LANDTECHNIK 70(5), 2015, 181–192

DOI:10.15150/lt.2015.2674

New NO_x reduction methods in utilizing agricultural residues as energy source

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From the points of view of economy and energy policy, the utilization as an energy source of agricultural residues, such as hay, straw and residues from cereal cleaning, is a major issue. However, in terms of firing technology, this is demanding compared to wood fuels due to the unfavourable fuel properties of residues. In a joint project, a new combustion concept has been developed and thoroughly tested. In addition to achieving a largely complete combustion especially the nitrogen oxide emissions could be significantly reduced. The examinations revealed a clear correlation of nitrogen oxide concentrations in the flue gas and the reducing conditions in the burnout zone, which could be imaged using numerical flow and combustion simulation. The knowledge gained provides valuable data for the development of new firing systems for agricultural residues and their optimal operation.

Keywords

Biomass, agricultural residues, combustion, nitrogen oxides, CFD simulation

The strong demand for wood fuels and the rising prices of energy sources lead to searching for alternative biomass fuels, such as hay, miscanthus, straw or grain residues. The firing systems with small and medium capacities currently available on the market for agricultural residues are, without a high maintenance effort, neither sufficiently reliable in operation nor do they comply with the emission limits for newly constructed plants. Therefore, the focus of the joint project was to examine the fundamental processes in the thermal decomposition of biogenic fuels in firing systems of small and medium capacities ranging from 50 to 500 kW. The tests included primary reduction measures for nitrogen oxides. These measures must be feasible along with the most complete combustion possible and thus low levels of incomplete combustion products over a wide capacity range. In the joint project with a firing system manufacturer, these requirements were translated into a prototype with a new combustion concept for the thermal utilization of agricultural residues. This prototype was used to carry out combustion experiments with hay pellets, representing agricultural residues, as well as with wood pellets in DINplus quality, as a reference fuel.

received 3 March 2015 | accepted 24 July 2015| published 1 October

Formation and reduction of nitrogen compounds

The nitrogen content of the fuel directly affects the nitrogen oxides emissions from biomass combustion, considered here in the power range up to several hundred kW (Keller 1994, Hartmann et al. 2007, Eder et al. 2006). The nitrogen oxide concentration in the flue gas, at comparable combustion conditions, increases with rising fuel nitrogen content. The oxidation of the nitrogen bound in the fuel is the main formation path for nitrogen oxides in this respect. The formation of thermal or prompt nitrogen oxides is only of secondary importance due to the combustion temperatures which are too low. Keller (1994), among others, shows this in combustion tests by substituting argon for the atmospheric nitrogen. Keller's work summarizes the process and the possible reaction pathways in nitric oxide formation. In the thermal decomposition of biomass, for instance, the predominant part of the fuel nitrogen is released as elemental nitrogen. A smaller proportion of the fuel nitrogen is released as nitrogen oxide-forming components such as hydrogen cyanide (HCN), ammonia (NH_3), and nitric oxide (NO) – the latter takes to a lesser extent part in forming nitrogen dioxide (NO_2). The components NO and NO_2 are collectively referred to as NO_x and are calculated as mass of NO_2. A certain fraction of the fuel nitrogen is not released and remains in the combustion residues.

The extent to which NO_x forms from the nitrogen oxide-forming components in the ongoing combustion process or already formed NO_x is maintained depends on the conditions in the subsequent reaction zones. In basically oxidative conditions, high NO_x concentrations result in the flue gas. An effective primary reduction of the NO_x concentration in the flue gas will only be achieved if a defined reduction zone is present at controlled combustion conditions. The main parameters having an influence on the decomposition of the formed nitrogen compounds are the temperature, the oxygen concentration, and the content of methane, hydrogen cyanide and ammonia in the reduction zone. The concentrations of hydrogen, water vapour, carbon monoxide and carbon dioxide have no significant impact on the reduction of the nitrogen compounds. In the homogeneous reduction of hydrogen cyanide and ammonia in the gas phase, maintaining the stoichiometric ratios decides whether they further react to NO_x or to molecular nitrogen (N_2). Under oxygen-deficient conditions, NO_x formation is suppressed and the equilibrium shifts in the direction of molecular nitrogen. For the complete decomposition of nitrogen compounds in the gas phase, the following conditions should be met (Keller 1994):

- Temperatures in the reduction zone 1100–1200 °C
- Air-deficient conditions
- Absence of methane
- NO/NH_3 mole ratio of 2
- Homogeneous concentration distribution of the reaction partners.

New combustion concept for agricultural residues

For agricultural residue combustion, small and medium-sized firing systems, designed for wood fuel, are only of limited use. The high ash content and low ash melting points of many agricultural residues often lead to operational problems through massive slagging in the fuel bed. This entails performance degradation, high emissions of incomplete combustion products and problems with discharging the combustion residues. The partially high nitrogen contents of agricultural residues result in high to very high nitrogen oxide emissions. In practice, this may lead to an exceedance of limit values for firing systems within the scope of TA Luft (2002) or, in the type test, to non-compliance with the emission limit requirements concerning appliances within the scope of the German Small Furnace Ordinance (1. BImSchV) of the Federal Emission Control Regulation (2010). In order to avoid these problems, a new combustion concept for the thermal utilization of agricultural residues has been developed in a joint project with a manufacturer. The concept design provides for the combustion phases being divided into separate reaction spaces, namely devolatilization, oxidation of the pyrolysis gases, and oxidation of the devolatilization residues.

Figure 1 shows the schematic diagram of the combustion concept, which was implemented in a prototype mounted on a commercially available heating boiler. To counteract sintering and slagging in the fuel bed, the fuel should devolatilize at the lowest possible temperatures. This is achieved by setting the lowest possible excess air ratio in the primary devolatilization zone. In addition, a moving component to prevent fouling and to dissolve already formed slagging is fitted in the primary devolatilization zone. The discharge of fuel and ash particles is minimized by the relatively low flow velocities in the primary devolatilization zone. This makes it possible to keep the dust concentrations in the flue gas comparatively low.

The pyrolysis gases developed in the primary devolatilization zone are mixed with secondary air and almost completely oxidized in the subsequent burnout zone in a flame tube. Excess air and devolatilization temperatures being on a low level in the primary devolatilization zone, the carbon in the fuel cannot be fully converted. This devolatilization residue consists of incompletely reacted fuel and ash. For full fuel conversion, the devolatilization residues get transferred to the underlying secondary devolatilization zone and further oxidized by adding combustion air. The presented experimental results were mostly obtained without using the secondary devolatilization zone. Involving this zone complicates the balancing of the material flows necessary for the study because, here, it is more difficult to set and reproduce steady-state conditions. In the secondary devolatilization zone, no fuel or only very little was converted. The combustion gas thus corresponds to the primary combustion air in this case.

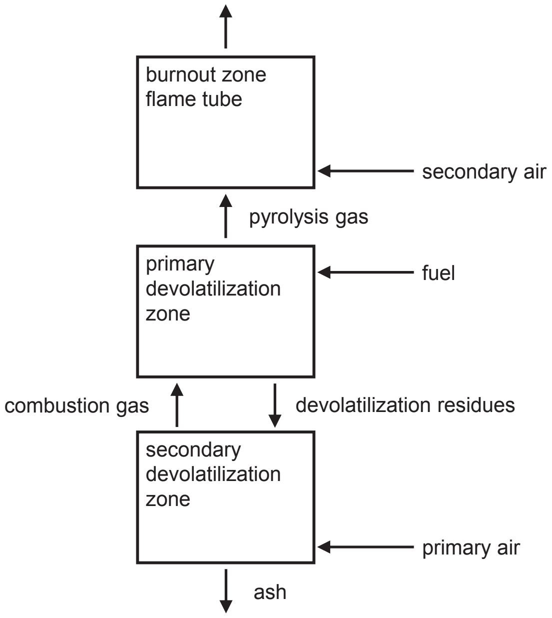

Figure 1: Schematic diagram of the combustion concept implemented in the prototype

Since the ignition and heat-up phases with hay pellets lasted relatively long and were accompanied by some higher emissions and odour pollution, the experiments were mainly carried out with wood pellets. Moreover, using hay pellets, a steady-state condition could not be ensured over a longer period regardless of the operational state, as slagging and irregular devolatilization processes occurred occasionally in spite of the moving component.

The prototype was installed at the Institute of Combustion and Power Plant Technology (IFK) and operated with wood and hay pellets for the measurement tests. For the evaluation of the prototype, a comprehensive material flow balance was created, making it possible to show the influencing parameters in the formation and reduction of nitrogen oxides. Figure 2 shows the balance diagram for the implemented combustion concept. The balance and control calculations could be compared with the measured values. It was possible this way to determine the degree of conversion of carbon into CO_2 (X_C) and the degree of conversion of fuel nitrogen to nitrogen oxides (X_N). The respective conversion degree is the molar ratio expressed as percentage of the released compound (CO_2 and NO_x as NO_2), measured in the flue gas, and the quantity of the substance (C and N) introduced by the fuel, minus the remaining amount of the substance (C and N) in the devolatilization residues. For the balance, the further oxidation of the devolatilization residues was dispensed with. These residues were discharged from the firing system by the ash screw after they had been removed from the primary devolatilization zone. Air infiltration through holes and leaks in the boiler and in the flue gas path happens within the balance area and must be determined in consequence. Being not measurable, this air leakage had to be estimated. The estimation was based on an experiment where the heat output, the primary air flow and the negative combustion chamber pressure were kept constant over a period of more than two hours. In this experiment, the flue gas was controlled to three different residual oxygen levels. The balance equation as shown in Figure 2 was solved by choosing the carbon conversion in all three sets of measurements in a way that the energy balances over the two-hour test period showed the smallest deviations. Thereafter, the infiltrated air was set for all three sets of measurements in a way that the results with all three of them were again the same

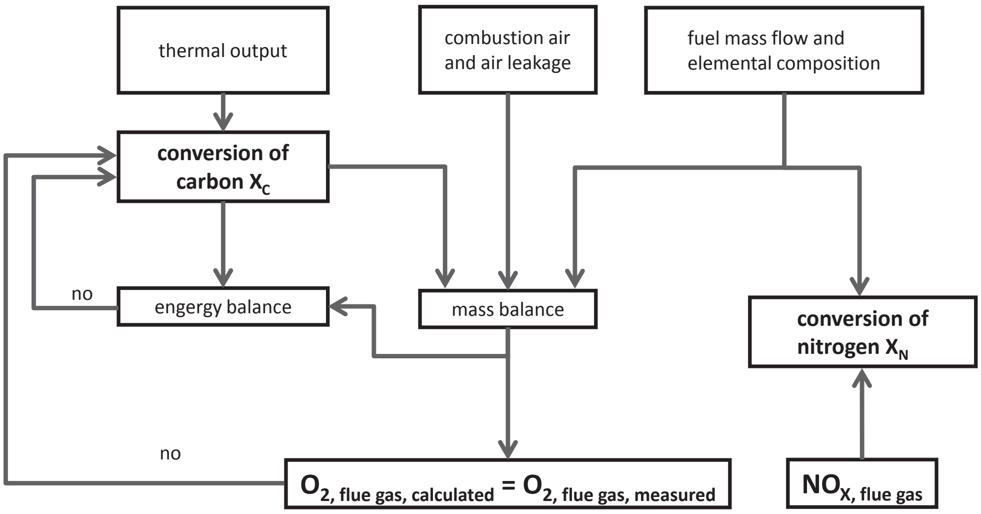

Figure 2: Schematic balance diagram for calculating the conversion degrees of X_C and X_N

values for both the calculated and the measured oxygen concentration in the flue gas. The leaked amount of air thus determined was then adopted for all tests and assumed to be constant at constant negative combustion chamber pressure.

Excess air ratios were calculated for each of the balance areas of the primary and secondary devolatilization zones and the burnout zone. The excess air ratio for the balance area comprising the primary and secondary devolatilization zones is specified as primary air ratio and the excess air ratio for the balance area of the burnout zone is the total air ratio. The primary and the total air ratios always refer to the total of the fuel, that is to say the quotient of the actual combustion air to the minimum combustion air required for complete fuel combustion is generated. The air ratios are thus independent of the degree of carbon conversion. Since the conditions in the fuel bed in the primary devolatilization zone could not be accurately determined, the calculated conversion degrees for carbon and nitrogen still bear some uncertainty. The influencing factors here include the local temperatures in the fuel bed, the fuel bed height, the ratio of fresh fuel to devolatilization residues, the intensity of the fuel movement and the local excess of oxygen in the fuel bed. To compare the various operating states and fuels, the measured values must be converted to a standardized reference oxygen content value. Therefore, all results are based on 13 % $O_{2.}$

Figure 3 shows as an example the degree of carbon conversion X_C over the primary air ratio $\lambda_{primary}$ for the combustion of wood pellets in the prototype. The individual points represent mean values calculated from various experiments with durations ranging from about 15 to 30 minutes, performed on different days. A dependency between the primary air ratio and the carbon conversion X_C can be recognized. However, there are test averages, where in addition to the primary air, the mentioned other factors have also affected the carbon conversion. These factors are likely to be regarded as a cause of the greater dispersion of the calculated test averages.

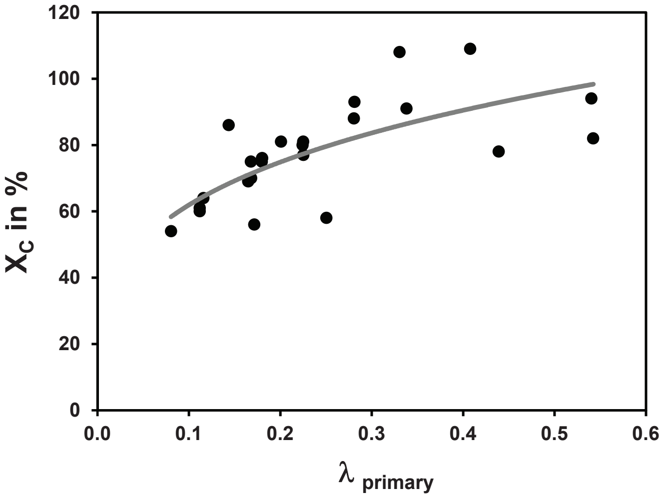

Figure 3: Correlation between primary air ratio $\lambda_{primary}$ and conversion degree X_C in the combustion of wood pellets in the prototype

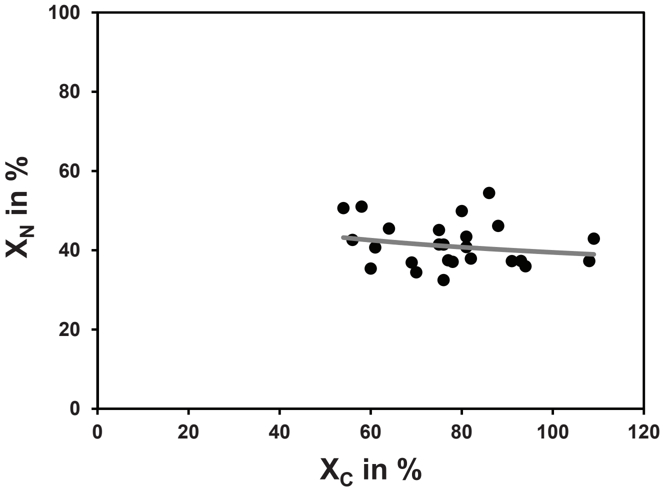

Figure 4: Correlation between the degree of carbon conversion X_C and nitrogen conversion X_N in the combustion of wood pellets in the prototype

For wood pellets, no correlation can be inferred from the conversion degree X_N of fuel nitrogen into NO_x and the conversion degree X_C of carbon into CO_2, as can be seen in Figure 4. This means that the level of the nitrogen oxide concentration in the flue gas of the prototype when wood pellets in DINPlus quality are fired is not determined by the primary air ratio and can therefore not be reduced by lower primary air ratios. In consequence, the proportion of nitrogen oxides which develop from the fuel nitrogen in the case of wood pellets is largely independent of the conversion degree of the carbon.

A correlation was discovered though between the total air ratio λ_{global} and the NO_x concentrations at equal fuel conversion. Figure 5 shows an example of this where, in addition to the NO_x concentrations, the CO concentrations are also given as functions of the total air ratio λ_{global}. The combustion

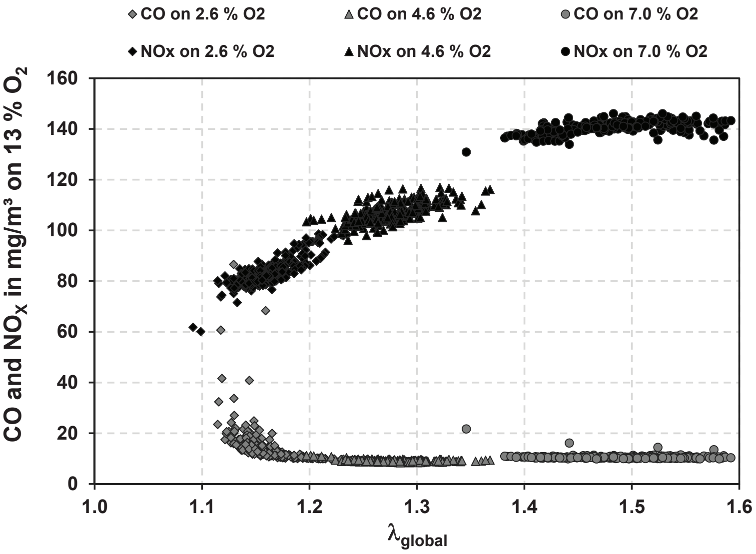

Figure 5: CO and NO_x concentrations as functions of the total air ratio λ_{global} in the combustion of wood pellets in the prototype

tests were performed with wood pellets in the prototype over a measurement period of about 40 minutes each. The figure shows mean values of measurement series of 10 seconds each with a primary air ratio of $\lambda_{primary}$ = 0.18 and a conversion degree X_C of 75–76 %, at differing average residual oxygen contents in the flue gas of 2.6 / 4.6, and 7.0 %. The result is NO_x concentrations in the flue gas of 140 mg/m³ at λ_{global} ranging from 1.4 to 1.6. With decreasing λ_{global}, the NO_x concentrations also diminish in a nearly linear manner down to a minimum of about 80 mg/m³. The reduction of NO_x happens in the area of the burnout zone in the flame tube. This will be described in the following section by means of numerical simulation. The CO concentrations are extremely low over a wide λ_{global} range. Only from a total air ratio of less than 1.2, the CO concentrations increase as well.

In Figure 6, mean NO_x concentrations (averaging time 10 sec each) are plotted at different primary air ratios and varying degree of carbon conversion X_C as functions of the total air ratio λ_{global}. It can be observed in these experiments that the NO_x concentrations diminish as λ_{global} is reduced, which holds for all primary air ratio adjustments and all different degrees of conversion X_C. The NO_x concentration levels and the decrease in concentration depend on additional influencing factors in the primary devolatilization zone. The evaluation of these factors and how they influence the NO_x concentrations needs further investigation.

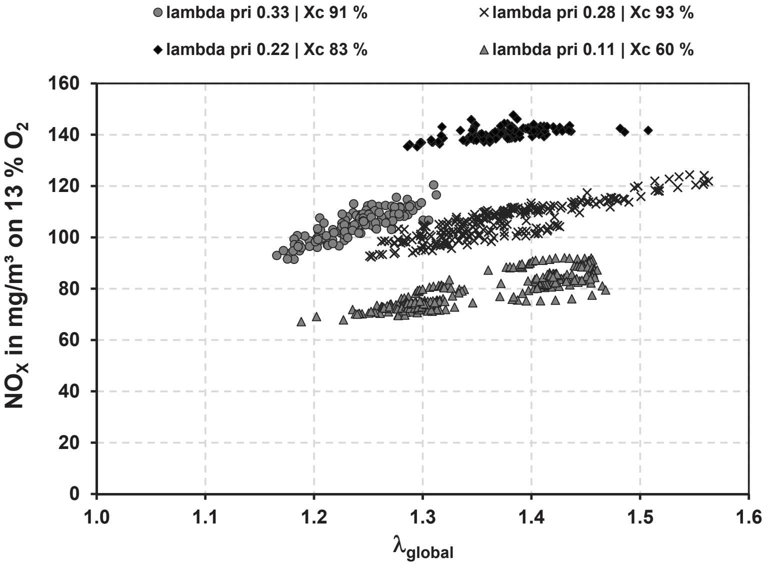

Figure 6: NO_x concentrations at different primary air ratios (lambda pri) and conversion degrees X_C as functions of the total air ratio λ_{global} in the combustion of wood pellets in the prototype

In the combustion of hay pellets in the prototype, some arising correlations differ from the combustion of wood pellets due to the difference in fuel characteristics (e.g. devolatilization behaviour) and concentrations of constituents (e.g. fuel nitrogen). Table 1 draws up a list opposing the main elements and heating values of the fuels used.

Table 1: Main elements and heating values of the wood and hay pellets used as fuels

		Wood pellets	Hay pellets
Volatile matter – raw –	%	79.1	67.5
Fixed C – raw–	%	15.6	15.7
Water (H_2O) – raw –	%	4.9	7.2
Carbon (C) – raw –	%	47.8	41.2
Organ. hydrogen (H) – raw –	%	5.33	5.15
Oxygen (O) – raw –	%	41.4	35.2
Nitrogen (N) – raw –	%	0.10[1)]	1.62
Ash (A) – raw –	%	0.42	9.55
Lower heating value – raw –	$^{MJ}/_{kg}$	17.68	15.11
Lower heating value – daf –	$^{MJ}/_{kg}$	19.69	19.80

raw: fuel as fired (moist); daf: water- and ash-free

[1)] Nitrogen content according to own analyses was below the limit value of quantification of 0.3 % so a reference value from literature was used (Hartmann et. al 2007)

Firing hay pellets, the conversion degree X_N of fuel nitrogen to NO_x for instance depends significantly on the conversion degree of the carbon X_C (Figure 7). With decreasing carbon conversion in the primary devolatilization zone, the conversion degree X_N also decreases. Thus, the primary air ratio has an indirect impact on the level of nitrogen oxide emissions. This correlation has to be verified by further experiments.

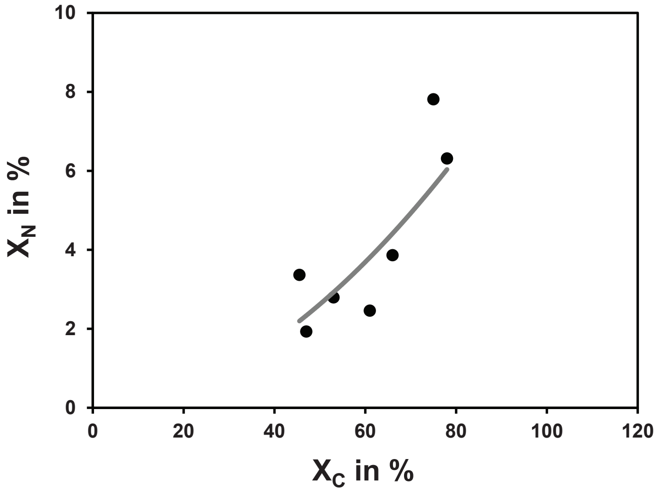

Figure 7: Correlation between the degree of carbon conversion X_C and of nitrogen conversion X_N in the combustion of hay pellets in the prototype

The combustion of hay pellets applying the new combustion concept reveals a clear dependence of the NO_x concentration on the total air ratio λ_{global} (Figure 8). The figure shows averages of 10 seconds from different sets of measurements at various test days. These measurements were carried out varying the primary air ratios which resulted, consequently, in a change in the degree of carbon conversion. At a primary air ratio of 0.22 and a conversion degree X_C of 75 %, the result is an average NO_x concentration of about 470 mg/m³ (averaging time 43 minutes) at a mean λ_{global} of 1.27. Reducing the primary air ratio $\lambda_{primary}$ to 0.14, the NO_x concentrations strongly decrease to a range around 200 mg/m³ (averaging time 63 minutes), with the conversion degree X_C decreasing to 53 %. If the primary air ratio remains constant at 0.14, the result, at a reduced carbon conversion of 47 %, is an average NO_x concentration at about 150 mg/m³ (averaging time 28 minutes).

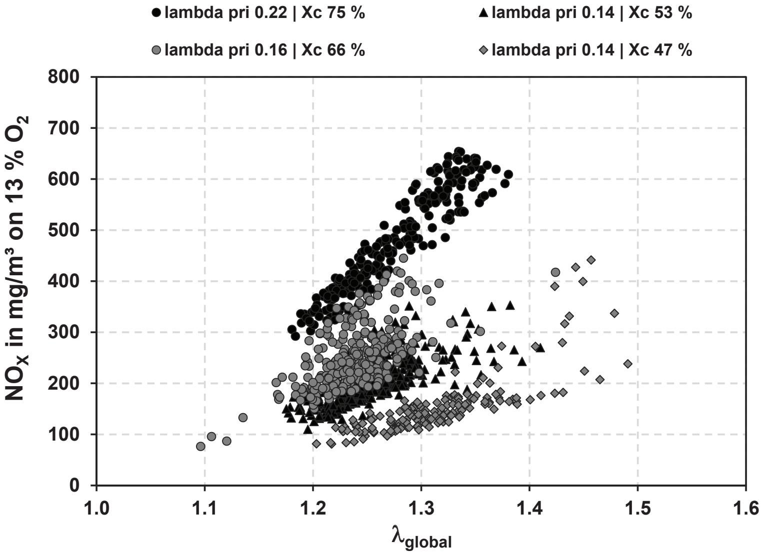

Figure 8: NO_x concentrations at varying primary air ratios (lambda pri) and conversion degrees X_C as functions of the total air ratio λ_{global} in the combustion of hay pellets in the prototype

The correlations presented here suggest the conclusion that the degree of carbon conversion, along with a diminished thermal output, has a substantial impact on the NO_x concentrations in the flue gas. λ_{global} remaining the same, a decrease in carbon conversion goes along with a marked decrease of NO_x concentrations. It seems reasonable to conclude that the conversion degree X_N of fuel nitrogen into nitrogen emissions does not only depend on the primary and total air ratios but also on the prevailing conditions in the primary devolatilization zone.

The demonstrated nitrogen oxide reduction in the combustion of wood and hay pellets takes place in the burnout zone in the flame tube due to a diminished total air ratio λ_{global}. In order to describe more precisely certain states such as temperature, flow behaviour, and oxygen concentrations in this area of the prototype, CFD (Computational Fluid Dynamics) simulations were carried out which will be explained in the following section.

Numerical simulation of the burnout zone

CFD is the simulation of flow processes by spatially resolved calculation. The quality of the simulation results highly depends on the flow and reaction models taken as a basis, on the mathematical computational grid and the constraints selected or to be determined. Numerical modelling requires a high degree of experience and knowledge in order to generate plausible calculation results because it is based on simplified chemical models and global reaction mechanisms.

As a reaction model, a two-step methane reaction was chosen. In the first step, methane reacts with oxygen to form carbon monoxide and water vapour. The carbon monoxide then reacts in a second step with oxygen to form carbon dioxide. The pyrolysis gas developed in the primary devolatilization zone during the test runs consists of a multitude of complex compounds which only in part can be identified by time-consuming and costly measurement technology. The pyrolysis gas values can therefore not be used as boundary condition for the simulation. The chemical processes in the fuel bed are too complex and cannot be described by mathematical analysis based on the current state of knowledge. For this reason, a synthesis gas consisting of CH_4, CO, CO_2, and H_2O is defined. By means of a typical fuel composition, complete combustion assumed, a mass balance equation can be set and the composition of the synthesis gas can be determined. The release of precursors from which nitrogen oxides can form, such as hydrogen cyanide, ammonia and nitrogen monoxide from the fuel bed, and the reaction pathways for the formation of nitrogen oxides can be determined only with great effort and are therefore difficult to describe by mathematical analysis. The effect of the reduction zone will therefore not be described by calculating the nitrogen oxide concentrations, but indirectly, via the temperature and oxygen distribution.

Simulations were carried out for three different total air ratios. The composition, temperature and the mass flow of the synthesis gas were maintained constant. Figure 9 illustrates the model for the CFD simulation. The synthesis gas is mixed with the secondary air flowing in by a ring duct and then enters the flame tube, which is mounted in the combustion chamber of the boiler. The burnout zone is located near the flame tube. The boiler functions as a heat exchanger. Heat loss through the surface was not taken into account. The temperatures calculated in the simulation therefore tend to be too high. Validation measurements of the temperatures occurring in the combustion chamber of the boiler or in the flame tube could not be carried out due to the inaccessibility. Likewise, air infiltrated through the boiler was not considered in the simulation because there were no data about the location of the leakage. Therefore, the calculated oxygen concentrations in the combustion chamber of the boiler are too low and not in exact accordance with the measurement results.

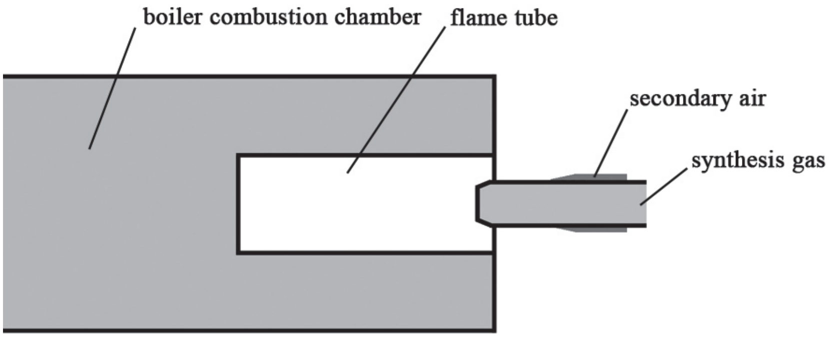

Figure 9: Model for the CFD simulation of the burnout zone with mixing unit for secondary air and synthesis gas, flame tube and boiler combustion chamber

Figure 10 shows the areal distribution of the oxygen concentrations and temperatures in the symmetrical plane of the simulation for the three total air ratios investigated. According to Keller (1994), a high NO_x reduction can be expected at a temperature of about 1200 °C with simultaneous absence of oxygen. In case 1 (C1), no reduction zone can be detected, although the temperatures exceed 1200 °C in the flame tube and in the combustion chamber of the boiler. In order to achieve reducing conditions and, in consequence, a reduction of nitrogen oxide emissions, the absence of oxygen is necessary. Case 1 reveals oxygen concentrations above 1.8 % in the burnout zone.

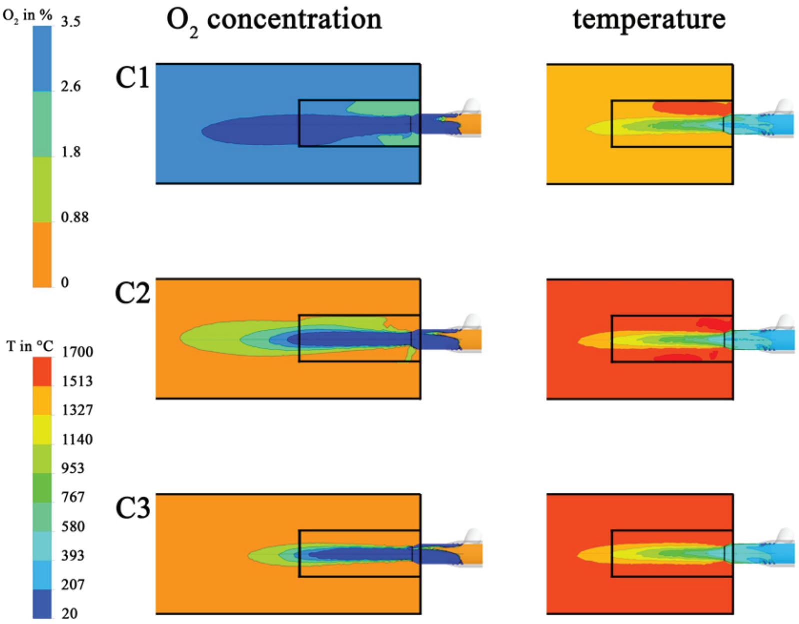

Figure 10: Calculated areal distribution of the oxygen concentration and the temperature in the burnout zone of the prototype at different total air ratios (Case 1: λ_{global} = 1.26; Case 2: λ_{global} = 1.05; Case 3: λ_{global} = 0.94)

If the total air ratio decreases by reducing the secondary air, a distribution of the oxygen concentration as calculated in case 2 (C2) can be observed. In this case, too, there are temperatures of > 1200 °C both in the flame tube and in the combustion chamber of the boiler. In addition, there is significantly less excess air in the hot area of the burnout zone. This produces reducing conditions in some areas of the flame tube. If the secondary air is even further reduced, so that combustible compounds would completely oxidize only by involving infiltrated air, a distinct reduction zone could be created in the flame tube. This is shown by the results of the simulation in case 3 (C3) with high temperatures and areas without any oxygen.

Conclusions

The thermal utilization of residual matter from agriculture makes high demands on firing and plant technology. Conventional plant technology cannot reliably guarantee the necessary low emission level and high operational reliability. By separating the reaction spaces, as implemented in the prototype, dividing the combustion phases into devolatilization of the fuel, oxidation of the pyrolysis gases and oxidation of the residues of devolatilization, it was possible to create a reduction zone in the burnout zone. This reduction zone helped to significantly reduce the NO_x concentrations in the flue gas. Compared to conventional combustion technology, the emission level of gaseous pollutants such as carbon monoxide and nitrogen oxides was well below the current limit values of the German Clean Air Code TA Luft (2002). However, there is still potential for improvement in the design of the reduction and burnout zones to achieve a comparable complete burnout along with further reduced nitrogen oxide at even lower overall excess air. The strict requirements of the German Small Furnace Ordinance (1. BImSchV) concerning the total suspended particulates (TSP) concentration of 0.02 g/m^3 (referring to 13 % O_2) were met partially in the combustion of wood pellets in the prototype. The limit values according to 1. BImSchV (2010) or TA-Luft (2002) concerning TSP can, with hay pellets as fuel, only be complied with using a downstream dust filter. Dust concentrations ranging from 70 to 140 mg/m^3 (referring to 13 % O_2) were thus determined in the combustion tests. The combustion concept implemented in the prototype, setting a very low primary air ratio and installing a moving component in the combustion chamber, was a means to mostly reduce but not prevent slagging completely in every operational condition. In this field, there is still considerable need for research and development.

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Acknowledgements

The present research was supported by the Fachagentur Nachwachsende Rohstoffe e.V. (FNR) (specialist agency for renewable resources) within the framework of the joint research project FKZ 22032111 - " Development of a burner firing system based on the AirRo® technology for the energetic use of agricultural residues; Subproject 1: Basic investigations" - funded by the Federal Ministry of Food, Agriculture and Consumer Protection (BMELV) following a decision of the German Bundestag.
The final report on the project can be obtained at http://www.ifk.uni-stuttgart.de/forschung/rdl/forschungsberichte.en.html.