EXPERIMENTAL VERIFICATION OF THE EFFICIENCY OF SELECTIVE NON-CATALYTIC REDUCTION IN A BUBBLING FLUIDIZED BED COMBUSTOR

Kristýna Michaliková*, Jan Hrdlička, Matěj Vodička, Pavel Skopec, Jitka Jeníková, Lukáš Pilař

Czech Technical University in Prague, Faculty of Mechanical Engineering, Department of Energy Engineering, Technická 4, 166 07 Prague, Czech Republic

* corresponding author: kristyna.michalikova@fs.cvut.cz

ABSTRACT. Controlling nitrogen oxide (NO_X) emissions is still a challenge as increasingly stringent emission limits are introduced. Strict regulations will lead to the need to introduce secondary measures even for boilers with bubbling fluidized bed (BFB), which are generally characterized by low NO_X emissions. Selective non-catalytic reduction has lower investment costs compared to other secondary measures for NO_X reduction, but the temperatures for its efficient utilization are difficult to achieve in BFBs. This paper studies the possibility of an effective application of selective non-catalytic reduction (SNCR) of nitrogen oxides in a pilot-scale facility with a bubbling fluidized bed. The effect of temperatures between 880 and 950 °C in the reagent injection zone on NO_X reduction was investigated. For the selected temperature, the effect of the amount of injected reagent, urea solution with concentration 32.5 % wt., was studied. The experiments were carried out using 500 kW_{th} pilot scale BFB unit combusting lignite. In addition, an experiment was performed with the combustion of wooden pellets. With reagent injection, all experiments led to the reduction of nitrogen oxides and the highest NO_X reduction of 58 % was achieved.

KEYWORDS: Selective non-catalytic reduction, SNCR, fluidized bed, BFB, denitrification.

1. INTRODUCTION

The future of the energy industry is inextricably linked to the need to prevent the release of pollutants and greenhouse gases. One of the monitored pollutants is nitrogen oxides, which is the collective term for nitric oxide (NO) and nitrogen dioxide (NO_2). Their formation is well known and is described even in fluidized bed combustion [1, 2]. Nitrogen oxides have a negative impact on the environment and contribute to problems such as acid rain, ozone depletion, and photochemical smog [3]. The nitrous oxide (N_2O) is a gas with a greenhouse effect. It is also formed during combustion, particularly at lower temperatures. At higher temperatures (greater than 1 500 K), it is rapidly decomposed, forming N_2 or NO [4]. Therefore, its emissions may be of significance in the case of combustion in fluidized beds, which are generally operated at lower temperatures and do not reach the temperature range for its oxidation. Besides the combustion process itself, its significant source can be an application of a selective non-catalytic reduction of NO_X [5], particularly at elevated ratios of the reducing agent [6].

Fluidized bed boilers are widely used for their advantages, such as fuel flexibility, uniform temperature distribution, and operation at low temperatures. Bubbling fluidized bed (BFBs) as well as circulation fluidized bed combustors (CFBs) allow the combustion of fuels of different sizes, moisture content, and

heating values, and therefore can be used not only for the combustion of coal, but also for the combustion of biomass or various alternative fuels. The operating temperatures in the fluidized bed are in the range of 800–950 °C [7]. This lower operating temperature range also leads to a lower formation of NO_X. The formation of nitrogen oxides can generally be realised by three mechanisms – thermal, prompt, and fuel NO_X [8, 9]. The thermal and prompt pathways become more important above the operating temperature range of fluidized bed combustors and are therefore negligible during fluidized bed combustion and fuel NO_X is then considered the main contributor to nitrogen oxides.

2. MEASURES FOR NO_X REDUCTION

Reduction of NO_X emissions can be achieved by modifying the combustion process, thereby preventing the formation of NO_X, known as primary measures, or by secondary measures, which are techniques for the reduction of already generated nitrogen oxides.

In principle, all primary measures involve adjustments leading to combustion conditions with a decreased O_2 availability at the early stage of the combustion process, a reduction of the maximum flame temperature, or a change in residence time in different parts of the combustion zone [5]. For fluidized bed combustors, the early stage of the combustion process takes place in the dense bed zone. One of
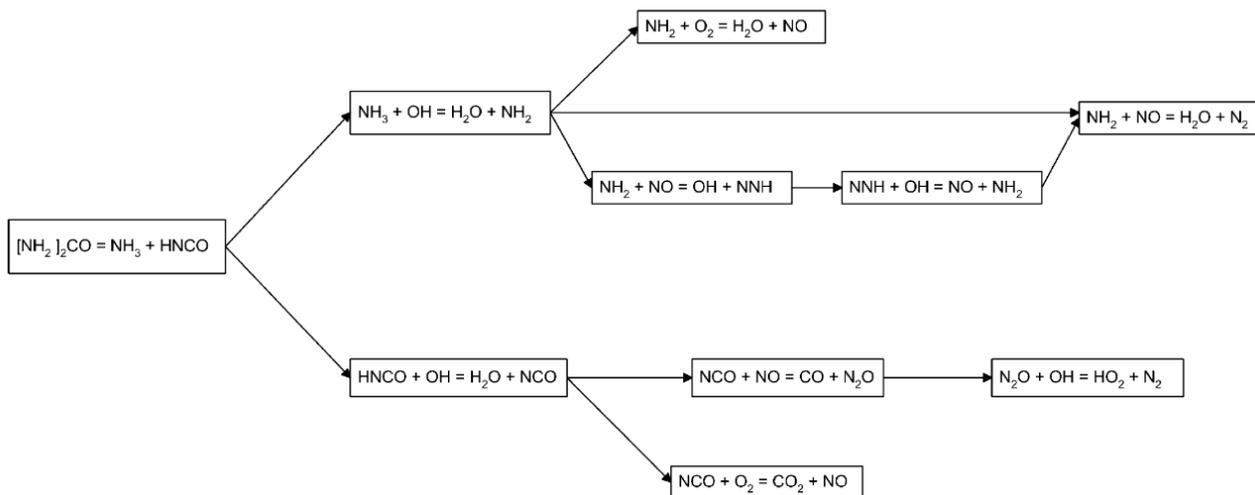
FIGURE 1. Reaction path diagram with urea as a reagent [5].

the measures can be air staging, which presents the oxygen-lean primary combustion zone and the oxygen-rich secondary combustion zone. It is realized by supplying secondary or even multi-stage air above the area of primary combustion, typically to the freeboard of the BFBs or to the lean bed zone of the CFBs. Air staging is often used in BFBs to control combustion and ensure the required temperature and overall oxygen stoichiometry. The use of flue gas recirculation is required for fluidized bed combustion because it provides the necessary volume flow to fluidize the bed material. Most primary measures are less effective in the case where the generated NO_X is predominantly formed by the oxidation of fuel nitrogen [5], which is a typical situation for fluidized bed combustors. Therefore, to meet the NO_X limits, secondary measures may be necessary.

Secondary measures are used to reduce nitrogen oxides that have been already formed. These post-combustion technologies that reduce NO_X are mainly selective catalytic (SCR) and selective non-catalytic reduction (SNCR). These flue gas treatments reduce NO_X to N_2 by reaction with an amine-based reagent, such as ammonia or urea. Both technologies are widely used.

In the process of SCR, the catalyst is present, reducing the activation energy of key reactions. Therefore, the reduction of NO to molecular nitrogen is realized in the temperature range 290–450 °C [10]. The efficiency of SCR at similar reducing agent stoichiometric ratio is higher than for SNCR and can reach above 90 %, however, the investment and operating costs are significant and its installation has a large space requirement [11]. This may limit its application as a retrofit to an existing facility. Additional problems can be fouling and catalyst poison. On the other hand, SNCR can be easily retrofitted, and its investment costs are lower because of the absence of the catalyst.

2.1. SELECTIVE NON-CATALYTIC REDUCTION

SNCR is a well-known and described technology [5], but its application in fluidized bed combustors is rare. This is mainly due to the lower formation of NO_X in fluidized bed combustion, which can then operate within the emission limits. The problem may arise if these limits for NO_X emissions are even stricter or fuels with higher fuel-nitrogen content are burned, for example, non-wooden biofuels.

Several different reducing agents can be used in the SNCR process. The reduction process with ammonia is called the Thermal DeNOx process, whereas the use of urea is called the NOxOUT process. A less common reducing agent is cyanuric acid within the RAPRENOx process. Since urea decomposes into ammonia and cyanuric acid, the SNCR process with urea can be considered as the combination of the other two [12]. The reaction path of urea within the selective non-catalytic reduction is shown in Figure 1, which describes the decomposition of urea into ammonia and cyanuric acid and subsequent reactions.

The reduction of NO_X occurs in a temperature range called a temperature window. This required temperature window is affected by many factors and the influence on it has parameters such as the reducing agent, the composition of the flue gas, the residence time, and the mixing between the reagent and the flue gas [5]. However, the interval is usually given in the range 800–1 100 °C; the temperature window for ammonia is 850–1 000 °C and for urea is the temperature window wider (800–1 100 °C) [13]. Below these temperatures, the reaction is too slow and most of the injected ammonia remains unreacted, increasing the slip of ammonia. At temperatures above 1 200 °C, the degree of NO_X reduction decreases due to the thermal decomposition of the reagent that subsequently oxidizes [5].

The amount of reagent injected is usually represented by a normalized stoichiometric ratio (NSR), which defines the number of moles of injected NH_2^- reagent relative to the number of moles of NO_X. For SNCR, the preferred normalized stoichiometric ratio is greater than 1, and a ratio NSR in the range of 1.5–2.5 is generally recommended [13].

As mentioned above, the temperatures in the dense bed of BFB are usually in the range $800 - 900\,°C$, and therefore it is evident that it is difficult to reach sufficiently high temperatures in the freeboard zone for efficient SNCR application. However, our previous work [14] that has been done in a laboratory-scale BFB combustor confirmed that such temperatures can be reached in the freeboard section of a BFB combustor through an intensively staged supply of combustion air. Such an intensive air staging, which means that understoichiometric conditions are established in the primary combustion zone in the dense bed, is not typically applied in the industrial practice. In parallel, the application of SNCR in a BFB combustor is not common, and the original experimental data from this study contribute to the possible realization of this technology.

In this article we have therefore focused on an experimental study of real performance of the selective non-catalytic reduction of NO_X in a $500\,kW_{th}$ pilot scale BFB combustor in connection with intensive air staging in order to increase the temperature of gas phase in the freeboard section, where the reducing agent was injected. This temperature was in the range for effective reduction of NO_X. In this work, the characterization of the SNCR performance in correlation with the NSR and the temperature in the freeboard section where the reducing agent was injected is presented.

3. Experiments

3.1. Experimental setup

The experiments were carried out in a pilot scale bubbling fluidized bed combustor with a thermal input of $500\,kW$, and its scheme is given in Figure 2. The facility is very variable as it allows combustion of different fuels with different oxidants; it is possible to use oxygen-enriched air up to the pure oxy-fuel regime. In the case of the air regime, a mixture of primary air and recirculated flue gas provides the fluidization, and its volume and mixture ratio can be changed arbitrarily. The combustion chamber together with the freeboard is insulated with fireclay lining, and the walls of the boiler are water-cooled. Four secondary air distributors are evenly spaced around the perimeter and each can supply secondary air at 4 heights. In addition, the inspection windows are located in the freeboard, which can be used for injection of reagent within the selective non-catalytic reduction process. The flue gas was continuously sampled. The volumetric fraction of O_2 was measured using a paramagnetic sensor and
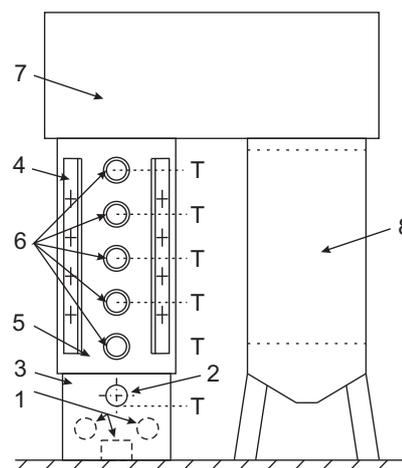
FIGURE 2. Scheme of the $500\,kW_{th}$ pilot-scale BFB facility. 1) primary gas inlets, 2) fuel feeder, 3) dense bed region, 4) secondary air distributors, 5) freeboard section, 6) inspection windows, 7) crossover pass, and 8) heat exchanger. The 'T' signs indicates the temperature measurement points.

FIGURE 3. Injection probe.

using a lambda probe (for operation). The volumetric fractions of SO_2, CO_2, CO, NO_X (sum of NO and NO_2), and N_2O were measured using NDIR sensors. The volumetric fraction of NH_3 was measured using a FTIR analyzer.

For selective non-catalytic reduction, the main part of realization is reagent injection. In this case, a single probe with a spray nozzle was used (Figure 3). The probe is water-cooled, and compressed air is used to atomize the reagent. The probe can be placed at five different heights along the freeboard zone using inspection windows. The reducing agent was transported from an accumulation vessel to the nozzle by increasing the air pressure above the level of the reducing agent in the accumulation vessel. The volumetric flow of the reducing agent was controlled by a manually operated proportional valve placed in the stream of the reducing agent. Two rotameters were used to measure the volumetric flow of the reducing agent, which
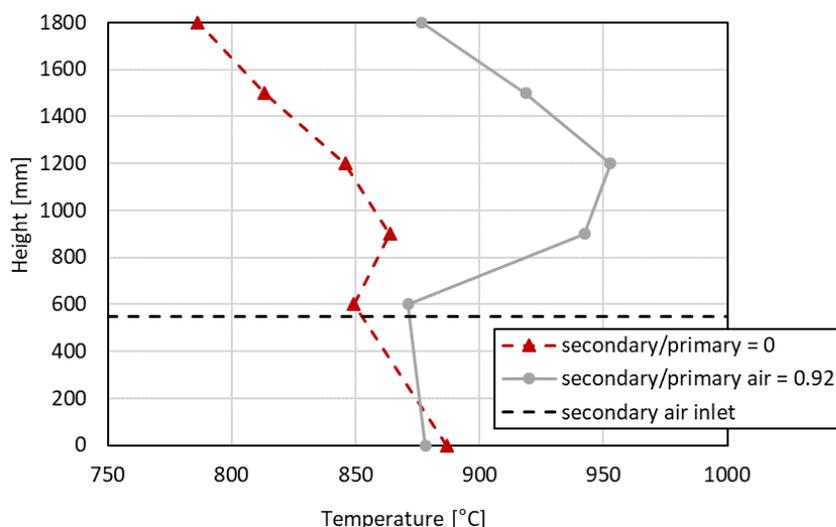
FIGURE 4. The temperature profile along the height of the facility with and without the use of secondary air.

	As received				Dry ash free					
	LHV [MJ·kg^{-1}]	Water [wt. %]	Ash [wt. %]	Comb.[*] [wt. %]	C [wt. %]	H [wt. %]	N [wt. %]	S [wt. %]	O[*] [wt. %]	Volatiles [wt. %]
Lignite	17.6	21.1	9.9	69.0	72.3	6.3	1.1	1.3	19.0	47.0
Wood	16.4	7.8	1.5	90.7	51.0	6.9	0.3	0.003	41.797	84.6

[*] Calculated as balance to 100 %.

TABLE 1. Proximate and ultimate analysis of the fuels used within the experiments.

differed in the operating range - the first measured flow in the range 0–1.2 l/h and the second in the range 1–5 l/h.

To achieve the temperature window for efficient injection of the reagent, air staging was realized. It leads to the primary zone with sub-stoichiometric conditions, above which the secondary air inlet is located that creates fuel-lean zone. Thanks to this measure, it was possible to obtain higher temperatures in the freeboard area while keeping the bed temperature below 900 °C. Air staging simultaneously serves as a primary measure that leads to a reduction of NO$_X$. A comparison of temperature profiles within the combustor during non-staged and staged combustion is given in Figure 4. The dashed horizontal line indicates the height level of secondary air supply in the combustor. Each point in the chart corresponds to a mean temperature value measured at that specific position. The locations of the thermocouples are indicated in Figure 2 by a 'T' sign. The height of 0 mm corresponds to the average temperature in the dense bed measured by 4 thermocouples. The temperatures in the freeboard section were measured by two thermocouples at each height. It can be seen that the temperature of the flue gas slightly higher than 950 °C was reached at a height of 1 200 mm above the dense bed. At this point, the reducing agent for SNCR was injected.

3.2. Materials and methods

The experiments were carried out using Czech lignite Bílina HP1 135 and wooden pellets as fuels. The proximate and ultimate analyses of the lignite and wooden pellets are given in Table 1.

During experiments with lignite coal, its inherent ash was used as a bed material. Experiments with biomass were realized combusting wooden pellets (according to the standard ENplus A1) and using a lightweight ceramic aggregate with a mean diameter of 1.12 mm as a bed material, which is described in detail in [7].

The reagent used in all experiments with lignite as fuel was a urea solution with a concentration of 32.5 % by weight. Since the wooden biomass combustion is expected to lead to a lower production of NO$_X$ due to the significantly lower nitrogen content in the fuel, it was necessary to adjust the concentration of reagent to 10.8 % wt. to ensure sufficient flow of the urea solution.

Several series of experiments were performed for lignite and one experiment for the combustion of wooden pellets. In order to achieve temperatures in the freeboard zone (where the injection takes place) suitable for effective nitrogen oxides reduction using SNCR, the high level of staged supply of combustion air had to be realized. The stoichiometry in the fluidized bed for individual experiments is given in Table 2 for lignite combustion. In the case of combusting wooden

Freeboard temperature [°C]	Required freeboard temperature [°C]	Air excess ratio in the dense bed [−]
Combustion of lignite		
870 ± 0.8	870	0.50
882 ± 0.8	880	0.94
885 ± 0.8	890	0.97
925 ± 2.0	920	0.63
949 ± 0.6	950	0.53
Combustion of wood		
886 ± 0.3	880	1.46

TABLE 2. Stoichiometry in the fluidized bed.

pellets, no secondary air was used and the air excess in the dense bed was 1.7. The value representing the freeboard temperature in Figure 2 is an average of values measured at the place of injection of the reducing agent sampled for at least 30 minutes in the interval of 1 s. The average value is given together with the interval of 95 % confidence.

The experiments were performed with a constant bed temperature of 880 °C and the oxygen level in the dry flue gas maintained at 6 % to diminish the impact of these parameters on the NO_X formation. Secondary air was injected 900 mm above the surface of the fluidized bed for lignite. A reference case was measured for each selected temperature and the measured values of the concentration of NO_X were used to calculate the corresponding values of NSR and the efficiency of NO_X reduction. During all experiments, the selected temperature in the freeboard area was kept constant and the amount of urea solution injected was increased in steps. In the case of lignite combustion, the volumetric flow of the urea solution was increased by 0.25 l/h, except for the measurement with the freeboard temperature 870 °C, when the step was 0.15 l/h. Consequently, steady-state cases with volumetric flows of the urea solution of 0, 0.25, 0.5, 0.75, 1, and 1.2 l/h were measured for freeboard temperatures 882, 885, 925, and 949 °C. For freeboard temperature of 870 °C, volumetric flows of the urea solution were 0, 0.15, 0.3, 0.45, 0.60, and 1.2 l/h. In the case of biomass combustion, steady states were measured with volumetric flows of the urea solution of 0, 0.4, 0.85, 1.3, 2, and 3 l/h. The volumetric flow of the urea solution was used together with the reference concentration of NO_X to determine the stoichiometric ratio NSR. In the case of urea $(NH_2)_2CO$, the normalized stoichiometric ratio is defined as two moles of urea in the urea solution to the mole of NO in the flue gas [15]:

$$NSR = 2 \cdot \frac{n_{urea}}{n_{NO}} \qquad (1)$$

The NSR ratio was used in the evaluation of the result as the variable parameter that describes the intensity

of the SNCR process. Each of the steady-state cases was measured in the average for 40 minutes (at least for 30 minutes). All measured values were sampled with an interval of 1 s except for the NH_3 concentrations and the NO_X concentrations measured downstream of the SNCR in the case of lignite combustion and freeboard temperature 920 °C, where the data were sampled with an interval of 1 minute. All sampled data reported in the results are expressed using averages with corresponding intervals of 95 % confidence.

4. RESULTS AND DISCUSSION

The measured data from all experiments relevant for this study can be found in Table 3 (for the combustion of lignite) and Table 4 (for the combustion of biomass). All concentrations reported in these tables are calculated for a reference content of O_2 in dry flue gas of 6 %.

Achieving different temperatures in the freeboard zone was realized by different mass flow of fuel, modification of the volume of fluidizing gas and its composition, and changing the volumetric flow of secondary air as well. These adjustments resulted in different initial concentrations of NO_X, which varied from 438 to 498 mg/m_N^3 for lignite combustion. The difference in the initial NO_X concentration could also be caused by a slightly different O_2 volumetric fraction in the flue gas. The formation of NO_X is significantly dependent on the availability of O_2 for the oxidation of the fuel N, which was confirmed by Krzywański et al. [16] or Vodička et al. [17]. Although a constant volumetric fraction of O_2 in dry flue gas was desired within all experimental cases, its value varied in the range from 4.3 to 7.3 %. It can be seen in Table 3 that the higher concentrations of NO_X were measured for higher volumetric fractions of O_2 and vice versa. The NO_X concentrations measured for wood combustion were significantly lower than those measured for lignite combustion, particularly due to the significantly lower nitrogen content in the fuel [18].

The measurement of CO concentration in the freeboard and of NH_3 concentration in the flue gas re-

Freeboard temp. (required) [°C]	NO_X before SNCR [mg/m$_N^3$]	NO_X after SNCR [mg/m$_N^3$]	NSR [mol/mol]	η_{NO_X} [%]	NH_3 [mg/m$_N^3$]	O_2 [% vol.]	CO [mg/m$_N^3$]	CO freeboard [mg/m$_N^3$]	N_2O [mg/m$_N^3$]
870±0.8 (870)	438±0.5	438±0.5	0.00	0.0	NA[*]	6.1±0.04	313±5.4	NA[*]	19.2±0.19
		396±0.5	0.43	9.6	NA[*]	6.4±0.05	294±3.5	843±9.8	32.4±0.24
		348±0.5	0.87	20.5	NA[*]	5.7±0.05	394±15.0	777±13.9	30.4±0.45
		312±0.4	1.30	28.8	0.1±0.02	5.5±0.05	326±10.0	703±5.4	37.8±0.34
		289±0.4	1.70	34.0	0.2±0.03	5.1±0.04	341±12.2	677±3.3	41.2±0.46
		276±0.9	3.47	37.0	0.4±0.08	5.4±0.06	385±9.8	NA[*]	47.1±0.88
882±0.8 (880)	460±0.6	460±0.6	0.00	0.0	NA[*]	6.7±0.04	268±1.9	NA[*]	23.2±0.18
		390±0.5	0.55	15.1	NA[*]	6.8±0.04	303±2.3	NA[*]	30.7±0.19
		303±0.4	1.10	34.1	NA[*]	5.9±0.03	294±2.2	NA[*]	43.5±0.22
		265±0.5	1.65	42.3	NA[*]	5.6±0.03	283±2.3	NA[*]	55.8±0.30
		256±0.5	2.20	44.4	NA[*]	5.7±0.03	345±2.5	NA[*]	72.0±0.29
		241±0.4	2.64	47.5	NA[*]	5.9±0.03	333±2.4	NA[*]	83.4±0.27
885±0.8 (890)	443±1.1	443±1.1	0.00	0.0	NA[*]	4.9±0.05	216±2.5	NA[*]	19.8±0.09
		415±0.8	0.62	6.4	NA[*]	5.3±0.04	196±1.0	NA[*]	30.8±0.12
		360±0.7	1.30	18.7	NA[*]	4.6±0.03	182±1.2	NA[*]	32.8±0.13
		299±1.2	1.89	32.5	NA[*]	4.4±0.05	225±2.1	NA[*]	33.4±0.23
		202±1.0	2.50	54.4	NA[*]	4.6±0.04	511±16.7	NA[*]	37.0±0.40
		181±0.6	3.00	59.6	NA[*]	4.6±0.04	265±7.3	NA[*]	73.8±0.61
925±2.0 (920)	498±3.8	498±3.8	0.00	0.0	NA[*]	7.0±0.08	221±4.8	539±15.7	NA[*]
		458±1.3	0.41	8.0	0.1±0.02	7.0±0.08	227±3.5	660±72.5	NA[*]
		450±1.9	0.81	9.5	0.01±0.01	7.2±0.07	283±7.0	1883±94.1	NA[*]
		410±3.6	1.23	17.7	0.01±0.01	7.2±0.04	216±5.9	1274±39.4	NA[*]
		364±10.8	1.97	26.9	0.3±0.04	7.3±0.20	265±21.3	1564±71.6	NA[*]
949±0.6 (950)	468±0.3	468±0.3	0.00	0.0	0.03±0.02	6.8±0.03	219±9.1	NA[*]	6.8±0.36
		454±0.6	0.57	2.9	0.03±0.01	6.3±0.03	306±24.2	773±34.9	16.0±0.43
		442±0.9	1.12	5.5	0±0	5.5±0.04	358±18.2	958±18.4	14.4±0.55
		430±0.4	1.70	8.3	0±0	4.3±0.02	321±20.7	1027±20.0	12.6±0.54
		399±0.7	2.70	14.7	0.77±0.10	4.7±0.04	282±14.5	833±19.6	23.0±0.69

[*] The value was not available for this experiment.

TABLE 3. Operating conditions during experiments for lignite combustion, $O_{2,ref} \approx 6\%$.

Freeboard temp. (required) [°C]	NO_X before SNCR [mg/m$_N^3$]	NO_X after SNCR [mg/m$_N^3$]	NSR [mol/mol]	η_{NO_X} [%]	NH_3 [mg/m$_N^3$]	O_2 [% vol.]	CO [mg/m$_N^3$]	CO freeboard [mg/m$_N^3$]	N_2O [mg/m$_N^3$]
886±0.3 (880)	145±0.5	145±0.5	0	0.0	NA[*]	6.7±0.02	76±0.4	NA[*]	4.2±0.14
		133±0.2	1	8.7	NA[*]	6.4±0.02	60±0.1	NA[*]	7.5±0.01
		113±0.3	2.2	22.0	NA[*]	5.4±0.02	55±0.1	NA[*]	12.6±0.03
		107±0.5	3.3	26.6	NA[*]	5.2±0.02	54±0.2	NA[*]	13.1±0.08
		86±0.4	5.1	40.9	NA[*]	4.8±0.02	52±0.2	NA[*]	18.9±0.11

[*] The value was not available for this experiment.

TABLE 4. Operating conditions during experiments for biomass combustion, $O_{2,ref} \approx 6\%$.

quired an additional analyzer. The absence of data of NH_3 and N_2O concentrations in the off-gas and CO concentrations in the freeboard section reported in Tables 3 and 4 was caused by non-availability of the additional FTIR analyzer during the corresponding experimental case.

In all experiments, injection of the reagent resulted in a reduction in nitrogen oxides even at the lowest volumetric flows of the urea solution corresponding to the lowest NSRs. The impact of injection of the urea solution on the concentration of NO_X in the

flue gas downstream of SNCR is demonstrated in Figure 5 with injection of reagent expressed as NSR. The NO_X reduction efficiency was calculated as the fraction of the difference in the NO_X concentration after and before SNCR over the NO_X concentration before the SNCR process. The best NO_X reduction efficiency of 58 % was achieved for temperature 885 °C and NSR 3.1 and this efficiency decreased with the use of higher or lower temperatures. This trend is shown in Figure 6 for four different NSRs in the range from 0.5 to 3.3. NO_X reduction was also affected by
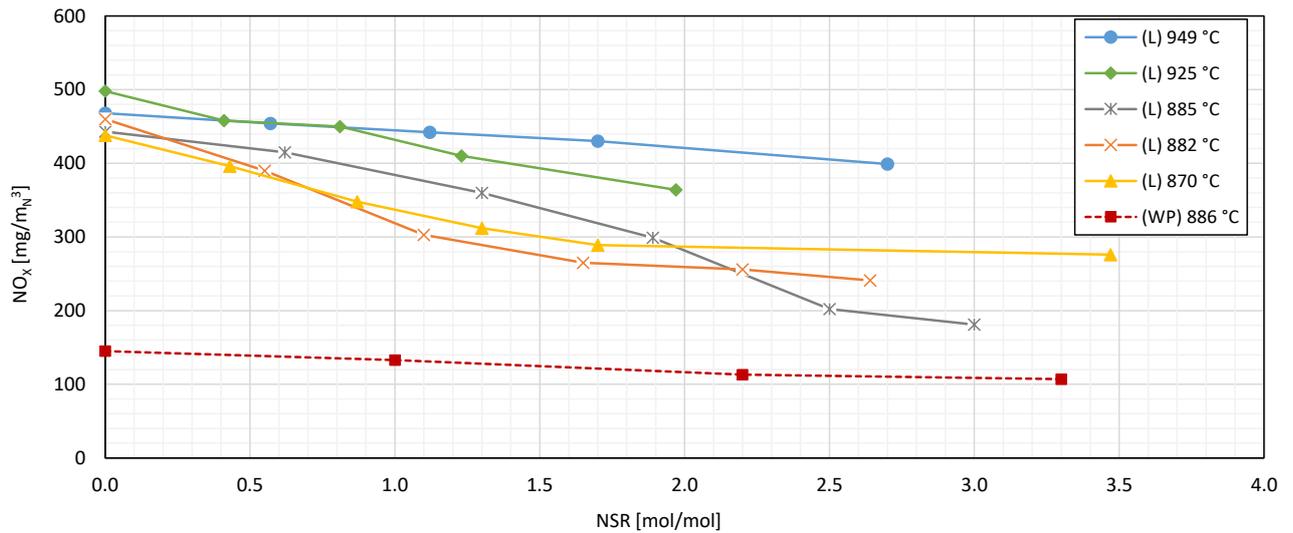
FIGURE 5. Dependence of NO$_X$ concentration in the flue gas downstream the SNCR on NSR for different temperatures, (L) – lignite, (WP) – wooden pellets.
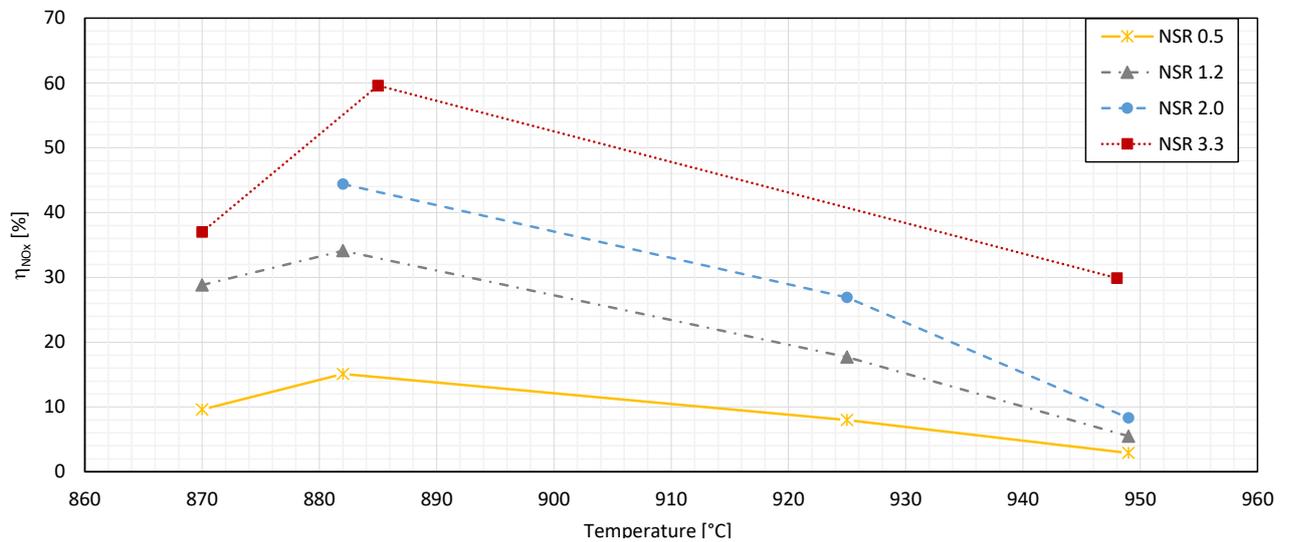
FIGURE 6. Dependence of NO$_X$ reduction efficiency on temperature for different $NSRs$.
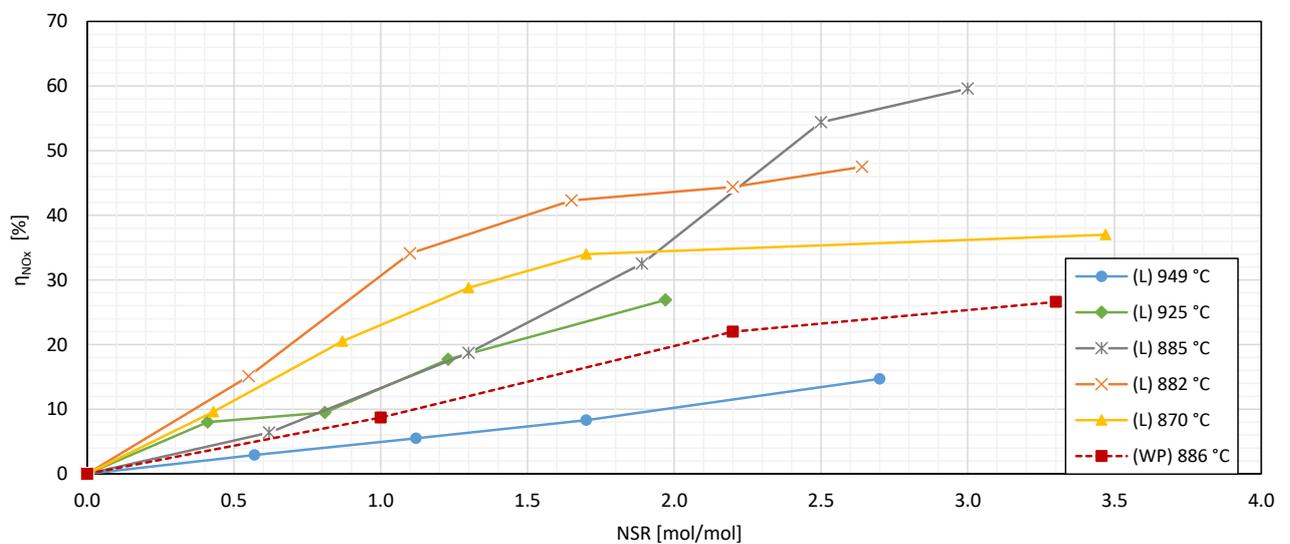
FIGURE 7. Dependence of NO$_X$ reduction efficiency on NSR for different temperatures.

the amount of injected reagent, expressed as NSR. An increase in NSR resulted in an increase in efficiency for all experiments, although the increase in efficiency of the NO_X reduction gradually decreased with increasing NSR, as can be seen in Figure 7, where the dependence of the NO_X reduction efficiency on NSR is given. In the cases where the ammonia slip was measured, the ammonia concentration never exceeded $1\,mg/m_N^3$ for lignite combustion, even for the highest NSRs indicating a strong over-stoichiometry of the urea solution.

N_2O is a greenhouse gas. Its emissions in the energy industry are not currently limited in EU legislation, however, they are negatively affected by selective non-catalytic reduction in the case when urea or cyanuric acid is used as the reducing agent [5]. N_2O concentrations increased with increasing reagent levels, up to four times its initial value, which can be seen in Tables 3 and 4. In the case of lignite combustion, the highest concentrations of N_2O were measured for the highest NSRs and freeboard temperatures 880 and 890 °C, where the NO_X reduction efficiency was the highest and the concentration of NO_X after SNCR was the lowest. For the freeboard temperature of 890 °C and $NSR = 3$, the concentration of N_2O was $73.8\,mg/m_N^3$, which was $40\,\%$ of the value of the concentration of NO_X. In the case of the combustion of wooden pellets and NSR 5.1, the concentration of nitrous oxide was $18.9\,mg/m_N^3$, whereas the concentration of NO_X achieved after reduction was $86\,mg/m_N^3$. Thus, the application of SNCR with urea solution can possibly be limited by N_2O emissions.

The best efficiency of nitrogen oxides reduction is achieved by injecting the reagent into the area with a temperature of around 890 °C, which is a lower temperature compared to previous work [5, 19]. This optimal temperature has been found independent of the NSR values. However, to evaluate the effect of temperature on the efficiency of the reduction of NO_X, it would be necessary to keep the other remaining combustion parameters constant, which is not feasible due to the control of the combustion process in a pilot-scale boiler. Therefore, the experiments vary not only in different temperatures in the combustion region but also by the flow rate of the fluidized medium and the ratio of secondary to primary air. These parameters may result in different reagent residence times and different mixing for each series of experiments, and may also affect NO_X reduction efficiency. For lignite combustion, the implementation of air staging increases the concentration of carbon monoxide in the flue gas, which can result in a shift of the temperature window for reagent injection into the lower temperature range [5, 20]. In the case of biomass combustion, only primary air and no air staging was used, and the temperature dependence will be the subject of further studies, but a lower initial level of NO_X can lead to lower reduction efficiency.

5. Conclusion

This paper presents an experimental study of selective non-catalytic reduction of NO_X in a bubbling fluidized bed boiler. Achieving the required temperatures for the reduction reactions was realized by modifying the combustion process by means of high degree of air staging with sub-stoichiometric conditions in the dense bed, which allowed controlling the freeboard temperature in the required range for the SNCR. In several series of experiments in the BFB boiler, efficient application of selective non-catalytic reduction of nitrogen oxides by injecting the urea solution was achieved. During the experiments, it was possible to achieve a nitrogen oxide reduction efficiency of 59.6 % for a normalized stoichiometric excess of reagent 3.0. High values of NSR resulted in a higher ammonia slip in the flue gas. The optimal temperature for the SNCR in this experimental setup was reached at approximately 890 °C, which is a value slightly below the typical optimum reported in the literature. It can be attributed to elevated CO levels in the high-degree air staging operation mode of the combustor. In all experiments, the injection of the reducing agent led to a significant increase in N_2O emissions, which in several cases was up to four times the initial value. The NO_X reduction in the case of biomass combustion was nearly 40 % but due to the different concentrations of urea solution, the results of lignite and biomass combustion are not directly comparable. Further experiments with biomass as fuel will be the subject of continued research, followed by oxy-fuel combustion of lignite and biomass, i.e., combustion with oxygen as an oxidant.

References

[1] J. E. Johnsson. Formation and reduction of nitrogen oxides in fluidized-bed combustion. *Fuel* **73**(9):1398–1415, 1994. https://doi.org/10.1016/0016-2361(94)90055-8.

[2] P. Skopec, J. Hrdlička, J. Opatřil, J. Štefanica. NO_X emissions from bubbling fluidized bed combustion of lignite coal. *Acta Polytechnica* **55**(4):275–281, 2015. https://doi.org/10.14311/AP.2015.55.0275.

[3] L. Muzio, G. Quartucy. Implementing NOx control: Research to application. *Progress in Energy and Combustion Science* **23**(3):233–266, 1997. https://doi.org/10.1016/S0360-1285(97)00002-6.

[4] C. T. Bowman. Control of combustion-generated nitrogen oxide emissions: Technology driven by regulation. *Symposium (International) on Combustion* **24**(1):859–878, 1992. https://doi.org/10.1016/S0082-0784(06)80104-9.

[5] M. Tayyeb Javed, N. Irfan, B. M. Gibbs. Control of combustion-generated nitrogen oxides by selective non-catalytic reduction. *Journal of Environmental Management* **83**(3):251–289, 2007. https://doi.org/10.1016/j.jenvman.2006.03.006.

[6] C. Mendoza-Covarrubiasr, C. E. Romero, F. Hernandez-Rosales, H. Agarwal. N2O Formation in Selective Non-Catalytic NOx Reduction Processes. *Journal of Environmental Protection,* **2**:1095–1100, 2011. https://doi.org/10.4236/jep.2011.28126.

[7] M. Vodička, K. Michaliková, J. Hrdlička, et al. External bed materials for the oxy-fuel combustion of biomass in a bubbling fluidized bed. *Journal of Cleaner Production* **321**:128882, 2021. https://doi.org/10.1016/j.jclepro.2021.128882.

[8] Y. B. Zeldovich. The oxidation of nitrogen in combustion explosions. *Acta Physiochiochimica USSR* **21**:577–628, 1946.

[9] C. Fenimore. Formation of nitric oxide in premixed hydrocarbon flames. *Symposium (International) on Combustion* **13**(1):373–380, 1971. https://doi.org/10.1016/S0082-0784(71)80040-1.

[10] J. He, K. Chen, J. Xu. *Urban Air Pollution and Control.* 2017. https://doi.org/10.1016/B978-0-12-409548-9.10182-4.

[11] K. Abul Hossain, M. Nazri Mohd Jaafar, A. Mustafa, et al. Application of selective non-catalytic reduction of NOx in small-scale combustion systems. *Atmospheric Environment* **38**(39):6823–6828, 2004. https://doi.org/10.1016/j.atmosenv.2004.09.012.

[12] J. A. Miller, C. T. Bowman. Mechanism and modeling of nitrogen chemistry in combustion. *Progress in Energy and Combustion Science* **15**(4):287–338, 1989. https://doi.org/10.1016/0360-1285(89)90017-8.

[13] M. Mladenović, M. Paprika, A. Marinković. Denitrification techniques for biomass combustion. *Renewable and Sustainable Energy Reviews* **82**:3350–3364, 2018. https://doi.org/10.1016/j.rser.2017.10.054.

[14] M. Vodička, K. Michaliková, J. Hrdlička, et al. Experimental verification of the impact of the air staging on the NO_X production and on the temperature profile in a BFB. *Acta Polytechnica* **62**(3):400–408, 2022. https://doi.org/10.14311/AP.2022.62.0400.

[15] N. Modliński. Numerical simulation of SNCR (selective non-catalytic reduction) process in coal fired grate boiler. *Energy* **92**:67–76, 2015. https://doi.org/10.1016/j.energy.2015.03.124.

[16] J. Krzywański, W. Nowak. Neurocomputing approach for the prediction of NOx emissions from CFBC in air-fired and oxygen-enriched atmospheres. *Journal of Power Technologies* **97**(2):75–84, 2017.

[17] M. Vodička, N. E. Haugen, A. Gruber, J. Hrdlička. NO_X formation in oxy-fuel combustion of lignite in a bubbling fluidized bed - Modelling and experimental verification. *International Journal of Greenhouse Gas Control* **76**:208–214, 2018. https://doi.org/10.1016/j.ijggc.2018.07.007.

[18] M. Lisý, H. Lisá, D. Jecha, et al. Characteristic properties of alternative biomass fuels. *Energies* **13**(6), 2020. https://doi.org/10.3390/en13061448.

[19] S. Daood, M. Javed, B. Gibbs, W. Nimmo. NOx control in coal combustion by combining biomass co-firing, oxygen enrichment and SNCR. *Fuel* **105**:283–292, 2013. https://doi.org/10.1016/j.fuel.2012.06.087.

[20] P. Lodder, J. Lefers. Effect of natural gas, C2H6 and CO on the homogeneous gas phase reduction of NOx by NH3. *The Chemical Engineering Journal* **30**(3):161–167, 1985. https://doi.org/10.1016/0300-9467(85)80026-5.