INFLUENCE OF FUEL ON THE EMISSION OF NITROGEN OXIDES (NO AND N_2O) FROM AN 8-MW FLUIDIZED BED BOILER

by

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Influence of Fuel on the Emission of Nitrogen Oxides (NO and N_2O) From an 8-MW Fluidized Bed Boiler

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Emissions of nitric oxide (NO) and nitrous oxide (N_2O) from an 8-MW circulating fluidized bed boiler have been measured. The influence of the volatile content of the fuel was investigated by using three different fuels and operating the boiler at different bed temperatures, primary air stoichiometries, and excess air ratios. The measurements show that the emissions of NO are extremely low and dependent upon the char loading of the boiler as well as on the existence of unburned combustible matter such as CO and H_2 in the gas phase. The char content and CO levels are influenced by the fuel, the bed temperature, and the air-to-fuel ratio in the combustion chamber. The levels of N_2O emission are high and caused by the low temperatures used in fluidized beds. The N_2O emission is influenced by bed temperature and oxygen concentration as well, but the influence of bed temperature is opposite compared to the dependence of bed temperature on the NO emission.

INTRODUCTION

The paths of formation and destruction of NO and N_2O in fluidized bed combustion are complex and not fully known. In addition, the present knowledge is difficult to apply on results from an existing fluidized bed boiler. Full-scale tests are therefore needed to obtain a better picture of the actual levels of emissions and if possible to track the reasons for the levels and trends of the emissions.

The aim of the present test program is to study the influence of the volatile content of the fuel on the emissions of NO and N_2O by means of a systematic variation of the influencing parameters, bed temperature, excess air ratio and primary air stoichiometry in test boilers of 8–12 MW but otherwise similar to large-scale commercial circulating fluidized bed (CFB) boilers.

EXPERIMENTAL

The Boilers

The tests were run in an 8-MW CFB boiler designed by Götaverken Energy in 1981 (Fig. 1). The combustion chamber is built up by membrane tube walls. The height is 8.5 m and the cross section is about 1.8 m^2. The walls are refractory-lined at the bottom. The bottom plate is plain and manufactured by membrane tubes as well. The primary air is introduced through nozzles welded between the tubes of the bottom plate. Secondary air is introduced through an air register located 1 m above the bottom of the combustion chamber. The secondary air register consists of rectangular ports in the fins of two of the four membrane walls located opposite each other on the same sides as the fuel and material coming from the cyclone return leg are introduced. The fuel is fed with a screw to the bottom of the combustion chamber as close as possible to the bottom plate. The fluidizing velocity is normally in the range of 3–6 m/s. The entrained bed material is captured in a hot cyclone of van Tongeren type that is refractory-lined as well. The separated particles are passed back to the combustion chamber through a return leg and a conventional particle seal. Silica sand was used as a bed material. No limestone was added during the test program. The boiler is further equipped with a data-acquisition system and on-line gas analyzers for fast and accurate sampling of data needed in the research program.

A few complementary tests were run in the

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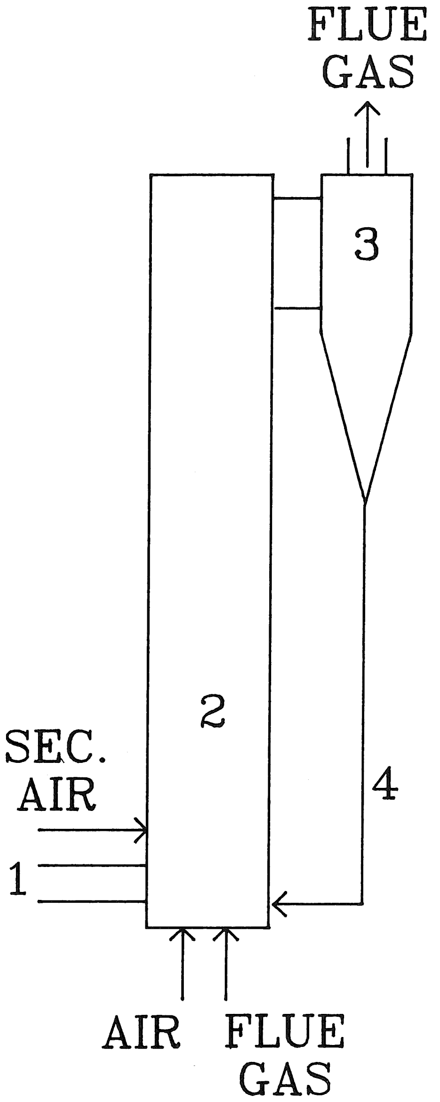

Fig. 1. Schematic picture of the boilers.
1—Fuel feed screw. 2—Combustion chamber with fluidized bed. 3—Cyclone. 4—Particle return leg.

12-MW CFB boiler located in Chalmers University of Technology. This boiler has the same features as that shown in Fig. 1, with a height of 14 m and a cross section of about 2 m^2.

The Fuels

The three fuels used were brown coal from the German Democratic Republic, a bituminous coal from Pennsylvania (USA), and a petroleum coke from a Dutch oil refinery. The fuel characteristics are listed in Table 1. The brown coal ash and the brown coal bed contain high levels of CaO and Fe_2O_3 compared to the bituminous coal and petroleum coke, which is important for the results of the tests with brown coal.

The results are reported in the form of resulting fuel-nitrogen conversion to either NO or N_2O. The nitrogen content of the fuel is critical for the accuracy of the calculation of this conversion. The analysis of the fuel have therefore been carried out at three different commercial coal laboratories, where the coal samples originate from the same general test. The procedure was repeated again after 3 months. The instruments used for the determination of the nitrogen content were elementary analyzers, where two of the laboratories used a LECO CHN-600 and the third laboratory a similar instrument from Carlo-Erba. The errors in determining the nitrogen content were estimated to be less than 5% of the values given in Table 1. The nitrogen leaving with the unburned char of the fly-ash is excluded from the calculation of the fuel-nitrogen conversion. Different combustion efficiencies caused by different fuel reactivities or operating conditions would therefore not affect the calculation of fuel-nitrogen conversion.

The Tests

The general aim in a parameter study is to vary one influencing parameter at a time, keeping all the others constant. Such a variation is difficult to carry out in practice because in a CFB reactor many parameters are intimately connected to one another. The hydrodynamic behavior of the boiler, for example, is connected to the heat transfer and the resulting temperature profile as well as the combustion process that is closely connected to the NO chemistry. Changing the relation between the primary and secondary air, for example, leads to influence on

the air-to-fuel ratio in the bottom zone (which is desired),

the devolatilization and combustion of volatiles and thereby the release of volatile nitrogen,

TABLE 1

Fuel Characteristics

	Brown Coal (German Dem. Rep.)	Bituminous Coal (Pennsylvania, USA)	Petroleum Coke (Oil refining)
Size, mass mean (mm)	[a]	6.5	7
% smaller than 1 mm	0	11	14
Volatiles % maf	53.1	35.5	14.3
Proximate analysis (%)			
Combustibles	80	87	91
Ash	5	7	2
Moisture	15	6	7
Ultimate analysis (% maf)			
C	67.1	82.7	89.8
H	4.9	5.2	4.1
O	25.9	8.8	2.7
S	0.8	1.6	2.0
N	0.9	1.7	1.4
Volatile nitrogen (% maf)	49.0	39.3	25.9
Ash analysis (%)			
P_2O_5	0.02 (0.05)[b]	0.54 (0.09)[b]	0.45 (0.04)[b]
SiO_2	20.6 (90.5)	46.9 (95.4)	49.0 (97.1)
Al_2O_3	5.70 (2.22)	23.7 (2.32)	22.7 (1.22)
CaO	17.5 (4.41)	3.50 (0.36)	3.21 (0.56)
Fe_2O_3	25.9 (2.11)	15.3 (1.06)	13.7 (0.58)
MgO	4.28 (0.33)	1.10 (0.22)	0.94 (0.10)
MnO	0.28 (0.02)	0.03 (0.01)	0.04 (0.01)
TiO_2	0.27 (0.14)	1.04 (0.16)	1.12 (0.07)
BaO	0.12 (0.03)	0.07 (0.02)	0.10 (0.01)
Na_2O	0.20 (0.14)	0.61 (0.19)	0.68 (0.12)
K_2O	0.42 (0.22)	1.64 (0.23)	1.66 (0.21)
SO_3	23.5 (0.1)	4.6 (0.1)	3.1 (0.1)

[a] The brown coal was supplied as uniform cylinders, diameter 60 mm, length 35 mm.

[b] The composition within brackets is corresponding bed material. As makeup bed pure silica sand has been used.

TABLE 2

NO-Influencing Parameters
(P Primary, S Secondary, D Design)

No.	Type	Name
1	P	Bed temperature (bottom)
2	P	Total excess air ratio
3	P	Primary air stoichiometry
4	S	Primary air ratio (from No. 3)
5	P	Fluidizing velocity
		a. Load
		b. Flue gas recirculation
6	P,S	Sort of bed material and size
7	P	Fixed carbon content in fuel
8	S	Char content bed
9	S	CO concentration in combustion chamber
10	S	Temperature distribution in combustion chamber and cyclone
11	S	Density at the top of the combustion chamber
12	D	Height of combustion chamber
13	D	Design of the combustion chamber (bottom and outlet to cyclone)
14	D	Location and design of secondary air nozzles
15	D	Cyclone efficiency and recycling rate from cyclone

the combustion of the char and thereby the release of char nitrogen,

the density profile along the combustion chamber, and

the internal recirculation of bed material in the combustion chamber as well as the external recirculation flow across the hot cyclone.

In order to sort out this rather confusing picture, a definition of the influencing parameters is given in Table 2, where the parameters have been divided into three groups—primary (P), secondary (S), and design parameters (D). Out of the parameters in Table 2, numbers 1, 2, 3, and 7 have been varied, one at a time, since these are considered to be the most important ones. The total air flow (primary + secondary air) has always been kept constant and therefore parameter 5b has been used to achieve the proper operating conditions. The parameter 8, 9, 10, and 11 have been free, but special attention to these is necessary and they are therefore reported qualitatively

TABLE 3

Variation of Secondary Parameters (Table 2) During the Bed Temperature Series[a]

Parameter	Brown Coal	Bituminous Coal	Petroleum Coke
Char content, bed (%)	0.3 ↘	7.5 →	19.5 ↘
Char content, return leg cyclone (%)	0 →	1.1 ↘	8.2 ↘
CO (2.8 m, %)	5.0 ↗	3.5 ↘	1.2 ↘
CO (8.5 m, %)	1.1 ↗	1.0 ↘	0.3 ↘
Temp. top (°C)	813 ↗	810 ↗	810 ↗
Density top (kg/m^3)	2.8 ↘	2.9 ↘	2.6 ↘

[a] Values are given for the reference case and the tendency at increasing bed temperature.

TABLE 5

Variation of Secondary Parameters (Table 2) During the Excess Air Series[a]

Parameter	Brown Coal	Bituminous Coal	Petroleum Coke
Char content, bed (%)	0.3 ↘	7.5 ↘	19.5 ↘
Char content, return leg cyclone (%)	0 →	1.1 ↘	8.2 ↘
CO (2.8 m, %)	5.0 ↘	3.5 ↘	1.2 ↘
CO (8.5 m, %)	1.1 ↘	1.0 ↘	0.3 ↘
Temperature top (°C)	813 ↘	810 ↘	810 ↘
Density top (kg/m^3)	2.8 ↘	2.9 ↘	2.6 ↘

[a] Values are given for the reference case and the tendency at increasing excess air ratio.

for each test series (Tables 3–5). A few other important factors have not been characterized. These are the penetration of secondary air into the combustion chamber and the devolatilization zone including the mixing with air and subsequent combustion. The CO levels reported in Tables 3–5 are sampled in the combustion chamber at a height of 2.8 m above the bottom plate and also in a location just before the hot cyclone. A substantial burning of CO takes place in the cyclone and the CO emissions in the stack never exceed 300 ppm.

As a starting point for the parameter study a reference case is defined as a run with a bed temperature of 850°C, an excess air ratio of 1.25, and a primary air stoichiometry of 0.8. Each parameter in the three series, the bed temperature series, the primary air stoichiometry series, and the excess air series, has been varied around this reference case to lower and higher values, keeping the two others constant. The variation is carried out for all three fuels.

TABLE 4

Variation of Secondary Parameters (Table 2) During the Primary Air Stoichiometry Series.[a]

Parameter	Brown Coal	Bituminous Coke	Petroleum
Char content, bed (%)	0.3 →	7.5 ↘	19.5 ↘
Char content, return leg cyclone (%)	0 →	1.1 ↘	8.2 ↘
CO (2.8 m, %)	5.0 ↷	3.5 ↷	1.2 ↘
CO (8.5 m, %)	1.1 ⤴	1.0 ⤴	0.3 →
Temperature top (°C)	813 ↺	810 ↘	810 ↘
Density top (kg/m^3)	2.8 ↗	2.9 ↗	2.6 ↗

[a] Values are given for the reference case and the tendency at increasing primary air stoichiometry.

The design parameters 12, 13, 14, and 15 are what they are and can only be varied in test programs where boilers of different design are compared with each other.

Measurement of N_2O

N_2O was measured by sampling of dry flue gas in bags made of aluminum foil. Subsequent analysis was made on a gas chromatograph (GC) equipped with an electron capture detector. Further details are reported in Ref. 1, where it is also concluded that the measurement of N_2O is accurate enough to form a basis for a conclusion on N_2O levels and emission. In the complementary tests in the 12-MW boiler a continuous infrared (IR) spectrometer was used (Spectran 647, Perkin Elmer). Further details on this analyzer are given in Ref. 2, from where it is evident that the use of the IR analyzer is dependent upon the existence of methane in the flue gas. The methane concentration was checked by GC and nothing was found at the location of gas sampling.

RESULTS

Figures 2–7 show the variation of NO and N_2O for the three series. From Figs. 2, 4, and 6 it is evident that, for the majority of tests, the order of

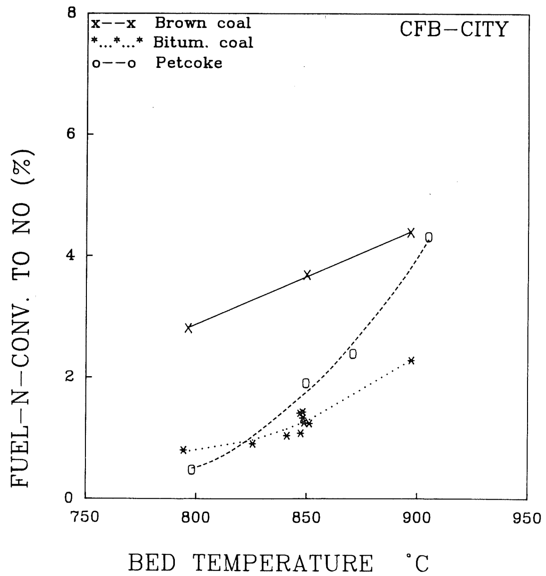

Fig. 2. Fuel-nitrogen conversion to NO in the bed temperature series. Primary air stoichiometry = 0.7-0.8. Excess air ratio = 1.20-1.25.

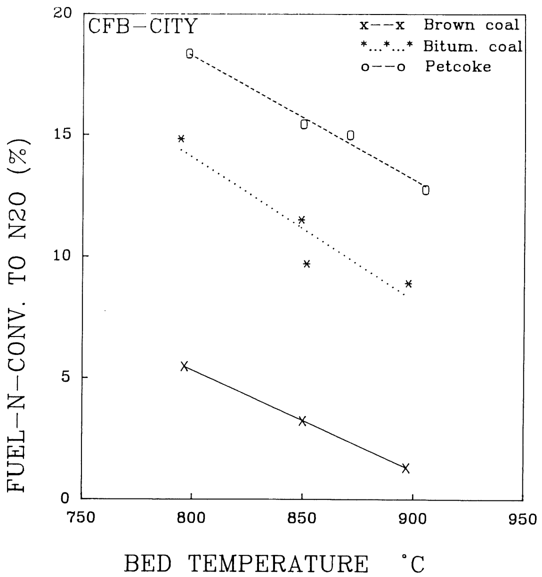

Fig. 3. Fuel-nitrogen conversion to N_2O in the bed temperature series. Primary air stoichiometry = 0.7-0.8. Excess air ratio = 1.20-1.25.

the fuels with respect to the fuel-nitrogen conversion to NO, from higher conversion to lower, is

Brown coal

Petroleum coke

Bituminous coal.

The conversion is extremely low in all tests. The NO emission level never exceeds 50 mg NO_2 /MJ fuel supplied (or 80 ppm NO at 6% O_2 dry).

As can be seen in Fig. 2, the conversion of fuel nitrogen to NO increases for all three fuels when the bed temperature is increased. This general influence of bed temperature has been seen in both stationary (bubbling) fluidized bed boilers and in other CFB boilers. However, in Fig. 2 the bed temperature dependence is different for different fuels, as shown by the heavier dependence for petroleum coke compared with the bituminous coal.

Figures 4 and 6 show the influence of primary air stoichiometry and excess air ratio on the conversion of fuel nitrogen to NO. Here the expected result is an increased fuel-nitrogen conversion at higher primary air stoichiometries and excess air ratios regardless of which fuels are used. In the primary air stoichiometry series only the petroleum coke follows the expected behavior while the bituminous coal shows no influence and for brown coal the fuel-nitrogen conversion to

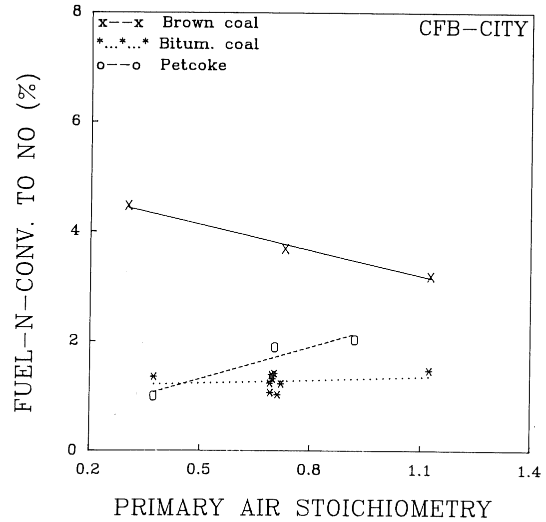

Fig. 4. Fuel-nitrogen conversion to NO in the primary air stoichiometry series. Bed temperature = 845°-850°C. Excess air ratio = 1.20-1.25.

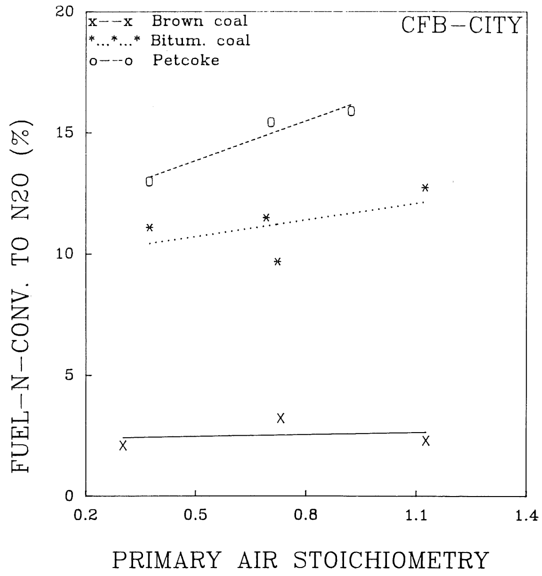

Fig. 5. Fuel-nitrogen conversion to N_2O in the primary air stoichiometry series. Bed temperature = 845°-850°C. Excess air ratio = 1.20-1.25.

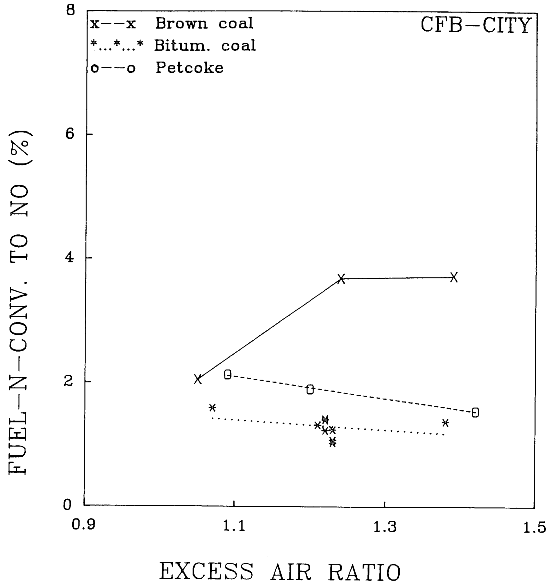

Fig. 6. Fuel-nitrogen conversion to NO in the excess air series. Primary air stoichiometry = 0.7-0.8. Bed temperature = 845°-850°C.

NO even decreases at higher primary air stoichiometries. Looking at Fig. 6, the picture becomes even more confused since here the brown coal follows the expected behaviour instead, while for the petroleum coke the fuel-nitrogen conversion starts to decrease at higher excess air ratios!

The fuel-nitrogen conversion to N_2O is seen in Figs. 3, 5, and 7, which give the following order of the fuels:

Petroleum coke

Bituminous coal

Brown coal.

Furthermore, the fuel-nitrogen conversion to N_2O is several times higher for petroleum coke and bituminous coal than the corresponding conversion to NO. For instance, the conversion to N_2O is 10% in the reference case with bituminous coal, whereas only 1% of the fuel nitrogen is converted to NO. Corresponding values for petroleum coke are 15% to N_2O and only 2% to NO.

In Fig. 3 it can be seen that the conversion of fuel nitrogen to N_2O decreases in a similar way for all three fuels when the bed temperature is increased. The primary air stoichiometry series shows that the fuel-nitrogen conversion is slightly increased for petroleum coke and more or less unaffected for brown coal and bituminous coal (Fig. 5). The results of the excess air ratio series

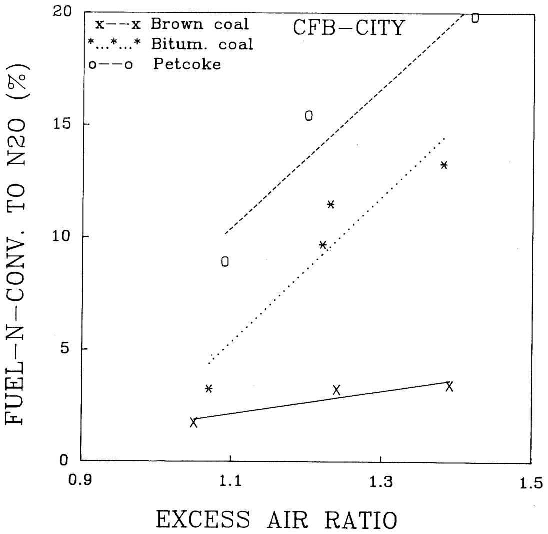

Fig. 7. Fuel-nitrogen conversion to N_2O in the excess air series. Primary air stoichiometry = 0.7-0.8. Bed temperature = 845°-850°C.

show an increasing fuel–nitrogen conversion to N_2O at higher excess air ratios for all three fuels (Fig. 7). However, the increase for the brown coal is not so large as for the other fuels.

Apart from the results given in Figs. 2–7, the following observations about the secondary parameters can be clearly seen in Tables 3–5:

The char concentration at the bottom of the combustion chamber, as well as in the material returning from the hot cyclone, depends directly on the fixed carbon content of the fuel and the reactivity of the corresponding char towards oxygen. Thus, the char concentration is highest for petroleum coke and lowest for brown coal.

The CO concentrations in the combustion chamber are directly connected to the content of volatile matter of the fuel, which leads to brown coal producing the highest levels of CO and petroleum coke producing the lowest.

INTERPRETATION OF THE RESULTS

General

In Fig. 8 the main paths of formation and destruction of NO and N_2O under the conditions of a fluidized bed combustor are outlined on the basis of present knowledge. The difference between the scheme in Fig. 8 and the NO schemes presented before Refs. 3–6 is that N_2O has been included, based on the discussion in Ref. 1.

The scheme in Fig. 8 expresses the amount of fuel nitrogen that is released during the combustion, and is to be found as either N_2, N_2O, or NO in the stack. On the left-hand side of Fig. 8 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. They can participate in NO reduction reactions (step 13) or they can be oxidized on char surfaces to N_2 (step 9) or NO (step 11). Part of the volatile nitrogen can be released as cyanides (HCN in the scheme, step 4), which is known to partly oxidize to N_2O [7] (step 12). The volatile fraction of the fuel results in species such as CO and H_2 (shown as CO in the scheme), which take part in the NO reduction reactions on char surfaces (step 16).

The char nitrogen is released during combustion as NO or NH_3, depending on the rank of the coal [8]. The char itself and the CO produced when the coal is not oxidized completely are both important for the reduction (step 15), which takes place more or less in the pores of the char, depending on where the NO is released, the size of the char, and the reactivity of the char towards reaction with oxygen. One of the products of the reaction of NO on char surfaces is N_2O (steps 15 and 16). The N_2O formed can be reduced by hydrogen radicals (step 14). The important reactions included in the NO–N_2O scheme are given in Table 6. If lime is used for sulfur capture or if the composition of the fuel ash makes the bed catalytically active, the situation becomes more complicated than with a bed of silica sand and the reactions below the dotted line in Table 6 should be considered. Reactions involving oxidation or decomposition of NH_3 (steps 20–22) and reduction of NO by CO catalyzed by the bed material (step 18) have to be included. Also included in Table 6 are reaction steps involving formation and destruction of N_2O. It is evident that the NO and N_2O chemistry within the walls of a fluidized bed reactor is extremely complex. Not only heterogeneous reactions, in which mass transfer is included, but also the combustion process itself, interact with the NO–N_2O chemistry.

Influence of Volatiles on the Fuel–Nitrogen Conversion to NO

Higher volatile content leads to a higher release of fuel nitrogen in the form of NH_3. In a particle-rich environment, where char is contained, the main part of this NH_3 is oxidized to N_2 or NO (step 9 or step 10, Fig. 8) [6], and thereby rendered harmless, or contributes to the formation of NO. According to Arai et al. [8] the char nitrogen of high volatile fuels is released more in the form of NH_3 than is the case with fuels of higher ranks due to a higher hydrogen content, and this NH_3 will be oxidized to N_2 or NO as well. On the other hand, a fuel with a

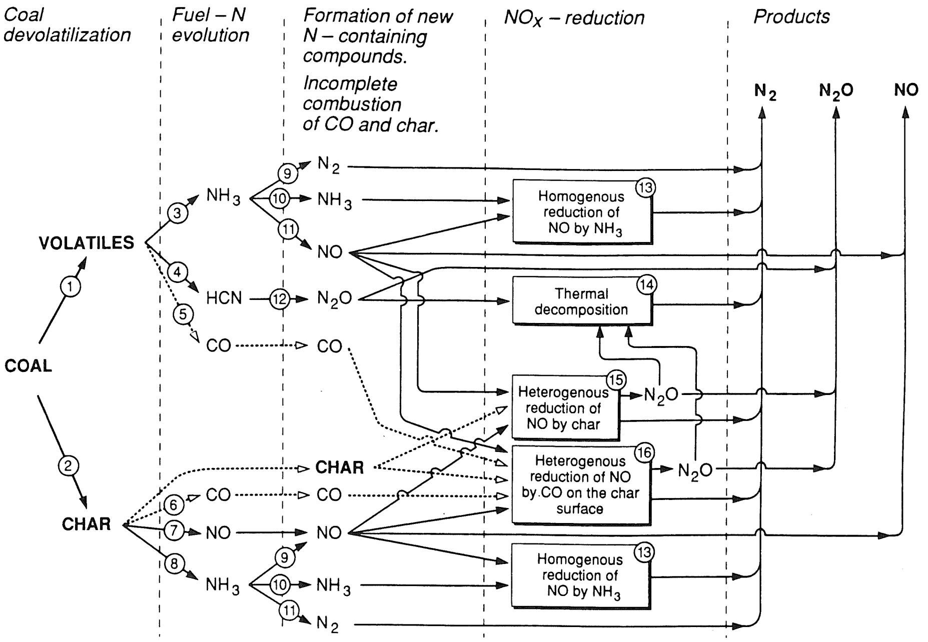

Fig. 8. Pathways involved in fuel-nitrogen formation to NO, N_2O, and N_2 in fluidized beds.

lower volatile content holds a greater part of the fuel nitrogen as char nitrogen which is released as NO within the pores of the char, where the conditions for NO reduction are probably extremely good. The net effect of the volatile content, therefore, is difficult to evaluate.

Fuels with a high volatile content produce less char, the most important surface for NO reduction reactions (in a bed of silica sand), but on the other hand the production of CO and other reducing species is favoured (step 5 followed by step 16, Fig. 8). However, one can only speculate about the importance of the bulk CO concentrations for the NO reduction on char surfaces, since CO is produced during the combustion of the char itself, which can be periodically inhibited due to reducing zones caused by the staged air supply and an incomplete mixing of fuel and air. In these zones high CO levels may promote the reduction of NO produced from oxidation of volatile nitrogen (e.g., NH_3) or NO produced somewhere else where the oxygen concentration is higher.

Petroleum coke yields the highest concentration of char in the combustion chamber, but this does not automatically result in optimum conditions for NO reduction. The reactivity of the char from petroleum coke towards reaction with oxygen is lower than that of the corresponding char from bituminous coal. This may influence the combustion process in the pores of the char and the local conditions for NO reduction.

Although an exact explanation of the influence of the volatile content cannot be given, the order of the fuels regarding the fuel-nitrogen conversion to NO of all the test series shows that the char and the char-related reactions are the key to a better understanding of the NO reduction reactions in the combustion chambers with high particle densities, since the volatile nitrogen (e.g., NH_3) is most probably oxidized to N_2 or NO.

Influence of Bed Temperature on the Fuel-Nitrogen Conversion to NO

The trends of the char concentrations and CO levels of Table 3 are opposite to the trends of the conversion of fuel nitrogen to NO at increasing

TABLE 6

Important Reactions Involving NO, N_2O, HCN and NH_3 Under Fluidized Bed Combustion Conditions [6, 7, 9, 10]

Reaction	Catalyst	Step in Fig. 8
Reduction of NO (bed of silica sand)		
$NO + char \rightarrow \frac{1}{2}N_2 + CO$	gas–solid reaction	15
$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$	char	16
$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$	bed material	17
$NO + \frac{2}{3}NH_3 \rightarrow \frac{5}{6}N_2 + H_2O$	homogeneous gas phase	13
Oxidation of NH_3 to NO (bed of silica sand)		
$NH_3 + \frac{5}{4}O_2 \rightarrow NO + \frac{3}{2}H_2O$	char	11
$NH_3 + \frac{5}{4}O_2 \rightarrow NO + \frac{3}{2}H_2O$	homogeneous gas phase	11
$NH_3 + \frac{5}{4}O_2 \rightarrow NO + \frac{3}{2}H_2O$	bed material	11
Oxidation of NH_3 to N_2 (bed of silica sand)		
$2NH_3 + \frac{3}{2}O_2 \rightarrow N_2 + 3H_2O$	char	9
$2NH_3 + \frac{3}{2}O_2 \rightarrow N_2 + 3H_2O$	bed material	9
Reactions concerning NO formation and destruction when lime is present in the bed		
$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$	CaO	18
$NO + \frac{2}{3}NH_3 \rightarrow \frac{5}{6}N_2 + H_2O$	$CaSO_4$	19
$NH_3 + \frac{5}{4}O_2 \rightarrow NO + \frac{3}{2}H_2O$	CaO	20
$2NH_3 \rightarrow N_2 + 3H_2$	CaO	21
$2NH_3 + \frac{3}{2}O_2 \rightarrow N_2 + 3H_2O$	CaO	22
Reactions involving formation and destruction of N_2O		
$HCN + O^* \rightarrow NCO + H^*$	homogeneous gas phase	12
$NCO + NO \rightarrow N_2O + CO$	homogeneous gas phase	
$NH + NO \rightarrow N_2O + H^*$	homogeneous gas phase	23
$N_2O + H^* \rightarrow N_2 + OH^*$	homogeneous gas phase	14
$2NO + char \rightarrow N_2O$	gas solid reaction	15,16
$char\text{-}N + \frac{1}{2}O_2 \rightarrow N_2O$	gas solid reaction	25
$volatile\text{-}N + \frac{1}{2}O_2 \rightarrow N_2O$	char	26

bed temperature. The increase of fuel-nitrogen conversion to NO at higher bed temperatures is believed to be connected to this reduction in CO and char concentrations. Furthermore, the conversion varies more for petroleum coke than for other fuels. The reason for this is probably the lower combustion reactivity and the processes in the pores of the char from petroleum coke.

Since the change of bed temperature had been carried out with flue gas recirculation, it may be argued that the observed results are rather an effect of a dilution of the oxygen concentration in the gas phase than a temperature effect. However, tests where a change of the bed temperature has been obtained either with flue gas recirculation *or* by adding cold sand give the same effect on the NO emission. In other words, the change of the bed temperature is important and the rather small dilution caused by the flue gas recirculation has a minor influence on the fuel-nitrogen conversion to NO.

Influence of Air-to-Fuel Ratio on the Fuel-Nitrogen Conversion to NO

The primary air stoichiometry series and the excess air series represent two ways of affecting the local ratio between air and fuel in the combustion chamber at a constant bottom bed temperature. This is not the only way of changing this ratio for the boiler. The different alternatives can be summarized as follows:

1. Changing the excess air ratio of the entire combustion chamber by
   a. increasing/decreasing both the primary and secondary air flows. Fuel flow constant.
   b. increasing/decreasing the fuel supply at constant primary and secondary air flows.
2. Changing the excess air ratio only at the location above the secondary air nozzles (equivalent to a constant primary air stoichiometry) by
   a. increasing/decreasing the fuel flow and *also* adjusting the primary and secondary air flows. Total air flow constant.
   b. increasing/decreasing the secondary air flow only, not touching either the fuel flow or the primary air flow.
3. Changing the primary air stoichiometry at a constant excess air ratio by changing the primary and secondary air flows. Fuel flow and total air flow are kept constant.

The alternative ways of changing the ratio of fuel and air may influence important factors differently, which leads to different fuel-nitrogen conversions to NO. Some of the important factors are

Distribution of the char between the bottom and the top of the combustion chamber.

The temperature profile above the location at the bottom of the combustion chamber where the temperature is kept constant.

The release of volatiles and the corresponding levels and distribution of CO.

Factors difficult to measure from outside of the combustion chamber, such as penetration of secondary air.

Catalytic activity of the fuel ash may give a catalytic bed that behaves differently compared to a pure sand bed towards changes in air–fuel ratio.

Below, these factors will be used as a starting point for the analysis of the results.

The last factor is most likely to play a role according to a parallel study in a plug flow laboratory reactor of the reactivity of the present chars and bed material [11]. This study showed that the bed material from the brown coal has an extremely high reactivity for NO reduction compared to the bed materials from bituminous coal and petroleum coke (Fig. 9). A visual inspection of the bed material shows that the color of silica sand has shifted into light brown. In other words, the ash from the brown coal coats the bed material.

The primary air stoichiometry series represents air supply alternative No. 3 and the excess air ratio series alternative No. 2a. The resulting speculations about the trends of the conversion of the three fuels in Figs. 4 and 6 are discussed below.

Brown Coal

The decrease in fuel-nitrogen conversion at higher primary air stoichiometries may be caused by the catalytic bed. Table 4 shows that the density at the top of the combustion chamber increased for all three fuels when the primary air stoichiometry is increased. In the case of the highly active brown coal bed, this increase of top density may favor the reduction of NO on the bed material at higher primary air stoichiometry. In the excess air series the density at the top decreases instead at higher excess air ratios (Table 5) and the fuel-nitrogen conversion increases.

Bituminous Coal

The fuel-nitrogen conversion is almost unaffected by either a change of primary air stoichiometry or a change of the excess air ratio. However, the temperature at the top of the combustion chamber

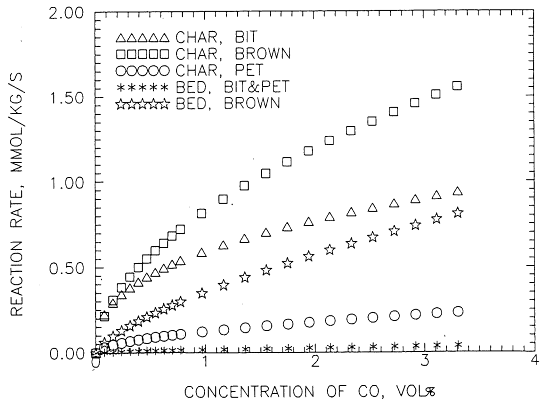

Fig. 9. Comparison of the catalytic activity at 850°C for the catalytic reduction of NO by CO for the material used. From Johnsson [11].

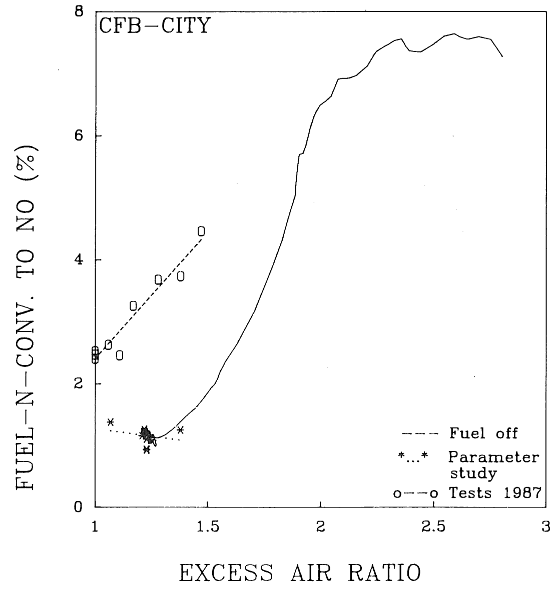

Fig. 11. Comparison of the fuel-nitrogen conversion to NO using different strategies to obtain different excess air ratios. Fuel: bituminous coal.

decreases when the primary air stoichiometry or the excess air ratio is increased, Tables 4 and 5. The influence of a decreasing temperature at the top has been studied separately by gradually decreasing the load at the boiler, keeping the bottom bed temperature constant with flue gas recirculation. The result is shown in Fig. 10, from which it is evident that a decreasing temperature at the top causes the fuel-nitrogen conversion to decrease. In other words, in the primary air stoichiometry series as well as in the excess air series the decreasing top temperatures have a moderating effect on the fuel-nitrogen conversion and the expected increase of fuel-nitrogen conversion at higher air–fuel ratios does not take place.

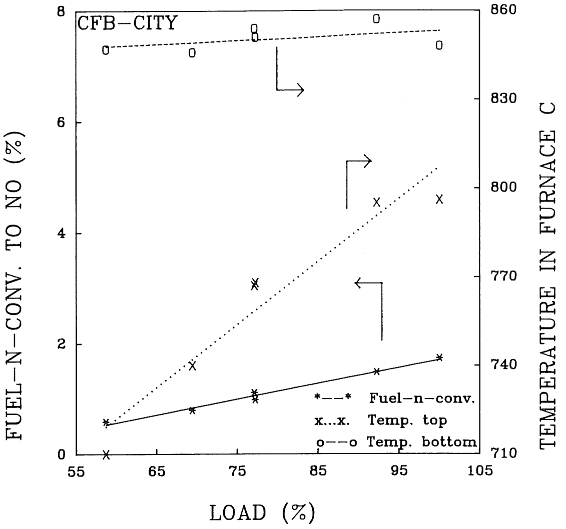

Fig. 10. Influence of the temperature at the top of the combustion chamber on the fuel-nitrogen conversion to NO. Fuel: bituminous coal. Excess air ratio = 1.20–1.25. Primary air stoichiometry = 0.7–0.8.

In Fig. 11 the results for the bituminous coal in Fig. 6 is shown together with two more strategies to obtain higher air–fuel ratios. The open rings represent results obtained in a previous test series [12] with the same fuel where alternative No. 2b was used. The solid line represents a step response test where the fuel feed had been shut off, which is an extreme form of alternative No. 1b. The tendency of a decreasing temperature is counterbalanced by gradually decreasing the flue gas recirculation. In both cases the fuel-nitrogen conversion is seen to increase at higher excess air ratios. The leveling off seen at the step response test at an excess air ratio higher than 2 is caused by a decrease of the bed temperature that can no longer be avoided since the flue gas recirculation is shut. The additional tests point out that the fuel-nitrogen conversion increases in two cases:

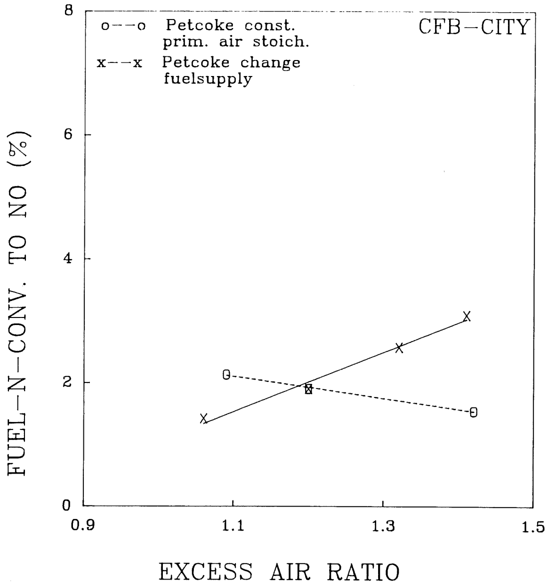

Fig. 12. Comparison of the fuel-nitrogen conversion to NO using different strategies to obtain different excess air ratios. Fuel: petroleum coke.

1. When the air–fuel ratio is increased all over the combustion chamber and not only above the secondary air inlet.
2. When the secondary air flow is increased, which probably improves the penetration of secondary air.

Petroleum Coke

When petroleum coke is used as fuel the different char contents and CO levels in the combustion chamber (Tables 4,5) compared to the case of bituminous coal might be important for the effect of changes of the air–fuel ratio on the fuel-nitrogen conversion to NO. The increase of fuel-nitrogen conversion seen in Fig. 4 may be due to the higher char content, since more char is affected this time, which might give a measurable effect. Another explanation is the lower CO levels, which means that we are now in a different range of CO concentration where small changes of CO concentration might have a larger influence on the reduction rate of the important reaction step 16 (Fig. 8).

The lack of influence of excess air seen in Fig. 6 at higher excess air ratios can be explained as partly being an effect of decreasing top temperature and partly the effect of increasing air–fuel ratio above the bottom zone of the combustion chamber, where the main part of the char is located. Additional tests with petroleum coke where the air–fuel ratio had been increased in the whole combustion chamber (Alternative No. 1b) has been carried out (Fig. 12). This time the fuel-nitrogen conversion to NO increases when the excess air ratio increases.

It can be concluded that the fuel-nitrogen conversion depends upon the air–fuel ratio in the combustion chamber. The strategy used to obtain the change of air–fuel ratio affects the location of this change relative to the location of the char, as well as other factors, which together play roles in the overall fuel-nitrogen conversion to NO in the boiler.

Influence of Volatiles on the Fuel-Nitrogen Conversion to N_2O

The N_2O that is emitted from the boiler is formed either from HCN (step 12, Fig. 8) or by an incomplete reduction of NO on char surfaces (steps 15 and 16, Fig. 8) and reduced by the thermal decomposition reaction with hydrogen radicals (step 14, Fig. 8).

The difference in char concentration (Table 3) between the beds of the three fuels is a possible reason for the order of fuel-nitrogen conversion to N_2O. For the petroleum coke, for example, 10%–18% of the fuel nitrogen is converted to N_2O. The fuel releases 26% of its nitrogen content during slow heating in a laboratory oven. Although the release of fuel nitrogen in the combustion chamber might be somewhat higher due to a higher heating rate, 40%–70% of the fuel nitrogen has to be released as HCN and further oxidized to N_2O without any decomposition at all in order to reach the higher level of conversion observed. In other words, the char concentration and the incomplete reduction of NO to N_2O on char surfaces should be important as well. Oxidation of volatile nitrogen on char surfaces is another likely explanation that would favor the initial formation of N_2O (step 26, Table 1).

Influence of Bed Temperature on the Fuel-Nitrogen Conversion to N_2O

The reason for the bed temperature dependence of the conversion to N_2O of all three fuels is probably the thermal decomposition step (step 14, Fig. 8) which has been shown to be very sensitive to changes in the bed temperature [1]. In Ref. 1, the conclusion was based on model calculations using a homogeneous reaction scheme. Since then experiments have been carried out in an entrained flow reactor [13] made of quartz (0.1 m diameter and 2 m in length) in which both formation and destruction of N_2O from different fuels have been studied in the temperature range of 750°C–970°C. Even if the experiments in Ref. 13 confirm the bed temperature dependence as being mainly caused by the thermal decomposition step, a decrease in the N_2O initially formed from volatile nitrogen (step 12, Fig. 8) at higher temperatures or a decrease in the CO and char concentrations (at higher temperatures) should reduce the formation of N_2O by steps 15 and 16 (Fig. 8) as well.

Influence of Air–Fuel Ratio on the Fuel-Nitrogen Conversion to N_2O

Both in the primary air stoichiometry series and in the excess air ratio series the temperature at the top of the combustion chamber decreases when the parameter studied is increased (Tables 4 and 5). This decrease of the top temperature is the most conceivable explanation for the observed results, judging from the strong temperature dependence already shown in the bed temperature series (Fig. 3). This is further confirmed by the additional step response tests carried out in the 12-MW CFB boiler. In these tests the change of the temperature in the combustion chamber was obtained by adding cold bed material and the change of N_2O was recorded (Fig. 13). Due to thermal inertia the change of the bottom bed temperature is much slower than the change of the temperature at the top when the cold bed material is added. The N_2O emission follows the top temperature closely, which indicates that the N_2O emission depends upon the temperature level in the whole combustion chamber, and the temperature of the bottom bed is not sufficient to give the entire picture.

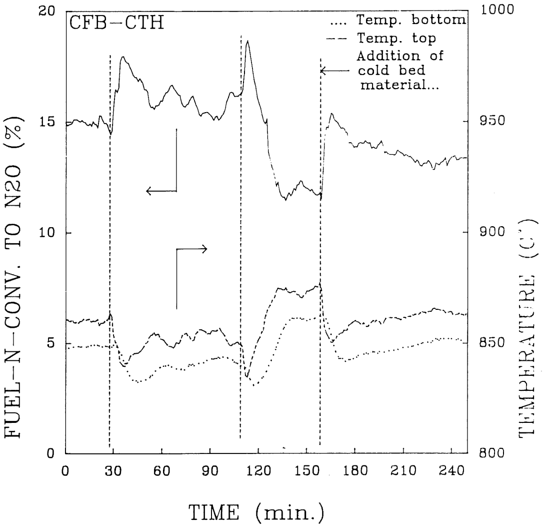

Fig. 13. Characterization of the dependence of the temperature on the fuel-nitrogen conversion to N_2O. Dotted vertical lines show times of addition of cold bed material.

Changes of the air–fuel ratio without keeping the temperature level constant in the entire combustion chamber cannot be used as a basis for any conclusion of the dependence of oxygen concentration on the fuel-nitrogen conversion to N_2O.

The next step was therefore to try to find a period during which different excess air ratios have been used without a change of either the bottom bed temperature or the top temperature. Such an evaluation of data from the 12-MW CFB boiler fired with bituminous coal is shown in Fig. 14. For comparison, the NO values are shown as well. From Fig. 14 it is evident that a dependence of an increasing air–fuel ratio on the fuel-nitrogen conversion exists, independent of the temperature dependence.

The next question is to ask is whether the air–fuel ratio influences the fuel-nitrogen conversion to N_2O through the formation step in which oxidation of volatile nitrogen to N_2O is favored by high oxygen levels (step 12 and step 26, Table 6) or through the influence of oxygen on the destruction mechanism involving hydrogen radicals?

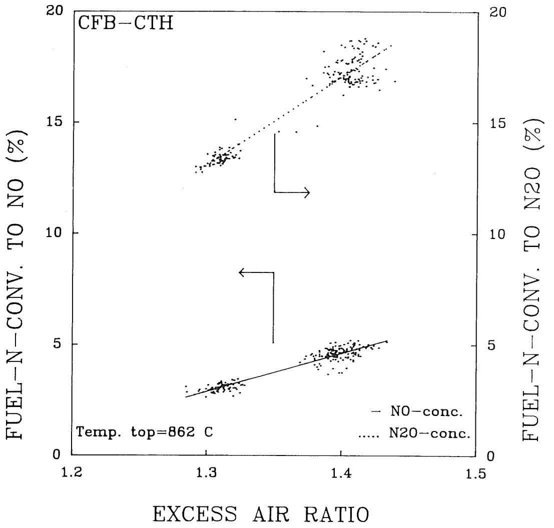

Fig. 14. Fuel-nitrogen conversion to NO and N_2O as a function of the excess air ratio. Evaluation of minute mean values during 8 h of continuous operation.

The tests by Aho et al. [13] give guidance. They have shown no influence of oxygen concentration on the formation of N_2O in the range of 3%–20% excess O_2, but the destruction of N_2O is greatly favored by low oxygen concentrations (1.5%–2.5% O_2 compared to 18%–20% O_2).

DISCUSSION AND CONCLUSIONS

Results Concerning the Emission of Nitric Oxide

The most significant result of the parameter study is the order of the fuels with respect to fuel-nitrogen conversion to NO, which is (in descending order of conversion)

Brown coal

Petroleum coke

Bituminous coal.

Depending on which reduction mechanism is considered to be most important in CFB boilers, step 15 and/or step 16 (involving char), here called "the char line," or step 13 (involving ammonia or other amines), here called "the ammonia line," one would expect the following orders of the fuel-nitrogen conversion to NO (in descending order):

Char line:

Brown coal

Bituminous coal

Petroleum coke

Ammonia line:

Petroleum coke

Bituminous coal

Brown coal.

At first glance, the result obtained does not fit either of the expected orders. However, the reduction of nitric oxide in fluidized beds is far too complicated to be answered by a simple look at the volatiles and char content of the fuel. Instead, the parameter study points to the following additional important factors:

the evolution of CO from the volatiles and their significance for the NO reduction on char surfaces;

the reactivity of the char towards reaction with oxygen; and

the reactivity of the char towards reaction with nitric oxide.

In this way an extended char line can be defined as reactions involving NO reduction on char surfaces, but with respect also to the additional factors mentioned. The reason the fuel with the highest fixed carbon content, the petroleum coke, does not have the lowest conversion of fuel nitrogen to NO can be

a lack of CO from the volatiles,

a lower combustion reactivity of the char, or

a lower reactivity of the char for the NO reaction with CO.

Data in the literature support the different char reactivities (for NO reduction) given by the tests of Johnsson [11], from which some results are shown in Fig. 9. However, the reactivity in Fig. 9 is expressed per grams of char and, taking into consideration the different porosity of the chars as well as how much of the pore volume is actually utilized for NO reduction, it is impossible at the moment to judge, from the laboratory study, which chars are most reactive.

The influence of combustion reactivity of the char on the char-nitrogen conversion to NO has been studied by Shimitzu et al. [14]. The tests have been carried out in a fixed bed reactor with a 20-mm-i.d. quartz tube. They show an increased char nitrogen conversion to NO for bituminous coals of low reactivity. Johnsson [15] has also carried out similar tests on the present chars and found an opposite dependence compared to Shimitzu. In other words, it remains to be explained in detail how different combustion reactivities influence the release and subsequent reduction of NO within the pores of a burning char particle.

As a final comment on the order of the fuels, one can compare with the situation in stationary fluidized bed boilers as well as in pulverized coal combustion (PCC) [16], which shows an opposite order of the fuels. In stationary fluidized bed boilers and in PCC the volatile nitrogen plays a different and more important role for the NO reduction than in CFB boilers.

In addition to the order of the fuels, the parameter study shows the dependence of temperature and oxygen concentration on the fuel-nitrogen conversion to NO. Generally, the conversion increases at higher temperatures and oxygen concentrations. This is in agreement with previous studies in stationary fluidized bed boilers. However, the situation in a CFB boiler is somewhat different. The parameter study shows that the temperature dependence is a function of not only the bottom bed temperature but also the temperature in the entire combustion chamber as well. Apart from this, the temperature dependence is different for different fuels, probably because of the different combustion reactivities of the fuels.

The influence of air–fuel ratio is affected by the method used to change the air supply to the boiler.

The fuel properties, such as the reactivity of the fuel as well as the catalytic activity of the bed material, also seem to be of importance.

Results Concerning the Emission of Nitrous Oxide

The order of the fuel–nitrogen conversion to N_2O is for all tests in the parameter study (from higher conversion to lower):

Petroleum coke

Bituminous coal

Brown coal.

For the moment, the reason for this order is unclear. It seems that the char loading of the bed has an influence on the fuel-nitrogen conversion to N_2O, but it is difficult to say whether the result is caused by an incomplete reduction of NO to N_2O on char surfaces (steps 15 and 16, Fig. 8), or if the char might influence the amount of volatile nitrogen that is oxidized to N_2O (step 26, Table 2), or if some other unknown reactions are important. At least it is clear that the fuel-nitrogen conversion to N_2O is very sensitive to changes of the temperature in the entire combustion chamber. The temperature dependence is opposite from that of the fuel-nitrogen conversion to NO, here the temperature dependence is in an indirect relationship, since an increased temperature causes the fuel-nitrogen conversion to N_2O to decrease.

From the additional tests it is evident that the fuel-nitrogen conversion to N_2O is dependent on oxygen concentration as well. The effect of an increased oxygen concentration is similar for the conversion to N_2O and NO, but the increase seems to be larger for N_2O than for NO. Because NO and N_2O have the dependence of oxygen concentration in common, it becomes desirable to operate the CFB boilers at as low excess air ratios as efficient burnout of CO will permit. Excess air levels between 1.05 and 1.10 are desirable. This leads to new demands regarding the air distribution to favor good mixing between fuel and air. A satisfactory burnout of CO and char fines in the particle separator also must be maintained. The amount of cooling of the cyclone and the corresponding temperature at the outlet of the cyclone are critical for a proper burnout at low excess air levels. Finally, the control system has to be optimized to counterbalance disturbances in fuel quality, so that temporary high concentrations of unburned volatiles in the stack can be avoided by avoiding excess air levels below 1.05 even during short moments.

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