

Christian Thulfaut
Aachen University
Institute of Heat Transfer
and Air Conditioning
Eilfschornsteinstrasse 18
D-52056 Aachen, Germany
phone: +49 241 80-95403
fax: +49 241 80-92143
e-mail: thulfaut@wuek.rwth-aachen.de
(Primary Contact)

Ulrich Renz
Aachen University
Institute of Heat Transfer
and Air Conditioning
Eilfschornsteinstrasse 18
D-52056 Aachen, Germany
phone: +49 241 80-95400
fax: +49 241 80-92143
e-mail: renz@wuek.rwth-aachen.de

Experimental and Numerical Investigations on Flue Gas Purification during Hot Gas Filtration

Keywords: Hot Gas Filtration, Purification of Gas, Pollutants, Reduction

Introduction

In recent years the necessity of minimising the overhead and investment expenses in the process and energy conversion industry leads to the development of integrated technologies which are able to perform several processes inside a single unit. In this context the combined removal of particulate matter and gaseous pollutants from flue gas during hot gas filtration seems to be a challenging task. Regarding the installed hot gas filtration units with rigid ceramic filter areas between 50 and 1.000 m² in coal fired power generation plants and municipal waste incinerators up to now the potential for an implemented catalytic reduction of gaseous pollutants is obvious, keeping in mind that the porosity of ceramic filter media multiplies the attainable regions for surface reactions (Klein et al. 1991, Halang 1997, Duo et al. 1998). The ranges in which these processes can be used are widespread (Peukert 1996, Gäng 1990, Möhring 1998, Hübner et al. 1996, Kwetkus et al. 1996).

But introducing these technologies into large scale facilities still faces some difficulties. On the one hand cheap catalysts with a maximum conversion rate regarding the favoured reaction path inside the special temperature window of hot gas filtration between 573 to 1173 K and different possibilities to integrate catalytic and supporting material into the filtration process without influencing the regeneration process of the filter medium is necessary. On the other hand efficient means for the design of appropriate apparatus which consider the kinetics of the reactions progressing during the reduction of gaseous pollutant components are missing.

Objective

The aim of the actual investigations is to integrate the catalytic reduction of carbon monoxide and particularly nitric oxides into the hot gas filtration process with ceramic filter elements of fluidized bed combustors which mainly represent an important N₂O-source. According to Klein (Klein 1994) worldwide approx. 260 coal-fired power plants with fluidized bed combustors in the power range > 50 MW_{el} existed in 1994, to which approx. 1 % of the global coal dissipation corresponds. These emitted dinitrogen oxide with 70 kt/a, however, 20 % of the entire N₂O amounts from stationary firing plants. After Kleins calculations an increase of coal-fired fluidized bed combustors only by 10 % triples the N₂O emission.

From this basis it is currently of interest to find out, how the origin and the reduction of the nitrogen oxides (NO, NO₂ and N₂O) in fluidized bed combustors can be influenced. This requires detailed knowledge of the formation and reduction mechanisms of the involved nitrogenous flue gas components on which the experimental and numerical investigations are focused.

Approach

Both experimental and numerical investigations were performed. A test rig was build up in which the reaction kinetics for synthetic flue gases of variable gas composition could be analysed at different temperatures. So far thermal decomposition and homogeneous catalysis were researched. In the latter case aqueous solutions of ammonia, urea and hydrogen peroxide were brought into the reactor at different positions as liquid or vaporised.

The results attained thereby were used to validate numerical investigations which were performed on the one hand with the standard CFD-Code FLUENT and on the other hand with an own one-dimensional steady-state software. This software is able to reduce the underlying system of elementary reactions by a sensitivity analysis to a set of only a few substantial reactions which were then used in the CFD-Code. Otherwise a simulation of complex three-dimensional geometry's is not practicable due to the enormous computational effort.

Project Description

The experimental investigations for the homogeneous reduction of nitrogenous gas components by adding appropriate reducing agents and further additives on condition of an atmospherically operated coal-fired fluidised bed combustor were carried out at a tubular reactor which is represented schematically in –figure 1–.

The equipment allows the investigation of different processes to reduce gaseous pollutant components in synthetic flue gases under atmospheric conditions up to 1173 K. So mechanisms also heterogeneously catalyzed and/or sped up by liquid additives with regard to their kinetics next to reactions activated thermally can be determined quantitatively.

The experimental set-up can be divided in five functional units which are explained in the following:

1. proportioning and mixing of gas components
2. additive proportioning to the preparation and supply of additives into the reactor
3. high temperature reactor of special steel with probe lances and proportioning capabilities
4. gas analysis for the recording of the local gas concentrations of some components
5. control technique, data acquisition, signal processing, visualization

The tubular reactor is produced as a steel tube made of a high temperature steel with a wall-thickness of 11 mm. The length amounts to 1,7 m and the diameter to 0,15 m.

In order to guarantee an homogenous mixture of the gaseous pollutant components (O₂, CO, CO₂, NO, NO₂, N₂O) with the carrier gas (N₂) in the reactor, the two gas streams must be premixed. To that they are introduced together into the reactor head by an aperture with a diameter of 13 mm and flow against a highly porous quartz frit which decollates the head of the reactor in a distance of 100 mm from the intermediate part. The fitting pressure difference makes a flow reversal which causes the mixing. Optionally a further filter plate e.g. a carrier plate for catalysts can be used for following investigations in the lower part of the reactor.

To compensate the dissipated heat flux with a maximum of 4 kW the reactor itself is surrounded by two electrical heaters arranged uprightly, that can produce a power output of

in total 5 kW. Three additional heating tapes guarantee maximally small temperature gradients at the reactor head, reactor foot and between the electrical heaters. The temperature of the heating and the reactor interior is measured and controlled by thermocouples along the reaction path continuously. The system is thermally very slow due to the high heat capacity of the steel and the complete isolation with a ceramic fleece.

Next to the five proportioning capabilities for the insertion of liquid or gaseous reducing agents and additives at four locations along the reaction path a side stream of the gas mixture is taken to a gas analyser unit after optionally being cooled down apart from temperatures below 373 K in the probe lance to prevent reactions of the gases on the way from the reactor to the analysers. The gas exits the reactor via a water cooled coil.

Concerning the numerical investigations a Fortran program with the intern denotation HOKINGA (homogenous kinetics of gas phase reactions) was developed to calculate homogenous gas phase reactions which was used to verify the experimental results (Gross 2002). The program makes it possible to reduce the detailed elementary kinetics with 42 species and 247 reactions according to different applications to a reaction system with about 10 reactions and 5 species since the complete system is not manageable with commercial CFD-codes because of its complexity and size at practical applications and two- or three-dimensional geometries. As input data the program needs only the original concentrations of the involved species, the initial values for temperature and pressure, geometric data, as length and diameter of the reactor as well as simulation-particular information as convergence criteria or under-relaxation factors.

The reduction principle employed in the program appertains to the group of the classification procedures based on 'brute-force' methods. The program proceeds into four stages. First of all, the complete reaction system with all reactions and species is solved. This solution serves as reference for the further reduction steps. In the first reduction stage the reactions whose species is not available in the system are removed from the system. With the here considered systems this concerns sulfur -containing components.

In the second reduction step reactions are checked by means of the size of their source terms. If the standardized contribution of the source term of a reaction to the formation of a species is at all grid points below an user-defined absolute threshold value, these reactions are removed, first of all, from the system. The so reduced mechanism is computed again and compared with the results of the complete system. The comparison takes place in this case not for all species contained in the system, but only for species defined before by the user. This means makes a precise reduction of the reaction system possible. It can absolutely occur from that, that the reduced mechanism represents the initial system sufficiently exactly only with respect to a few species that stand in the focal point of interest.

If the deviation of the resultant concentration profiles in accordance with preset error bounds for these target species is not acceptable, the reduced system is rejected and a new reduced system with a smaller barrier concerning the source term is used. This iterative procedure is continued so long until the deviations in the concentration profiles correspond to the default error bounds or a minimum source term contribution for a reaction is reached. In the latter case the reaction is retained, and no reduction of the system occurs.

As a criterion for the deviation of the reduced one of the complete reaction system the local deviation of the concentration of every target species at every grid point is evaluated. This computes itself as follows:

$$\text{err}_{i,n} = \left| \frac{c_{0i,n} - c_{i,n}}{c_{0i,n}} \right| \quad (1)$$

with $\text{err}_{i,n}$: relative error of the concentration of species i in grid point n

$c_{0i,n}$: concentration of the species i according to the origin system in grid point n

$c_{i,n}$: concentration of the species i according to the reduced system in grid point n

In the third reduction step those still available species and the appropriate reactions are removed after each other from the system. In turn the matching with the origin system is regarded as a criterion for the admissibility of the reduction with regard to the concentration of the target species at every grid point. In the last step the same procedure with the still remained reactions is carried out. Ultimately one receives a reduced reaction system which yields to comparable results with respect to the target species as the origin system. With this system it is now possible to carry out two- or three-dimensional simulations with CFD codes.

An advantage of the described reduction procedure is the simple implementation as well as the fact that the user does not have to know the real reaction kinetics. But these advantages are bought with a high computational effort which is, however, more than compensated with the use of the reduced mechanism with complex fluid flow calculations. The calculation duration is in particular dependent on the residence time to be considered since the difference between the rapid and slow modes of the elementary kinetics becomes noticeable. Although the fast reactions are completed after a few milliseconds, they remain to the system, however, until at the end of the residence time. Furthermore such a procedure does not lead automatically to an optimum with reference to the possible reduction potential.

Results

First of all, the efficiency of the reduction mechanism implemented in HOKNGA should be represented for a system of the components N_2O , CO , CO_2 and N_2 . The examined mixture is described in table 1.

The reduced kinetics were implemented into the CFD-code FLUENT, to be able to simulate the reactor also two-dimensionally. Through that the influence of the fluid flow is supposed to be examined in particular for the axial concentration distribution of important species in the mixing zone between inert gas and gaseous pollutants in the reactor head up to the quartz frit as well as the effect of the form of the flow section with fixed wall temperatures. The calculations were accomplished in this case for the temperatures 573, 973, 1073 and 1173 K and compared with the calculations from HOKINGA and the results of measurement.

In –figure 2– the process is represented to the N_2O -concentration as it shows during the two-dimensional calculation with FLUENT.

The conversion is defined as:

$$\text{conversion} = \left(1 - \frac{c}{c_0}\right) \cdot 100 \text{ [%]} \quad (2)$$

With regard to the dinitrogen oxide distribution one can see, that at 1173 K within the mixing zone between the admission and the quartz frit a field with high concentration gradients both in axial as also a radial direction exists. The gradients are not available with smaller temperatures, here 773 K, since dinitrogen oxide is thermally stable in this temperature range. Below the quartz frit the radial concentration profile which developed in the mixing zone remains preserved due to the plug flow and the small radial diffusion rate within the reactor

up to the outlet. With high temperatures dinitrogen oxide is thermally removed in axial direction about the entire length of the reactor completely.

A comparison of the axial data for the CO- and N₂O-concentration from the FLUENT calculations with the data from the simulation with HOKINGA and the measurements, represented in –figure 3a– for N₂O and 3b for CO, shows the good agreement between the calculation methods. Since the underlying kinetics is identical for both calculations, the recognizable deviations must depend on the fluid flow that can not be considered realistically using the one-dimensional simulation with HOKINGA.

An approach to explain this effect is in the consideration of the flow circumstances above the porous quartz frit in the mixing zone. Due to the mixing procedure locally lower temperatures occur there as in the one-dimensional calculations. From this basis the N₂O and CO conversions are lower at the two-dimensional FLUENT simulations at the beginning and resemble first after some seconds with the concentration level of the HOKINGA calculations.

The next case which will be presented here includes the injection of H₂O₂ as additive. –Figure 4– represents the processes of the N₂O and CO-conversion (–figure 4a and 4b–) as well as those of the concentrations of NO and NO₂ (–figure 4c and 4d–) of the series of experiments I, II and III. The most important limiting conditions for these series of experiments under presence of oxygen are presented in table 2.

The agreement between the computed and measured data, in particular for high temperatures for all species shown in –figure 4– at all, N₂O, CO, NO and NO₂ is quite good; only for 773 K the simulation can calculate the data of CO, NO and NO₂ only tendentially.

The investigation of the elementary kinetics of the series of experiments I, II and III reduced through the simulation program HOKINGA, consisting of 17 reactions with 17 species, shows, that the decomposition of dinitrogen oxide after 0,02 s residence time in the reactor is based to almost 100 % on OH-radicals from the dissociation of the hydrogen peroxide.

Considering the concentration profiles of NO (–figure 4c–) and NO₂ (–figure 4d–), in particular the data for 773 and 973 K, it must be explained, that with higher temperatures both NO as also NO₂ hardly deviate from the entry concentrations. At the beginning of the reaction at temperatures of 773 and 973 K the computed concentrations for NO decrease within a few milliseconds from an original concentration of 670 mg/m_N³ to zero, whereas in the same period the concentration of NO₂ increases from 0 to more than 800 mg/m_N³.

The combustion of NO is responsible for this mechanism. According to the following equation at first HO₂ radicals were formed:



Due to the elementary reaction



next to OH also NO₂ arises. With increasing residence time the NO₂ reacts then with free H-radicals according to the following equation



so that the origin concentration of NO is reached again.

The differences in the concentration profiles of NO (–figure 4c–) and NO₂ (–figure 4d–) between measurement and simulation that occur in particular at 773 K could be explained through the short period of few milliseconds in which the radical reaction (4) happens and that can be represented only inadequately through the available test setup that has the first measurement point in the reactor at a distance of 25 cm below the gas pipe.

The investigations showed that for the reduction of dinitrogen oxide in the first place the thermal decomposition which increases with increasing temperature clearly is leading. The thermal decomposition can be sped up particularly by the presence of NH₂ radicals from the disintegration of urea or ammonia and/or about H and OH radicals through the addition of hydrogen peroxide at the beginning of the reaction. Generally the conversion of dinitrogen oxide at increasing residence time remains thermally controlled because of the rapid disassembly of the free radicals contained in the system.

Concerning the reduction of the NO with the reducing agents ammonia and urea, as well as for the combination of hydrogen peroxide and ammonia or hydrogen peroxide and urea with temperatures between 1073 and 1173 K an almost complete NO reduction was obtained. The temperature optimum for the conversion of the nitrogen oxide rests in agreement with the literature below 1173 K.

Future Activities

The investigations have shown that there is a unspecified catalytic wall influence of the steel reactor onto the kinetics of the reactions. So comparative measurements with a reactor of silica glass are desirable. With this reactor also investigations of the heterogeneous nitrogen kinetics should be carried out at conditions of atmospheric fluidized bed combustors with presence of ash, bed material as well as catalysts to reduce NO_x and N₂O. The definition of heterogeneous Arrhenius-rates can be used then for a further development of the simulation program HOKINGA concerning the heterogeneously catalyzed kinetics of nitrogenous gas components.

References

- Klein, M., Köser, H., Rosenthal, J., 1991. Modelluntersuchungen zur chemischen Reaktivität der Stickstoffoxide an Bettaschen von Wirbelschichtfeuerungen. Proceedings of the VGB Conference Chemie im Kraftwerk
- Halang, S., 1997. Experimentelle Untersuchungen zum katalytischen Einfluß der Aschebestandteile auf die NO_x-Bildung bei der Kohleverbrennung. Dissertation TU Bergakademie Freiberg
- Duo, W., Grace, J.R., Lim, C.J., Brereton, C.M.H., Watkinson, A.P., Laursen, K. 1998. The Role of the Filter Cake in Hot Gas Cleaning with Ceramic Filters. Annual Report. Department of Chemical and Bio Resource Engineering. University of British Columbia.
- Peukert, W., 1996. Combined Processes for High Temperature Gas Cleaning. 3th International Symposium on Gas Cleaning at High Temperatures, Karlsruhe
- Gäng, P., 1990. Die kombinierte Abscheidung von Stäuben und Gasen mit Abreinigungsfiltern bei hohen Temperaturen. Dissertation Universität Karlsruhe
- Möhring, S., 1998. Simultane Staub- und Schadgasabscheidung mittels katalytisch aktivierter faserkeramischer Filter. GVC-Tagung

Hübner, K., Pape, A., Weber, E.A., 1996. Simultaneous Removal of Gaseous and Particulate Components from Gases by Catalytically Activated Ceramic Filters. 3th International Symposium on Gas Cleaning at High Temperatures, Karlsruhe

Kwetkus, B.A., Egli, W., 1996. The Ceramic Monolithic Filter Modul: Filtration Properties and DeNOx Potential. 3th International Symposium on Gas Cleaning at High Temperatures, Karlsruhe

Gross, R. F., 2002. Zur Kinetik homogener Gasphasenreaktionen nitroser Komponenten in Rauchgasen einer kohlebefeuereten Wirbelschicht, Dissertation, RWTH Aachen

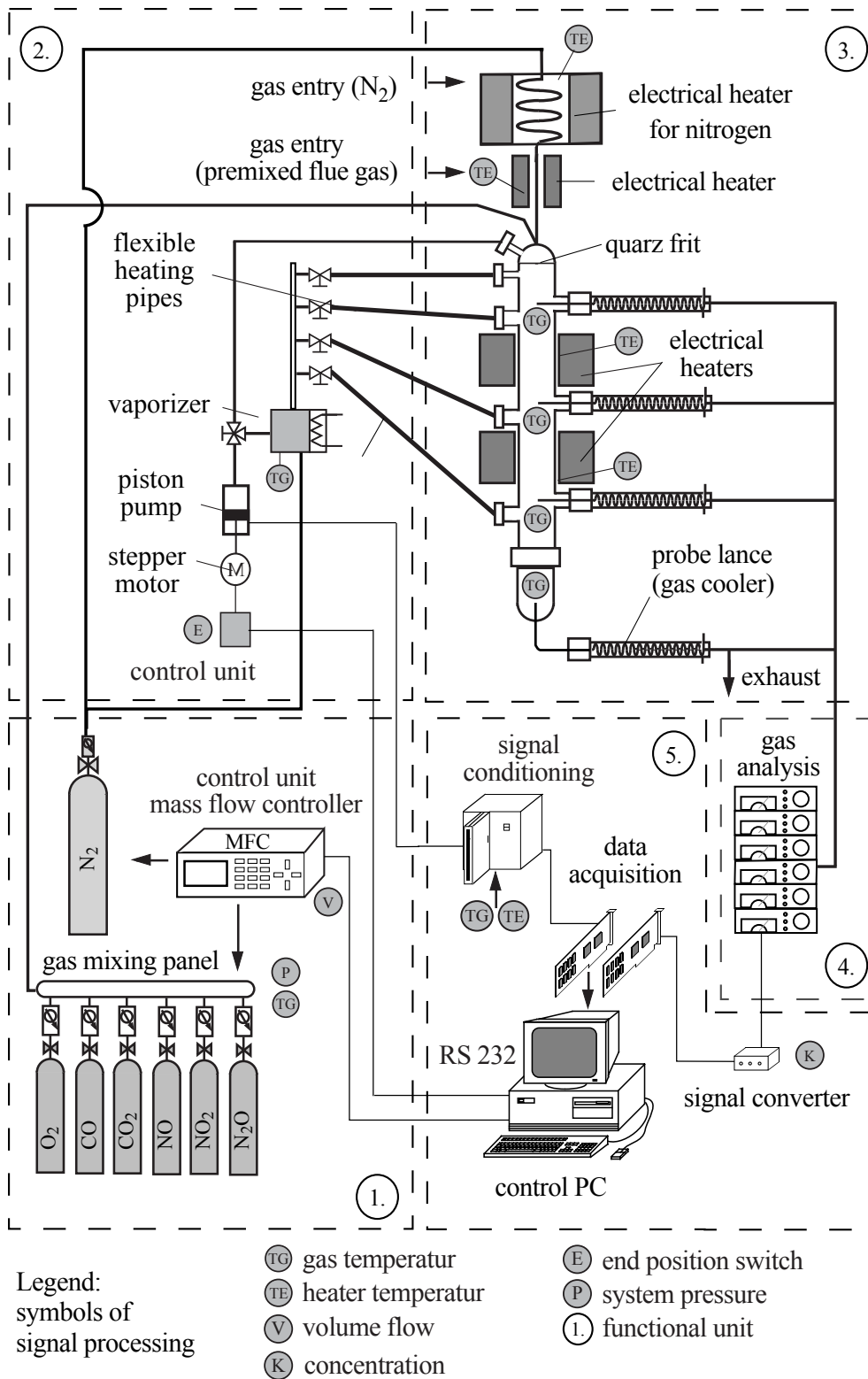


Figure 1: Schematic Construction of the Reactor and its Periphery

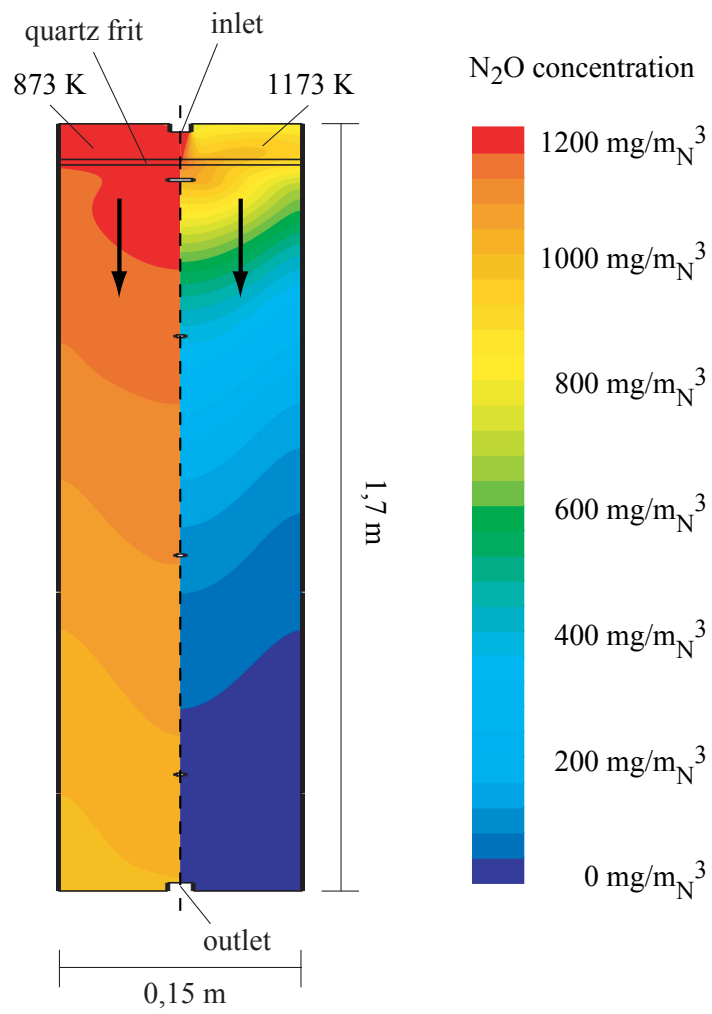


Figure 2: 2D-Simulation with FLUENT, N_2O Concentration Profiles in the Reactor (not to scale)

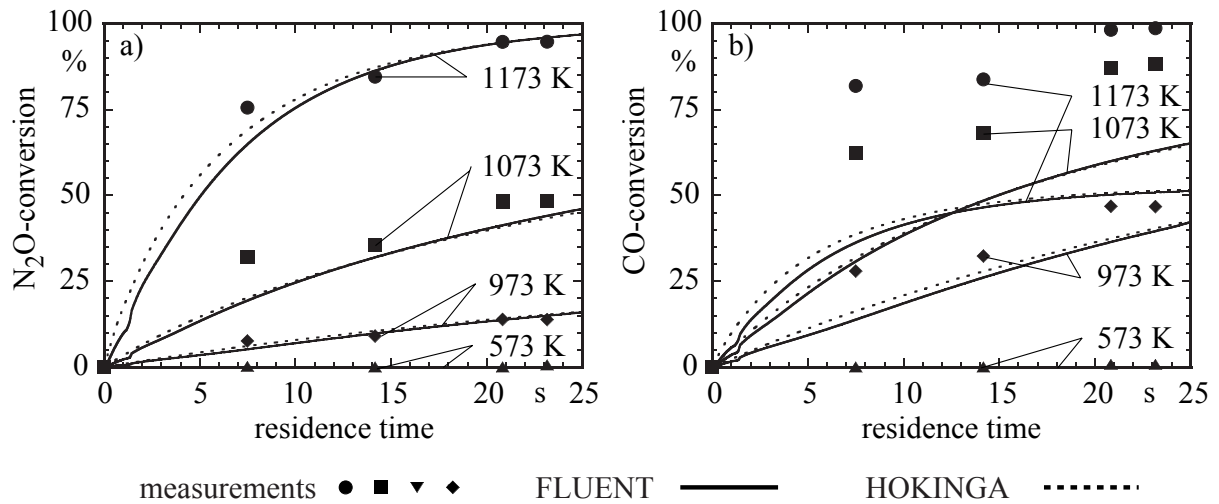


Figure 3: N₂O-Reduction Through Thermal Decomposition and Combustion of CO, Comparison Between Measurement and Simulation (HOKINGA (1D) and FLUENT (2D))

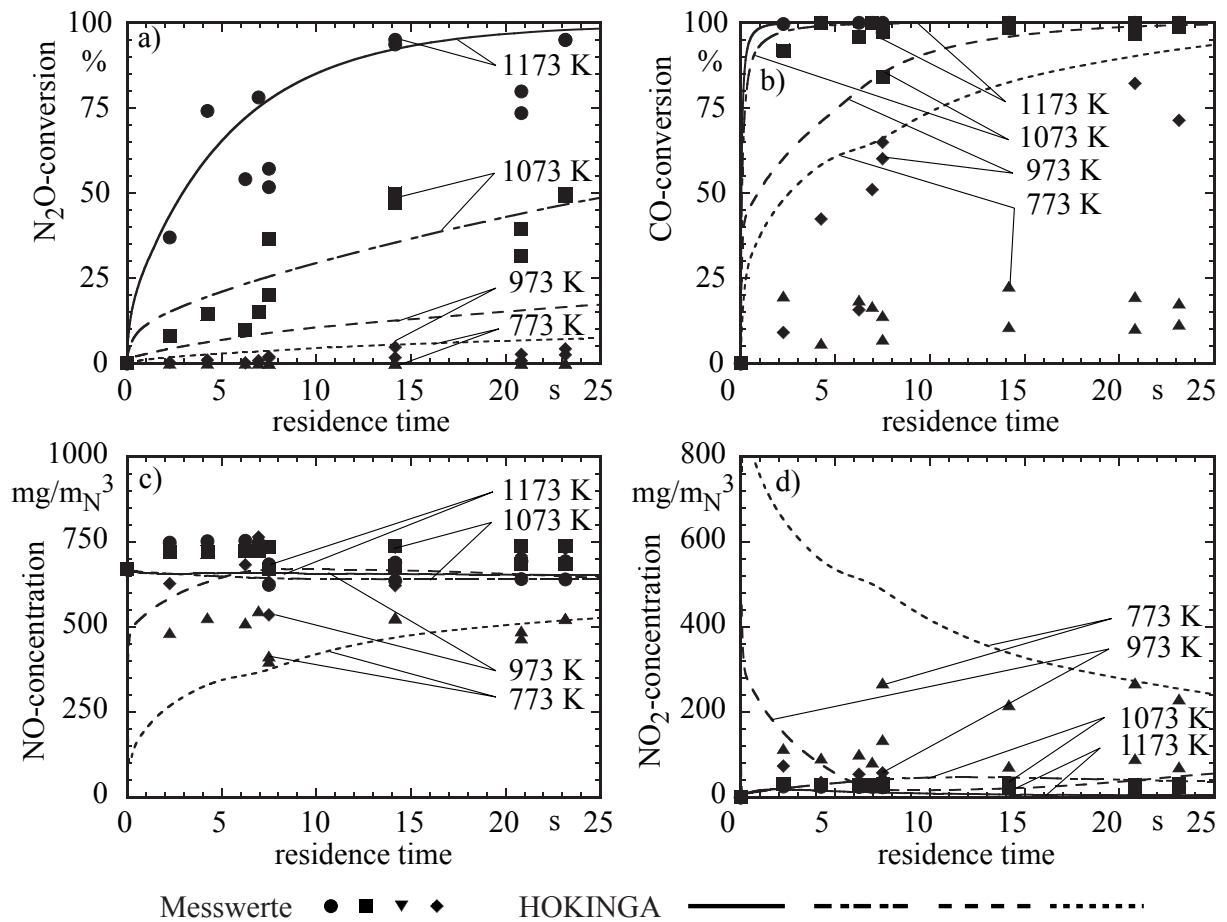


Figure 4: Concentration Profiles of Nitrogenous Components and Conversion of CO

Table 1: Examined Gas Mixture

N ₂ O [mg/m _N ³]	NO [mg/m _N ³]	NO ₂ [mg/m _N ³]	CO [mg/m _N ³]	CO ₂ [g/m _N ³]	O ₂ [g/m _N ³]	N ₂ [g/m _N ³]	u [cm/s]
1179	---	---	250	59	---	1212	6

Table 2: Examined Gas Mixtures with Additive Injection

No.	NO [mg/m _N ³]	O ₂ [g/m _N ³]	N ₂ [g/m _N ³]	H ₂ O ₂ [mg/m _N ³]	H ₂ O [mg/m _N ³]	injection type	u [cm/s]
I	670	29	1181	1229	2285	vaporized	6
II	670	29	1181	1229	2285	liquid	6
III	670	29	1181	1229	2285	liquid	20
other gas components: N ₂ O = 1179 mg/m _N ³ , CO = 625 mg/m _N ³ , CO ₂ = 59 g/m _N ³							