

4.11 Chemistry of nitrogen oxides at atmospheric fluidized bed combustion

In fluidized bed combustion, the combustion takes place in a bed of particles that is being fluidized by means of air blown through the bed from below. The bed is composed of sand, ash, char residue, and, possibly, SO_2 sorbent. Fluidized bed combustion may be divided into two main groups:

- Bubbling fluidized bed combustion (BFBC) is a combustion method where the velocity of the gasflow upwards is between 1 and 3 m/s. A distinct fluidized bed and a freeboard zone that is almost free of bed material may be discerned in a BFBC reactor.

- In circulating fluidized bed combustion (CFBC) the air velocity is so high, some 5 to 10 m/s, that the bed material suspension fills the whole combustion chamber. Entrained particles are caught in a cyclone and returned to the combustion chamber.

The NO emission from fluidized bed combustion is, as a rule, significantly less than that resulting from burner operation. This is partly explained by the low fluidized bed combustion temperature (800 - 900 °C) as a result of which the formation of thermal NO is negligible, and almost all of the nitric oxide originates from fuel nitrogen. In circulating fluidized bed combustion, the low NO emission is partly explained also by the efficient reduction of nitric oxide by air staging, and reduction of nitric oxide with char. In circulating fluidized bed combustion, significant amounts of char are present everywhere in the furnace, and the efficient interaction between nitric oxide and char is possible in the whole reactor volume. With air staging the amount of char in the furnace increases even more.

Describing the formation and decomposition of nitrogen oxides in fluidized bed combustion is more complicated than describing that related to burner combustion. Apart from the nitric oxide emission, the laughing gas emission at fluidized bed combustion must be accounted for too, because the low temperature favors the formation of laughing gas, whereby the N_2O emission at fluidized bed combustion is markedly higher than that with burner combustion. The dependences on combustion parameters are often contradictory for NO and N_2O . Moreover, at fluidized bed combustion, many heterogeneous reactions between gas and particles become important, *e.g.*, reduction of nitric oxide with char, which, aside from the homogeneous gas reactions, must be considered. This concerns especially circulating fluidized bed combustion, where the interaction between gas and particles is more intensive than in bubbling fluidized bed combustion.

The heterogeneous reactions of fluidized bed combustion may be either catalytic or noncatalytic. For example, the reduction of nitric oxide with char

may take place also catalytically if sufficient concentrations of reducing gases, such as carbon monoxide, are present. Apart from char, it has been found that an efficient catalyst for nitrogen reactions is, *e.g.*, calcium oxide (CaO), which is added to the combustion chamber in the form of limestone, (CaCO₃) for binding sulfur dioxide (Chapter 3). Limestone itself and sulfated limestone (CaSO₄) are generally less efficient catalysts than CaO.

A simplified diagram of the formation and decomposition reactions of nitrogen oxides during fluidized bed combustion is shown in Figure 4.38 and Table 4.8. The NO reactions of fluidized bed combustion have been under closer scrutiny only a couple of decades, and the discovery of the N₂O emission in the 1980s made the studies even more troublesome.

In the following we are to examine the main formation and decomposition reactions of nitric oxide and laughing gas, but the proportional significance of the reactions is not yet fully clarified. Research in this area is lively at this time. *Reaction numbers in the text that follows refer to Figure 4.38/ Table 4.8, indicated with the extra number sign #.*

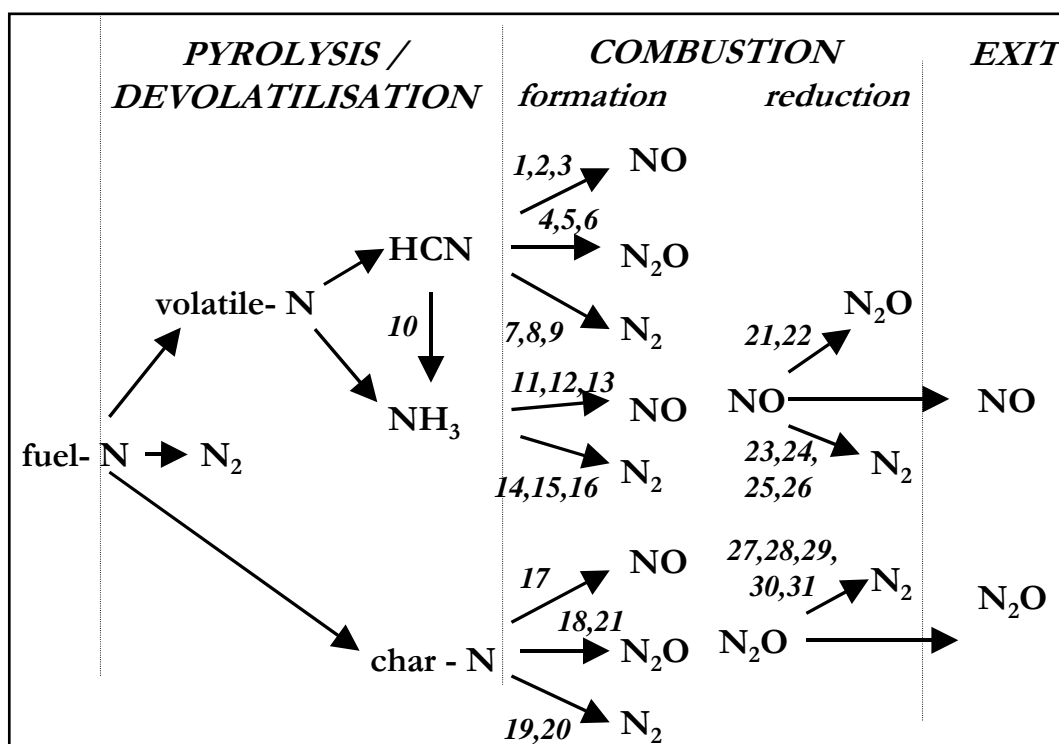


Figure 4.38 Most important reactions involved in nitrogen oxides formation and reduction in fluidised bed combustion (Kilpinen, 1995)

Table 4.8 Most important reactions involved in nitrogen oxides formation and reduction in fluidised bed combustion (see Figure 4.38)

NOTE: (-Y) stands for species Y absorbed on char surface carbon

#	REACTION :	homo- geneous	hetero- geneous
1	$\text{HCN} + \text{O}, +\text{OH} \rightarrow \text{H}_i\text{NCO} \xrightarrow{+\text{H}} \text{NH}_i \xrightarrow{+\text{O}_2, +\text{OH}, +\text{O}} \text{NO}$	♦	
2	$\text{HCN} + \text{CaO}, \text{O}_2 \rightarrow \text{NO}$		♦
3	$\text{HCN} + \text{char}, \text{O}_2 \rightarrow \text{NO}$		♦
4	$\text{HCN} + \text{O} \rightarrow \text{NCO} \xrightarrow{+\text{NO}} \text{N}_2\text{O}$	♦	
5	$\text{HCN} + \text{CaO}, \text{O}_2, (\text{NO}) \rightarrow \text{N}_2\text{O}$		♦
6	$\text{HCN} + \text{char}, \text{O}_2, (\text{NO}) \rightarrow \text{N}_2\text{O}$		♦
7	$\text{HCN} + \text{O}, +\text{OH} \rightarrow \text{H}_i\text{NCO} \xrightarrow{+\text{H}} \text{NH}_i \xrightarrow{+\text{NO}} \text{N}_2$	♦	
8	$\text{HCN} + \text{CaO}, (\text{O}_2), \text{NO} \rightarrow \text{N}_2$		♦
9	$\text{HCN} + \text{char}, (\text{O}_2), \text{NO} \rightarrow \text{N}_2$		♦
10a	$\text{HCN} + \text{O}_2 + \text{H}_2 \xrightarrow{+\text{CaO}} \text{NH}_3$		♦
10b	$\text{HCN} + \text{O}_2, +\text{OH} \rightarrow \text{H}_i\text{NCO} \xrightarrow{+\text{H}} \text{NH}_i \xrightarrow{+\text{H}_2\text{O}, +\text{H}_2} \text{NH}_3$	♦	
11	$\text{NH}_3 + \text{O}, +\text{OH} \rightarrow \text{NH}_i \xrightarrow{+\text{O}_2, +\text{OH}, +\text{O}} \text{NO}$	♦	
12	$\text{NH}_3 + \text{CaO}, \text{O}_2 \rightarrow \text{NO}$		♦
13	$\text{NH}_3 + \text{char}, \text{O}_2 \rightarrow \text{NO}$		♦
14	$\text{NH}_3 + \text{H}, +\text{OH} \rightarrow \text{NH}_i \xrightarrow{+\text{NO}} \text{N}_2$	♦	
15	$\text{NH}_3 + \text{CaO}, (\text{O}_2), (\text{NO}) \rightarrow \text{N}_2$		♦
16	$\text{NH}_3 + \text{char}, (\text{O}_2), (\text{NO}) \rightarrow \text{N}_2$		♦
17	$\text{O}_2 + (-\text{C}) + (-\text{CN}) \rightarrow (-\text{CO}) + (-\text{CNO})$ $(-\text{CNO}) \rightarrow \text{NO} + (-\text{C})$		♦ ♦
18	$\text{O}_2 + (-\text{C}) + (-\text{CN}) \rightarrow (-\text{CO}) + (-\text{CNO})$ $(-\text{CN}) + (-\text{CNO}) \rightarrow \text{N}_2\text{O} + 2(-\text{C})$		♦ ♦
19	$\text{NO} + (-\text{C}) \rightarrow \frac{1}{2}\text{N}_2 + (-\text{CO})$		♦
20	$\text{N}_2\text{O} + (-\text{C}) \rightarrow \text{N}_2 + (-\text{CO})$		♦
21	$\text{O}_2 + (-\text{C}) + (-\text{CN}) \rightarrow (-\text{CO}) + (-\text{CNO})$ $(-\text{CNO}) \rightarrow \text{NO} + (-\text{C})$ $\text{NO} + (-\text{CNO}) \rightarrow \text{N}_2\text{O} + (-\text{CO})$		♦ ♦ ♦
22	$2\text{NO} + \text{CaSO}_R (\text{s}) \rightarrow \text{N}_2\text{O} + \text{CaSO}_4 (\text{s})$		♦
23	$\text{NO} + (-\text{C}) \rightarrow \frac{1}{2}\text{N}_2 + (-\text{CO})$		♦
24	$\text{NO} + \text{char} + \text{CO} \rightarrow \text{N}_2$		♦
25	$\text{NO} + \text{CaO} + \text{CO} \rightarrow \text{N}_2$		♦
26	$\text{NO} + \text{CaO} + \text{H}_2 \rightarrow \text{N}_2$		♦
27	$\text{N}_2\text{O} + \text{H} \rightarrow \text{N}_2 + \text{OH}$	♦	
28	$\text{N}_2\text{O} + \text{OH} \rightarrow \text{N}_2 + \text{HO}_2$	♦	
29	$\text{N}_2\text{O} + \text{M} \rightarrow \text{N}_2 + \text{O} + \text{M}$	♦	
30	$\text{N}_2\text{O} + (-\text{C}) \rightarrow \text{N}_2 + (-\text{CO})$		♦
31	$\text{N}_2\text{O} + \text{CaO} \rightarrow \text{N}_2$		♦

4.11.1 N₂O formation mechanisms

Homogeneous oxidation of hydrogen cyanide

At fluidized bed combustion temperatures, about 10 to 50 %, of the volatile cyan and cyanide compounds of the fuel nitrogen, such as HCN, is oxidized homogeneously to laughing gas. The main reaction path from hydrogen cyanide to laughing gas is:



Conversion of hydrogen cyanide to laughing gas is sensitive to temperature and it diminishes with rising temperature. When the temperature exceeds approximately 950 °C, no more laughing gas is formed: the intermediate

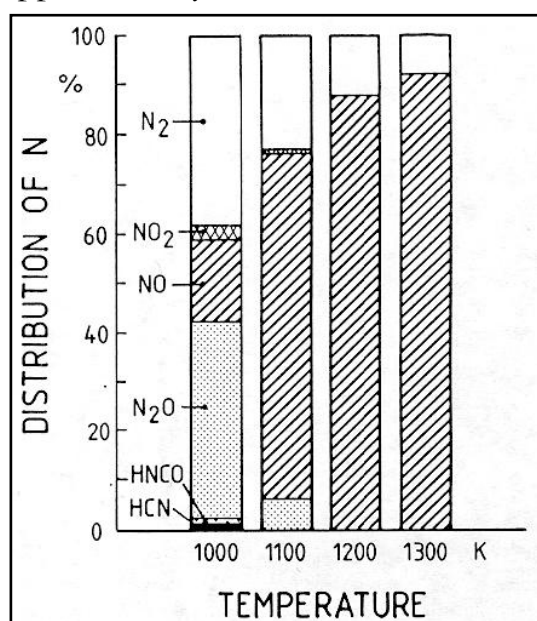


Figure 4.39 Detailed kinetic modelling of N₂O formation from HCN combustion at 1000-1300 K. Inlet 500 ppm HCN, staging with $\lambda_{\text{primary}} = 0.7$, $\lambda_{\text{total}} = 1.2$. (picture from Kilpinen and Hupa, 1991)

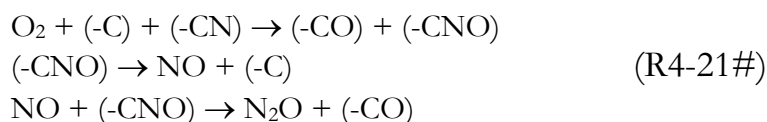
product NCO radical then reacts mainly to nitric oxide. This is illustrated by Figure 4.39, which gives the results of detailed kinetic modelling work on the staged combustion of a gas that contains HCN. According to model calculations, the formation of laughing gas increases also by an increased air factor.

It has been observed that laughing gas is also formed when hydrogen cyanide is oxidized catalytically on CaO and char surfaces, but the N₂O conversion has been distinctly less than with homogeneous oxidation. As compared to oxidation of hydrogen cyanide, homogeneous or heterogeneous oxidation of ammonia forms hardly any laughing gas.

Oxidation of char residue, and reduction of NO with char

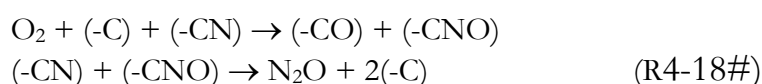
During combustion of coal, part of the char residue forms laughing gas at fluidized bed combustion temperatures. The N₂O that is generated from char nitrogen varies, depending on fuel type and pyrolysis conditions,

between 1 and 20 %. The formation mechanism of laughing gas from char nitrogen is not yet fully clarified, but, *e.g.*, the following mechanism has been proposed:



where $(-\text{Y})$ in the formulae refers to molecule Y bound to char. In this mechanism, oxygen oxidizes the nitrogen bound in char $(-\text{CN})$ producing a suitable intermediate product such as $(-\text{CNO})$. This intermediate $(-\text{CNO})$ may be decomposed further to nitric oxide or react together with the nitric oxide to laughing gas.

Alternative reaction mechanisms for formation of laughing gas from char nitrogen have been proposed also:



The first step of both above reaction mechanisms is the same. The intermediate product $(-\text{CNO})$ reacts to laughing gas either with another nitrogen atom on the char surface $(-\text{CN})$ (R4-18#) or with nitric oxide NO (R4-21#). Since the probability of two adjacent nitrogen atoms occurring on the char surface is very small, the significance of (R4-18#) is assumed to be less than that of (R4-21#).

The NO reacting in the last phase of mechanism (R4-21#) may, aside from resulting from oxidation of char nitrogen, originate from other sources, whereby it may later diffuse into the char pores.

4.11.2 N₂O decomposition mechanisms

Homogeneous decomposition

Laughing gas may be decomposed both homogeneously and heterogeneously. Under fluidized bed combustion conditions the main homogeneous N₂O decomposition mechanism is usually a reaction with a hydrogen atom.



The reaction rate constant and the concentration of H atoms increase strongly with rising temperature and the decomposition of laughing gas is markedly accelerated at high temperatures. As the laughing gas in a burner

flame enters hot zones of the flame, any or all of the N_2O formed at lower temperatures is decomposed according to the reaction above. Also at fluidized bed combustion temperatures, the concentration of H atoms during oxidation is high enough to allow decomposition of a considerable part of the laughing gas.

If the concentration of H atoms is low and the temperature over, say, 900°C , laughing gas decomposes also thermally:



where M represents any third (gas) component.

Heterogeneous decomposition

The main heterogeneous N_2O decomposition mechanisms are those with char and calcium oxide:



The N_2O decomposing efficiency of char and calcium oxide varies somewhat depending on the types of fuel and calcium.

4.11.3 N_2O emission at fluidized bed combustion

The main factors affecting the emission of laughing gas from fluidized bed combustion are the type of fuel, the temperature, and the air factor. The N_2O emission increases when the temperature drops and the air factor increases. The N_2O emission is higher for geologically older fuels (*e.g.*, coal) than for younger fuels (*e.g.*, peat and wood). A typical N_2O emission for coal ranges between 50 and 150 ppmv. For peat at circulating fluidized bed combustion, the typical N_2O emission is less than 30 ppmv, and for wood, less than 10 ppmv. The N_2O emission from bubbling fluidized bed combustion is usually somewhat lower than in circulating fluidized bed combustion.

It has frequently been observed that also the age of different coals or peats affects the N_2O emission: the older the fuel, the higher is the N_2O emission. The correlation is, however, not so clear as between coal, peat, and wood, since the fuel nitrogen content begins to have an increasing effect on the

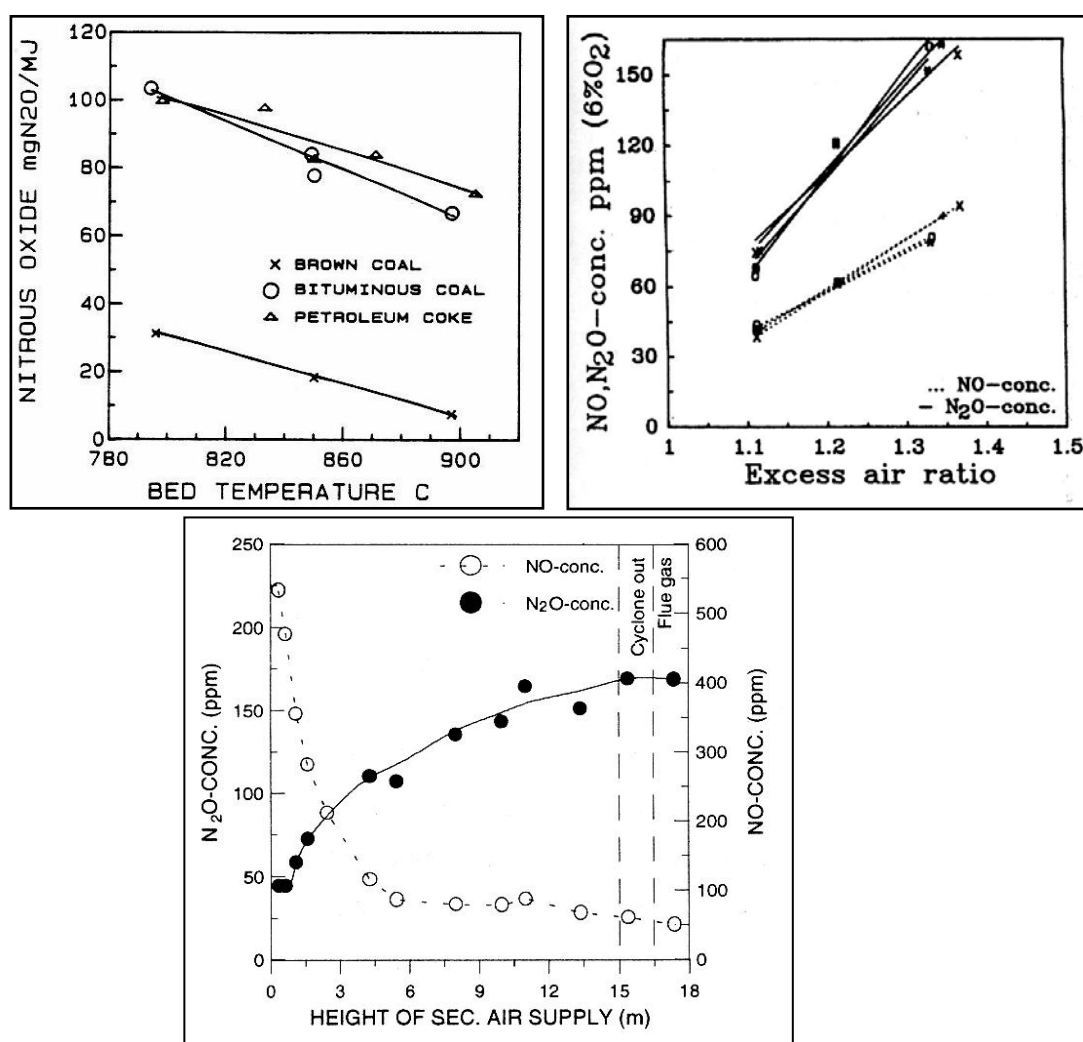


Figure 4.40 *Top left* : Effect of temperature on N₂O emission, for different fuels in an 8 MW CFB boiler. Excess air ratio 1.2, bed material sand (picture from Åmand and Andersson, 1989). *Top right* : Effect of excess air ratio on N₂O and NO emission in a 12 MW CFBC boiler firing bituminous coal. The excess air ratio was varied in different ways by means of adjusting the total air supply or fuel feed. Bed material sand (picture from Åmand and Leckner, 1992) *Bottom* : Typical measured N₂O and NO concentration profiles in a 12 MW CFB boiler firing bituminous coal. Bed temperature 850 °C, air factor 1.2, primary stoichiometry 0.75, bed material sand. (picture from Åmand *et al.*, 1991)

N₂O emission. Figure 4.40 demonstrates the effects of fuel type, temperature, and air factor on the N₂O emission and shows typical N₂O concentration profiles measured at a full scale circulating fluidized bed combustion plant.

Several methods have been proposed for reducing the N₂O emission during fluidized bed combustion. One is based on optimizing the combustion parameters to minimize the formation of laughing gas. This is possible, *e.g.*, by means of raising the temperature. A problem, however, arises as the various emissions from fluidized bed combustion are largely dependent on

each other. Reducing one emission often increases another. For example, when the temperature is raised, the N_2O emission decreases but the emissions of NO and SO_2 increase.

Another method proposed was to operate the boiler under conditions which minimize the NO and SO_2 emissions at the cost of the N_2O emission. To decrease the laughing gas, a secondary fuel, *e.g.*, natural gas, may be supplied to the cyclone. The burning gas would raise the cyclone temperature and, *e.g.*, the H-atom concentration, and part of the laughing gas decomposes through homogeneous reactions. Studies regarding catalytic decomposition of laughing gas in a separate reactor with, *e.g.*, limestone have also been made.

4.11.4 NO formation mechanisms

Homogeneous reaction of ammonia (R4-11#), or heterogeneous oxidation with calcium oxide (R4-12#), and oxidation of char nitrogen (R4-17#) have been suggested to be the most important formation mechanisms of nitric oxide.

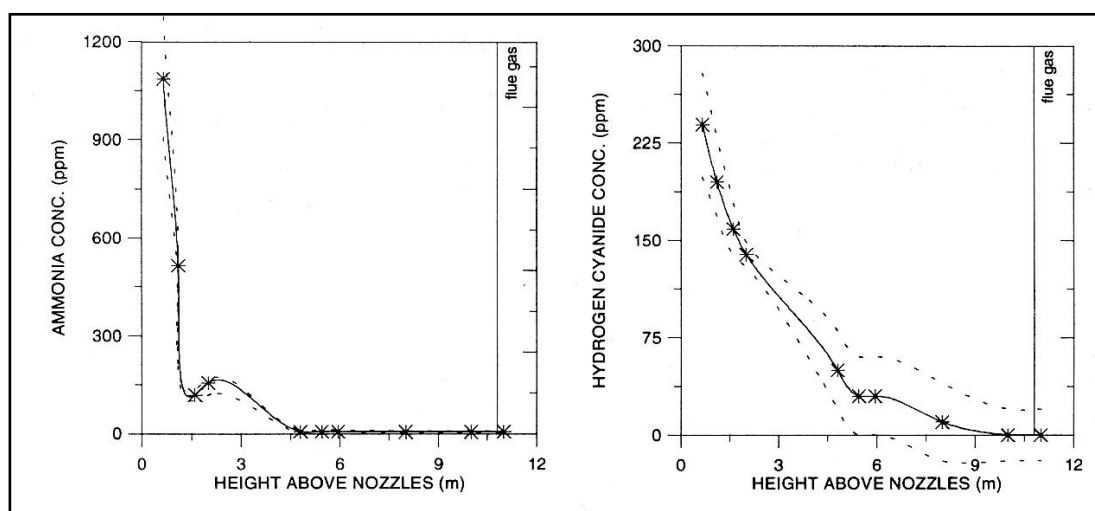
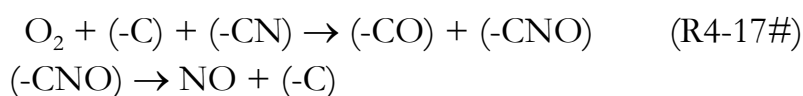
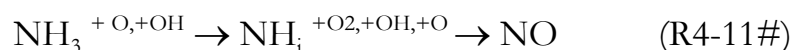


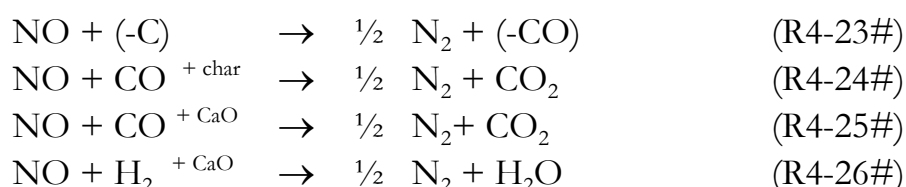
Figure 4.41 Typical measurement data for NH_3 and HCN concentration profiles in a 12 MW CFBC boiler firing bituminous coal. Bed temperature 850°C , air factor 1.2-1.25, primary air factor 0.7-0.75 (picture from Åmand and Leckner 1994)

The ammonia originates from the volatile fuel nitrogen. During fluidized bed combustion, generally, the NH_3 concentration is considerably higher than the concentration of HCN (Figure 4.41).

At this moment, however, it is not clear how the ammonia is formed, since the number of amino groups forming ammonia during pyrolysis/devolatilisation is not enough to explain all ammonia measured. One suggestion is that part of the hydrogen cyanide previously formed reacts to ammonia in the presence of suitable gas components. For example, calcium oxide has been observed to catalyze the HCN conversion to NH_3 in the presence of hydrogen and oxygen (R4-10#). Also, ammonia was observed to form when nitric oxide is reduced with hydrogen on CaO surfaces. Further research is necessary to fully clarify the formation of ammonia.

4.11.5 NO decomposition mechanisms

Heterogeneous reactions govern nitric oxide decomposition at fluidized bed combustion. The main reactions involve reduction of NO with char, which may take place noncatalytically (R4-23#), or catalytically if suitable reducing gases are present (R4-24#). Calcium oxide, too, catalyzes decomposition of nitrous oxide when reducing gases are present (R4-25# and R4-26#):



Experiments by Zevenhoven and Hupa (1998) on chars from coal, peat and wood showed that reaction (R4-24#) is generally an order of magnitude faster than (R4-23#) when the CO concentration is much larger than the NO concentration. Peat char was found to be more catalytically active than char from coal or wood.

4.11.6 NO emission at fluidized bed combustion

The main factors affecting nitrous oxide emissions from fluidized bed combustion are fuel type, temperature, and air factor. The NO emissions increase when the temperature or the air factor increases. The dependence of nitric oxide on fuel type is more complicated than that of N_2O emission, and there is no clear correlation between NO emission and fuel age. Moreover, the NO emission from bubbling fluidized bed combustion may be very different from corresponding emissions at circulating fluidized bed combustion.

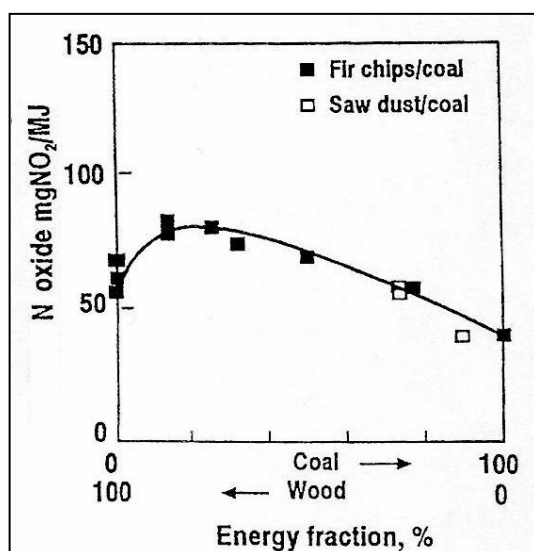


Figure 4.42 NO emission at firing spruce chips and/or coal in a 12 MW CFB boiler. Bed temperature 850 °C, air factor 1.25, bed material sand (picture from Leckner, 1992)

The NO emission is strongly dependent on the fuel nitrogen content of young fuels such as wood: the NO emission increases with increased fuel nitrogen content. Corresponding distinctive NO emission dependence of fuel nitrogen content of older fuels such as coal is not always found. Furthermore, it has been observed that, during circulating fluidized bed combustion, the NO emission of coal may even be less than that of wood although the nitrogen content of coal is markedly higher than the nitrogen content of wood (Figure 4.42). This is probably due to the larger amount of char in the boiler during coal combustion, whereby the nitric oxide may be reduced with char.

The typical NO emission for coal during circulating fluidized bed combustion when combustion-specific abatement techniques such as air staging has been applied ranges between some 100 and 200 ppmv. During bubbling fluidized bed combustion, the NO emission for coal is somewhat higher, about 150 to 300 ppmv. Also the SNCR method may be used to decrease the NO emission during fluidized bed combustion, this method has

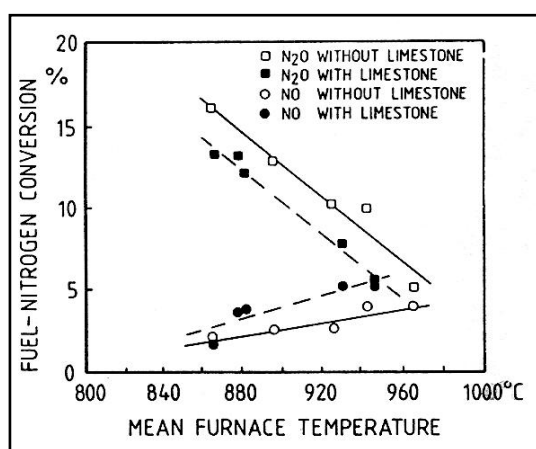


Figure 4.43 Effect of adding limestone on emissions of N₂O and NO in a 0.8 MW CFB boiler. Petchora coal, Ca/S = 1.5, Gotland limestone. (picture from Hiltunen *et al.*, 1991)

resulted in decreasing the NO emissions down to below 50 ppmv for fluidized bed combustion of coal.

Also the addition of limestone to the boiler furnace has a substantial effect on the emissions of both NO and N₂O. At circulating fluidized bed combustion, adding limestone increases the NO emission and decreases the N₂O emission (Figure 4.43). It has been suggested that the increase of NO emission is caused by ammonia catalyzed by calcium oxide, which is oxidized to nitric

oxide (R4-12#), whereas the decrease of N_2O emission is a result of decomposition of laughing gas catalyzed by calcium oxide (R4-31#).

At this moment, knowledge on the effects of limestone addition on the NO and N_2O emissions is not conclusive, because alternative explanations have also been given, as for instance:

- When limestone is added the oxidizing reaction of hydrogen cyanide shifts from homogeneous (R4-1#, R4-4#, R4-7#) to heterogeneous (R4-2#, R4-5#, R4-8#). Heterogeneous oxidation of HCN catalyzed by calcium oxide produces, according to laboratory experiments, substantially more nitric oxide and less laughing gas than corresponding homogeneous oxidation of HCN at fluidized bed combustion temperatures.

- When limestone is added the concentrations of sulfur dioxide and carbon monoxide decrease. According to laboratory experiments the decrease of SO_2 increases the NO conversion of the nitrogen compounds in the fuel to some extent and decreases the N_2O conversion. The decrease of the CO concentration, too, increases the NO emission, since the reduction of nitric oxide becomes less intense.

4.11.7 NO_x and N_2O from FBC - overview

A summary on the effect of various combustion parameters on the NO and N_2O emissions at fluidized bed combustion is made in Table 4.9. The effect of pressure is still to be discussed below.

Table 4.9 *Effect of process parameters on N_2O and NO emissions from bubbling and circulating FBC (Kilpinen, 1995)*

Increasing parameter	N_2O emissions	NO emissions
Temperature	↓	↑
Fuel volatile nitrogen content	↓ (BFB), ↓ (CFB)	↓ (BFB), ↑ (CFB)
Fuel nitrogen content	↑	↑
Excess air	↑	↑
Air staging	↓	↓
Limestone addition	↓, -	↓ (BFB), ↑ (CFB)
SO_2 level	↑	↓
SNCR – NH_3	↑, -	↓
SNCR – urea	↑	↓
SCR	-	↓
Pressure	↑, ↓	↓ (but NO_2 ↑)

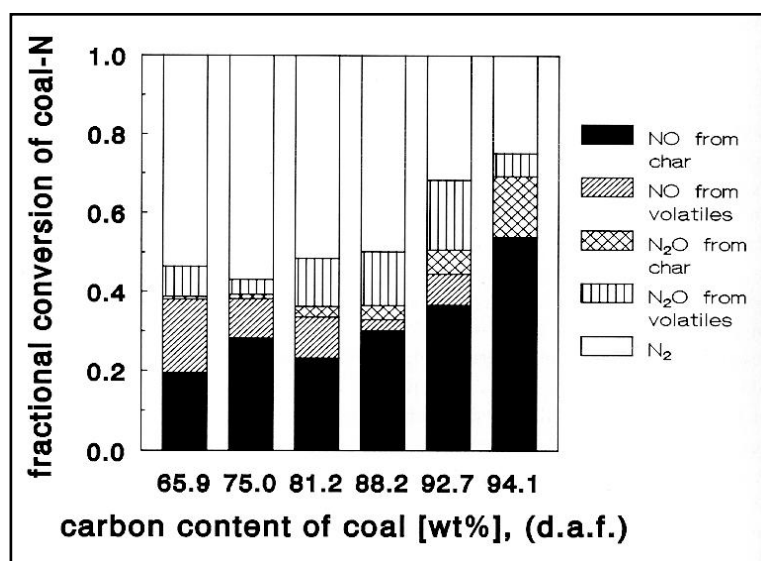


Figure 4.44 Fractional conversion of fuel-nitrogen into NO and N₂O and N₂, via volatile-N and char-N for coals with increasing carbon content. Laboratory scale FBC, 850°C, ~ 6% oxygen. (picture from Pels, 1995)

The influence of coal rank on the fate of fuel-N is shown in Figure 4.44 for coals with increasing carbon content (Pels, 1995). Both NO and N₂O from char increase with coal carbon content, the N₂O from volatiles increases but then decreases, whilst NO from volatiles decreases with coal rank. The sum of N₂O + NO increases continuously with carbon content.

For a 72 MW_{elec} CFBC furnace (Pforzheim, Germany) the influence of bed temperature and excess air on NO_x and N₂O emissions were reported by Boemer *et al.* in 1993. Some results are given in Figure 4.45, all in accordance with Table 4.9. It is noted that N₂O emissions are of the same level as or higher than the NO_x emissions.

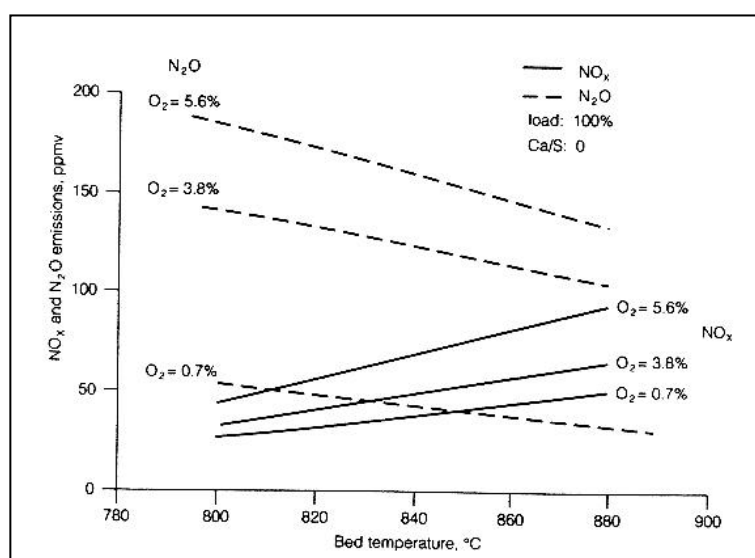


Figure 4.45 NO_x and N₂O emissions from a full scale CFBC firing hard coal (Boemer *et al.*, 1993, picture from Takeshita, 1994).

A comparison between the char residues from various types of solid fuels ranging from lignite to anthracite was reported by Johnsson, considering NO and N₂O emissions *versus* FBC temperature. Results are given in Figure 4.46, which agree with what is given above in Table 4.9 and Figure 4.44.

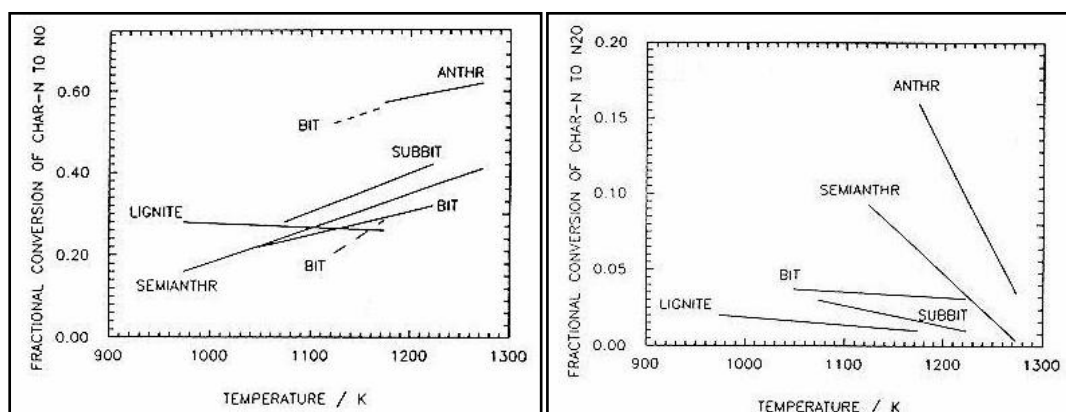


Figure 4.46 Conversion of char-N to NO (*left*) and N₂O (*right*) versus temperature for FBC, fuels ranging from lignite to anthracite. (pictures from Johnsson, 1994)

A comparison between NO emissions from pulverised coal (PC) and FBC firing, with additional low NO_x technologies is given in Table 4.10. This clearly shows the superiority of FBC considering NO emissions, which often do not need any further control measures.

Table 4.10 *NO emissions : pulverised coal versus coal – fired FBC (taken from Takeshita, 1994)*

Method	PC-fired plant	FBC
(1) Standard	550–800	100–150
(2) Low excess air	450–650	70–120
(3) (2) + Air staging	300–500	50–80
(4) (2) + Flue gas recirculation	350–550	–
(5) (3) + Flue gas recirculation	200–400	–
(6) (5) + Low NO _x burner	150–300	–
(7) (6) + SNCR or SCR	10–50	10–50

For N₂O emissions typical values would be 0.5 – 2 ppmv for PC firing, 50 – 150 ppmv for atmospheric FBC, and probably of the order of 20 ppmv for pressurised FBC. Similar to the situation with pulverised coal combustion the char-N appears to be responsible for a significant, if not the major part of the NO_x emissions. Moreover, due to the temperature of firing in FBC there is a potential of N₂O emissions of the same level as the NO_x emissions.

Finalising this discussion on atmospheric FBC Table 4.11 gives a comparison of two approaches for simultaneous abatement of NO_x, SO_x and N₂O. Method “A” is based on “high” temperature combustion followed by NO_x control downstream (Leckner), method “B” is based on “low” temperature combustion and N₂O control (Wójtowicz).

Table 4.11 Comparison of two methods for combined NO_x/SO_x/N₂O abatement for FBC (from Pels, 1995)

(A) low N₂O, high NO_x combined with NO_x control	
○ high temperature (~ 1173 K)	low N ₂ O, high NO _x (most of fuel-N converted into NO _x)
○ limestone addition (Ca/S ~ 3)	low SO _x , low N ₂ O, high NO _x
○ low excess air (~ 1.2 may be possible due to improved process control)	low N ₂ O, low NO _x (approach (2) used)
○ gas afterburning in the cyclone	low N ₂ O
○ ammonia injection (SNCR)	NO _x control (ammonia slip? increased N ₂ O?)
(B) low NO_x, high N₂O combined with N₂O control	
○ low temperature (~ 1073 K)	low NO _x , high N ₂ O (most of fuel-N converted into N ₂ O)
○ two-stage operation (O ₂ -lean, then O ₂ -rich)	low NO _x
○ limestone addition only in the O ₂ -rich section	low SO _x , low NO _x (no catalytic enhancement of NH ₃ oxidation during devolatilisation, no catalytic conversion of HCN into NH ₃ , HCN reacts to form N ₂ O rather than NO _x , high SO _x in O ₂ -lean section); high N ₂ O in O ₂ -lean section, lower N ₂ O in O ₂ -rich section
○ catalytic N ₂ O decomposition	N ₂ O control
○ afterburning	N ₂ O control

Method “A” mentioned in Table 4.11 has been developed further at Chalmers University of Technology (Sweden) and is nowadays referred to as “reversed air staging” for FBC (Lyngfelt *et al.*, 1995, 1998). The approach is to do the opposite of what is done with air staging: with reversed air staging the oxygen levels are high in the bottom part of the FBC, adding some additional air after the cyclone. As the result, N₂O emissions are significantly reduced, whilst the emissions of NO, SO₂ and CO remain low.

4.12 Reaction of nitrogen oxides at pressurised combustion

Pressurized combustion processes in heat and power generation are likely to gain importance. These processes comprise combustion or gasification stages at elevated pressure (typically 10~20 bar) and gas or steam turbines. In production of electricity, the efficiency of the processes is calculated to be 45 % or even more, *i.e.*, ~ 10 % units higher than conventional condensing power plant techniques. (More details: **L** Chapter 2).

Little information concerning the effect of pressure on the formation of

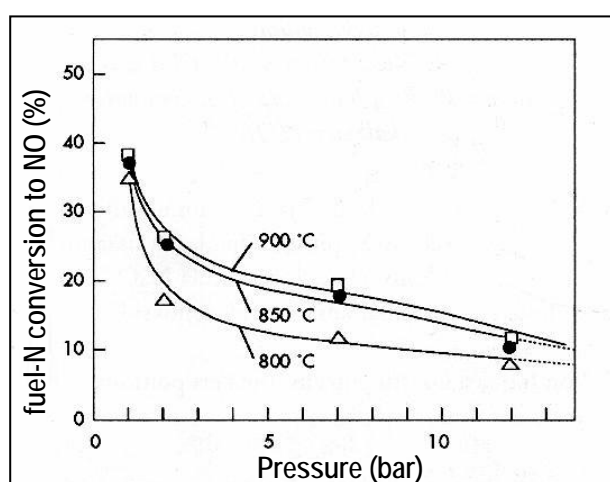


Figure 4.47 Effect of pressure on coal nitrogen NO conversion at different temperatures. Experiments made in laboratory flow reactor. Residence time 1 s, O₂ concentration 19 to 20 % by volume. (results from Aho *et al.*, 1994)

nitrogen oxides and the function of the NO abatement techniques exists at this time. According to the information available it seems that pressure decreases the formation of nitric oxide, *e.g.*, under fluidized bed combustion conditions (Figure 4.47). Less is known of the effect of pressure on laughing gas, but, as a general rule, pressure has not affected N₂O emission significantly, or the N₂O emission has slightly decreased. Pressure has increased the formation of nitrogen dioxide somewhat (Kilpinen *et al.*, 1999).

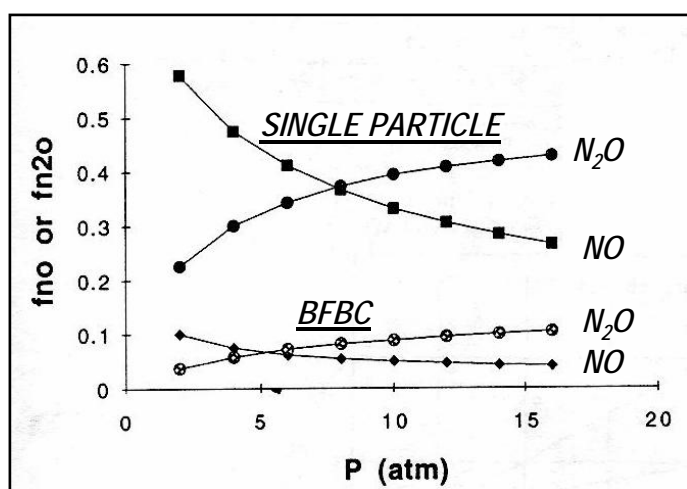


Figure 4.48 Fractional conversion of fuel-N to NO and N₂O as function of pressure: modelling work by Goel (picture from Sarofim *et al.*, 1994)

Similar results for NO were calculated by Goel when modelling single char particle combustion as well as a bubbling FBC furnace: see Figure 4.48. The same work suggests also that N₂O emissions would be increasing with pressure, which has not been supported by hard evidence yet.

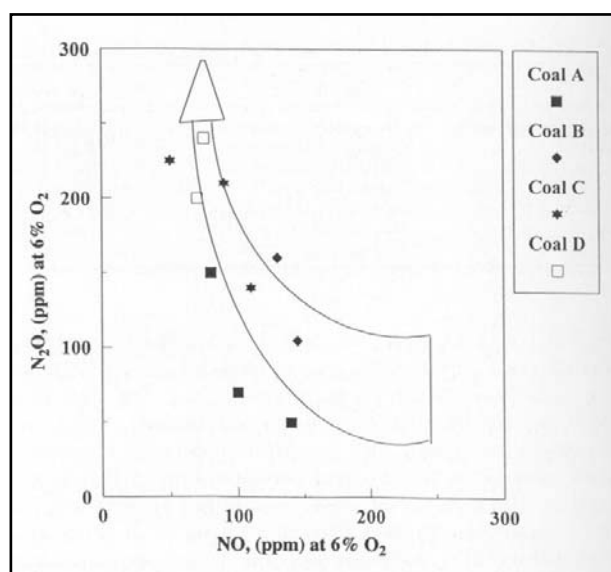


Figure 4.49 The trade-off between NO and N₂O of PFBC combustion of coal (reported by Moritomi, 1994; picture from Grace *et al.*, 1997)

Moritomi measured the NO and N₂O from PFBC for a series of coals, with fuel-nitrogen content varying between 1.1 and 1.8 %-wt. The results are shown in Figure 4.49: increasing NO emissions results in decreasing N₂O emissions, and *vice versa*.

Verification and explanation of the effect of pressure requires further research. However, based on the research results available, it may be concluded that pressure does not *per se* increase NO_x or N₂O emissions at fluidized bed combustion. Thus both emissions, looking at the quantity of electricity

produced, are considerably less in pressurized fluidized bed combustion processes.

4.13 Reactions of nitrogen compounds in gasification processes

4.13.1 Formation of nitrogen species during gasification

In gasification, a solid or liquid fuel is converted into combustible gases and ash by partial oxidation (air factor $\lambda \sim 0.3..0.4$). One of the challenges met at developing the (pressurized) gasification technique called the IGCC process (Integrated Gasification Combined Cycle, + Chapter 2) relates to the high concentration of nitrogen compounds in the gasification gases. Typical data on NH₃ and HCN in gasifier product gases is given in Table 4.12 (Alderliesten, 1990; Leppälähti *et al.* 1991, 1995).

Table 4.12 NH₃ and HCN concentrations in gasifier product gases

Gasifier facility	Fuel	NH ₃ (ppmv)	HCN (ppmv)
Texaco-type entrained bed	Coal	~ 800	~40
Shell-type entrained bed	Coal	~ 300	~150
VTT air blown FB	Coal	~2000	~ 50
“	Peat	~3000	~100
“	Wood	~ 600	~ 20

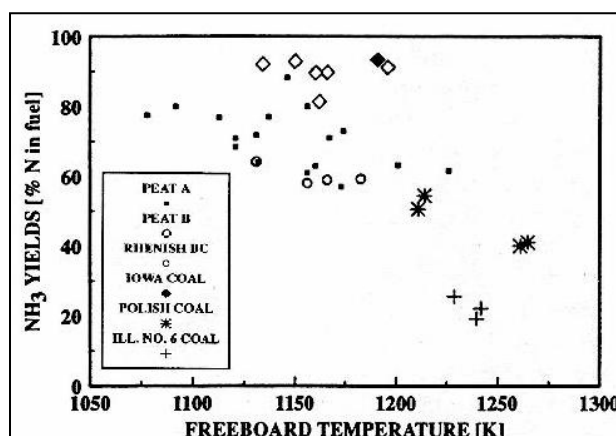


Figure 4.50 NH_3 conversion of fuel nitrogen from pressurized gasification in air. Pressure 4 ~ 9 bar (picture from Leppälähti and Koljonen, 1991)

In fluidized bed gasification, especially the concentration of ammonia in the gas is high, between 1000 and 10000 ppmv; smaller amounts of hydrogen cyanide and nitrogenous organic compounds or tars occur as well.

The ammonia in gasification gas originates from fuel nitrogen. Its formation mechanisms, however, are not fully explained (+ section 4.11 on fluidized bed combustion). The NH_3 conversion during FB gasification varies between 20 and 50 % for coal and as high as 70 to 90 % for peat and wood (Figure 4.50).

4.13.2 Nitrogen compounds in combustion of gasifier product gas

During combustion of gasification gas, ammonia reacts easily to nitric oxide and causes a high NO emission if no abatement techniques are applied. Figure 4.51 shows factors affecting oxidation of ammonia in the "low NO_x " burner of a gas turbine under development. Although the conversion of ammonia to nitric oxide increases when the NH_3 concentration decreases, the NO emission itself decreases at the same time. From the viewpoint of minimizing the NO emission, minimizing the NH_3 concentration of the gasification gas is always desirable. Figure 4.51 shows also that the NO emission

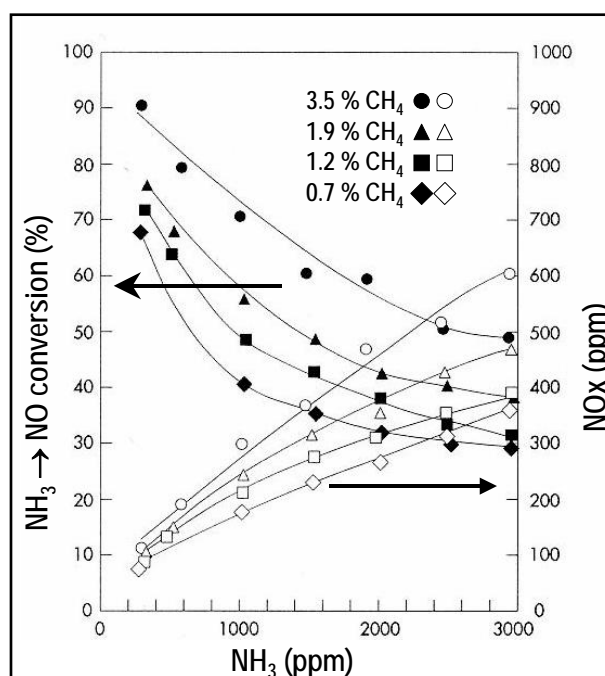


Figure 4.51 Effects of concentrations of ammonia and methane on ammonia NO conversion and NO emission at combustion of gasification gas. Data given holds at atmospheric pressure for the low NO_x burner of a gas turbine under development. Total air factor 2.0. (picture from Nakata *et al.*, 1994)

increases if methane is present in the gasification gas.

Little data is available today on the effect of pressure on the NO emission during combustion of gasification gas. According to preliminary results, the formation of nitric oxide is somewhat decreased by pressure (Coda Zabetta *et al.*, 2000).

Often combustion-specific NO abatement methods alone are not enough for sufficient reduction of the NO emission from gasification processes. An interesting auxiliary method for controlling the NO emission from gasification processes would be to decompose the ammonia in the gasification gas to molecular nitrogen before combustion in a gas turbine. The quantity of gas to be handled is considerably smaller before combustion than after it. Several methods are being developed, based on catalytic or noncatalytic decomposition, with or without suitable additives – as will be discussed below.

4.14 Removal of nitrogen compounds from gasifier product gas

The removal of NH_3 and HCN from gasifier product gas is dictated by the application of this gas. Further chemical processing may involve sensitive catalysts, or “combustion” in a fuel cell (+Chapter 2). Combustion of the gas in a gas turbine or engine may result in oxidation to nitrogen oxides. Four options are available for dealing with gasifier product-gas nitrogen compounds:

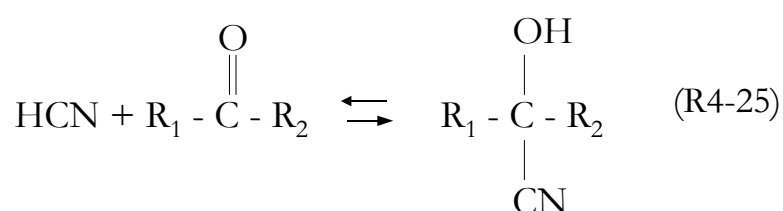
1. Removal at low temperatures, using an acidic ($\text{pH} < 7$) water wash or a selective sorbent.
2. High temperature (and high pressure, HTHP) removal, before the inlet of the gas turbine where the gas is burnt
3. Adjustments to the combustion chamber of the gas turbine, optimise the combustion process
4. Let the nitrogen species be oxidised to NO_x in the combustor and apply SCR or SNCR to the exit gas

For chemical industries option 1 is often chosen, in gas turbine combustion option 4 is generally selected since option 2 and 3 have not yet matured and more importantly, because SCR or SNCR will also remove the thermal NO_x formed during fuel gas combustion.

4.14.1 Low temperature processes for NH₃ and HCN removal from fuel gas

At low temperatures (≈ 300 °C) NH₃ and HCN can be removed from a gas stream by a gas/liquid absorption process. In general this is accomplished simultaneously with removal of H₂S and CO₂. Three major routes were studied by Boon (1995) for removal of NH₃ and/or HCN:

1. NH₃ and HCN are both very well soluble in water, making it a good solvent, allowing for reversible processing
2. Ketones (organic groups R₁ and R₂) and aldehydes (R₁ or R₂ = H) can reversibly absorb HCN:



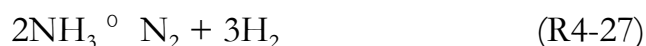
3. Polysulphides such as Na₂S_x can absorb HCN via formation of thiocyanates, a fast reaction which is irreversible:



4.14.2 High temperature processes for NH₃ and HCN removal from fuel gas

For the removal of nitrogen species from gasifier product gas or other fuel gases at high temperatures ($> 300^\circ\text{C}$), mainly aiming at gas turbine combustion, several approaches are receiving much R&D attention nowadays. The three most important, focussing mainly on NH₃, are:

1. Catalytic decomposition of NH₃ to N₂, at 550 – 900 °C, via the global reaction



a) This involves a catalytic process, using nickel as the active component, with magnesium or iridium, on an alumina support: Ni/Mg/Al₂O₃ or Ni/Ir/Al₂O₃ (Alderliesten *et al.*, 1990). Qader *et al.* (1996) report NH₃ decomposition of the order of 80-90% at approx. 650 - 850°C using an aluminum silicate catalytic material (RA-330). One problematic aspect is the thermodynamics of the process: at $\sim 800^\circ\text{C}$ for a typical gasifier gas the equilibrium concentration of NH₃ is ~ 200 ppmv. (Norman *et al.*, 1995).

Some other decomposition studies consider the use of the zinc titanate catalyst for H_2S removal (+ Chapter 3) as a basis for catalytic NH_3 decomposition (Jothimurugesan and Gangwal, 1996), or methanol injection (Qader *et al.*, 1996).

b) Inexpensive materials for nitrogen compounds conversion in gasification gas were analysed by Leppälahti *et al.* (1991). At the temperature that is considered, 900°C , these materials could be used *in situ* in a fluidised bed gasifier. Some results of that work are shown in Figure 4.52 for NH_3 and HCN , respectively. It appears that some Ni-based catalysts remove NH_3 without any effect on HCN , though.

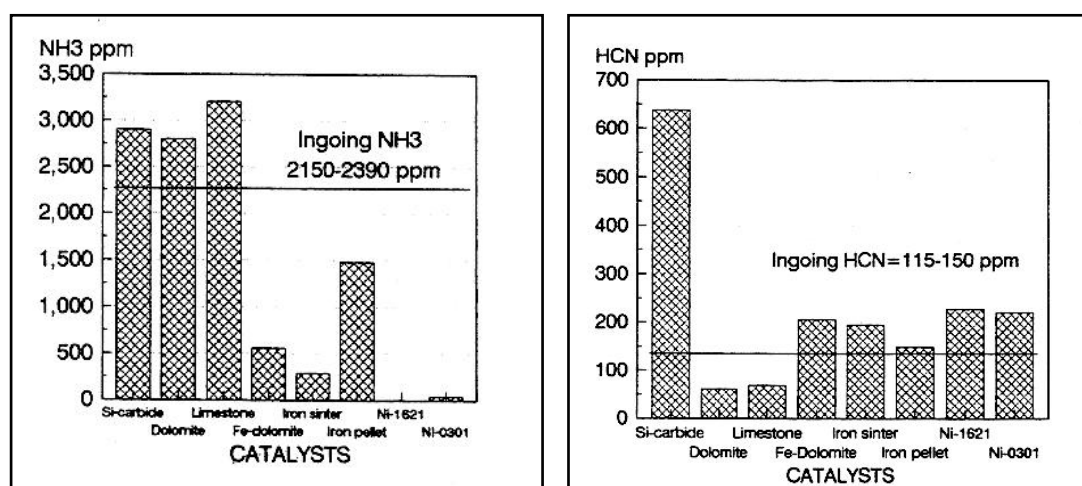


Figure 4.52 Effectivity of catalysts for *in situ* NH_3 and HCN conversion in fluidised bed gasification (of peat and biomass) (pictures from Leppälahti *et al.*, 1991)

2. Selective catalytic oxidation (SCO) at $300 - 550^\circ\text{C}$. This process uses a molybdenum (Mo) based catalyst on silica/alumina. (Alderliesten *et al.*, 1990, Gangwal *et al.*, 1996). This requires the presence of $2 \sim 2.5$ % vol oxygen in the gas, *i.e.* stoichiometries slightly above $\lambda = 1$. This results in some oxidation of CO and H_2 in the gasifier product gas. Qader *et al.* (1996) report conversions of $80 - 95\%$ at approx. $450 - 550^\circ\text{C}$. Leppälahti *et al.* (1997) showed that aluminum oxides and aluminum silicates allow for NH_3 reductions of $50 - 60\%$ from (synthetic) gasifier gas at $\sim 2\%$ O_2 in the temperature window $600-700^\circ\text{C}$.
3. Adsorption/desorption on zeolites (highly porous aluminum silicates also known as molecular sieves). Drawbacks are the low efficiency ($\sim 1\%$) and the sensitivity to water. (Alderliesten *et al.*, 1990).

4.15 Nitrogen oxides formation and reduction in gas turbines



Figure 4.53 Combustion chamber of a Pratt & Whitney's FT-4 gas turbine (picture from Phillips and Roby, 2000)

A gas turbine is a rotary combustion engine that is composed of a compressor, a combustion chamber and an expansion turbine (+ Chapter 2). A combustible gas (usually natural gas or the product gas from a solid fuel gasifier) is injected into the combustion chamber, which results in a pressurised flue gas at temperatures of the order 1200 – 1500°C. Figure 4.53 shows the combustion chamber of a

turbine: visible are six burner inlets. Clearly under these conditions, despite the short residence time of typically 0.002 s NO_x formation from N₂ can be expected, plus oxidation of fuel-N derived nitrogen compounds if these have not been removed or converted to N₂.

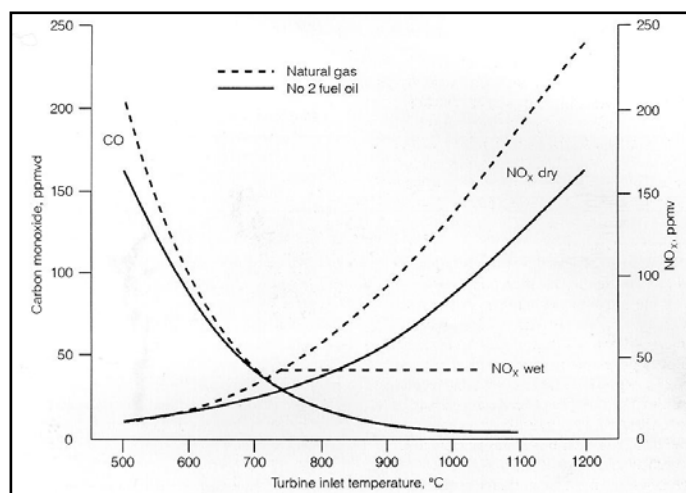


Figure 4.54 CO and NO_x versus firing temperature for a conventional gas turbine (picture from Maude and Kirchner, 1995)

Figure 4.54 gives the CO and NO_x emissions from a conventional gas turbine firing natural gas or light fuel oil *versus* the firing temperature (= expansion turbine inlet temperature). A distinction is made for “dry” operation or “wet”, *i.e.* using water injection for NO_x control. A big drawback of steam and water injection is that the reduced flame temperature results in higher CO emissions. For example,

for the gas turbine shown in Figure 4.53, 75 ppm NO with 100 ppm CO shifts to 25 ppm NO with 250 ppm CO emissions with water injection (Phillips and Roby, 2000).

Several methods are available to control the NO_x formation in a gas turbine. Two methods are referred to in Figure 4.55 which shows the temperature

profile inside the combustion chamber without special measures, with diluent injection or lean burn, or with use of a catalyst.

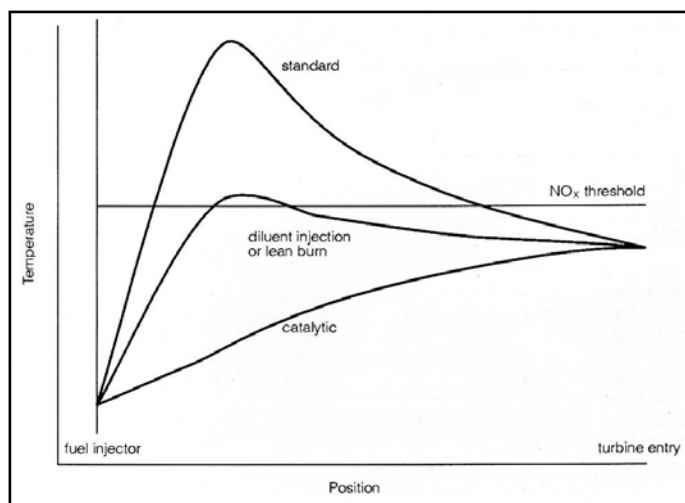


Figure 4.55 Gas turbine combustion chamber temperature/ distance profiles (picture from Maude and Kirchner, 1995)

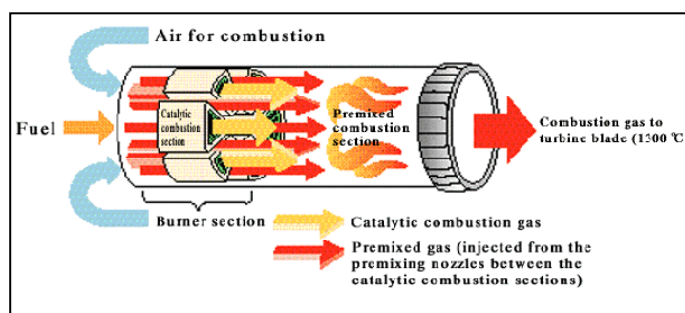


Figure 4.56 Reduced NO_x emissions from a gas turbine by catalytic combustion (picture from CRIEPI 1996a)

As diluent, water or steam, or nitrogen is applied. Catalytic combustion is being optimised at CRIEPI in Japan. For a 1300°C class gas turbine a catalytic combustion section is used that keeps the temperature below 1000°C, followed by lean premixed combustion at 1300°C. The result is NO_x emission below 10 ppm @ 16% O₂, at combustion efficiency near 100% (CRIEPI 1996a). An illustration is given by Figure 4.56.

In a second project at CRIEPI a two-stage combustion chamber was optimised for a class 1500°C turbine for IGCC application. NO_x emissions are ~ 60 ppm @ 16% O₂, with less than 20 ppm CO. This technology

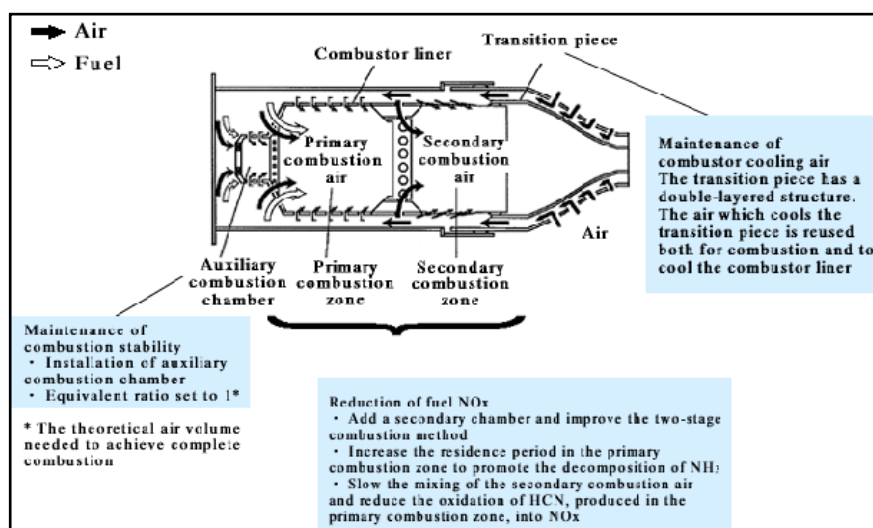


Figure 4.67 Reduced NO_x emissions from a gas turbine by two-stage combustion (picture from CRIEPI, 1996b)

is illustrated by Figure 4.57.

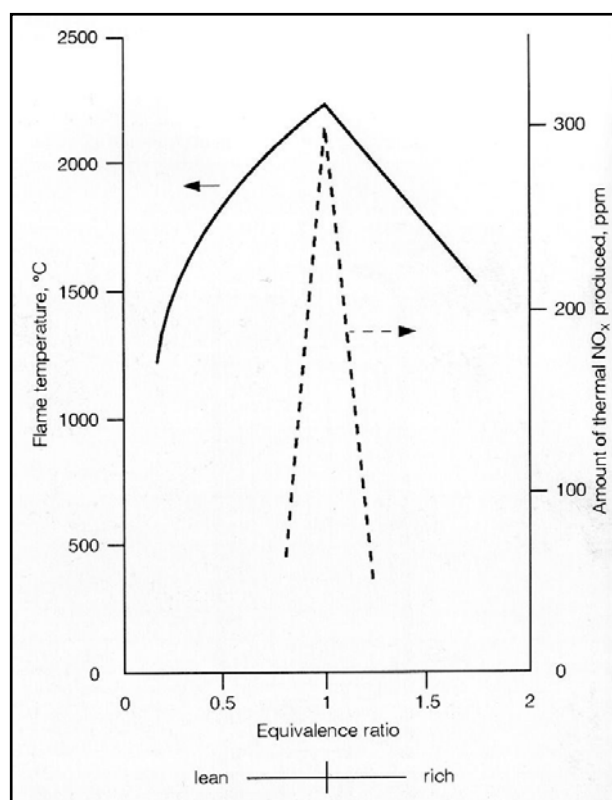


Figure 4.58 Combustion temperature and NO_x formation versus equivalence ratio (= 1/air factor) (picture from Maude and Kirchner, 1995)

Optimal combustion performance of a gas turbine corresponds to air factors close to unity. This results in the maximum achievable temperature (generally too high for the expansion turbine) but the maximum thermal NO_x formation as well: see Figure 4.58. Switching to fuel-rich firing may result in smoke, whilst fuel-lean will eventually lead to unstable combustion and increased CO emissions.

As an alternative to steam or water injection, dry low NO_x (DLN) gas turbines were developed which are based on pre-mixed combustion. Fuel and air are mixed in a region where ignition does not yet occur. The presence of larger amounts of air results in lower

temperatures due to increased thermal inertia, similar to when steam or water is injected. (Maude and Kirchner, 1995). Unfortunately operation under partial load with DLN combustors can give flame stability problems with natural gas when the lower flammability limit is approached (+ Chapter 2). In response to this, gas turbine manufacturers have developed methods that add much complexity to a DLN combustor, however (Phillips and Roby, 2000).

An alternative for NO_x emissions control downstream of the turbine by SCR, for example (+ 4.9.1) seems to be pointed out by experiences with coal-fired IGCC plants. Figure 4.59 shows the NO_x emissions and adiabatic flame temperatures of a Siemens V94.2 gas turbine at the Demkolec IGCC facility at Buggenum in the Netherlands. Natural gas gives significantly higher combustion temperatures than syngas, *i.e.* a mixture of CO and H₂ diluted with water and N₂. The presence of hydrogen in the gas is extremely beneficial due to its high flame speed and wide flammability range. In practice this allows for stable flames at conditions where natural gas flames are unstable, and the burnout of CO is better.

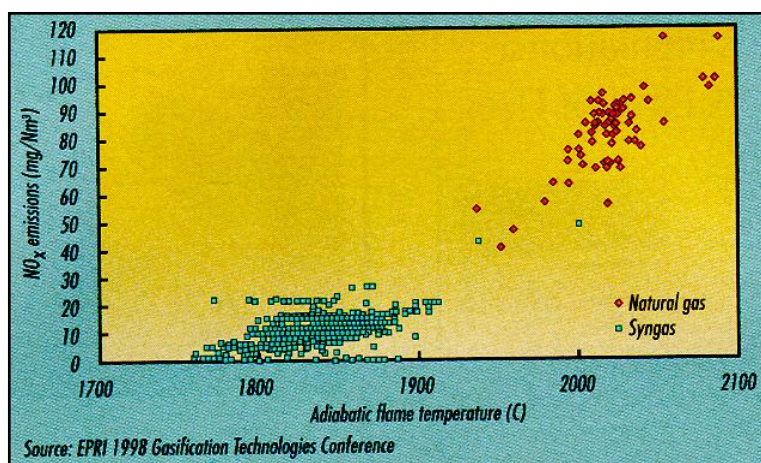


Figure 4.59 NO_x emissions from the Demkolec IGCC facility (picture from Phillips and Roby, 2000)

Therefore, adding H₂ to natural gas would be very beneficial for reducing CO emissions during “wet” firing, and can solve the stability problems during partial load operation of a DLN system (Phillips and Roby, 2000). What remains, for a natural gas fired system, is the problem

of a H₂ supply, for example by steam reforming of the natural gas. From a costs point of view, purchasing liquid hydrogen from an external supplier may be more attractive (Phillips and Roby, 2000).

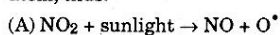
4.16 Nitrogen oxides formation and reduction in (transport vehicle) engines

Nitrogen oxides (NO+NO₂) are emitted from automobile engines at a rate of 1-2 g/km NO₂ or 20 g/kg fuel, *i.e.* 500-1000 ppm (Heywood, 1988). This explains why the transport sector is responsible for ~ 60% of the NO_x emissions in a modern society. Methods available for reducing these emissions are 1) optimisation of the combustion section and 2) gas clean-up in the exhaust pipe. These two options will be discussed below.

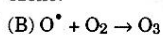
How ozone is formed

Ozone is formed as a result of various chemical processes, which are complicated and often obscure. A simplified description might be:

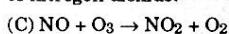
A prerequisite is the decomposition of nitrogen dioxide by sunlight, forming in the process a highly reactive oxygen atom, thus:



The freed oxygen atom can react with oxygen gas to form ozone:



If there are no volatile organic compounds in the air, the ozone reacts again with the nitrogen monoxide, reforming to nitrogen dioxide:



In this process no really high concentrations of ozone will be formed – since forming and using up take place at about the same rate.

For the formation of greater quantities of ozone, other substances have to enter the process and convert nitrogen monoxide to nitrogen dioxide – so that the ozone molecule will not be consumed, as in reaction (C), but “saved.” Fueling the process are the so-called radicals that are formed when volatile organic compounds become decomposed by sunlight.

High concentrations of ozone will thus be built up when volatile organic compounds, nitrogen dioxide, and sunlight all coincide. The nitrogen dioxide that is formed in the reaction in which volatile organic compounds are involved can become re-used many times over in accordance with reactions (A) and (B).

Figure 4.60 “How ozone is formed” – the role of NO_x in photochemical smog formation (from Ågren and Elvingsson, 1997)

A direct effect of these NO_x emissions is the formation of photochemical smog, apart from the toxicity effects of mainly NO₂. The role of NO_x in smog formation with groundlevel ozone is explained in Figure 4.60.

The development of emission limits regulations by the European Commission is given in Table 4.13 (Acid News, 1996). Emissions of the species other than NO_x will be discussed in later chapters.

Table 4.13 Emission limits for passenger cars in the EU (g/km)

	1996/1997	2000	2005
Petrol Driven			
CO	2.7	2.3	1.0
Hydrocarbons	0.341	0.20	0.10
NO _x	0.252	0.15	0.08
Diesel			
CO	1.06	0.64	0.50
Hydrocarbons	0.71	0.56	0.30
NO _x	0.63	0.50	0.25
Particulates	0.08	0.05	0.025

For ships, NO_x emissions may become the major contributor to acidification within the European Union, as discussed in Chapter 3 considering SO₂ emissions from shipping (+ section 3.15).

Air transport, finally, is relatively “clean” from a NO_x per km per passenger point of view. It must be noted, though that at an altitude of 10000 m NO_x emissions are very harmful, being closer to participating in ozone layer destruction (+ Figure 4.2).

4.16.1 Formation of nitrogen oxides in engines

The process of NO formation, in combination with that of CO and hydrocarbons (C_xH_y) inside a cylinder during an internal combustion engine cycle is presented in Figure 4.61 for a spark-ignition engine. Since fuel-N levels are practically zero in transport fuels (a situation that may change when more bio-fuels penetrate the market), the NO_x formation follows the thermal NO_x (Zeldovich) and prompt NO_x routes. In short, the NO is formed during the short high temperature period shortly after the point of maximum pressure/minimum volume (top dead centre, TDC), followed by rapid quenching of the NO_x chemistry due to the increasing volume/decreasing pressure stage as a result of the lowering of the piston.

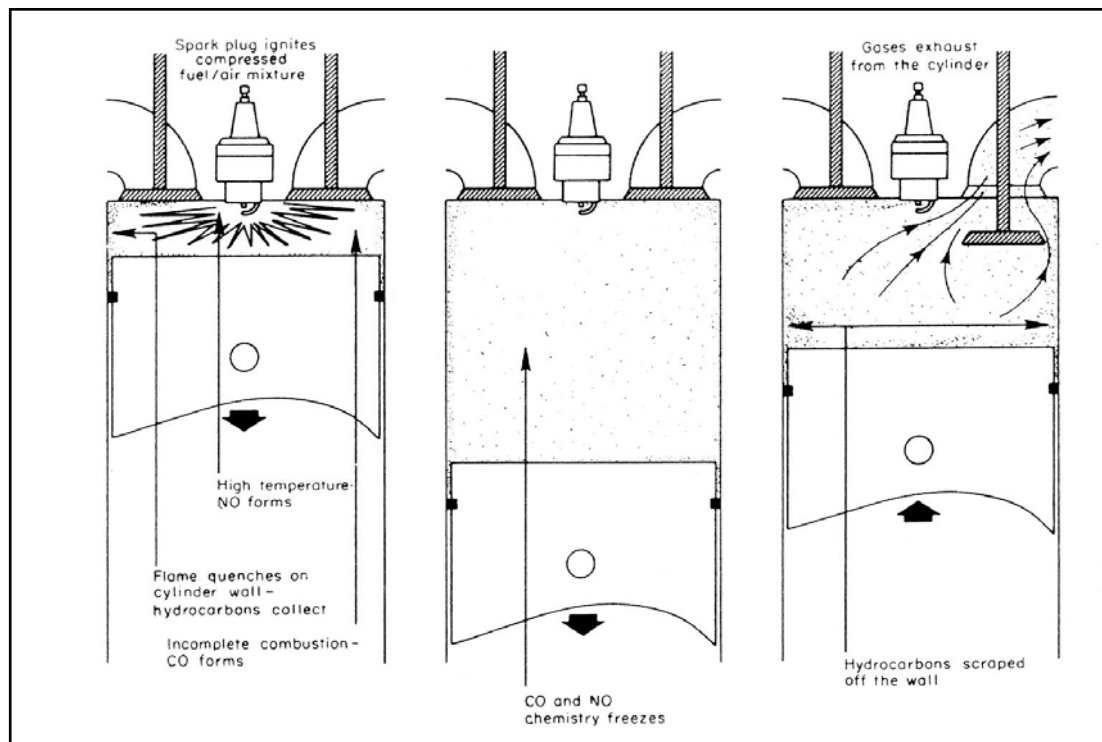


Figure 4.61 Formation of NO, CO and hydrocarbon pollutant during spark-ignition combustion (picture from Heywood, 1988)

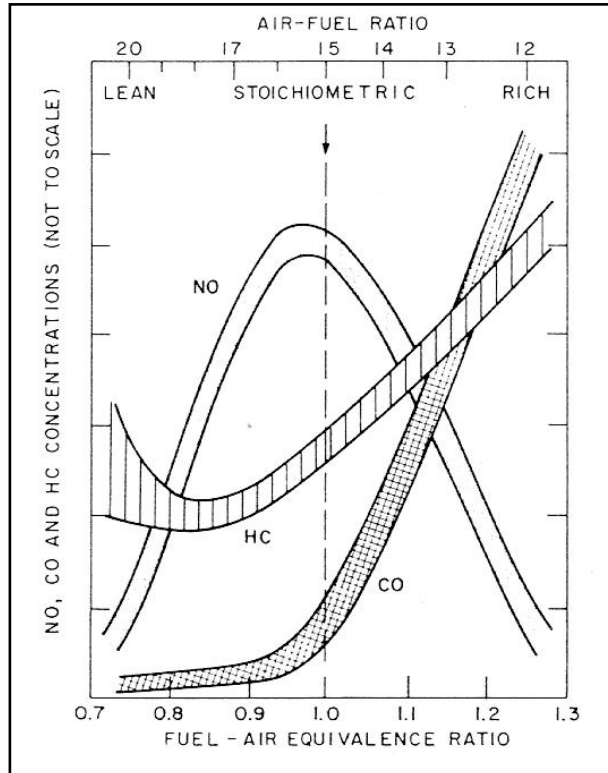


Figure 4.62 Effect of fuel / air equivalence ($\lambda = 1/\text{air factor}$) on NO, CO and hydrocarbon emissions from a spark-ignition engine (picture from Heywood, 1988)

Regarding process parameters, engine NO_x is mainly determined by 1) the compression ratio, 2) the design of the compression chamber (this defines flame speed, flame length and where hot/cold spots are), 3) inlet pressure/temperature, 4) spark or fuel injection timing and 5) fuel-to-air ratio.

The last of these points is illustrated by Figure 4.62, which shows that NO_x emissions are highest in a spark ignition engine operated at slightly lean conditions (stoichiometry $\lambda \sim 1.05$). A λ value slightly above 1 compensates for non-perfect mixing limitations.

For direct ignition, “diesel” engines (+ Chapter 2) the NO_x formation is a bit more complicated due to the heterogeneous combustion process. Erroneously, knowledge and theoretical concepts from spark-ignition engines are directly applied to direct ignition engines. Moreover, concepts such as NO reduction and N₂O-NO are not taken into account in theoretical models for NO_x emissions from spark-ignition as well as direct ignition engines: future work is needed here (Coda Zabetta and Kilpinen, 2000).

4.16.2 Removal of nitrogen oxides from engine exhaust gases

As mentioned above, two options are open to reduced NO_x emissions from engines: 1) improvements to the combustion process and 2) removal of NO_x from the exhaust. For combustion engine improvement a wide, highly specialised literature exists (see *e.g.* Heywood, 1988): only the second approach is addressed here, *i.e.* reduction of NO using a catalyst.

The tasks of a modern three-way catalyst for car engine exhaust gas are illustrated by Figure 4.63: reduction of NO has to be accomplished as well as

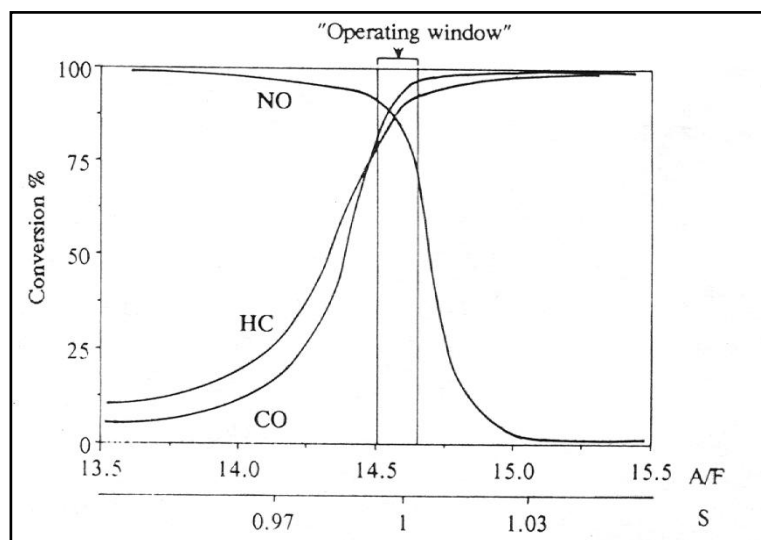


Figure 4.63 The operating window for a three-way catalyst system for car engine exhaust gas (picture from Barbier Jr., and Duprez, 1994)

oxidation of CO and hydrocarbons. This requires operation in a very narrow operating window for stoichiometry ($0.99 < \lambda < 1.01$), to which purpose a “lambda sonde” is applied that controls the operation of the engine.

For the selection of the catalytically active component several criteria have to be met: apart from chemical activity and selectivity the catalyst must be durable and stable against poisoning by *e.g.* sulphur or trace metals, plus the obvious requirement of reasonable cost.

Pollutant emissions from car engines are typically cut by 90-95% by a well-operating catalyst. Drawbacks are that a certain heating time (*i.e.* driving distance) of 5~ 10 km is needed to heat up the catalyst to its working temperature. Furthermore, N₂O emissions are generated which are of the

order 6×10^{-5} g N₂O/g CO₂ for a car with a catalyst, being virtually zero for a car without it (Becker *et al.*, 1999).

For direct ignition / diesel engines a different catalyst system is needed since also relatively high emissions of particulates (soot, tar) must be dealt with. These emissions are discussed in a later Chapter.

4.17 REFERENCES

- Acid News (1996) **4** Oct. 1996, The Swedish NGO Secretariat on Acid Rain, Gothenburg, Sweden
- Acid News (2000) **3** Oct. 2000, The Swedish NGO Secretariat on Acid Rain, Gothenburg, Sweden
- Aho, M.J., Paakkinen, K.M., Pirkonen, P.M., Kilpinen, P., Hupa, M. (1994) "The effects of pressure, oxygen, partial pressure and temperature on the formation of N₂O, NO and NO₂ from pulverised coal", *Combustion & Flame* **102** 387-400
- Alderliesten, P.T. *et al.* (1990) "System study high temperature gas cleanup at IGCC systems" NOVEM, the Netherlands, report 90-310
- Barbier Jr., J., Duprez, D. (1994) "Steam effects in three-way catalysts", *Applied Catalysis B: Environmental* **4** 105-130
- Becker, K.H., Lörzer, J.C., Kurtenbach, R., Wiesen, P., Jensen, T.E., Wallington, T.J. (1999) "Nitrous oxide (N₂O) emissions from vehicles" *Environ. Sci. Technol.* **33** 4134-4139
- Bockhorn, H., Hornung, A., Hornung, U., Teepe, S., Weichmann, J. (1996) "Investigation of the kinetics of thermal degradation of commodity plastics" *Comb. Sci. & Technol.* **116-117**, 129-151
- Boon, J.P. (1995) "Removal of hydrogen cyanide from gaseous streams by means of gas/liquid processes", Twente University, the Netherlands
<http://www.ct.utwente.nl/~ospt/minipost95/ut/boon>
- Cassidy, P. (2002) "New European laws target", *Modern Power Systems* **22(3)** 18-21
- Coda Zabetta, E., Kilpinen, P. (2000) "Development of an improved NO submodel for in-cylinder simulation of medium-low speed compression ignition engines" presented at the Topical Meeting on Modelling of Combustion and Combustion Processes", Turku, Finland, Nov. 2000.
- Coda Zabetta, E. *et al.* (2000) "Kinetic modelling study on the potential of staged combustion in gas turbines for the reduction of nitrogen oxide emissions from biomass IGCC plants" *Energy & Fuels* **2000** 751-761
- Cooper C.D., Alley, F.C (1994) "Air pollution control – a design approach", 2nd Ed., Waveland Press Inc., Illinois, Chapter 15.
- CRIEPI (1996a) "Development of a low NO_x catalytic combustor for a gas turbine", CRIEPI, Japan, <http://criepi.denken.or.jp/RD/nenpo/1996E/96seika14>
- CRIEPI (1996b) "Development of a 1500°C-class gas turbine combustor for use in IGCC, CRIEPI, Japan, <http://criepi.denken.or.jp/RD/nenpo/1996E/96seika17>
- Cullis, C.F., Hirschler, M.M. (1981) "The combustion of organic polymers", Clarendon Press, Oxford
- Doig, A., Morrison, G. (1997) "The use of natural gas in coal-fired boilers" IEA Coal Research, Report IEAPER/35, London, UK

- EU (2000) Directive 2000/76/EC of the European parliament and of the Council of 4 December 2000 on the incineration of waste
- EU (2001) Directive 2001/80/EC of the European parliament and of the Council of 23 October 2001 on the limitation of emissions of certain pollutants into the atmosphere from large combustion plants
- Flagan, R.C, Seinfeld, J.H. (1988) "Fundamentals of air pollution control engineering", Prentice-Hill, New Jersey Chapter 8.5
- Gangwal, S.K. *et al.* (1996) "Catalytic ammonia decomposition for coal-derived fuel gas" in: Proc. of the Advance Coal-Fired Power Systems '96 review meeting, Morgantown, June 1996.
- Glarborg, P. (1993) "NO_x chemistry in pulse combustion", keynote lecture, Workshop on Pulsating Combustion and its Applications, Lund, Sweden, August 1993.
- Grace, J.R., Avidan, A.A., Knowlton, T.M. (Eds.) (1997) "Circulating fluidised beds", Chapman & Hall, London
- Heywood, J.B. (1988) "Internal combustion engine fundamentals" McGraw-Hill, New York
- Hiltunen, M., Kilpinen, P., Hupa, M., Lee, Y.Y. (1991) "N₂O emissions from CFB boilers: experimental results and chemical interpretation" Proc. of the 11th Int. Conf. on FBC, E.J. Anthony, (Ed.), ASME, New York, p. 687-694
- Hämäläinen, J.P., Aho, M.J., Tummavuori, J.L. (1994) "Formation of nitrogen oxides from fuel-N through HCN and NH₃ : a model-compound study" FUEL **73(12)** 1894-1898
- Johnsson, J.E. (1993) "Formation and reduction of nitrogen oxides in fluidized-bed combustion", FUEL, **73(9)** 1398-1415
- Jothimurugesan, K., Gangwal, S.K. "Advances in ammonia removal from hot coal gas" in: Proc. of the Advance Coal-Fired Power Systems '96 review meeting, Morgantown, June 1996.
- Kilpinen, P. (1990) "Kinetic modelling of gas phase nitrogen chemistry in combustion" lic. tech. thesis / report 90-13, Åbo Akademi University, Combustion Chemistry Research Group, Turku, Finland
- Kilpinen, P. (1995) "Tyten oksidien muodostuminen ja hajoaminen", Chapter 9 in: "Poltto ja palaminen", R. Raiko et al. (Eds.), IFRF, Gummerus, Jyväskylä, Finland
- Kilpinen, P., Hupa, M. (1991) "Homogeneous N₂O chemistry at fluidised bed combustion: a kinetic modelling study" Combustion and Flame **85** 94-104
- Kilpinen, P., Aho, M., Seetula, J., Hupa, M. (1994) "Gas phase chemistry of NO_x and N₂O at pressurised combustion between temperatures 700 and 1000 °C" Proc. of the 6th Int. Workshop on Nitrous oxide emissions", Turku, Finland June 1994, p. 333-344
- Kilpinen, P., Norström, T., Mueller, C., Kallio, S., Hupa, M. (1999) "Homogeneous NO and N₂O chemistry in FBC" Proc. of the 38th IEA FBC meeting, Savannah (GA) May 1999
- Kilpinen, P. (2000) course material "Chemistry of Combustion Processes – Part 1", May 2000, Åbo Akademi University, Combustion Chemistry Research Group, Turku, Finland
- van der Lans, R.P. (1997) "Influence of process parameters on coal combustion performance" PhD thesis Technical Univ. of Denmark, Lyngby
- Leckner, B., Karlsson, M., Dam-Johansen, K., Weinell, C.E., Kilpinen, P., Hupa, M. (1991) "Influence of additives on selective noncatalytic reduction of NO with NH₃ in circulating fluidised bed combustors" Ind. & Eng. Chem. Res. **30** 2396-2404
- Leckner, B. (1992) "Emissioner vid förbränning av biobränslen i fluidiserad bädd", ABBs Energidag, 21.10.1992

- Leppälahti, J., Koljonen, T., Hupa, M., Kilpinen, P. (1997) "Selective catalytic oxidation of NH_3 in gasification gas. 2. Oxidation on aluminum oxides and aluminum silicates" *Energy & Fuels*, **11(1)** 39-45
- Leppälahti, J., Koljonen, T. (1995) "Nitrogen evolution from coal, peat and wood during gasification: literature review" *Fuel Proc. Technol.* **43** 1-45
- Leppälahti, J., Simell, P., Kurkela, E. (1991) "Catalytic conversion of nitrogen compounds in gasification gas" *Fuel Proc. Technol.* **29** 43-56
- Lyngfelt, A., Åmand, L.-E., Leckner, B. (1998) "Reversed air staging – a method for reduction of N_2O emissions from fluidized bed combustion of coal" *Fuel* **77(9/10)** 953-959
- Lyngfelt, A., Åmand, L.-E., Leckner, B. (1995) "Obtaining low N_2O , NO and SO_2 emissions from circulating fluidized bed boilers by reversing the air staging conditions" *Energy & Fuels* **9**, 386-387
- Maude, C.W., Kirchner, A.T. (1995) "Gas turbine developments", Report IEACR/84, IEA Coal Research, London
- McConville, A. (1997) "Emission standards handbook 1996: air pollutant standards for coal-fired plant" Report IEACR/96, IEA Coal Research, London
- Miller, J.A., Bowman, C.T. (1989) "Mechanism and modelling of nitrogen chemistry in combustion" *Prog. Energy Combust. Sci.* **15** 287-338
- Mitchell, S. (1998) "NO_x in pulverised coal combustion", Report CCC/05, IEA Coal Research, London
- MPS(2000) Modern Power Systems, 20(12) Dec. 2000 p. 11
- Nakata, T., Ninomiya, T., Sato, M. (1990) "Development of a gas turbine combustor fired on low BTU gases. Experimental evaluation of an advanced type combustor" Report EW90009, Yokosuka Research Laboratory
- Nelson, P.F., Buckley, A.N., Kelly, M.D. (1992) "Functional forms of nitrogen in coals and the release of nitrogen as NO_x precursors (HCN and NH_3)" *Proc. of the Combustion Institute, The Combustion Institute, Pittsburgh (PA)* **24** 1259-1267
- Norman, J.S., Pourkashanian, M., Williams, A. (1995) "Ammonia and its control in clean coal technology systems" *Proc. of the 12th Annual Pittsburgh Coal Conf.*, S.-H. Shiang (Ed.), Pittsburgh (PA) 193-198
- OECD/IEA & ETSU (1993) "Clean coal technology – options for the future" Paris, France
- Qader, S.A., Qader, Q.A., Muzio, L.J. (1996) "Decomposition of ammonia in IGCC fuel gas streams" in: *Proc. of the Advance Coal-Fired Power Systems '96 review meeting*, Morgantown, June 1996.
- Pels, J.R. (1995) "Nitrous oxide in coal combustion", PhD thesis, Delft Univ. of Technol., the Netherlands
- Phillips, J.N, Roby, R.J. (2000) "Hydrogen enriched natural gas offers economic NO_x reduction alternative" *Power Engineering*, **104(5)** / May 2000 36-40.
- Rozendaal, M. (1999) "Impact of coal quality on NO_x emissions for power plants", PhD thesis, Delft Univ. of Technol., the Netherlands
- Sarofim, A.F., Goel, S.K., Morihara, A. (1994) "Fluidized bed combustion and control issues", *Proc. Int. Clean Coal Symp. on PFBC*, Kitakyushu, Japan, July 1994, p. 12-17
- de Soete, G.G. (1988) "The nitrous oxide problem" Helsinki Univ. of Technol., Dept. of Energy Engineering, Seminar 21.10.1988, report 28
- Soud, H. Fukasawa, K. (1996) "Developments in NO_x abatement and control", Report IEACR/89, IEA Coal Research, London
- Takeshita, M. (1994) "Environmental performance of coal-fired FBC", Report IEACR/75, IEA Coal Research, London

- Takeshita, M. (1995) "Air pollution control costs for coal-fired power stations", Perspectives # 17, IEA Coal Research, London
- US (1997) "Six greenhouse gases", Fact sheet US Delegation to the 3rd Conf. of the Parties, United Nations Committee on Climate Change, Kyoto, Japan, Dec. 5, 1997 (http://www.state.gov/www/global/oes/fs_sixgas_cop.html)
- US DOE (1996) "Reducing emissions of nitrogen oxides via low-NO_x burner techniques" Clean Coal Technology, Topical Report 5 (Sept. 1996)
- US DOE (1997) "Control of nitrogen oxide emissions: selective catalytic reduction (SCR)" Clean Coal Technology, Topical Report 9 (July 1997)
- US DOE (1999) "Technologies for the combined control of sulphur dioxide and nitrogen oxides emissions from coal-fired boilers" Clean Coal Technology, Topical Report 13 (May 1999)
- US DOE (2000) "Clean coal technology demonstration program" Program Update September 1999, US DOE, Washington (DC) (April 2000).
- Werther, J., Ogada, T. (1999) "Sewage sludge combustion" Progr. Energy Comb. Sci. **25** 55-116
- Wójtowicz, M.A., Pels, J.R., Moulijn, J.A. (1993) "Combustion of coal as a source on N₂O emission", Fuel Proc. Technol. **34** 1-71
- Zevenhoven, R., Axelsen, E.P., Kilpinen, P., Hupa, M. (1999) "Nitrogen oxides from nitrogen-containing waste fuels at FBC conditions – # 1" Proc. 39th IEA FBC meeting, Madrid, Spain, Nov. 1999
- Zevenhoven, R., Axelsen, E.P., Elomaa, M., Liukkonen, V.-P., Kilpinen, P., Hupa, M. (2000) "Nitrogen oxides from nitrogen-containing waste fuels at FBC conditions – # 2" Proc. 40th IEA FBC meeting, Turku, Finland, May 2000
- Zevenhoven, R., Hupa, M. (1998) "The reduction of NO on chars from coal, peat and wood, with and without CO", FUEL **77(11)** 1169-1176
- Åbo Akademi University (2001)
http://www.abo.fi/fak/ktf/cmc/research/r_schemes.html
- Ågren, C., Elvingson, P. (1997) "Still with us - the acidification of the environment is still going on", The Swedish NGO Secretariat on Acid Rain, Gothenburg, Sweden
- Åmand, L.E., Andersson, S. (1989) "Emissions of nitrous oxides (N₂O) from fluidised bed boilers" Proc. of the 10th Int. Conf. on FBC, A.M. Manaker (Ed.) ASME, New York, 49-56
- Åmand, L.-E., Leckner, B., Andersson, S. (1991) "Formation of N₂O in circulating fluidized bed boilers", Energy & Fuels **5** 815-823
- Åmand, L.-E., Leckner, B. (1992) "Influence of air supply on the emissions of NO and N₂O from a circulating fluidized bed" Proc. of the Combustion Institute/ The Combustion Institute, Pittsburgh (PA) **24** 1407-1414
- Åmand, L.-E., Leckner, B. (1994) "Homogeneous and heterogeneous reactions for formation and destruction of N₂O – Results from the 12 MW CFB boiler at Chalmers", Proc. of the 6th Int. Workshop on Nitrous oxide emissions", Turku, Finland June 1994, pp. 95-113

