Formation of N₂O in a Circulating Fluidized-Bed Combustor

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Formation of N_2O was studied in a circulating fluidized bed boiler by means of injection of CH_3CN, NH_3, or NO to various locations in the combustion chamber. The resulting changes in the emissions of NO and N_2O were registered and the formation of N_2O was estimated by means of the measured reduction (from similar experiments with injection of N_2O to the combustion chamber). This was done while burning fuels with high as well as low volatile content: wood chips, bituminous coal and metallurgical coke. The results show that homogeneous gas-phase reactions are important for the formation of N_2O despite the high particle loading in the combustion chamber. Cyanides show a higher tendency to form N_2O than ammonia. The concentration of NO and char are also important factors contributing to the formation of N_2O.

Introduction

Formation and destruction of N_2O in connection to combustion in fluidized bed have been intensively studied during the last few years and a number of reviews have been published.[1-3] Furthermore, the problem of N_2O has been treated in a series of biannual workshops.[4-6] Extensive experimental work has been carried out on small laboratory-scale fluidized bed reactors[7,8] as well as on larger test facilities such as the 12 MW_{th} circulating fluidized bed (CFB) boiler at Chalmers University of Technology.[9,10] Recently, the reduction of N_2O has been studied by injecting N_2O into the combustion chamber of this boiler.[11] In conjunction with the reduction tests, formation of N_2O was investigated, by similarly injecting various species that could contribute to the formation of N_2O. This is the subject of the present paper, which is focused on the formation of N_2O.

Formation of N₂O

The reaction mechanisms presented below are selected to be the most relevant ones for the present work. All reactions where lime or sulfur are involved have been excluded, since the full-scale experiments were carried out with low-sulfur fuels using a bed of silica sand.

Homogeneous Formation of N_2O. The formation of N_2O from injection of HCN, NH_3, and CH_3CN (CH_3CN decomposes into cyano species) into flames was first studied by Kramlich *et al.*[12] with the interest focused on pulverized coal flames. Modeling of the kinetics of the homogeneous reactions involving formation and destruction of N_2O under fluidized bed conditions was carried out by Kilpinen and Hupa,[13] and extensive measurements in a laboratory reactor combined with kinetic modeling were made by Hulgaard.[14] The basis for modeling in the works quoted is the reaction kinetic mechanism of Glarborg *et al*,[15] but in the latter works[13,14] a number of revisions and modifications were included, among them those suggested by Miller and Bowman.[16] It was shown that under conditions of fluidized bed combustion the predominant path to N_2O is

$$HCN + O \rightarrow NCO + H \qquad (R1)$$

$$NCO + NO \rightarrow N_2O + CO \qquad (R2)$$
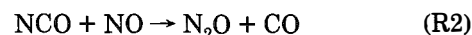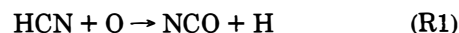
Amines can also form N_2O, although the yield is smaller than that of formation from cyanides,

$$NH_3 + NO \rightarrow N_2O + H_2 \qquad (R3)$$

$$NH + NO \rightarrow N_2O + H \qquad (R4)$$
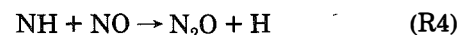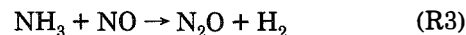
Heterogeneous Formation of N_2O Involving Char. Three mechanisms for formation of N_2O related to char have been proposed:[12] (1) oxidation of char nitrogen to N_2O (M1); (2) formation of N_2O as a byproduct of NO

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reduction on char surfaces (M2); (3) release of fuel nitrogen from the char to form HCN or NH₃, followed by gas-phase oxidation according to reactions R1–R4 (M3).

Extensive measurements on highly devolatilized chars have been carried out by de Soete[17,18] with the aim of determining the mechanism of N_2O formation from char. Mechanism M1 was found to be the only mechanism of some importance under the experimental conditions used. Mechanism M2 was ruled out on the basis of separate NO reduction experiments on the same chars since no N_2O was found. Similar NO reduction tests on char with a negligible N_2O yield have been made by others.[19–21] It should be emphasized that these NO reduction tests were made without oxygen present, except for the work by Mochizuki et al.[21] where the influence of oxygen was studied in separate tests. The influence of oxygen has also been noticed in other investigations.[22,23] The N_2O formation detected in the presence of oxygen was explained as an effect of NO reduction on char, but details of the mechanism were not given.

The conversion of char nitrogen to N_2O by mechanism M1 was typically 1–6%.[18] Similar results, but with slightly higher yields of N_2O (up to 10%), have been obtained in a laboratory-scale fluidized bed combustion experiment.[7] The reason for the higher yields may be explained by tests with a fuel which was devolatilized at various temperatures.[24] In an extreme case when the fuel was devolatilized at a temperature of 100 K below the combustion temperature, a conversion of char nitrogen to N_2O of 15% was achieved. The authors[24] explain this effect as an "indirect formation of N_2O with gases from char". This explanation is identical to mechanism M3. Further support for this mechanism is given by Suzuki et al.[25] who show the influence of residence time and NO concentration on mechanism M3. Tests on combustion of small batches of coal in electrically heated laboratory-scale fluidized beds have also been carried out by Tullin et al.[23] and Hayhurst and Lawrence.[2] In these studies the aim was to determine the relative importance of N_2O formation from volatile and char combustion. In the study of Tullin et al.[23] char combustion was found to be most important, while Hayhurst and Lawrence[2] claim that volatiles combustion is the most important source of N_2O. The reason for this discrepancy is unclear. On the basis of experimental work, Tullin et al.[23] state that the M2 mechanism is responsible for the formation of N_2O during char combustion. They also state that oxygen and NO are important. Oxygen

breaks up the aromatic structure of the char, and the nitrogen in the disrupted rings then reacts either with oxygen to form NO or with NO to form N_2O. This mechanism was tested in a combustion model to support the experimental findings.[26]

Purpose

The purpose of the present work is to study the significance of cyanides and amines for the formation of N_2O in a circulating fluidized bed boiler. The fact that cyanide tend to form N_2O in a homogeneous system according to reactions R1 and R2 at the bed-temperature level of a fluidized bed boiler does not mean that this actually takes place in a boiler. This uncertainty is caused by the unknown influence of particles such as sand, lime, char, and ashes which may disturb the transformation of radicals and also may catalyze other reactions, for instance, the oxidation of cyanides and amines to NO or the transformation of cyanides to amines.[27,28] The approach of the present tests was to add acetonitrile (CH_3CN) or ammonia (NH_3) to the combustion chamber of a circulating fluidized bed boiler in order to simulate the formation of cyanides or amines respectively. In the literature two tests of a similar kind have been reported.[29,30] In the tests by Bramer and Valk,[29] CH_3CN and NH_3 were added to the bed of a small laboratory fluidized bed reactor (diameter 10 cm). The tests by Buchtela and Hofbauer[30] were carried out in a 15-kW bubbling fluidized bed. Urea was used to simulate amines and kinoline to simulate cyanides. In both test facilities the injection tests were part of larger projects and reported very briefly. Furthermore, the results are not applicable to a circulating fluidized bed.

A second purpose was to study the three possible mechanisms of heterogeneous formation of N_2O by injecting NO to the combustion chamber in the same way as CH_3CN and NH_3. At least, it should be possible to notice if mechanisms M2 and M3 are active, since NO is involved in both of them.

In order to produce combustion situations dominated by volatiles or char, as well as intermediate cases, three fuels were selected which are quite different from each other with respect to volatile content: wood, bituminous coal, and metallurgical coke.

Experimental Section

The Boiler. The tests were run in the 12-MW$_{th}$ CFB boiler at Chalmers University of Technology (Figure 1). The boiler is built in the form of a commercial boiler with the combustion chamber made up of membrane tube walls with a height of 13.5 m and a cross section of about 2.9 m². Fuel is fed to the bottom of the combustion chamber through a fuel chute (1). The bed material entrained is separated from the gases in the hot cyclone

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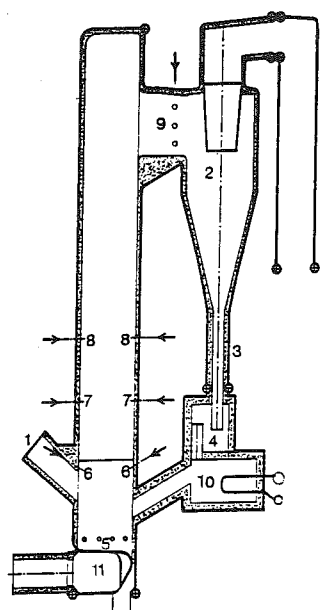
Figure 1. The 12-MW CFB boiler at Chalmers University of Technology: (1) fuel feed chute; (2) cyclone; (3) particle return leg; (4) particle seal; (5) bottom plate; (6) secondary air inlet at 2.2 m; (7) secondary air inlet at 3.8 m; (8) secondary air inlet at 5.5 m; (9) secondary air inlet in the inlet channel to the cyclone; (10) heat exchanger; (11) air plenum.
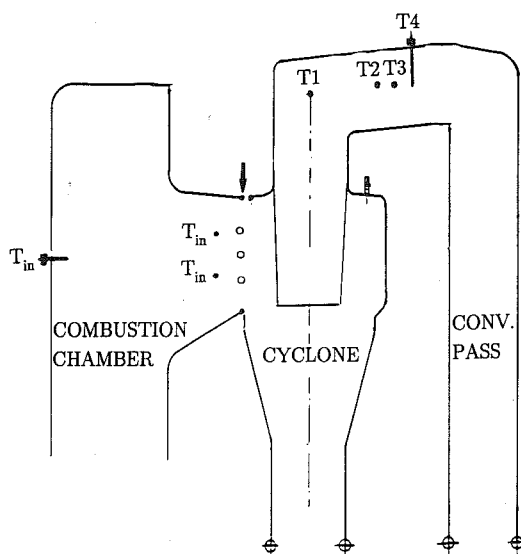
Table I. Fuel Characteristics

type	wood chips	bituminous coal[a]	bituminous coal[b]	coke
size, mass mean (mm)	9.6	6.0	not analyzed	2.5
% smaller than 1 mm	0.0	28.5	not analyzed	54.5
volatiles, % maf	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, % maf				
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.

thermocouples are important for the determination of the reaction environment when CH₃CN, NH₃, or NO were supplied to the cyclone.

Measurement Equipment. Data needed for the evaluation procedure were collected with a data-acquisition system. The concentrations of O₂, NO, N₂O, and CO were measured in the stack with continuous gas analyzers. A chemiluminescence analyzer was used for NO, a nondispersive infrared (NDIR) for N₂O and CO, and a paramagnetic analyzer for O₂. The analyses were made on dry gas, and the flue gases sampled therefore first passed a refrigerator before they were conducted to the various analyzers. The N₂O analyzer is cross-sensitive toward methane (CH₄). Also, a disturbance from SO₂ at concentrations higher than 500 ppm can cause a problem, but this level of SO₂ was not reached due to the low sulfur content of the fuels used. During normal operation CH₄ is not present in the flue gases leaving the plant. This was the case also during wood chips combustion according to regular checks by an on-line total hydrocarbon analyzer. Gas analysis was carried out at two locations in the combustion chamber in addition to the measurement in the stack. Gas was withdrawn through a cooled filter located at the end of each of two probes, and the particle-free gas was sent to on-line analysis for O₂, CO, NO, and total hydrocarbons. Gas from the probes was also collected (after drying) in Tedlar bags for further analyses of N₂O, H₂ and hydrocarbons on three gas chromatographs equipped with different columns and detectors: a thermal conductivity detector for H₂, an electron-capture detector for N₂O, and a flame-ionization detector for hydrocarbons.

In order to verify that all CH₃CN and and NH₃ reacted, especially when they were added into the entrance of the cyclone, an FTIR (Fourier transform infrared) analyzer, Bomem M110 with a resolution of 4 cm⁻¹, was used. NH₃ was analyzed at a wave number of 965 cm⁻¹ and HCN at 714 cm⁻¹. Gas to the FTIR analyzer was sampled from the flue gas duct in heated sample lines, and a heated sample cell was used as well. The volume of the cell is 0.5 L and the optical path length was set to 3.6 m.

Fuels. The reference fuel was a bituminous coal from Colombia. In addition, high-volatile wood chips and low-volatile coke were chosen for comparison. The wood chips were produced for research purposes out of dried pieces of pine which had been left as waste from furniture and house manufacture. The coke, normally used in the steel industry, was produced in a cokery in Oxelösund out of a blend of eight commercial imported bituminous coals. The rest-volatile content after devolatilization at the cokery was only 3.4% measured on a dry and ash-free basis. Fuel analyses are given in Table I. The three fuels burned differently in the CFB boiler. The coke burned slowly (low reactivity) which led to an accumulation of large quantities of char in the combustion chamber. On the other hand, when coke was burned the concentration of hydrocarbons in the combustion chamber was very low. The wood chips behaved in an opposite way: there was almost no accumulation of char, but the concentration of hydrocarbons (and hydrogen) was very high. The bituminous coal showed values in between those of the two

Figure 2. Top of the combustion chamber, the cyclone, and the cyclone exit duct (cf. Figure 1). Temperature measurement locations (T) are shown.

(2) and passed back to the combustion chamber through the return leg (3) and particle seal (4). Primary air is introduced through nozzles in the bottom plate (5), and secondary air can be injected through several inlets, consisting of sets of nozzles, located along the combustion chamber at various heights as indicated by arrows in Figure 1. The lowest secondary-air inlet (6) is located at 2.2 m, the second inlet level (7) at 3.8 m, and the third and highest level (8) at 5.5 m. Secondary air can also be introduced to the entrance of the hot cyclone (9). In the present tests only the lowest inlet at 2.2 m was used. The inlet at 5.5 m and at the entrance of the cyclone can be supplied with recycled flue gases, which were used as carrier gas for the injection of concentrated CH₃CN, NH₃, or NO into the combustion chamber.

The bed temperature is controlled by a heat exchanger (10) located in connection to the particle seal and by recycled flue gases which are mixed with the primary air in the air plenum (11) before entering the combustion chamber. Figure 2 shows the location of various thermocouples at the top of the combustion chamber as well as in the exit duct of the cyclone. These

Table II. Content of Solids and Char in the Combustion Chamber for the Three Fuels (kg)

	wood chips		bituminous coal		coke	
	0–2.3[a]	2.3–13[a]	0–2.3[a]	2.3–13[a]	0–2.3[a]	2.3–13[a]
solids	1160	290	1040	310	1540	580
char	1.3	0.3	22.4	3.1	184	45.2

[a] Location from the bottom, in meters.

Table III. Concentration of Reducing Species, O_2, NO, and N_2O at Two Locations in the Combustion Chamber for the Three Fuels[a]

	wood chips		bituminous coal		coke	
	2.5 m above bottom[b]	11.0 m above bottom[b]	2.5 m above bottom[b]	11.0 m above bottom[b]	2.5 m above bottom[b]	11.0 m above bottom[b]
O_2	3.04	1.75	4.04	4.38	2.31	4.82
NO	85	75	159	99	324	118
N_2O	1	2	110	143	70	108
CO	35900	15100	9000	1200	12900	340
H_2	14200	6500	2100	60	80	BDL[f]
CH_4	4900	2000	1000	20	6	1
C_2H_6	400	300	50	1	BDL	BDL
C_2H_4	2000	500	400	7	1	BDL
C_2H_2	200	30	65	0.5	BDL	BDL
ΣC_3	200	15	50	BDL	BDL	BDL
ΣC_4	100	10	BDL	BDL	BDL	BDL
ΣC_5	10	BDL	BDL	BDL	BDL	BDL
ΣHC^c	7700	2900	1600	30	7	1
ΣHC^d	6100	1900	1800	50	20	3
ΣRS^e	57800	24500	12700	1290	13000	340

[a] In ppm, except O_2 which is given in percent. [b] Location of the probe. [c] Total hydrocarbon concentration based on gas chromatograph analysis. [d] Total hydrocarbon concentration based on on-line analyzer. [e] Total concentration of reducing species (CO, H_2, C1–C5 hydrocarbons). [f] BDL = below detection limit = 0.5 ppm for hydrocarbons and 50 ppm for H_2.

other fuels. The char content in the combustion chamber is shown in Table II, and Table III gives the corresponding hydrocarbon content. Table II is based on bed density measurements by pressure drops and on char samples taken along the height of the combustion chamber and Table III on measurements with the gas sampling probes.

Test Program. The boiler was operated with all three fuels under constant conditions: a bottom-bed temperature of 850 °C, an excess-air ratio of 1.20–1.25, and a quotation of primary to secondary air corresponding to a calculated primary-air stoichiometry between 0.70 and 0.75. The calculated primary-air stoichiometry expresses the ratio of primary-air feed rate and stoichiometric air demand corresponding to the fuel feed rate. This definition presupposes that all fuel burns below the secondary-air inlet, but this is not the case. The actual excess air in the bottom zone below the secondary-air inlet is therefore higher than 0.75 and also dependent on the type of fuel.

The boiler load was maintained at about 8 MW during all tests. With the air ratio chosen, this load gives a fluidization velocity of about 6 m/s at the top of the combustion chamber. Since calcined lime is known to influence the formation of N_2O as well as to catalyze the decomposition,[10,17] the tests were carried out without lime addition. The bed consisted of commercial silica sand mixed with some fuel ash and char from the combustion of the various fuels.

CH_3CN, NH_3, or NO were added to the combustion chamber at three locations: the primary-air duct (11, Figure 1), the secondary-air inlet at 5.5 m (8, Figure 1), and the entrance of the cyclone (9, Figure 1).

Gas Concentrations. All gas concentrations are given as measured. With the excess-air ratio chosen, this corresponds to an oxygen concentration of 3.5% O_2 in the flue gases.

Injection Equipment. CH_3CN is a liquid at room temperature. It was supplied by two parallel piston pumps with variable speed control to an injection nozzle mounted in the primary-air duct or in the duct of the flue gases which were used as carrier
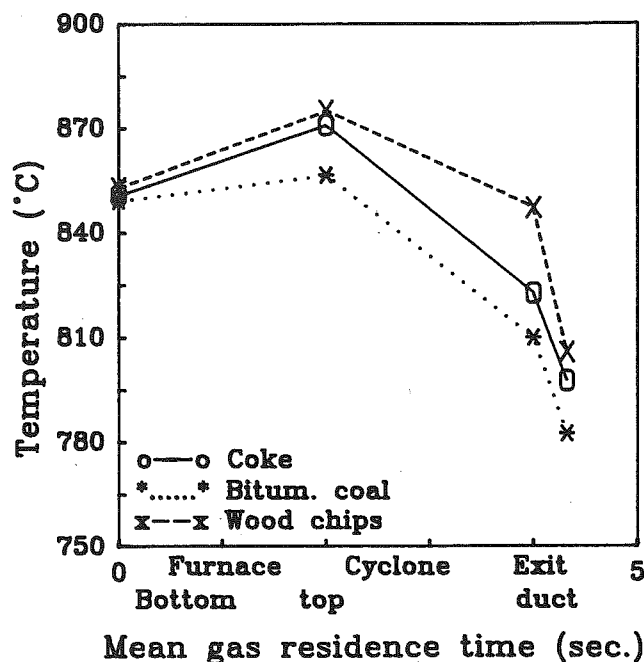

Figure 3. Temperatures along the path of gases from the bottom of the combustion chamber to the entrance of the boiler convection section. The locations of the various thermocouples are given in Figure 2.
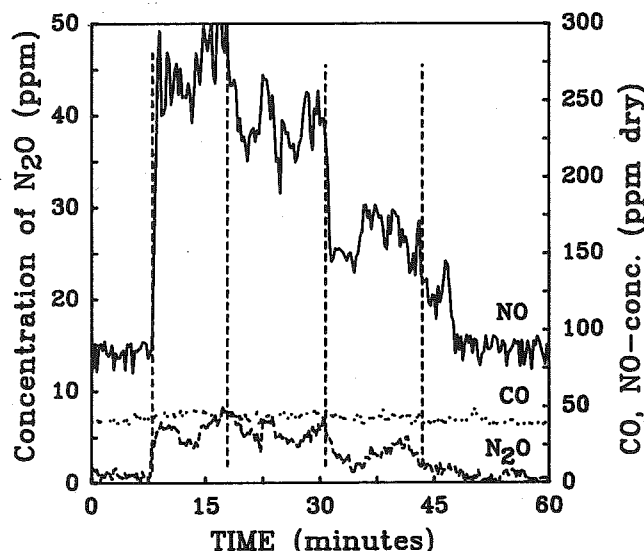

Figure 4. Supply of CH_3CN to the primary air duct. Fuel: Wood chips. Between 8 and 18 min, 1150 ppm CH_3CN; between 10 and 31 min, 760 ppm CH_3CN; between 31 and 43 min, 360 ppm CH_3CN.

gas. At the prevailing temperatures (48 °C in the primary-air duct after the fluidization fan or 115 °C in the duct of recirculated flue gases) the droplets from the injection nozzle were instantaneously vaporized and the CH_3CN was well mixed in the carrier medium before reaching the combustion chamber.

NH_3 was stored as a liquid in pressurized cylinders. During the tests, the NH_3 liquid was first vaporized in a special heat exchanger and then fed as a gas via a rotameter directly into the primary-air or flue-gas duct for mixing before it reached the combustion chamber.

NO was stored as a gas in pressurized cylinders and therefore no evaporation was needed prior to the feeding of the NO to the rotameter.

The gas containers were weighed continuously during an injection test and the flow rate was calculated afterwards. The set points for operation of the pumps and the position of the rotameter throttle were determined during a series of preliminary tests.
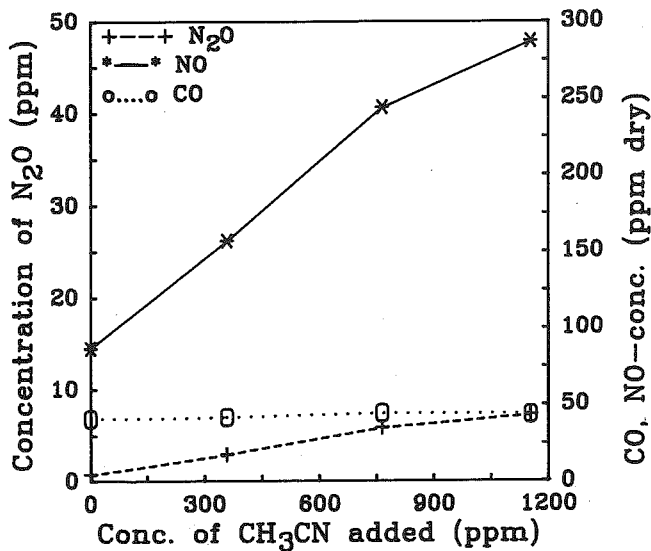
Figure 5. Concentration of NO, N$_2$O and CO in the stack as function of amount of CH$_3$CN added to the primary air duct. Fuel: wood chips.

Temperature Control. N$_2$O formation and especially the reduction are dependent on temperature. Therefore, it is desirable to maintain a constant temperature in the combustion chamber and this is feasible at the load chosen. However, minor temperature variations occur and these have to be considered. Figure 3 shows the temperature profile in the combustion chamber, cyclone, and cyclone exit duct. The temperature at the bottom of the combustion chamber was always maintained at 850 °C by the control system. With wood and coke there was more combustion in the top part of the combustion chamber than in the case with bituminous coal. During combustion of wood chips the volatiles were responsible for the temperature rise in the top of the combustion chamber seen in Figure 3, while in the case of coke the temperature rise was caused by combustion of accumulated char (Table II). In the cyclone, the temperature fell due to cooling by the walls of the cyclone. The temperature drop was smaller in the case of wood chips because of combustion of larger quantities of CO, hydrocarbons, and hydrogen in the cyclone (see Table III) than with the other fuels.

In the cyclone exit duct a further fall in temperature was measured, shown by the measurement point on the right-hand side of the diagram in Figure 3. This temperature is represented by an average of the three thermocouples T2, T3, and T4 (Figure
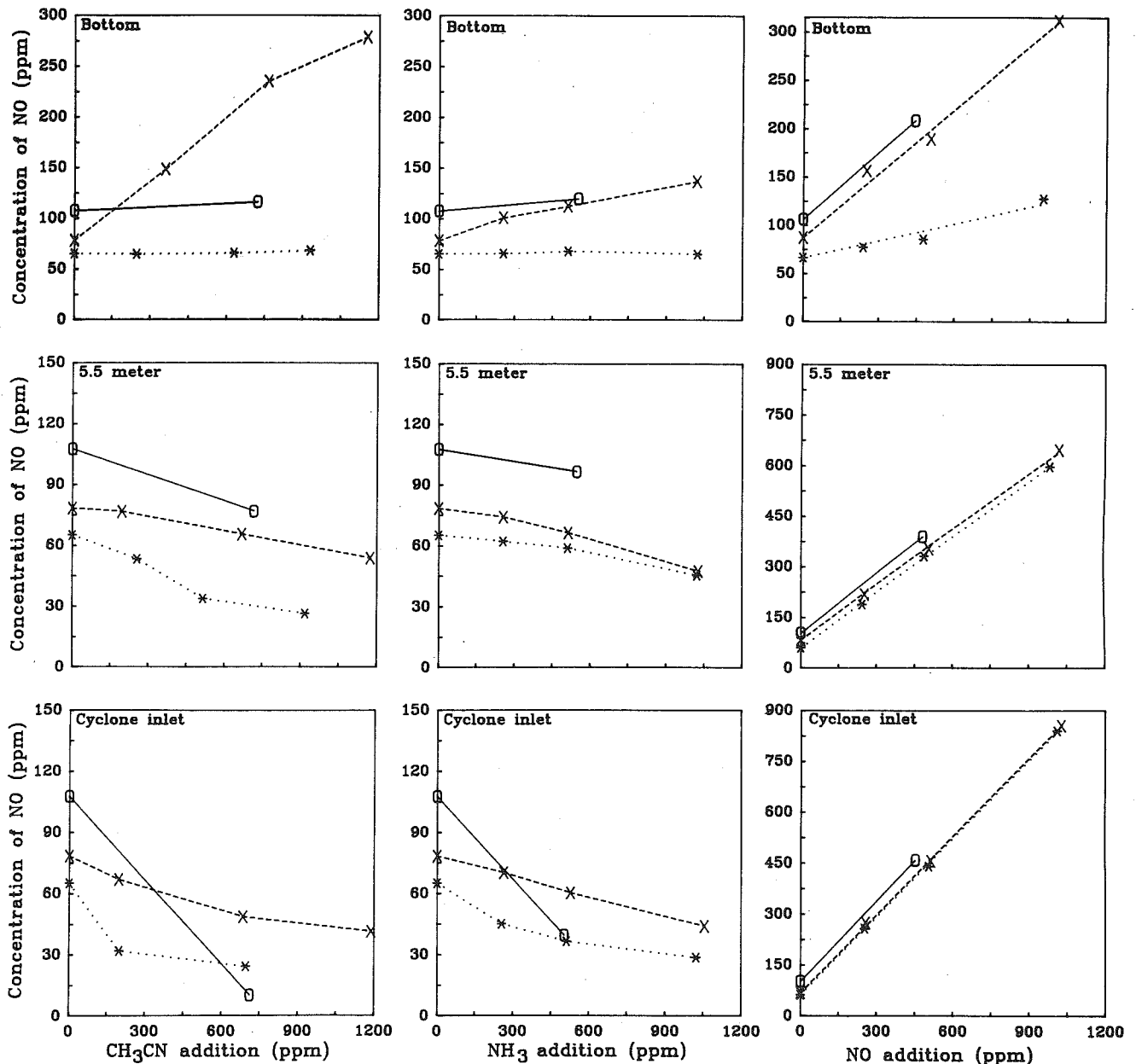

Figure 6. NO emissions (concentration in the stack) resulting from injection of CH$_3$CN, NH$_3$ or NO during combustion of wood, coal, or coke. The concentration scales are different. (✕– –✕) wood chips, (*⋯*) bituminous coal, (○—○) coke.
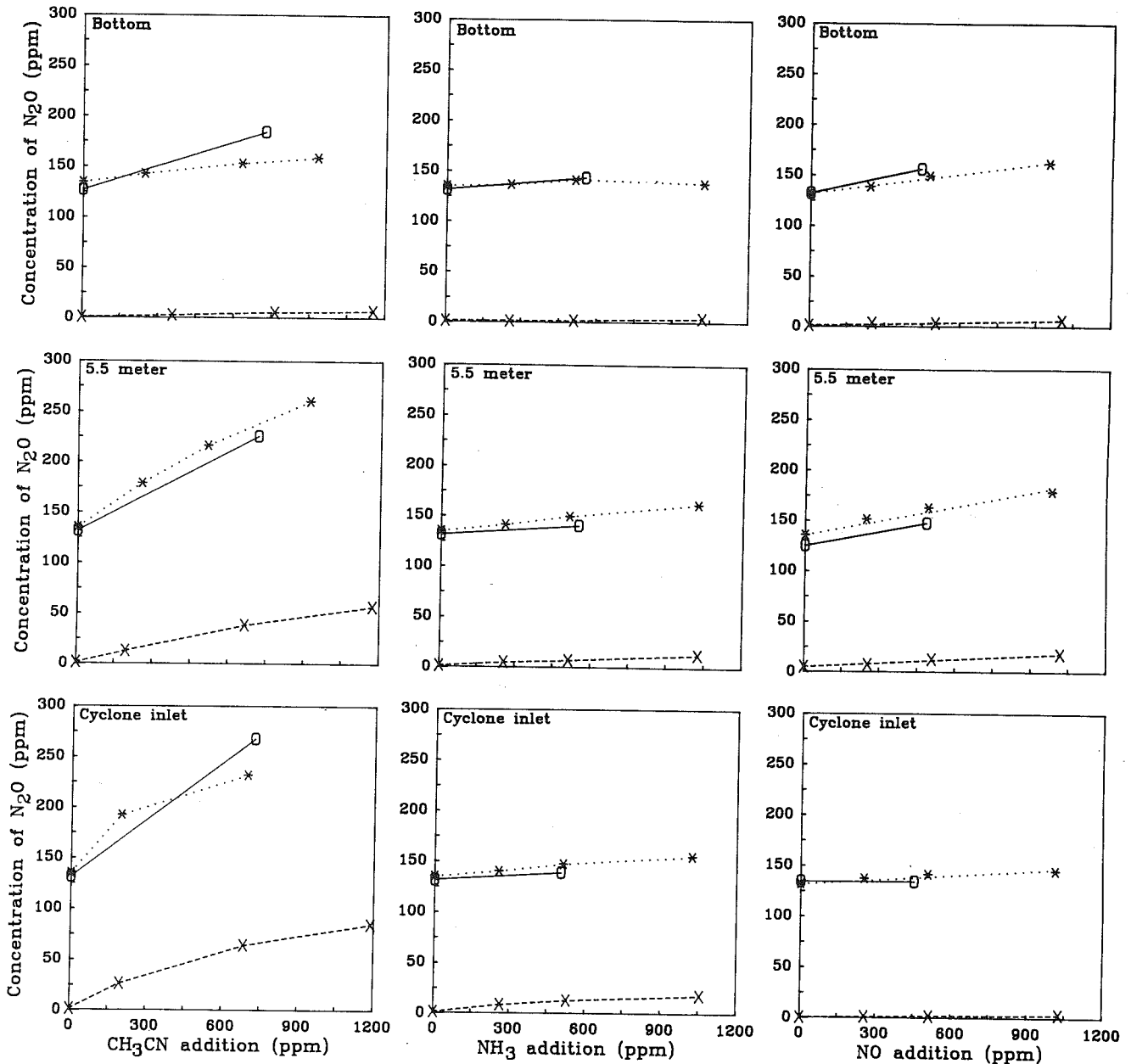
Figure 7. N₂O emissions (concentration in the stack) resulting from injection of CH₃CN, NH₃ or NO during combustion of wood, coal, or coke: (×− −×) wood chips; (*···*) bituminous coal, (O—O) coke.

2). These thermocouples show almost the same temperature, but unfortunately they are all affected by the cold walls of the boiler convection section. This means that the temperature decline in the cyclone exit duct is 20–30 °C less than that shown in Figure 3.

Results

General. Figure 4 presents the result of a test with CH₃CN addition to the primary air during combustion of wood chips. The concentrations of NO, N₂O, and CO in the stack during the 1-h test are shown. The rise of the NO concentration with rate of CH₃CN addition is evident, but there is also a certain formation of N₂O. The added quantities of CH₃CN were 360, 760, and 1150 ppm if related to the total amount of air supplied during the test. The feed rate of air was rigorously constant and identical to that of all other tests, because the control system of the boiler makes it possible to fix the total flow of air. The maximum account of CH₃CN can be compared to the amount of nitrogen released with the volatiles of the coal, which would be 1300 ppm of HCN and NH₃ if related to

the total air flow and assuming the nitrogen concentration in the volatiles to be the same as in the original coal.

In Figure 5 the levels of emissions from Figure 4 are plotted *versus* amount of CH₃CN added. The tests with injection of NH₃ or NO can be represented in a similar way. If the curves of Figure 5 were straight lines the data could be represented in a quite condensed way, since the inclination of a curve expresses rate of formation or reduction. Unfortunately, the relationships are not always straight lines and, therefore, before approximations are introduced; the entire material is plotted in Figures 6 and 7.

Preliminary tests were carried out in order to adjust the equipment some weeks before the main tests, and other boiler operation conditions and fuels were used in between. Since the main tests were merely a repetition of the preliminary tests, the results can be compared to verify the accuracy of the tests. It can be concluded from such comparisons that small deviations occurred in some test conditions, but in no case were the trends different, and the general conclusion is that the reproducibility was good
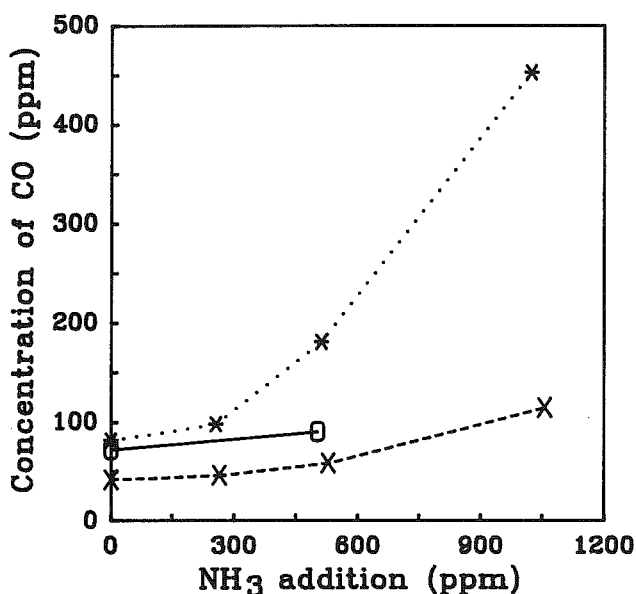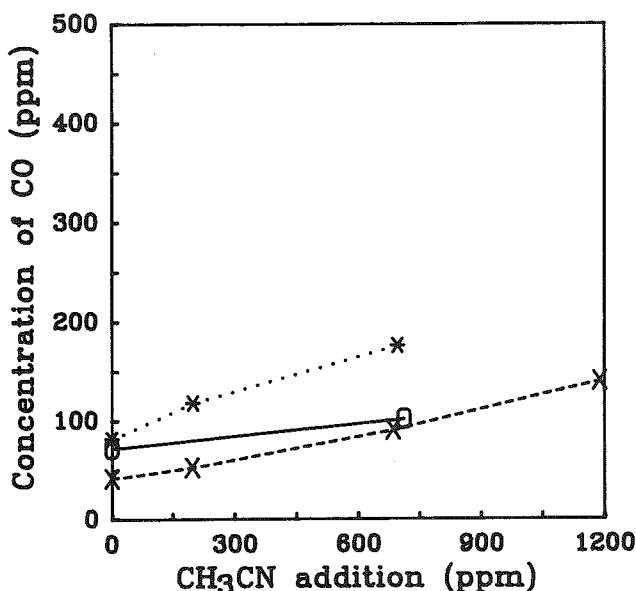
Figure 9. Reduction of NO added as a function of the location of the NO supply for the three fuels.

Figure 8. CO emissions (concentration in the stack) resulting from injection of CH_3CN or NH_3 to the inlet of the cyclone during combustion of wood, coal, or coke: (X--X) wood chips, (*...*) bituminous coal, (O—O) coke.

considering the intention of the investigation. Below, only results from the main tests will be presented.

Main Tests: CH_3CN and NH_3 Addition. Addition of CH_3CN or NH_3 to the primary air (i.e., to the air nozzles of the water-cooled bottom of the combustion chamber) did not affect the emission of NO, except in the case of wood combustion, where a considerable rise in the emission was noted, more for CH_3CN than for NH_3 (Figure 6). When the addition was moved to higher positions in the combustor, to the 5.5-m level and to the inlet of the cyclone, the emission of NO decreased for all three fuels used.

Addition of CH_3CN resulted in a rise in the emission of N_2O. The rise was small during addition to the bottom of the combustor, but more pronounced at higher levels (Figure 7). This took place for all fuels used. On the other hand, NH_3 only produced a small rise in the N_2O emission in all cases investigated.

The CO emission was never much affected except during addition of large quantities of NH_3 to the cyclone (Figure 8).

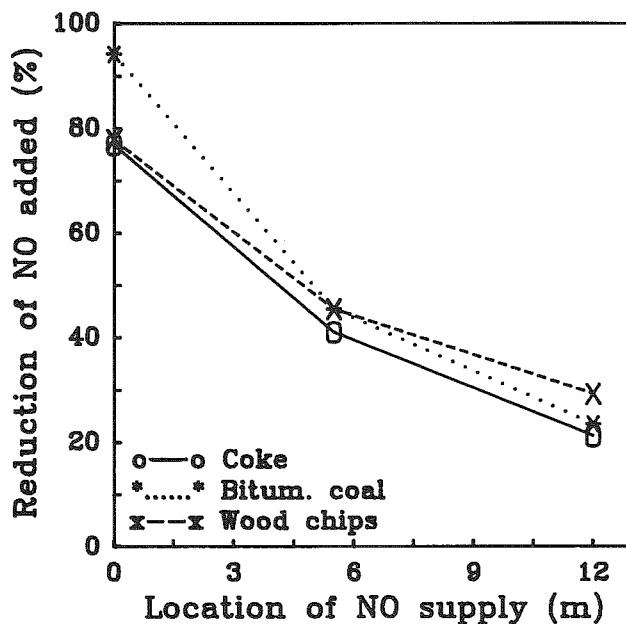**Main Tests: NO Addition.** The CH_3CN or NH_3 added are almost entirely converted or broken down in the

combustor, but the NO added survives to a certain extent and the NO emission increases with addition as seen in Figure 6. The inclination of the curves is a measure of the reduction of the NO added and the straight line relationships allow a more compact representation of the reduction as a function of the location of addition (Figure 9). This figure shows that there is a considerable reduction of the NO added, especially in the bottom where 80–95% is reduced. Somewhat surprising is the similarity between the case of wood and coke combustion, since the situation in the bed is quite different in these cases (cf. Tables II and III) and the simple idea that reduction of NO on char predominates does not hold in this case.

A part of the conversion of the NO added is spent on formation of N_2O according to mechanism M2 or M3. Figure 7 shows that the N_2O emission increases with the amount of NO added, more in the case of coke and bituminous coal than with wood as a fuel. The increase in emission is greatest during injection at the 5.5-m level, and it falls rapidly, especially in the case of coke when addition took place in the entrance of the cyclone. This behavior can be represented in the form of excess emission of N_2O *vs* location of addition, as in Figure 10, where reduction data from Figure 9 were employed in order to express the excess emission of N_2O in relation to the amount of NO reduced (or converted).

Data Reduction. The emission of N_2O is not linearly related to the addition of CH_3CN or NH_3. Therefore, these data cannot be so simply reduced as in the case of NO addition. However, the relationships are nearly linear and, if a linear approximation is permitted, the data can be treated in the same way as in Figure 10. Such data express the emission, that is, the result of formation and subsequent reduction during the passage through combustor and cyclone. Fortunately, it is possible to compensate for reduction with fairly good accuracy since, in conjunction with the present tests, N_2O was also injected, and its reduction was studied under the same conditions as in the present tests.[11] The results from the reduction tests are shown in Figure 11. For each fuel and location of N_2O supply a degree of reduction of the N_2O added can be calculated. This measured degree of reduction is then applied on all injection tests with CH_3CN, NH_3, and NO
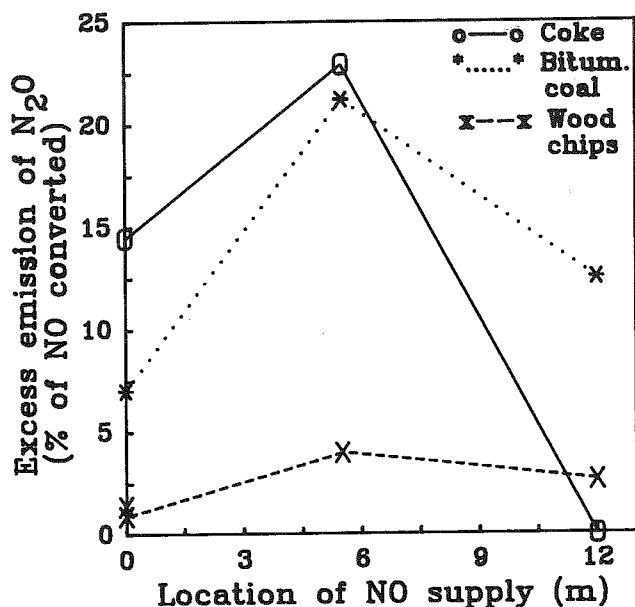
Figure 10. Excess emission of N_2O based on amount of NO reduced as function of the location of NO supply for the three fuels.
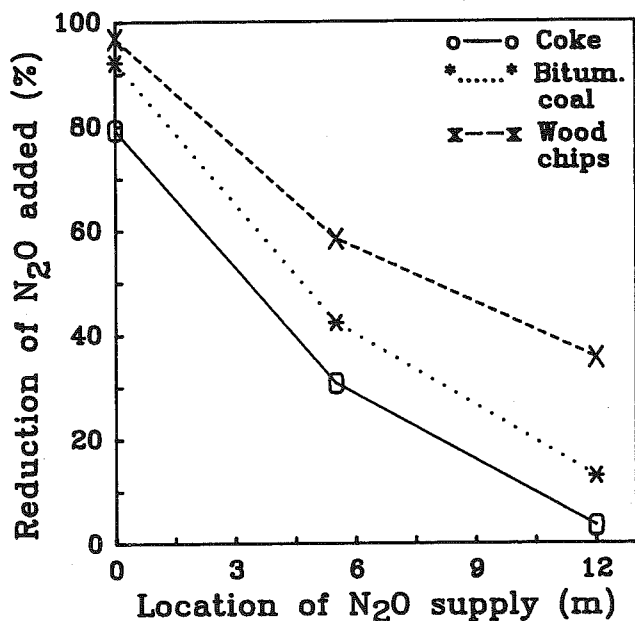

Figure 11. Reduction of N_2O added to the boiler as a function of the location of injection:[11] (×--×) wood chips, (*...*) bituminous coal, (O—O) coke.

Figure 12. Primary formation of N_2O as a function of the location of CH_3CN supply for the three fuels.
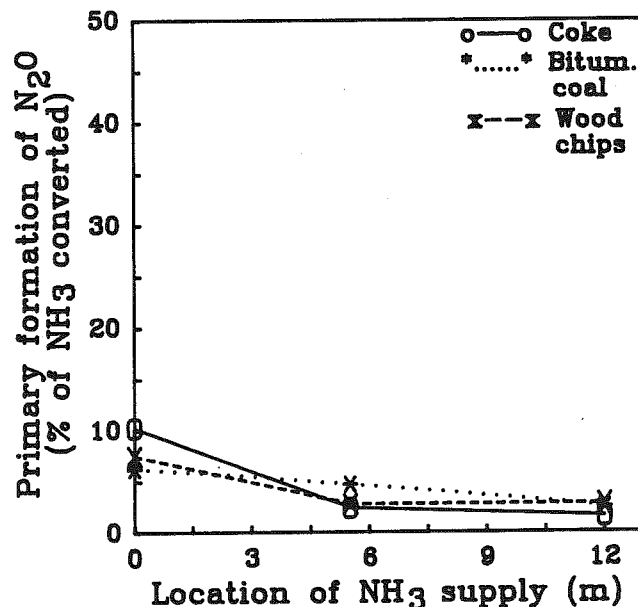
Figure 13. Primary formation of N_2O as a function of the location of NH_3 supply for the three fuels.

in order to remove the influence of the reduction of N_2O. It is then possible to represent the present data in the form of formation of N_2O in percent of the amount of CH_3CN, NH_3, or NO converted (Figures 12, 13, and 14). In the calculation of conversion it was assumed that one cyanide, ammonia, or nitrogen oxide molecule was consumed to form one molecule of N_2O by reactions R1 and R2. The other nitrogen atom in N_2O comes from NO which is normally available in excess.

Due to the low concentrations of N_2O involved in the tests with N_2O, NO, CH_3CN, and NH_3 supply to the bottom, small changes in the N_2O have a great effect on the final result of primary formation of N_2O (Figures 12, 13, and 14). In order to minimize this uncertainty, the calculation is based on four points (Figure 7) and the effect of an error in an individual test on the calculation of the slope is reduced. Also, the preliminary tests give a guideline to judge the uncertainty. Nevertheless, the
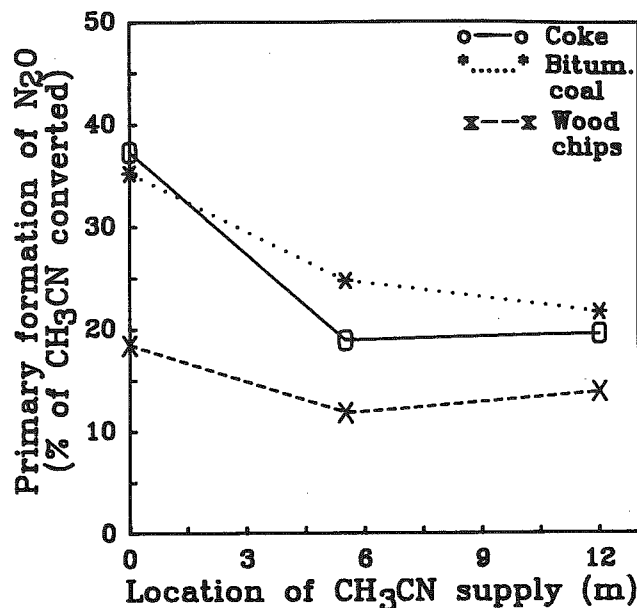
uncertainty in the calculation of the primary formation of N_2O is in the order of 25% for CH_3CN and NO and 50% for NH_3 in Figures 12–14 in the worst case of wood chips and supply of CH_3CN, NH_3, or NO to the bottom. In the other cases shown in Figures 12–14 the accuracy is much higher.

Figures 12 and 13 show, in agreement with the homogeneous reaction kinetic calculations, that the formation of N_2O from NH_3 is very small compared to that from cyanides. In all cases the formation is highest in the bottom part of the combustion chamber. In the case of NO addition, Figure 14, the dependence on the location of addition of NO is evident, and the conversion is also in this case quite high in the bottom zone of the combustion chamber.

Discussion

Ability of CH_3CN To Form N_2O. In contrast to NH_3, CH_3CN gave rise to a considerable formation of N_2O for all three fuels. This proves that N_2O is formed from
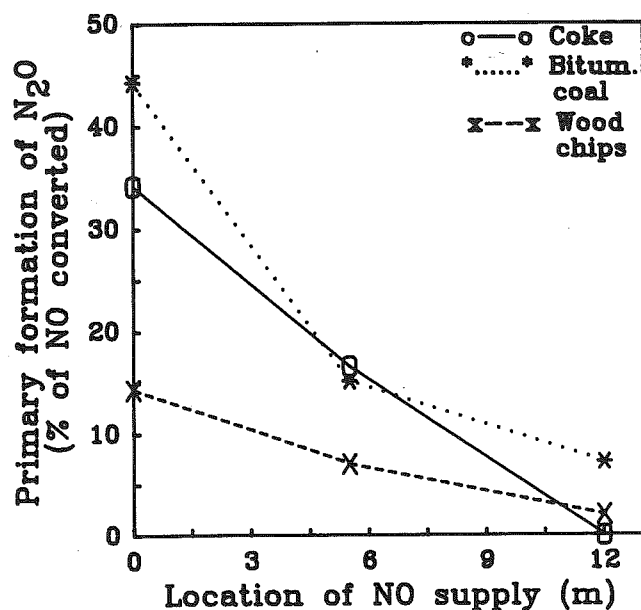
Figure 14. Primary formation of N_2O as a function of the location of NO supply for the three fuels.

Figure 15. N_2O and NO concentration profiles in the center of the combustion chamber:[31] (O—O) N_2O concentration, (×--×) NO concentration.

cyanides, as shown by the models of homogeneous reaction kinetics, in spite of the high concentration of particles in the circulating fluidized bed. The contribution to the emission of N_2O is, however, heavily dependent on the location of injection as seen in Figure 10, where the balance between formation and subsequent reduction during the passage of gas through the combustion chamber resulted in an optimum contribution to N_2O emission from the injection at the 5.5-m level. (Figure 10 illustrates the case of NO injection, but the picture is similar for the other species injected.) When reduction of N_2O according to Figure 11 is taken into account, Figure 12 shows that most formation occurs in the bottom of the combustion chamber where 35% of the CH_3CN added is converted into N_2O. The corresponding number for NH_3 addition is only 10% according to Figure 13.

Figure 12 thus proves that a homogeneous formation of N_2O is possible, in spite of the presence of particles. This observation is further supported by the rather even formation during injection in the upper parts of the combustion chamber and the cyclone where the particle loading is lower. The greater N_2O formation in the lower part of the combustor is most probably caused by the higher NO concentration in this zone. As shown by the NO addition tests, NO enhances the homogeneous formation of N_2O, probably through reaction R2, and this could explain the higher formation of N_2O in the bottom zone during CH_3CN addition.

Concentration Profiles in the Combustion Chamber. Table III shows that the amount of volatiles is great in the bottom part of the combustion chamber but less in the top. Hardly any volatiles were measured for coke, since the large CO concentration in the bottom may be explained as an intermediate product from char combustion. Complete profiles of NO and N_2O in the combustion chamber were not measured during the present tests, but profiles are available from a previous measurement[31] with another but similar bituminous coal under the same operation conditions as in the present tests (Figure 15). This figure shows a steady rise in N_2O concentration with height in the combustion chamber; formation dominates
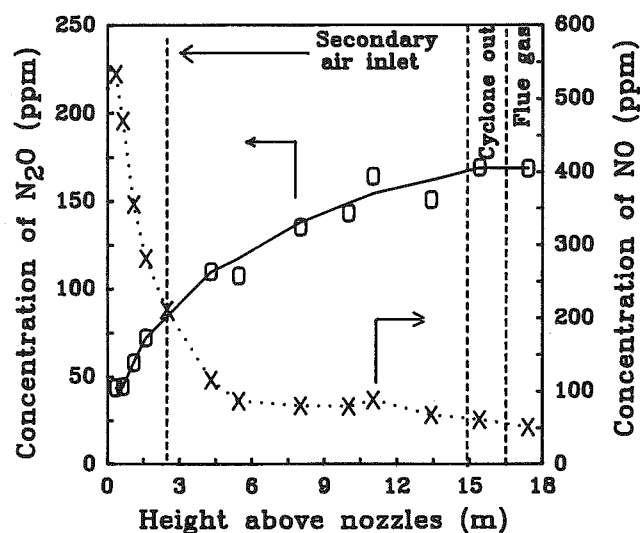
(31) Åmand, L.-E.; Leckner, B. *Energy Fuels* **1991**, *5*, 815.

over reduction and is still important in the upper parts of the furnace. Simultaneously, there is a continuous reduction of NO with height. The measurement of the NO and N_2O concentration during the present tests at two locations in the combustion chamber shows (Table III) the same qualitative picture as the complete profiles in Figure 15.

Considering the preponderant conversion of volatiles in the bottom and the more extended combustion of char over the combustion chamber, it can be assumed that most N_2O connected to volatile release is formed in the bottom, but due to the strong reduction this N_2O does not survive. The remaining volatiles and, most probably, the char contribute to the formation of N_2O in the upper parts of the furnace, but it is not possible to distinguish between formation originating from the volatiles or from the char. However, a comparison between the cases with combustion of coke and bituminous coal might give an indication on the contributions from char and volatiles.

Heterogeneous Mechanisms. Without additions to the bed, Figure 7 shows that the N_2O emissions from combustion of coal and coke are fairly similar. This is surprising since the volatile contents of the two fuels are quite different and so are the resulting compositions of combustibles in the combustion chamber (Tables II and III). It would be straightforward to assume that the formation of N_2O from volatile nitrogen in the form of HCN by reactions R1 and R2 would be more important for the bituminous coal than for coke. Then, what is the origin of N_2O during combustion of the nonvolatile coke? It has been shown[17,18] that very little N_2O is formed by mechanism M1. However, the NO addition experiments might provide an answer; the NO added was partly converted to N_2O (Figures 7 and 14), and this should be the case also for the NO produced during the combustion process without NO addition.

The M2 mechanism in which, according to Tullin *et al.*,[23] oxygen breaks up the aromatic structure of the char and the nitrogen in the disrupted rings reacts with NO to form N_2O is a plausible alternative which explains the char-related N_2O formation. However, in this mechanism, M2, N_2O is formed directly from the char without any gas-phase reactions according to (R1) and R2), and therefore it cannot explain the influence of residence time found by Suzuki *et al.*[25] and the detection of HCN in the

experiments of de Soete.[17,18] Suzuki *et al.*[25] changed the residence time in their fixed-bed reactor experiments by using the same amounts of char and bed material and the same gas flow rate, and only changing the length of the heated outlet section after the fixed bed. An increase in gas residence time in the outlet section increased the N_2O yield, which indicates that gas-phase reactions are involved in the char-related N_2O formation as well.

In the experiments by de Soete,[17] NO was reduced on a highly devolatilized char without oxygen present, and 10% of the NO reduced was found as HCN at 850 °C. Based on the two facts that char-related N_2O formation is influenced by residence time and that HCN is a possible product from NO reduction on char, an extension of the M2 and M3 mechanisms is proposed. This mechanism (called M4) involves a primary formation of a cyano compound (HCN or HNCO for example) as a result of the reaction of the disrupted aromatic rings with O_2 and/or NO. The HCN or HNCO then reacts further to N_2O according to reactions R1 and R2. Tests of either of the two mechanisms, M2 or M4, do not exist. They are both results of an interpretation of laboratory experiments and further detailed measurements in this area are certainly needed. In both the mechanisms discussed, M2 and M4, the presence of nitrogen oxide and oxygen is critical for the formation of N_2O. Several studies[17,19-21] have failed to detect any formation of N_2O in experiments with NO reduction on char in the absence of oxygen, whereas others[21-23] indicated that N_2O is produced if oxygen is added to the reactor.

The negligible amount of volatiles, the considerable amount of char, and oxygen present in the case of NO injection during combustion of coke favors the interpretation that either mechanism M2 or M4 (or both) is the dominant heterogeneous path for N_2O formation in this particular case.

The Case of Wood Chips. Both mechanisms M2 and M4 are related to char combustion and should not be important in the case of NO addition during combustion of wood-chips due to the low char loading. In spite of this, the reduction of NO in Figure 9 is high, and Figure 14 shows a certain primary formation of N_2O, at least in the lower part of the combustion chamber. This is a relevant result, although the accuracy of the determination of the primary N_2O formation is low when NO is supplied to the bottom. Neither the NO reduction nor the N_2O formation can be explained on the basis of the present knowledge of the NO/N_2O chemistry in an FBC boiler. According to Figure 13, the NH_3 supply leads to a small primary formation of N_2O, probably through reactions R3 and R4. By injecting NO into the combustion chamber and thereby increasing the NO concentration, a larger fraction of the volatile nitrogen could be expected to form N_2O. However, it is seen in Figure 14 that the increase in the N_2O formation did not become large. Furthermore, contributions from small amounts of HCN and char cannot be excluded even in this case of wood chips combustion.

CH_3CN or NH_3 and NO Reduction. CH_3CN or NH_3 did not affect the emission of NO during combustion of coal or coke as long as the addition took place in the bottom of the combustion chamber, whereas a decline in the NO emission was noticed during injection at the 5.5-m level and especially into the inlet of the cyclone (Figure 6). The interpretation of these results is that CH_3CN and NH_3 are oxidized to NO in the bottom part of the combustor where the particle concentration is high, whereas they
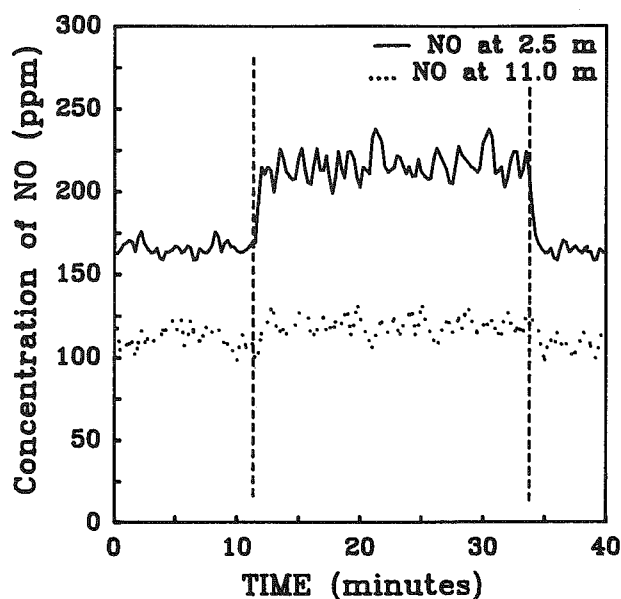

Figure 16. Concentration of NO at the 2.5- and 11-m level in the combustion chamber during injection of NH_3 to the primary air duct. Fuel: Bituminous coal. Between 11 and 34 min, 440 ppm NH_3 was injected.

contribute to the reduction of NO in the upper part of the combustor and in the cyclone according to the SNR (selective noncatalytic reduction) process which works under fluidized bed conditions under influence of CO and other combustion products.[32]

Production of NO from nitrogen-containing volatiles in a highly particle-laden environment of a circulating fluidized bed has been stated as a hypothesis in several previous works.[33,34] It has been argued[33,34] that a comparison with pulverized fuel combustion, where staged combustion favors the reduction of NO with NH_3 formed from the fuel volatiles,[35] is not applicable in a circulating fluidized bed. In the lower, "staged" part of a circulating fluidized bed, NH_3 instead forms NO as shown in Figure 16. This formation, which was measured at 2.5 m from the bottom, is, however, not observed as an emission since the NO formed is reduced during its passage through the combustion chamber (promoting formation of N_2O) and the concentration of NO remains constant at the 11-m level as shown by the measurement in Figure 16. This significant interaction with the bed material is not noticed during injection into the upper part of the combustor and into the cyclone where CH_3CN and NH_3 do reduce NO.

In the case of wood combustion the behavior is almost the opposite: the NO emission is increased by injection of CH_3CN or NH_3 in the bottom, and the reduction in the cyclone seems to be less than that obtained for the other fuels. It can be speculated that there is a formation of NO during injection to the bottom of the bed also in this case, but, since the reduction of NO is less due to the lower concentration of char in the combustor, the emission of NO increases. The reason for the less effective reduction of NO in the cyclone during injection of CH_3CN and NH_3 (seen in Figure 6) is not understood for the moment, but

(32) Leckner, B.; Karlsson, M.; Dam-Johansen, K.; Weinell, C. E.; Kilpinen, P.; Hupa, M. *Ind. Eng. Chem. Res.* **1991**, *30*, 2396.
(33) Amand, L.-E.; Leckner, B. *Proceedings of the Twenty-third Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1990; p 927.
(34) Amand, L.-E.; Leckner, B. *Energy Fuels*, **1991**, *5*, 809.
(35) Bose, A. C.; Dannecker, K. M.; Wendt, J. O. L. *Energy Fuels* **1988**, *2*, 301.

it may have to do with combustion in the cyclone displacing the temperature range of the selective noncatalytic reduction.

Conclusions

The following conclusions can be made about N$_2$O formation in a circulating fluidized bed combustor to which limestone is not added: 1. Cyanides show a greater tendency than ammonia to form N$_2$O. 2. Homogeneous gas-phase reactions are important in spite of the high particle concentrations. 3. The significance of the cyanides for the N$_2$O emission is highest in the upper parts of the combustor because of the parallel reduction of N$_2$O which is extremely large in the bottom part. 4. Cyanides or amines, which are formed in the bottom part of the combustor, do not contribute to a decrease of the emission of NO, such as is the case in staged combustion of a pulverized coal flame. 5. Cyanides or amines decrease the emission of NO if they are present in the upper part of the combustion chamber or in the cyclone. 6. The concentration of NO and the char loading of the combustion chamber are important for the formation of N$_2$O during combustion of char particles.

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