

Co-Combustion of Wood and Straw in a Circulating Fluidized Bed Boiler – reduction of NO_x emission

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Abstract

The nitrogen oxides (NO_x) reduction through selective non-catalytic reduction in the flue gas stream from the co-combustion of wood chips and straw pellets in a circulating fluidized bed boiler has been investigated. Injection of ammonium sulphate (AmSulphate) to the inlet of the hot cyclone decreases the emissions of NO_x but a low overall efficiency for the reduction process is obtained in this work. No ammonia-slip (increased concentration of ammonia in the flue gas) was observed when the ammonium sulphate was added.

Introduction

Fluidized bed combustion (FBC), especially circulating fluidized bed (CFB) combustion, is an advantageous method for burning solid fuels of different types, including biomass and waste. Fluidized bed boilers are fuel flexible and due to turbulent mixing between the bed material and combustion products, the technique presents an opportunity for emission control through additives lacking in other combustion techniques.

Throughout the years, the FBC technique has become frequently used for biomass and waste incineration, fuels with a higher fuel nitrogen conversion to NO_x than coal. New types of biofuels such as rice husk and straw are known to be high in alkali and nitrogen. These compounds are often associated with high emissions and problematic operation and present a challenge not only for efficient boiler operation but also efficient gaseous emission control. The purpose of this work is to investigate the NO_x-reduction capability of ammonium sulphate injected into the flue gas stream from the co-combustion of wood chips and straw pellets in a 12 MW CFB boiler. The concentration of the nitrogen oxides in the flue gas is determined with the analytical measuring technique Fourier transform infra red (FTIR) spectroscopy.

Theory

Formation and reduction of nitrogen oxides

The emissions of nitrogen oxides from biomass fired CFB boilers have been reported as higher than for corresponding operation with coal [1] but low in comparison to other combustion techniques [2]. The research regarding emissions of nitrogen oxides from stationary combustion systems have been mainly targeted towards NO and NO₂ but also the emission of N₂O has awoken interest since it is considered a greenhouse gas [2].

Nitrogen oxides (NO_x) formation in combustion involves three main processes, [2-3].

- Formation of thermal NO_x from the nitrogen in the combustion air. The thermal mechanism involves the O and OH radicals, thus the temperature has to be high enough to dissociate of the atmospheric O_2 and N_2 molecules.
- Formation of NO_x from nitrogen in the fuel. As the fuel is converted, nitrogen volatilizes and readily reacts to form NO_x .
- Formation of prompt NO_x involving the nitrogen in the combustion air and hydrocarbon radicals formed in the flame zone.

The formation of NO and NO_2 is strongly dependent on the nitrogen content of the fuel and to a smaller extent on the operational parameters [1]. The relatively low temperature in fluidized bed combustion limits the formation of thermal NO_x from the combustion air. Prompt NO_x is mostly associated to the flame zone but the significance of prompt NO_x is often overlooked in biomass related investigations [2].

The formation of N_2O involves both homogeneous and heterogeneous reactions and originates primarily from the nitrogen bound in the fuel [4], hence the fuel properties have a significant impact not only on the formation of NO_x but also on N_2O . The formation of N_2O is temperature dependent, the higher the combustion temperature the lower the emissions due to thermal decomposition. Hence the low temperature in fluidized bed combustion favours low emissions of NO_x but increases the N_2O emissions [5 and references therein]. Despite the low formation of NO_x in biomass fired fluidized bed boilers, to ensure that the emission levels of NO_x meets the legislated limits a post-combustion reduction system can in some cases be required.

Two major post-combustion processes for NO_x reduction are available:

- Selective catalytic reduction (SCR)
- Selective non-catalytic reduction (SNCR) also known as thermal DeNO_x.

In this work, the investigated method is SNCR, thus, SCR is given no further attention. The NO_x in the flue gas is reduced to N_2 by reactions with ammonia (NH_3), through the simplified reaction paths shown in figure 1. In this work, the NH_3 is supplied to the system through a water solution of AmSulphate ($(\text{NH}_4)_2\text{SO}_4$).

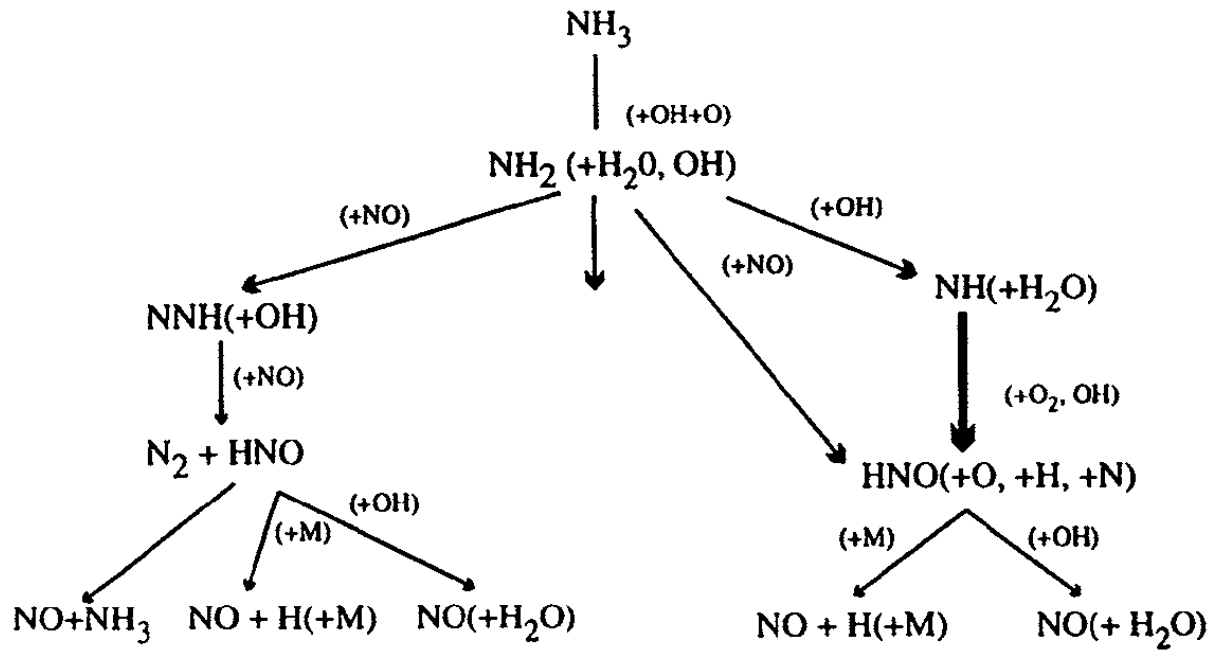


Figure 1: Thermal reduction scheme of NO by NH₃ [5]

The efficiency of the SNCR process depends on several factors including the temperature, NO_x level, reagent-flue gas mixing, NH₃/NO_x ratio and reaction time. Some of the problems with SNCR are ammonia slip, formation of NH₄HSO₄ (corrosive and fouling) and of N₂O. Thermal DeNO_x gives an expected reduction of NO_x between 30 and 70% but efficiencies as high as 80% have been reported [6 and references therein].

Reduction of NO_x by NH₃ is temperature sensitive with an optimum at about 1250 K and only efficient in an interval between 1100 and 1400 K, thus the temperature of FBC is favourable for efficient reduction using SNCR. At the lower temperature, the reaction path shown to the left in figure 1 is favoured, resulting in a net reduction of NO. At 1400 K and higher temperatures the reaction path shown to the right in figure 1 is favoured, resulting in a net increase of NO [3]. NH₃/NO_x ratio well above the stoichiometric equilibrium ratio promotes high NO_x reduction but may result in an increased and undesired ammonia-slip [2].

Gas concentration measurements with Fourier transform infrared spectroscopy

Gas concentration measurements with the FTIR technique is based on the analysis of the infrared light transmitted by an extracted gas sample. The principle of IR spectroscopy, illustrated in figure 2, is based on the splitting of a beam from a light source in the mid-infrared region into two coherent beams via a mirror that after reflection from separate mirrors will interfere before passing through a sample and arriving at the detector. As the beams interact with the molecules of the sample, energy is absorbed at specific frequencies determined by the discrete rotation and vibration energy modes of molecules. As these energy modes are dependent on quantum properties as well as mass and bond strength of the molecule constituents, the absorbed frequencies acts as a fingerprint of the compound.

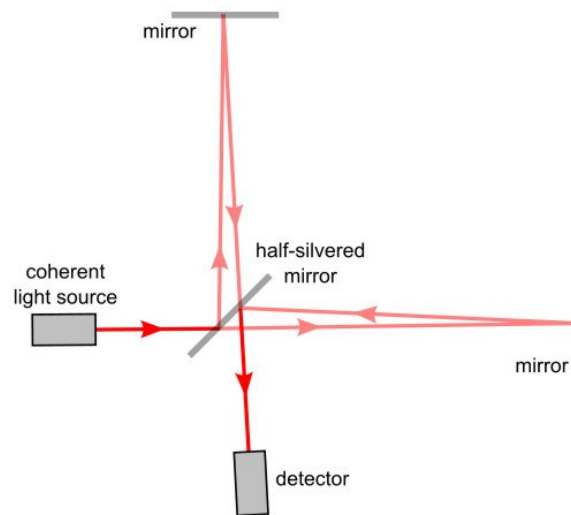


Figure 2: The principle of FTIR spectroscopy

The spectrometer has the advantage of detecting all incoming wavelengths at the same time. By measuring the intensity of the light transmitted through the sample, the wavelength at which light was absorbed is determined. One of the mirrors in the spectrometer is movable, which means that the measured intensity of transmitted light is a function of the displacement of the mirror. The signal obtained is the result of constructive and destructive interference between the light waves reflected off the mirrors. By applying a Fourier transformation on this signal, the signal becomes a function of the wavenumber, the inverse of the wavelength, instead of mirror displacement. The wavenumber is used in the analysis of the gas sample.

Chemiluminescence is another common technique when measuring NO_x , but cannot be used for measuring ammonia concentrations. There are several problems with measuring ammonia concentrations. FTIR spectroscopy becomes a powerful tool when the gas sample to be analyzed has a high temperature, since a method of analysis based on IR spectroscopy in the appropriate spectral window is needed. As the inherent property of FTIR enables detection of all incoming wavelengths at the same time, it is possible to measure a wide range of gaseous compounds with one single instrument.

The analysis of the obtained spectrum is computer aided. The software used in this work is called Grams and provides two alternative analytical methods. Both methods use the principle of spectral subtraction of calibration spectra (spectra obtained from pure samples of known concentration) of compounds of interest from the untreated or raw signal. It should be mentioned that all experimental data presented in the discussion of this section are taken from the actual measurements. The gas sample used in this discussion of the FTIR analysis was taken from the combustion chamber, at the level of the fuel chute.

The first method available is automated and based on an algorithm called partial least squares (PLS), which is a multivariable method of analysis. By importing approximately 20 different calibration spectra for each compound of interest into Grams, the PLS technique is able to automatically identify which compounds the gas contains through identification of the corresponding wavenumbers. Each calibration spectrum corresponds to different concentrations of the compound so that a least squares solution can be found for the investigated sample. The FTIR analysis both identifies the compounds themselves and determines their respective concentrations in the sample.

The second method, demonstrated with an example further down, is based on manual spectral subtraction. Provided that the spectral resolution is high enough, a calibration spectrum with a known concentration for the investigated compound is imported into Grams. Subtracting the calibration spectrum from the raw signal spectrum with an appropriate constant of proportionality, the resulting spectrum will be free from influence of the compound of interest. The calibration spectra used in the subtraction should be for a concentration as close as possible to the concentration in the sample, i.e. keeping the constant of proportionality as close to unity as possible. By repeating the subtraction procedure for different compounds suspected to be present in the sample, the remaining spectrum includes only signals from unknown compounds or noise. The constant of proportionality is needed as the concentration used for the calibration spectra rarely matches the concentration in the sample. The closer the constant is to unity, the smaller the error in the subtraction will be.

Several compounds may absorb energy at the same wavenumber, overlap the signals and making the spectrum difficult to analyze. When this occurs, identification of the compounds has to be made through the use of alternative peaks uniquely originating from the overlapping compounds in the spectrum.

Figure 3 shows a series of spectra from Grams to illustrate the principle of manual spectral subtraction. The figure shows the untreated or raw signal (red) derived from the analysis in the spectral window of 1020-880 cm^{-1} . The peak at approximately 950 cm^{-1} is identified as the main absorbance wavenumber of ethylene/ethene (C_2H_4). Subtracting a calibration spectrum for ethene at a concentration of 440 ppm (green), multiplied by the proportionality constant 0.974 from the raw signal, cancel the influence of ethene on the raw signal with a very high accuracy.

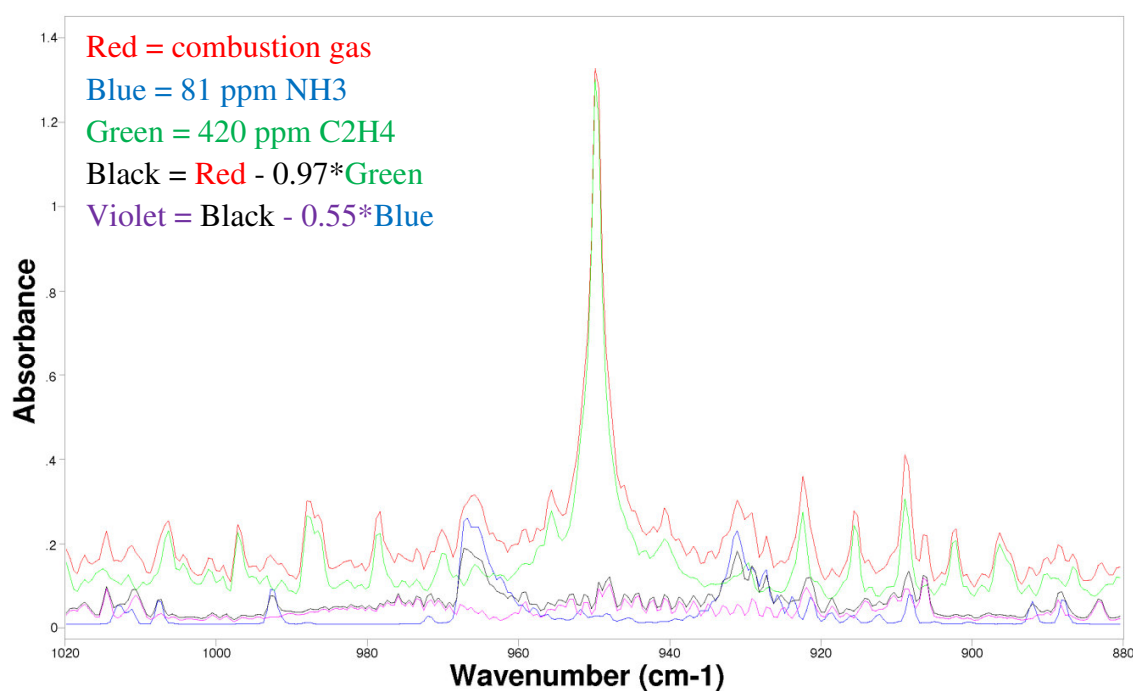


Figure 3: FTIR analysis spectrum for the raw signal and through subtraction of ethane and ammonia

The resulting spectrum (black) shows, after rescaling, two distinct peaks at approximately 965 cm^{-1} and 930 cm^{-1} . The chemical compound absorbing energy of these wavenumbers is

available in literature. By consulting the appropriate tables of resonant wavenumbers, ammonia can be identified as the compound generating peaks at the specified wavenumbers. Subtracting a calibration spectrum for ammonia at a concentration of 81 ppm (blue), multiplied by the proportionality constant 0.546, the resulting spectrum (violet) consists of background noise, possibly originating from the influence of CO₂ or other compounds present in the sample. It was found that the concentration of C₂H₄ was $0.974 \cdot 440 = 429$ ppm and the concentration of NH₃ was $0.546 \cdot 81 = 44$ ppm.

Experimental

The co-combustion experiments with wood chips and straw pellets were performed in the 12 MW CFB-boiler, schematically illustrated in figure 4, at Chalmers University of Technology. The combustion chamber (1) has a square cross-section of 2.25 m² and a height of 13.6 m. The fuel is feed on to the bed surface via the fuel chute (2). The entrained bed material is separated from the flue gases in the cyclone (9) and recirculated to the combustion chamber via the particle return leg (10) and the particle cooler (12). The flue gases leave the boiler via the cyclone and through the convection pass. The flue gas stream exiting the convection pass is cleaned from ashes with a secondary cyclone (16) and bag filters (17). The AmSulphate is injected into the flue gas stream in the upper part of the combustor (25) as the gas is entering the cyclone. The increased gas velocity in the cyclone facilitates good gas mixing. The gas sampling is performed with a heat resistant suction probe after the convection pass (15).

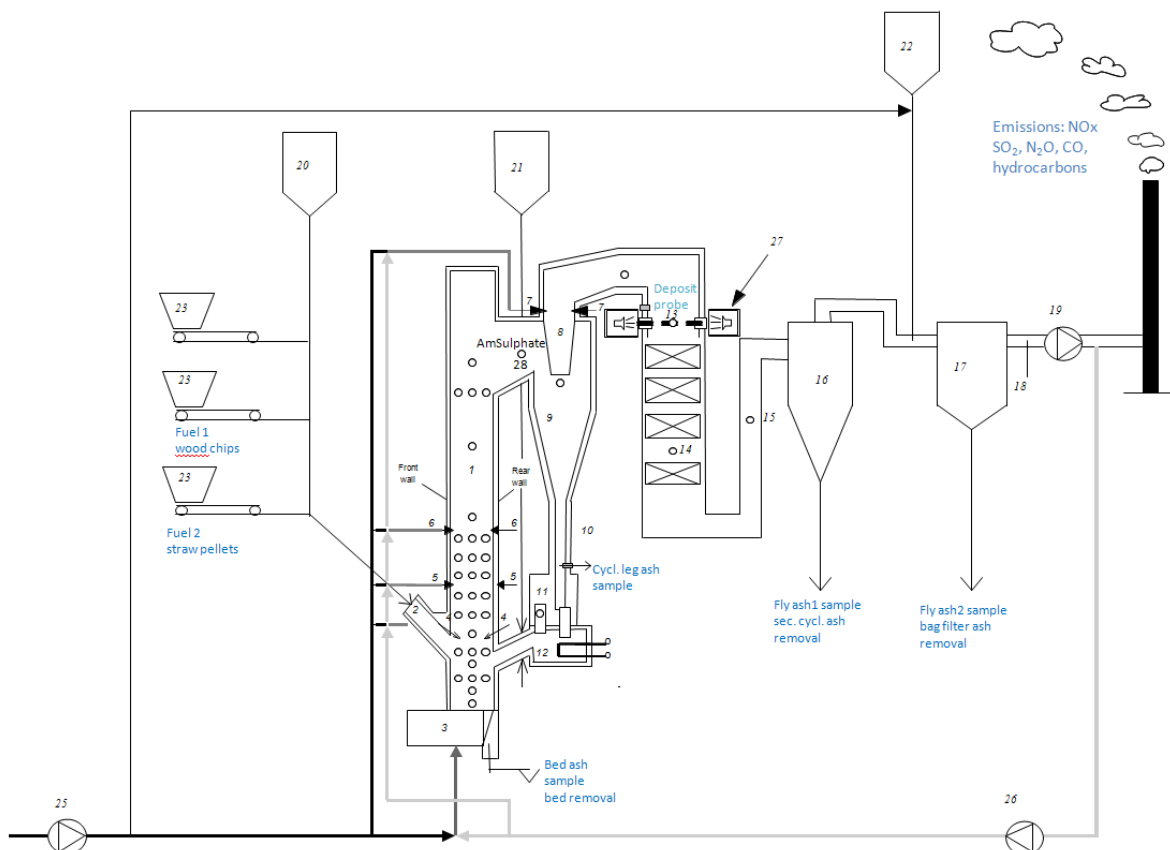


Figure 4: The 12 MW CFB-boiler at Chalmers University of Technology

(1) Combustion chamber, (2) Fuel feed chute, (3) Air plenum, (4) Secondary air inlet at 2.1 m, (5) Secondary air inlet at 3.7 m, (6) Secondary air inlet at 5.4 m, (7) Secondary air inlet into cyclone exit duct, (8) Cyclone exit duct, (9) Hot primary cyclone, (10) Particle return leg, (11) Particle seal, (12) Particle cooler, (13) Measurement hole cr1, (14) Measurement hole cr2, (15) Extraction probe for gas sampling, (16) Cold secondary cyclone, (17) Bag house filter, Lime bin, (18) Gas extraction probe for emission monitoring, (19) Flue gas fan, (20) Sand bin, (21) Lime bin, (22) Hydrated lime bin, (23) Fuel bunkers, (25) Air fan, (26) Flue gas recirculation fan, (27) IACM instrument, (28) AmSulphate injection position

Flue gas sampling system

A gas sampling probe, with an electrically heated sampling tube surrounded by water cooled jacketed, was mounted in the measurement port after the convection pass. The tip of the probe is equipped with a high temperature filter to avoid particles entering the gas analysis system. The gases are transported in heated Teflon tubes from the probe to the analysis instruments by an electrically heated pump. The hot flue gases are continuously analysed in the FTIR instrument and after cooling and water condensation, the flue gas is further analysed in the series of online instruments outlined in figure 5.

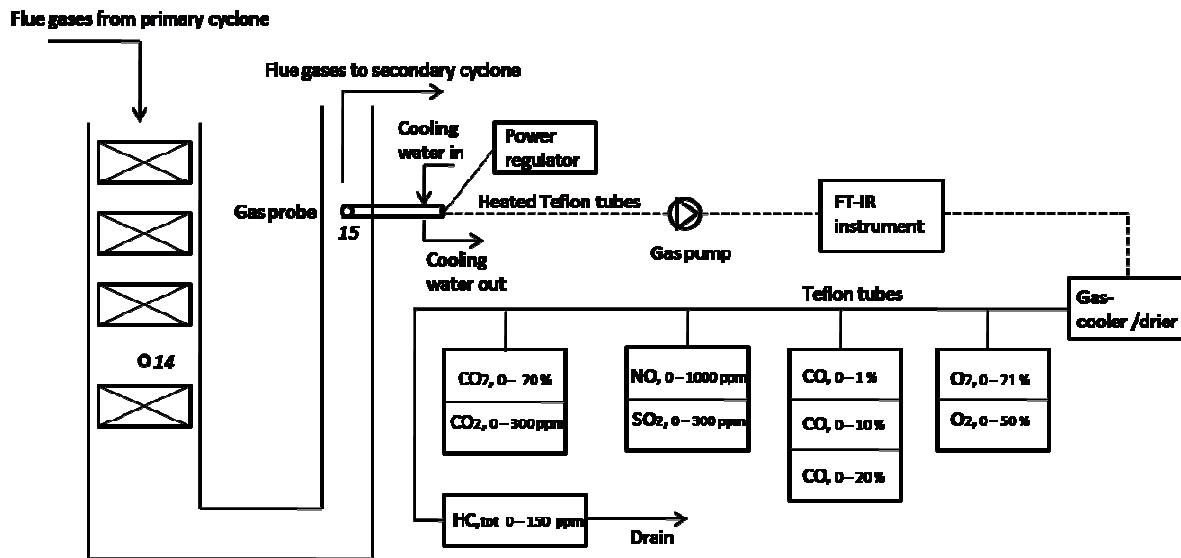


Figure 5: Gas sampling and gas analysis equipment

Experimental method

The co-combustion experiments were performed during a period of two days. Details of the experiments and fuel properties are outlined in tables 1-3. A base case, scenario I, with co-combustion of wood chips and straw pellets and without AmSulphate was performed during the first day. This scenario was used for mapping the nitrogen emissions and conversion in the CFB boiler. During the second day, scenario II, the fuel feeding and operation parameters were kept similar to those in scenario I. In this scenario, AmSulphate was introduced in the flue gas entering the cyclone.

- Scenario I. Co-combustion of wood chips and straw pellets
- Scenario II. Co-combustion of wood chips and straw pellets with AmSulphate injection

Table 1: Fuel and additive feeding rate

Scenario	Components	Unit	Wood chips	Straw pellets
I	Fuel _{input}	kg/h Ds	897	271
	Fuel Nitrogen	kg/h	1.16	2.35
II	Fuel _{input}	kg/h Ds	979	273
	Fuel Nitrogen	kg/h	1.27	2.37
	AmSulphate	kg/h		12.3

Ds = Dry substance

Table 2: Operational parameters

Parameter	Scenario I	Scenario II
Bed temperature [K]	1122	1121
Cyclone inlet temperature [K]	1137	1123
Exit temperature after burner chamber [K]	1139	1125
Load [MW]	5.6	5.4
Excess air ratio	1.18	1.22
Primary airflow/total air flow	0.76	0.77
Superficial velocity [m/s]	4.5	4.4

Table 3: Fuel properties

Proximate analysis	Wood chips	Straw pellets
Water (wt-%, raw)	41.6	13.1
Ash (wt-%, dry)	0.5	3.7
Combustibles (wt-%, dry)	99.5	96.3
Ultimate analysis (wt-%, daf)		
C	50.2	49.4
H	6	6.2
O	43.6	43.2
S	0.01	0.1
N	0.13	0.90
Cl	0.01	0.19
Volatiles	81.4	80.3
Lower Heating Value (MJ/kg)	18.7	18.5

raw = as received, daf = dry ash free

Results and discussion

The measured emissions of nitrogen oxides detected in the flue gas for both scenarios, with and without injection of AmSulphate, are presented in figure 6. The emissions of NO constitute 95% and 88%, respectively, of the total molar flow of oxides in each scenario. From figure 6 it can be seen that in the case with injection of AmSulphate, the emissions of NO decreases, the emissions of NO₂ increases slightly and the emissions of N₂O increases significantly. The measured emissions of NH₃ remain constant in both scenarios.

The decrease of NO does not correspond to the added amount of ammonia, a NH₃/NO ratio of about 5, which suggests an excess of NH₃ which should be detectable as an ammonia-slip in the flue gas but this is not the case.

The emissions of NO₂ increase with nearly 21% and N₂O increase with as much as 297%. Due to the low combustion temperature in biomass fed fluidized beds, relatively high emissions of N₂O are not unusual but injection of NH₃ for NO emissions control can further increase the N₂O emissions [4], which also can be seen in this work. The increase in molar flow of both NO₂ and N₂O in scenario II does not correspond to the decrease of NO, suggesting a reduction of NO_x to N₂ as intended.

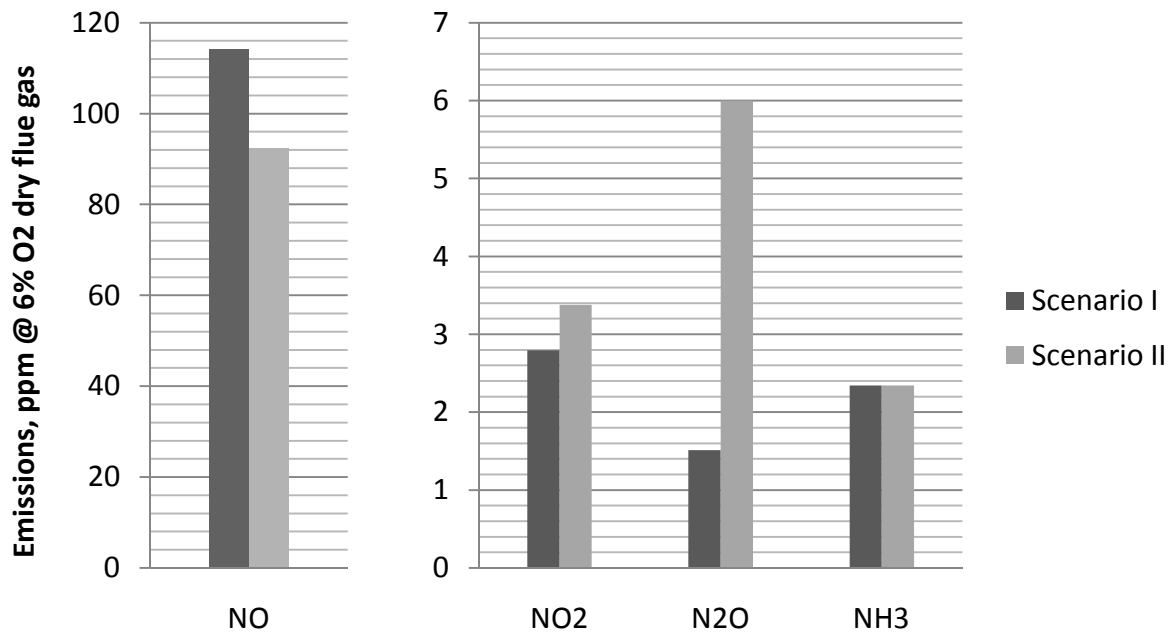


Figure 6: Emissions of nitrogen oxides measured in the flue gas with (Scenario II) and without (Scenario I) the injection of AmSulphate

The conversion of the organically bounded nitrogen in the fuel is calculated, assuming that the nitrogen oxides found in the flue gas originate entirely from the fuel, and shown in figure 7. The fuel-N conversion to nitrogen oxides in Scenario I is only 16%. A significant amount of the nitrogen released from the fuel is not detected as oxides in the flue gas. NO is without a doubt the largest constituent in the emissions, as would be expected. 15% of the fuel-N or 93% of the converted nitrogen is oxidised to NO. In scenario I, a small amount of the fuel-N is converted into NO₂, N₂O and NH₃ (not included in figure 6), 0.37%, 0.40% and 0.31% respectively.

The total conversion of fuel-N to nitrogen oxides in scenario II is 15%, decreased by 1% point compared to scenario I. The conversion of fuel-N to NO reduces to 13% but the conversion to NO₂ and N₂O increases to 0.48% and 1.69% respectively. Since the ammonia concentration in the flue gas is unaffected by the injection of AmSulphate, no conclusions about the ammonia-slip nor the conversion into NH₃ in scenario II can be made.

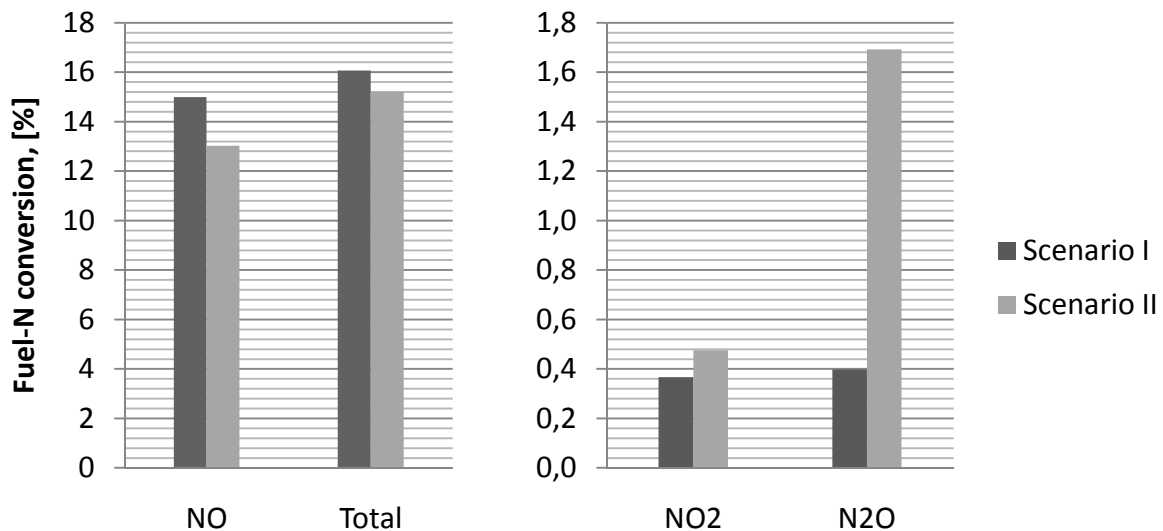


Figure 7: Fuel-N conversion with (Scenario II) and without (Scenario I) injection of AmSulphate

The low reduction of NO emissions, only 19%, achieved by injection of AmSulphate indicates a low efficiency of the thermal DeNO_x process which can be due to several factors.

- Low temperature; the optimum for thermal reduction of NO_x is 1250 K but the flue gases exiting the cyclone only holds a temperature of about 1130 K which is too low for an efficient reduction.
- A high sensitivity towards the level of oxygen concentration at the injection point of AmSulphate; increasing the excess air ratio has a strong impact on the thermal DeNO_x process especially in the present research boiler [7]
- Low NO_x levels; the FBC process generates low NO_x levels also for fuels with high nitrogen content. If the levels are low, a reduction becomes more difficult due to equilibrium limitations.
- High NH₃/NO_x ratio; an excess of ammonia would benefit the reduction of NO_x but would also increase the risk of ammonia-slip and N₂O formation.
- Injection site; the gas mixing is a key parameter and poor mixing will influence the efficiency of the thermal reduction negatively.
- Reaction time; thermal reduction of NO_x requires the reagents to have sufficient residence time, determined by the reaction rate, in the high temperature zone for the process to be efficient. A too high gas velocity, a short mixing zone or a combination of these two would have a negative effect on the efficiency.

Conclusion

The NO_x-reduction capability of ammonium sulphate (AmSulphate) injected into the flue gas stream from the co-combustion of wood chips and straw pellets in a circulating fluidized bed boiler has been investigated. Addition of AmSulphate to the flue gas stream entering the cyclone decreases the emissions of nitrogen oxides (NO_x), and thereby the conversion of organically bound nitrogen in the fuel to nitrogen oxides. The overall reduction of emissions of nitrogen oxides is small, thus a low efficiency for the thermal reduction process is obtained in this work. When the ammonium sulphate was added, no ammonia-slip (increased concentration of ammonia in the flue gas) was observed.

References

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