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Measurement of the concentration of ammonia and ethene in the combustion chamber of a circulating fluidised-bed boiler

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This paper presents the results of measuring the ammonia and ethene concentration profiles in the combustion chamber of a circulating fluidised-bed boiler. The boiler was operated in three air-staging conditions with peat as fuel, and with the addition of lime. Two sampling techniques were used for the analysis of ammonia: gas-sampling probe connected to a Fourier transformed infra-red (FTIR) instrument, and a gas-quenching (GQ) probe where the sample was quenched directly in the probe tip by a trapper solution. Both techniques are accurate enough to distinguish the influence on air staging of the level of ammonia in the combustion chamber. Comparison of the concentration profiles for ammonia measured by the two procedures shows similar results. The levels of ammonia and ethene measured by FTIR follow each other in the combustion chamber for all three staging conditions. The FTIR spectra were evaluated by three methods: spectral subtraction, differential absorbance and the multiple variable analysis method named 'partial least square' (PLS). Almost equal levels of concentration of ammonia and ethene were found, regardless of the method employed. The measurement error from reactions with ammonia at the GQ probe tip was estimated in a simple model.

1 Introduction

NH_3 and HCN are the major nitrogen-containing components released during pyrolysis and combustion of solid fuels. Both of them act as gas-phase precursors to the formation of NO and N_2O. N_2O is preferentially formed from cyano species, and NH_3-based compounds tend to react mainly to NO[1]. These processes are not completely known, especially not in the complex environment of a fluidised bed; therefore measurements of the NH_3 and HCN concentrations in the combustion chamber during combustion of different fuels can support prediction of the final emissions of NO and N_2O. Such results would be important, for instance, to support modelling of the nitrogen chemistry in real boilers[2,3]. Another factor of environmental concern is the potential emissions of unburned volatiles, especially during combustion of highly volatile fuels such as peat and wood. Here NH_3 and ethene are key components in volatiles conversion, representing nitrogen chemistry and hydrocarbons.

It is also important to measure NH_3 during NO_x abatement in low-NO_x processes. In this case the goal is to find efficient ways of reducing NO with a minimal NH_3 slip from the stack and without conversion of added reducing nitrogen species to HCN. For this reason much effort has been put into the development of analytical methods for determining NH_3 and HCN in flue gases[4,5] and these new methods have been developed in parallel with established wet chemical methods[6]. After the development of a quenching probe, wet chemistry was used at higher temperatures in furnaces, such as in pulverised-coal combustion (PCC)[7,8] and in fuel-oil flames[9]. The temperature in the combustion chamber of a CFB boiler is lower than in PCC, but the presence of particles and the complexity of the gas composition have the effect of complicating measurement. Also, in order to measure the true gas concentration in a combustion chamber with a sampling probe, the gases must be cooled rapidly to stop further reactions. Especially critical in a fluidised-bed combustion chamber is the passage through a particle filter in the probe tip. Secondary reactions could occur both in a filter cake and in the filter material itself.

Hitherto, measurements of NH_3 and HCN profiles at temperatures of fluidised-bed combustors have been carried out in an entrained-flow reactor[10] and in a laboratory CFB[11]. Furthermore, attempts to measure NH_3 and HCN in the combustion chamber of the 12 MW CFB boiler at Chalmers have been made by Åmand[12] with a gas-sampling probe connected to a Fourier transform infra-red (FTIR) instrument and by Kassman *et al*[13] with a gas-quenching (GQ) probe. The design of the GQ probe originated at the International Flame Research Foundation (IFRF), IJmuiden.

The purpose of the present project was to improve methods already applied in the combustion chamber of a CFB boiler[12,13] and to compare the results from the two sampling techniques. The NH_3 concentration profile was measured with the GQ probe previously used, but the GQ probe sampling system was improved to increase the measurement accuracy. There was a possibility that reactions with NH_3 at the GQ probe tip[13] could influence the result; therefore the measurement errors from these reactions were estimated by a simple model (which will be the subject of a later paper). The gas-concentration profile was also measured by means of the same equipment as in Ref.12, but the evaluation procedure was improved, as demonstrated by the determination of ammonia (NH_3) and ethene (C_2H_4). Three methods of evaluating FTIR spectra are compared. Other gas components such as HCN will be treated elsewhere. The parallel NH_3 measurements made possible a comparison between the concentration profiles obtained by the two techniques; the concentration profiles of the two volatile species ethene and ammonia in the combustion chamber measured by FTIR can also be compared.

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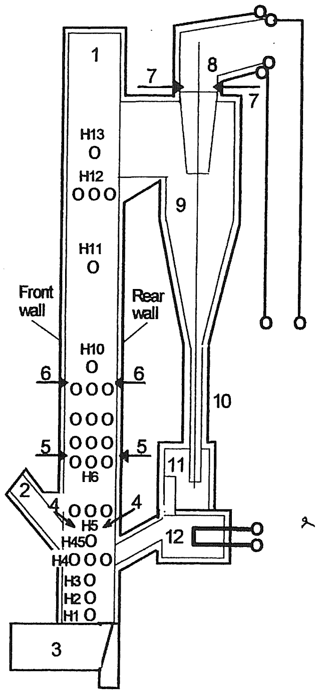

Fig.1 The 12-MW$_{th}$ CFB boiler at Chalmers University of Technology: (1) combustion chamber; (2) fuel feed chute; (3) air plenum; (4) secondary air inlet at 2.1 m; (5) secondary air inlet at 3.7 m; (6) secondary air inlet at 5.4 m; (7) secondary air inlet into cyclone exit duct; (8) cyclone exit duct; (9) cyclone; (10) particle return leg; (11) particle seal; (12) heat-exchanger. Measurement ports H1 to H13 on the right-hand boiler wall are indicated.

2 Experimental

2.1 The boiler

The tests were performed in the 12 MW CFB boiler[14] at Chalmers University of Technology. The measurement ports on the wall of the combustion chamber (Fig.1) are of particular interest in this project: they make it possible to sample gas inside the combustor and to characterise the combustion behaviour more closely. The boiler is equipped with on-line conventional flue-gas analysers for continuous monitoring of O_2, CO, SO_2, NO and N_2O in the stack, and of O_2, NO, CO, CO_2, SO_2, H_2 and total hydrocarbons (HC-tot) in the combustion gas from the gas-sampling probe.

2.2 Operating conditions

The measurements were performed in conjunction with a larger project concerning the influence of air supply on the emissions of NO, N_2O and SO_2[15,16]. For this purpose the boiler was operated in three air-staging cases, and limestone was supplied at a molar ratio of 2.5:1 to 3:1 for sulphur capture. The fuel was peat of the following composition: ash 4%, moisture 27% and content of combustibles 69%, analysed as delivered; C 59%, H 6.3%, O 32%, S 0.6% and N 2.2%, expressed on a moisture- and ash-free (maf) basis. The volatile content was 69% on the maf basis. Peat was supplied as cylinders of 30 mm diameter and up to 150 mm long; this shape was not maintained during the fuel-handling process, but large pieces of peat were still supplied to the boiler, and the production of fines was small.

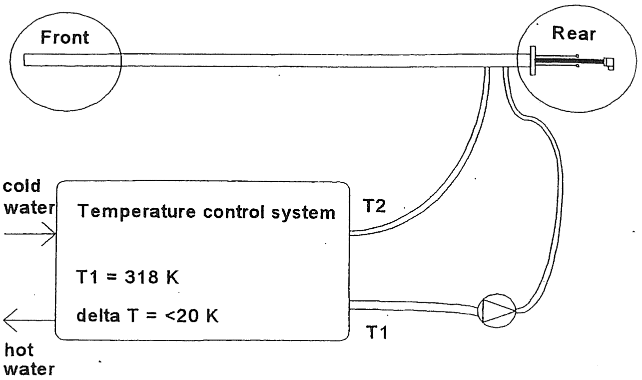

Fig.2a Gas-sampling probe used for analysis of hot gases from the combustion chamber.

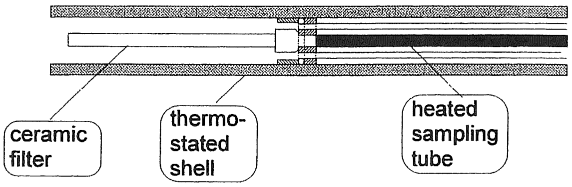

Fig.2b Front part of the gas-sampling probe.

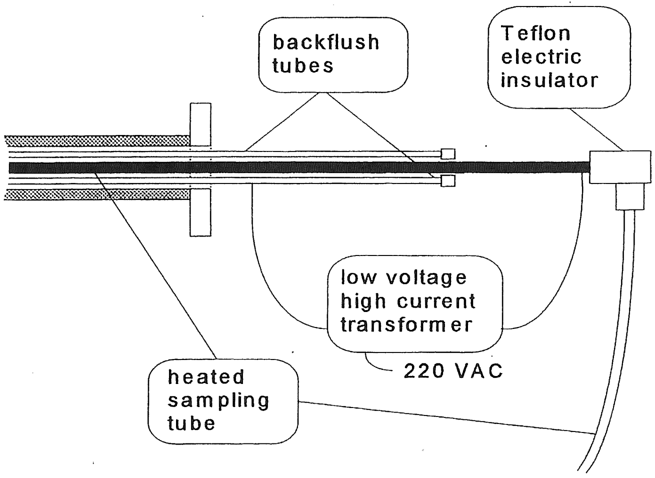

Fig.2c Rear part of the gas-sampling probe.

The air-staging[15] cases are:

Normal staging (reference case): 60% primary air and 40 % secondary air (introduced 2.1 m above the air distributor).

No staging: no secondary air, all air added at the bottom of the combustion chamber, and the conditions were significantly more oxidising in the bottom part of the combustor relative to the reference case.

Reversed staging: no secondary air in the combustion chamber, but about 20% of the total air added downstream of the cyclone for final combustion. This meant less oxidising conditions in the upper part and more oxidising in the bottom part relative to the reference case.

2.3 The gas-sampling probe

The probe shown in Fig.2a was designed for wet combustion gases; this is important in the analysis of NH_3. Combustion gas first passes a ceramic filter mounted at the probe tip, Fig.2b, protected and cooled by the cooling shield of the probe. The gas is then transported through the centre pipe, which is electrically heated to 200 °C, Figs.2b and 2c. In order to control the temperature of the centre pipe the probe is water-cooled, Fig.2a, having a temperature of 45-95 °C. Downstream of the probe the combustion gas is transported to the gas analysers through heated gas lines. The ceramic filter is cleaned of ash and bed material by back-flushing with pressurised air at regular time intervals.

2.4 The FTIR analyser

The FTIR analyser is connected in series with the continuous gas analysers. The FTIR is a Bomem M110-D11 with a 500 cm^3 quartz glass cell having an optical path-length of 3.6 m. The instrument is equipped with an MCT detector. The maximum resolution of 4 cm^{-1} was used in all tests. The gas cell was heated to 200 °C. The Spectra Calc software package[17] was used for evaluation and control of the spectrometer. During the present tests, spectra were collected in a continuous mode, where 28 mirror scans (each scan lasting approximately one second) were sampled for each single-beam spectrum stored. 27 stored single-beam spectra were added to form an average single-beam spectrum corresponding to a measurement time of about 15 minutes. An absorbance spectrum was produced from the ratio of this average spectrum and a reference spectrum (100% nitrogen) collected immediately before the sampling of the single-beam spectra. Three methods of evaluating spectra from FTIR were compared: spectral subtraction (SS), differential absorbance (DA) and a multiple variable analysis method named partial least square (PLS). Generally, the differences between the methods were small and did not affect the trends of NH_3 and ethene in the combustion chamber, nor the absolute levels[18].

2.5 The gas-quenching (GQ) probe

The GQ probe and the sampling system shown in Figs.3a and 3b is described in detail by Kassman[19]. A sintered quartz filter (3b:1) attached to an uncooled steel pipe (3b:2) in the probe tip, Fig.3b, prevented particles contaminating the trapper solution injected through a distributor (3b:3). Sampled combustion gas was withdrawn through the water-cooled quartz-lined (3a:2) probe. The acidic trapper solution (3a:4) was sprayed uniformly through the distributor into the tip of the quartz-lined suction line, to provide immediate gas quenching without losing any trapper solution. The trapper solution was circulated from a reservoir (3a:5) by a peristaltic pump (3a:3). The gas flow rate was 3-5 L/min, and a sampling time of about 15 minutes gave a total gas volume of 50-80 litres. The total volume of gas withdrawn was measured by a mass-flow controller (3a:7) connected to a data-acquisition system, and a gas meter (3a:9) was used as a back-up. Each test was started and stopped in exactly the same procedure. The change of measurement port made it possible to collect any filter-cake on the probe tip. The amount of filter-cake during peat combustion varied with limestone addition, height above the nozzles and air-staging conditions. However, the appearance of the filter-cakes was similar.

2.6 Analytical procedure

The acidic (1 mMol dm^{-3} H_2SO_4) trapper solution was analysed by means of both ion-selective electrodes (ISE) and distillation followed by titration[13]. The two methods gave similar concentrations of NH_4^+ in the trapper solution. In the present project, the samples were analysed only with ISE, which permitted immediate preliminary analysis and evaluation to reconfirm the results before the measurement port was changed. In the evaluation the average NH_3 concentration from a final accurate analysis of a reliable double sample was used. The concentration of NH_3 in the combustion gas was calculated, assuming an absorption efficiency of 100 % in the trapper solution. The calculation was performed by means of the ideal gas law together with the measured amount of gas that passed the mass-flow controller and the exact volume of trapper solution (approximately 250 ml).

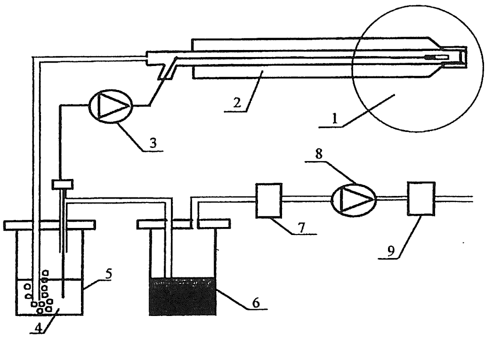

Fig.3a The gas-quenching (GQ) probe and the sampling system: (1) the tip of the probe (Fig.3b); (2) water-cooled quartz-lined probe; (3) peristaltic pump; (4) trapper solution; (5) reservoir; (6) dryer; (7) mass flow controller; (8) gas pump; (9) gas meter.

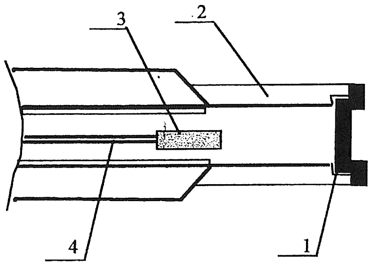

Fig. 3b The tip of the GQ probe: (1) sintered quartz filter; (2) uncooled steel pipe; (3) distributor; (4) injection line for the trapper solution.

3 Results

3.1 Measurement of ammonia and ethene concentrations

The concentration profiles of NH_3 and C_2H_4 measured by FTIR are plotted for the three air-staging cases in Figs.4 and 5. In all cases, NH_3 fell as a function of height above the bottom air nozzles in the combustion chamber. Fig.6 shows a comparison of the three air-staging cases for the NH_3 measurements with the GQ probe. The operating conditions have an impact on the measured levels of NH_3 and C_2H_4, which can be distinguished with the evaluation methods used. No staging (which means more oxidising conditions in the lower part of the boiler) resulted in the lowest concentrations, except in the upper part of the combustion chamber. Relative to normal staging, both reversed and no-staging lead to a dilution effect caused by higher air flows in the lower part of the combustion chamber. Dilution could also explain the lower concentration values of NH_3 and C_2H_4 for reversed and no staging (Figs. 4-6) in the lower part of the combustor.

3.2 Comparison of the ammonia concentrations measured by the two probes

Extracted gases in the gas-sampling probe were cooled to 200 °C and transported in a heated sampling line to an FTIR analyser, without any quenching. But when the GQ probe was used, NH_3 was quenched by the circulating trapper solution sprayed through the distributor in the probe tip immediately behind the sintered quartz filter. Afterwards, the trapper solution was analysed for NH_4^+ by wet chemistry.

This procedure changed the measurement conditions considerably. The result did not change however, as can be seen in Fig.7, where the NH_3 concentrations measured by the two sampling systems are compared for the normal staging conditions. The GQ probe measurement shows a good correlation with the parallel FTIR measurement in almost every measurement position. The dependence of

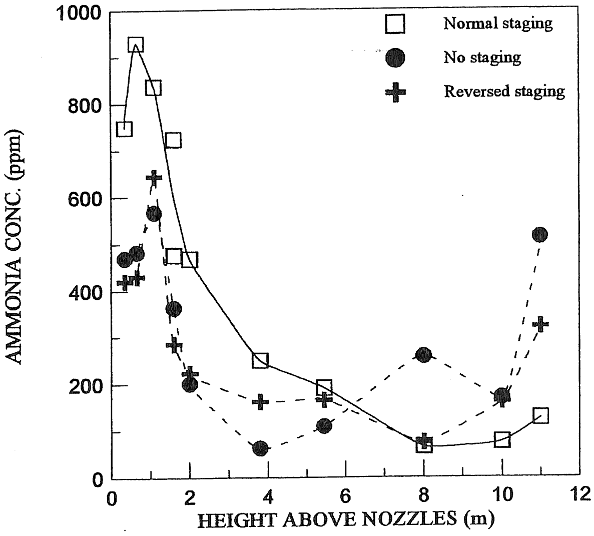

Fig.4 Concentration of ammonia as a function of height in the combustion chamber for the three air-staging cases. Analysed with FTIR. Spectral evaluation: PLS.

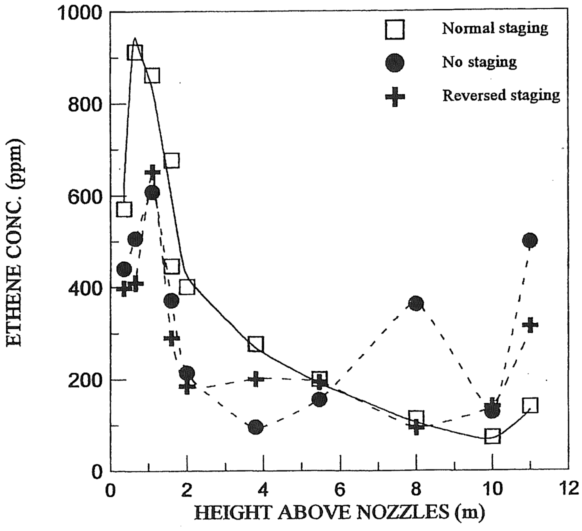

Fig.5 Concentration of ethene as a function of height in the combustion chamber for the three air-staging cases. Analysed with FTIR. Spectral evaluation: PLS.

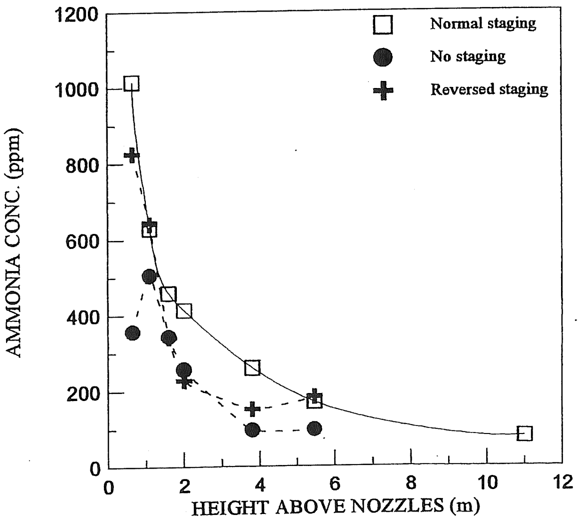

Fig.6 Concentration of ammonia as a function of height in the combustion chamber for the three air-staging cases. The gas-quenching probe (wet chemistry analysis).

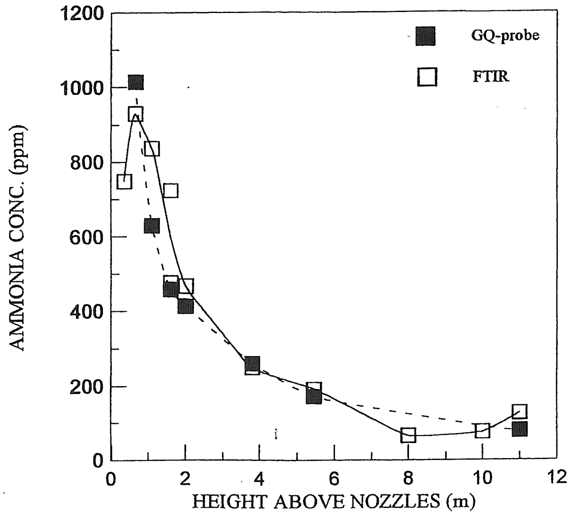

Fig.7 Comparison of the results of the measurement of ammonia with the gas-quenching probe (wet chemistry analysis) and the gas-sampling probe connected to the FTIR analyser. Operating conditions: normal air staging. Spectral evaluation method on FTIR: PLS.

air-staging condition on the NH_3 levels in the combustor is therefore confirmed by the two independent methods. Unfortunately, NH_3 could not be measured in position H1 with the GQ probe, where the FTIR measurement always showed a lower result than in the H2 position. Such behaviour can be suspected, however, if the NH_3 profiles are compared with the profiles for ethene, where also a lower concentration is measured in position H1 relative to H2 for all air-staging cases (Fig.5). The comparison in Fig.7 indicates that the gas-sampling probe, together with the FTIR and the GQ measurements, give reliable levels of NH_3 in the combustion chamber.

3.3 Comparison of the results for ammonia and ethene

The concentration profiles for NH_3 and ethene in Figs.4 and 5 have similar trends: large concentrations at the bottom of the combustor and falling concentration profiles from there upwards. It is striking that the changes in NH_3 are followed by identical changes in C_2H_4, for example in the last measurement port H13, where both NH_3 and C_2H_4 rose in all three operating cases. This port is at 10.9 m, where the combustion gases flow towards the exit of the combustion chamber (Fig.1). The reason for the increase could be that excess amount of volatiles containing NH_3 and C_2H_4 are present along the front wall, where the fuel is supplied. Close to the exit of the combustion chamber, this excess amount of volatiles is mixed with the centre flow containing fewer volatiles, and this leads to the observed rise in concentrations of NH_3 and C_2H_4. The explanation given is supported by the fact that the observed increase of volatiles is larger for the two cases where no secondary air was supplied to the combustion chamber. Lack of secondary air leads to poorer mixing, and more primary air pushes the devolatilisation up to higher levels; both factors increase the volatile content along the front wall. If the volatiles entering the cyclone were not burned completely, emissions of NH_3 and ethene from the boiler would occur. This requires to be investigated further.

4 Discussion and conclusions

The accuracy of the measurements by means of the improved GQ probe sampling system and the gas-sampling probe connected to an FTIR, is high enough to follow the influence of air-staging on the levels of NH_3 and C_2H_4 in the combustion chamber of the boiler.

A comparison between the NH_3 concentration profiles for the two probes using different sampling procedures showed almost identical results for NH_3 during the three air-staging conditions. This can be explained in two ways: either the measurement is correct for both methods, or they are equally influenced by secondary reactions. However, it is not likely that two probes with different sampling procedures are influenced by the same secondary reactions during different air-staging conditions. Nevertheless, an attempt to estimate the influence of potential secondary reactions with NH_3 was performed in a simple plug-flow model. This will be the subject of a later paper.

NH_3 and C_2H_4 follow each other closely in the combustion chamber in all three air-staging cases. The concentrations of NH_3 and ethene increase towards the exit of the combustion chamber. This could be important for the emissions of hydrocarbons and NH_3 from the boiler.

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