INVESTIGATION OF NO_x FORMATION FOR FLAMELESS COAL COMBUSTION

Dragisa Ristic[1]*, Maik Schneider[1], Anja Schuster[1],
Prof. Dr. techn. Günter Scheffknecht[1,]
Dr. Joachim G. Wünning[2]
[1]Institute of Process Engineering and Power Plant Tecnology (IVD) Universität Stuttgart
[2]WS Wärmeprozesstechnik GmbH, Germany
* dragisa.ristic@ivd.uni-stuttgart.de

Abstract: *In recent years flameless combustion technology has been developed in order to reduce NO_x emissions in combustion proceses. Within this work a significant reduction of NO_x emissions was achieved by developing a novel coal flameless burner design. The objective of this paper is to examine mechanisms forming NO_x in the pulverised coal air staging combustion.*

Within this research, determination of the fuel-NO portion out of total-NO concentrations has been done by evaluating the flue gas measurements and using Ar/O_2 mixture instead of combustion air in flameless and flame mode. Nitrogen-containing species such as HCN and NH_3 and gaseous species used for calibration have been recorded using a high resolution FTIR spectrophotometer in flameless and flame mode. The effect of stoichiometry in the fuel-rich zone and the effect of furnace wall temperature were examined in flameless mode.

The results show strong influence of volatile matter content in coal on NO_x emission. The thermal-NO could be reduced double within flameless mode. Within flameless mode in primary combustion zone under fuel-rich conditions reducing components HCN and NH_3 are dominant volatile nitrogenous species. Amount of yielded total fuel volatile nitrogen within primary combustion zone under fuel-rich condition depend on local stoichiometry. Increasing furnace wall temperature decreases fuel-NO.

Key Words: Flameless combustion / Fuel-NO / NO of air nitrogen / Total volatile fuel nitrogen

1. INTRODUCTION

Flameless Oxidation (FLOX®) mode, also known as flameless combustion, has been originally developed for gaseous hydrocarbon fuels [1]. Its extension to other fuels is a challenge for further development. In recent years oil and gas flameless burners with high flue gas recirculation rates have been developed successfully to reduce NO_x-emission. The hot recirculating flue gas dampens the temperature fluctuations and reduces the maximum temperatures within the reaction zone which leads to reduction of NO_x-emission. Therefore, flameless combustion has also high potential to reduce NO_x formation in the pulverized coal combustion applications.

The combustion of pulverized coal in steam generating boilers is the most widely process for power generation, supplying over 40 % of the electricity worldwide. However, coal-fired plants are a source of NO_x (sum of NO, NO_2). Most of the NO_x emitted from coal-fired power plant is in the form of nitric oxide (NO), more than 95 %. Oxides of nitrogen remain one major pollutant from pulverized coal combustion and are receiving increased international attention because of their role as precursor to acid rain and photochemical smog and greenhouse effect.

Within the EU Project FLOX-COAL flameless combustion of pulverised coal is investigated at IVD (University Stuttgart) using novel designs of flameless coal burners. The novel flameless coal burners were developed in cooperation with the company WS Wärmeprozesstechnik GmbH on basis of gas FLOX® burners previously developed by WS as well as on basis of earlier experimental results [2, 3]. The tests were carried out in a bench-scale drop tube Pulverised Coal Combustor (PCC) at IVD. Flameless coal combustion within these tests was confirmed visually, by chemiluminescence imaging and velocity measurement using Laser Doppler Anemometry (LDV) [4, 5].

The main aim of this research is to investigate the possibility of using flameless technology in coal combustion to reduce the formation of NO_x, both through the fuel mechanism and thermal mechanism. For gaseous fuels this can be achieved by flameless technology due to the relatively high content of hydrocarbon radicals provided all over the combustion chamber and because of the different way fuel combusts in diluted conditions (experienced with gaseous fuels) [6]. Chemical time scales are significantly larger in the flameless oxidation mode than in other combustion modes, while temperature distributions in the primary reaction zone are more homogeneous. The improvement of combustion efficiency and the minimization of pollutant emission are the main goals of this experimental research. Moreover, to achieve a higher pollution control, the possibility of coupling flameless combustion with air staging conditions was investigated.

The mechanisms occuring during air staged combustion of pulverised coal are depicted in Figure 1.

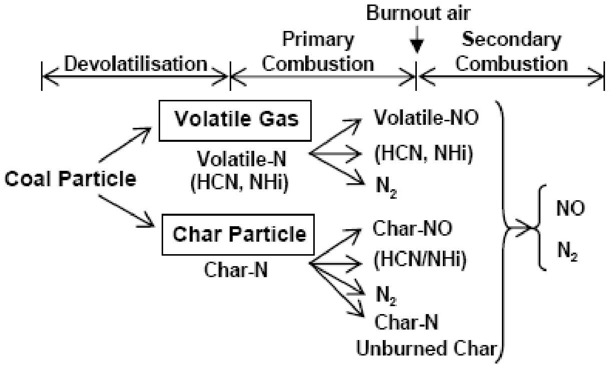

Fig. 1. Combustion of pulverised coal [7]

In the devolatilisation zone, primary and secondary combustion zone, fuel-NO is formed via various reaction pathways. The devolatilisation zone involves short time scales of roughly 100 ms. Here most of the coal and thus coal nitrogen are devolatilized, the pyrolysis products are partially oxidised, and HCN, NH_3, NO and char nitrogen are formed. The primary combustion zone, under fuel-rich conditions, involves long time scales between 2-3 s. Although concentrations of major species may not change significantly in this zone, much happens to those of the trace nitrogenous species [8], and a substantial fraction of the original coal nitrogen is converted to N_2. The third zone commences at the point of burnout air addition to provide an overall fuel-lean environment. NO_x can either be formed or destroyed in this zone.

2. EXPERIMENTAL SECTION

2.1. Furnace

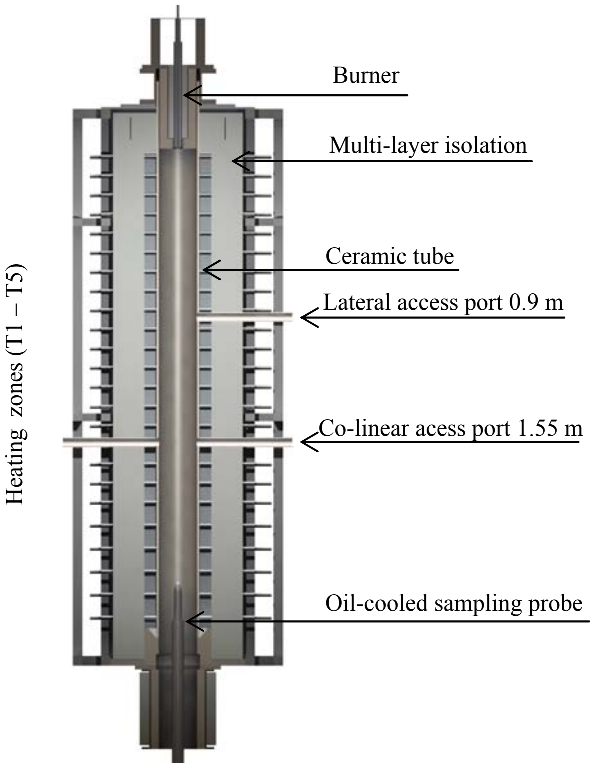

Fig. 2. Sheme of the drop tube PCC

Tests in this study were carried out on a bench-scale drop tube Pulverised Coal Combustor (PCC). The electrically heated part of the combustion chamber has a length of 2.5 m and a diameter of 0.2 m. The electrical heating allows to adjust a constant wall temperature as well as a temperature profile along the combustion chamber. Combustion chamber wall temperatures (further: wall temperature) used during this study were 1000 °C, 1100 °C and 1300 °C. Pulverized coal is supplied by primary air to the top-mounted burner through which it is injected into the combustion chamber. The feeding system consists of a volumetric conveyor and a screw feeder. The facility provides a good environment to investigate combustion in air staging conditions. Burnout air can be added at each position along the combustion chamber by axialy movable probe from below.

2.2. Burner

The burner thermal load based on coal flow is 8 kW_{th}. Primary air and pulverised coal are injected into the furnace through a fuel pipe. Preheated air is injected by the secondary air pipe into the combustion chamber through air nozzles located equidistantly on a pitch circle around the primary pipe. The diameters of the secondary air nozzles are designed for high velocity air injection. The high secondary air momentum induces a recirculation of large amounts of hot combustion products back in to the primary reaction zone, diluting the fuel and combustion air with combustion products. This dilution in the reaction zone leads to a volumetric combustion where chemical reactions occur within a large volume of the combustion chamber instead of the distinct flame fronts with high temperatures found in conventional combustion flame modes.

2.3. Sampling

The flue gas is extracted at the final section of the heated reaction tube at 2.5 m. Standard emissions analysed are O_2, CO_2, CO, SO_2, NO_x. Profile measurements of the gas composition were carried out in the combustion chamber using an oil-cooled sampling probe which transports the extracted flue gas to the standard analyzers. The oil-cooled sampling probe can be adjusted along the centre axis of the combustion chamber from the burner mouth to the burnout section with high flexibility.

2.4. FTIR spectrophotometer

A Fourier Transformed InfraRed spectrophotometer (FTIR), which uses a heated gas cell whith an optical path length of 1 m, is applied for identification and quantification of H_2O, NH_3, HCN, C_2H_2 and C_2H_4. For calibration and analysis of each measured gaseous species there were six spectral windows used in order to obtain optimal mean value. The mean values were corrected regarding interfering species [9].

2.5. Coal composition

Four different coal types are examined within this experimental study. Lignite coal Lausitz (L) was specified as a high volatile lignite coal. Kleinkopje (K) was specified as a low volatile bituminous coal. The

Kleinkopje coal has high content of fixed carbon, which represents nearly the whole carbon fraction. Budryk (B) was specified as a medium volatile bituminous coal. This coal has a higher volatile content but less carbon than Kleinkopje coal. Third bituminous coal represents blend of Polish Hard Coals (PHC) and it is specified as high volatile bituminous coal. Proximate and ultimate analyses of the tested coals are shown in Table 1.

Table 1. Fuel analyses

	K	B	PHC	L
Carbon (C) [%]	65.30	57.30	80.9	56.70
Hydrogen (H) [%]	3.90	4.00	5.0	5.60
Oxygen (O) [%]	7.02	3.52	2.94	21.44
Nitrogen (N) [%]	1.30	0.77	1.2	0.55
Sulphur (S) [%]	0.28	0.64	<0.3	0.61
Fixed Carbon [%]	56.20	43.20	64.2	36.20
Volatiles [%]	21.60	23.30	29.8	48.70
Ash [%]	18.60	26.30	4.0	4.90
Moisture [%]	3.60	6.90	2.0	10.20
LCV [MJ/kg]	23.94	22.69	32.35	18.97

3. EXPERIMENTAL RESULTS

3.1. NO_x emission

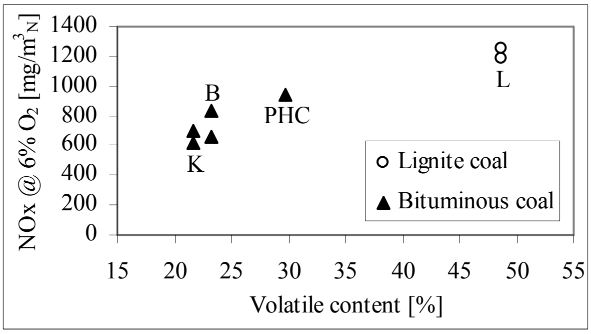

Fig. 3. Relationship between NO_x and volatile matter content in coal (unstaged flameless coal combustion; λ_{total}=1.16; wall temperature 1300 °C)

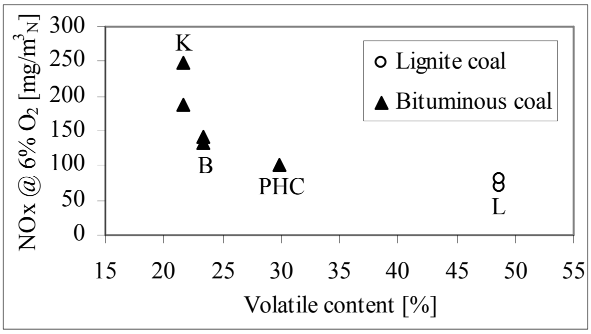

Fig. 4. Relationship between NO_x and volatile matter content in coal (air staging flameless coal combustion; λ_{local}=0.8, λ_{total}=1.16; wall temperature 1300 °C)

The impact of volatiles contained in each tested coal on NO_x emissions is presented in Figures 3 and 4. Without air staging conditions, NO_x formation increase with increasing volatile content (Figure 3), but with air staging contitions, NO_x emission decreases with increasing volatile content (Figure 4). The similar influence of volatiles on NO_x emission under fuel-rich and fuel-lean conditions is experienced for flame coal combustion within the same test facility [10].

In Figure 5 the influence of air stoichiometry on NO_x emissions for the investigated coals is shown. Tests with Lausitz coal were conducted at two different furnace wall temperatures. With intendancy to stay below regulatory limit of 200 mg/m^3_N, for lignite coal Lausitz it was possible to reduce local air stoichiometry in the primary combustion zone to 0.95, whereas for tested bituminous coals local air stoichiometry between 0.75 and 0.85 is necessary. The results were confirmed by 40 kW$_{th}$ pilot-scale tests at RWTH Aachen with up-scaled coal flameless burner [11].

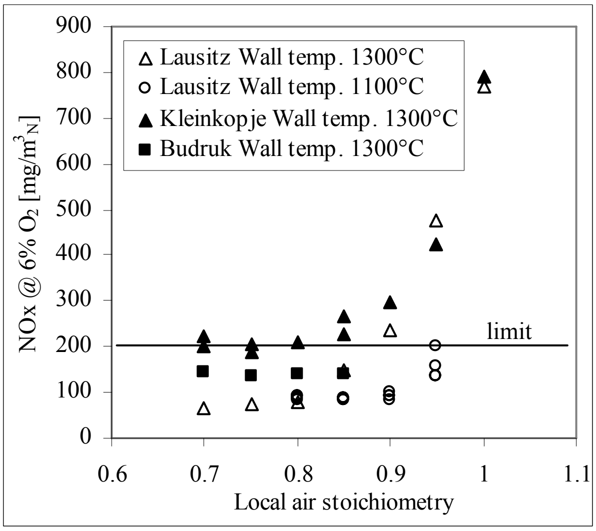

Fig. 5. Effect of air stoichiometry on NO_x emission (air staging flameless coal combustion; λ_{total}=1.16)

3.2. Fuel-NO formation in flameless and flame mode

Figures 6 and 7 represent the effect of combustion mode on NO_x formation mechanism. Tests were carried out at same boundary conditions both within air and Ar/O_2 (79 % of argon and 21 % of oxygen) mixture under air staging conditions. The measured NO concentrations decrease continuously with distance to the burner, confirming air staging technology as appropriate for NO reduction. On the other hand the only nitrogen source for NO formation which has to be considered in case of combustion with Ar/O_2 mixture is fuel bound nitrogen, so that the difference of formed NO between the use of normal combustion air and Ar/O_2 mixture can be attributed to air nitrogen. The formation of thermal NO from air nitrogen depends on temparature. Within flameless combustion recirculating flue gas smooths down temperature peaks inside the combustion chamber by mixing with the reactants. Since the reacting mixture is diluted, the adiabatic flame temperature decreases and thus peak temperatures within the furnace are reduced. Therefore, compared to flame combustion formed NO from air nitrogen is significantly lower. Regarding fuel-NO is slightly higher. Results of these measurements are summarised and shown in Figures 6 and 7.

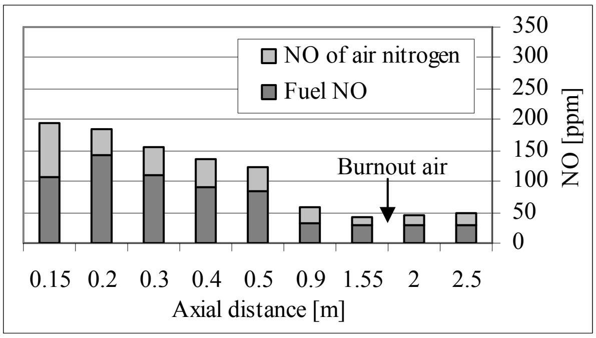

Fig. 6. Fuel-NO portion out of total NO concentration (air staging flameless Lausitz coal combustion; $\lambda_{local}=0.8$, $\lambda_{total}=1.16$; wall temperature 1300 °C)

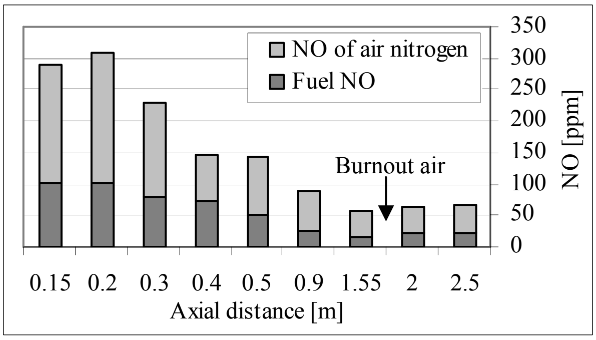

Fig. 7. Fuel-NO portion out of total NO emission (air staging flame Lausitz coal combustion; $\lambda_{local}=0.8$, $\lambda_{total}=1.16$; wall temperature 1300 °C)

3.3. Total volatile fuel nitrogen concentration

Total Volatile Fuel Nitrogen (TVFN) comprises the sum of fuel-NO, HCN, and NH_3. Within the primary combustion zone besides fuel-NO, the main part will be HCN at first and than later and slower transformed into NH-components. Figures 8 and 9 represent TVFN produced within flameless and flame air staged combustions of Lausitz coal. Experiments were performed to determine the distribution of nitrogeneous species, especially the relative magnitudes of HCN and NH_3, resulted from flame and flameless combustion under the same boundary conditions.

Within both flameless combustion and flame combustion the maximum level of fuel-NO was on the axial distance of 0.2 m, downstream combustion chamber fuel-NO was decreasing, finally in the burnout area fuel-NO concentration keep constant value under fuel-lean conditions. In these tests fuel-NO is slightly lower along the whole combustion chamber within flame combustion. Within both combustion modes at axial distance of 0.2 m HCN and NH_3 levels are low, however at axial distance of 0.4 m HCN was dominant volatile nitrogenous species. Within flameless combustion mode HCN concentration was significantly higher than in flame combustion mode. With flameless combustion at axial distance of 0.4 and 0.5 m HCN is dominant nitrogenous compound higher than both fuel-NO and NH_3. The results of these measurements are summarised and shown in Figures 8 and 9.

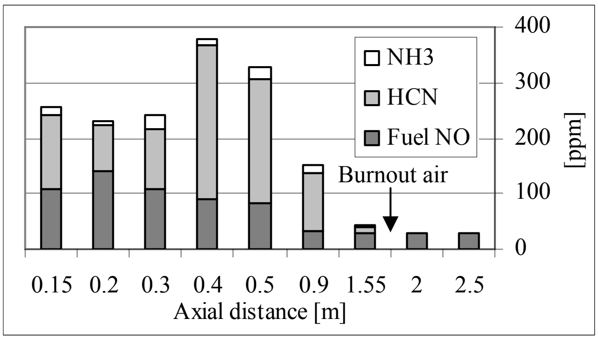

Fig. 8. Total volatile fuel nitrogen (air staging flameless Lausitz coal combustion; $\lambda_{local}=0.8$, $\lambda_{total}=1.16$; wall temperature 1300 °C)

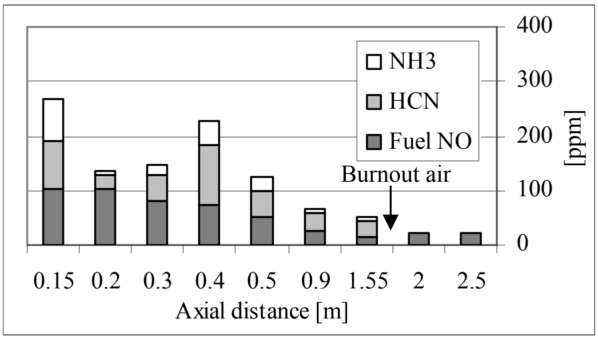

Fig. 9. Total volatile fuel nitrogen (air staging flame Lausitz coal combustion, $\lambda_{local}=0.8$, $\lambda_{total}=1.16$; wall temperature 1300 °C)

3.4. Influence of local air stoichiometry on fuel-NO

In order to investigate the effect of air stoichiometry on NO formation via the fuel mechanism, changes in fuel-NO, HCN, and NH_3 concentrations were measured in an atmosphere without air nitrogen (Ar/O_2 mixture). Both tested air stoichiometries indicate destruction of fuel-NO and formation of HCN and NH_3. Accordingly, NO reacts rapidly with hydrocarbons to form HCN, which generates NH_3 and N_2 [8]. These reactons are favoured for decreasing oxygen availability. Namely, under local air stoichiometry of 0.7 concentrations of HCN in primary combustion zone are double and fuel-NO is less. For both tested local air stoichiometries concentrations of NH_3 are similar and ranging between 0 and 70 ppm. Results of these measurements are summarised and shown in Figures 10 and 11.

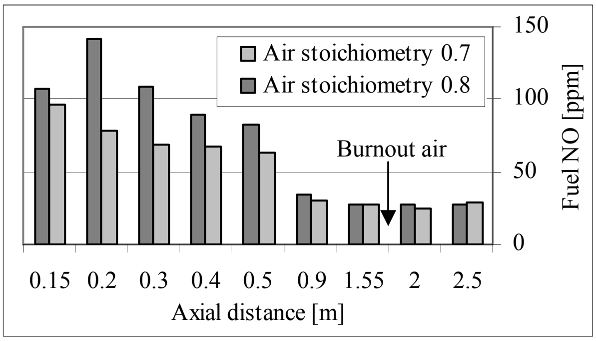

Fig. 10. Effect of air stoichiometry on fuel-NO emission (air staging flameless Lausitz coal combustion; $\lambda_{local}=0.8$, $\lambda_{total}=1.16$; wall temperature 1300 °C)

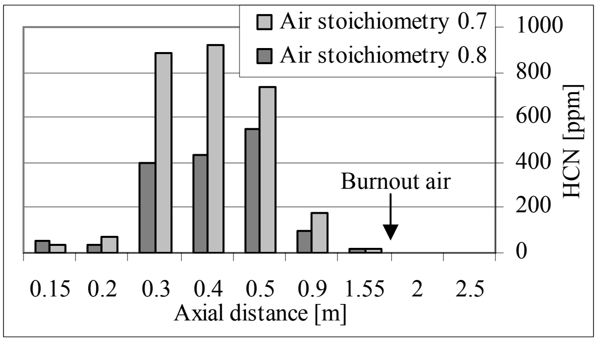

Fig. 10. Effect of air stoichiometry on fuel-NO emission (air staging flameless Lausitz coal combustion; λ_{local}=0.8, λ_{total}=1.16; wall temperature 1300 °C)

3.5. Influence of wall temperature on fuel-NO

The influence of the wall temperature on the fuel-NO emission under the unstaged flameless lignite coal combustion is presented in Figure 12.

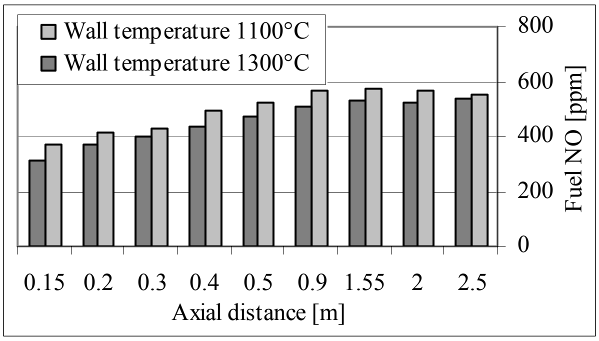

Fig. 12. Effect of wall temperature on fuel-NO emission (unstaged flameless Lausitz coal combustion)

These tests were carried out within Ar/O_2 atmosphere and two different wall temperatures of 1100 and 1300 °C. Comparing these results and the results presented in Figures 6-9 assuming that temperature within the primary combustion zone is lower for flameless combustion due to the reduced adiabatic temperature, TVFN is decreasing with increasing temperature. This had also observed for flame combustion by Bose [8].

4. CONCLUSIONS

The impact of both, the flameless coal combustion and the flame coal combustion on the formation of nitrogeneous species is very complex and comprises of different factors. Besides the fuel nitrogen, very important factors are the volatile content.

The impact on NO formation via nitrogen in air is double reduced within flameless combustion mode. This is more evident within primary combustion zone due to reducing high temperature peak under flameless regime.

In this study the main measured compositions of volatile nitrogen are HCN, NH_3, and NO. Their yields depend on tested combustion modes. The fuel nitrogen conversion to NH_3 tends to level off within both combustion mode. HCN is dominant volatile nitrogenous species and fuel-NO is slightly higher within primary reaction zone in flameless mode.

Combustion parameters such as wall temperature and air stoichiometry are very important for the fuel-NO yield within flameless mode. The fuel-NO yield decreased with increasing wall temperature and decreasing air stoichiometry. This implies that the combustion conditions are of major importance for fuel-NO formation.

5. ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support from the European Commission which supported this project within the Research Fund for Coal and Steel (Project number RFCR-CR-2005-00010).

6. REFERENCES

[1] Wünning, J. A., Wünning, J. G.: Flameless oxidation to reduce thermal NO-formation. Prog. Energy Combust. Sci., 23:81-94 (1997).
[2] Orsino, S., Tamura, M., Stabat, P., Constantini, S., Prado, O., Weber, R. : Excess Enthalpy Combustion of Coal. IFRF Research Report, 2000.
[3] Fielenbach, C., Holfeld, Th., von Petery, C., Renz, U., Wünning, J.: NO_x-Reduction in a Pressurized Pulverized Coal Flame by Flue Gas Recirculation. 20th International Pittsburgh Coal Conference, 2003.
[4] Ristic, D., Berger, R., Scheffknecht, G., Lacour, C., Honoré, D., Wünning, J.: Experimental study on flameless oxidation of pulverised coal under air staging conditions. 15th IFRF member's conference Pisa, Italia, 2007.
[5] Ristic, D., Schuster, A., Scheffknecht, G., Stadler, H., Foerster, M., Kneer, R.: Experimental study on flameless oxidation of pulverised coal in bench and pilot scale. 23. Deutscher Flammentag, Berlin, Germany, 2007.
[6] Galbiati, M. A., Cavigiolo, A., Effuggi, A., Gelosa, D., Rota, R.: Mild combustion for fuel-NO_x reduction. Combust. Sci. and Tech., 176:1035-1054 (2004).
[7] Greul, U.: Experimentelle Untersuchung feuerungstechnischer NOx-Minderungsverfahren bei der Kohlenstaubverbrennung. VDI Fortschrittberichte Reihe 6: Energieerzeugung Nr. 388, VDI Verlag GmbH, Düsseldorf 1998.
[8] Bose, C. A., Dannecker, M. K., Wendt, J. O. L.: Coal composition effects on mechanisms governing the destruction of NO and other nitrogenous species during fuel-rich combustion. Energy & Fuels 1988, 2, 301-308.
[9] Wiebren de J.: Nitrogen compounds in pressurized fluidized bed gasification of biomass and fossil fuels. PhD thesis, Netherlands, 2005.
[10] Wörner, H. P., Maier, J., Hein, K. R. G.: Formation and reduction of NO: comparison of coals for unstaged, air staged and fuel staged combustion. 19th Pittsburgh Coal Conference, 2002.
[11] Stadler, H., Tschunko, S., Förster, M., Kneer, R., Fielenbach, C.: NOx reduction in a pulverised coal flame by flue gas recirculation. VGB Workshop Flue Gas Cleaning 2007, Vienna, Austria.