

SELECTIVE NON-CATALYTIC DENITRIFICATION OF BIOMASS COMBUSTION FLUE GASES (SYNTHETIC MIXTURE)

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Abstract: *Despite many benefits of agricultural biomass utilization as an energy source, there are certain disadvantages such as the possible high emission of nitrogen oxides (NO_x). NO_x emission represents one of the key challenges for agricultural biomass use as a fuel. The experimental denitrification chamber was used to evaluate the impact of initial NO content, NH₃:NO molar ratio, flue gas temperature, and the temperature difference between two denitrification chamber sections on NO_x reduction using ammonia aqueous solution. The optimization of experimental conditions was done in the NO concentration range from 200 to 800 ppm, NH₃:NO molar ratios from 0.31 to 3 and second chamber section temperature range from 770 to 867°C. The denitrification process under controlled conditions is the starting point for the optimization of the secondary denitrification technique of selective non-catalytic reduction (SNCR) process on real-scale plants combusting biomass or any other fuels with increased NO_x emission.*

Key words: *Agricultural biomass combustion, NO_x reduction, denitrification chamber, SNCR*

1. Introduction

To mitigate climate change and follow the principles of sustainable development, the use of biomass, as a high-value and CO₂ - neutral - carbon-rich fuel, for green energy production is widely promoted. Even though the emission of certain pollutants during agricultural biomass combustion is not negligible [1], their concentrations are usually less pronounced than from coal and/or fuel oil combustion. Since agricultural biomass has increased protein content [2-4], to which intensive use of nitrogen fertilizers additionally contributes, the emission of nitrogen oxides (NO_x) may exceed legal limits [5, 6]. Although emitted NO_x could cause numerous environmental and health problems, the potential of agricultural biomass use as an energy source is immense, which imposes the necessity to minimize NO_x emissions.

The most dominant among NO_x are nitric oxide NO (around 90%) and nitrogen dioxide NO₂ [2, 5]. Numerous strategies are employed to reduce NO_x emissions [2, 7-9] including pre-combustion

measures for total nitrogen reduction in biomass, combustion control measures with modifying the design and operating features of the combustion unit, as well as flue gas treatment (FGT) after combustion. Tab. 1 provides a brief summary of the most common and a few novel NO_x abatement methods together with key details about their main features.

Table 1. Brief summary of the most common NO_x abatement methods and their characteristics

Strategy	Control technique	NO _x reduction [%]	Temp. range [°C]	Characteristics		Ref.
				Advantages	Weakness	
Pre-treatment	- biomass washing - additives - blending	low	ambient temp.	- simple - low cost	insufficient NO _x reduction	[10-12]
Combustion control	AS	20–56	combust. temp.	combustion optimization	mostly insufficient at biomass combustion	[2, 8, 13-17]
	FS	≈ 50	500-900	without additional pollution abatement equipment		
	FGR	> 20				
Flue gas treatment (FGT)	SCR	75–85	200–500	- mature technology - high efficiency and selectivity - catalysts utilization	- high costs - limited life span of catalysts	[2, 8, 16, 18-20]
	SNCR	30–60	800–1100	- mature technology - high efficiency and selectivity	- more cost effective than SCR at higher NO _x and PM levels - high reactant consumption	
	WS	≤ 90	4-40 (water) 165 (NaClO aqueous solution)	- simultaneous deNO _x and deSO _x	- limited to small waste stream cleanup - high amount of liquid waste	
	EB	80	lab. scale temp. 40-65	- simultaneous deNO _x and deSO _x - promising novel technologies	- high energy consumption - not reached industrial application	
	PC	60		- promising novel technologies	- high capital and operating costs	
AS -air staging		SCR - Selective catalytic reduction		PC - Pulse corona-induced plasma		
FS - Fuel staging (re-burning)		SNCR - Selective non-catalytic reduction		EB - Electron beam		
FGR - Flue gas recirculation		WS - Wet scrubbing		PM- particulate matter		

As the influence of N-fuel content dominates the NO_x emission during biomass combustion [2], the primary - combustion control measures are often insufficient to meet strict emission limits and/or are inapplicable in existing furnaces. If baled agricultural biomass is used, pre-combustion mixing with other types of biomass is also not an option. The required NO_x reduction is achieved by additional FGT, and for biomass of agricultural origin, rich in nitrogen, denitrification is often necessary. Therefore, selective non-catalytic reduction (SNCR) is considered herein as the most common and economically justified technology.

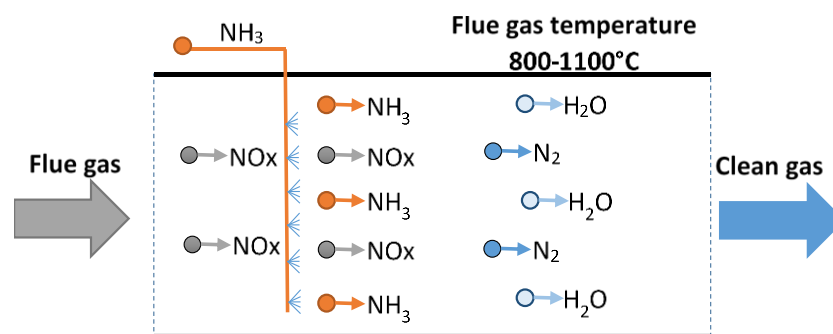
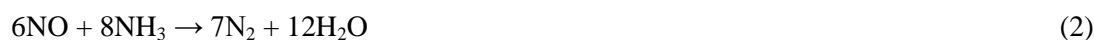


Figure 1. Scheme of selective non-catalytic reduction (SNCR)

In the SNCR process, the reducing agents, mainly ammonia or urea, are injected into the hot flue gas stream to selectively reduce NO_x into N₂ without any catalysts (Fig. 1). Although ammonia is toxic, its application as the reducing agent is often, especially for small experimental installations. The key to the SNCR process is an optimization of reagent injection into flue gases within a specific temperature range ("temperature window"). According to literature, optimal temperature window for ammonia is between 850 to 1000°C [2, 18-23]. The temperatures for biomass combustion in large-scale plants vary within this range.

Dominant reactions in the case of ammonia application [2, 24] as a deNO_x reagent are:



These reactions of complete conversion to N₂ and water are achievable by optimization of NO reduction processes, but in non-ideal cases, unwanted oxidation reactions can also occur.

The aim of this study was to examine the influencing parameters of NO reduction under conditions as close as possible to the SNCR process in real scaled biomass combustion furnaces. Therefore, the experimental denitrification chamber was designed. Much smaller compared to the real scale facility and, consequently, with low inertia, it allows quick change of operating parameters and achievement of stationary conditions, which is very suitable for performing several experiments by varying the different parameters in a short time interval. So the objectives are: to critically assess the impact of temperature and homogeneity of the temperature field in the deNO_x chamber, the influence of the reducing agent injection site, the NH₃:NO ratio, moisture in the gas mixture, as well as the influence of initial NO concentration on the NO reduction, all in order to optimize the NO_x reduction process.

2. Materials and methods

2.1. Chemicals

A synthetic gas mixture that simulates real flue gases generated during biomass combustion was obtained by mixing nitrogen (N₂, 3.5, 40 L, 150 bar, Messer) as the balance gas, carbon dioxide (CO₂, 3.8, 40 L, 150 bar, Messer) and nitric oxide (NO, 2% vol. NO balance nitrogen, 10 L, 150 bar, Messer) with air. An ammonia aqueous solution (25%, LabExpert) was used as a reagent for denitrification.

2.2. Experimental installation

The experimental setup (Fig. 2) includes an adiabatically isolated deNO_x chamber along with measuring and acquisition equipment (peristaltic pump, device for experimental conditions control, gas cylinders filled with commercial gases).

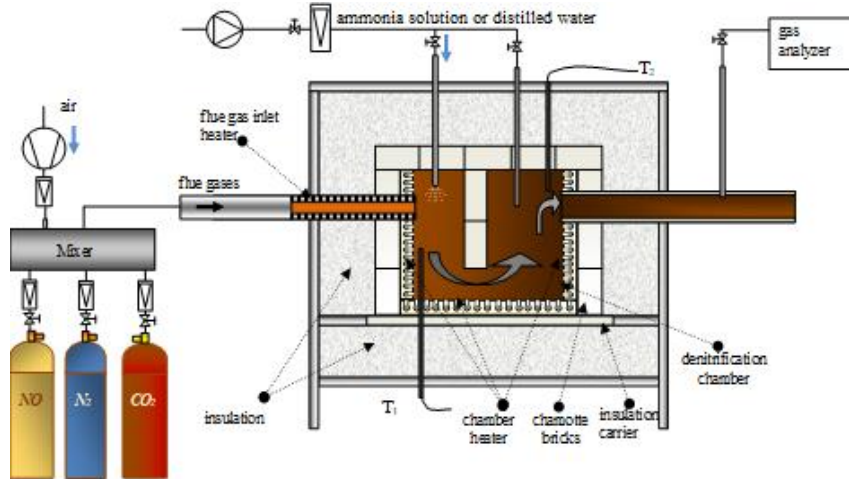


Figure 2. Denitrification experiment setup

The denitrification chamber is made of chamotte bricks, coated with multilayer insulation (total thickness 180 mm) and a tin cover. Chamber dimensions are 120 mm × 400 mm × 500 mm, with a bulkhead, enabling better mixing of synthetic gases. The gases were premixed and introduced through a heating tube into the denitrification chamber. The chamber has electric heaters: one at the flue gas inlet and four inside the chamber. The rotameters set the inlet flows of the synthetic gas mixture components. The temperatures (T₁ and T₂) were continuously recorded by the KEITHLEY acquisition system connected with thermocouples placed in both chamber sections. Flue gas analysis was done at the deNO_x chamber gas outlet by MRU Airfare Varioplus Industrial gas analyzer. Ammonia solutions or distilled water were injected into the deNO_x chamber by a low-flow peristaltic pump VELP Scientifica SP 311 (flow rates 200 - 950 mL/h) at marked points (Fig. 2).

2.3. Experimental conditions

The contents of all components in the synthetic gas mixture were set to simulate real flue gases emitted during biomass combustion [25-27]. The flows of nitrogen, CO₂ and air were adjusted to provide the following contents of gases in the final gas mixture: CO₂ in the range of 4-8%, oxygen content between 9 and 11%, while excess air coefficient was around two, at a total flow from 6500 to 7500 L/h. The retention time of the gas mixture in the deNO_x chamber was approximately 1 s. In conducted experiments, the following parameters were varied: temperature of chamber sections, synthetic flue gas mixture content, initial NO concentration in the mixture, the concentration of ammonia solution, NH₃:NO molar ratio, dosing site position, and water content (moisture). NO concentrations were in the range of 200 to 800 ppm. The SNCR reagent (0.5% to 4%) is directly injected into the chamber within temperature range between 770°C and 867°C. Denitrification was investigated for NH₃:NO molar ratios from 0.31- 3.

3. Results and discussion

To better understand the impact of different experimental parameters on NO_x reduction, a series of experiments in an adiabatic deNO_x chamber were done.

3.1. Kinetic curves

The decrease in NO concentration induced by NH₃(aq) injection (A), as well as the re-growth of NO induced by water addition to the gas mixture (W), can be described by the kinetics of pseudo-first-order. These kinetic reaction curves (exponential dependence of NO and NO₂ concentrations on time) are shown in Figs. 3 and 4, while in Tab. 2 denitrification parameters are given.

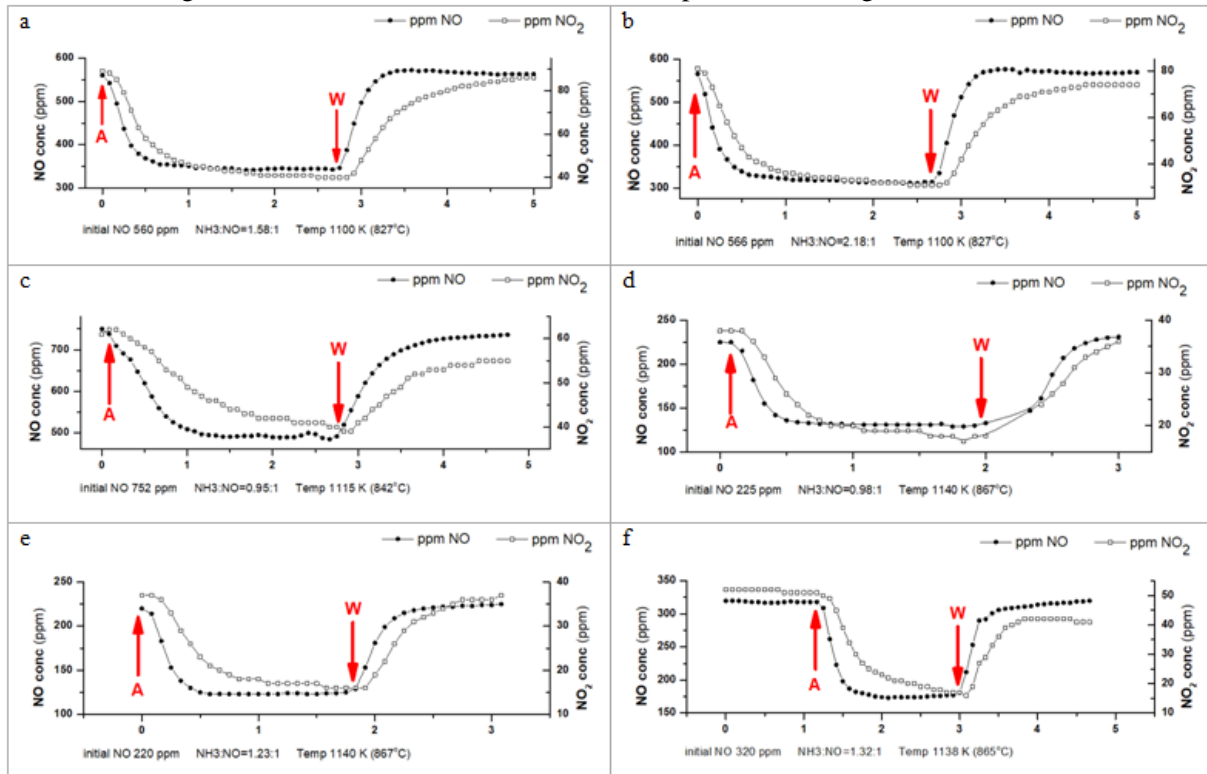


Figure 3. Representative time dependences of NO and NO₂ concentrations (a-f) after the addition of ammonia solution (A) and distilled water (W) (arrows indicate injection times)

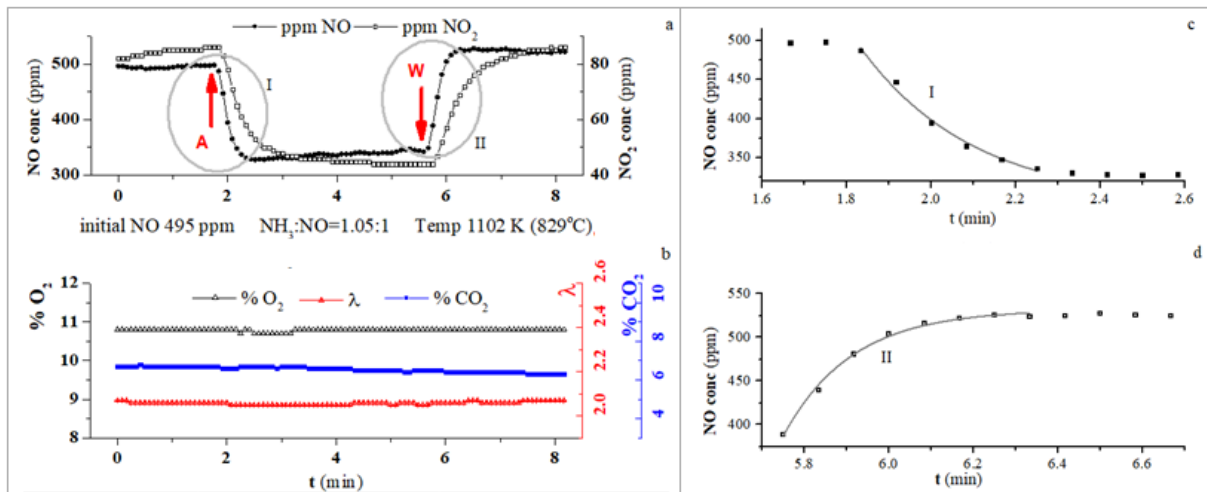


Figure 4. Representative time dependences of NO, NO₂, O₂ and CO₂ concentrations and excess air coefficient - λ (a, b) after addition of ammonia solution (A) and distilled water (W); experimental data fitting with the exponential curves for pseudo-first-order kinetics (c, d)

The experimental findings demonstrate that NO content in the gas mixture is greatly reduced by the addition of an ammonia solution and that NO concentration returns to its initial concentration following water addition. NO₂ content variation followed the same pattern as NO, but these changes are less pronounced.

Table 2. Denitrification parameters for the regimes shown in Figs. 3 and 4

Fig	NO ¹ ppm	NO _{reduct} %	NH ₃ :NO -	λ -	O ₂ %	CO ₂ %	T ₁ °C	T ₂ °C	k _{NOreduct} min ⁻¹	k _{NOregrow} min ⁻¹
3a	560	36.96	1.58	2.05	10.7	5.6	753	827	4.35	4.55
3b	566	44.88	2.18	2.04	10.7	5.2	752	827	6.25	3.70
3c	752	35.51	0.95	1.99	10.4	4.1	672	840	2.02	2.73
3d	225	42.67	0.98	1.77	9.1	6.5	739	867	6.44	3.85
3e	220	44.09	1.23	1.79	9.2	6.6	743	867	7.69	3.70
3f	320	45.63	1.32	1.74	8.9	6.6	730	865	5.78	5.38
4a,b	495	33.74	1.05	2.06	10.8	6.6	764	829	3.70	6.25

NO¹ - initial concentration of NO in the synthetic flue gas mixture at the inlet of the deNO_x chamber

T₁ and T₂ - temperatures measured in the first and second sections of the deNO_x chamber

k_{NOreduct}, k_{NOregrow} - rate constants of the exponential curves of pseudo-first order (for NO reduction and re-growth)

As shown in Tab. 2 and Figs. 3 and 4, the NO reduction process is more intensive for higher NH₃:NO molar ratios and within a higher temperature range [18, 19, 28].

3.2. The influence of experimental conditions on NO reduction

The influence of NH₃:NO molar ratio on NO reduction for different temperatures for the same initial NO content (265 ppm) and initial NO concentrations at the same temperature of the second chamber section (825°C), are shown in Figure 5 (a and b), respectively.

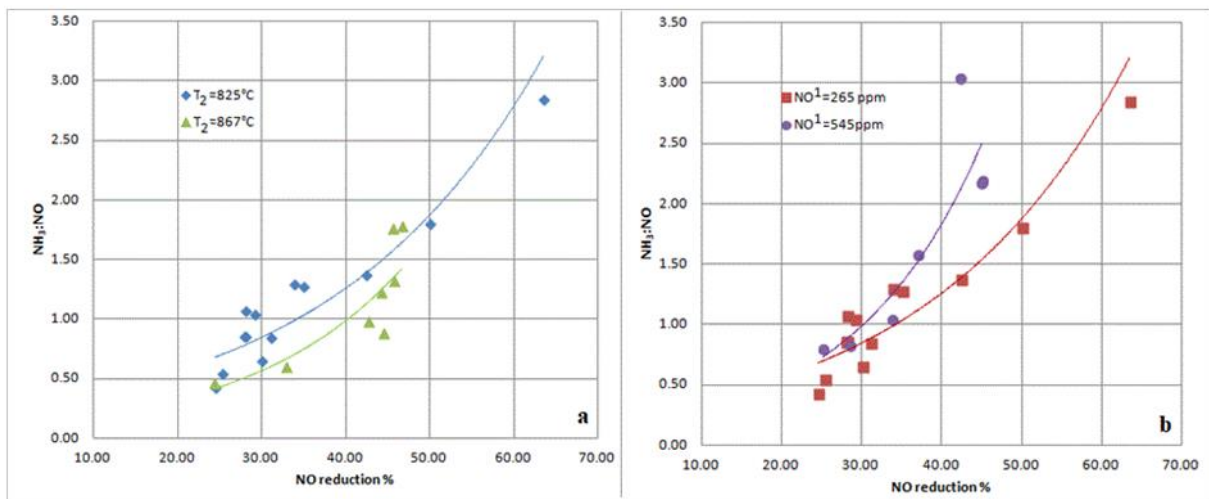


Figure 5. Influence of temperature and NH₃:NO molar ratio on NO reduction for a series of experiments at two temperatures for initial NO concentration 265 ppm (a) and two initial NO concentrations at second chamber temperature T₂ = 825°C (b)

For the same NH₃:NO molar ratio, the NO reduction degree increases if second chamber temperatures are higher (Fig. 5a). Also it is noticeable that at the same temperature (Fig. 5b), the reduction is more pronounced if the initial NO content is lower. In Tab. 3 the influence of chamber sections temperatures and temperature differences between chamber sections on NO reduction for series of experiments with NH₃:NO molar ratios from 0.72 to 0.98 is shown.

Table 3. List of experimental conditions for NO reduction

NO ¹ ppm	NO _{reduct} %	H ₂ O %	NH ₃ :NO -	O ₂ %	CO ₂ %	T ₁ °C	T ₂ °C	ΔT °C
351	47.58	5.89	0.72	10.4	4.4	837	821	-16
311	47.27	5.82	0.80	10.5	4.4	823	822	-1
504	49.40	5.55	0.96	10.0	6.1	790	812	22
410	46.83	5.78	0.98	10.5	4.2	772	838	66
320	44.38	3.27	0.88	8.9	6.6	728	865	137
225	42.67	3.19	0.98	9.1	6.5	739	867	128
753	35.99	5.64	0.98	10.4	4.2	689	840	151
752	35.51	5.49	0.95	10.4	4.1	672	842	170
302	31.13	2.93	0.84	9.7	7.8	745	822	77
236	27.97	2.95	0.85	9.8	7.7	747	822	75
508	22.44	10.18 ^{**}	0.86	10.4	3.9	726	820	94
523	21.80	10.18 ^{**}	0.84	10.4	3.9	734	816	82
519	18.30	10.06 ^{**}	0.83	10.1	6.2	724	812	88
483	33.13	6.20 [*]	0.88	10.5	4.3	766	840	74
283	28.27	6.28 [*]	0.95	10.6	4.4	721	840	119
293	24.57	6.28 [*]	0.94	10.6	4.4	663	840	177

^{*} ammonia solution injection into the second chamber section
^{**} ammonia solution injection into both chamber sections simultaneously

For the first two regimes (Tab. 3) the temperatures at both chamber sections were higher than 800°C, resulting in a very pronounced NO reduction ($\approx 47\%$) even at lower NH₃:NO molar ratios (0.72 and 0.80) compared to results of other conducted experiments given within this table. Even though the premixed gases were preheated, the temperature of the first chamber section is typically lower than the temperature of the second in most conducted experiments.

The influence of NH₃:NO molar ratios on NO reduction at a constant temperature of the second chamber section (841°C) in the case of temperature differences among chamber sections of 152°C and 78°C ($\Delta T = |T_2 - T_1|$), is presented in Fig. 6.

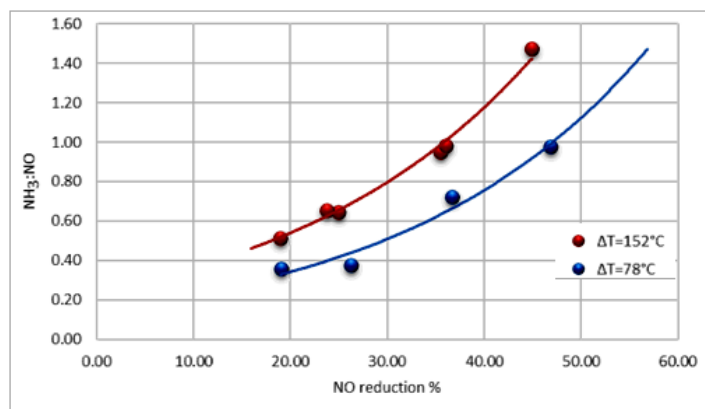


Figure 6. Influence of NH₃:NO molar ratios on NO reduction at T₂ 841°C (temperature differences between chamber sections ΔT of 152°C and 78°C)

From Fig. 6, it is obvious that similar NO reduction is achieved for higher NH₃:NO molar ratios if the temperature difference between chamber sections is higher, *i.e.* NO reduction is higher if the temperature difference is lower.

In the conducted experiments NO reduction that has been achieved was usually no higher than 50% for chamber temperature that did not exceed 867°C and NH₃:NO molar ratios in the range from 1 to 2 which is consistent with literature [18]. The maximal NO reduction of 84% is found at higher temperatures [19, 29].

The agriculture biomass has high alkaline content and consequently low ash melting temperature (shrinkage temperature around 700°C) [30-32]. Furthermore, when lower-quality biomass (with higher ballast content, *e.g.* dirty wet bales) enters the combustion system, temperature fluctuations become more pronounced [32]. Hence, experimental investigations of denitrification by ammonia solution at temperatures up to 800°C are highly encouraged.

Tab. 4 demonstrates that when both chamber sections' temperatures are lower than 800°C and with increase in NH₃:NO molar ratios, NO content increases instead of being reduced (so-called ammonia sleep effect) [2, 19]. No matter how much the amount of reagent increases, the temperature is insufficient to initiate the reduction process and undesirable oxidation reactions of NH₃ take place, such as: $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$ (4)

Table 4. Denitrification parameters at temperatures in both chamber sections below 800°C (moisture content 3.16%)

NO ¹	NO _{reduct}	NH ₃ :NO	O ₂	CO ₂	T ₁	T ₂	T _{aver}
ppm	%	x	%	%	°C	°C	°C
201	-54.23	2.05	11.0	7.7	732	781	756.5
207	-41.06	1.33	11.0	7.8	727	780	753.5
315	-39.05	1.30	10.8	7.8	722	778	750.0
201	-17.91	0.67	11.1	7.7	738	782	760.0

T_{aver} - average deNO_x chamber temperature

The influence of the ammonia solution injection site (first chamber section, both sections simultaneously or second chamber section) on the degree of NO reduction was also examined and presented in Fig. 7 and Tab. 3.

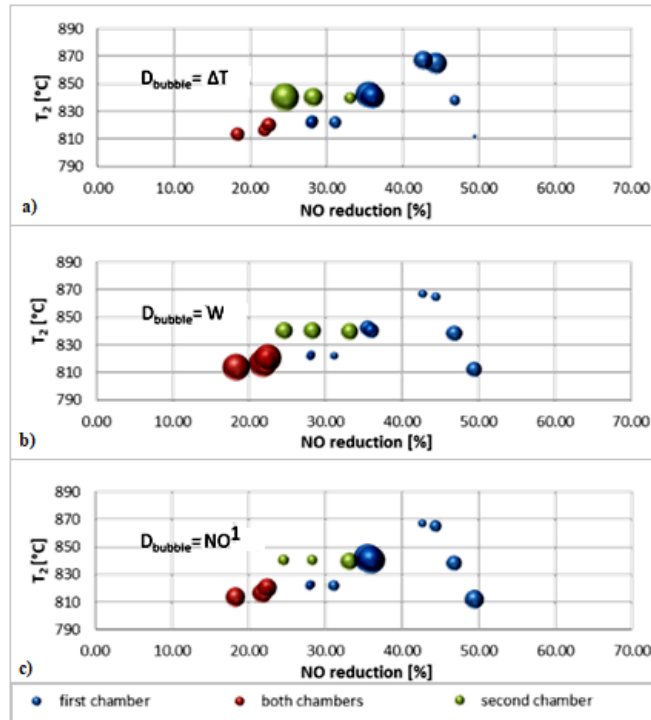


Figure 7. Influence of deNOx reactant injection site on NO reduction at $NH_3:NO = 0.8 - 1$

According to obtained results, NO reduction is the highest if the ammonia solution is injected into the first chamber section. The reason is the longer distance that the reactant passes *i.e.* longer retention times of reactants in the chamber. The reduction is more intensive if the temperature difference between chamber sections (ΔT) is lower (Fig. 7a). In addition, the higher moisture content (W) in the synthetic flue gas mixture accelerates NO reduction (Fig. 7b). The effect of NO initial concentration (NO^1) is not as obvious as the effect of the previous two parameters, except that a greater NO reduction is achieved for lower NO^1 at temperatures around 825°C (Fig. 7c).

Fig. 8 depicts the effect of moisture on NO reduction when using ammonia solution as a reducing agent. It shows that the presence of moisture has a certain promoting effect on NO reduction. The obtained data show that, at the same temperature ($T_2=823^\circ C$), increasing the moisture content from 2.95% to 5.7% promotes NO reduction [22, 33].

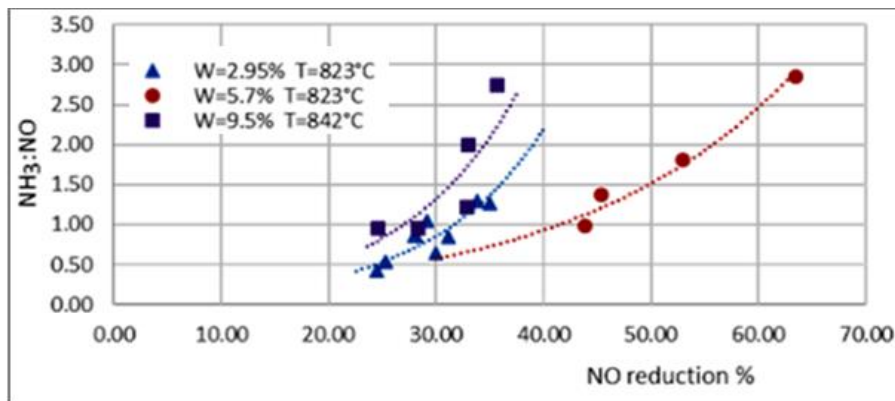
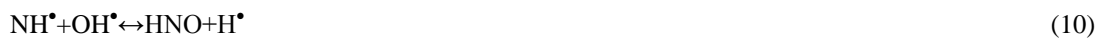
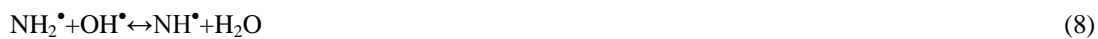


Figure 8. Influence of molar $NH_3:NO$ ratio on NOx reduction for a series of experiments for different moisture contents and second chamber temperatures

It can be explained by the fact that the moisture in the flue gas via reaction (5) produces additional OH radicals (OH[•]). The increasing OH radicals further enhance the positive reaction rate of reaction (6) to produce more NH₂[•] radicals and promote NO reduction via reaction (7).



However, at a higher moisture content of 9.5% and increased second chamber temperature ($T_2 = 842^{\circ}\text{C}$), lower NO reduction is obtained even though the temperature at which the reduction process takes place is higher. (Fig. 8). This can be explained by the influence of the reducing reagent injection site given in Fig.7b, where decreased NO reduction is noticed with an injection of ammonia solution to both chambers. Further, this also can be explained by the fact that the increased moisture promotes the NO reduction only up to a certain optimum value. The moisture content of 9.5% is obviously more than optimum value, so the OH[•] radical concentration starts to increase, resulting in NH formation *via* reaction (8) which leads directly to NO formation through the following reactions [33]:



3.3. A brief overview of the experimental research with a similar laboratory setting

Since SNCR has demonstrated to be an efficient method for NO_x reduction, studies on this technique have become increasingly thorough in recent years. Thus, Tab. 5 gives a comparative view of recent relevant papers with laboratory setups using synthetic gas mixtures to investigate the influencing parameters of the SNCR process.

Table 5. Literature overview – comparison of DeNO_x reactors

Laboratory-scale deNO _x reactor/investigations	Temperature range R ¹ /NO molar ratio Residence time	Synthetic gas mixture	Reducing agents/additives	Findings	Ref.
Tubular stainless steel reactor (inside a heating furnace)/ SNCR	800 - 1150°C 1 - 2 1 s	NO (900 ppm) NO ₂ (10 vol% of NO) O ₂ (0 - 10 vol%) Ar (balance gas)	methane, ammonia, urea/ Na ₂ CO ₃ , CH ₃ OH	NO _x reduction 80–85% (ammonia) 66–68% (urea) 32–34% (methane)	[29]
Four specific tubular plug flow reactors/ impact of O ₂ , CO, CO ₂ or combined O ₂ /CO/CO ₂ atmosphere	800 - 1500°C 1 - 2 / /	NO (500 ppm) O ₂ (0% - 4%)/CO CO ₂ (0-4%) Ar (balance gas)	NH ₃	NO reduction CO and CO ₂ negligible impact O ₂ significant impact	[34-36]
Electricity-heated tube reactor/ influence of multicomponent additives on NO reduction by SNCR	600 - 1200°C 1.5 /	NO (300 ppm) O ₂ (4%) N ₂ (balance gas)	NH ₃ / CO, H ₂ , CH ₄	additives shift temperature window to lower temperature	[37]
Laminar flow reactor (3 concentric quartz tubes in a muffle furnace)/influence of synthetic gas content, mixing, temperature and residence time	700 - 1100°C 2.1 /	NO (400ppm) O ₂ (1-6%) N ₂ (balance gas)	NH ₃ (N ₂ carrier gas)	extended residence time shifts NO _x reduction temperature to lower values long residence time, the optimum temperature	[38]

				900°C	
Drop tube furnace/ SNCR in O₂/CO₂ atmosphere	800 - 1200°C 1.5 1.2 s	O ₂ (3%) CO ₂ /Ar/N ₂	NH ₃ and SO ₂ / Na ₂ CO ₃ , C ₂ H ₅ OH and FeCl ₃	no NO reduction under 750°C NO reduction efficiency increases at higher temperatures (max at 900 °C) SO ₂ inhibit NO reduction other additives shift the reaction temperature to lower one	[39]
deNOx chamber/ NO reduction - influence of reducing agent injection site, NH₃:NO molar ratio, moisture content, initial NO concentration	770 - 867°C 0.31 – 3 1 s	NO (200 – 800 ppm) CO ₂ (4 – 8%) O ₂ (9- 11%) N ₂ (balance gas)	ammonia aqueous solution (0.5 – 4%)	NO reduction around 50% chambers temperature, moisture and injection site (residence time) have strong impact on NO reduction	This paper
¹ reducing agent					

Various laboratory setups include diverse reducing agents and additives (Tab. 5). Previously mentioned denitrification reactors generally are less complex design than deNOx chamber investigated in this paper. All of them are tube flow reactors with lower flow rates [29, 34-39]. NO reduction using ammonia was achieved at higher temperatures [29] than in this study and NO reduction is not achievable below 750°C [39]. From the point of view of biomass burning, it is significant that the addition of the mentioned additives lowers the temperature of the NO reduction reaction [39].

This study makes a contribution by using an ammonia aqueous solution as a deNOx reagent for the first time and by using a novel deNOx chamber design.

4. Conclusion

Unlike the experimental apparatus available from literature, which mainly has drop tube furnaces, this denitrification chamber is built of chamotte bricks with a bulkhead that enables better mixing of gases, as well as uses ammonia solution as a deNOx reagent instead ammonia as a gaseous reactant. Based on the results presented in the paper, the following conclusions can be stated:

- The decrease in NO content induced by NH₃(aq) addition, as well as the re-growth of NO induced by water addition to the gas mixture, can be described by the kinetics of pseudo-first-order (exponential dependence).
- The temperature has a strong impact on NO reduction.
- A significant NO reduction is noticed if the temperature of both chamber sections is higher than 800°C, even at an NH₃:NO molar ratio of 0.72. Quite a high NO reduction was noticed for NH₃:NO molar ratios in the range from 0.8 to 1, if the second chamber temperature is between 800 and 850°C, no matter if the first chamber section temperature is lower than 800°C. At temperatures of both chamber sections below 800°C, the production of NO through ammonia sleep was noticed.
- The appropriate mixing of deNOx reagent with synthetic flue gas mixture is necessary to obtain efficient NO reduction, so if ammonia solution is introduced into the first chamber section, a reduction is more favorable due to the longer path length and retention time in the chamber.
- For the examined temperature interval of 810-867°C, the NO reduction is higher at higher temperatures and, at the same temperature, the NO reduction is more pronounced for a lower initial NO content.

- The water vapor promoting effect on NO reduction was recorded if moisture content is not too high.
- For the tested temperature range and stoichiometric ratios of 1.0–2.0, the maximum NO_x reduction yield that has been achieved, was usually no greater than 50%.
- Although the largest part of NO_x in biomass of agricultural origin is generated from volatiles, whose content dominates over the coke residue, it should not be completely ignored that biomass ash can act catalytically on the reduction of NO_x. This is crucial for biomass with high calcium oxide (CaO) content, which can catalyze the reduction of NO. Since in this study just the gas mixture was considered, without taking biomass ash into account, in real cases, for the same range of temperatures, a greater reduction can be anticipated.
- The drawback of the performed experiments is the lower temperature achieved in the first deNO_x chamber section, where the NO reduction process begins, compared to the second chamber section. Notwithstanding, the obtained results provide guidelines for improving the apparatus and methods of conducting future experiments.

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