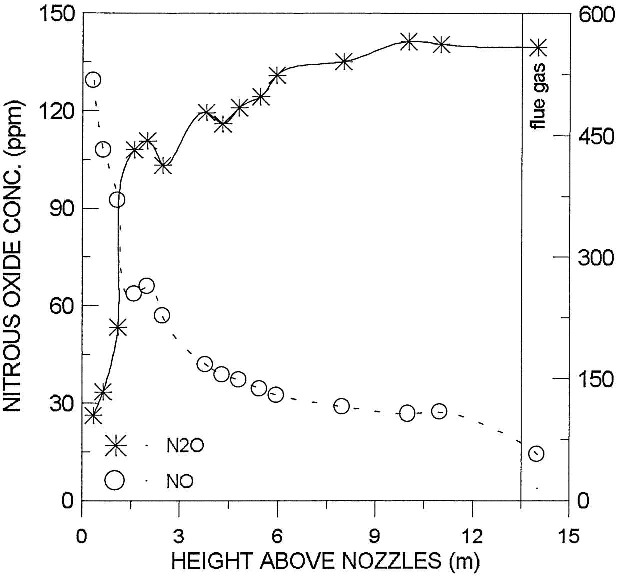

Figure 2. Vertical profiles of N_2O and NO along the centerline in the combustion chamber. Fuel: bituminous coal. Operating conditions: reference case.

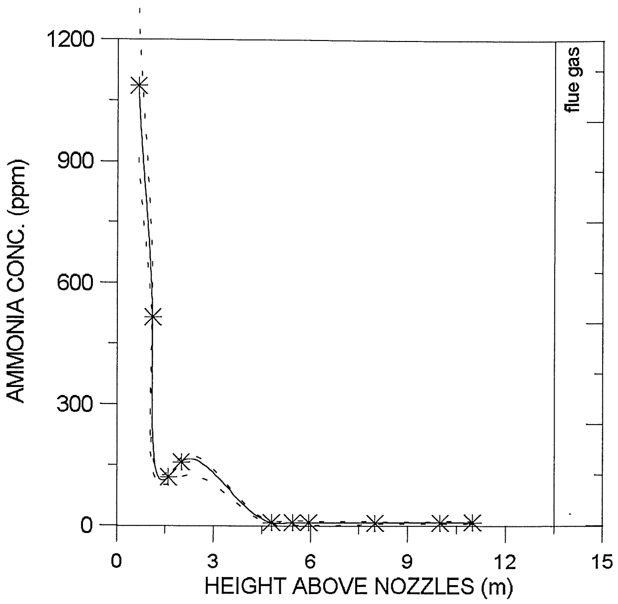

Figure 3. Vertical profiles of NH_3 along the centerline in the combustion chamber. Dotted lines indicate the uncertainy in the NH_3 determination. Fuel:bituminous coal. Operating conditions: reference case.

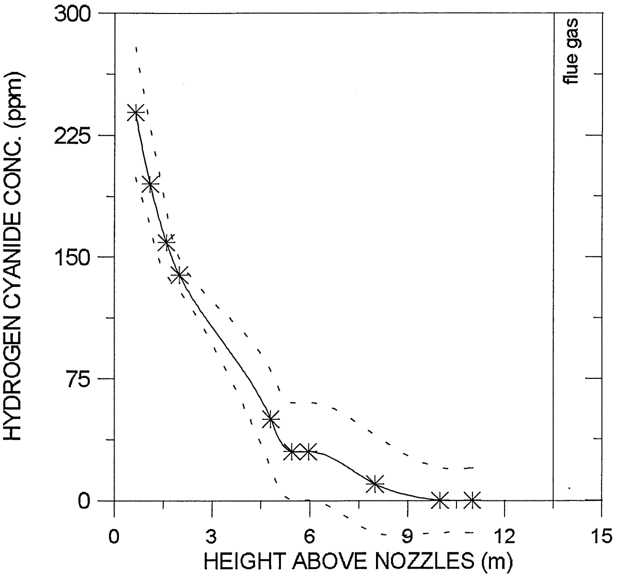

Figure 4. Vertical profiles of HCN along the centerline in the combustion chamber. Dotted lines indicate the uncertainy in the HCN determination. Fuel: bituminous coal. Operating conditions: reference case.

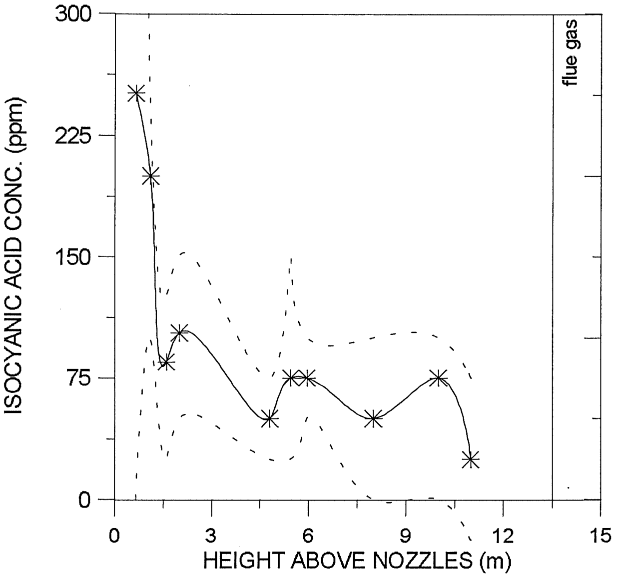

Figure 5. Vertical profiles of HNCO along the centerline in the combustion chamber. Dotted lines indicate the uncertainy in the HNCO determination. Fuel: bituminous coal. Operating conditions: reference case.

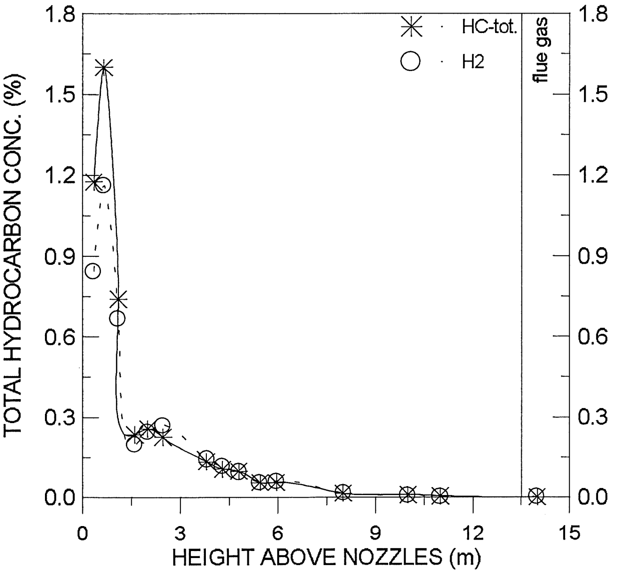

Figure 6. Vertical profiles of HC-tot and H_2 along the centerline in the combustion chamber. Fuel: bituminous coal. Operating conditions: reference case.

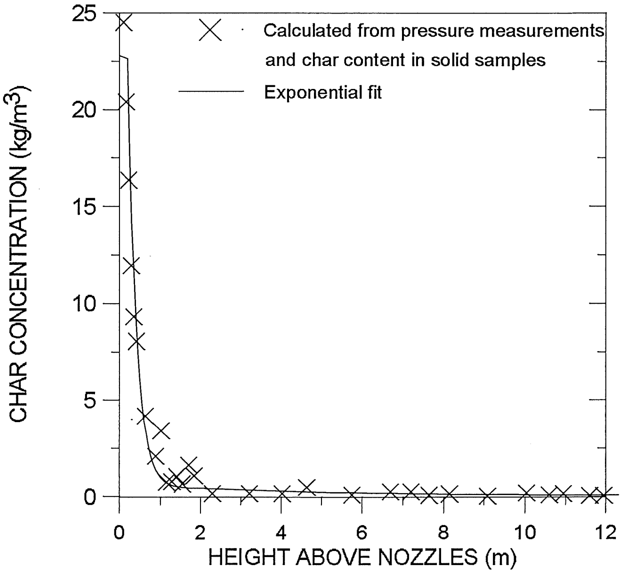

Figure 7. Char concentration in the combustion chamber based on pressure drop measurements and solid samples extracted from the combustion chamber. Fuel: bituminous coal. Operating conditions: reference case.

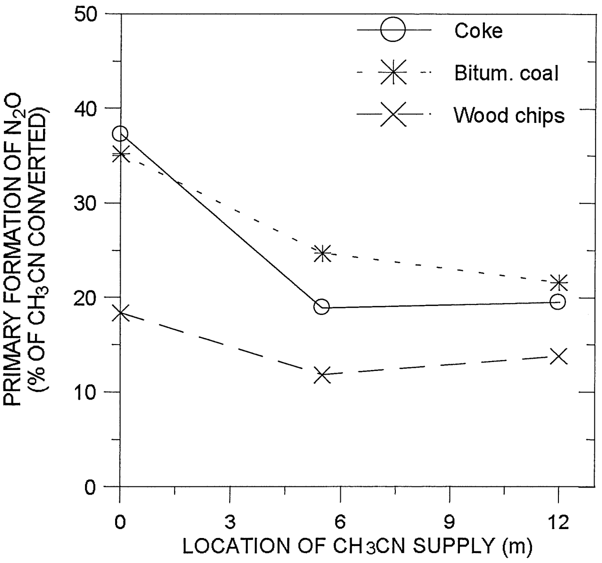

Figure 8. Primary formation of N_2O as a function of the location of CH_3CN supply for the three fuels. Operating conditions: reference case. Rewritten from [5].

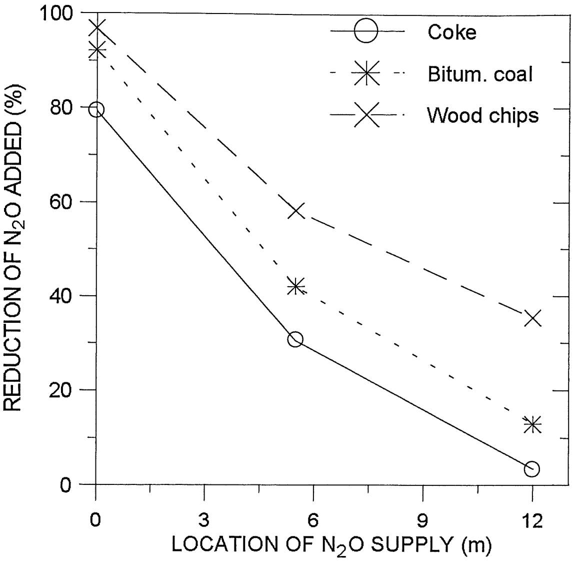

Figure 9. Reduction of N_2O added to the boiler as a function of the location of injection for three fuels. Operating conditions: reference case. Rewritten from [17].

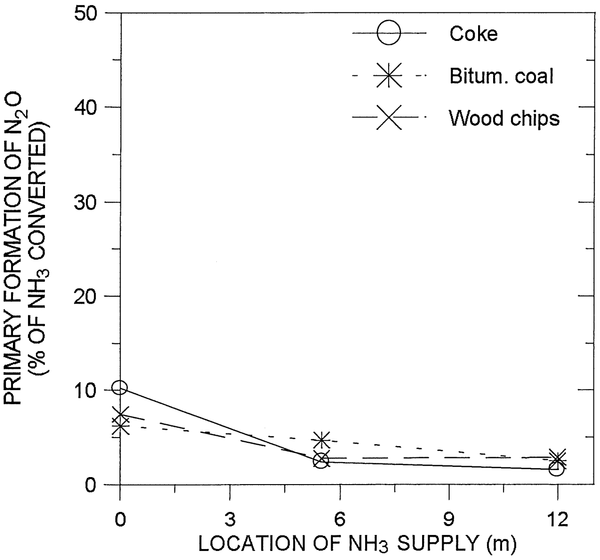

Figure 10. Primary formation of N_2O as a function of the location of NH_3 supply for the three fuels. Operating conditions: reference case. Rewritten from [5].

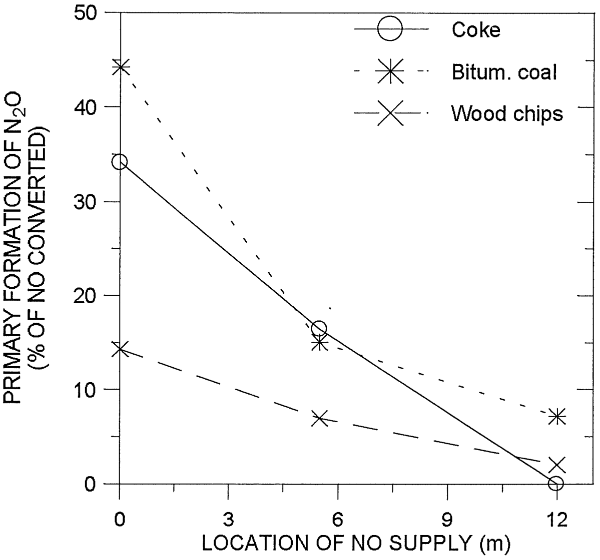

Figure 11. Primary formation of N_2O as a function of the location of NO supply for the three fuels. Operating conditions: reference case. Rewritten from [5].

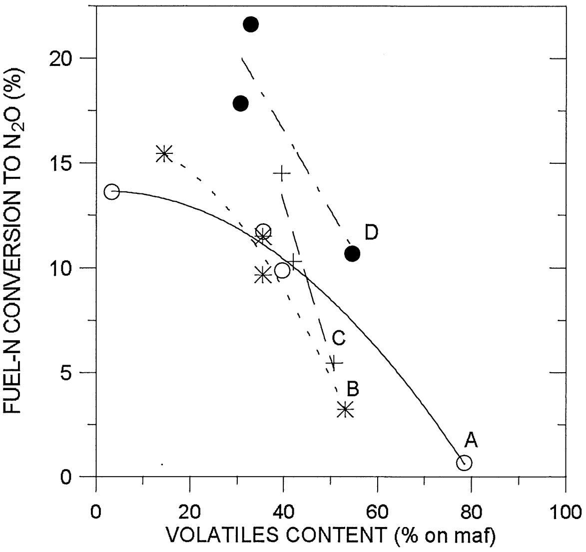

Figure 12. Influence of fuel volatiles on the conversion of fuel nitrogen to N_2O during combustion in CFB reactors without limestone supply, Key: see Table 2.

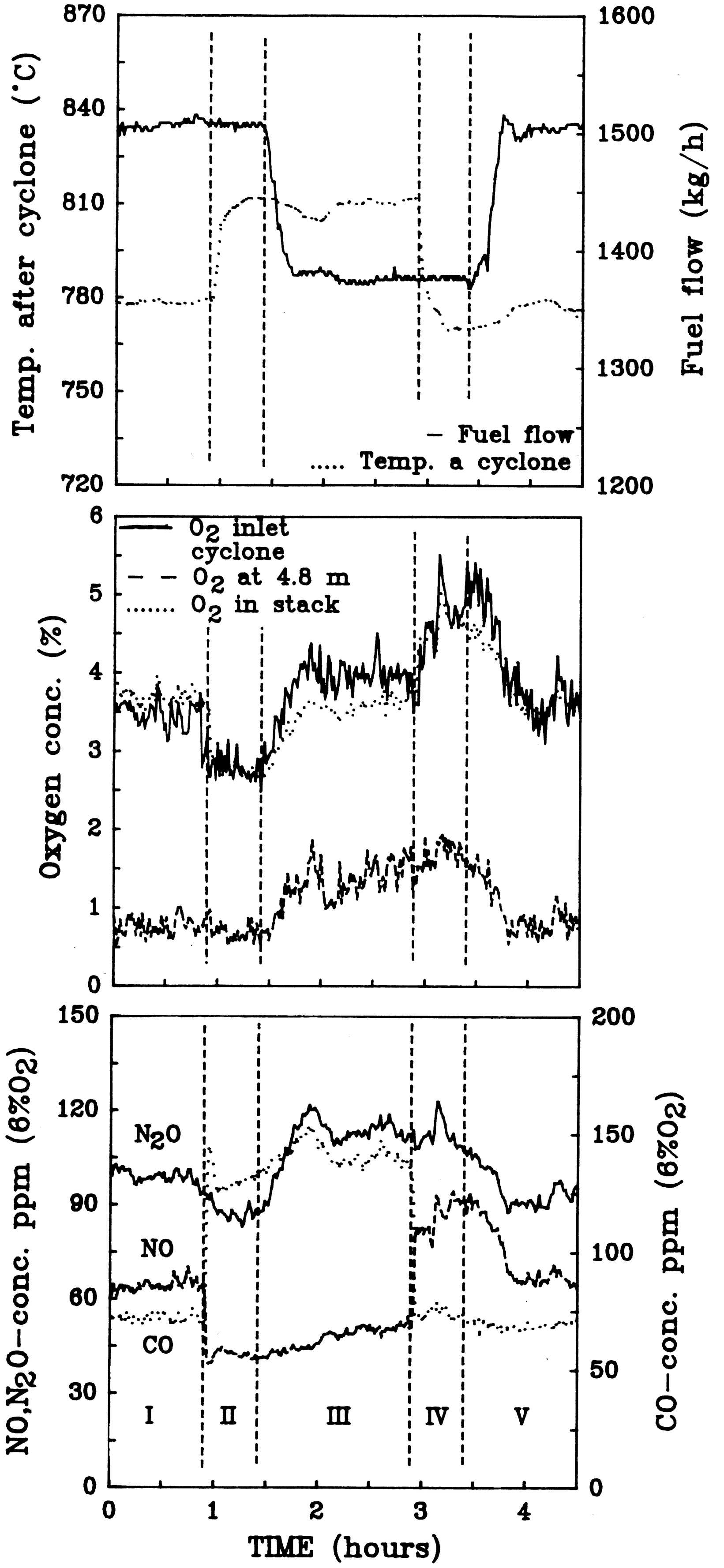

Figure 13. Flyash recirculation test with bituminous coal.
Operating conditions: reference case. Events:
Period I: flyash recirc./fuelflow=0
Period II: flyash recirc./fuelflow=0.6; no change of fuel flow
Period III: flyash recirc./fuelflow=0.6; change of fuel flow
Period IV: flyash recirc./fuelflow=0; no change of fuel flow
Period V: flyash recirc./fuelflow=0; change of fuel flow

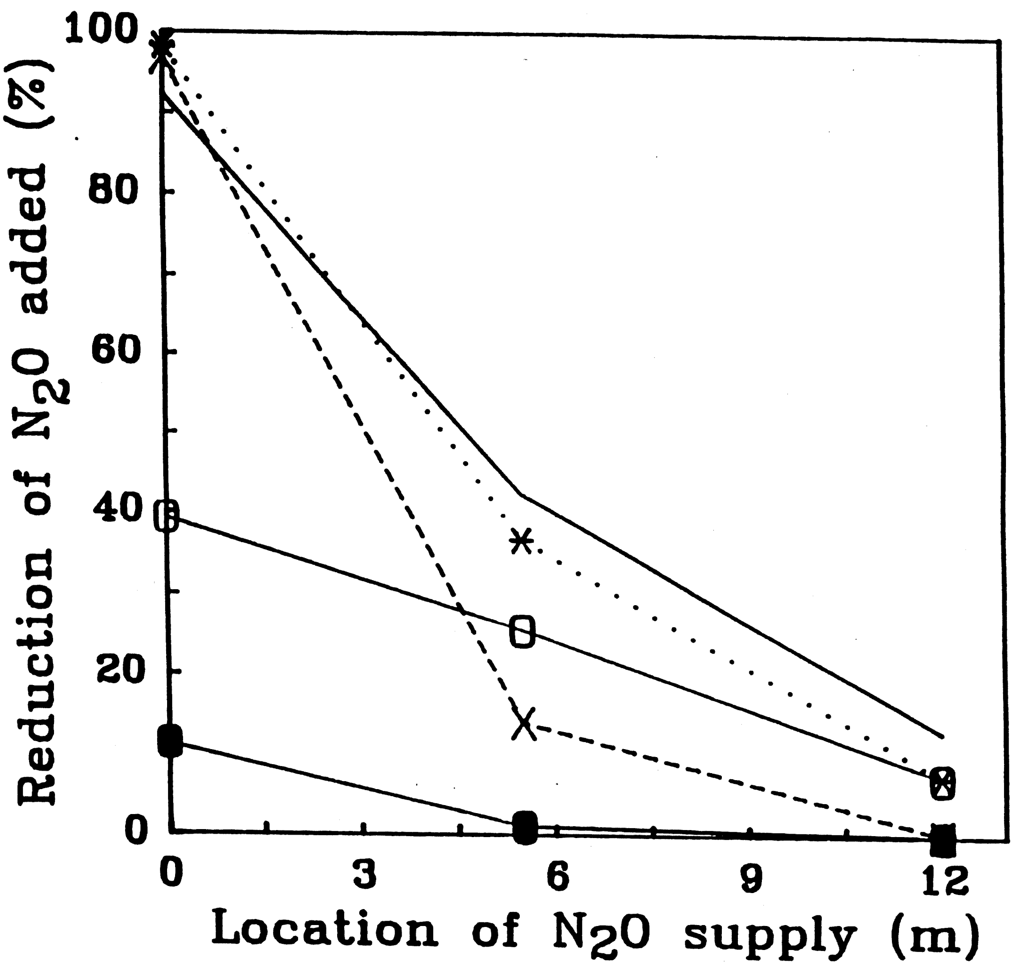

Figure 14. Comparison between measured and calculated reduction of N_2O. The bituminous coal case is taken from Figure 11 and the calculation is based on an evaluation of kintetics in [18].

●——●	Quartz sand analytical grade [19]
x - - - x	"Cedar Grove" char [15]
o——o	Thermal decomposition [20]
. . . . .	Parallel reactions
———	Measured N_2O reduction for bituminous coal (upper line)