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*Andra Nordiska Konferensen om Svaveldioxid och
Kväveoxidbegränsning vid Förbränning av Fasta Bränslen
Danmarks Tekniska Högskola, Lyngby, november 1990*

FORMATION OF N₂O IN CIRCULATING FLUIDIZED BED BOILERS

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ABSTRACT

The N₂O formation in circulating fluidized bed boilers is assumed to be influenced by two formation routes, either by char or by hydrogen cyanide originating from the fuel volatiles. A test program has been carried out with the purpose to better understand the formation routes. The test program consists of step response tests in a 12 MW circulating fluidized bed boiler. Concentration profiles of O₂, CO₂, CO, NO, HCN, NH₃ and C₁ to C₃ hydrocarbons in the combustion chamber of the boiler were also measured in order to support the conclusions from the step response tests. The importance of the two routes is discussed but no conclusions can be made about their magnitude.

INTRODUCTION

One of the advantages with fluidized bed combustion (FBC) is the low emissions of NO and SO₂, a consequence of the combustion temperatures of 800 to 900°C which are low in comparison with the temperatures of flame combustion, 1000 to 1600°C. The low temperatures in FBC prevent thermal NO formation and promote NO-reducing reactions during the combustion process. The temperature range is also suitable for sulphur capture by lime addition.

The circulating type of FB boiler (CFB boiler) takes even better advantage of these properties [1] and interest has gradually been focussed on this type of boiler.

However, the advantage of the lower emissions of NO and SO₂ has lately been found to be offset by high emissions of N₂O from FB boilers [2] but not from other combustion equipment [3]. N₂O is one of the greenhouse gases, and contributes also to ozone depletion in the stratosphere [4], [5].

The present work is a continuation of a project, previously published in [2] and [6]. Characterizations of NO and N₂O have been carried out simultaneously, but for convenience results of the present work which are related to NO are reported separately in [7].

The N₂O emission has been found to depend on the bed temperature. A higher temperature leads to lower emissions of N₂O, opposite to the bed temperature dependence of NO. In [2] it was discussed if the N₂O formation from volatile nitrogen species (especially HCN) or the heterogeneous reactions on char surface play an active role for the N₂O formation. No definite answer to this question could be given. In [6] it was found that the char loading of the boiler influenced the fuel-nitrogen conversion to N₂O. This could be seen by comparing N₂O emission results from tests where three kinds of fuel with different volatile content were used. The temperature dependence on N₂O was shown to include the entire combustion chamber and not only the bed temperature at the bottom. Finally, a dependence on oxygen concentration was evaluated. In [8] it was shown that the decomposition of N₂O in the cyclone depends upon the temperature level. An increase of the cyclone temperature by gas injection leads to a substantial reduction of the N₂O produced in the combustion chamber.

The present work is focused on the formation of N₂O in the combustion chamber. Results from measurements in a 12 MW commercial-type CFB boiler are presented. These measurements include transient response tests with changes of the flyash recirculation and fuel feed rates. Gas concentration profiles of O₂, CO₂, CO, NH₃, HCN, NO and C₁ to C₃ hydrocarbons are also measured. The aim of the work is to continue the discussion of the importance of formation of N₂O from the nitrogen-containing volatiles (e.g. HCN) compared to the formation related to char.

FORMATION AND DESTRUCTION OF N_2O

The formation and destruction of N_2O at fluidized bed conditions are not well understood. For gas flames, where the chemical reactions are homogeneous, there are reaction schemes available [9] but the knowledge of the heterogeneous processes, which are more relevant for fluidized bed conditions, is poor. In a fluidized bed there is not only coal present but also sand, ash and limestone, making interpretation even more difficult. As a simplification limestone is not employed in the present experiments and sand is regarded to be rather inert, which leaves the char and ash as the only remaining surfaces of interest. Of these two surfaces ash is regarded to be less important in comparison with char.

In Figure 1 the important formation and reduction steps of N_2O at fluidized bed conditions are outlined. The scheme is based on the literature and detailed reactions and references can be found in Table I.

The scheme in Figure 1 expresses the amount of fuel nitrogen which is released during the combustion, and found in the stack as N_2 , N_2O and NO . On the left-hand side of Figure 1 the nitrogen content of the fuel is seen to be released either in the volatile fraction of the fuel, step 1, or in the char fraction, step 2. The volatile nitrogen is released in the form of intermediaries such as amines (in the scheme equivalent to NH_3) step 3 or cyanides (HCN in the scheme) step 4, or oxidized directly to NO , step 5. The relation between the amount of NH_3 and HCN is important and depends on fuel type. Studies of bituminous coals [16], [17], [18] have shown that almost all coal nitrogen is contained in tightly-bound heterocyclic rings such as pyridines and pyrroles, with small amounts of nitrogen contained in side chains. It is generally accepted that the primary nitrogen-containing product of pyrolysis of coal is HCN [18] [19], [20], apart from the nitrogen in the tar fraction, which remains in the same form as in the parent coal [17], [18]. Measurements of the gas concentration profiles in staged pulverized coal flames [21], [22], [23] support the devolatilization studies and in [23] it is stressed that during oxidative pyrolysis conditions NH_3 is derived from HCN and HCN originates from the light gas fraction of the pyrolysis or from the tar nitrogen. The pyrolysis studies in [14] and [15] were closer to the situation in large fluidized beds than any of the work reported previously [18], [16], [24], [25]. In [14], [15] it is concluded that the primary nitrogen-containing species is HCN from the cleavage of hetero-aromatic compounds, and NH_3 can be formed by hydrogenation of HCN ,

step 11. This was also observed in oxidative pyrolysis studies, in the same experimental setup at a bed temperature of 600°C. Similar formation of NH_3 from HCN is modelled by Kilpinen [11] for higher temperatures and shown experimentally at pulverized coal combustion conditions [18], [23].

The volatiles also contain H_2 and CO , step 6, 7, which are important for the NO - N_2O chemistry as well. The NH_3 formed is believed [7] to be oxidized to either NO or N_2 on the char surfaces present, step 8, 9 and the homogeneous reduction of NO with NH_3 is therefore considered less important and is excluded from the scheme. Laboratory studies of a similar oxidation of HCN on char surfaces are not found in the literature. Instead model calculations of N_2O formation at fluidized bed temperatures [11] show that HCN is the dominating nitrogen source, step 10. Experimental evidence of this formation route is given by Aho et al. [26] who carried out tests in an entrained flow reactor with low particle loadings. The N_2O formed can be reduced either homogeneously with H and OH radicals, step 12, or heterogeneously on char surfaces, step 13.

As a simplification, the nitrogen in the char is assumed to produce only NO and N_2O , step 14, 15. The CO is produced from an incomplete combustion of the char, step 16, and the char itself is the main surface and reducing species for the reduction of NO to N_2 in CFB boilers, step 17, 18. NO can then be reduced to N_2O as well, step 19.

EXPERIMENTAL

The Boiler

The tests were run in a 12 MW_{th} boiler at Chalmers University of Technology, Figure 2. 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 meters 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 (2) and passed back to the combustion chamber through the return leg (3) and the particle seal (4). Primary air is introduced through nozzles in the bottom plate (5) and secondary air can be injected through several registers, located along the combustion chamber as indicated by the arrows in Figure 2. The

lowest level (6) is located at 2.2 m and the second level (7) at 3.8 m. An additional cold cyclone, which is not seen in Figure 2, makes it possible to recycle flyash back to the combustion chamber.

The boiler is equipped for research purposes with a data-acquisition system and on-line gas analysers. The N_2O is measured with a continuous IR analyser (Spectran 647 from Perkin Elmer). This analyser is cross sensitive of methane in the gas [27] and therefore gas-chromatograph analysis of N_2O was carried out as well. The N_2O analyser has an extra large gas-sampling cell which gives a longer response time compared to the other gas analysers. This makes it difficult to make on-line compensation of the N_2O signal for changes in oxygen concentration. Thus the gas concentrations in the following figures are expressed as measured without conversion to a certain O_2 concentration in the gas.

The Tests

A reference case was defined, where the bottom bed temperature was kept at 850°C , the primary air stoichiometry was around 0.75 and the excess ratio 1.2. The fluidizing velocity was 6 m/s. This reference case was used for all tests except in the case when the flyash recirculation was stopped, where a bed temperature of 830°C , a primary-air stoichiometry of 1.0 and an excess-air ratio of 1.3 were used. The fuel was a bituminous coal with the following composition: Ash, moisture and content of combustibles: 9.5%, 12.5% and 78.0% analysed as delivered. C, H, O, S and N: 84%, 5%, 9%, 0.5%, and 1.9% expressed on moisture and ash-free basis (maf). The volatile content was 30% on maf basis. The size of the coal was 0–30 mm with a mean size on mass basis of 11 mm. 13% of the fuel had a size less than 1 mm.

The Gas-Sampling Probes

The concentration profiles were measured inside the combustion chamber with gas-sampling probes. Gas was withdrawn through a cooled filter located at the top of the probe. The particle-free gas was then sent to on-line analysis for O_2 , CO , CO_2 and NO . Also the HCN and NH_3 profile and the concentrations of C_1 to C_3 hydrocarbons were measured. The NH_3 and HCN concentrations were determined

by trapping the gases in wash bottles, containing a diluted acidic water solution for NH_3 and a basic water solution for HCN . The analysis was then carried out by ion-selective electrodes for NH_3 and argentometry (Liebig-Deniges method) for HCN . After drying, gas from the probes was also collected in Tedlar bags for further analyses of N_2O and hydrocarbons on a gas chromatograph equipped with an electron-capture detector (for N_2O) and a flame-ionisation detector (for hydrocarbons).

DESCRIPTION OF THE RESULTS

Step Response Test with Stop of Flyash Recirculation

Figure 3 a,b,c show the transient response of the concentrations of O_2 , CO_2 , CO , NO and N_2O together with the temperatures in the combustion chamber and the cyclone after a stop of the flyash recirculation. Before the stop the flyash recirculation had been kept at the same rate for more than 6 hours and the char content of the flyash had reached a steady state which is seen in the figure for a period of 9 minutes.

When the flyash recirculation was stopped the oxygen concentration increased from 6% to 8% (Figure 3 a) and the CO_2 concentration decreased correspondingly (Figure 3 b) as a consequence of a loss of combustible matter. Part of this loss consists of fine particles which burned in the cyclone before the stop and the temperature of the gas leaving the cyclone dropped 50°C after the stop (Figure 3 a). Probably CO was also produced in the cyclone from an incomplete oxidation of the char in the flyash since the CO concentration dropped as well (Figure 3 b).

In Figure 3 c the change of N_2O and NO can be followed. The increase of NO from 70 ppm (expressed at 6% O_2) to 160 ppm was expected judging from the experience with flyash recirculation in a similar CFB boiler [28], but the corresponding decrease of the N_2O emission with 6% from 200 ppm (at 6% O_2) down to 185 ppm came as a surprise. The decrease of N_2O occurred in spite of the decrease of the temperature in the cyclone and the increase of the oxygen concentration. A similar independent change of these parameters leads to an increase of the N_2O emission.

Tests with flyash recirculation have also been carried out in a 1 MW_{th} stationary (bubbling) fluidized bed boiler by Bramer and Valk [29]. They found the same influence on NO and N₂O as reported in the present work.

Step Response Test with Batch Supply of Fuel

At stable operating conditions, a batch of fuel was dropped into the fuel chute together with the normal fuel feed. Not more than 30 seconds elapsed for the whole batch to be fed into the combustion chamber. The batch corresponds to an increase of the fuel feed rate of 2.3 times the normal fuel feed. The normal fuel was used for batch fuel, but the size of the fuel was varied. The first test used a coarse fraction of the fuel with a size between 15 and 40 mm and the second test the fine fraction, which was further crushed down to a mean size (mass based) of only 0.25 mm. Both tests are shown in Figure 4 in the same way as the flyash recirculation test. When the batch of fuel was dropped into the combustion chamber, the oxygen concentration decreased, Figure 4 a, and the CO₂ increased correspondingly, Figure 4 b. The coarse fuel gave a much smaller O₂ peak, but the time needed for the O₂ to recover back to its original level was much longer than that of the same amount of crushed fuel. The change of the temperatures can be followed in Figure 4 a. The coarse fuel only resulted in a minor increase of the temperature in the top of the combustion chamber compared with the fine fuel, which caused an almost instantaneous increase of both the top temperature and the temperature of the gas leaving the cyclone. This is an effect of an increased combustion in the cyclone, similar to that observed during the flyash recirculation test. The bottom bed temperature also increased to some extent, but due to thermal inertia this small increase is delayed a few minutes (Figure 4 a).

The change of the CO concentration in the stack can be seen in Figure 4 b. The coarse fuel with its more prolonged devolatilization period, did not produce more CO than could be oxidized before the flue gas reached the stack. This is in contrast to the fine-sized fuel batch where a CO peak of 4000 ppm was produced.

The NO concentration decreased in both cases. A decrease of the N₂O can be seen as well for the coarse-sized fuel batch, while a large N₂O signal was recorded for the crushed fuel. However, this large peak is not N₂O, since CH₄ was emitted simultaneously. Instead, the N₂O concentration decreased in this case as well. Both

the CH_4 -top and the decrease of N_2O were confirmed by gas-chromatograph measurements and the level of N_2O was found to be as low as 60 ppm.

Step Response of the Stop and Start of the Fuel Feed

The last series of step response tests are reported in Figure 5. The control system was switched to manual mode, in order to prevent changes of the air and the flue-gas recirculation flows. The fuel was stopped for a period of 4 minutes. The heavy drop of the temperatures in the combustion chamber is limiting for the shut off time of the fuel supply without a total turn down of the boiler. If the boiler stops a restart would be needed and half of the step response test is spoiled. The critical time was investigated in some preliminary tests. After the 4 minutes without fuel supply, the fuel feed was started again at the same rate as during the steady state operation, and no extra fuel was supplied to speed up the recovery period. The control system was switched on after 15 minutes and stable operating conditions were attained after another 30 minutes. This period is not included in the figure in order to increase the resolution of the more interesting parts of the transient. As can be seen in Figure 5 a a stop of the fuel feed caused the oxygen concentration to increase from 4% to 11% and the CO_2 to fall from 15.5% down to 10% (Figure 5 b). The CO concentration was almost unchanged until the drop of the top temperatures became large. The CO increased even more when the fuel feed was started again and a release of large amounts of CO from the volatiles at low combustion temperatures occurred.

The NO concentration corrected to 6% O_2 increased from 60 ppm up to 200 ppm. The decrease of the NO concentration after the top (1 minute before the fuel supply was started) was probably due to the falling combustion temperatures, but the NO decrease was enhanced even more when the fuel supply was started again. For N_2O an opposite behaviour was seen. However, the first decrease of N_2O was not more than what can be explained as a dilution effect. But when the fuel supply was restarted, an increase of the N_2O emission up to 280 ppm (at 6% O_2) was recorded, which should be compared to the reference level of N_2O before the start of the step-response test which was 150 ppm (at 6% O_2). The increase of N_2O observed in this case should be compared to the N_2O emission when batches of fuel were supplied and the emission decreased instead (Figure 4). A check for CH_4 in the flue gas was carried out in this case as well, but nothing was found.

Measurement of Gas Concentration Profiles in the Combustion Chamber

Figure 6 shows the oxygen concentration profiles in the centre of the combustion chamber when the height of the secondary air supply was changed. The profile looks different from oxygen-concentration profiles obtained in a laboratory-scale CFB combustor [30]. In [30] falling oxygen-concentration profiles are measured also above the secondary air supply. The reason for the difference between the small laboratory unit with a diameter of only 0.1 m and the large 12 MW boiler can be found in the secondary air penetration. This is illustrated in Figure 7, which shows the horizontal profiles of oxygen at heights of 4.8 m (lower figure) and 8.0 m (upper figure), when the secondary air was supplied to the 3.8 m level. The base plane of Figure 7 is the cross-section of the combustion chamber. Secondary air is introduced from the front and rear walls of the combustion chamber. One meter above the secondary air nozzles an increase of the oxygen concentrations could be registered at the 6 measurement points located parallel to the front and rear walls at a distance of 0.37 m. Along the center line located 0.85 m from the walls no change of oxygen was observed. Moving another 3.2 m upwards, a more even concentration profile could be seen and a higher average oxygen concentration along the centerline. This means that more oxygen is transported to the middle of the combustion chamber from the oxygen-rich sides than what is consumed by combustion. Measurement of horizontal profiles was carried out at the same time for CO_2 , CO and NO as well, but not for N_2O due to high CH_4 concentrations.

The CO_2 profiles are the inverse of the oxygen profile. Both the CO and NO were influenced by the large differences in oxygen concentration. Higher CO concentrations and lower NO concentrations were measured at the centerline than at the oxygen-rich sides of the combustion chamber. The measurement in the middle of the combustion chamber (1 point) is representative for the whole centerline. This centerline represents about 10% of the cross-section area of the combustion chamber. The remaining vertical profiles of NO, N_2O , HCN, NH_3 , CO and C_1 to C_3 hydrocarbons were recorded only in the middle of the combustion chamber, but these profiles are most likely representative for the centerline as well.

Figure 8 shows the vertical profiles of N_2O and NO. High concentrations of NO were found near the bottom, but the NO decreased higher up in the combustion chamber as an effect of reducing reactions and dilution by secondary air, which is

gradually mixed with the primary air. On the other hand, only 50 ppm N_2O was measured at the bottom and a slow increase of the concentration was seen along the entire height of the combustion chamber in spite of the dilution effect of secondary air. Similar profiles of NO and N_2O from the combustion chamber of a 8 MW_{th} CFB boiler were reported in [2] and have also been confirmed in a small laboratory unit with a diameter of only 0.1 m [31].

In Figure 9 the concentrations of NH_3 and HCN can be followed. For these species a rapid formation of the gas occurred near the bottom, followed by an almost immediate decrease again down to only about 5 ppm. NH_3 dominated over HCN and the ratio of NH_3/HCN at the maximum concentrations (at $h = 0.65$ m) was 8.5. When the secondary air starts to reach the centerline, a second small maximum in the NH_3 and HCN concentration was observed. Here the ratio of NH_3/HCN is 1.0. Also the hydrocarbon concentrations showed a large maximum at 0.65 m above the bottom of the combustion chamber, Figure 10. The ratio of the three classes of hydrocarbons at the maximum was $\text{CH}_4/\text{C}_2 = 2.7$ and $\text{CH}_4/\text{C}_3 = 12$. The hydrocarbons were oxidized almost completely before the secondary air reached the centerline. The levels of CO were between 2% and 500 ppm in the combustion chamber. A maximum of CO could not be registered, since the CO instrument reached its upper limit. The decrease of CO is much slower than that of the hydrocarbons. There are several reasons for this. First, CO is also produced as an intermediate of hydrocarbon oxidation. Second, the CO oxidation is a much slower reaction than the corresponding oxidation steps of hydrocarbons. Third, CO is also produced from an incomplete combustion of char and this char combustion takes place higher up in the combustion chamber, and not only at the bottom. Finally, a comparison of the N_2O and NO profiles when the secondary air was supplied to different heights can be followed. Moving the secondary air to a higher level caused the N_2O to increase more slowly, up to a lower level of 128 ppm (corrected to 6%), than the case shown in Figure 8 where a N_2O concentration of 155 ppm (at 6%) was recorded. The NO profiles were very similar up to the 6 m level from which the NO decreases faster for the case of secondary air at 3.8 m. The exit concentration dropped 45% from 47 ppm (corrected to 6% O_2) down to 26 ppm (at 6% O_2).

INTERPRETATION OF THE RESULTS

General

It is assumed that there are two principal formation routes for N_2O in CFB boilers, formation involving char or formation from HCN. The formation involving char can either be a direct consequence of the combustion of char and the conversion of fuel nitrogen according to step 15, Figure 1, or a result of NO reduction with char surface serving as a catalyst, step 19.

The results presented in Figure 3 to 11 will be analyzed with the purpose of better understanding the two formation routes of N_2O . It is evident, however, that the observations are affected by destruction of N_2O as well. One of the most extreme examples is given in [8] where the homogeneous reduction with radicals (step 12, Figure 1) was utilized to reduce N_2O by firing of gas in the cyclone independent of the processes in the combustion chamber.

N_2O formation from char

Several test results indicate that the char content in the combustion chamber influences the formation of N_2O .

A proof of the influence of char is given by the step-response test with flyash recirculation, Figure 3. Here, a N_2O reduction was recorded as a consequence of the decrease of the amount of char when the recirculation was stopped in spite of a simultaneous decrease in cyclone temperature. A change in cyclone temperature has been shown by independent tests [8] to have the opposite effect on N_2O from what was shown in Figure 3, which further supports the influence of char, since fuel volatiles are insignificant in the cyclone during the present test conditions.

The vertical concentration profiles, Figures 8 to 11, indicate that the concentration of HCN is small in the upper part of the combustion chamber, which supports the assumption that the increase of N_2O with height is a result either of char combustion or of reduction of NO on char surfaces. The continuous decrease of NO as the N_2O increases supports the suspicion that the latter source of N_2O plays a role through step 19, Figure 1. Figure 11 shows that the NO concentration was

decreased by 400 ppm between 1 and 5 meters above the bottom of the combustion chamber, while the N_2O increased by 50 ppm (in the case of secondary air at 3.8 meter). Assuming the mechanism of Kramlich in which NO reacts with char nitrogen to form N_2O (see Table I) one molecule of NO reduced is needed in order to produce one molecule of N_2O and 12% of the NO reduced would produce the 50 ppm N_2O . If NO molecules are absorbed on the char surface instead, two moles are needed and 24% of the NO reduced would be spent to produce N_2O . It is seen that these conversions are at least possible from a mass-balance point of view.

The tests with stop and start of the fuel feed, Figure 5, can be interpreted as an effect of char as well as of volatiles. If formation of N_2O as a consequence of NO reduction on char surfaces is relevant, the following interpretation could partly support the observations: When the fuel was stopped, the NO increased in spite of a decreasing release rate of fuel nitrogen and falling temperatures (Figure 5 c). This is explained as an effect of the fast decrease of the CO levels in the combustion chamber, and thus a lower reduction rate of NO on char surfaces. The corresponding decrease of N_2O is partly hidden behind the influence of the drop in the temperature, but on the other hand, when the fuel was started again the NO reduction on char surfaces came back and a heavy increase of the N_2O emission was observed, certainly to some extent also caused by the volatiles.

A few results taken from previous tests support the discussion around the influence of char.

In the parameter study reported in [6] three fuels with different volatile contents were used. In order to compare the fuels with each other, the results are rewritten in Figure 12 in the form of fuel-nitrogen conversion to N_2O . The char content of bed material taken from the return leg of the hot cyclone is plotted in Figure 12 as well. It is evident that the conversion of fuel-nitrogen to N_2O is related to the char content. However, also in this example other factors may influence the N_2O trends observed.

The only test available where the N_2O formation from NO reduction is isolated from other influencing factors is taken from [2], where the fluidizing air was doped with 2200 ppm NO. In the case where bituminous coal was used as fuel, 85% of the NO added was reduced to N_2 , but 5% was found as N_2O . Similar NO doping tests

have been carried out in a laboratory fluidized bed [32] and similar results were obtained. The conversion of 5% is not the primary formation of N_2O , since reduction of N_2O (step 12 and 13, Figure 1) is expected to occur also.

N_2O formation from HCN

Homogeneous formation of N_2O , step 10, Figure 1, is a possible route. In the calculations by Kilpinen and Hupa [11] 500 ppm of HCN was needed to form about 100 ppm N_2O at 800°C . The maximum values measured in the present tests never exceeded 40 ppm, Figure 9, and the HCN levels rapidly decreased with height in the combustion chamber to 10 ppm without a corresponding increase of the concentrations of N_2O . It appears then, that the relationship between the quantities of HCN needed according to calculations for an essential contribution to N_2O formation and the measured values of HCN require further discussion.

The first question to be answered is if the relation between the measured concentrations of NH_3 and HCN is reasonable. Above, it was mentioned that NH_3 could be produced from HCN by hydrogenation. This may be an explanation to the high concentrations of NH_3 measured at a height of 0.65 m in the 12 MW boiler. Actually, the NH_3 produced from the side chains of the coal structure (amino groups) may not be sufficient to reach the 350 ppm level measured. If data from [15] concerning the NH_3 yield in the light gas fraction from pyrolysis of bituminous coal are applied, a maximum concentration of 200 ppm NH_3 in the primary zone of the 12 MW CFB boiler would be obtained. Fast hydrogenation of HCN may be an explanation of the high NH_3 levels measured, but still the N_2O formation route from HCN does not explain the levels of N_2O measured in the boiler. Further measurements of HCN are needed in the 12 MW boiler in order to cover a larger part of the bottom zone area, since higher HCN concentrations can be expected closer to the fuel-feed point. Furthermore, a conversion of HCN to NH_3 , either on the filter of the probe or in the gas sampling probe itself cannot be excluded in spite of the cooled probe used.

Although the HCN measured seems to be insufficient to explain a large part of the N_2O emission, other factors than the NO reduction on char certainly play a role for the N_2O formation. Examples of this is shown in Figure 11 where the increase in the height of the primary air zone by moving the secondary air to a higher level

resulted in a decrease in both the NO and the N₂O emission. Similarly, in the batch supply tests shown in Figure 4 the NO and the N₂O emissions decreased simultaneously.

The trends in Figure 5, especially the ones obtained when the fuel feed was restarted at an oxygen level of 11% need further comments. In addition to what was said about the influence of char, the large values of N₂O can also be a result of a contribution from HCN according to step 10, Figure 1, if the hydrogen released from the volatiles is predominantly oxidized to water in the oxygen-rich atmosphere instead of converting HCN into NH₃.

The results of Figure 13 showing the N₂O emissions from fuels with different volatile content could possibly have been influenced also by the volatiles. Unfortunately the comments to be made are mere speculations: The high conversion of fuel nitrogen to N₂O in the case of petroleum coke would partly be a result of a low release of H₂ which means that relatively seen more HCN would be available for N₂O formation. In the case of brown coal which is characterized of a low N₂O emission in spite of a high volatile content, a larger part of the volatiles might have been released as NH₃, since more fuel nitrogen is contained in the side chains compared with fuels of higher rank.

DISCUSSION AND CONCLUSIONS

The tests were carried out in a bed of sand-ash without limestone addition.

Formation – Destruction of N₂O

Among the homogeneous reduction mechanisms, the reduction by radicals is deemed to be the most important one [8]. The heterogeneous reduction of N₂O on char surfaces (step 13) was found by de Soete [12] to be higher than that of NO in his fixed bed reactor in the absence of CO. This may shift to a higher NO reduction in the combustion chamber of a CFB boiler with CO concentrations between 20 000 and 500 ppm. However, if formation and reduction are compared, it is evident that the formation is dominant in the combustion chamber, since the N₂O concentration increases with height according to Figure 8.

Conversion of HCN

HCN is important for the formation of N_2O , at least in a homogeneous reaction situation. However, laboratory scale studies show that hydrogenation of primary produced HCN to NH_3 may occur, which would withdraw HCN from the N_2O formation route.

HCN versus char

There are no verifications of the importance of HCN for N_2O production in the heterogeneous surrounding of a fluidized bed. Also, the low concentrations of HCN measured indicates that its importance may be limited. Measurement errors and strong concentration variations in the horizontal plane have to be further checked, however.

The char is more important than HCN for the successive formation of N_2O seen in Figure 11. It was mentioned above that a conversion of 10 to 30% of the NO converted would be sufficient to explain the N_2O formation. This should be compared with a possible contribution from char combustion (step 15). de Soete [12] has found that up to 5% of the char nitrogen was converted to N_2O in his experiments. This value corresponds to 50 ppm N_2O assuming a complete combustion of the char. The figure of 5% is too small to explain the increase of the N_2O concentration with height as an effect of char combustion only.

The general conclusion from this discussion then becomes: The principal contribution to the N_2O emission originates from the reduction of NO on char surfaces. HCN and char combustion make minor contributions. This conclusion has of course to be further verified since the basic knowledge of N_2O formation and reduction still has to be improved.

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Table I

Important formation and reduction steps for N_2O at fluidized bed conditions. Reactions involving lime are excluded.

Reaction	Catalyst	Step in Fig.1	References
<i>Formation of N_2O</i>			
$\begin{cases} \text{HCN} + \text{O}^* \rightarrow \text{NCO}^* + \text{H}^* \\ \text{NCO}^* + \text{NO} \rightarrow \text{N}_2\text{O} + \text{CO} \end{cases}$	homogeneous gas phase	10	[10],[11]
$2\text{NO} \rightarrow \text{N}_2\text{O}$	char	19	[9],[12]
$\text{NO} + \text{char-N} \rightarrow \text{N}_2\text{O}$	gas-solid reaction	19	[9],[12]
$\text{char-N} + 1/2 \text{O}_2 \rightarrow \text{N}_2\text{O}$	gas-solid reaction	15	[12]
<i>Reduction of N_2O</i>			
$\begin{cases} \text{N}_2\text{O} + \text{H}^* \rightarrow \text{N}_2 + \text{OH}^* \\ \text{N}_2\text{O} + \text{OH}^* \rightarrow \text{N}_2 + \text{HO}_2^* \end{cases}$	homogeneous gas phase	12	[10],[11]
$2\text{N}_2\text{O} + \text{char} \rightarrow \text{N}_2 + \text{CO}$	gas-solid reaction	13	[12]
<i>Other important reactions</i>			
$2\text{NH}_3 + 3/2 \text{O}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O}$	char	8	[13]
$\text{NH}_3 + 5/4 \text{O}_2 \rightarrow \text{NO} + 3/2 \text{H}_2\text{O}$	char	9	[13]
$\text{HCN} + 3 \text{H}_2 \rightarrow \text{NH}_3 + \text{CH}_4$	homogeneous gas phase	11	[14],[15]
$\text{NO} + \text{char} \rightarrow 1/2 \text{N}_2 + \text{H}_2\text{O}$	gas-solid reaction	17	[13]
$\text{NO} + \text{CO} \rightarrow 1/2 \text{N}_2 + \text{CO}_2$	char	18	[13]

Table II

Support for N₂O formation mechanisms

Sort of test	Figure or reference	N ₂ O formation Step 10, Fig.1	N ₂ O formation Step 19, Fig.1	N ₂ O formation Step 15, Fig.1
Stop of fly ash recirculation	3,[31]		x	x
Batch supply of fuel	4	x		
Stop of fuel supply	5	x	x	
Start of fuel supply	5	x	x	
NO, N ₂ O profiles in com- bustion chamber	8,[2],[30]	x	x	x
NH ₃ , HCN profiles in com- bustion chamber	9		x	x
Secondary air, different levels	11	x		
NO doping of fluidizing air	[2],[20]		x	
Tests with three different fuels	13	x	x	x

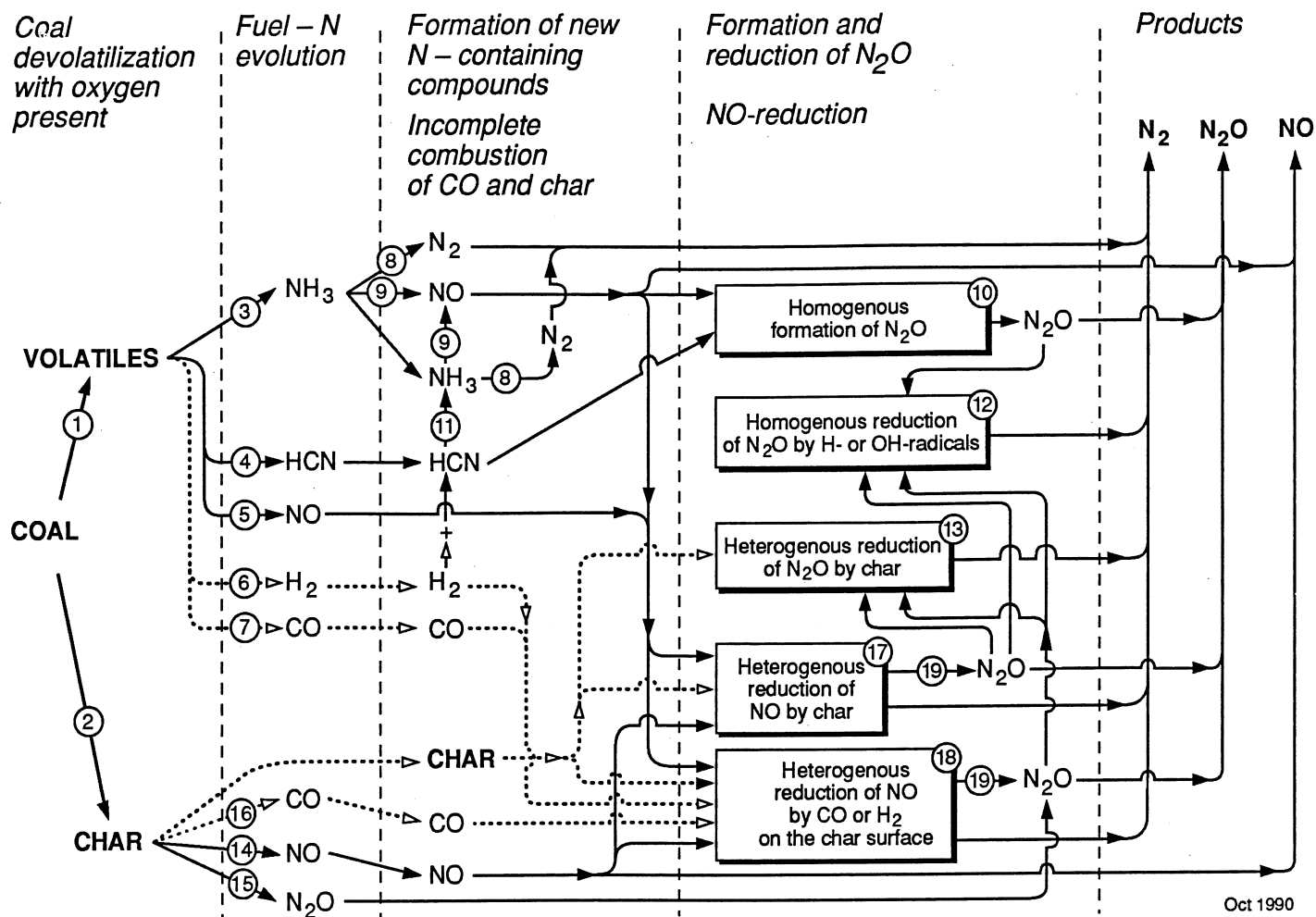


Figure 1. Pathways of in-fuel-nitrogen formation to N_2O in fluidized beds.

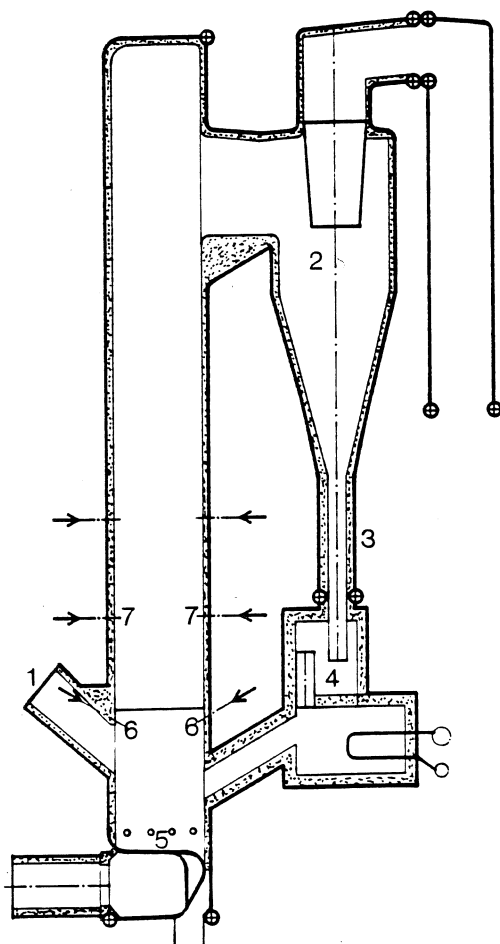


Figure 2. The 12 MW CFB boiler at Chalmers University of Technology.

1. Fuel feed chute.
2. Cyclone. 3. Particle return leg.
4. Particle seal. 5. Bottom plate.
6. Secondary air inlet at 2.2 meters.
7. Secondary air inlet at 3.8 meters.

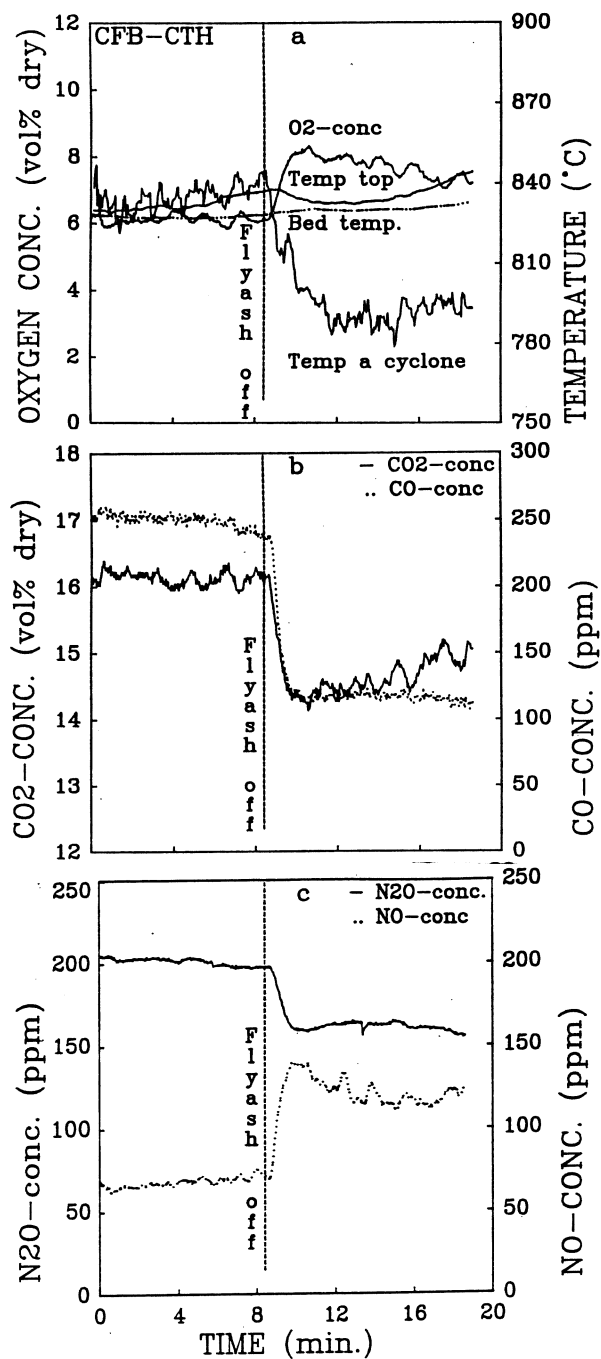


Figure 3a,b,c. Step response test with stop of fly ash recirculation.
 Fly ash flow/fuel flow = 1.0.
 Operating conditions:
 Bed temperature = 830°C.
 Excess air ratio = 1.3.
 Primary air stoichiometry = 1.0.

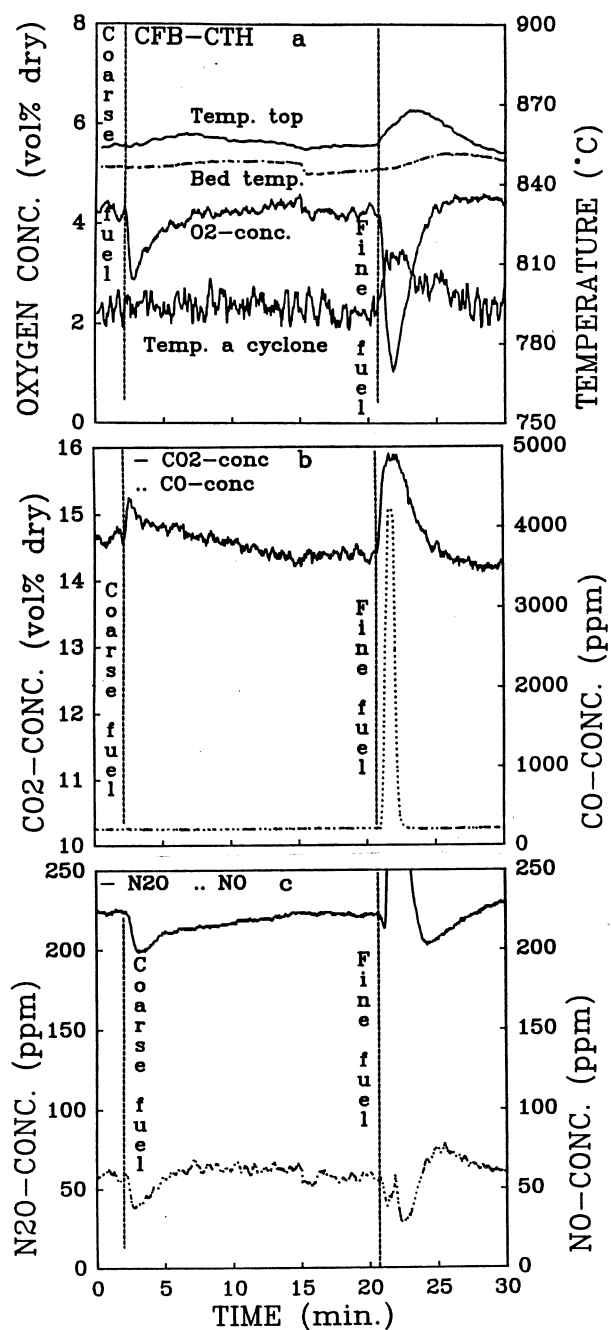


Figure 4 a,b,c. Step response test with batch supplies of bituminous coal. Batch size/fuel flow = 2.3.
 Operating conditions: Reference case.

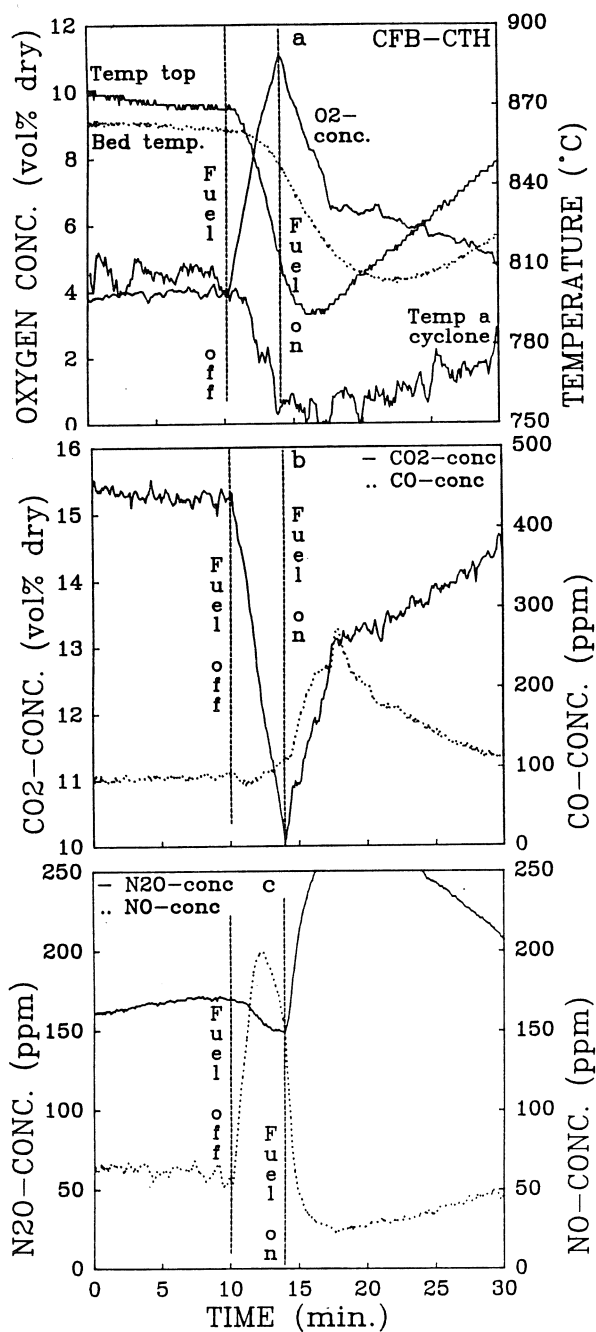


Figure 5 a,b,c. Step response test with stop and start of fuel feed.
Operating conditions: Reference case.

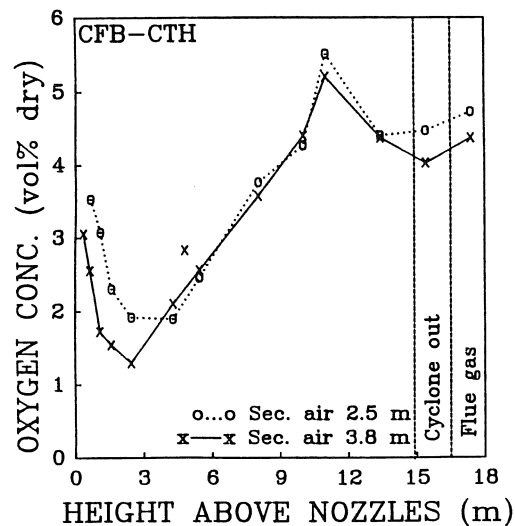


Fig.6. Oxygen concentration in the centre of the combustion chamber with secondary air at 2.2 m or 3.8 m.
Operating conditions: Reference case.

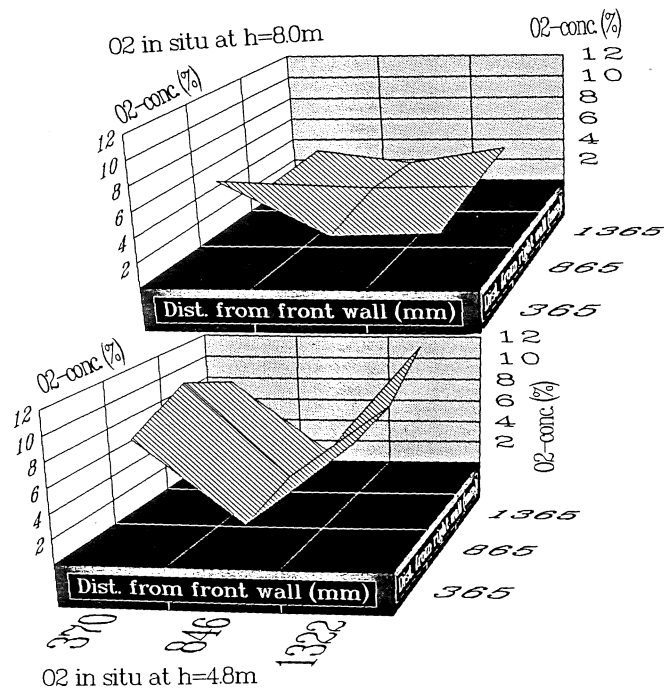


Figure 7. Horizontal profiles of oxygen at 4.8 m and 8.0 m above the bottom of the combustion chamber. Secondary air is supplied at 3.8 m. Depth of figure shows the distance from the right wall.
Operating conditions: Reference case.

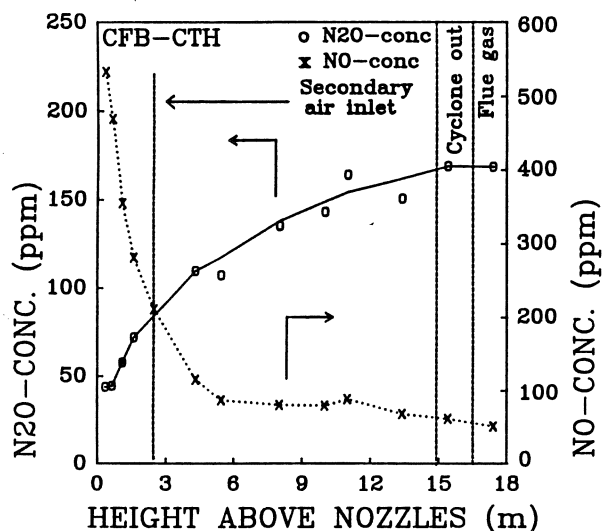


Fig. 8. N_2O and NO concentration profiles in the centre of the combustion chamber with secondary air at 2.2 m. Operating conditions: Reference case.

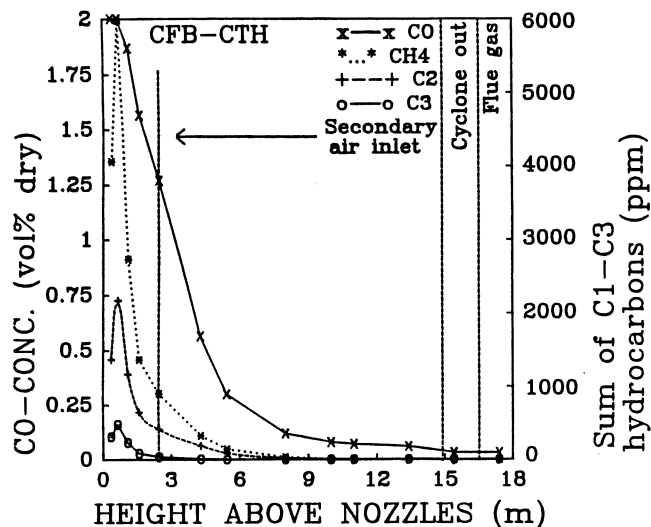


Figure 10. CO and C_1 to C_3 hydrocarbon concentrations in the centre of the combustion chamber with secondary air at 2.2 m. Operating conditions: Reference case.

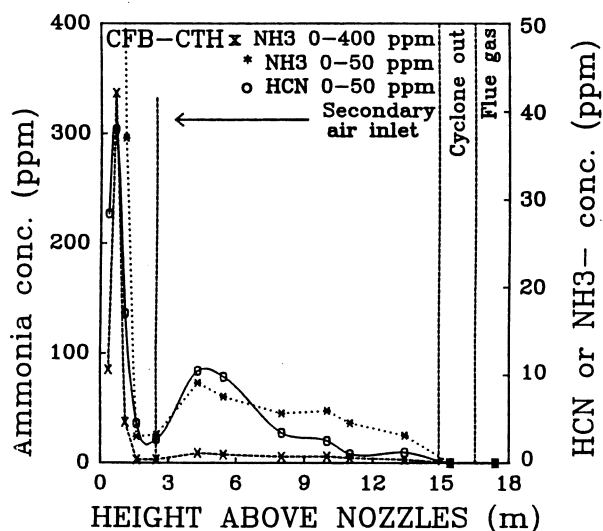


Fig.9. NH_3 and HCN concentration profiles in the centre of the combustion chamber with secondary air at 2.2 m. NH_3 concentration shown at 0-400 ppm range on left axis and 0-50 ppm range on right axis. Operating conditions: Reference case.

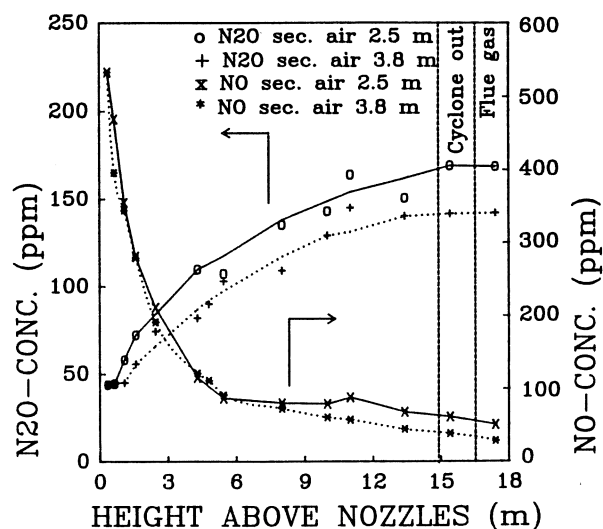


Figure 11. Comparison of the vertical profiles of N_2O and NO at different heights of secondary air supply. Operating conditions: Reference case.

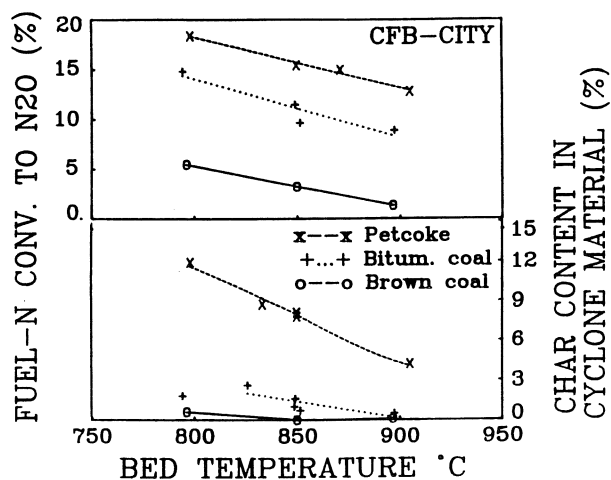


Figure 12. Fuel-nitrogen conversion to N_2O and char content in the material returning from the hot cyclone as function of bed temperature for three different fuels. Operating conditions: Reference case. Rewritten from data in [6].