RELEASE OF NO$_X$ PRECURSORS FROM BIOMASS FUEL BEDS AND APPLICATION FOR CFD-BASED NO$_X$ POSTPROCESSING WITH DETAILED CHEMISTRY

E. Widmann [1], R. Scharler [1,2], G. Stubenberger [1], I. Obernberger[1,2]
[1]Institute for Resource Efficient and Sustainable Systems, Graz University of Technology, Inffeldgasse 25, A - 8010 Graz
Tel.: +43 (0)316 481300 34, Fax: +43 (0)316 481300 4; Email: widmann@rns.tugraz.at
[2]BIOS BIOENERGIESYSTEME GmbH, Sandgasse 47, A-8010 Graz, Austria

ABSTRACT: In this work the development and test of a combined model for NO$_x$ formation in biomass fixed bed furnaces is presented. Pot furnace experiments were performed with the fuels bark, waste wood and fibreboard in order to measure the composition of the flue gas above the fuel bed. Conversion rates from fuel nitrogen to the NO$_x$ precursor species NH$_3$, HCN and NO were derived from this experiments and implemented in an empirical model for the combustion of the biomass fuel layer in a fixed bed furnace. The results of this model are used as boundary conditions for subsequent calculations with a newly developed CFD-based NO$_x$ postprocessor. This technology allows for spatially resolved calculation of NO$_x$ formation with detailed reaction kinetics. Simulations of a pilot-plant were performed in order to validate the combined model and the results showed good qualitative and quantitative agreement with measurements. It is concluded, that the presented combined model of NO$_x$ formation allows to investigate NO$_x$ reduction in biomass grate furnaces by primary measures in detail and is therefore a powerful tool for the optimisation of furnace designs and process control.
Keywords: combustion, emission reduction, modeling, NO$_x$ formation, CFD

1 INTRODUCTION

While NO$_x$ emissions from fossil fuel combustion mainly emerge from oxidation of N$_2$ at high temperatures, NO$_x$ emissions from biomass fuel combustion arise from oxidation of fuel bound nitrogen. Biomass fuels with a high nitrogen content – amongst those some commercially highly interesting fuels like waste wood or fibreboard residues from furniture production – yield potentially high NO$_x$ emissions and demand costly secondary measures (SNCR/SCR).

CFD (computational fluid dynamics) was successfully applied to optimise the design of biomass furnaces concerning flue gas burnout and temperature distribution [1]. Up to now the CFD simulation of NO$_x$ formation was limited by the necessity to include detailed chemistry in the models which caused unrealistically long computation times. Furthermore, CFD models need mass flow, composition and temperature of the flue gas arising from the fuel bed as boundary conditions. Knowledge about the concentration of NO$_x$ precursors in the flue gas released from the surface of the fuel layer on the grate is crucial for the subsequent NO$_x$ formation in the gas phase. The scope of this work is to present recent experimental and modelling work which covers the release of NH$_3$, NO and HCN from the fuel bed and the subsequent CFD simulation of NO$_x$ formation in the furnace based on the CFD simulation of combustion (NO$_x$ postprocessing). This new approach allows to account for the interaction of turbulence and detailed chemistry and requires acceptable computation time.

2 METHODOLOGY

Considering the complexity of the processes in biomass fuel beds, a detailed mathematical treatment seems, on the one hand, too time-consuming for engineering applications and, on the other hand, not completely understood so far. An empirical fuel layer model was thus applied for the combustion of the solid biomass fuel on the grate and the model parameters were based on pot furnace (batch reactor) experiments. The transfer of the results of those experiments to the combustion of a biomass fuel layer on a grate is valid, if diffusional transport and mixing effects in direction of the grate can be neglected compared to the transport of the fuel along the grate (see Figure 1). Although this condition is not fulfilled in general due to mixing effects on the grate, the approach was adopted for this work as a first experimental approximation. Consequently, the pot furnace experiments were designed in a way to represent the burning biomass fuel layer in a grate furnace as good as possible.
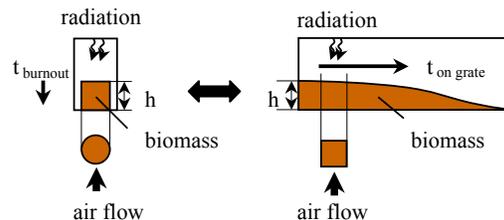

Figure 1: Transfer of pot furnace experiments to the fuel layer in a grate furnace

While an empirical approach for modeling the fuel bed was used, CFD calculations are used as a standard tool for the calculation of gas phase combustion to optimise the design of biomass furnaces. However it is a demanding task to combine the detailed calculation of the reacting flow with a suitable chemical model for fuel NO$_x$ formation. First tests with global 2-step and 3-step NO$_x$ mechanisms in combination with a simple break up combustion model showed a false prediction of NO$_x$ formation in biomass grate furnaces. Therefore it was concluded, that a more detailed description of the complex interactions of turbulence and NO$_x$ kinetics is needed.

2.1 Pot furnace experiments

Three different fuels with different content of nitrogen were investigated in the pot furnace. The fuels were fibreboard, waste wood and bark (nitrogen contents:

3.1 / 1.0 / 0.3 wt% d.b. respectively).

The pot furnace that was used for the experimental work is a cylindrical batch reactor (see Figure 2). The fuel was placed in a sample holder, which rested on a weight balance. Heater elements are installed in order to heat up the reactor to a specified temperature.
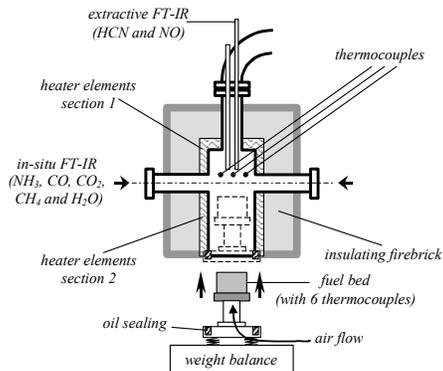

Figure 2: Scheme of the pot furnace

Inside the fuel bed 6 thermocouples were installed in order to measure the temperature in different heights of the fuel bed as well as the propagation speed of the ignition front in the bed. Combustion air is introduced through a porous plate at the bottom of the fuel bed. To avoid false air, the reactor was sealed with thermo oil. In the upper part of the retort there are two channels which allow measurement of gas phase concentrations of H_2O, CH_4, CO, CO_2 and NH_3 just above the fuel bed using a specially developed hot gas in-situ FT-IR technique [2]. Three thermocouples are placed above the sample holder to measure the temperature of the flue gas leaving the fuel bed. Extractive gas measurements were performed using a heated suction probe and extractive FT-IR as well as CLD for HCN and NO

In addition, O_2 was measured (paramagnetic) and a wide-band ZrO_2 sensor provided information about the stoichiometry conditions. The combined information of the various measurements performed was used for the calculation of elemental balances for each pot furnace experiment. Following this approach, rates of conversion from fuel compounds to flue gas species, especially from fuel bound nitrogen to NO_x precursors, could be obtained.

2.2 Empirical fuel layer model

The fuel bed is divided into small slices and mass and energy equations are solved. The model applies a 2-step approach. The first step covers the decomposition of the biomass fuel and the release of the fuel components C, H, O, N and H_2O. The model uses pre-defined 1-D elemental release profiles along the grate, which were derived from grate furnace experiments [3].

The second step covers the conversion of the fuel components to the flue gas species CO_2, CO, H_2O, O_2, N_2, CH_4, NH_3, NO and HCN using functions, which are dependent on the stoichiometric ratio in the fuel bed. For the major combustion species the conversion functions yielded results close to equilibrium concentrations. The conversion of the fuel-N to NO_x precursors showed a strong dependency on the nitrogen content of the fuel. Therefore, the conversion of fuel nitrogen was made

dependent on the stoichiometric ratio as well as on the nitrogen content of the fuel.

It is possible to apply different conversion functions for different biomass fuels. This is of relevance to account for special fuel characteristics, which can be derived by pot furnace experiments. Moreover, it is important to state, that only NH_3, NO and HCN are implemented at present. Other possible NO_x precursor species like NO_2, N_2O and $HNCO$ are not included in the model. However, the experiments performed yielded only low concentrations of these species, therefore the restriction on NH_3, HCN and NO seems to be justified.

The empirical fuel layer model supplies profiles of flue gas velocity, temperature and species concentrations above the fuel layer as results.

2.3 CFD-based NO_x postprocessing

Under the assumption that the NO_x formation reactions do not significantly influence the flow pattern in the furnace, a time saving 2-step approach was applied for the CFD simulations. The Realizable k-ε Turbulence model, the Eddy Dissipation combustion model in combination with a global methane 3-step mechanism (CH_4, CO, CO_2, H_2, H_2O) and the Discrete Ordinates Radiation model where used for basic gas phase combustion simulation in the presented case. The sub-models were validated for combustion simulation in biomass furnaces with lab-scale test cases [1].

The subsequent CFD simulation of gas phase fuel NO_x formation in a postprocessor mode was performed with the Eddy Dissipation Concept in combination with a detailed reaction mechanism with 50 species and 253 reactions (Kilpinen 92), which was developed under the consideration of NO_x kinetics in biomass combustion systems. This model allows for a detailed consideration of both flow and chemistry.

2.4 Model validation

In order to validate the combined model of NO_x formation two different operating conditions of a 440 kW$_{th}$ pilot-scale plant (see Figure 4) were simulated. The pilot plant is divided in a primary and a secondary combustion zone. The primary combustion zone is designed with sufficient residence time (about 0.6 – 0.8 seconds) in order to allow for an effective reduction of nitrogen oxides under fuel-lean conditions. The secondary combustion zone is designed as an oxygen rich zone (air ratio λ > 1), in order to ensure flue gas burnout. A further important feature of this furnace type is the possibility of a staged flue gas re-circulation for temperature control in the furnace. Measurements of temperatures and species concentrations inside the furnace (CO, CO_2, CH_4, H_2O and NH_3 using in-situ FT-IR) were performed in order to validate the basic CFD combustion model [2]. NO_x emissions were measured at the boiler outlet using conventional flue gas analysis equipment to validate the combined model for NO_x formation.

One simulation (case A) was performed for fuel rich conditions in the primary combustion zone ($λ_{prim}$>1) and one simulation was performed for fuel-lean conditions (case B). The results of the simulations were then compared to measurements of NO_x emissions at the boiler outlet.
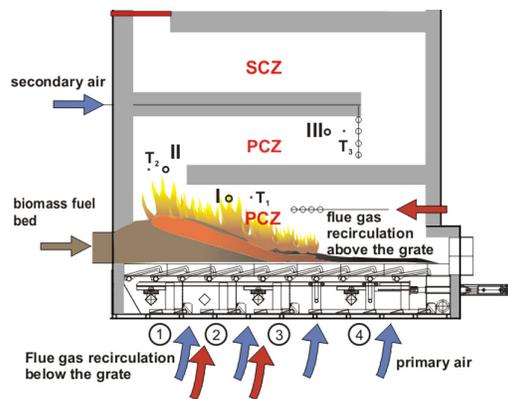
Figure 3: Scheme of the pilot plant used for model validation

Explanations: PCZ...primary combustion zone; SCZ…secondary combustion zone; measurement positions: I, II, III…FT-IR; T1, T2, T3…thermocouples; boundaries of CFD simulation: from entrance (surface fuel bed as well as inlet re-circulated flue gas and secondary air) to exit of the furnace (red line)

3 DISCUSSION OF RESULTS

3.1 Pot furnace experiments

After the insertion of the fuel sample in the pre-heated reactor the uppermost fuel layer heated up and drying and pyrolysis processes started. After the ignition of the fuel, a reaction front propagated through the fuel bed towards the grate.

Gas phase concentrations above the fuel bed were measured and the release of NO_x precursors from the fuel was studied. By elemental mass balances it was possible to calculate overall conversion rates of fuel nitrogen to NH_3, NO and HCN.

The major NO_x precursors released from the fuel bed were NH_3 and NO, only small concentrations of HCN were measured. HCN was not detected at all (using wet chemical analysis) at the experiments with fibreboard. Moreover, the experiments confirmed the thesis, that the overall conversion rates from fuel N to NO_x precursors are higher for fuels with a lower content of nitrogen (see Table I).

Table I: Results of pot furnace experiments

Explanations: nitrogen contents for bark, waste wood and fibreboard 0.3 / 1.0 / 3.1 wt% d.b., respectively; u-NO, u-NH_3, u-HCN ratios of fuel nitrogen to NO_x precursor species

	u-NO	u-NH_3	u-HCN
bark	8% - 15%	73% - 88%	1% – 2%
waste wood	3% - 10%	38% - 46%	3% - 5%
fibreboard	2% - 3%	25% - 48%	not detected

Although the experiments performed within the scope of this work strongly support a high NH_3/HCN ratio regarding the release of fuel N, this result should not be generalised without care. Additional experiments with various biomass fuels and under consideration of different combustion conditions are necessary to confirm the results. At present it seems to be the best-practice strategy to study the combustion and fuel-N conversion

of individual fuels in pot reactor experiments and establish conversion characteristics for each fuel separately. However, it is possible to give estimations of the expected conversion ranges depending on the nitrogen content of the fuel using the results of Table I.

3.2 Empirical fuel layer model

The model parameters of conversion were fitted to individual pot reactor experiments. Figure 4 shows a comparison of model calculations with the experimental results for fibreboard. Adaptation of the model parameters depending on the stoichiometric conditions inside the fuel layer resulted in a satisfying quantitative and qualitative agreement between the model calculations and the experiments. NH_3 is released mainly under air-lean conditions, while NO is released from the fuel bed under air-rich conditions. It was concluded, that the empirical fuel layer model can be used as an engineering tool to calculate the boundary conditions for the CFD based NO_x postprocessing (NH_3 and NO release from the fuel bed).
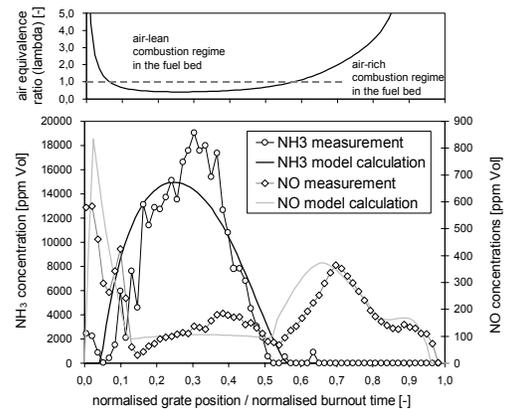

Figure 4: Fit of model parameters to the results of the pot furnace experiments

Explanations: normalised grate position…model calculations; normalised burnout time…pot furnace experiments

3.3 Results of CFD based NO_x postprocessing

First 3D CFD simulations of NO_x formation based on the basic combustion simulation (NO_x postprocessing) were performed for the above mentioned pilot scale plant for two different operating conditions (case A: fuel rich conditions in the primary combustion zone, $\lambda_{prim} < 1$; case B: fuel lean conditions in the primary combustion zone, $\lambda_{prim} > 1$). First calculations needed about 2 weeks on a single PC processor for a grid size of 275,000 cells, but a considerable speed up can be achieved with parallel processing. For both operating conditions, a good qualitative agreement of relevant nitrogen species concentrations (NO_x precursors NH_3 and HCN as well as NO and NO_2 with measurements as well as data from lab-scale experiments and literature could be achieved. Figure 5 shows calculated mole fraction profiles of NH_3 and NO in the vertical symmetry plane of the furnace. The calculated NO emissions at the furnace outlet where about an order of magnitude higher than the corresponding NO_2 emissions, which is in compliance with literature data and measurements (conventional flue gas analysis). The calculated NO_x emissions (NO + NO_2)

were only 10% higher than measurements at the boiler outlet for fuel rich conditions and fuel lean conditions (see Table II).

Table II: Results of model validation

	λ_{prim} [-]	NO_x measured [ppm Vol]	NO_x calculated [ppm Vol]
case A	0.97	264	287
case B	1.63	303	332

Following, the effect of air staging could be reproduced correctly. Only small concentrations of HCN and NH_3 where calculated at the furnace outlet which is in accordance with literature and experience. Furthermore, the simulations showed, that NH_3 is not immediately consumed above the fuel bed but nearly completely in the primary combustion zone (see Figure 5 B) depending on the effective air ratio in the primary combustion zone (earlier for larger λ).

This is in qualitative agreement with FT-IR measurements at the pot-furnace reactor (NH_3 was not immediately consumed above the fuel bed) as well as with FT-IR measurements at the pilot-scale plant (no NH_3 was measured at port III for case A and no NH_3 was measured at port II for case B). Additionally, this trend is in agreement with the above-mentioned data concerning the NH_3 concentration level at boiler outlet [3].

4   SUMMARY

A combined model for NO_x formation in biomass fixed bed furnaces was developed. The model consists of an empirical model of the combustion of the biomass fuel layer in the furnace and a newly developed CFD-based NO_x postprocessor, based on a basic combustion simulation and a subsequent calculation of NO_x formation using the EDC model in combination with detailed kinetics.

In order to determine the conversion parameters of the empirical fuel layer model, pot furnace experiments where performed with bark, waste wood and fibreboard. The experiments yielded fuel nitrogen conversion mainly to NH_3 and NO, only low concentrations of HCN were measured. Moreover, the conversion rates increased with decreasing nitrogen content of the fuel and were dependent on the stoichiometric conditions in the fuel layer. The empirical fuel layer model was used in order to calculate boundary conditions for subsequent CFD calculations with a newly developed CFD-based NO_x postprocessor. Simulations were carried out for a 440 kW_{th} pilot plant (fuel: fibreboard) and simulation results were in good qualitative and quantitative agreement with measurements.

Concluding, it can be stated that the combined model of NO_x formation was successfully tested for 3D simulations of biomass grate furnaces. The newly developed NO_x postprocessor allows to investigate in detail NO_x reduction measures in biomass grate furnaces and, therefore, is a powerful tool for the optimisation of furnace designs and process control. But more tests and comparisons with measurements are necessary and ongoing in order to improve and validate the model (including the fixed bed and the gas phase combustion sub-models).
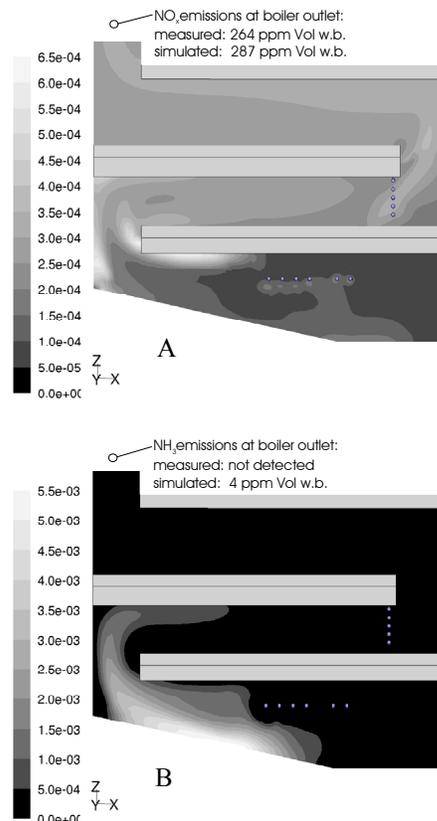

Figure 5: Calculated mole fraction profiles of NO (A) and NH_3 (B) in the vertical symmetry plan of the pilot plant
Explanations: fuel-rich conditions in the primary combustion zone (case A)

5   ACKNOWLEDGEMENTS

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