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### **Oxidation of Volatile Nitrogen Compounds During Combustion in Circulating Fluidized Bed Boilers**

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

## OXIDATION OF VOLATILE NITROGEN COMPOUNDS DURING COMBUSTION IN CIRCULATING FLUIDIZED BED BOILERS

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### ABSTRACT

In circulating fluidized bed boilers, the volatile nitrogen species of the fuel are mostly oxidized to NO. This is shown in a test programme where the effect of batch supply of fuel on the NO emission has been carried out in two different commercial-type fluidized bed boilers. Measurements of gas concentration profiles of CO, NO, HCN, NH<sub>3</sub> and C<sub>1</sub> to C<sub>3</sub> hydrocarbons in the boilers support the conclusions from the batch supply tests.

### INTRODUCTION

Fluidized bed combustion (FBC) is a convenient way of burning solid fuels in order to achieve low emissions of NO and SO<sub>2</sub>. The reason for this is the combustion temperatures of 800 to 900°C which are low in comparison with the temperatures of pulverized coal combustion, 1000 to 1600°C. The low temperatures in FBC prevent thermal NO formation and promote NO reducing reactions during combustion. 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 aspects [1] and interest has gradually been focussed on this type of boiler. However, the advantage of the lower emissions of NO and SO<sub>2</sub> has lately been

found to be offset by high emissions of  $N_2O$  as a consequence of the temperature levels. This has been reported for FB boilers [2] but not for other combustion techniques [3].  $N_2O$  is one of the greenhouse gases, and  $N_2O$  also contributes to the ozone depletion in the stratosphere [4].

This paper is a continuation of a project previously reported in [2], [5], [6] and [7]. Characterization of  $N_2O$  is included in the  $NO_x$  emission projects but, for convenience, results related to  $N_2O$  are reported separately in [8]. In [5], [6], and [7], it has been stressed that in CFB boilers, reactions involving NO reduction on char surfaces are favoured more than reactions involving ammonia ( $NH_3$ ) or other amines ( $NH_1$ ). This should be compared with the situation in the stationary (bubbling) fluidized bed (SFB) boiler, where the char is concentrated at the dense bed at the bottom of the combustion chamber and a freeboard with low particle densities plays a role different from that of the upper part of the combustion chamber of the CFB-type of FB boiler. In other words, it is possible for the homogeneous reduction of NO by  $NH_3$  (or other amines) to take place in the freeboard of the SFB boiler. In order to prove that this reaction is not of significance for the NO reduction in CFB boilers, a test programme has been carried out. The tests combine measurements and comparative studies of the effect of batch supply of fuel in two different, commercial-type CFB boilers. In addition, the gas-concentration profiles taken in the combustion chambers of the two boilers are valuable for the establishment of a general characterization of the NO reduction in CFB boilers. This shows that the NO-char reaction plays a dominant role. Although the importance of the char and CO for the NO reduction during FB combustion has already been discussed in [9], [10] and [11], and is referred to in most publications concerning NO emissions from FB boilers, there are still new aspects of this reaction that can be seen in the test programme presented below. These new aspects confirm the observations made in [5] and [6] that

- The volatile nitrogen species are mostly oxidized to NO in a CFB boiler using bituminous coal or fuels of higher rank.
- The CO level is important for the NO reduction on char surfaces.

## EXPERIMENTAL

### The Boilers

The tests were run in two CFB boilers, one 8 MW<sub>th</sub> boiler designed and built by Götaverken Energy in 1981 at Cityvarvet, and one 12 MW<sub>th</sub> boiler built by Generator Industri AB in 1989 at Chalmers University of Technology, Figure 1. Both boilers are built in the form of commercial boilers with the combustion chamber made up of membrane tube walls. The height of the combustion chamber is 7.8 meters and the cross section is about 1.8 m<sup>2</sup> for the 8 MW boiler. Corresponding data for the 12 MW unit are 13.5 meters and 2.9 m<sup>2</sup>. Fuel is fed to the bottom of the combustion chamber through a fuel screw in the 8MW boiler, while a fuel chute (1) is used in the 12 MW boiler. In both boilers bed material 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 air nozzles in the bottom plate (5) and secondary air can be introduced through several secondary air registers located along the combustion chamber. The lowest level (6) is located at 2.2 meters in the 12 MW boiler while the lowest secondary air level in the 8 MW boiler is located only one meter above the bottom plate. Both boilers are equipped with data-acquisition systems and on-line gas analyzers for sampling of data needed in the research program.

### The Fuels

In both boilers high volatile bituminous coals have been used as fuel having the properties shown in Table 1. In the 8 MW boiler anthracite and petroleum coke were also employed in some tests.

### 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 air ratio 1.2. The fluidizing velocities were between 4 and 6 m/s. In this reference case, batches of fuels of different volatile content were dropped into the combustion chamber of the 8 MW boiler and the effect on the O<sub>2</sub> and NO emissions was followed during the

burnout period. In the 12 MW boiler similar tests were carried out, however only one type of fuel was used as a batch fuel. The fuel particle size and amounts of fuel in the batches were varied instead.

In the reference case, concentration profiles of NO and CO in the combustion chambers of both boilers were measured. In the 12 MW boiler the profiles of NH<sub>3</sub> and HCN together with C<sub>1</sub> to C<sub>3</sub> hydrocarbons were also included.

### The Gas Sampling Probes

The concentration profiles were taken inside the combustion chambers by means of 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<sub>2</sub>, CO, and NO. In the 12 MW CFBB boiler also the HCN and NH<sub>3</sub> profile and the concentrations of C<sub>1</sub> to C<sub>3</sub> hydrocarbons were also measured. The NH<sub>3</sub> and HCN concentrations were determined by trapping the gases in wash bottles containing a diluted acidic water solution for NH<sub>3</sub> and a basic water solution for HCN. The analysis could then be carried out by means of selective electrodes for NH<sub>3</sub> and argentometry (Liebig-Deniges method) for HCN. After drying, gas from the probes was also collected in Tedlar bags for further analyses for N<sub>2</sub>O and hydrocarbons on a gas chromatograph equipped with an electron-capture detector (for N<sub>2</sub>O) and a flame-ionization detector (for hydrocarbons).

## RESULTS

### Burnout of Batches of Fuels in the 8 MW Boiler (CFB Cityvarvet)

In the test series involving batches of fuel the 8 MW boiler was operated under the reference conditions with the low sulphur coal, see Table 1. At stable operating conditions a batch was dropped into the fuel feed screw corresponding to an increase of the fuel feed rate by a factor of about 7 to 8. Not more than 30 seconds elapsed before the entire batch of fuel was fed into the combustion chamber. Three fuels, each with a different content of volatiles, were used as batch fuels. The effect of the batch fuel on the concentrations of oxygen, CO and NO in the stack, as well as the bottom-bed temperature, was followed during the burnout period and is

shown for the three tests in Figure 2, 3 and Figure 4. For all three fuels the effect is more or less the same. There is a decrease in the oxygen concentration and bed temperature and an increase in the CO and NO concentrations during the volatile release period. Higher volatile content of the fuel leads to larger peaks in CO and NO.

#### Burnout of Batches of Fuel in the 12 MW Boiler (CFB Chalmers)

The tests using batches of fuel were carried out in a somewhat different way in the 12 MW boiler. The operating conditions were those of the reference case, however, instead of using batches of fuels of different volatile contents, the same fuel was fed, and the size and amount of fuel were varied. The results of the tests with the same amount of batch fuel are shown in Figure 5. The coarse fuel was tested first. This fraction of the fuel contained only pieces between 15 and 40 mm (mass mean size of 22 mm). The fine fraction was removed and further crushed down to a size corresponding to a mean size (mass based) of only 0.25 mm. In order to avoid as large peaks in CO as were recorded in the 8 MW boiler the batch size in the 12 MW boiler was only about one third of the one used in the 8 MW boiler. The effect on the oxygen, CO and NO concentrations was different in the 12 MW boiler. The slow and prolonged devolatilization, which was caused by the coarse batch fuel, did not influence the bed temperature at all. The oxygen concentration dropped only a little and a long, delayed recovery period followed. No CO peak was found and the NO concentration dropped and did not increase as it did in the 8 MW boiler. On the other hand, the rapid devolatilization of the crushed fuel increased the bed temperature and caused the oxygen concentration to drop quickly, after which it returned to the original concentration very fast. There is also a large CO peak, but still no increase of the NO concentration. In the last test, shown in Figure 6, the batch size was therefore made 3.5 times larger. Mixed fuel was used, of a size between 1 and 25 mm. This time the exit oxygen concentration dropped to zero and a long, slow recovery period of 25 minutes was recorded. The bed temperature decreased a little in the beginning, after which a large and slow increase took place. The CO peak is tremendous and could not be recorded completely, since a lower range on the CO analyzer was used by mistake. However, the CO disappeared as soon as the oxygen concentration started to increase again. The effect of the large batch of fuel on the NO emission is interesting. This time there was a small increase of the NO concentration in the stack, but the NO decreased again as soon

as the CO concentration started to decrease. Again there was no recording of an NO peak similar to those seen in the 8 MW boiler.

### Gas Concentration Profiles in the Combustion Chambers

The results of the measurement of the gas concentration profiles are found in Figure 7 to Figure 10. The vertical profiles were taken in the centre from bottom to exit of the combustion chambers and include also measurements in the cyclone outlet and stack. In the 12 MW boiler, measurements of the horizontal profiles were carried out at a few locations for some of the components as well. The staged air supply causes concentration gradients in the horizontal direction of the combustion chamber. This is an effect of the size of the boiler rather than an effect of uneven distribution of the secondary air between the nozzles. Problems with incomplete penetration of secondary air are always present in evaluation of data from larger commercial boilers and the data presented below are representative for this class of experimental facilities. Further discussion of these problems together with a more complete presentation of all profiles taken in the 12 MW boiler are given in [8].

In Figure 7 a comparison of the NO profiles from the two boilers is shown. In both cases there are high levels of NO at the bottom of the combustion chamber. The NO concentration decreases higher up in the combustion chamber. This decrease is partly an effect of dilution by secondary air and partly because of reduction of NO. The reduction of NO is almost complete at the exit, down to only 40 ppm for the 12 MW boiler and 30 ppm for the 8 MW boiler.

The concentration of C<sub>1</sub> to C<sub>3</sub> hydrocarbons was measured only in the 12 MW boiler and the result is plotted in Figure 8. The high levels of CH<sub>4</sub> and the drastic drop in the concentration of the higher hydrocarbons C<sub>2</sub> and C<sub>3</sub> can be seen. For all three classes of hydrocarbons, there is a rapid evolution at the bottom of the combustion chamber similar to that of the nitrogen-containing constituent of the volatiles, NH<sub>3</sub> and HCN, Figure 9. After the maximum concentration is reached at 0.65 meters above the bottom plate, a rapid oxidation of the hydrocarbons takes place. As a matter of fact, the hydrocarbon profile shows that the major part of the volatiles is released close to the bottom of the combustion chamber (below one meter).

A comparison of the CO levels of the two boilers is shown in Figure 10. In the 8 MW boiler CO levels between 1 and 6% are found in the combustion chamber, while only 0.05 to 2% are found in the 12 MW boiler. The reason for this large difference in CO level is probably due to the mixing of air and fuel. In the 8 MW boiler the secondary air was introduced at one meter, where the particle density is high, through poorly designed and worn air ports, while in the new 12 MW boiler the secondary air supply has been moved up to the 2.2 meter level where there are air ports of a new and better design. The difference in fuel supply of the boilers, described earlier, might also be of importance. The third difference of importance is, possibly, the location of the inlet of recycled char from the hot cyclone. The distribution of these large amounts of combustible matter might affect the oxygen concentration in the bottom zone of the combustion chamber.

## INTERPRETATION OF THE RESULTS

### The Effect of Batches of Fuel on NO Emissions in CFBs

Transient tests for which batches of fuel have been burnt under fluidized bed conditions have been reported in the literature [9], [10]. In these tests a small electrically-heated bubbling bed laboratory unit was used (diameter 7.5 cm). Batches of coal particles were dropped into this unit under various conditions and the NO concentrations were recorded. This technique was also used in the large CFB boilers in this study. However, the large-scale tests differed somewhat from the laboratory tests, since the batch fuel was thrown into the combustion chamber in addition to the normal fuel. The normal NO reduction was then disturbed by the large amounts of volatiles produced and the changes were followed through the burnout period.

During the devolatilization period, two competing reactions prevail. The first one is caused by the large amounts of CO produced from the volatiles. This CO takes part in the NO reducing reaction on the surface of the char already present from the devolatilization of the normal fuel supplied at a constant feed rate. The second reaction is related to the large amounts of volatile nitrogen species which can be oxidized on the same char surface. The competing reaction that dominates can be identified by observing that there is an increase of the NO when oxidation of volatile nitrogen dominates, or a decrease of NO when the CO effect on NO char



reactions dominates. In the 8 MW CFB boiler the oxidation of volatile nitrogen dominates and in Figure 11 the results from Figure 2, 3 and Figure 4 have been rewritten to show the normalized amounts of excess NO emitted during the NO peak caused by the batch fuel. For this normalization, attention has been paid to the different amounts of combustibles in each batch (due to different moisture and ash content) and the varying nitrogen content. It is evident from Figure 11 that there is a strong correlation between the amount of volatile nitrogen in the fuel and the amount of NO produced during the NO peak.

The lack of an NO peak for the batch tests in the 12 MW boiler (Figure 5) is taken as proof of the dominance of the CO concentration on the NO-char reactions. The different CO levels in the two boilers shown in Figure 10 are, in combination with Figure 12, the key to the understanding of the different behaviours of the two boilers regarding the NO chemistry. The data in Figure 12 is based on kinetic studies of the NO reduction on graphite [20] and char from bituminous coal [19]. As can be seen in Figure 12, an increase of the CO concentration increases the NO reduction rate on the char. However, the levelling of of CO at high CO concentrations depends on the NO level and the material studied (graphite or char from bituminous coal). The CO effect can be understood by looking at the NO kinetics proposed by Chan [20]. In the mechanism proposed by Chan, CO reacts with chemisorbed oxygen on the surface, thereby increasing the overall reaction rate. However the positive effect of CO can be expected to be active only as long as the desorption of chemisorbed oxygen molecules is the rate determining step, therefore a state of saturation of CO can be expected at high CO levels. In the combustion chamber of a fluidized bed boiler, this means that the effect of a given increment of the CO level depends on the CO level from which the increase starts. In other words, the increase of the CO level caused by the batch supply of fuel in the 8 MW boiler, does not lead to any further significant NO reduction on char surfaces. The oxidation of volatile nitrogen species to NO can be followed instead since the effect of CO has already been saturated.

The difference in NO reduction behaviour of the two boilers was further investigated by the two more tests in the 12 MW boiler, the aim of which was to reach the critical CO levels of the boiler either by increasing the release rate of volatiles (crushed fuel, Figure 5) or by increasing the batch size, Figure 6. This strategy was expected to cause an NO peak. However, the crushed fuel did not

produce sufficient CO in spite of the large CO peak, shown in Figure 5. It was not until the batch of fuel had been increased 3.5 times that a state of saturation of the CO level was reached and a small NO top could be recorded.

### The Gas Concentration Profiles

Concentration profiles of NO from the combustion chamber similar to those shown in Figure 7 have been measured in stationary fluidized bed boilers, [9], [10], [12], [13] and [14]. These measurements have shown an increase of NO at the bottom of the bed, followed by a drop further up in the bed and in the freeboard. The general shape of the NO profile in fluidized bed boilers is taken as evidence of the importance of NO-reducing reactions such as the NO-char reaction and the homogeneous reduction of NO by amines. Especially the amines are considered important for the NO reduction in the freeboard region of the SFB boiler, [13], [17].

In most work involving models and experiments on the reactions of the volatile nitrogen in fluidized beds, it is simply assumed that the volatile nitrogen is released as ammonia ( $\text{NH}_3$ ) or amines ( $\text{NH}_i$ ) in spite of the fact that no measurements of either  $\text{NH}_3$  or HCN concentrations have been reported for fluidized beds so far. The result shown in Figure 9 is strong proof of the relevance of the assumption that  $\text{NH}_3$  is the dominating volatile nitrogen specie. Further support of the dominance of  $\text{NH}_3$  under fluidized-bed conditions is found in the literature [15], [16] and is discussed in [8].

Concentrations of  $\text{NH}_3$  in the freeboard of a stationary fluidized bed test facility have been measured by Hirama and coworkers [17]. They found that the  $\text{NH}_3$  level just above the bed varied greatly with the primary to secondary air ratio. The largest  $\text{NH}_3$  concentrations together with the lowest NO emissions were measured for a primary air stoichiometry of 0.75. This result was taken as a proof of the importance of the volatile nitrogen species for the reduction of NO in stationary fluidized bed boilers.

In the case of the 12 MW CFB boiler, the  $\text{NH}_3$  disappears long before the NO reduction is completed. As a matter of fact, the  $\text{NH}_3$  disappears faster than the hydrocarbons which were produced at the same time. This can be seen by comparing the  $\text{NH}_3$  profile in Figure 9 with the profiles of  $\text{C}_1$  to  $\text{C}_3$  in Figure 8. The

fast disappearance of the  $\text{NH}_3$  in the combustion chamber can be explained as an effect of the oxidation of ammonia on char particles to either  $\text{N}_2$  or  $\text{NO}$ . This result is in accordance with measurements carried out by Hirama and coworkers in a small-scale CFB test rig [17]. They measured only above the secondary air inlet and there they found the same low levels of  $\text{NH}_3$  as those shown in Figure 9. Evidence of the oxidation of ammonia can be found in the experimental results of [17] and [19], as well as in the results of the modelling calculations of  $\text{NO}$  formation in the 8 MW CFB boiler reported in [7]. The results obtained for the two CFB boilers, when batches of fuel were dropped into the combustion chambers, are also in agreement with the fast disappearance of the  $\text{NH}_3$  in the 12 MW CFB boiler.

The gas concentration profiles and the fuel batch test series in the two boilers are two independent proofs of the fact that ammonia does not contribute to the  $\text{NO}$  reduction in either of the CFB boilers.

## CONCLUSIONS

The measurements reported here, together with the results of laboratory investigations previously reported, make it possible to draw the following conclusions.

- In circulating fluidized-bed boilers, the main part of the volatile nitrogen species is found as ammonia or amines.
- The  $\text{NH}_i$  species produced from the volatiles are removed faster from the system than the  $\text{C}_1$  to  $\text{C}_3$  hydrocarbons.
- In CFB boilers burning bituminous coal or other fuels of higher rank, the  $\text{NH}_i$  species do not contribute to the  $\text{NO}$  reduction, due to the fast oxidation to  $\text{N}_2$  or  $\text{NO}$  on char surfaces.
- In CFB boilers burning bituminous coal, the  $\text{CO}$  level in the combustion chamber is the key to the understanding of  $\text{NO}$  reduction in the boiler. The different  $\text{CO}$  levels in different CFB boilers, due to design and size of the boilers can explain the  $\text{NO}$  reduction behaviour seen under the burnout of batches of fuel which have been supplied to the boilers under normal operating conditions.

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**Table I**  
The fuels

Type	Bitu- minous coal No 1	Bitu- minous coal No 2	Bitu- minous coal No 3	Bitu- minous coal No 4	Petro- leum coke	Anth- racite
Size, mm, mass mean	6.5	2.5	16	11	14	1.9
% < 1 mm	11	35	0	13	0	50
Volatiles, % maf	35.5	30.3	30.3	30.0	14.3	11.1
Prox. analyse % as delivered:						
Combustibles	87	82.0	82.0	78.0	95.2	81
Ash	7	9.0	9.2	12.5	3.10	16.5
Moisture	6	9.0	8.8	9.5	1.7	2.5
Ultimate analyse, % maf:						
C	82.7	85.3	85.3	84	89.8	92.1
H	5.2	4.5	4.5	5	4.1	1.6
O	8.8	7.4	7.4	9	2.7	2.6
S	1.6	1.1	1.1	0.5	2.0	2.3
N	1.7	1.7	1.7	1.9	1.4	1.4
Heating value, lower, MJ/kg maf	33.1	33.2	33.2	33.1	35.4	32.0

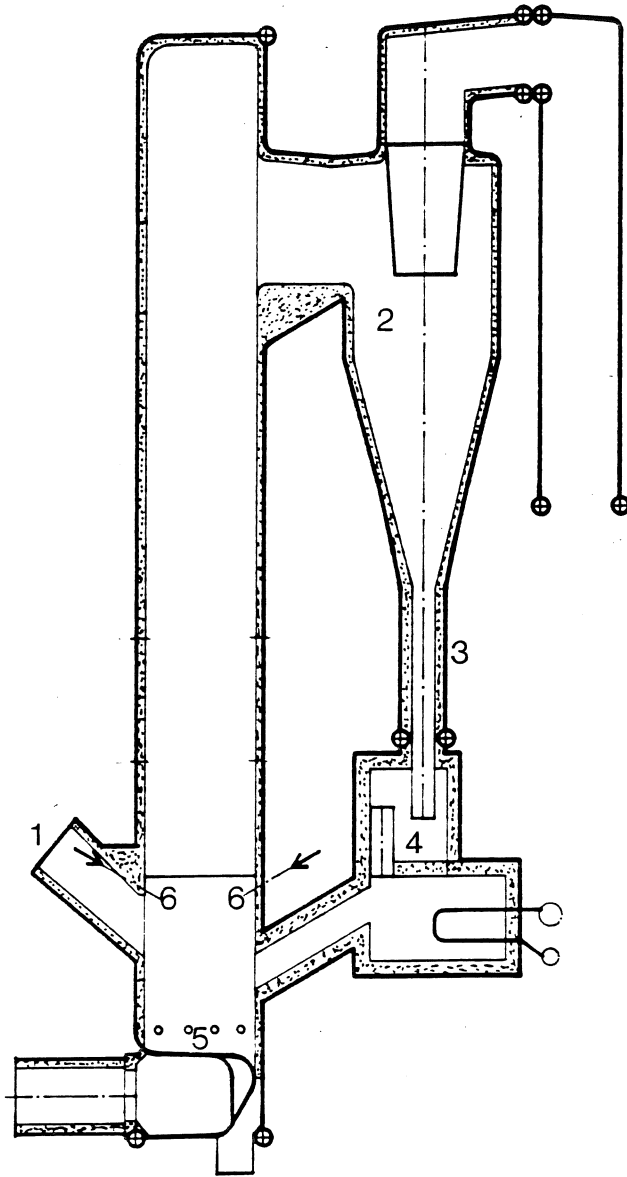


Figure 1. The 12 MW<sub>th</sub> CFB boiler at Chalmers University of Technology. 1-Fuel feed chute, 2-Cyclone, 3-Particle return leg, 4-Particle seal, 5-Bottom plate, 6-Secondary air inlet.



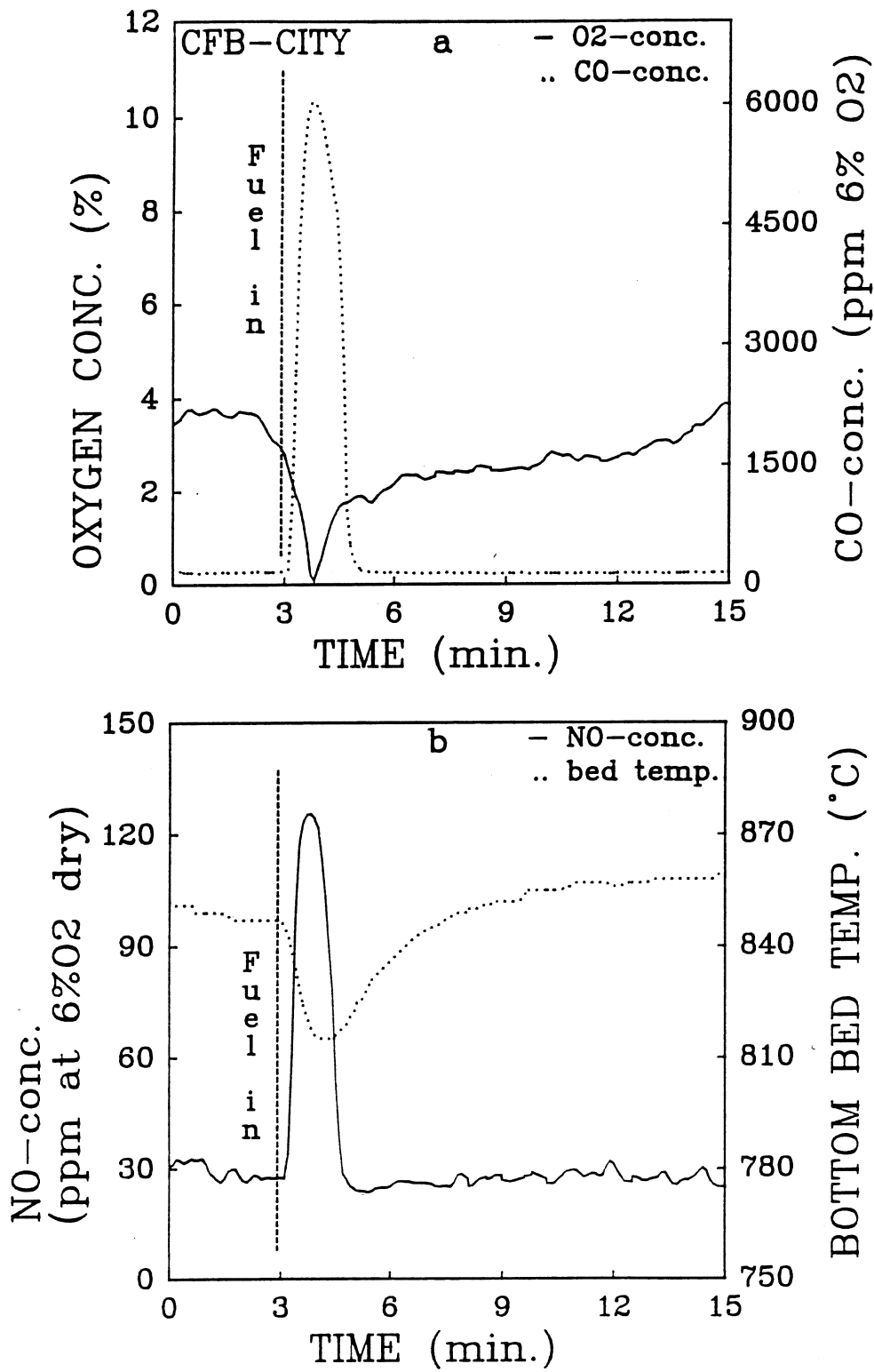


Fig. 2 a, b.

Batch supply of bituminous coal No. 3. Effect on O<sub>2</sub>-CO-NO concentrations and bed temperature during the burnout period. Batch size/fuel flow = 7.3, Reference fuel: bituminous coal No. 2. 8 MW CFB boiler.

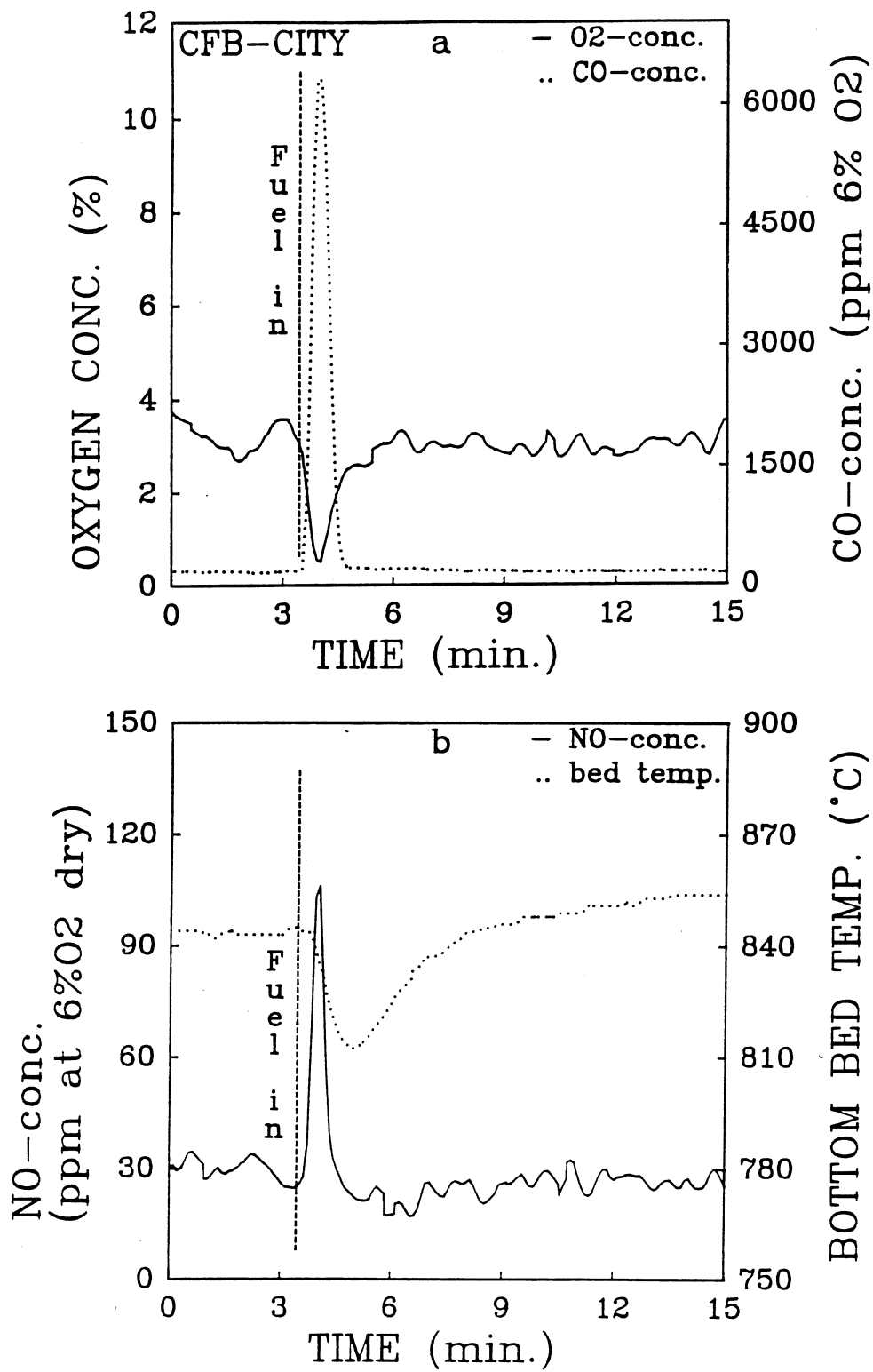


Fig. 3 a, b.

Batch supply of petroleum coke. Effect on O<sub>2</sub>-CO-NO concentrations and bed temperature during the burnout period. Batch size/fuel flow = 8.5. Reference fuel: bituminous coal No. 2. 8 MW CFB boiler.

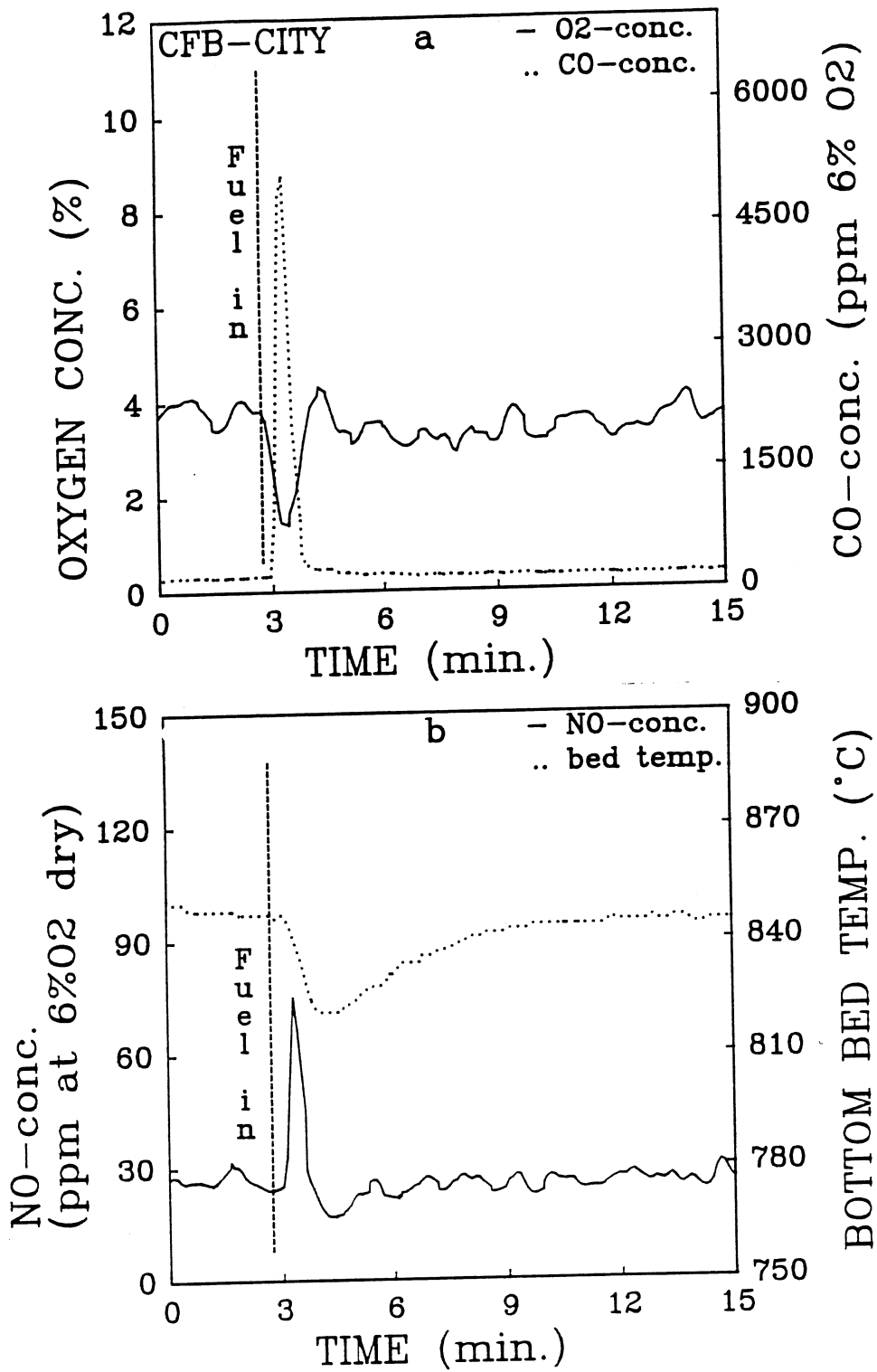


Fig. 4 a, b.

Batch supply of anthracite. Effect on O<sub>2</sub>-CO-NO concentration during the burnout period. Batch size/fuel flow = 6.5. Reference fuel: bituminous coal No. 2. 8 MW boiler.

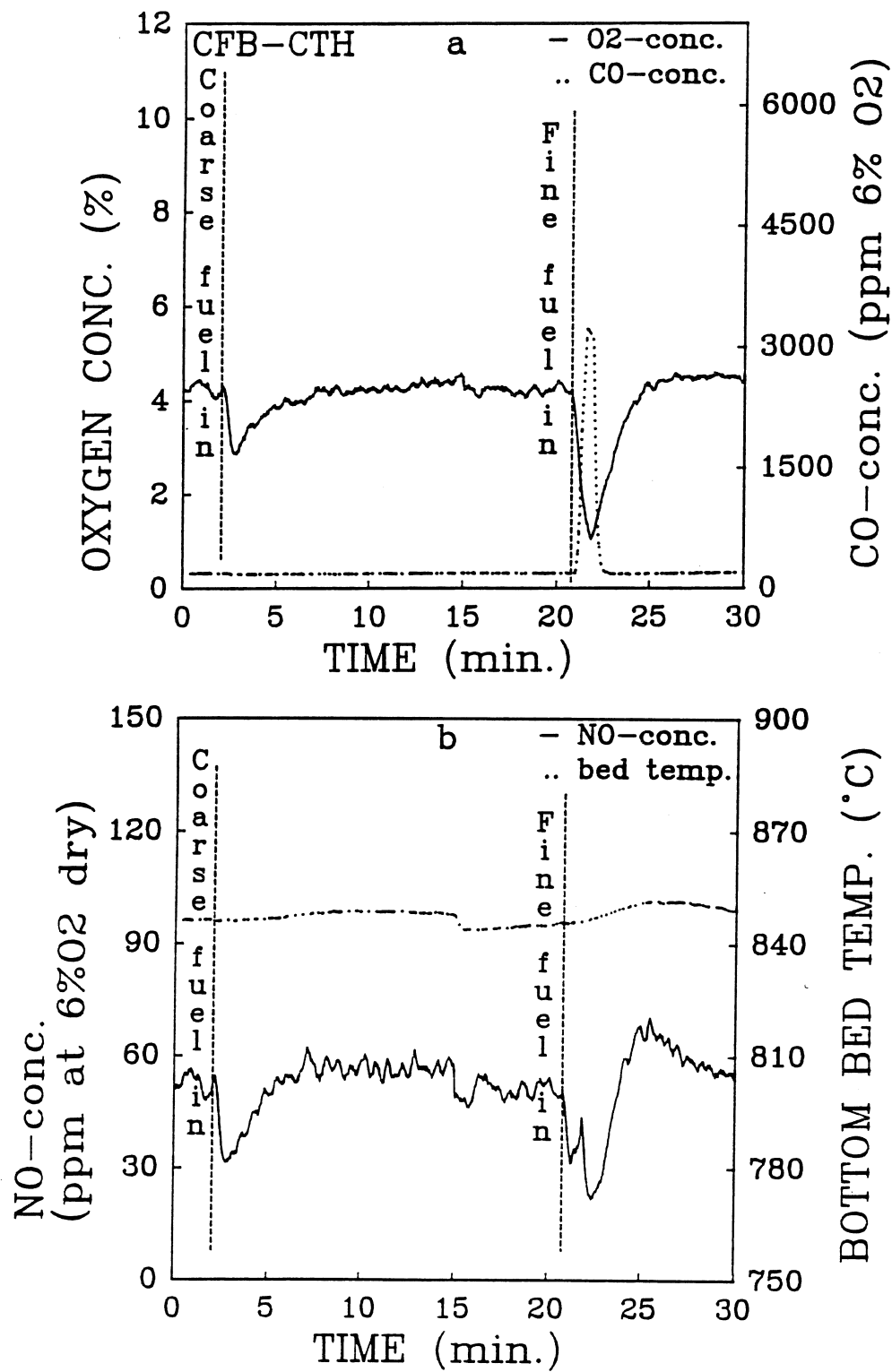


Fig. 5. a, b.

Batch supplies of equal amounts of bituminous coal No. 4 of coarse and fine size. Effect on O<sub>2</sub>-CO-NO concentrations and bed temperature. Reference fuel: bituminous coal No. 4. Batch size/fuel flow = 2.3. 12 MW CFB boiler.

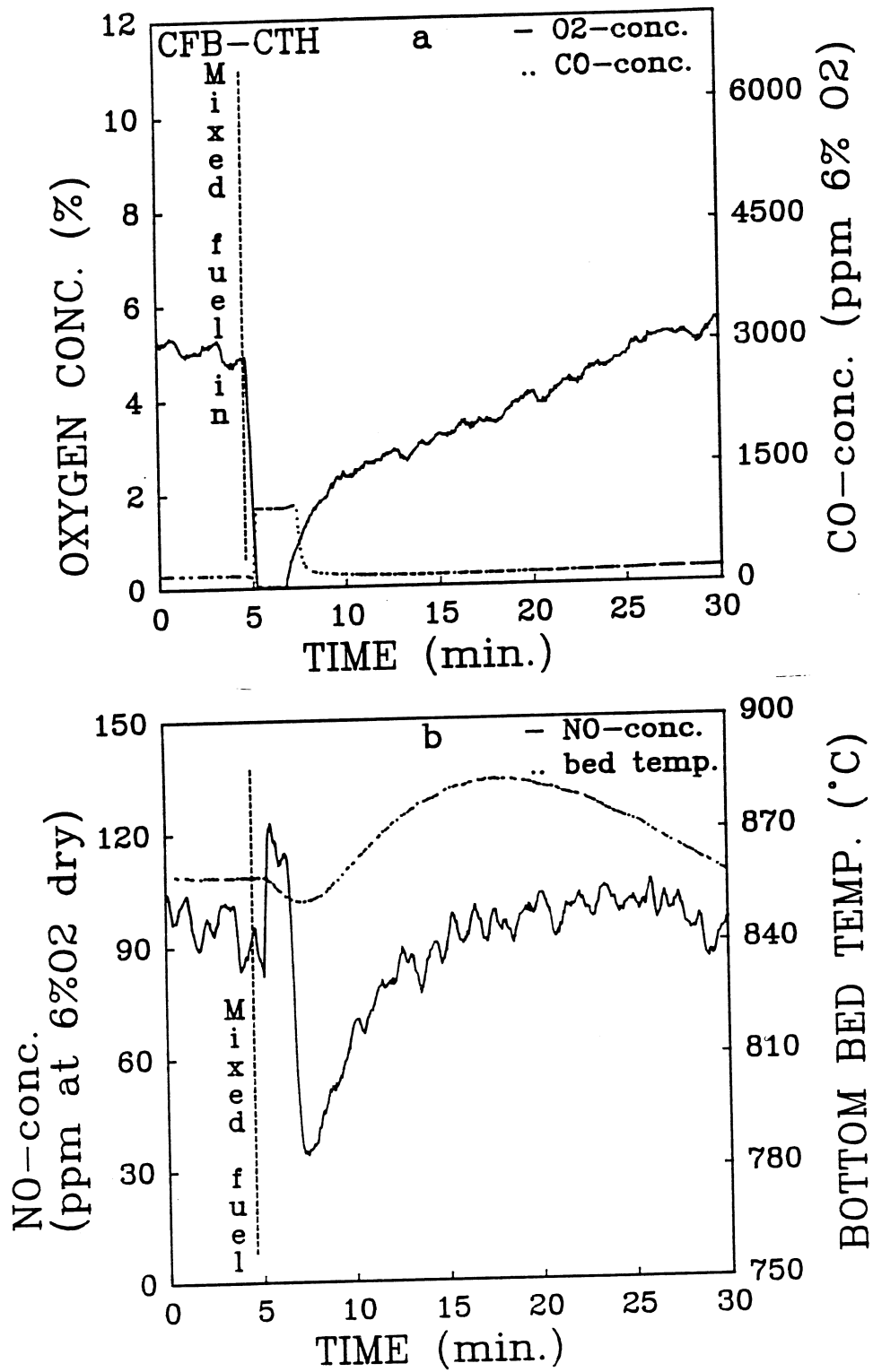


Fig. 6 a. b.

Large batch supply of bituminous coal No. 4. Effect on O<sub>2</sub>-CO-NO concentrations and bed temperature. Batch supply/fuel flow = 8.1. Reference fuel: bituminous coal No. 3. 12 MW CFB boiler.

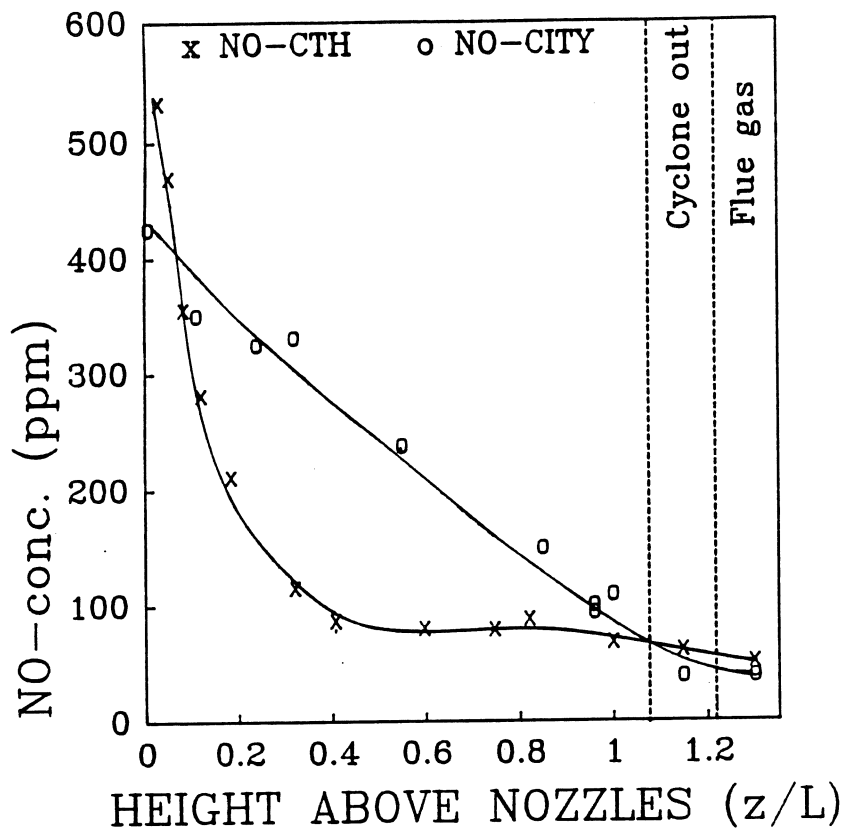


Fig. 7. Comparison of the NO profiles in combustion chambers of the 8 MW and 12 MW CFB boilers. Operating conditions: Reference case. Fuel 8 MW boiler: bituminous coal No. 1. Fuel 12 MW boiler: bituminous coal No. 4.

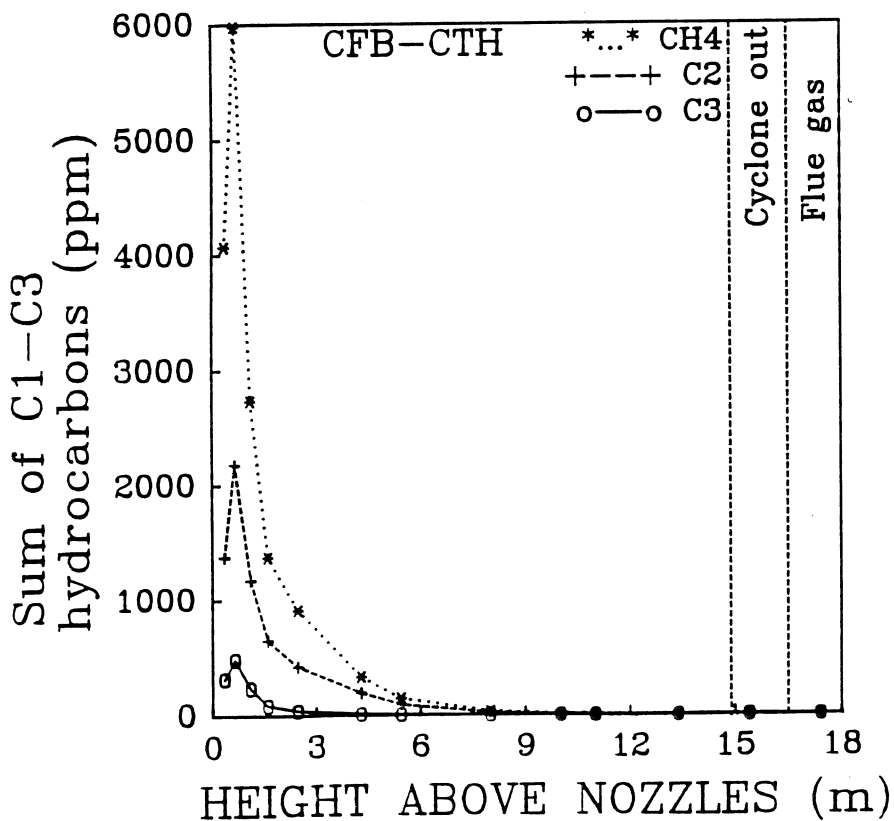


Fig. 8. C<sub>1</sub> to C<sub>3</sub> profiles in the centre of the combustion chamber of the 12 MW CFB boiler. Operating conditions: Reference case. Fuel: bituminous coal No. 4.

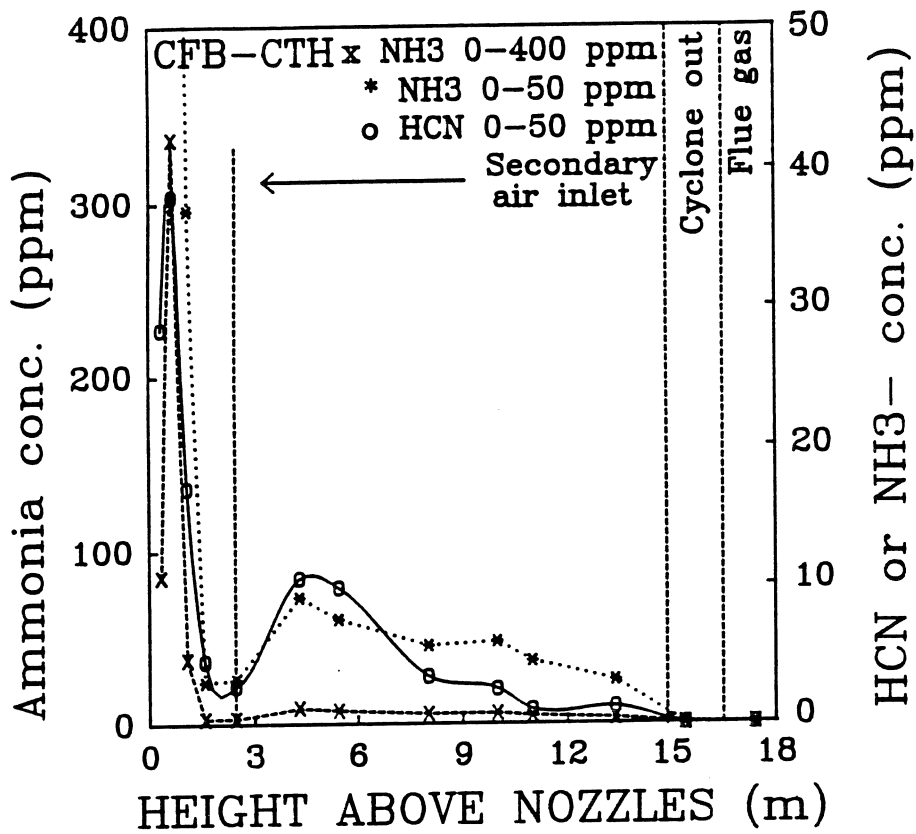


Fig. 9. NH<sub>3</sub> and HCN profiles in the centre of the combustion chamber of the 12 MW CFB boiler. NH<sub>3</sub> concentration shown at 0-400 ppm range on left axis and 0-50 ppm range on right axis. Operating conditions: Reference case. Fuel: bituminous coal No. 4.

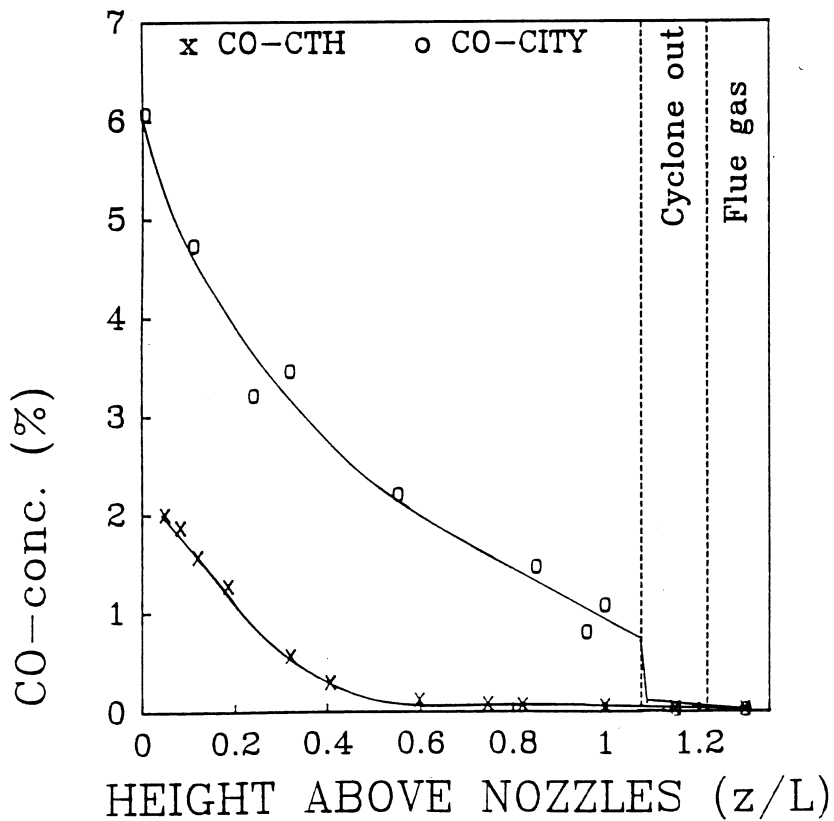


Fig. 10. Comparison of the CO profiles in the combustion chambers of the 8 MW and 12 MW CFB boilers. Operating conditions: Reference case. Fuel 8 MW boiler: bituminous coal No. 1. Fuel 12 MW boiler: bituminous coal No. 4.

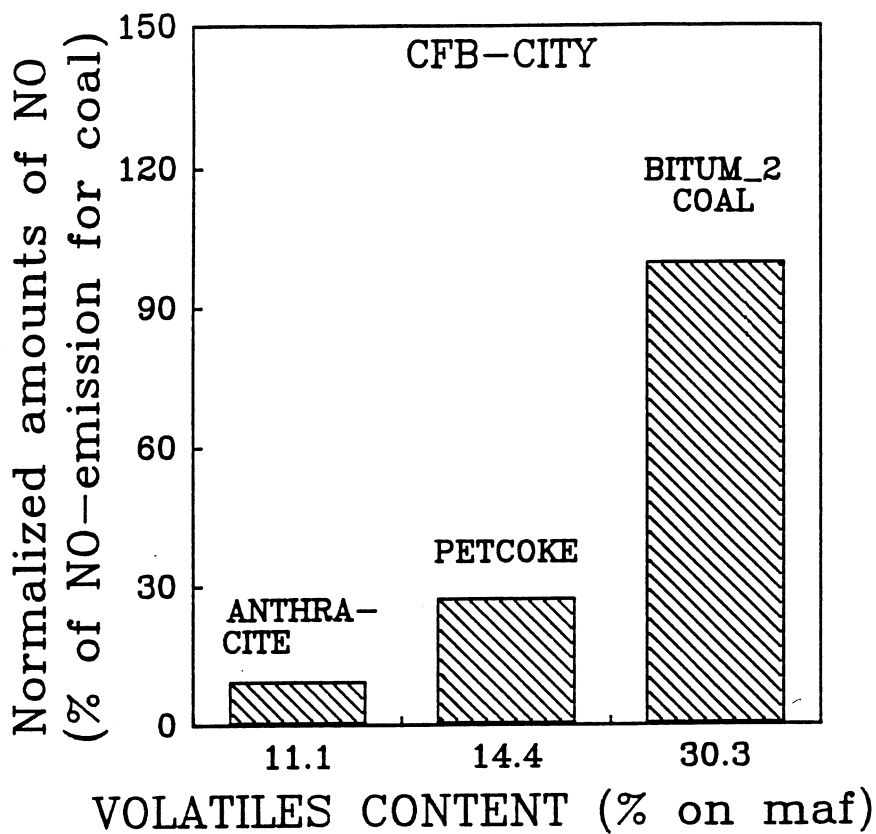


Fig. 11. Normalization of the amounts of NO produced during the devolatilization period of the batch fuels in the 8 MW CFB boiler.

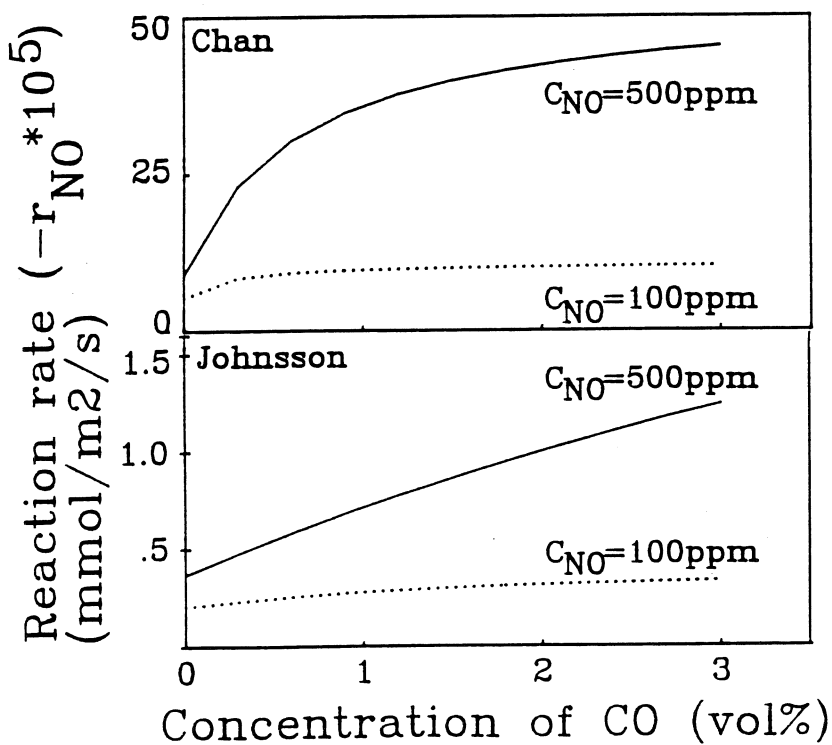


Fig. 12. Comparison of the calculated reaction rates for the reduction of NO by CO with graphite [20] and char from bituminous coal [19] as catalysts, at 800°C, 1.013 bar. Rewritten from data in [20].