PRIMARY AND SECONDARY MEASURES FOR THE REDUCTION OF NITRIC OXIDE EMISSIONS FROM BIOMASS COMBUSTION

NO_X reduction in biomass combustion

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Abstract

Nitric oxide emissions from biomass combustion originate mainly from the fuel bound nitrogen, thermal NO_X are only of minor importance. Since biomass combustion leads to higher NO_X emissions than gas or light fuel oil combustion primary or secondary measures for NO_X reduction are necessary for future combustion plants.

To minimize NO_X emissions by primary measures, the fuel nitrogen must be reduced to molecular nitrogen in zones with an excess air ratio < 1. The following techniques for the reduction of fuel NO_X have been investigated: Air staging with and without separate reduction chamber, fuel staging and flue gas recirculation. It is shown that an NO_X reduction of 40% to 75% can be reached by air staging with separate reduction chamber if the following conditions are met: Primary excess air ratio ≈ 0.7 – 0.8, temperature in the reduction chamber ≈ 1'100° – 1'200°C, residence time ≈ 0.3 – 0.5 s. Fuel staging shows a similar potential of NO_X reduction. As for air staging the NOx reduction is mainly influenced by the excess air ratio in the reduction chamber. Fuel staging can only be used for large combustion plants while air staging can be used for automatic wood furnaces from app. 200 kW up to large scale combustion.

If primary measures are not sufficient, secondary measures as the selective catalytic and non-catalytic reduction (SCR, SNCR) through the injection of sal ammoniac, ammonia or urea can be taken. The NO_X reduction in the SNCR process is limited by the ammonia slippage. Further an accurate process control is neceassary to ensure the temperature window of app. 840°C – 920°C. To operate the combustion at low excess air ratio without exceeding the temperature limit, a partial extraction of heat before the SNCR process is necessary. By the SNCR process 60% – 80% reduction can be reached, depending on the fuel composition and the operation conditions. With SCR more than 80% (up to 95%) reduction can be achieved. However there is only little experience with the long term behaviour of catalysts in wood combustion systems.

For large combustion plants combinations of low NO_X and denox-techniques are considered.

Keywords: NO_X, low NO_X, air staging, fuel staging, reburning, staged combustion, ammonia injection, SCR, SNCR, denox.

1 Introduction

Nitric oxides NO and NO_2, summarized as NO_X, from combustion processes are formed in three different reactions:

- Thermal NO_X are formed at high temperature (relevant concetrations can be found > 1'300°C) by the oxidation of nitrogen in the air
- Prompt NO_X can be formed during the combustion of hydrocarbons in reactions of molecular nitrogen with free radicals in the flame
- Fuel NO_X are formed from the nitrogen contained in the fuel.

Fuel NO_X as an oxidation product are usually maximally at high combustion quality. Since typical combustion temperatures in todays wood firings are between 800° and 1200°C only fuel NO_X are of great importance. Therefore nitric oxide emissions typically increase with increasing nitrogen content in the wood (table 1). Furthermore the analysis of flue gas from wood combustion shows that the emission of NO_2 is usually much smaller than the emission of NO.

The NO_X concentration which can be calculated by the Zeldovic mechanism of thermal NO_X formation is neclictible in relation to the measured NO_X emissions from wood firings. This fact was confirmed in different experimental investigations [1] [2] [3]: Wood was burnt in a conventional furnace a) with air and b) with a nitrogen free mixture of oxygen and argon. Since no difference in the emission of NO_X was found the nitrogen in the air is not responsible for the formation of NO_X. Further it was shown in a laboratory furnace that the emission of NO_X from different wood samples are independent of the combustion temperature in the range from 800° – 1300°C.

Table 1. Nitrogen content of pine wood, beech and chip board, concentration of NO_X and conversion rate (NO_X/N) of fuel nitrogen to NO_X resulting from the isothermal combustion in a laboratory furnace (NO_X at 11 Vol.-% O_2) [1].

	Fuel-N	NO_X [Wt. %]	NO_X/N [mg/Nm^3]
[%]			
Pine wood	0.07	173	67.3
Beech	0.2	231	36.0
Chip board (UF)	2.85	921	8.4

During the pyrolisis of wood approximately 20% of the nitrogen compounds remain in the char and 80% form volatile substances. As a first approximation, the volatile nitrogen conversion to NO and the char conversion to NO can be assumed as independent [4].

The volatile fraction consists of HCN, NH-compounds (NH, NH_2, NH_3) NO and N_2. HCN is converted homogenously to NH_2/NH_3 which can be oxidized to NO or react with NO to N_2 [5] [6] [7]. The overall reaction from fuel nitrogen to NO or N_2 can be influenced by the reaction conditions, especially by the temperature, the concentration of oxidizing agents as O_2 and H_2O, the residence time in the different zones of the combustion and the turbulence.

2 Primary measures for NO_X reduction

2.1 Fundamentals

To ensure combustion with low NO_X emissions the fuel nitrogen must be converted to N_2. Different concepts of staged combustion for NO_X reduction have been investigated for the combustion of coal, oil and gas [8] [9] [10] [11] [12]. For the combustion of wood the following reactions are considered to be important for the NO_X emissions [2] [5]: During the gasification HCN and NH_i radicals as NH_2 and NH_3 are formed. These components can react in different reactions to form molecular oxygen (simplified):

$$NO + NH_2 \rightarrow N_2 + H_2O \qquad (1)$$

Where there is a shortage of oxygen NO_X acts as an oxidizing agent for carbon monoxide, methane, hydrocarbons, hydrogen and carbon:

$$NO + CO \rightarrow CO_2 + 0.5\,N_2 \qquad (2)$$
$$NO + CH_4 \rightarrow CO + 2\,H_2 + 0.5\,N_2 \qquad (3)$$
$$NO + H_2 \rightarrow H_2O + 0.5\,N_2 \qquad (4)$$
$$NO + C \rightarrow CO + 0.5\,N_2 \qquad (5)$$

Fig. 1 shows the main reactions of the fuel nitrogen during gasification and oxidation. The gas phase reactions are dominant for the NO formation. From HCN which is released from the fuel, NH_i radicals are formed. Under oxidizing atmosphere the NH_i-components are mainly converted to NO, while under reducing conditions, the NH_i-radicals can be reduced to N_2. The already formed NO can react to N_2 in the presence of NH_i or other reducing components such as CH_i, CO etc.. Furthermore NO can react with CH_i to form HCN in the so called NO recycle.

Since in oxidizing and reducing atmosphere different reactions are dominant for the fuel nitrogen, the primary excess air ratio plays an important role for the NO_X formation (Fig. 2, Fig. 3, Fig. 4).

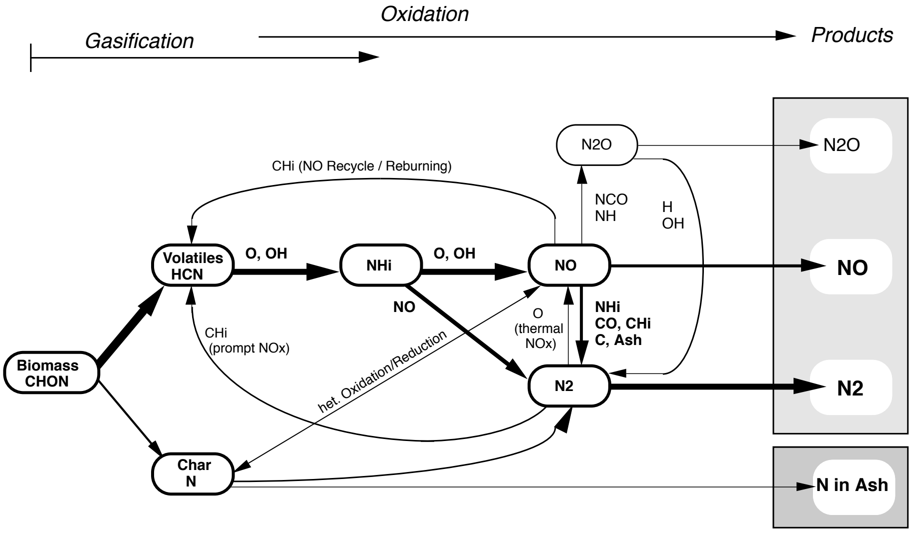

Fig. 1 Reactions of fuel nitrogen during combustion (main paths thick).

2.2 Staged combustion with reduction chamber and air staging

To investigate under which conditions the above mentioned reactions (1) to (5) can significantly reduce NO_X during combustion, a 25 kW test reactor with fixed bed updaft gasification followed by a gas phase combustion was built (Fig. 2). The test reactor can be operated as an under stoker firing, which allows to receive reference NO_X values for conventional combustion. The following concepts of staged combustion have been investigated:

- air staging with separate reduction chamber between the gasification and the combustion chamber
- air staging in the gasification chamber
- flue gas recirculation
- combinations of the listed measures.

Due to the results of different experiments carried out in the fixed bed reactor reaction (1) is supposed to be most important for fixed bed combustion of wood. Reaction (2) might be of importance together with catalytic effects on ash while for reaction (4) and (5) no effects were found during wood combustion in the test reactor. Reaction (5) is supposed to be of major influence during fluidized bed combustion of coal [8]. However for NO_X reduction by air staging in biomass combustion, the heterogenous reactions are of minor importance.

In the test reactor an NO_X reduction > 50% for native wood and > 75% for UF chipboards (N-content app. 3 wt.-%) compared to conventional fixed bed combustion is optained by air staging with a separate reduction chamber between the gasification and the combustion. Table 2 shows the results of different primary measures for native wood and UF chipboards at different operation conditions. However to reach minimal NO_X emissions the reaction conditions must be as follows:

- residence time in the reduction chamber ≈ 0.5 s (> 0.3 s) and sufficient mixing quality (turbulence) to ensure mixing
- reduction temperature ≈ 1’100C° – 1’200C°
- primary excess air ratio ≈ 0.7 – 0.8

The primary excess air ratio in the gasification chamber is of great influence on the NO_X emissions (Fig. 4):

- Primary air ratio << 0.7 (gasification): Mainly NH-components (and) HCN are formed during the gasification, while the NO concentration is low. The NH-components are oxidized in the combustion chamber to NO.
- Primary air ratio > 1: The pyrolisis gases are burnt immediately in the gasification chamber (= combustion). The concentration of NH-components to reduce NO in the reduction chamber is close to 0.

An additional NO_X reduction can be achieved by air staging in the gasification chamber (3 stage combustion compared to 2 stage combustion in table 2). Flue gas recirculation was found to have a minor influence on NO_X emissions. The temperature window for the reduction of NO_X by staged combustion with reduction chamber is about 300°C higher than for the SNCR process. It is assumed that methane in the gas consumes OH radicals and therefore inhibits the formation of NH_2 radicals which are necessary for the NO reduction [7]. The experimental results correspond to datas from a kinetic model acc. to Kilpinen et al. [13].

To ensure a constant primary air ratio and a reduction temperature of app. 1’150°C a suitable process design as well as an accurate combustion and gasification control are necessary. As a consequence, a 250 kW grate firing with reduction chamber has been designed (Fig. 5). To reduce heat losses from the reduction chamber, the combustion chamber is surrounding the reduction chamber. In the grate firing similar results as shown in Fig. 4 have been achieved. However measures must be taken to limit the temperature if dry biomass is burnt. Flue gas recirculation, secondary air preheating with convective heat from the primary chamber and wall cooling in the primary zone are considered as measures to limit the temperature < 1’200°C if dry wood is burnt and are investigated in ongoing research.

Fig. 2 Laboratory furnace for staged combustion (25 kW).

From left to right: Automatic feeding with under stoker. Updraft-gasification chamber with primary air injection on one level (2 stage combustion) or several levels (staged gasification; 3 stage combustion). Reduction chamber which can be heated for isothermal conditions and with a residence time which can be varied between 0.05 s to 2.0 s. Secondary air injection, combustion chamber and boiler. Option (not shown): Flue gas recirculation. Raw gas analysis after the gasification chamber with FTIR, flue gas analysis by NDIR, CLD and paramagnetic analyzers.

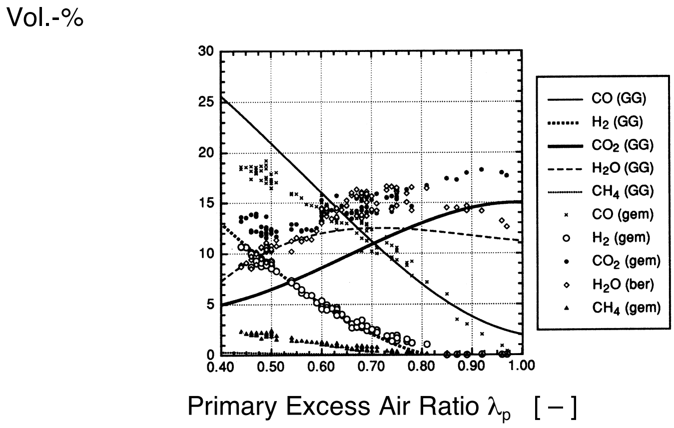

Fig. 3 Composition of the raw gas from the under stoker gasification in the laboratory furnace in function of the primary excess air *(gem)* in comparison to calculated datas *(GG)* [7], [14].

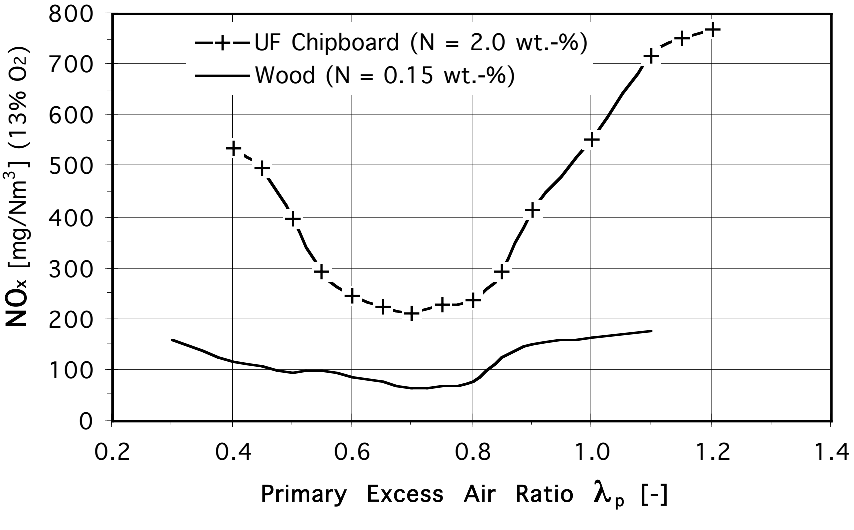

Fig. 4 NO_X emissions in function of the primary excess air ratio during the combustion of wood and UF chipboards in the laboratory furnace with reduction chamber (2 stage combustion, temperature in the reduction chamber = 1’150°C). Similar results are found in the low-NOx grate firing (Fig. 5).

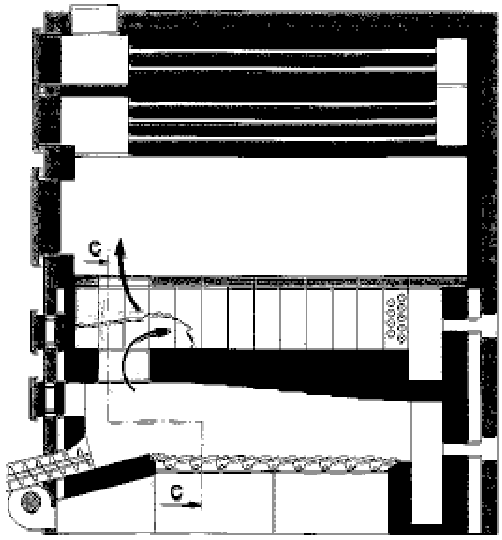

Fig. 5 Prototype grate firing (250 kW) with reduction chamber, which is surrounded by the combustion chamber to reduce heat losses.

Table 2. NOx emissions and conversion rate of fuel-N to NOx for the combustion of native wood and UF chipboars for different primary air excess ratios [7]. Temperature in the reduction chamber = 1'160°C, residence time = 0.3 – 0.6 s.

Fuel Type	**Combustion technology**	**Primary excess air**	**NO$_X$**	**Conversion of fuel N to NO$_X$**	**NO$_X$ reduction**
		[–]	[mg/Nm^3] as NO$_2$ at 13 Vol.-% O$_2$	[%]	[%]
Wood N = 0.15 wt.-%	**2 stage** combustion without reduction chamber (**ref.**)	1 – 1.3	200	39.8	0
	2 stage combustion with understoichiometric operation	0.6 – 0.8	140	28.0	30
	2 stage combustion **with** reduction chamber	0.7	76	15.1	62
	3 stage combustion **with** reduction chamber	0.8	60	12.0	70
UF Chipboard N = 2.0 wt.-%	**2 stage** combustion without reduction chamber (**ref.**)	1 – 1.3	848	15.3	0
	2 stage combustion with Low-NOx operation	0.6 – 0.8	440	8.1	48
	2 stage combustion **with** reduction chamber	0.7	216	4.0	75
	3 stage combustion **with** reduction chamber	0.8	176	3.2	79

2.3 Fuel staging

To reduce NO$_X$ emissions by fuel staging, the primary fuel is burnt with excess air ($\lambda > 1$). A secondary fuel or reburn fuel is injected in the hot flue gas of the primary fuel. In the mixing zone a reducing atmosphere can be achieved if the excess air ratio is smaller than 1. As in the reactions shown in Fig. 1, NO$_X$ in the flue gas of the primary fuel can be reduced with CH$_i$, NH$_i$ and other components of the gas from the secondary fuel by the above mentioned reactions. Fuel nitrogen from primary and secondary fuel and also thermal NO$_X$ from the primary fuel can be converted to N$_2$.

The potential of fuel staging in small scale wood combustion has been investigated in an under stoker furnace [15]. The secondary fuel was introduced on a second grate above the main fuel bed with an energy input ratio of app. 70% primary and 30% secondary fuel. In comparison to unstaged combustion, an NO$_X$ reduction between 52% – 73% has been achieved at a reduction temperature of app. 700°C. In comparison to air staging a NO$_X$ reduction can be achieved at lower temperatures. The influence of the reduction temperature, the residence time and the fuel composition will be investigated in future work.

The application of fuel staging in practice requires an automatic feeding of the primary and the secondary fuel. For this purpose the secondary fuel must be easily dosable. Therefore natural gas, light fuel oil, biomass powder, saw dust or similar fuels can be used. The nitrogen content in the reburn fuel has a positive effect on reducing NO_X emissions. Furthermore the high volatile matter of biomass has a positive effect on the reburn efficiency. However if solid fuels are used as reburn fuel, fine grinding is necessary to achieve high reburn efficiencies and a good burnout [16].

Pyrolisis gas is also a suitable reburn fuel. Beside NH_i, CH_i and other gaseous components, tars in the pyrolisis gas are supposed to improve the reburn efficiency. As air staging (Fig. 4), also fuel staging leads to minimal NO_X emissions for a primary excess air ratio between app. 0.7 – 0.9 [16] [17] [18] (Fig. 6). The heterogenous reactions were found to be of minor importance for the NO_X reduction [19]. Since two feeding systems are necessary, fuel staging is mainly an option for larger biomass combustion systems.

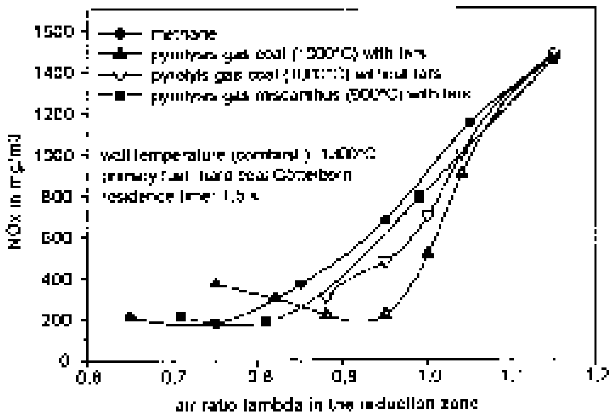

Fig. 6 NO_X emissions in function of the primary excess air ratio for different reburning fuels [16].

3. Secondary measures for NO_X reduction

3.1 Fundamentals

For native wood the NO_X emissions are usually between 150 and 300 mg/m^3 at 11 Vol.-% O_2 (calculated as NO_2). If chipboards or similar wood residues are burnt, the nitrogen contained in glue and bonding agents (urea) lead to typical NO_X emissions between 500 and 1000 mg/m^3. For biofuels such as straw, miscanthus and grass NO_X emissions are close to those of wood residues since short rotation plants generally show a significantly higher nitrogen content than wood.

In Switzerland secondary measures can be necessary for larger boilers (> 1 – 2 MWth) to fit the emission standard of 250 mg/m^3 of the ordinance on air pollution control (OAPC).

For the secondary measures a reduction agent is injected for a selective NO_X reduction. The most important reduction agents are:

- Ammonia (NH_3) which is gasous at atmospheric pressure and is usually stored in a pressurized tank. NH_3 is toxic and has a low smell limit.

- Sal ammonia (ammonia aq., max. 24 wt.%) is easier to store than ammonia. Smell problems by leackage are similar to ammonia.
- Urea $(NH_2)_2CO$ is a white solid powder which is usually stored as a granulate. To use it as a reduction agent it is dissolved in water. Urea is easy to handle and gives no smell problems.

The reactions in the SCR and SNCR process are similar. The desired reaction is the reduction of NO with NH-reactants, mainly NH_2 (as reaction (1) for primary measures). If urea is used, it has to be decomposed before the reaction with NO_X. Therefore a temperature of at least 250°C – 300°C is necessary.

Desired reaction:

$$4\,NO + 4\,NH_3 + O_2 \longrightarrow 4\,N_2 + 6\,H_2O \qquad (6)$$

Side reactions and slippage of reducing agent (4):

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O \qquad (7)$$
$$4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O \qquad (8)$$
$$NH_3 \longrightarrow NH_3 \qquad (9)$$

In reality reaction (6) is a radical reaction mainly with NH_2 as described for reaction (1) for primary measures: $NO + NH_2 \rightarrow N_2 + H_2O$. Therefore a temperature of about 850°C or the use of a catalyst is necessary for reaction (6).

If the temperature exceeds 950°C the side reactions (7) and (8) become more and more important. Therefore the reaction conditions for the NO_X reduction show an optimum in the temperature window between 850°C to 950°C. Because of the side reaction (8) an over stochiometric amount of reducing agent is necessary. The molar ratio of reducing agent is defined as follows:

$$n = NH_3/NO_X \text{ (mol/mol)} \quad \text{where } NO_X = NO + NO_2 \text{ (mol)} \qquad (10)$$

If a high molar ratio is needed ammonia slippage can lead to high emissions of NH_3 (9). Furthermore N_2O can be formed in undesired side reactions especially when urea is used as reduction agent.

3.2 Selective non-catalytic reduction SNCR

The reaction temperature is most important for the non-catalytic reduction. The highest reduction rate is usually achieved in the temperature window from 850° to 950°C depending on the reducing agent used and other parameters [20]. Own experiments with SNCR with urea in a grate firing with reduction chamber showed an optimum temperature window between 840°C to 920°C [21]. The temperature window can be shifted to lower temperatures by adding H_2 or alcohols which generate OH-radicals. CH_4 can shift the reactions to higher temperatures because it consumes OH-radicals.

Experiments with non-catalytic NO_X reduction in an existing 500 kW grate firing showed unsufficient results. To achieve an NO_X reduction of 50% a highly over stoichiometric amount of reduction agent is needed (n = 3 – 5) which leads to a high NH_3-slippage (> 30 mg/m^3). It was found that the non-ideal mixing of the gases is responsible for the slippage of ammonia [22]. Hence a special reduction chamber with a residence time > 0.3 – 0.5 s is needed for the application of SNCR. To investigate the potential of SNCR processes for biomass combustion, an experimental setup with a pre oven firing and a separate reduction chamber for the SNCR process has been realized (Fig. 7). For wood residues an NO_X-reduction of 60% to 90% was obtained at a molar ratio n = 2 with NH_3-slippage < 10 mg/m^3 at a reaction temperature of app. 900°C. For gaseous ammonia a residence time of app. 0.3 s is sufficent, while for urea and sal ammonia app. 1 s is necessary (Fig. 8).

Laboratory experiments have shown that N_2O can be formed under certain condition when urea is used (Fig. 8) [23]. In several experiments at wood firings no increase of N_2O emissions, which typically were < 5 mg/m^3, has been found [21] [22]. In one case N_2O concentrations > 30 mg/m^3 have been found. The influence on N_2O formation will be studied in future investigations.

From these results several a commercial grate firing was built (Fig. 10). It was shown that an accurate process control is necessary to ensure high NO_X reduction and low NH_3-slippage [22]. Three different control systems to optimize the molar ratio with the aim of minimal NO_X emissions without significant ammonia slippage have been tested:

a Addition of the reducing agent in function of the load signal
b Control of the reducing agent in function of the NO_X concentration in the raw gas (in front of the ammonia injection).
c Control of the reducing agent in function of the NO_X concentration in the flue gas.

Similar results can be achieved with control type *a*, *b* and *c* if the setpoints for type *a* can be precisely optimized for the actual fuel type. However control type *a* can only be used in practice if the fuel composition, especially the nitrogen content, is constant. The continous NO_X measurement in the hot raw gas, as needed for control type *b*, is more complicated than the measurement in the flue gas needed for type *c*. Since no significant advantages have been achieved with control type *b*, the measurement of NO_X in the flue gas *c* is proposed for practical applications.

The test results show that the hot reduction chamber also has a positive effect on the reduction of unburnt pollutants (CO, HC and also PCDD/F) [21]. However the temperature control in the reduction chamber is a major problem in practice. If the grate firing as shown in Fig. 10 is operated at low excess air (< 2), the temperature in the reduction chamber exceeds 950°C and the injected reducing agent immediately reacts to form N_2 and H_2O as described in reaction (8). To ensure high efficiency (low excess air level) and high NO_X reduction efficency, a partial heat extraction from the flue gas is necessary before entering the reduction chamber. Respective design modifications are under investigation.

Fig. 11 shows the design of a large wood combustion plant with combined low-NOx and SNCR process. If saw dust is injected as reburn fuel, a NO_X reduction is achieved by fuel staging. Without saw dust injection, the grate has to be operated with an understoichiometric excess air ratio and the chamber above the grate is used as reduction chamber for air staging. In addition, ammonia or urea can be injected for the SNCR process at different levels in the boiler. At full load operation, the injection is after the first heat exchanger section to avoid temperatures > 950°C, at part load operation, the reducing agent is injected in front of the first heat exchanger section.

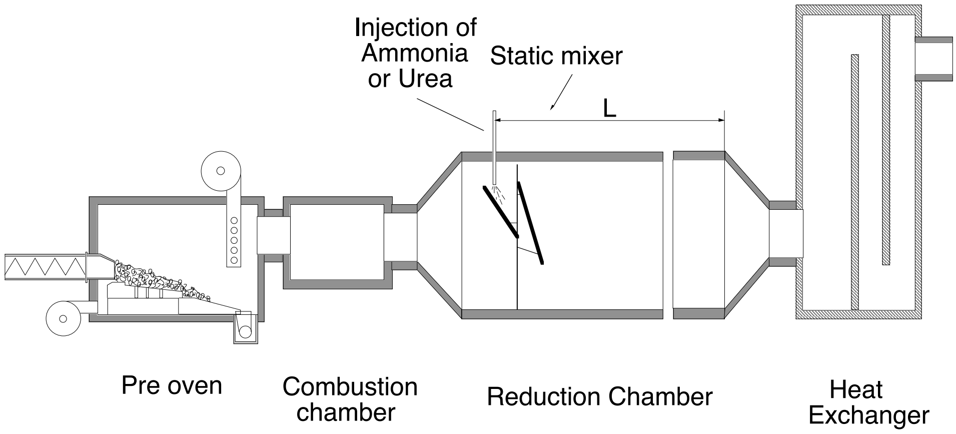

Fig. 7 Pre oven firing with SNCR process in a separate reduction chamber [22]. The residence time can be varied from 0.3 s to 3 s.

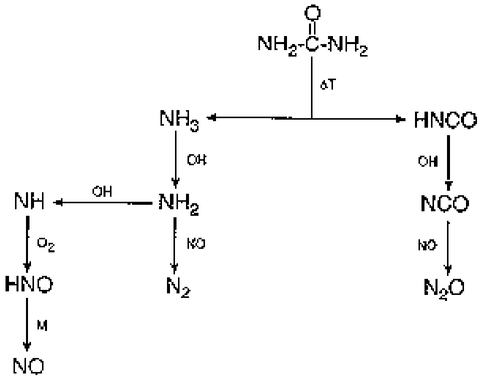

Fig. 8 Reactions during decomposition of urea. Under certain conditions HNCO and N_2O can be formed [23].

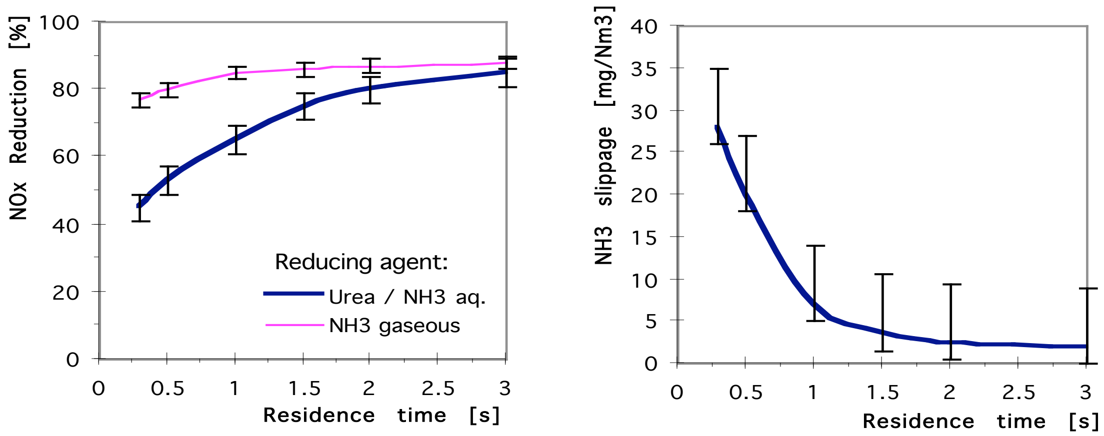

Fig. 9 NO_X reduction by SNCR process with urea and ammonia. Fuel: wood residues, urban waste wood, N content 1 – 2 wt.-%, NO_X level without denox = 700 – 800 mg/Nm3, temperature = 850°C – 930°C°C, n = 1.5 .... 2.2 [22].

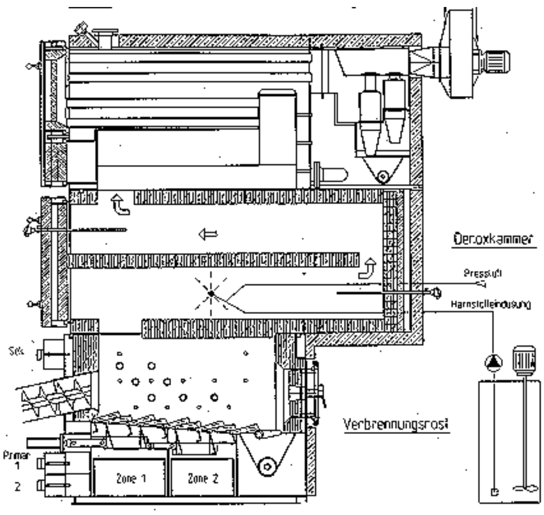

Fig. 10 Grate firing with SNCR process in a separate reduction chamber [21]. Residence time = 0.8 s. At a molar ratio of n = 2.2 up to 90% NOx reduction can be achieved, average reduction in practical operation = 60% – 70%.

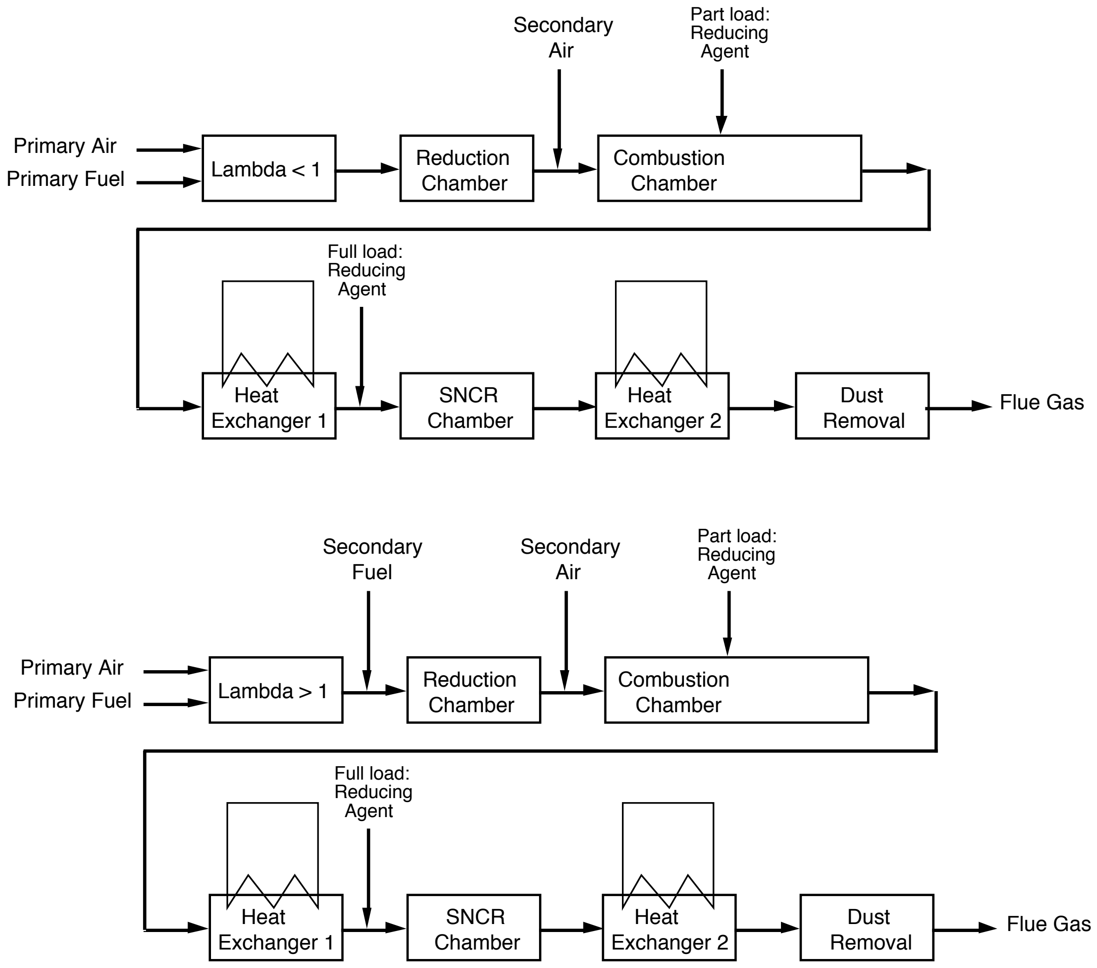

Fig. 11 Combustion plant with combined low-NOx and denox technology. Above: Low NO_X by air staging, below: low NO_X by fuel staging.

3.3 Selective catalytic reduction SCR

In previous investigations monolithic catalysts ($TiO_2/V_2O_5/WO_3$) have been used with sal ammonia at temperatures between 220° – 270°C and with urea at temperatures between 400° – 450°C. The catalyst was used in low dust and in high dust configuration. For wood residues an NO_X-reduction > 90% was obtained with a molar ratio n = 0.9 – 1 at a catalyst temperature > 250°C. The NH_3-slippage was well below 10 mg/m^3 for $0.7 < n < 2$. N_2O emissions were usually low (< 10 mg/m^3), with the exception of one measurement with a catalyst temperature > 350°C [22]. It is assumed that at high catalyst temperature N_2O formation can be significant. Detailed results from the SCR process have been presented in earlier papers [22, 24].

The SCR process shows a high potential for NOx reduction. Similar process control systems as for the SNCR process are necessary to optimize the injection of reducing agents, although ammonia slippage is a minor problem for SCR. The formation of salts in the presence of sulfur and chlorine ($(NH_4)HSO_4$, $(NH_4)SO_4$, NH_4Cl etc.) can lead to severe fouling problems in the catalyst, especially at catalyst temperatures below 250°C and in high dust configuration. Due to high costs only few biomass plants have been equipped with SCR and there is only few long term experience. Further development is needed to bring SCR techniques into practice for biomass combustion systems.

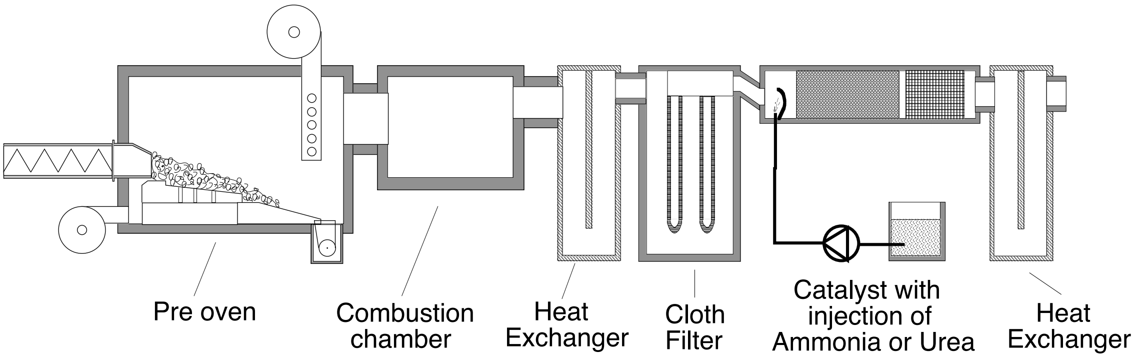

Fig. 12 Wood firing system with NO_X reduction by SCR low dust process.

4. Conclusions

4.1 Primary measures

Air staging can be considered as a primary measure for NO_X reduction in biomass combustion. By optimizing the excess air ratio towards understoichiometric conditions in the first section of the combustion, a certain NO_X reduction – depending on the furnace design and the fuel – can be achieved in existing combustion systems.

In comparison to such optimized operation of conventional furnaces, air staging with a separate reduction chamber and shows a potential for further NO_X reduction in the order of 40% – 60% for biofuels with low nitrogen content (< 0.5 wt.-%) and 50% – 75% for biofuels with high nitrogen content i.e. UF-chipboards (> 1 wt.-%). For the combustion of natural wood NO_X emissions < 150 mg/Nm^3 (calculated as NO_2 at 13 Vol.-% O_2) were reached in a 250 kW grate firing equipped with air staging and reduction chamber, while for wood residues with a nitrogen content of 2.75 wt.-% NO_X emissions < 250 mg/Nm^3 were reached

The NO_X reduction by air staging is mainly influenced by the excess air ratio in the reducing zone, the residence time, the temperature and the mixing quality. Optimal conditions for air staging are: Excess air = 0.7 – 0.8, residence time > 0.3 – 0.5 s, temperature = 1’100° – 1’200°C. To ensure a residence time of 0.3 – 0.5 s in the reducing zone, a separate reduction chamber is needed to achieve high NO_X reduction. Furthermore the realisation of the proposed low-NO_X concept needs an accurate process control to enable a primary excess air ratio below 1 during practical operation. Air staging in the gasification chamber can slightly improve the NO_X reduction rate. However mainly the gas-phase reactions are responsible for the NO_X reduction, while the heterogenous reactions are of minor importance.

Fuel staging shows a similar potential for NO_X reduction as air staging with separate reduction chamber. However fuel staging seems to be effective in a wider temperature range and especially at lower temperatures, while the conditions for the excess air ratio and the residence time are similar to those for air staging. Furthermore a fine grinding of the reburn fuel is needed to achieve significant NO_X reduction. Since two independent automatic fuel feeding systems are necessary for fuel staging, its application is limited to larger biomass plants.

4.2 Secondary measures

To achieve a relevant NO_X reduction without ammonia slippage by the selective non-catalytic reduction (SNCR), a temperature between 850°C and 950°C is needed. To achieve 60% – 70% reduction with ammonia slippage < 10 mg/Nm^3 a residence time in the reduction chamber of app. 1 s is needed for urea (aq) or ammonia (aq), while for gaseous ammonia app. 0.3 s is sufficient. For practical application a separate reduction chamber has to be introduced after the combustion zone. A relevant problem for the SNCR process is the very narrow temperature window. Without heat extraction before the reduction chamber, the temperature generally exceeds 950°C at low excess air ratios. Therefore a partial heat extraction before entering the reduction chamber and an accurate process control for the temperature window and the injection of reducing agent are necessary to ensure optimal results in practice. If urea is used N_2O can be formed in the SNCR process under certain conditions. The formation of N_2O will be investigated in future studies.

The selective catalytic reduction (SCR) shows the highest reduction potential of > 80% (up to 95%) at nearly stoichiometric operation with ammonia or urea. Due to high costs only few plants have been equipped in practice with catalysts and only few long term experiences are available. Technical problems have to be considered concerning the possible fouling in the catalyst at low catalyst temperatures (< 300°C), while at high catalyst temperatures the heat management of the combustion plant becomes more complicate.

As an option for large combustion plants low NO_X and denox techniques can be combined in an appropriate way i.e. air staging, fuel staging and SNCR or air staging, fuel staging and SCR.

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Fig. 13 Emission of NO (above) and NH_3 slippage in function of the molar ratio n (NH_3/NO) for SCR process with sal ammoniac.

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