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INFLUENCE OF AIR-STAGING ON THE CONCENTRATION PROFILES OF NH$_3$ AND HCN IN THE COMBUSTION CHAMBER OF A CFB BOILER BURNING COAL

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ABSTRACT

The characterisation of the concentration profiles of NH$_3$ and HCN are of great importance for increasing the knowledge of the formation and destruction pathways of NO and N$_2$O in a fluidized bed boiler. Further improvements of the sampling methods for the determination of both NH$_3$ and HCN in the combustion chamber in full-scale CFB boilers are also needed. A gas-sampling probe connected to a Fourier Transform Infra Red (FTIR) instrument and a gas-quenching (GQ) probe in which the sample is quenched directly in the probe tip by a circulating trapper solution were used. The FTIR technique is based on analysis of hot combustion gases, whereas the trapper solutions from the GQ probe were analysed by means of wet chemistry.

The tests were performed during coal combustion in a 12 MW CFB boiler, which was operated at three air-staging cases with the addition of limestone for sulphur capture. The concentration profiles of NH$_3$ and HCN in the combustion chamber showed a different pattern concerning the influence of air-staging. The highest levels of NH$_3$ were observed during reducing conditions (severe air-staging), and the lowest were found under oxidising conditions (no air-staging). The levels of HCN were much lower than those measured for NH$_3$. The highest levels of HCN were observed for reversed air-staging and severe air-staging showed almost no HCN. The potential reactions involving NH$_3$ and HCN in the combustion chamber as well as the potential measurement errors in each sampling technique are discussed for the three air-staging cases.

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1 Introduction

The simultaneous minimisation of the total emissions of N$_2$O, NO$_x$, SO$_2$ and CO are an environmental concern during combustion of coal in a fluidized bed boiler (FBB). The two major parameters for controlling the environment in the combustion chamber of an FBB are temperature and air supply. Reversed air-staging was first described in (Lyngfelt et al 1995b), as a method for reduction of N$_2$O without creating adverse effects on the other emissions and combustion efficiency. In reversed air-staging (Lyngfelt et al 1995a, Lyngfelt et al 1995b, Lyngfelt et al 1998), the air-ratio (= primary air-ratio/total air-ratio) in the bottom of the combustion chamber is raised, whereas that in the upper part is lowered, as compared to normal air-staging. More oxidising conditions in the bottom are beneficial for sulphur capture and have no effect on the N$_2$O emission. The lower air-ratio in the upper part and the cyclone, however, results in significantly reduced NO and N$_2$O emissions. Measurements of the NH$_3$ and HCN concentration profiles in the combustion chamber during combustion of different fuels and under different air-staging conditions could improve our understanding of the formation and reduction paths of NO and N$_2$O in an FBB. Such results would also be important, for instance, in supporting modelling of the nitrogen chemistry in real boilers (Goel et al 1996, Hannes et al 1995, Philippek et al 1997, Särnbratt 1998, Tsuo et al 1995).

Several measurement techniques have been used for determination ammonia and/or HCN at combustion conditions. FTIR analysis of nitrogen species have been carried out in both combustion laboratories (Li et al 1998, Tullin 1995, Wartha

1998) and in full-scale boilers (Andries et al 1997, Kassman et al 1995, Tullin et al 1996, Åmand 1994, Åmand et al 1997). The measurements with FTIR in full-scale have often been performed in parallel with wet chemistry (Kassman et al 1995, Åmand et al 1997). Wet chemical methods have also been applied in for instance pulverised coal combustion (PCC) (Smart and Maalman 1987), in fuel-oil flames (Nimmo et al 1995) and in an electrically heated fluidised bed combustor (Boavida et al 1997). The temperature in the combustion chamber of a circulating fluidized bed (CFB) boiler is lower than in PCC, nevertheless the measurements are complicated due to the presence of particles and the complexity of the gas composition. Also, in order to measure the gas concentration in a combustion chamber with a sampling probe, the gases must be cooled rapidly to stop further reactions. Especially critical in the combustion chamber of a CFB bolier is the passage through a particle filter in a probe tip. Secondary reactions could occur both in a potential filter cake and in the filter material itself (Åmand et al 1997).

Experiments regarding the influence of air-staging on emissions during coal combustion have previously been carried out in a 0.1 MW CFB test unit (Reidick and Kremer 1996) and during peat combustion in a full-scale CFB boiler (Åmand et al 1997). In the present paper, the influence of air-staging on the concentration profiles of NH_3 and HCN was studied in the combustion chamber of a CFB boiler burning coal. Here a rather extreme air-staging case, where reducing conditions prevailed in the whole combustor and primary cyclone is included in the investigation. The measurement was carried out by means of two sampling techniques already applied in the boiler (Kassman et al 1995, Åmand 1994, Åmand et al 1997). It was a gas-sampling probe connected to an FTIR analyser and a gas-quenching (GQ) probe in which the sample is quenched directly in the probe tip by a trapper solution. Both the sampling systems and the evaluation procedures have been improved since the last measurements of NH_3 and HCN (Kassman et al 1995).

2 Nitrogen Chemistry

During fluidized bed combustion (FBC) of coal with addition of limestone, many heterogeneous and homogeneous reactions are important for the formation and reduction of NO and N_2O, Figure 1 (Johnsson 1994). NH_3 and HCN are the major nitrogen-containing components, the characterisation of which is relevant to the formation of NO and N_2O (Hämäläinen and Aho 1994, Johnsson 1994, Pels et al 1995, Winther et al 1996, Wójtowicz et al 1995). N_2O is formed preferentially from cyano-species, and NH_3-based compounds have a tendency to react mainly to NO. The reaction pathways of NO and N_2O are not well understood. There are reaction schemes available for homogeneous reactions in gas flames (Kilpinen and Hupa 1991, Kramlich et al 1989), but the knowledge of the heterogeneous processes taking place in the combustion chamber of an FBB remains insufficient. There are char, ash, sand and limestone present in the bed material during combustion of coal building up a complex environment, which also depends on the operating conditions and thereby the sulphur capture behaviour of the added limestone.

The secondary reactions during FBC, where NH_3 and HCN are either oxidised, decomposed or reduced to other species are of special interest for this paper. In many of these reactions, both NH_3 and HCN occur in parallel reaction pathways catalysed by the same solids such as CaO, $CaSO_4$, char and ash (Johnsson 1994). Even if similar secondary reactions occur, the reaction rate is sometimes much faster for one of them. Oxidation of HCN over CaO is one such example. There are also some important differences in the behaviour of HCN and NH_3 due to air-staging conditions. For instance, HCN may be reduced by H_2 over CaO to form NH_3 under reducing conditions (Jensen et al 1993) and reactions between HCN and $CaSO_4$ forming either CaO or CaS during reductive decomposition of $CaSO_4$ have been suggested (Jensen et al 1997). No such reactions for NH_3 under reducing conditions have been found. There is also no knowledge available regarding the influence of reactions between NH_3 or HCN and CaS, formed during reducing
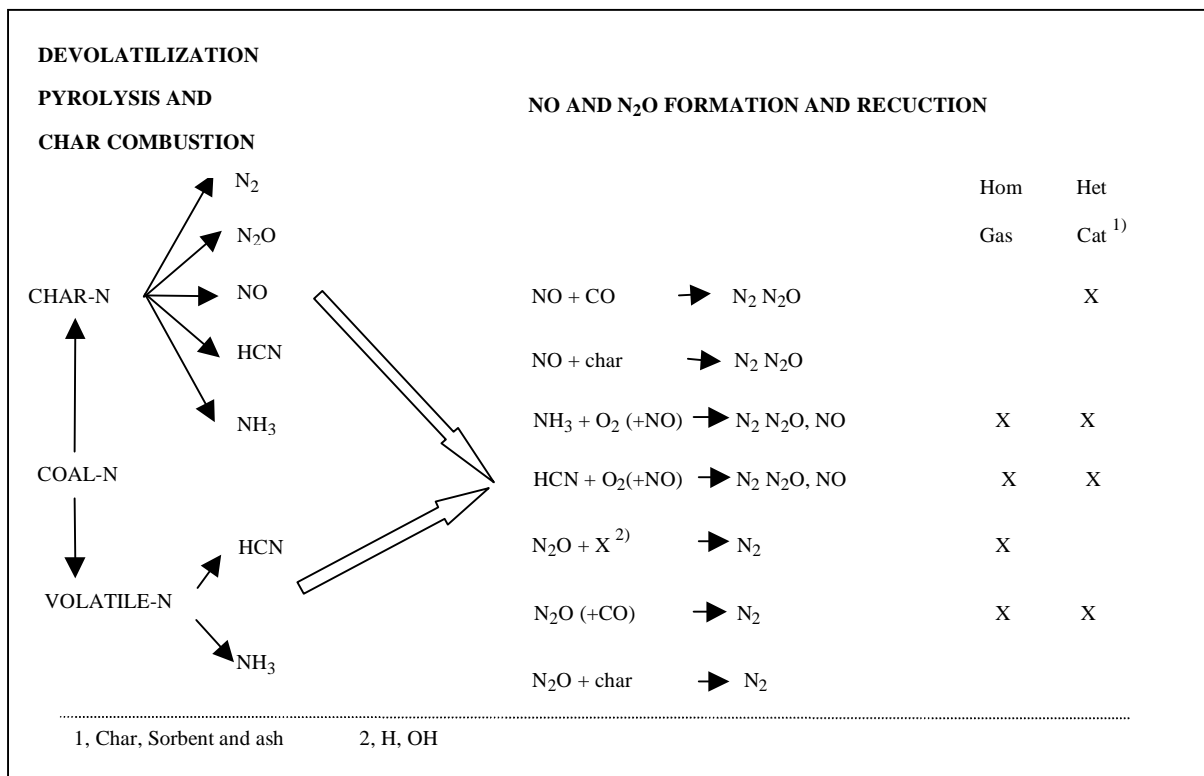
DEVOLATILIZATION PYROLYSIS AND CHAR COMBUSTION

$CHAR-N \rightarrow N_2, N_2O, NO, HCN, NH_3$

$COAL-N$

$VOLATILE-N \rightarrow HCN, NH_3$

NO AND N_2O FORMATION AND RECUCTION

Reaction	Hom Gas	Het Cat [1]
$NO + CO \rightarrow N_2\ N_2O$		X
$NO + char \rightarrow N_2\ N_2O$		
$NH_3 + O_2\ (+NO) \rightarrow N_2\ N_2O, NO$	X	X
$HCN + O_2(+NO) \rightarrow N_2\ N_2O, NO$	X	X
$N_2O + X$ [2] $\rightarrow N_2$	X	
$N_2O\ (+CO) \rightarrow N_2$	X	X
$N_2O + char \rightarrow N_2$		

1, Char, Sorbent and ash   2, H, OH

Figure 1 Simplified reaction scheme for the formation and reduction of NO and N_2O adapted from (Johnsson 1994).

conditions in the combustion chamber (Mattisson and Lyngfelt 1995).

3   Experimental

3.1 The boiler

The tests were performed in the 12 MW CFB boiler (Lyngfelt et al 1998, Åmand and Leckner 1993) at Chalmers University of Technology. The measurement ports on the wall of the combustion chamber, Figure 2, are of particular interest for this project. These ports enable the sampling of gas inside the combustor and a more detailed characterisation of the combustion behaviour. The boiler is equipped with daily calibrated on-line conventional flue-gas analysers for the continuous monitoring of O_2, CO, SO_2, NO and N_2O in the stack and O_2, NO, CO, CO_2, SO_2, and total hydrocarbons (HC-tot) in the combustion gas from the gas-sampling probe.

3.2 Operating conditions

The boiler was operated at three different air-staging cases and limestone was supplied at a molar ratio of 1.8 to 2.0 for sulphur capture. The excess air-ratio was kept constant at 1.23 during all air-staging cases. The temperature in the bottom of the combustion chamber was held between 848 and 851°C with the help of the particle cooler in the solids return leg and flue-gas recirculation added to the primary air duct. The fuel, a coal from Katowice in Poland had the following composition: ash, moisture and content of combustibles, 14.4%, 10.8% and 74.7% respectively, analysed as delivered; C, H, O, S and N, 81.4%, 5.7%, 10.4%, 0.9% and 1.6%, respectively, expressed on a moisture and ash-free basis (maf). The volatile content was 35.8% on the maf basis.

The air-staging cases are:

Reversed air-staging: no secondary air in the combustion chamber, but about 20% of the total air added in the cyclone outlet for final combustion (see (7) in Figure 2). This case gives
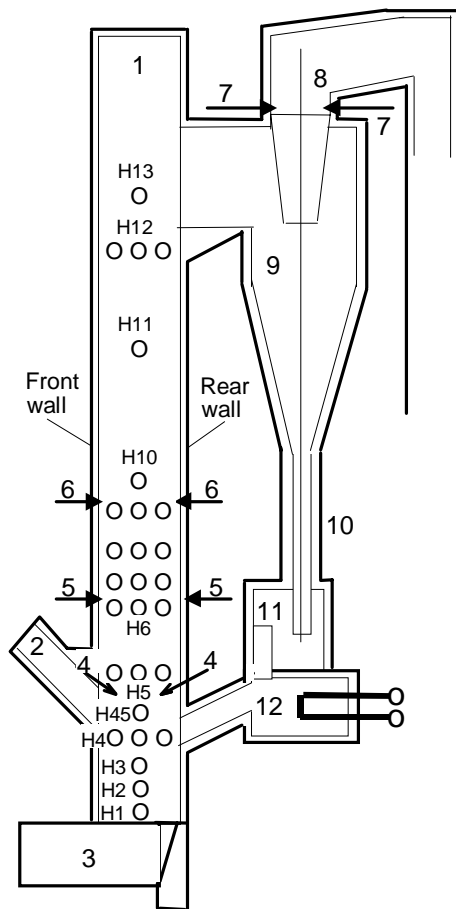
Figure 2 The 12-MW$_{th}$ CFB boiler at Chalmers University of Technology (1) combustion chamber; (2) fuel feed chute; (3) air plenum; (4) secondary air inlet at 2.1m; (5) secondary air inlet at 3.7m; (6) secondary air inlet at 5.4m; (7) secondary air inlet into cyclone exit duct; (8) cyclone exit duct; (9) cyclone; (10) particle return leg; (11) particle seal; (12) heat exchanger. Measurement ports (H1 to H13) on the right boiler wall indicated

an air-ratio λ_c of 1.05 in the combustion chamber and cyclone, calculated according to (Lyngfelt et al 1998).

No air-staging: no secondary air, all air added to the bottom of the combustion chamber except a small amount for fluidization of the particle seal and particle cooler. The conditions were significantly more oxidising in the lower part of the combustion chamber compared to reversed air-staging (λ_c= 1.23).

Severe air-staging: Increased amount of air in the cyclone outlet (see (7) in Figure 2) leading to a combustor air-ratio λ_c of only 0.94. This means significantly more reducing conditions in both the combustor and the cyclone compared to reversed air-staging.

3.3 The gas-quenching (GQ) probe and wet chemical analysis

The gas-quenching (GQ) probe and the sampling system, Figure 3, are described in detail in Kassman et al 1995 and the present sampling procedure can be found in Åmand et al 1997. Sampled combustion gas was withdrawn through a water-cooled quartz-lined probe. A trapper solution (acidic or basic) was circulated from a reservoir by a peristaltic pump and evenly sprayed through a distributor to obtain an immediate gas quenching without losing any solution. A sintered quartz filter in the probe tip, Figure 3b, prevented particles from contaminating the trapper solution. An additional wash bottle (see (6) in Figure 3a) was used to collect any HCN or NH$_3$ not absorbed in the reservoir.

Afterwards, the ammonia and cyanide content in the trapper solutions were analysed by means of wet chemistry. It was taken into consideration that HNCO can be converted to NH$_3$ when absorbed (Kassman et al 1995), and acetylene interferes with HCN excluding the use of ion selective electrodes in the analysis (Lin et al 1994).
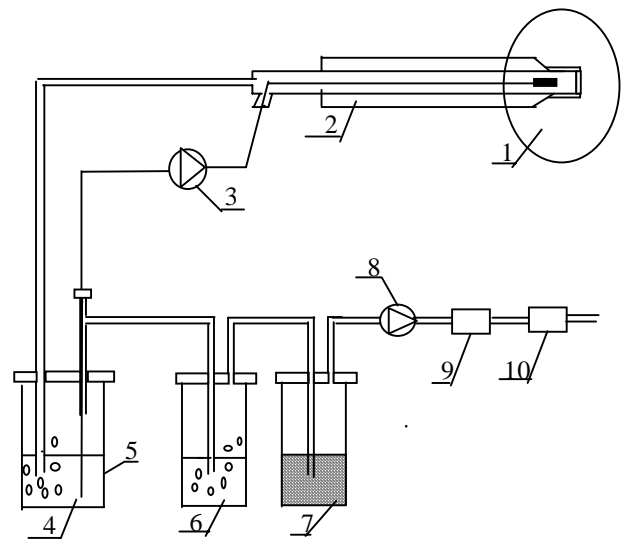

Figure 3a The gas quenching (GQ) probe and the sampling system (1) the tip of the probe; (2) water-cooled quartz-lined probe;(3) peristaltic pump; (4) trapper solution (acidic or basic);(5) reservoir; (6) wash bottle (trapper solution); (7) dryer; (8) gas pump; (9) mass flow controller; (10) gas meter
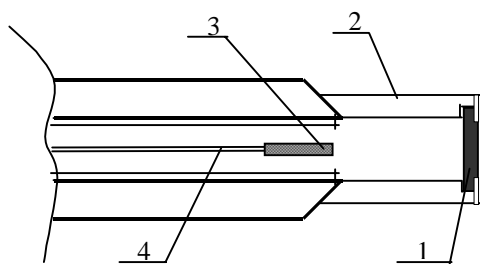
Figure 3b The tip of the GQ probe (1) sintered quartz filter; (2) uncooled steel pipe; (3) distributor, injection point of trapper solution; (4) injection line of teflon

The gas flow rate was approximately 3-5 litres/minute. The total volume of gas withdrawn was measured by a gas meter and a mass flow controller connected to a data acquisition system.

The ammonia content in the acidic (10 mmol/dm^3 H_2SO_4) trapper solution was analysed by means of a distillation followed by a titration (Foss Tecator 1993). The ammonia content in the additional bottle was found to be negligible and therefore only analysis of solutions from the reservoir were necessary. The concentration of NH_3 in the combustion gas was calculated using the ideal gas law. The cyanide content in the basic trapper solution (0.5 and 1.0 mol/dm^3 NaOH) was analysed by means of a distillation followed by a titration ($AgNO_3$) (Foss Tecator 1997). Any sulphides present in the samples were precipitated prior to analysis. A significant amount of HCN (5 – 20%) was found in the additional bottle, which consequently was included in the evaluation. The concentration of HCN was calculated using a similar principle as NH_3. An overall absorption efficiency of 100% was assumed
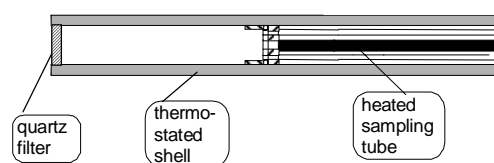
in the trapper solutions taken from the reservoir and the additional bottle, although it can not be excluded that HCN to some extent also escaped the additional bottle.

3.4 The gas-sampling probe and FTIR analysis

The gas-sampling probe, Figure 4, has been described earlier (Kassman et al 1995, Åmand et al 1997). However, the probe tip, Figure 4a, has been reconstructed in order to prevent bed material from being accumulated on the filter. A sintered quartz filter, instead of a ceramic one, was attached to the probe tip in an arrangement similar to what was used in the GQ probe. The combustion gas passed the quartz filter and was then transported through the centre-pipe, which was electrically heated to 200°C. Downstream of the probe the combustion gas was transported to the gas analysers through heated gas lines (200°C).

The FTIR analyser was connected in series upstream of the continuous gas analysers. The FTIR is a Bomem MB9100 with a 2 dm^3 quartz glass cell with an optical path-length of 6.4 metres. The instrument is equipped with a DTGS detector. The maximum resolution 1 cm^{-1} was used in all tests. The gas cell is heated to 174 °C. The Grams 32 software package (Galactic 1998) is used for evaluation and control of the spectrometer. During the present tests, spectra were collected in a continuous mode where 12 mirror scans, approximately five seconds in length, were sampled for each single-beam spectrum stored. 10 stored single-beam spectra were added to form an average

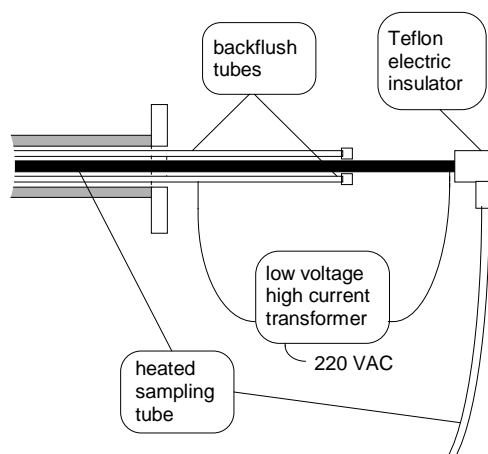

Figure 4a Front part of the gas-sampling probe

Figure 4b Rear part of the gas-sampling probe

single-beam spectrum corresponding to a measurement time of about 11 minutes. An absorbance spectrum was produced from the ratio of this average spectrum and a reference spectrum (100% nitrogen) was collected immediately before the sampling of the single-beam spectra.

A comparison was made in Karlsson and Åmand 1996 of three procedures for spectral evaluation, one of which was selected in this project: a multiple variable analysis method known as partial least square (PLS). The evaluation of low concentrations of trace compounds such as NH_3 and HCN in the presence of large quantities of water, CO_2 and hydrocarbons such as methane and ethene is especially complicated. The PLS software has been improved since Karlsson and Åmand 1996, by means of producing a rest spectrum, which could be visualised making a judgement of the quality of the prediction easier. However, there still remains a degree of uncertainty when using the PLS for HCN at low concentrations.

During severe air-staging the combustion gas had to be diluted with nitrogen in order to avoid too high absorbance when using the FTIR. The evaluation of spectra was improved by means of dilution. However, the determination of the dilution-ratio introduced further uncertainties. These were minimised by doping the dilution gas with sulphurhexaflouride (SF_6), the level of which was also determined by the FTIR
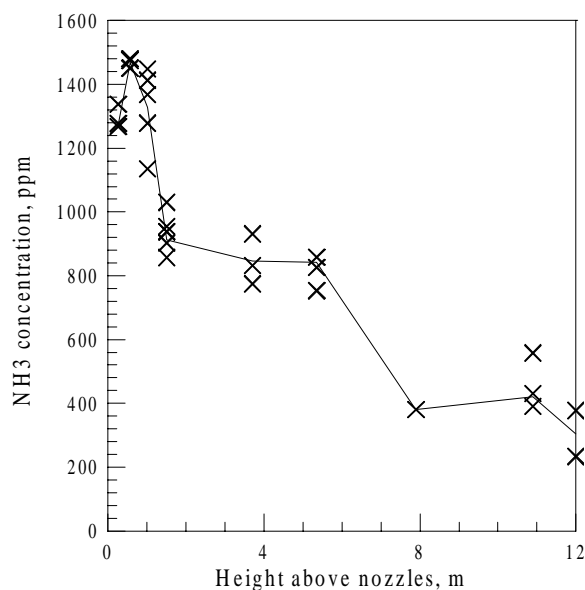

Figure 5 Concentration of ammonia as a function of height in the combustion chamber for severe air-staging. The gas-quenching probe (wet chemistry analysis)

4 Results

In a previous measurement (Åmand et al 1997) using peat as fuel, a comparison of the two sampling techniques showed almost identical results for NH_3 during three air-staging conditions. The NH_3 profile was also compared to that of ethene (using FTIR). It was observed that each change in NH_3 was followed by an identical change in ethene (C_2H_4). Consequently, if the concentration profiles of NH_3 and ethene do not follow each other, it could be taken as an indication of a measurement error.

4.1 Concentration profiles of ammonia

Figure 5 presents the scattering around an average value of ammonia measured by the GQ probe at severe air-staging conditions. Excellent repeatability was achieved in almost all the measurement ports, despite the measurements being carried out on different days. This indicates an accurate result and the existence of only minor changes in the NH_3 levels over a period of time. The highest values of NH_3 were found in measurement port H2 below the fuel chute, above which NH_3 fell as a function of height in the combustor. Less NH_3 compared to port H2 was found in measurement port H1 closer to the primary air
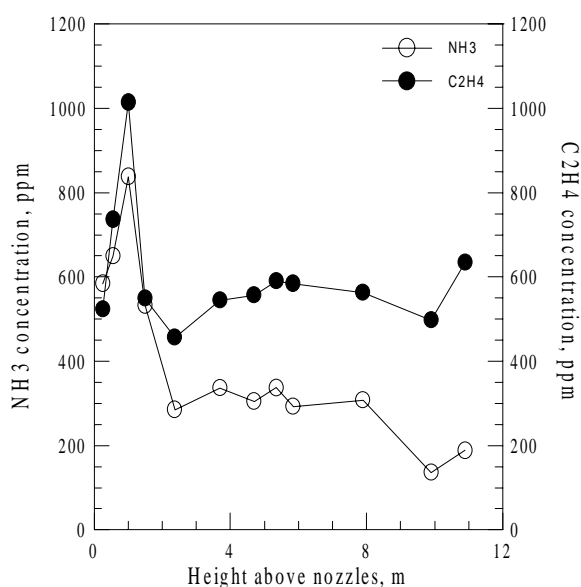

Figure 6 Concentration of ammonia and ethene as a function of height in the combustion chamber for severe air-staging. Diluted sample used in the evaluation of FTIR spectra. The gas-sampling probe (FTIR analysis)
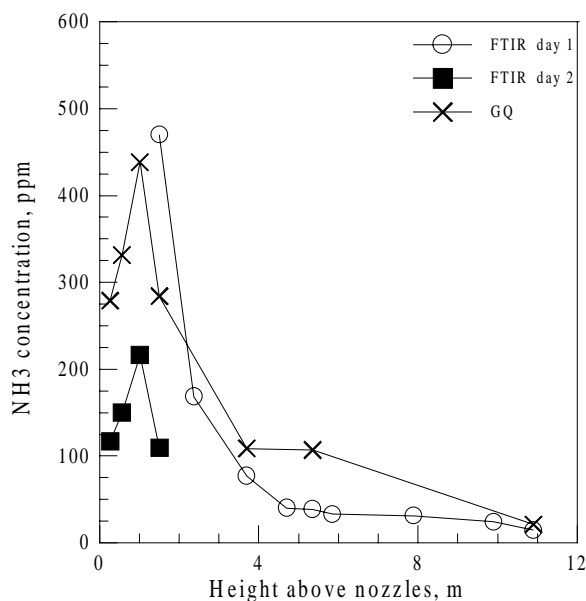
Figure 7 Comparison of the measurements of ammonia with the gas-quenching probe (wet chemistry analysis), ammonia and ethene with the gas-sampling probe (FTIR analysis) during reversed air-staging.
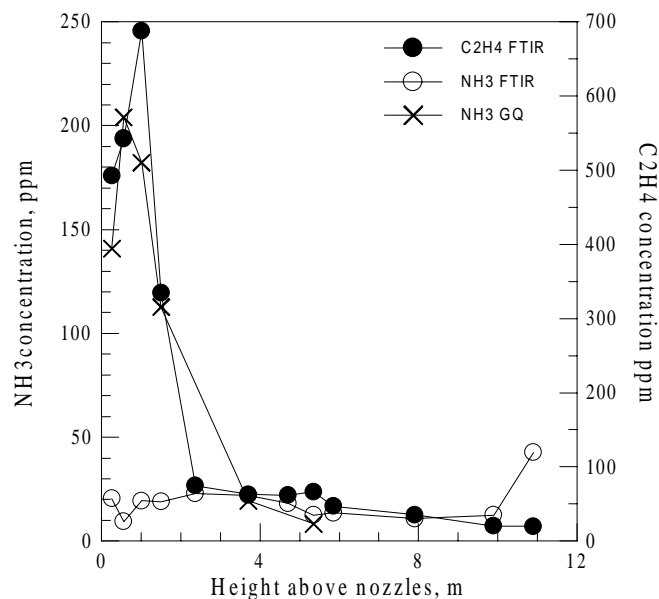

Figure 8 Comparison of the measurements of ammonia with the gas-quenching probe (wet chemistry analysis) and the gas-sampling probe (FTIR analysis) during no air-staging.

distributor, which was similar to what was observed in Åmand et al 1997. Figure 6 shows the concentration profiles of NH_3 and ethene obtained from FTIR analysis at severe air-staging. NH_3 followed ethene but was somewhat lower compared to NH_3 measured with the GQ probe in Figure 5.

Figure 7 presents the concentration profiles of NH_3 for both sampling probes at reversed air-staging conditions. The highest values of NH_3 (GQ probe) were found in measurement port H3 below the fuel chute and NH_3 fell as a function of height above the air nozzles. Although the level of NH_3 was lower, the trend is similar to that observed during severe air-staging. A comparison of the NH_3 levels obtained from FTIR during two different days indicated the influence of a measurement error. This error was significant for all the results from one particular day, independent of measurement port. Figure 8 shows the results for both NH_3 and ethene during no air-staging. The trends for NH_3 (GQ probe) and ethene are similar but the value of NH_3 is much lower compared to the other air-staging cases. In these more oxidising conditions, the inaccuracy of the measurement with FTIR in the lower part of the combustor is even more apparent. The error most likely depends on secondary reactions in an old filter, which is discussed in

Section 5.1. Due to the errors in measuring NH_3 with the gas-sampling probe, it can only be justified to compare the concentration profiles obtained from measurements with the GQ probe. Figure 9 presents the influence of air-staging on NH_3 and the three air-staging cases are clearly distinguished. The highest levels of NH_3 were observed during reducing conditions (severe air-staging), the lowest at no air-staging.
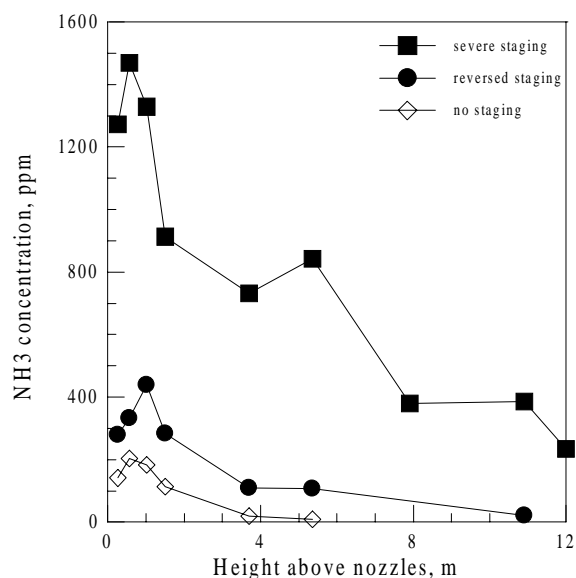

Figure 9 Concentration of ammonia as a function of height in the combustion chamber for the three air-staging cases. The gas-quenching probe (wet chemistry analysis)
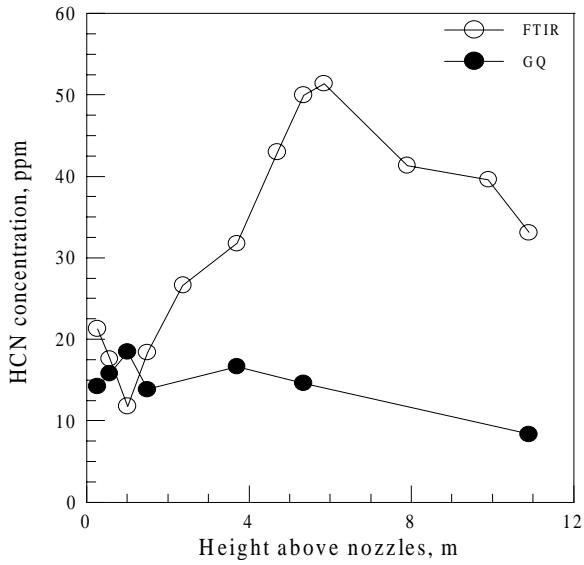
Figure 10 Comparison of the measurements of HCN with the gas-quenching probe (wet chemistry analysis), and the gas-sampling probe (FTIR analysis) during reversed air-staging.

4.2 Concentration profiles of HCN

The measured levels of HCN were rather low in all the measurement ports regardless of air-staging conditions and sampling technique. This made an accurate evaluation complicated and influence from the analytical uncertainty could have remained in both sampling techniques. Thus, the results could to some extent be an effect of the analytical uncertainty instead of the gas concentration in the combustion chamber. Figure 10 presents a comparison of the concentration profiles of HCN obtained from the two sampling probes at reversed air-staging conditions. The levels of HCN are, as previously mentioned, much lower than those of NH_3. A correlation between FTIR and wet chemistry was found in the lower part of the combustion chamber. The FTIR analysis indicates an increased concentration of HCN in the upper part. The opposite was indicated in wet chemistry analysis, however, too few measurements were carried out for a verification of this trend. Figure 11 shows a comparison of the HCN concentration profile at the three air-staging cases for the GQ probe. The levels of HCN measured at no air-staging were lower than those at reversed air-staging. Only small amounts of HCN were found in wet chemistry analysis of trapper solutions taken at severe air-staging. A similar comparison of HCN obtained from FTIR
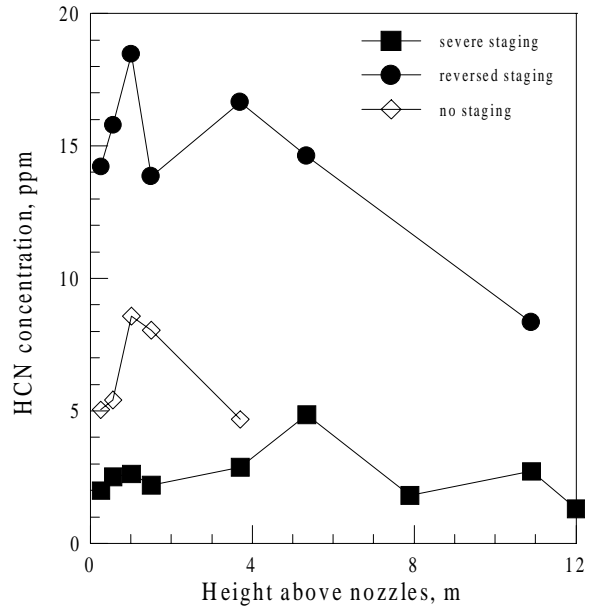

Figure 11 Concentration of HCN as a function of height in the combustion chamber for the three air-staging cases. The gas-quenching probe (wet chemistry analysis)

analysis is presented in Figure 12. Here the levels of HCN at severe and no air-staging were also lower than those of reversed air-staging. The FTIR analysis at no air-staging indicates that the concentration of HCN increased with height over air nozzles, which was also observed at reversed air-staging. This trend could not be verified at no air-staging due to a lack of measurements with the GQ probe in the upper part of the combustor.
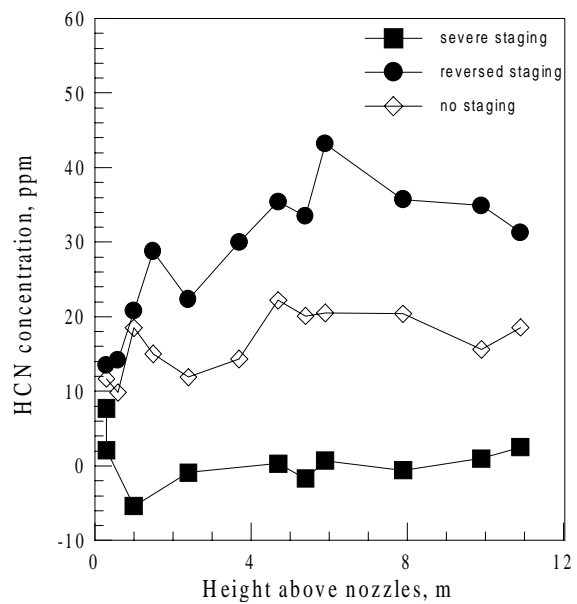

Figure 12 Concentration of HCN as a function of height in the combustion chamber for the three air-staging cases. The gas-sampling probe (FTIR analysis)

Despite the much lower levels of HCN, it is still possible to distinguish between the three air-staging cases. The highest levels are observed for reversed staging and severe staging shows almost no HCN. The same internal relation between the concentration profiles of HCN for the three air-staging cases was found using both sampling probes. The concentration profile for HCN shows a different pattern than NH_3 concerning the influence of air-staging.

5   Discussion

A measurement of the true gas concentration in the combustion chamber of a CFB boiler with a sampling probe is no easy task. Errors due to both the sampling and the analytical procedure could have an impact on the result.

The influence of air-staging on the concentration profiles of NH_3 and HCN is not the same. The possible reaction paths depend on the composition of the gases and particles present in the combustion chamber during the different air-staging cases.

5.1 Sampling and analysis of ammonia

The potential secondary reactions and measurement errors in sampling ammonia with the two sampling probes were investigated in ref. (Kassman et al 1997), where it was found that the passing of a particle filter in the probe tip was especially critical for accuracy. Here, secondary reactions could occur both in a possible filtercake and in the filter material itself. Laboratory studies (Kassman et al 1995) verified that HNCO could be measured as NH_3 when wet chemistry is applied. There were no indications in the FTIR analysis of the presence of HNCO in the combustion chamber.

The best correlation between the measurement with FTIR and the GQ probe was achieved in severe air-staging, where reducing conditions prevailed in the whole combustion chamber and in the cyclone. Oxidising conditions emphasised the inaccuracy in the NH_3 measurement with FTIR enhancing secondary reactions with NH_3. A measurement error due to a filtercake in the tip of the gas-sampling probe would be of the same magnitude from one day to the next during the same air-staging conditions. The results from reversed air-staging

(Figure 7) prove that the filtercake was not the cause. Possible reactions in the filters can be reduced by the use of pure and less active filter materials (Kassman et al 1997). The quartz filter in the GQ probe tip was regularly replaced with a new one, except at the end of the project. The filter in the tip of the gas-sampling probe was only replaced when a visual inspection indicated a breakdown. The concentration levels from measurements carried out with an old filter were significantly lower than with a new filter. It is believed that impurities of entrained bed material in an old filter caused an increased oxidation of NH_3, which explains the lower result achieved in FTIR during no air-staging.

The concentration profiles of NH_3 achieved from measurements by means of the GQ probe are believed to be more accurate than those obtained from FTIR analysis.

5.2 Sampling and analysis of HCN

The comparison of the concentration profiles of HCN (Figures 11 and 12) shows the same relation with the highest levels found at reversed air-staging. The FTIR analysis indicates that HCN increases with height above nozzles, but such a trend could not be verified by wet chemistry analysis.

Significant amounts of HCN were found in the additional wash bottle when using the GQ probe. An influence on the absorption efficiency in the reservoir from both the concentration of the basic trapper solution and sampled gas volume was observed. This indicated that a measurement error could occur if HCN is released from the reservoir without the presence of an additional wash bottle. Circulation of solutions with known cyanide content in the GQ probe sampling system at reversed air-staging showed that no absorbed HCN leaves the reservoir and the additional wash bottle if the trapper solution is strong enough. One month after the first analysis, these and several other samples were analysed a second time with a similar result. The cyanide content did not, therefore, change due to storage in samples from reversed air-staging.

In Figure 13 the H_2S concentration found in a previous measurement campaign using a gas chromatograph equipped With a mass spectrometer (GC-MS) clearly shows a large
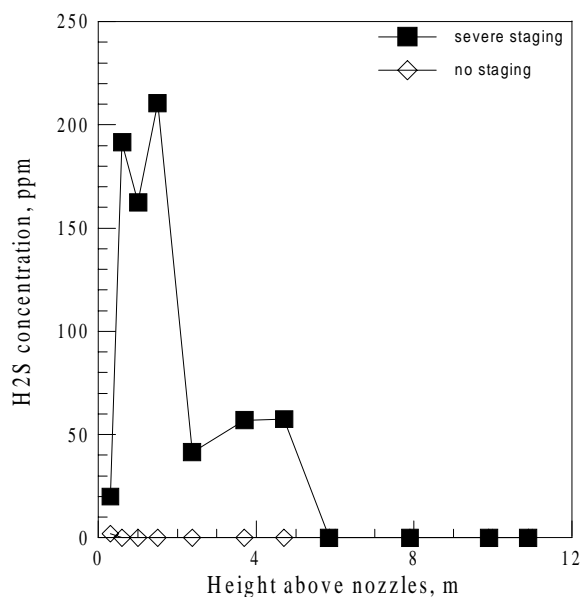
Figure 13 Concentration of H_2S as a function of height in the combustion chamber at two different air-staging cases. Obtained from a measurement campaign in 1994.

Figure 14 Comparison of the result from four evaluation procedures for HCN using the PLS routine (FTIR analysis) during severe air-staging.

difference between no air-staging and severe air-staging in the lower part of the combustor. A similar relationship was also measured for COS (carbonyl sulphide). This result is consistent with results obtained in Mattisson and Lyngfelt 1995 where CaS could only be detected in solid samples withdrawn from the combustion chamber during severe air-staging and not during no air-staging conditions. It should be emphasised that these solid samples were taken in parallel to the use of the gas-sampling probe, which supplied the GC-MS on-line with hot combustion gases. This means that sulphides, such as H_2S and COS, were most likely present in the lower part of the combustor during severe air-staging. These sulphides could have been absorbed in parallel with HCN in the basic trapper solution and were precipitated prior to the analysis of HCN to avoid interferences. It was found that cyanides in an aqueous solution were not reactive with monosulfide species (HS^-) at high pH values (Luthy and Bruce 1979). The cyanides could, however, react with oxidised products of sulphides (polysulphide) to produce thiocyanate (SCN^-). On the other hand, the formation of polysulphides is neither rapid nor extensive at pH values greater than 8.2 (Luthy and Bruce 1979). It is, therefore, not likely that the presence of sulphides during severe air-staging had any significant effect on the result when
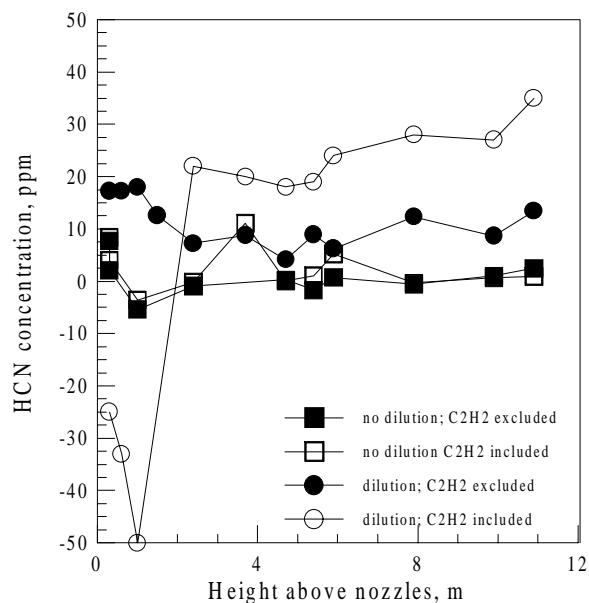
using the GQ probe.

The spectrum of acetylene (C_2H_2) is known to interfere with the HCN spectrum. Thus, the PLS evaluation was setup with C_2H_2 included or excluded in the routine. This was justified by looking at the main absorbance peak of C_2H_2 located in a separate infra-red (IR) region from HCN. Here no absorbance due to C_2H_2 was found. Another interesting aspect is the comparison of the influence of dilution of the sample on the evaluation of HCN. Figure 14 shows the concentration profile of HCN at severe air-staging resulting from the four methods. The choice of method had an effect on the level, indicating the analytical uncertainty in the FTIR evaluation. The largest impact on the HCN result was the combination of a diluted sample and having C_2H_2 included in the evaluation routine. This gave negative HCN concentrations in the lower part of the combustion chamber and too high concentrations in the other measurement positions. This method was therefore excluded. Nevertheless, severe air-staging is still the most difficult air-staging case to evaluate. The three remaining methods chosen vary much less for the two other air-staging cases resulting in the same order between the profiles in Figure 12 regardless of which method that was used for the FTIR evaluation.

5.3 Influence of air-staging on the concentration profiles

It is possible to distinguish between the three air-staging cases for both ammonia and HCN and their concentration profiles show different patterns depending on the air-staging conditions. The highest levels of ammonia are observed for severe air-staging and no air-staging shows the lowest values. Severe air-staging resulted in almost no HCN and the highest levels were found at reversed air-staging. This is due to differences in the environment of the combustion chamber in combination with different reaction pathways for NH_3 and HCN.

Oxidation reactions seem to be of great importance for the level of ammonia in the combustion chamber. Strangling the air supply to the boiler (the severe air-staging case) stopped the sulphur capture process completely. Two important parameters thus change simultaneously: the oxidation potential and the composition of the bed material. Still decomposition of NH_3 on the bed material could be of importance, but the rate of heterogeneous decomposition is probably slower than the oxidation reactions. In the case of char acting as a catalyst only an oxidation reaction with NH_3 has been found, and no decomposition of NH_3 on char has been observed (Johnsson 1994). The severe air-staging case is unique in many ways. In this case the highest NH_3 values were obtained but almost no HCN. The question arises whether there is a link between HCN reduction and NH_3 formation. There is a reaction suggested in Section 2; HCN reduction by H_2 catalysed by CaO (Jensen et al 1993). Two conditions regarding the severe air-staging case favour this reaction: (1) the high concentrations of H_2 measured during the present tests by gas chromatography (GC) and (2) $CaSO_4$ decomposes into CaO (and CaS) during severe air-staging increasing the amount of available catalyst for this reaction. The other reactions suggested in (Jensen et al 1997) to proceed during reductive decomposition of $CaSO_4$, where HCN and CaSO4 reacts with each other forming CaO and CaS, would indeed remove HCN from the combustion chamber. However, these reactions do not simultaneously lead to an increase in the formation of NH_3.

6   Conclusions

The dependence of air-staging conditions on the NH_3 and HCN levels in the combustion chamber of an FBB burning coal with the addition of limestone was confirmed by means of two independent sampling methods.

A comparison of the sampling methods gave concentration profiles in the same range of NH_3 and HCN, unless the filter in the probe tip was aged leading to secondary reactions over it. This effect was especially obvious in the measurements of NH_3 by means of FTIR during oxidising conditions.

A measurement error could occur during wet chemistry analysis of HCN if not an additional wash bottle is used.

Addition of limestone in combination with the air-staging conditions was important for the reaction pathways of NH_3 and HCN.

The concentration profiles of NH_3 and HCN in the combustion chamber show different patterns concerning the influence of air-staging.

The highest levels of NH_3 were observed during reducing conditions (severe air-staging), the lowest at no air-staging. The destruction pathways of ammonia are thus determined by the level of oxygen in the combustion chamber.

The levels of HCN are much lower than those found for NH_3.

The highest levels of HCN are observed for reversed air-staging and severe shows almost no HCN.

7   Acknowledgements

8   References

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