

WEISSINGER Alexander, OBERNBERGER Ingwald, Günter LÄNGLE, Alfred STEURER, 1998: NO_x - reduction by primary measures for grate furnaces in combination with in-situ measurements in the hot primary combustion zone and chemical kinetic simulations. In: Proceedings of the 10th European Bioenergy Conference, June 1998, Würzburg, Germany, C.A.R.M.E.N. (ed), Rimpf, Germany, pp. 1474-1478

NO_x – REDUCTION BY PRIMARY MEASURES FOR GRATE FURNACES IN COMBINATION WITH IN-SITU MEASUREMENTS IN THE HOT PRIMARY COMBUSTION ZONE AND CHEMICAL KINETIC SIMULATIONS

Authors: Alexander Weissinger*, Ingwald Obernberger**, Günter Längle***, Alfred Steurer***
* Technical University Graz, Institute of Chemical Engineering,
Inffeldgasse 25, A- 8010 Graz,
TEL: +43 316 481300; FAX: +43 316 4813004 E-MAIL: weissing@sbox.tu-graz.ac.at.
** BIOS Research and Development
Sandgasse 47, A-8010 Graz,
*** MAWERA Holzfeuerungsanlagen GmbH & Co KG,
Neulandstraße 30, A- 6971 Hard/Bregenz,

ABSTRACT: Primary measures for the reduction of NO_x emissions, meaning the conversion of the volatile N-species (NH₃, HCN) to molecular nitrogen (N₂), are an important part of scientific research in the field of biomass combustion. Reaction mechanisms describing the reactions leading to the reduction of N-species have been developed and the optimum conditions in the primary combustion chamber for low NO_x emissions of underfeed furnaces have been investigated. In order to be able to simulate the chemical reaction kinetics relevant for the reduction of nitrogen species to molecular N₂ of a grate furnace, a new model has to be developed for describing the conversion rates and concentrations of nitrogen compounds and other important gaseous species relevant for N-reaction mechanisms in the hot flue gas right above the different grate sections.

Investigations of NO_x formation have to focus on that part of the grate where most N-species are released, which is supposed to be the gasification zone. To locate this zone test runs will be performed under controlled conditions (air supply to different grate sections, gas temperature in different sections) at a specially designed pilot plant, combined with fuel analyses of samples taken from different locations of the grate (in order to determine the amount of C and N released from the biomass fuel) and in-situ measurements of the flue gas composition in the primary combustion zone by means of FT-IR (in order to detect relevant compounds directly in the hot gas).

This combination of wet-chemical fuel analysis, in-situ flue gas measurements and simulation tools (chemical reaction kinetics, flow conditions) will make it possible to describe the releasing process of the fuel nitrogen and to define the optimum temperature profile and air staging conditions for best results concerning NO_x reduction in grate furnaces by primary measures.

1 Overview

NO_x emission reduction is one of the major tasks in the optimisation of biomass combustion [6].

In order to achieve this goal by primary measures the reduction of volatile N-species (NH₃, HCN) to molecular nitrogen (N₂) must be optimised. Reaction mechanisms describing these reactions have been developed. The most complete model, which also includes hydrocarbon reactions, was developed by Kilpinen [2].

Experimental studies for describing the influence of air staging on NO_x reduction have been performed for underfeed furnaces. The optimum conditions in the primary combustion chamber found for low NO_x emissions are an air ratio in the primary combustion zone of 0.6 – 0.8, a residence time in this reduction zone of about 0.5 seconds and temperatures between 1,100°C – 1,200°C [3].

These conditions are valid for underfeed furnaces but cannot be transferred to grate furnaces without modifications. Contrary to underfeed furnaces the three stages of biomass combustion (drying, gasification, charcoal combustion) take place in different sections of the grate. Former investigations have shown that for grate furnaces with primary stoichiometric air ratios between 0.8 and 1.2, a minimum of NO_x emissions can be achieved. Investigations concerning NO_x formation have to focus on that part of the grate where most of the N-species are released. Hence, an air ratio of 0.6 to 0.8 should be achieved in the gasification zone because about 70 % of the fuel nitrogen are volatile, passing to the gaseous phase in the respective grate section [3].

The difficulty is to locate this zone of gasification in dependence on the grate technology and the biomass fuel used and to measure the conversion rates and the concentrations of nitrogen compounds and other important gaseous species relevant for N reaction mechanisms in the hot flue gas right above the different grate sections.

These measurements are essential in order to be able to simulate the chemical reaction kinetics required for the conversion of nitrogen species to molecular N₂. This can only be achieved by test runs under controlled conditions (air supply to different grate sections, gas temperature in different sections) combined with fuel analyses of samples taken from different locations on the grate (in order to determine the amount of C and N released from the biomass fuel) and in-situ measurements of the flue gas composition in the primary combustion zone by means of FT-IR (in order to detect relevant compounds directly in the hot gas).

Conventional methods rely on extractive measurements where the gas is sampled, cooled, filtered and then analysed. This method has the disadvantage that no predictions are possible concerning chemical reactions taking place during sampling and pre-treatment of the gas. The new in-situ FT-IR method can analyse the gas directly in the combustion chamber by comparing the IR spectra achieved for relevant compounds with representative high-temperature calibration spectra.

Based on these analytical results chemical reaction kinetics for N reactions will be simulated in order to investigate the relevant influencing variables.

Consequently, combining wet-chemical fuel analysis, in-situ flue gas measurements and simulation tools will make

it possible to define the optimum temperature profile and air staging conditions for best results concerning NO_x reduction by primary measures.

2 Description of the pilot plant grate furnace

The furnace is a newly developed travelling grate with a nominal boiler capacity of 440 kW_{th} which was designed and built by the biomass furnace and boiler manufacturer MAWERA (Hard, Austria) in co-operation with BIOS Research and Development, Graz, and the Institute of Chemical Engineering at the Technical University Graz, Austria. The new experimental furnace was designed for testing primary measures as well as secondary measures as to their potential concerning NO_x reduction.

The innovative furnace design features a three-staged combustion chamber with selective flue gas recirculation and secondary air injection. For the investigation of primary measures flue gas recirculation can take place in the primary combustion zone (above or under the grate) or at the beginning of the secondary combustion zone in order to investigate the effect of different temperature and flow conditions on NO_x reduction. Furthermore, the secondary air can be injected at the beginning or at the end of the secondary combustion chamber. In the later mentioned case an additional hot reduction chamber is

achieved and the effect of a longer residence time of the flue gas in reducing conditions can be investigated. If secondary measures are tested, secondary air injection will take place at the beginning of the secondary combustion chamber and ammonia injection will take place at the end of this zone using the third combustion zone as a reaction chamber. Temperature control before ammonia injection is achieved by flue gas recirculation. Consequently, the new design of the experimental furnace allows high flexibility in the investigation of variables influencing NO_x reduction.

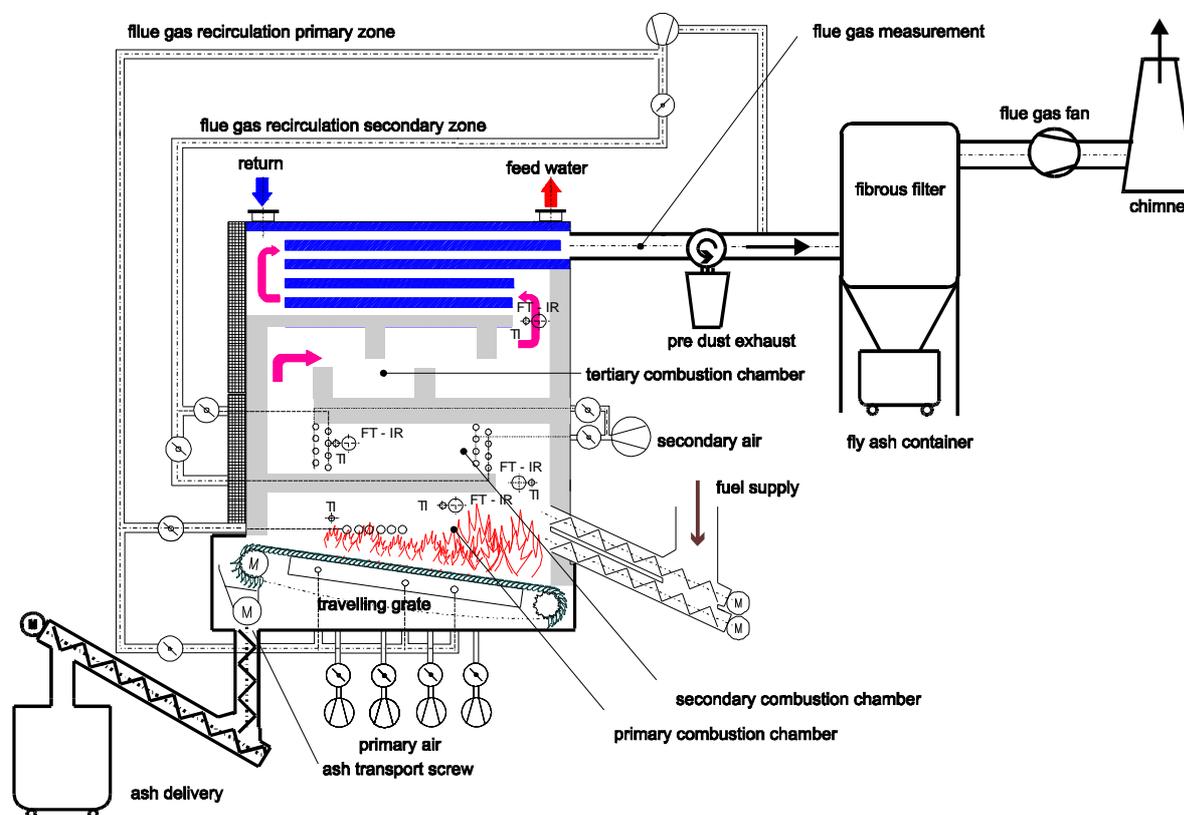
The tertiary combustion zone is designed for high turbulence in order to achieve good mixing conditions of the flue gas, air and reducing agent, respectively.

The emissions of CO, O₂ and NO with the flue gas are measured and recorded continuously. NO₂, C_xH_y and dust measurements are also available, if necessary. All emission data and a great number of selected operating data (all air flows and flue gas flows entering the furnace or leaving the boiler, the boiler load, temperatures as well as differential pressures over the whole system) are measured, visualised and recorded by a PC on a continuous basis.

Figure 1: Schematic view of the pilot plant grate furnace and the measurement parameters

Explanations: Test stand located at the MAWERA company, Hard, Austria; combustion system: travelling grate furnace; boiler: hot water (fire tube) boiler; biomass fuels tested: wood chips, sawdust, bark, residual and selected waste wood fractions.

Abbreviations: FT-IR...FT-IR measurement position (Temperature measurement included); TI...temperature indication



All fans are frequency controlled. Moreover, in relevant locations along the grate and in the post-combustion zones ZnSe-windows are provided in both walls of the primary combustion chamber. They are arranged at the same height in order to be able to pass an IR beam through the combustion chamber for in-situ measurements of hot flue gas compounds (see figure 1). These windows are designed to allow multiple reflection of the IR beam through the combustion chamber in order to improve the detection limits for certain compounds.

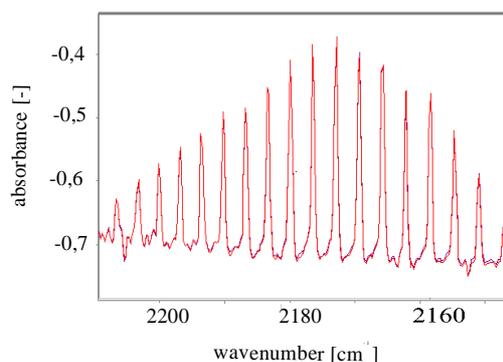
3 FT-IR in-situ measurement

FT-IR spectroscopy (Fourier Transform Infrared spectroscopy) is based on the effect of the absorption of infrared radiation by polyatomic molecules and heteronuclear diatomic molecules. Each molecule has its characteristic absorption and emission "spikes" at different frequencies in the infrared spectrum (emission and absorption "spikes" are located at the same frequencies of the IR spectrum). By comparing the IR spectrum of a gas with the characteristic spectra of a substance at known concentrations the substance in the gas can be quantified (see Figure 2).

The height of the characteristic "spikes" of a substance in a sample gas is dependent on the concentration and the temperature of the gas. To be able to perform in-situ measurements in the hot combustion zone it is necessary to create high-temperature calibration spectra under laboratory conditions using gases with defined and approved concentrations.

Figure 2: Example of an IR spectrum

Explanations: Substance CO, concentration 3.78 ppm, temperature 27°C



FT-IR spectroscopy allows for both active and passive measurements of the gas investigated. Active means leading an IR beam through the substance and measuring the absorption spectrum, passive measurement means measuring the emission spectrum of the hot substance [8], [9], [10]. FT-IR measurements can be performed by passing the gas through a built-in cell (extractive), or by passing the IR beam through a gas or ambient air to a detector (open path).

The FT-IR spectrometer used is a MIDAC M-2401-C equipped with a midband MCT detector with a resolution of 0.5 cm^{-1} , which allows measurements to be performed in a wavenumber range of 600 cm^{-1} to 4500 cm^{-1} . It can be used for open path analysis, both active (measuring the emission-spectra) and passive (measuring the absorption spectrum) as well as for extractive measurements of exhaust gases in a built-in 10 m gas cell with ZnSe windows. First measurements have shown an influence of the temperature gradient in direction of the path of the IR beam. In the case of a negative temperature gradient, the beam received in the passive open path analysis is a mixture of an active and a passive spectrum and cannot be quantified. Therefore the active open path analysis seems to be the best suitable method for in-situ analysis of gas species at higher temperatures. Using a multiple reflection system the sensitivity of the active open path analysis should be increased. The software for evaluating spectra analysis are AUTOQUANT and HITRAN databases [10]. Appropriate high-temperature calibration spectra will be created by laboratory test runs.

4 Simulation data

First simulations were performed studying a moving grate furnace. Based on literature data on the conversion of fuel nitrogen to volatile compounds for the influence of the air ratio and temperature on the conversion of these compounds, the simulations were performed using the CHEMKIN II program code [7].

These simulations of chemical N-reaction kinetics displayed an additional influence of the flow conditions in the secondary zone on the reduction of NH_3 and HCN to N_2 . Using the model of a perfectly stirred reactor (PSR) for simulating the secondary zone the reduction rate of all nitrogen compounds TFN (total fixed nitrogen) was better at lower temperatures (900°C – 1000°C) in the secondary zone, and it was better than the rate of reduction achieved using the model of an ideal plug flow reactor (PFR) (see Figure 3). In both cases the primary zone was simulated as a plug flow reactor at the same temperature level as the secondary zone.

Furthermore the reduction rate achieved in the secondary zone was higher than the reduction rate achieved in the primary zone. A delayed burn-out of the CO due to the reaction kinetics of the PSR model is supposed to be the reason for this.

These calculations showed that it is important to investigate the flow conditions in the whole post-combustion zone in more detail and to adjust the reactor model to the respective flow conditions by a cascaded arrangement.

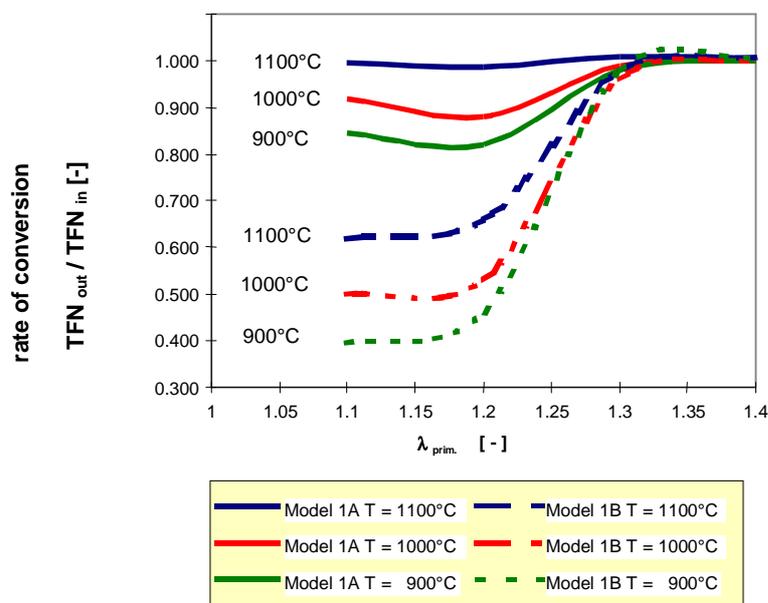
To be able to increase the certainty of the simulation of the chemical N-reaction kinetics and to investigate which reaction models or combinations of models (PSR/PFR or combinations of both) are best to be applied for achieving the highest accuracy, these chemical simulations will be combined with the simulation of the flow conditions and temperature profiles in the furnace.

This approach is supposed to be well suitable for the modelling of gas phase reactions in biomass combustion furnaces.

Figure 3: Rate of conversion of volatile N compounds (TFN) in the flue gas in the secondary combustion zone in dependence on gas temperature, primary excess air ratio and calculation model applied.

Explanations: Source [7]; Model 1A: plug flow without recirculation of the flue gas ; Modell 1B: perfectly stirred reactor without recirculation of the flue gas. The calculations were performed for woodchips in bark with a fuel nitrogen content of 0.4 wt.%dm, $\tau = 1.5 - 1.8$ s

Abbreviations: TFN in: total fixed nitrogen input secondary zone; TFN out: total fixed nitrogen output secondary zone.



5 References

1. FERREIRA, J.; NUSSBAUMER, T. 1997: Modellierung von Verbrennungsprozessen Zwischenbericht Projekt Auslegungsgrundlagen von Holzfeuerungsanlagen, Laboratory for Thermodynamics (Ed.), ETH Zürich, Switzerland
2. KILPINEN, P., 1992 : Kinetic Modelling of Gas-Phase Nitrogen Reactions in Advanced Combustion Processes, Report 92-7, PhD - thesis, Åbo Akademi University, Finland
3. KELLER, R., 1994 : Primärmaßnahmen zur NO_x Minderung bei der Holzverbrennung mit dem Schwerpunkt Luftstufung, Forschungsbericht Nr. 18 (1994) , Laboratory for Thermodynamics (Ed.), ETH Zürich, Schweiz
4. NUSSBAUMER, T. , 1995 : Zweistufige Verbrennung mit Reduktionskammer und Brennstoffstufung als Primärmaßnahmen zur Stickoxidminderung bei Holzfeuerungen, , Laboratory for Thermodynamics (Ed.), ETH Zürich, Schweiz
5. NUSSBAUMER T, 1997: NO_x -Reduction by primary and secondary measures, technologies, experiences, potential, 2nd Biomass Summer School Proceedings, Institute of Chemical Engineering (Ed.), Technical University Graz, Austria
6. OBERNBERGER, I., 1997: Nutzung fester Biomasse in Verbrennungsanlagen, Schriftenreihe Thermische Biomassenutzung Band 1, Institute of Chemical Engineering (Ed.), Technical University Graz, Austria
7. WEISSINGER A., 1997: Erstellung eines kinetischen Modells zur Simulation der Entstehung von Stickoxiden bei einer Biomasserostfeuerung, Thesis for diploma Institut of Chemical Engineering (Ed.), Technical University Graz, Austria
8. WÜLBERN K., WINDPASSINGER R., On-line Measurements of Exhaust Gas with a FTIR-Spectrometer, Lehrstuhl für Elektrische Meßtechnik (Ed.), Technische Universität München
9. NELSON C. M., KNIGHTK. S., BONONNO A. S., SERIO M. A., SOLOMON P. R., 1993: On-line FT-IR Analysis of Fossil Fuel-Fired Power Plants, Proceedings of the Air and Waste Management International Symposium on Optical Sensing for Environmental Monitoring, October 11-14, Atlanta, Air and Waste Management Association (Ed.), Pittsburgh
10. YOKELSON R.J., GRIFFITH D.W.T., BURKHOLDER J.B., WARD D. E., 1995: Accuracy and Advantages of Synthetic Calibration of Smoke Spectra, Proceedings of the Air and Waste Management Association Symposium Sept. 25-27 1995, San Francisco, Air and Waste Management Association (Ed.), Pittsburgh