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PRODUCTION AND REDUCTION OF NITROGEN OXIDE IN CONVENTIONAL- AND OXYFUEL- COMBUSTION BASED ON DRY PULVERIZED LIGNITE

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1 INTRODUCTION

The oxyfuel process is one of the CCS-Technologies applied in the separation of carbon dioxide from the combustion gases from fossil fuel fired combustion units. Compared to the conventional combustion powered with air, the combustion operated the oxyfuel process with pure oxygen, the lack of atmospheric nitrogen is replaced with recirculated flue gas. From that it results in other process conditions, which have an effect on the combustion behavior of coal and also to the pollutants formation and reduction. The investigations of these relationships are not yet complete. In this paper, there will be an emphasis on a few differences, that occur during nitrogen formation/reduction, and are clearly recognizable in oxyfuel fired combustion units as compared to the ones that conventionally fired by air. Detailed experiments were hence undertaken in a 50 kW_{therm} pulverized coal combustion test facility.

In this paper, the consideration of the relevant formation mechanism and a short description of the test facility are initially explained and furthermore the information into the flame investigations in the combustion chamber are described. After the introduction of the measuring technology and the undertaken measurement test series – the results of the investigations are shown and discussed.

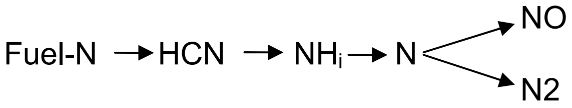
2 FORMATION PROCESS OF NITROGEN OXIDE

In this presented paper, the dominant NO formation mechanism from fuel nitrogen is considered for coal combustion under oxyfuel conditions.

Homogeneous fuel nitrogen release

The homogeneous nitrogen fuel release occurs when volatile matter is released from the coal. About half up to two thirds of fuel bound nitrogen can be released with the volatile matter [1]. That is dependent on the type of coal, petrographic structure, pyrolysis temperature and the heating rate [3].

After the volatile matter released, very fast reactions occur forming the typical nitrogen containing light gas species of HCN and NH_3. They form the starting reaction components for the nitrogen containing end products of NO_x, N_2O and N_2.The simplified reaction path for the conversion of the intermediate products into end products can be given as follows:



The rate-limiting reactions for the NO formation and reduction are after [2] described as follows:

$$N + OH \rightarrow NO + H \tag{R1}$$

$$N + NO \rightarrow N_2 + O \tag{R2}$$

In the oxyfuel process, however, the recirculated flue gas with NO load should be considered, provided that the flue gas is not discharged after a denitrification plant. The reaction R2 therefore becomes more important. Also other reactions to fuel rich conditions in the burner area as possible, such as

$$NO + NH \rightarrow N_2O + H. \tag{R3}$$

Heterogeneous fuel nitrogen release

The remaining amount of nitrogen in the coke is released parallel to carbon combustion. The nitrogen (-CN) bound in the coke is initially chemisorbed with oxygen and subsequently desorbed to NO [4]. However the NO in the pore system of the coal particle can be reduced again through the carbon. Thereby the decomposition rate of the NO strongly dependents on the temperature. With an increasing temperature there is a clear increase in the decomposition rate. The decomposed amount of NO is furthermore proportional to the formation of CO and N_2 [3].The conversion rate of the coke bound nitrogen in NO is therefore relatively small, at substoichiometric process operation it lies under 10 % and at overstoichiometric process operation between 30 and 50 % [1].

The reduction of NO from carbon proceeds after the following heterogeneous reaction [1,3]

$$C + 2\,NO \rightarrow CO_2 + N_2 \tag{R4}$$

$$2\,C + 2\,NO \rightarrow 2\,CO + N_2 \tag{R5 .}$$

The reaction R5 is initially relevant at temperatures above 700 K, which mostly occurs in coal combustion. With the help of catalytic influence of solid particles (coal or ash) the reaction can proceed as follows

$$2\,CO + 2\,NO \rightarrow 2\,CO_2 + N_2 \tag{R6}$$

Because of the already mentioned high rates of NO load by the flue gas recirculation, that can be implemented by improving fuel-rich conditions are in the oxyfuel process, further NO reduction pathways of importance, for example:

$CN + NO$	→	$N_2 + CO$	R7
$CN + NO$	→	$NCO + N$	R8
$NCO + NO$	→	$N_2O + CO$	R9.

The complexity of the reaction processes can be a consideration of NO formation or reduction of individual reactions not to. For this, the whole mechanism be investigated with the appropriate process conditions.

3 EXPERIMENTAL TEST FACILITY

Brief description and process diagram

The investigations into the oxyfuel process were carried out [7] in a test facility (Fig.1)

The test facility has a thermal power of 50 kW_{therm} and alongside the conventional operational mode with air with varying options, it also allows the possibility of coal combustion with pure oxygen and recirculation flue gas (oxyfuel) to be investigated.

In Fig 2 the process diagram of the test facility is shown. The core of the test facility is formed from the modular cylindrical combustion chamber and with a central assembled roof burner for pulverized fuels.

After the combustion chamber, the cooling of the flue gas occurs at about 200°C and filtration of the fly ash. A ventilator re-circulates the flue gas proportionally. The primary flue gas flow aids to the conveyance of the fuel. The oxygen in the secondary flue gas flow is dosed in a pre-mixture chamber of the process. The test plant is gas-tight and can represent an ideal oxyfuel process. It means that in dry flue gas conditions, carbon dioxide concentrations well over 95 % can be measured.

Through defined dosing of inleaked air (*false air*), a real oxyfuel process can be investigated [7,8]

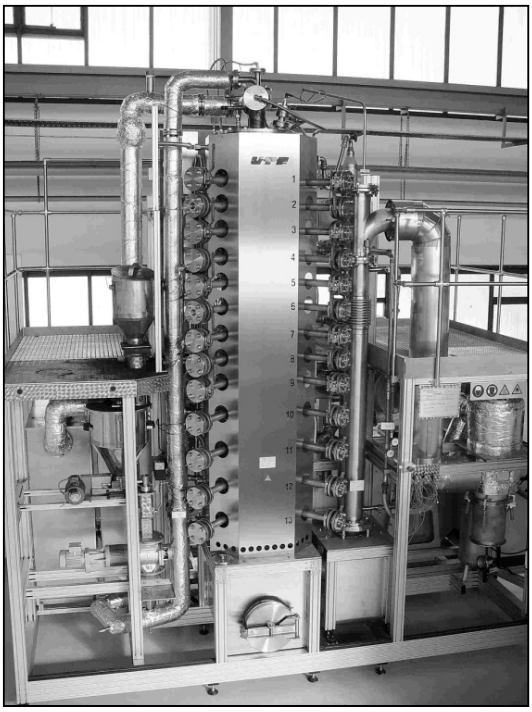


Fig 1 Pulverized coal combustion test facility at Technische Universität Dresden

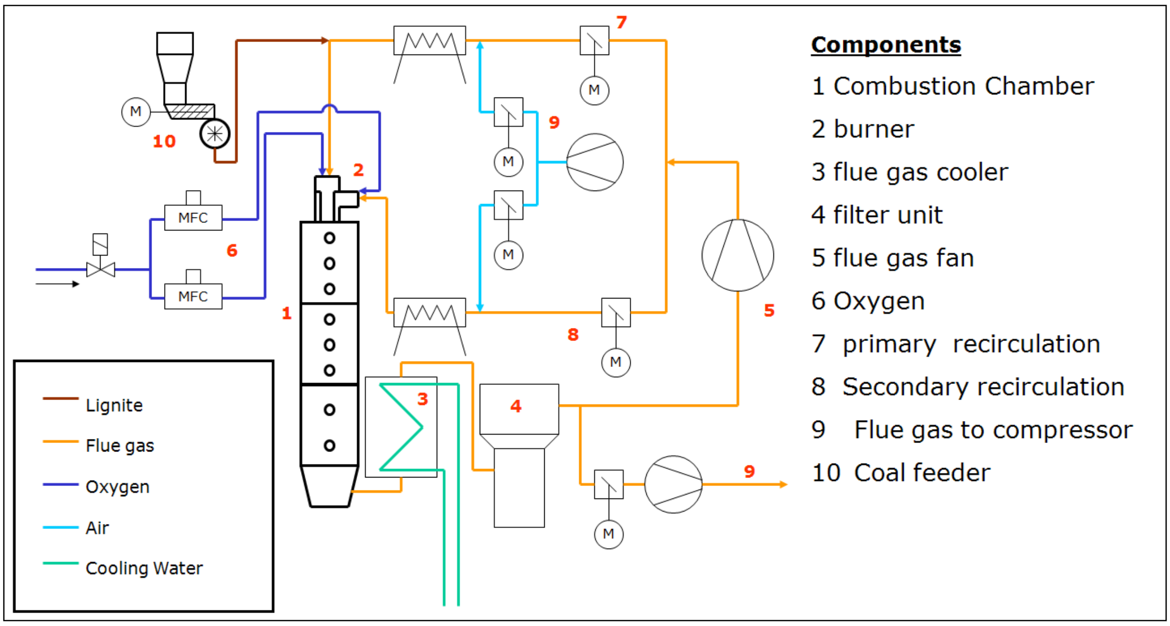


Fig 2 Process diagram of test facility

4 FLAME INVESTIGATIONS IN THE COMBUSTION CHAMBER

4.1 Flue Gas Measuring Technology

The flue gas composition at the end of the combustion chamber is measured through a conventional flue gas measuring technology of infrared basis. To that a partial flow is sucked, dried and analyzed. The acquisition of the measured values is done continually.

For the flame investigations a raster is placed, as shown in Fig 3. In the top of the combustion chamber more measurement points were arranged, as can be expected here, most reactions and conversions. A lock system enables the special sensors application across the combustion chamber length without false air inflow.

For the measurement of the flue gas composition there is a special sensor that was developed. The sensor is only cooled at the front part of the sampling area such that the reaction is stopped. Further on the gas is fed to an analyzer through a heated probe and a heated tube at a temperature of 180°C. From that the ability of strongly water containing flue gas to reach temperatures below the dew point for oxyfuel process is inhibited. Additionally the decomposition reaction is slowed down for example nitrogen monoxide from nitrogen dioxide.

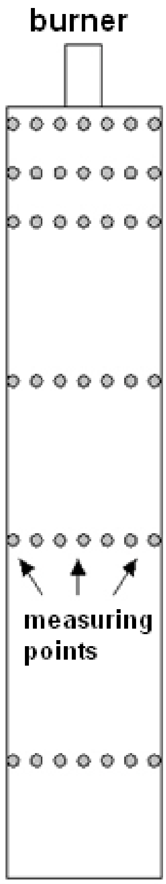


Fig 3 Measuring point raster in the combustion chamber

For analysis the multi-component measuring system MCS 100E from the company SICK MAIHAK was used. The MCS 100 E represents a standard solution for the flue gas monitoring in incineration plants after the air pollution law *17. BImSchV* (Germany) and also applications in plants with high acid dew point. The measuring principle is based on infrared spectral photometer with an image frequency and gas filter correlation process, and the measuring is through a transmitted light process. The system allows quasi simultaneous up to 8 components and oxygen, through a zirconium probe to be detected. In order to prevent the gas from being below the dew point, all components that are in contact with the gas are heated from the sampling place [5]. The composition of the components therefore does not change. The analysis system is initially designed for high flow rates of approximately 600 l/h, such that the adsorption and desorption forces are prevented [5].

4.2 Temperature Measuring Technology

For the measurement of the temperature in the combustion chamber a suction pyrometer is used after the standards norm VDI/VDE 3511 [6] and with a type s thermo-element (Pt/Rh/PT). In Fig 3 the shown measuring points illustrate how the measurements were carried out, similar to the flue gas measurements. The reaction conditions in the flame area correlate quite well.

4.3 Series Of Measurements

The formation and reduction of nitrogen oxide is strongly dependent on the temperature and the residence time in the combustion chamber. The oxyfuel process allows the possibility to vary the temperature and the residence time through variations of the recirculation rate. The 50 kW pulverized coal combustion test facility enables the recirculation of an amount between 60 and 80 % of the wet flue gas. Through that oxygen content of approximately between 17 and 33 vol.-$\%_{wet}$ is achieved in the combustion chamber entrance [7].

For the investigations into nitrogen formation and also reduction 3 different types of oxyfuel experimental set-up were chosen i.e. oxyfuel 20 (20 vol.-$\%_{wet}$ O_2 amount in combustion chamber entrance), oxyfuel 25 and oxyfuel 30. For comparison, a case with air (conventional combustion with air) was used, which like the oxyfuel case shows a rest oxygen content of 4 vol.-$\%_{wet}$ at the combustion chamber exit.

5 RESULTS

In Fig 4 the results of the measurement of the nitrogen monoxide concentration is shown. The values are in mg/m^3 and are based on the wet gas. The water content in the flue gas for the oxyfuel case lies between 35 and 39 vol.-% and thus it has clearly a higher amount compared to the conventional combustion with air (air operated case), with water content of approx. 9 vol.-%. For the comparison of the waste gas species between air and oxyfuel combustion it is therefore important to base on the wet flue gas.

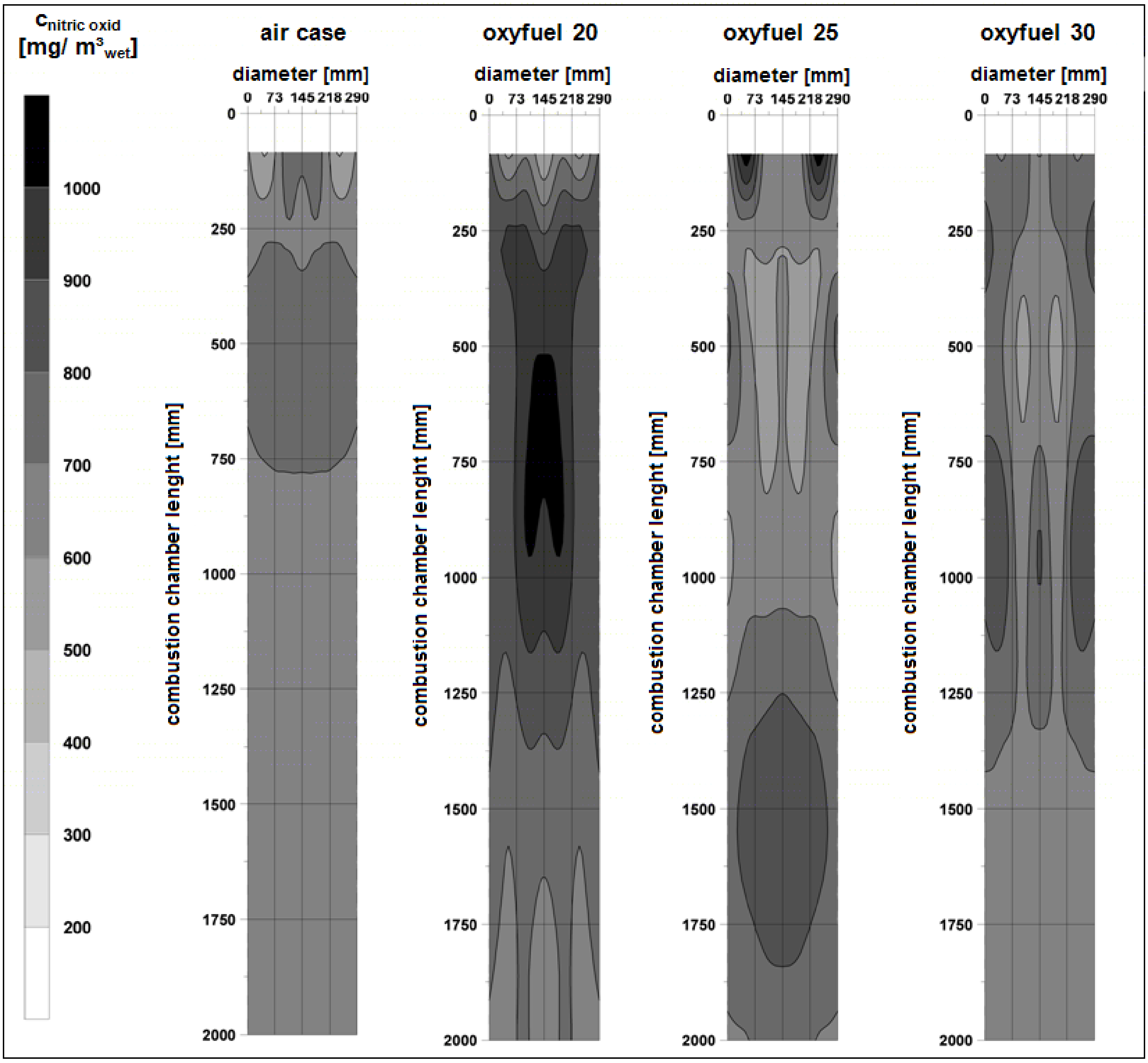


Fig 4 Nitrogen monoxide [mg/Nm$^3_{\text{wet}}$], distribution in combustion chamber

Comparison between conventional combustion with air (air case) and oxyfuel case 20

For a comparison between the air and oxyfuel case there is oxyfuel case 20 is suitable, since the mass flow in the gas phase in almost the same and the mixing ratio in the combustion chamber is comparable. The average residence time in the gas phase in the combustion chamber lies approx. at 1,6 s for the air case and for the oxyfuel case it lies approx. at 1,9 s. The oxygen concentration at the burner entry for the air case is 17,5 vol.-%, since the coal is fed in burner with recirculated flue gas.

From the lacking nitrogen in the oxyfuel process there is an expected smaller NO concentration as compared to the air case. However the thermal NO formation has no relevance also for the air case since the process temperature (see Fig 5) is very small. The fuel NO formation is decisive, for the oxyfuel case and as well as for the air case, as explained in section 2.

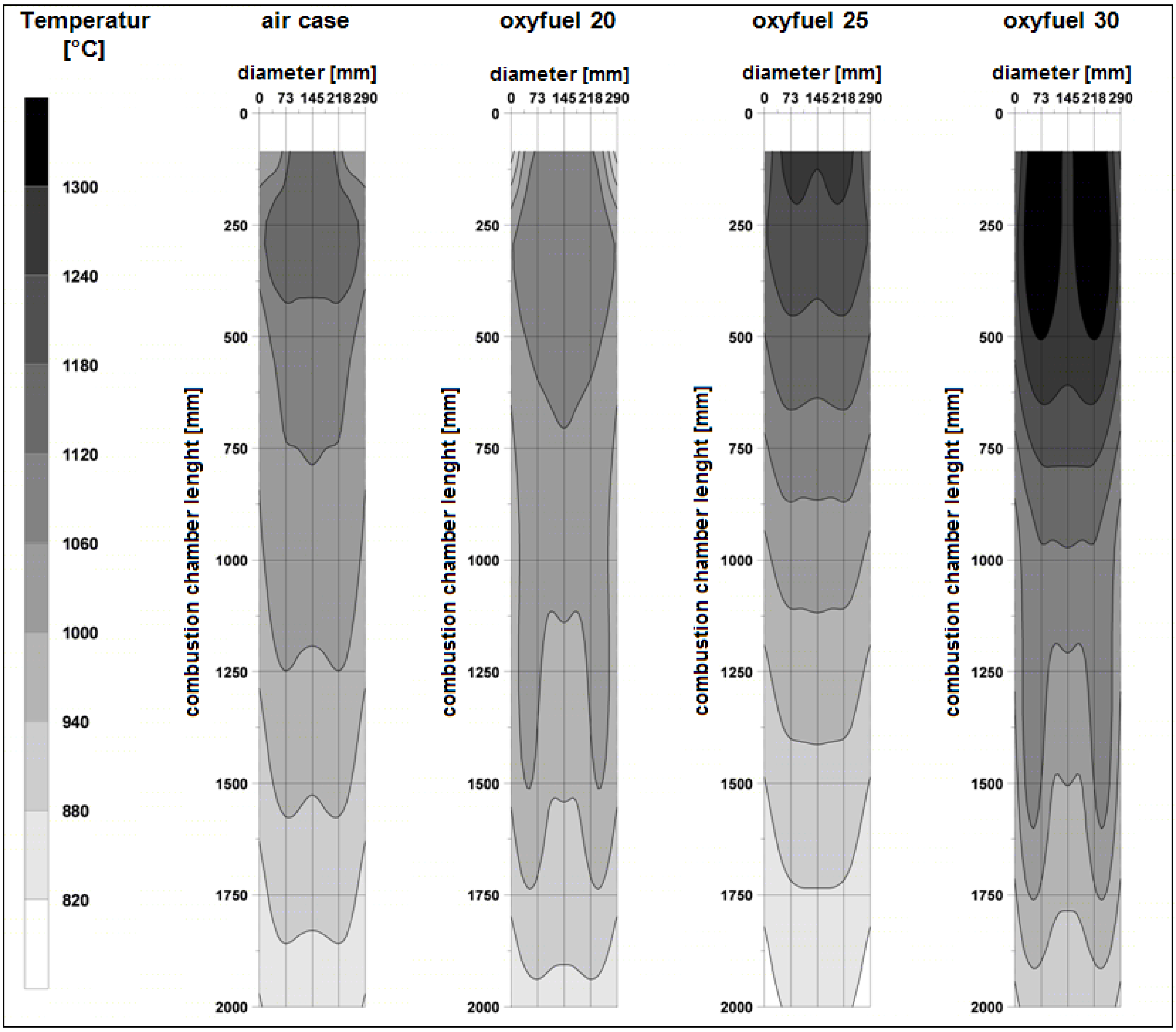


Fig 5 Temperature distribution [°C] in the combustion chamber

For a comparison between the NO concentration along the combustion chamber (Fig 4) it shows a local high NO concentration for oxyfuel case 20. On the other hand this can be attributed to the slightly high oxygen partial pressure at the entrance of the combustion chamber for the oxyfuel case (see Fig 6) and on the other hand to the recirculation of refeed fraction of NO. At the exit of the combustion chamber the concentration of NO again almost the same. Due to the clearly smaller flue gas flow rate for the Oxyfuel case the carried fraction of the NO_x is considerably smaller [8]. As explained in section 2, from the flue gas recirculation without denitrification plant, the reduction of NO to molecular nitrogen is activated (e.g. after R2).

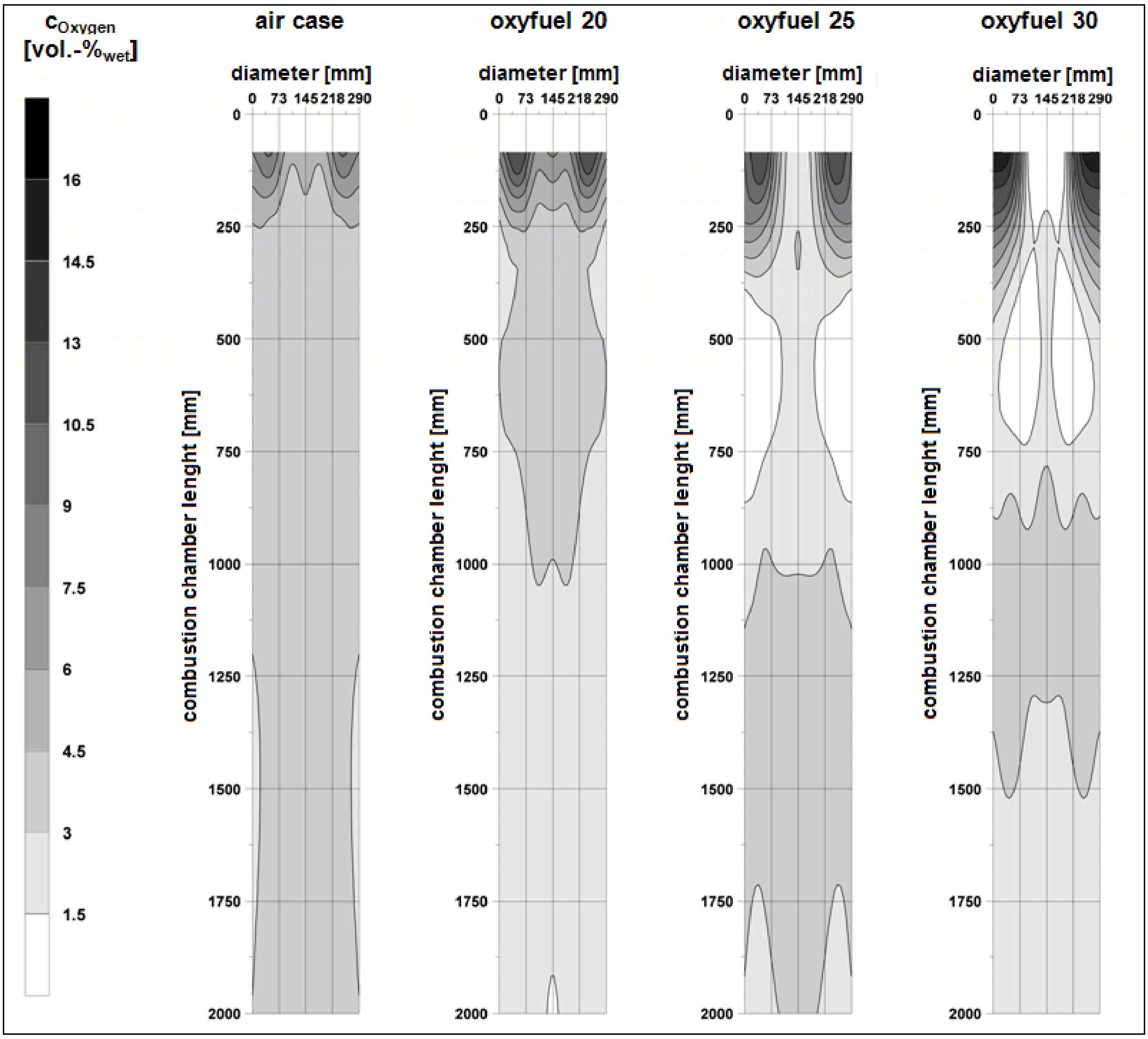


Fig 6 Oxygen [vol.-%$_{wet}$] distribution in the combustion chamber

Comparison of oxyfuel cases

With the increase in the oxygen content at the combustion chamber entry for oxyfuel process (Fig. 6), the temperature expectedly increases, as noticeable in Fig 5. The average residence time at the combustion chamber increases for oxyfuel 20 from 1,9 s to 2,5 s for oxyfuel 25 and to 2,9 s for oxyfuel 30. That is in accordance to the low recirculation rate. Compared to the oxyfuel case 20 are in the oxyfuel case 25 enforced about 22% less mass, the oxyfuel 30 is 35%. Thus the mixing in the combustion chamber decreases significantly with increasing oxyfuel case.

The reduced mixing produces a poorer burnout, which show the increased concentrations of CO, which are shown in Fig 7. The particle burnout however occurs 90 % in all cases after approx. 250 mm distance from the burner entry.

In particular, the oxyfuel case 30 demonstrates the influence of the missing mixing in the gas phase close to the burner. At the upper boundary area of the combustion chamber, very high oxygen concentration are present whilst at the center there is no oxygen present, as shown clearly in Fig 6. In this strongly under-stoichiometric area, CO is mainly formed (compare to Fig 7). The mentioned reaction R6 (see section 2) plays a more important role and the NO can be reduced to N_2 and CO_2 with the CO. A comparison of Fig 4 and Fig 5 shows on the example of Oxyfuel 30 very well the influence of this reaction. Areas with high CO concentration indicate lower NO concentrations.

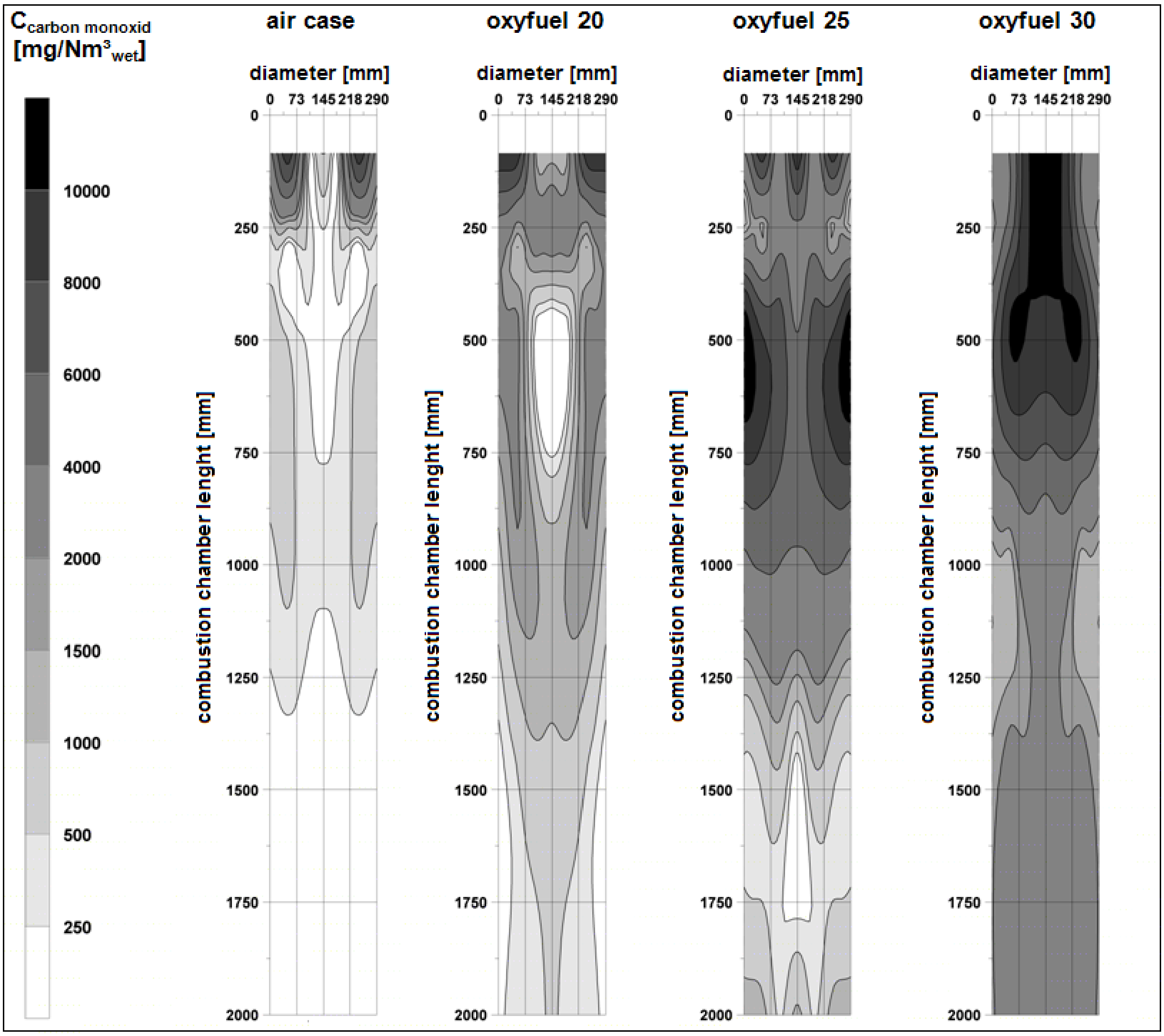


Fig 7 Carbon monoxide [mg/Nm$^3_{wet}$] distribution in the combustion chamber

The measurements of the N_2O concentration, which are shown in Fig 8, show that also the in section 2 mentioned reactions R3 and R9 are important.

In areas with high CO concentrations where the N2O concentrations are also very high (most notably that is clearly seen for Oxyfuel 30), it thus appears the reaction R9 is dominant. The N_2O formation is for the cases with high process temperatures i.e. oxyfuel case 25 and 30, dominant especially in the areas of substoichiometric, as shown by the low oxygen concentrations (Fig 6). In the oxyfuel case 20, which has lower temperatures, the N_2O is also at high O_2 concentrations in the burner area. N_2O formation is here probably already formed by reduction of N_2 reactions at the reaction

$$\text{N2 + O2 + M} \quad \rightarrow \quad \text{N2O + M} \qquad \text{R10 .}$$

The molecule M does this impact parameter is an inert [9].

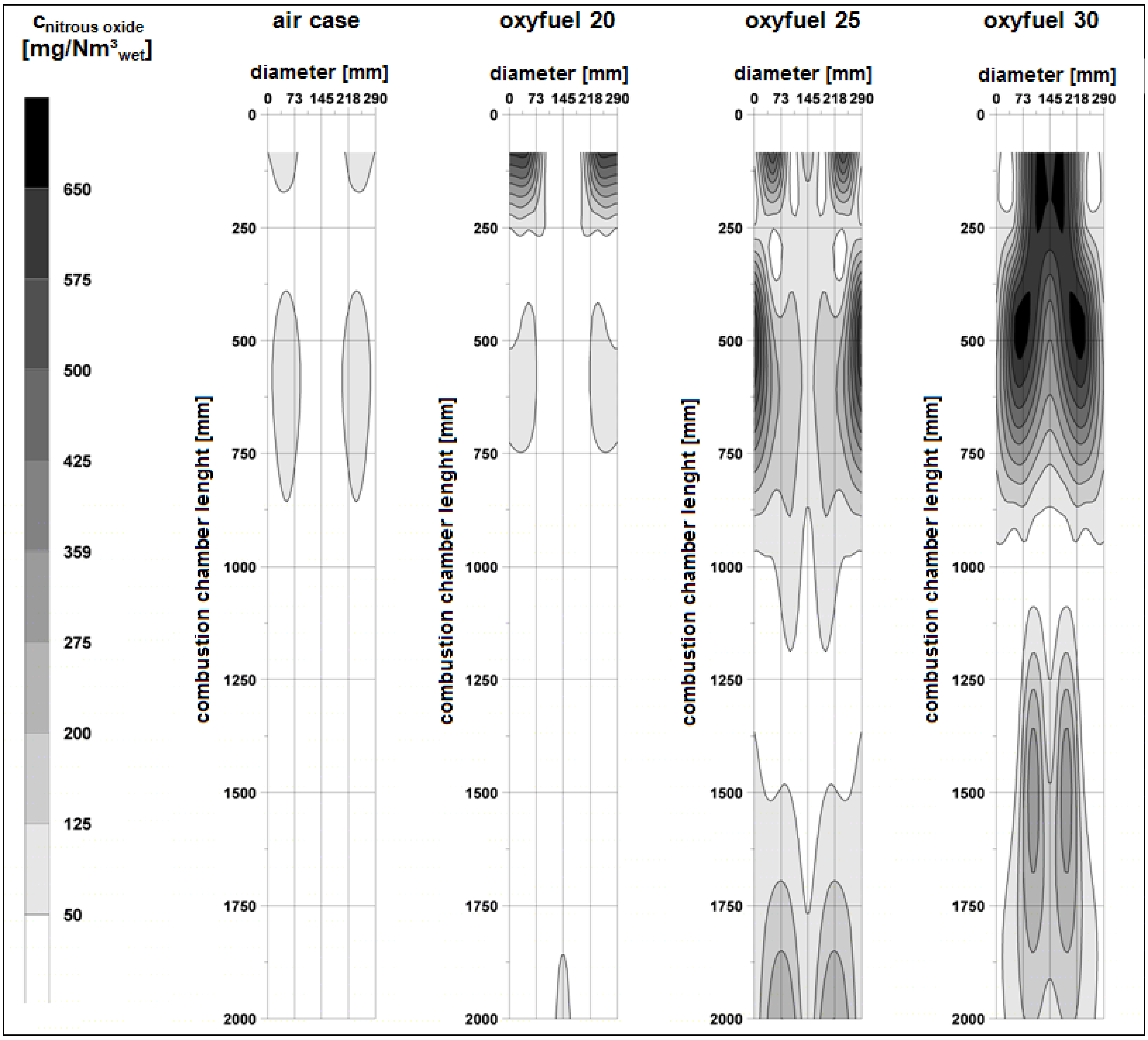


Fig 8 Nitrous oxide [mg/Nm³$_{wet}$] distribution in the combustion chamber

6 CONCLUSION

The results from flame investigations have shown that different mechanisms for the NO formation and reduction can be identified for the considered series of measurements. The mechanism can be difficulty described through single reaction and in this case, the modeling of the complete mechanism is required. The residence time and the mixing in the combustion chamber are the determining factors for a comparison of the different cases. Since the oxygen fuel concentration at the burner is controlled through the recirculation, a constant volume consideration (similar residence time and mixing) between the oxyfuel cases for a broad spectrum is very difficult. The excess oxygen, the geometry of the combustion chamber or also the geometry of the burner must be conformed to each other for such an experimental consideration.

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