

EXPERIMENTAL INVESTIGATIONS FOR THE REDUCTION OF NO_x IN AN ENTRAINED FLOW REACTOR

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ABSTRACT

Among the thermochemical conversion technologies, combustion is the only proven technology for heat and power production. In the biomass combustion process, fuel N in biomass can be oxidized into NO_x, causing acid rain or smog. The pollutant formation of NO_x occurs due to fuel constituents like N, Cl, K, Mg, Na, Mg and Ca. Air staging has been developed as a primary measuring to reduce the NO emissions. The NO reduction potential of 50% to 80 % is mainly depending on the combustion temperature, the air ratio, the fuel and the residence time in the combustion chamber.

For the high-temperature combustion investigations of in-furnace DeNO_x technology are carried out using air staging in an electrically heated entrained flow reactor. For the investigations to reduce the NO_x emissions, torrefied biomass (e.g. alder, spruce, birch) and HTC-coals (consisting of compost, grass clipping and leaves) are used. The investigated parameters are temperature from 900 to 1200 °C, the residence time and stoichiometry in the fuel rich primary zone from 0.6 to 1.15.

The experimental results show that the thermal NO becomes important from a temperature of 1200 °C. From a combustion temperature of 900 °C to 1200 °C the NO emissions of HTC-coal increased (at the not staged experiments) by 30 %. Moreover, the effect of air staging in the combustion process was shown to enhance NO reduction over biomass to different degrees. At 1200 °C with a mass flow of 0.8 kg/h and an air ratio of 0.71 in the substoichiometric zone a maximum reduction of NO (75%) can be seen. In addition a strong dependency of the fuel N with the NO emissions is investigated. The burnout values of the cyclone ash reached up to 99.8 %.

1 NO_x FORMATION

1.1 NO_x formation through combustion of biogenic solid fuels

Generally nitrogen oxides (NO_x) are formed through oxidation of nitrogen contained in the air and through oxidation of nitrogen contained in fuels. It is distinguished between three forms of nitrogen oxides [1–4]:

- Thermal nitrogen oxides are formed through oxidation of atmospheric nitrogen with the help of combustion air at high temperatures
- Prompt nitrogen oxides are formed from atmospheric nitrogen and atmospheric oxygen in the presence of radicals of hydrocarbons
- Fuel nitrogen oxides are formed through oxidation of nitrogen, which is chemically bonded in fuel

1.2 NO_x mitigation

NO_x mitigation generally differentiates between primary and secondary measures. Primary measures can either directly reduce the conversion of fuel nitrogen to nitrogen oxides or convert the already built NO_x from intermediates of the combustion to N₂, which is not

harmful to the environment [5]. Possible firing processes of the primary measures are air and fuel staging or exhaust fume circulation. Additionally to a reduction of NO_x in the fuel, the measures of air and fuel staging can reduce emissions from thermally formed NO_x [6]. When NO_x emissions cannot be reduced sufficiently by primary measures, secondary measures are utilized for mitigation. Thus exhaust fumes are added to the nitrogenous reducing agents, which convert the NO_x to harmless N_2 . One differentiates between the selective non-catalytic reduction (SNCR) and the selective catalytic reduction (SRC) [7, 8].

1.3 Air staging

For this work the primary measure of air staging is of particular relevance. The addition of combustion air during air staging takes place in two zones of the combustion chamber (see Figure 1). In the first zone ($\lambda < 1$) a part of the combustion air, namely the primary air, is reacted with the fuel. At first a short gasification zone forms, in which the volatile nitrogen compounds are released from the fuel. In the following reduction zone they are transformed to N_2 . The differentiation between the gasification and the reduction zone serves for a clarification that firstly the volatiles need to be released from the fuel. Especially for the biomass, which can contain up to 80 % volatiles, this step is not negligible. In practice, however, the gasification zone and the reduction zone are merged so that no difference can be observed [6].

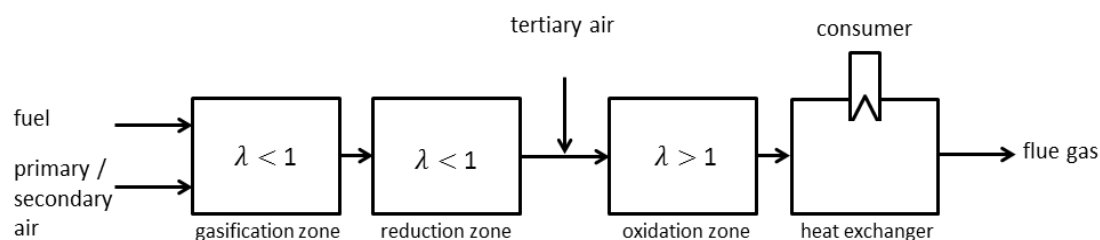
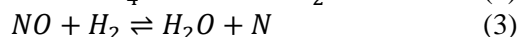
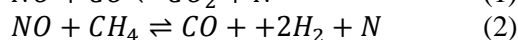
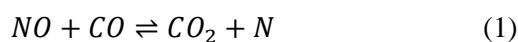


Figure 1. Principle of air staging [6]

Thus direct oxidation from nitrogen compounds to NO_x is prevented by the defined reducing conditions (lack of air). So an increased amount of NH intermediates forms which is converted to N_2 with the already existing NO_x . In addition to that, the reducing conditions of the first zone affect other compounds of the combustion process. Unburned compounds, such as CO , C_nH_m and H_2 , can additionally use NO_x according to the following reactions and with that contribute to a reduction of emissions [6, 9, 10].



The introduction of the secondary air, also called burnout air, into the secondary combustion chamber ($\lambda > 1$) shall finally provide a proper burnout of the fuel.

With the help of air staging and under suitable conditions, the NO_x emissions can be reduced to approximately 50 %. In the literature the following test conditions are recommended to achieve a minimal NO_x emission by means of air staging [6]:

- Residence time > 0.3 s (ideally approx. 0.5 s) and proper mixing of the gases in the reduction zone
- Temperature in the reduction zone between 1100 and 1200 °C
- Primary air ratio λ between 0.7 and 0.8

The correct configuration of the air ratio is particularly important. When the value is set lower than 0.7 there is hardly any NO_x in the reduction zone. NH compounds that are increasingly formed under reducing conditions can no longer react with the NO_x and thus are oxidized to NO_x in the secondary combustion chamber. For $\lambda > 1$ in the primary zone the

nitrogen compounds of the fuel are already oxidized in the gasification zone. Therefore the formation of NH compounds in the reduction zone is prevented which would have led to a NO_x reduction. Thus the two described configurations of the air ratio affect the NO_x reduction negatively [6].

In practice it can be observed that for a λ_{total} , which only marginally exceeds 1 (minimal total excess air), the lowest NO_x emissions can be measured. The λ_{total} represents the air ratio in the secondary combustion chamber. Consequently a CO- λ -Control is recommended for the combustion of biogenic fuels, for the excess air can be set to a minimum without an increase of the CO emissions.

Beside the correct selection of the primary air ratio, the temperature and the residence time, the location of the secondary air supply (burnout air) plays an important role for the NO_x mitigation. When the burnout air reaches the combustion chamber too soon, i.e. the residence time of the fuel particles in the reduction zone is too short, this can, in the worst case, lead to NO_x emissions that are even higher than they are during a not-staged combustion.

2 METHODS

2.1 Gas analysis

The flue gas is analysed with ULTRAMAT 23. It is a multi-component design with NDIR sensors for IR-active gases and has an electrochemical cell for oxygen measurement.

2.2 Ash treatment

The methods used for the ashing or incineration heat-up and holding periods are according to DIN EN 14775. A holding period of 13 h was chosen to ensure a full implementation of larger sample volumes during incineration.

2.3 Data evaluation from gas analysis

The measured NO emissions in the measuring cabinet have to be converted for a reference oxygen content $x_{O_2,B}$ of 6 Vol-%. This value mostly applies for biomass combustions and is therefore used in this work. So the NO concentration is calculated as follows [11]:

$$c_{NO,ref} = \frac{21-x_{O_2,ref}}{21-x_{O_2,m}} \cdot c_{NO,m} \quad (4)$$

where $c_{NO,ref}$ is the NO concentration in ppm, which is referenced to 6 Vol-% O₂ and $c_{NO,m}$ is the measured NO concentration in ppm. $x_{O_2,ref}$ and $x_{O_2,m}$ stand for the reference and measured oxygen content in Vol-%.

For better comparability the data obtained from gas analysis is evaluated using linear regression [12]. The measured NO values during a test series are plotted against the corrected residual oxygen values. The correction of the residual oxygen is carried out using mass balances for combustion reaction measurements. In doing so, the reference period between NO and O₂ has to be maintained. As known from combustion calculation, a λ of 1.15 requires a residual oxygen of 2.80 Vol-%. Inserting this value of 2.80 Vol-% in the equation of the trend line the corresponding mean NO value is obtained, which belongs to $\lambda = 1.15$.

To calculate the residence time ideal plug flow is assumed:

$$\tau = \frac{L_{reaktor} \cdot \left(\frac{d_{tube}}{T}\right)}{\dot{V}_{fg,w} \cdot \frac{T}{T_{STP}}} \quad (5)$$

The length of the reaction zone $L_{reaktor}$ [m] is determined depending on the configuration. The diameter of the ceramic tube d_{tube} is 0.15 m. $\dot{V}_{fg,w}$ [Nm³/s] refers to the volume flow rate of the wet flue gas $\dot{V}_{fg,w}$ under standard conditions (STP). With the aid of the factor T/T_{STP} the actual flow rate at the reaction temperature T is obtained.

3 EXPERIMENTAL SETUP

The reactor is 2.3 m high and consists of five segments which are arranged horizontally, as pictured in figure 2. A heat resistant ceramic tube inside the reactor forms the actual combustion chamber. This ceramic consists of five segments. Each ceramic tube section is surrounded by six heating units, which are arranged in a circle around the tube. The heating units have a combined power of 50 kW and can heat the ceramic tube to the desired operating temperature. Via a vibrating chute of a small quantity proportional scale a homogeneous transport of the fuel into the reactor is ensured. When the combustion chamber is heated up to the desired temperature the fuel is introduced from above through the dosing system and air. When there are steady-state operating conditions the measurement can be started. Every metering point is remained constant for at least 10 minutes.

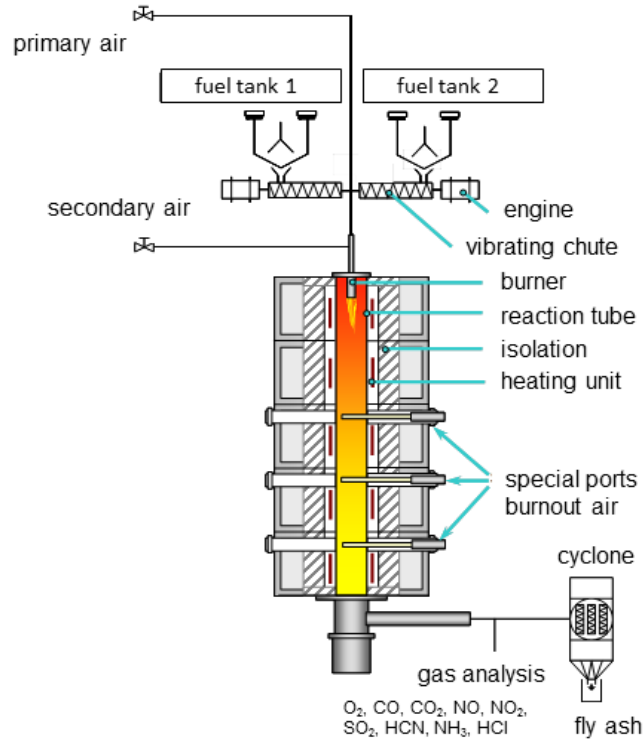


Figure 2. Entrained flow reactor

In this experiments algae, wheat straw, torrefied woods and HTC-coal were used as fuels. The raw material of the hydrothermal carbonized coal are a mixture of leaves, grass clipping, compost and other biogenic residues. The following table shows the mean particle size of the used fuels:

particle size	d50 [μm]
algae	514
wheat straw	82
torr. birch	90
torr. spruce	84
torr. alder	95
HTC-coal	80

Table 1. Mean particle sizes

4 RESULTS

The total nitrogen content of the used fuels is presented in figure 3. The nitrogen content rises significantly from the wooden biomasses to the straw-based and the HTC-coal up to the algae.

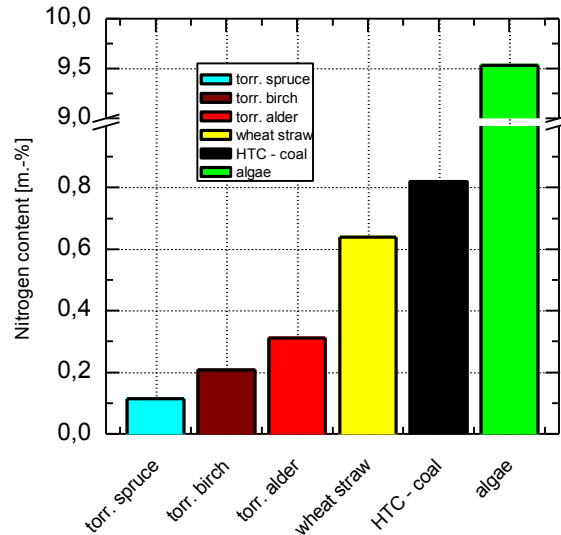


Figure 3. Nitrogen content of the used fuels

The following figure 4 shows the experimental setups for the different test series. Test series 1 helps to examine the influence of temperature and fuel at a constant air ratio ($\lambda = 1.15$) and constant fuel mass flow rate (1 kg/h). Based on this, at test series 2 the fuel mass flow is varied (0.8, 1.2, 1.4 and 1.6 kg/h) whereas the air mass flow rates remain constant. The main focus is to investigate the influence of temperature and stoichiometry and the associated nitrogen oxide mitigation. Test series 3 shows air staging, where staging occurs in port 1 or 2 (in this case at port 2) and sampling of the gas phase takes place at port 3.

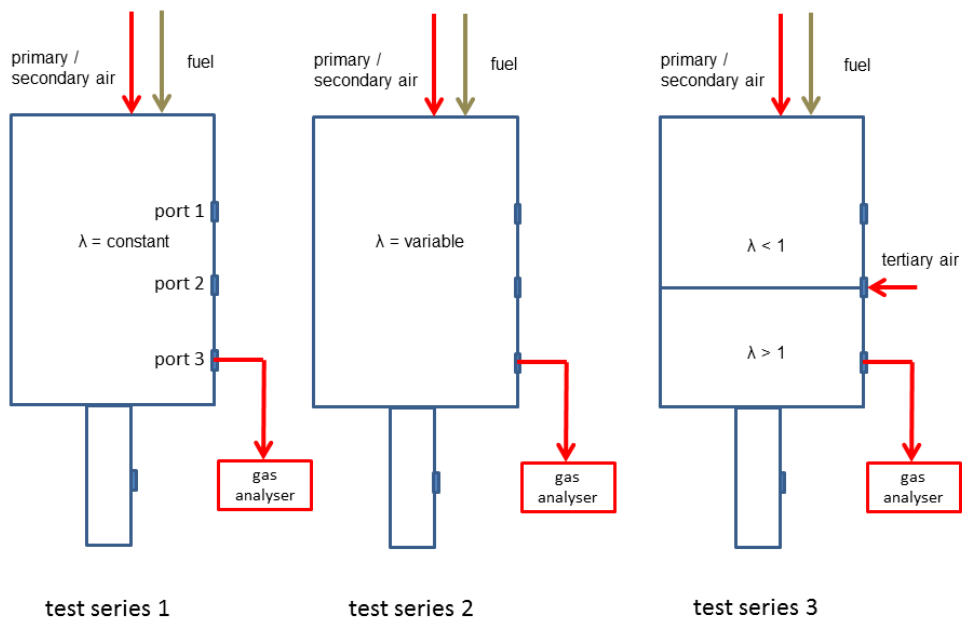


Figure 4. Schematic description of the test series

4.1 Experiments of the test series 1

This series of experiments is conducted at a reactor temperature of 900 °C, 1200 °C, 1300 °C and 1400 °C and with a constant fuel mass flow of 1.0 kg/h. The objective is to compare the different fuels for the same stoichiometry ($\lambda = 1.15$). If necessary, the temperature dependence of the emissions shall be observed as well. The fuels are torrefied birch, torrefied spruce, torrefied alder, algae, HTC coal and wheat straw. The gas analysis in this series of experiments takes place in port 3. When looking at Figure 5, the emissions of algae show an increase of NO emissions with increasing temperature. This increase can mainly be attributed to thermal NO. At temperatures higher than 1300 °C the release of nitrogen from the fuel only plays a subordinate role. Comparing the different NO emissions of the fuels, each of them shows the same trend. Fuels with higher nitrogen content show higher NO emissions. With 1100 ppm the algae has the highest NO emissions. The HTC-coal shows the second highest emissions with about 450 ppm. Wheat straw shows the third highest values which are in the range of 220 ppm to 360 ppm. The critical value for NO_x, stated as NO₂, for a daily average of the rated thermal input of 500-100 MW is at 250 mg/Nm³ (in terms of 6 % O₂). Converted, this equals a concentration of 122 ppm [13]. Since at atmospheric conditions NO is converted to NO₂, therefore this limit is representative for the conducted measurements. In this test series the critical value is not achieved.

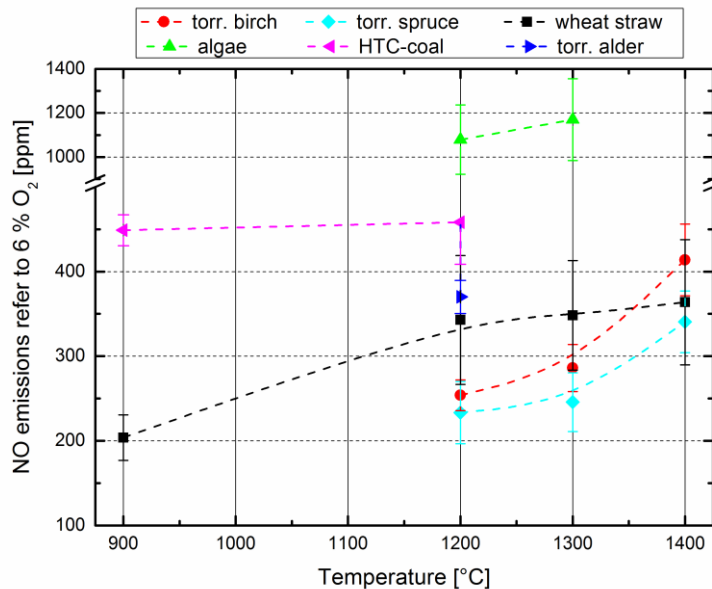


Figure 5. NO emissions as a function of the fuels and the temperature for $\lambda=1.15$

Figure 6 shows the overall conversion of the cyclone ash, calculated using the ash tracer method [14]. The torrefied spruce shows the highest values for the burnout. The values increase with a rising reactor temperature and at 1400 °C they almost reach 100 %. The burnout values of the cyclone ash of the torrefied birch are constantly above 99.8 %. No clear trend for the spruce with regard to the temperature can be seen. But since the burnout of more than 99.8 % is particularly high, this could be attributed to measurement inaccuracies. In comparison to the torrefied woods, the wheat straw has constantly low burnout values. At 1200 °C the value is 99.55 % and therefore it is particularly lower than the values for the woods. The worst values for the burnout of the cyclone ash can be observed for the algae. The values are between 98.5 % and 99.0 % and with that are almost one percentage lower than for the remaining fuels. This could be attributed to the particularly larger fuel particles and therefore in the resulting shorter residence time.

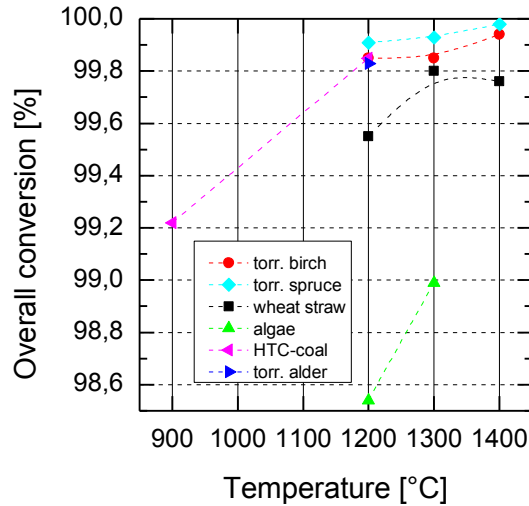


Figure 6. Overall conversion of the cyclone ash as a function of the temperature. The values belong to the NO and λ -values from Figure 5

In summary, it can be stated that the burnout values of the cyclone ash are no less than 98.54 %. In average, wheat straw, spruce and birch show burnout values of 99.8 % and higher. The burnout is almost complete for all temperatures and should not influence the increasing NO emissions with rising temperatures. The burnout of the HTC-coal increases sharply from 900 to 1200 °C and has almost the same value as torr. alder and torr. birch at 1200 °C.

4.2 Experiments of the test series 2

The experiments at variable mass flow shall display the dependency of NO emissions on the air ratio λ . Therewith additional insights can be gained according to the NO mitigation by a reducing zone in the reactor (see Figure 4; test series 2). In Figure 7 some results of this series of experiments at variable mass flow is shown for 1200 °C (on the left) and for 1400 °C (on the right). In both diagrams the estimated trend is apparent: The higher λ and the related air ratio during the combustion, the higher the NO emissions. Similarly, the already stated dependency of the NO values on the N content of the fuel can be seen once again. Algae shows the highest, the torrefied birch shows the lowest NO values. Furthermore, a slight temperature influence on the NO emissions can be observed. For a constant λ averaged NO concentrations at 1400 °C are higher than those at 1200 °C.

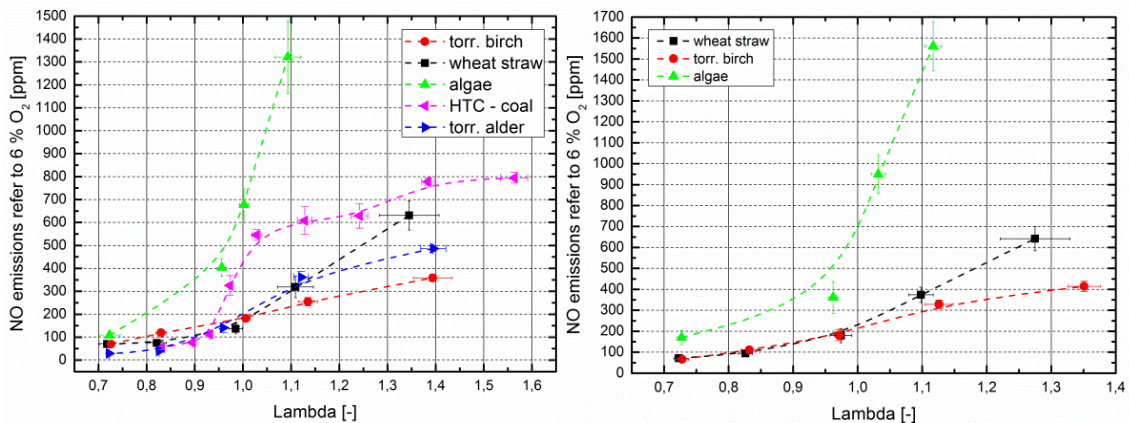


Figure 7. NO emissions as a function of λ at 1200°C (on the left) and 1400°C (on the right)

With the help of the two diagrams the strong NO reduction potential for the reduction of the air ratio can already be seen. For instance, comparing the NO emissions of birch (1400°C) at approximately $\lambda=1.1$ and $\lambda=0.8$, the values drop from 300 ppm to approximately 100 ppm. This equals a mitigation of 67 %. For wheat straw the values at the respective air ratios drop from approximately 370 ppm to around 90 ppm, so the NO mitigation is higher than 67 %. For algae the NO values drop from approx. 1400 ppm to around 300 ppm. Here the reduction rate is highest with a value of 78 %. Therefore a clear trend can be seen: The higher the nitrogen content of the fuel, the higher the mitigation potential. Thus algae shows the highest mitigation potential followed by wheat straw and torrefied birch. Here the recommendations in literature for the selection of the reduction fuel for fuel staging are reflected. It is recommended to create reducing burning conditions by means of a secondary fuel with a volatile content that is as high as possible and a high nitrogen content in order to produce as many NH_i - and CH_i -compounds as possible. These compounds convert the existing NO to N_2 . The algae shows a higher volatile content and by far the highest N content in this campaign. This explains why the algae shows the highest mitigation rate when the air ratio is decreased. The increase of the HTC-coal at 1200 °C follows neither a linear nor an exponential developing of values. At an air ratio from 1.0 to 1.3 the NO emissions increase insignificantly.

4.3 Experiments of the test series 3 (air staging)

At the air staging (test series 3) three different measuring points are measured. In the following, the procedure at port 1 is shortly described: In the beginning the fuel mass flow, here named basis mass flow, is set to a certain value (0.6 kg/h). With a suitable air mass flow a particular air ratio (here: 1.15) at port 1 can be obtained. Then, at constant air mass flow, the fuel mass flow is raised (0.8, 1.0 and 1.2 kg/h) and the NO emissions of this substoichiometric zone ($\lambda < 1$; see Figure 8 above; marked with black columns) are measured. These experiments are repeated with a basis mass flow of 1.2 kg/h and a raise of the fuel mass flow to 1.6 and 2.0 kg/h ($\lambda < 1$; see Figure 8 below; marked with black columns). The objective is to determine the influence of different residence times. Next, the mass flows higher than the basis mass flows are set and tertiary air is injected in port 1. The withdrawal of gas takes place at port 3 ($\lambda = 1.15$; see Figure 8; marked with blue columns). To compare and to evaluate the staging effect, non-staged experiments are run for all mass flow rates, which means that the primary and secondary air are adjusted to the fuel mass flow so that in port 3 an air ration of 1.15 can be determined. Examinations at port 2 are carried out in the same manner ($\lambda = 1.15$; see Figure 8; marked with red columns).

Looking at Figure 8 and 9, the effect of air staging becomes particularly apparent when comparing the staged and the non-staged experiments. Since the air ratio is identical the differences in NO concentrations can completely be attributed to the effect of air staging. The staging experiments are grouped by temperature and contain five measurements at each temperature: three at a basis mass flow of 0.6 kg/h and two at a basis mass flow of 1.2 kg/h. All experiments were carried out with HTC-coal. The values show that air staging has a serious influence on NO concentration: in the majority of the experiments a reduction of NO of over 50 % compared to the non-staged value can be observed. The effect of air staging decreases with rising basis mass flow at 900 °C, which is equivalent to a shorter residence time. Within one set of basis mass flow, one trend repeats itself (see Figure 8): the effect of air staging declines slightly with a decreasing λ in the reduction zone. So at a fuel mass flow of 0.8 kg/h the relative NO reduction averaged over port 1 and port 2 is approximately 65 %. Increasing the mass flow to 1.0 kg/h already results in a lower NO reduction %. A further increase to 1.2 kg/h is followed by a further decrease to 58 %. Furthermore, the low values of NO reduction in port 2 at mass flows of 1.0 kg/h and 1.2 kg/h can be noticed. However the reduction of NO concentration remains more than 50 %.

At a basis mass flow of 1.2 kg/h the experiments at 1.6 kg/h such as at 2.0 kg/h show a minor decreasing NO concentration from port 1 to port 2. At a basis mass flow of 0.6 kg/h the port has a significant influence. All three measurements clearly show a higher reduction at port 1.

The difference of NO mitigation between port 1 and port 2 is around 13 %. This trend cannot be observed at a basis mass flow of 1.2 kg/h.

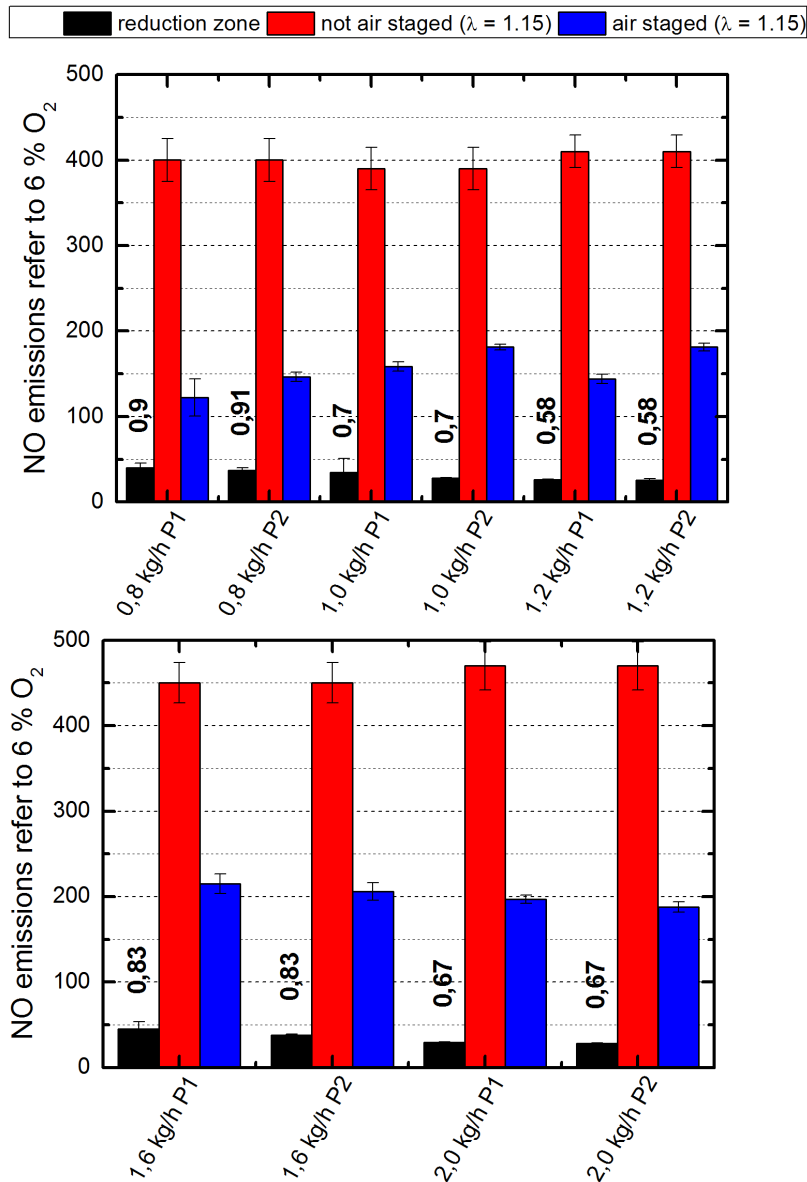


Figure 8. Comparison of the substoichiometric (λ is marked above the black columns), the unstaged and the air staged NO emissions at 900 °C. Above: Based on the basis mass flow of 0.6 kg/h. Below: Based on the basis mass flow of 1.2 kg/h

Looking at NO concentrations of non-staged experiments at different temperatures, a higher value at 1200 °C can be observed (see Figure 9). The difference in the values reaches up to 200 ppm. The difference in concentration between the temperatures can be explained with the formation of thermal NO. At temperatures higher than 1200 °C, thermal NO is formed from nitrogen in the combustion air. Therefore at 900 °C it can be ignored. At 1200 °C, the formed thermal NO correlates with the air ratio λ : The more oxygen is available for combustion, the more thermal NO can be formed. With increasing mass flow at constant air mass flows the air ratio λ is decreasing and therefore the formation of thermal NO decreases, too.

In contrast to air staging at 900 °C, only a minor increase in the effect of staging with increasing basis mass flow can be observed (from 1.6 to 2.0 kg/h). Whereas at 900 °C the NO concentration at a basis mass flow of 0.6 kg/h throughoutly drops by over 55 %, at 1200 °C the values lie around 65 % and therefore are 10 % above the values for 900 °C.

Comparing the NO reduction between port 1 and port 2 at a basis mass flow of 1.2 kg/h at 1200 °C, the same trend as already stated at 900 °C can be observed: for both mass flows 1.6 kg/h and 2.0 kg/h the air staging at port 2 shows slightly better results than staging at port 1, which applies for the absolute concentration as well as for the relative reduction.

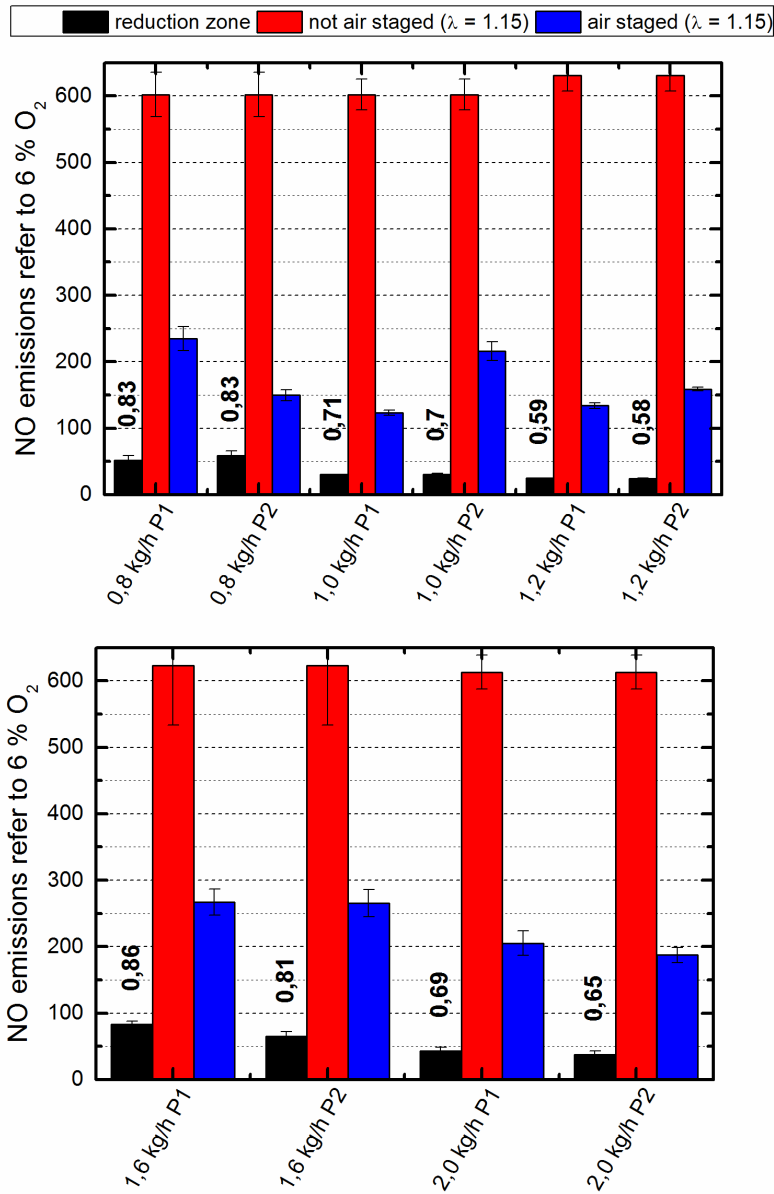


Figure 9. Comparison of the substoichiometric (λ is marked above the black columns), the unstaged and the air staged NO emissions at 1200 °C. Above: Based on the basis mass flow of 0.6 kg/h. Below: Based on the basis mass flow of 1.2 kg/h

5 SUMMARY

The experiments of the test series 1 show that NO emissions rise with an increasing combustion temperature. The rise is neither caused by a higher burnout nor by the release of the nitrogen contained in the fuels but rather occurs due to the formation of thermal NO. The burnout is not less than 98.5 % for all tested temperatures and thus is very high. The algae shows by far the highest NO emissions. The N content of the fuels is reflected in the NO emissions for all fuels. The nitrogen release was determined by means of the ash tracer method and was found to be more than 99 %. Thus the fuels with higher N content, such as straw and algae, show the highest release values.

The experiments of the test series 2 display the dependency of the stoichiometry on NO emissions. As expected, the NO emissions increased with an increasing air ratio. The algae showed the highest NO mitigation potential. With a reduction of the air ratio from 1.1 to 0.8 the NO concentration of the exhaust fumes can be reduced by 78 %. A trend was revealed: with increasing N content in the fuel the mitigation potential increases. Test series 3 revealed a significant reduction of NO emissions through air staging. The maximum reduction of the NO emissions can be detected at 1200 °C with an air ratio of 0.7 in the substoichiometric zone.

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