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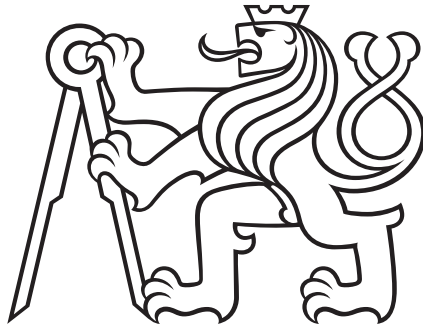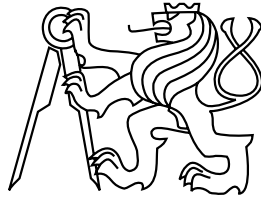
FACULTY OF MECHANICAL ENGINEERING

DOCTORAL THESIS STATEMENT

Czech Technical University in Prague
Faculty of Mechanical Engineering
Department of Energy Engineering

Doctoral thesis statement

Formation of NO$_X$ in oxy-fuel combustion in a bubbling fluidized bed

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Study Programme: Energy and Process Engineering

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Contents

1 Motivation and scope of the thesis

The oxy-fuel combustion belongs to the group of the 'carbon capture and storage' or 'carbon capture and sequestration' technologies (also referred as CCS), where a nearly pure oxygen is used for the oxidation of fuel, which results in significant increase of the carbon dioxide concentration in the flue gas. Oxy-fuel combustion is characterized by different volumetric flows and different concentration levels of the gases, which significantly affects the combustion process.

The application of oxy-fuel combustion on bubbling fluidized bed boilers is a specific case that is studied within this thesis. Bubbling fluidized bed (BFB) boilers are facilities with a power load that typically varies between $10 - 50$ MW. They are capable of combusting various types of solid fuels and even a variety of low-grade fuels with high moisture content [1]. The fluidized bed temperature typically varies in the range from 800 to 1 000 °C. Such a low combustion temperature contributes to the decrease in the formation of gaseous pollutants (particularly NO_X) and allows in situ desulfurization in the fluidized bed [2], [3]. The operation of BFB boilers in the oxy-fuel combustion regime requires significant flue gas recirculation (FGR) not only to provide the heat carrier, but also to keep sufficient fluidization of the bed. Into the FGR stream, the primary oxygen is introduced. Then, the fluidizing gas consists mostly from CO_2, oxygen and possibly water vapor. Therefore, the density, viscosity and heat capacity of the fluidizing gas are significantly different in the oxy- and air-combustion regime. This means that it is not possible to keep equal inlet gas velocity, maintain equally developed fluidization, and keep equal bed temperature, all at the same time, as in the case for conventional air-combustion.

Particularly, this thesis is focused on characterization of the formation of nitrogen oxides in oxy-fuel combustion in a BFB. The term 'nitrogen oxides' comprise generally all oxides of nitrogen, but in terms of gaseous products of combustion of solid fuels, we speak mainly about nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O). The former two are dangerous gaseous pollutants and their emissions are regulated and restricted in the case of conventional air-combustion of solid fuels. N_2O is not a harmful gas, however it has a strong greenhouse effect. Because it is present in flue gases only in small concentrations (in units or tens of ppmv), it is not an object of emission limits. In the case of oxy-fuel combustion (and other combustion

systems combined with CCS technologies), the maximum concentrations of impurities are not specified due to emission limits in general, because it is assumed that no gas is emitted to the atmosphere. They are based on technical demands for transport and storage and on environmental demands in the place of deployment. It is generally accepted that the concentration of NO_X (comprising NO and NO_2) in the leaving CO_2 stream should not be higher than 100 ppm [4]. This limit is set mainly due to health and safety reasons (in the case of gas leakage) [5] and because of risks of corrosion. NO can catalyze the conversion of SO_2 to H_2SO_4, which has a strong corrosive potential [6]. NO oxidizes to NO_2 at lower temperatures and higher pressures (e.g. in the CPU) and NO_2 can react with H_2O forming HNO_3, which is also a strong corrosive acid. In the case of CO_2 storage, NO and NO_2 can react with formation and cap rocks and affect the injectivity and storage integrity [6]. Therefore it is necessary to characterize the impacts of the operation parameters of the oxy-fuel combustion process in a BFB on the formation and reduction of NO_X, since it is crucial to minimize their presence in the outlet CO_2 stream.

Although the NO_X formation mechanisms as well as their reducing measures are well known in the conventional air-combustion mode [2], [7]–[10], the combustion of solid fuels in the oxy-fuel combustion regime brings a number of inevitable consequences [11], which make the research of NO_X formation and reduction within such systems necessary.

2 State of the art

2.1 Oxy-fuel combustion

It should be noted that the oxy-fuel fludized bed combustion has not yet been deployed in the industry on a commercial scale. It can be seen in the review of experimental studies on oxy-fuel combustion carried out in the world between 2011 and 2020 that most of the studies were performed using facilities with fluidized beds, particularly with CFBs. Several studies on nitrogen formation in oxy-fuel combustion in a BFB have also been published. However, in almost all of them, the real FGR was substituted by a dry mixture of clean gases from pressurized cylinders. Only de las Obras-Loscertales et al. [12] and de Diego et al. [13] included in their FGR water vapor and in only about 15 % vol., which is significantly lower than could be reached in the

case of lignite or biomass combustion. Several large-scale projects focused on the oxy-fuel combustion were carried out around 2010. However, only very limited results from these projects have been published (except for the Callide project, which was, however, focused only on the combustion of pulverized coal).

It is essential to study the oxy-fuel combustion in a BFB with real wet FGR, as there is a significant lack of knowledge. In particular for the study of formation gaseous pollutants, it is necessary to bring the conditions of the experiments as close as possible to the future large-scale applications. It can be expected that operation of BFB combustors under oxy-fuel conditions with real wet FGR will bring lesser freedom of choice of operating parameters and only narrower ranges of these parameters will be possible compared to laboratory-scale experiments with artificial atmospheres or electrically heated devices. However, such results will surely have a greater benefit for a real practice despite these drawbacks.

2.2   Modeling of NO$_X$ formation under oxy-fuel conditions

Modeling of NO$_X$ chemistry in a combustion process has been of scientific interest for almost as long as it has been studied. Many authors published models that employed various numerical approaches and different mechanisms of chemical kinetics. Glarborg et al. [14] published a comprehensive state of the art on NO$_X$ formation and destruction in combustion based on the work reported over the last four decades. The NO$_X$ modeling in oxy-fuel combustion process has been also a subject of a few studies, but none of these are focused on combustion in a BFB or on combustion at conditions similar to those usually reached in BFBs. Within most of them, combustion of natural gas or pulverized coal at temperatures in a range from $1\,000$ to $1\,500\,°C$ was modeled. Sometimes even at elevated pressures. Only Krzywański et al. [15] modeled oxy-fuel combustion of coal in a circulating fluidized bed, however, with a small set of chemical reactions. The residence times of fuel particles in an oxidation zone are significantly different in CFBs compared to those in BFBs. Therefore, the results of this study are hardly comparable with the results reached in BFBs. Based on the review, it can be concluded that numerical studies of the formation of nitrogen oxides in BFBs are missing in the current state of the art.

The conversion of nitrogen through homogeneous reactions can be modeled using a number of detailed kinetic mechanisms consisting of hundreds of elementary reactions. Usually, these mechanisms are based on kinetic parameters experimentally determined at particular conditions, and hence they should be used for modeling of process at similar conditions. However, modeling of heterogeneous reactions brings significant uncertainties in the size of the available reaction surface and its activity. Therefore, published numerical studies of solid fuel combustion are simplified and often rely on the chemistry of homogeneous reactions. Within the numerical studies of oxy-fuel combustion of solid fuels published by Hashemi et al. [16], Yadav and Mondal [17] or Liang et al. [18], it was considered that char-N converts to NO fully or at a rate proportional to the conversion of char-C to CO with the rest released as N_2. Krzywański et al. [15] considered that char-N reacts only with NO forming N_2O. No other heterogeneous reactions were involved in these studies.

3   Goals and novelty of the thesis

This thesis is focused on the formation of nitrogen oxides in oxy-fuel combustion in a BFB. A review of the current state of the art revealed that there is a lack of both numerical and experimental studies that would comprehensively cover this topic. Within the published numerical studies, no special interest has been given to the environment of BFBs or at least to conditions that would be similar to those of atmospheric oxy-fuel BFBs. Within the published experimental studies, almost all works were performed with simulated FGR consisting of an artificial mixture of pure gases and not with real wet FGR. This thesis contributes to the state-of-the-art and brings the missing information. Goals of this thesis can be described by the following points:

1. design of a numerical model of the formation of nitrogen oxides in a BFB combustor operating under oxy-fuel conditions using chemical kinetics,

2. numerical simulation of the formation of nitrogen oxides in a BFB combustor operating under oxy-fuel conditions,

3. design and construction of an experimental $30\,\mathrm{kW_{th}}$ laboratory-scale BFB combustor, which could be operated under full oxy-fuel conditions with real wet FGR and with various fuels,

4. experimental verification of the nitrogen oxides formation in the $30\,\mathrm{kW_{th}}$ BFB facility operating under full oxy-fuel conditions with real flue gas recirculation, and experimental validation of the numerical model.

The purpose of the numerical model is to clarify the effects of the operational parameters of the combustion process and their importance in the formation of nitrogen oxides (rather than to precisely predict their concentrations in the flue gas from different types of combustors). In addition, the model can be used to explain the observed experimental results in detail. The PFR model is based on physical parameters of the $30\,\mathrm{kW_{th}}$ laboratory-scale BFB combustor to ensure the highest possible comparability of obtained results.

Both the numerical and experimental studies presented in this thesis are performed for two different types of fuel, Czech lignite and wooden biomass. These types of fuel are typical for their application in BFBs and differ significantly in their nitrogen content, share of volatiles, and structure of nitrogen compounds. The fact that the full oxy-fuel combustion process is realized in a facility equipped with a real FGR makes the experimental results of great importance. It also verifies the limits of the attainable operating parameters and shows the possible drawbacks of the technology.

4 Material and methods

4.1 Numerical modeling

An one-dimensional mathematical model of the BFB combustor was proposed using a plug flow reactor (PFR) concept to gain a deeper understanding of the formation of nitrogen oxides in the oxy-fuel combustion in the BFB. The model was assembled using the Cantera [19] toolkit to calculate chemical kinetics, thermodynamics, and transport processes in Python code. Within the proposed model, the hydrodynamics of the fluidized bed was omitted as well as heterogeneous reactions, which were replaced with homogeneous reactions of typical char-reaction products. To provide model
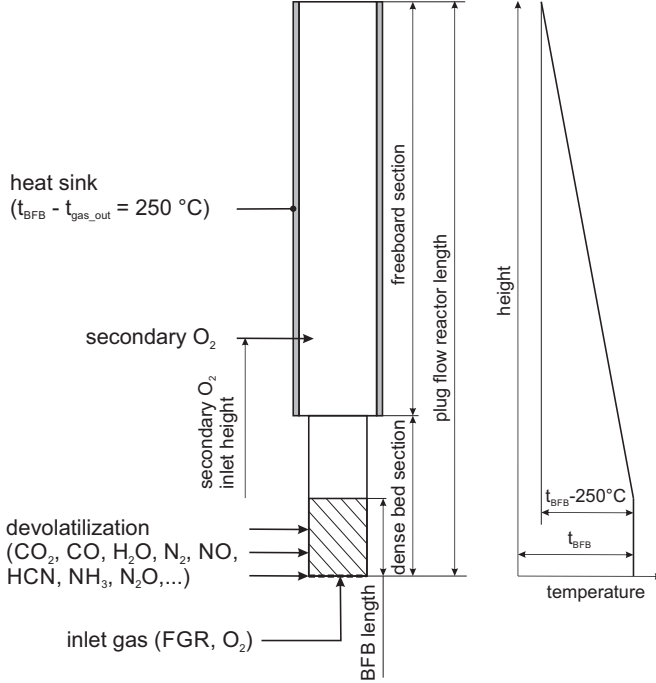
Figure 1: Scheme of the plug flow reactor model with an indicated temperature height profile.

outputs comparable with experimental results, the physical and operating parameters of the PFR were set according to the corresponding parameters of the facility used in the experimental part of this thesis. The PFR scheme is given in Figure 1. The grid of the numerical PFR reactor model was based on time steps. The duration of each time step was chosen according to the residence time of the gas - differently in the fluidized bed zone $(0.0004\,\text{s})$ and in the freeboard zone $(0.00473\,\text{s})$ providing 400 steps in the fluidized bed and 600 steps in the freeboard section.

The numerical model was based on the calculation of homogeneous combustion reaction kinetics. First, the GRI-mech 3.0 mechanism [20] had been used within the proposed model. The results achieved were published in a peer-reviewed journal [29] and in a conference proceedings [30]. However,

Table 1: Shares of volatile components and gaseous products of char combustion used within the numerical model.

Component	Lignite		Wooden biomass	
	Volatiles [g/kg$_{fuel}$]	Char [g/kg$_{fuel}$]	Volatiles [g/kg$_{fuel}$]	Char [g/kg$_{fuel}$]
NH_3	1.137	0.171	0.557	0.436
HCN	0.601	0.316	1.473	1.152
NO	2.671	1.803	0.491	0.384
N_2O	0.147	0.037	0.012	0.009
N_2	0.530	3.506	0.069	0.054
CH_4	91.839	0	171.455	0
C_2H_6	61.478	0	45.909	0
CO	160.350	70.388	427.655	22.343
CO_2	35.992	995.343	67.193	315.949
H_2	5.426	2.581	8.667	1.319
O_2	-8.224	-745.287	80.775	-237.763
H_2O	211.2		78	

the model predicted unrealistically high concentrations of NO_2 in the flue gas using the GRI-mech 3.0 mechanism. Therefore, a comparison of the performance of the model with the four most cited mechanisms of nitrogen chemistry in combustion process was realized. The mechanisms published by Glarborg et al. [14], Hashemi et al. [16], and Miller and Bowman [21] were compared with the GRI-mech 3.0 mechanism. On the basis of this comparison, the mechanism presented by Hashemi et al. was found to be the most suitable for the application on oxy-fuel combustion in a BFB and was further used within the model.

The composition of volatiles after devolatilization and char combustion was determined using data published by Winter et al. [7] and Konttinen et al. [9] (for combustion of lignite), by Konttinen et al., Anca-Couce et al. [22], and Brunner et al. [23] (for combustion of wooden biomass), based on fuel properties and the stoichiometry of the oxy-fuel combustion. The corresponding shares of volatile components and char combustion products used in the numerical simulations are given in Table 1.

4.2   Experimental tests

30 kW$_{th}$ BFB facility

The main experimental part of this thesis was carried out using a 30 kW$_{th}$ BFB combustor. This facility was built in 2013/2014 and has since been used for a number of studies on air- and oxy-fuel combustion, for example [31]–[39]. The author of this thesis contributed to the original design and construction of this facility. Its overall scheme is given in Figure 2. The reactor itself has a modular construction made of stainless steel. Its walls are insulated from the outside. The height of the combustor is 2.7 m (2.05 m from the fluidizing gas distributor (1) to the top of the reactor). Its cross section is 0.15×0.225 m in the dense bed section (2) and 0.2×0.3 m in the freeboard section (3). Fuel is supplied by a screw conveyor (4), the height of the fluidized bed is limited by the spillway (5) mounted in the wall (265 mm above the distributor of the fluidizing gas). Fly ash is separated from the flue gas stream by the cyclone particle separator (6). In the oxy-fuel combustion
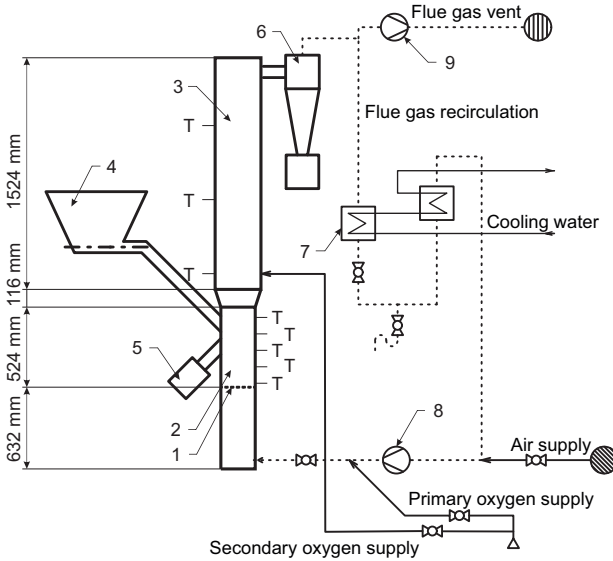

Figure 2: Scheme of the 30 kW$_{th}$ experimental BFB facility.

regime, oxygen of 99.5% purity from pressurized or cryogenic vessels is used as an oxidizer. The bed material is fluidized by a mixture of recirculated flue gas and oxygen. The FGR is taken downstream of the cyclone particle separator, through two water coolers (7) to the suction pipe of the primary fan (8). At the pressure pipe of the primary fan, the primary oxygen is mixed with the recirculated flue gas. To protect the primary fan from high temperatures and from the risks that could be caused by the condensation of water vapor simultaneously, the FGR is cooled to approximately 150 °C in the water coolers. The facility is also equipped with a secondary supply of oxygen to study the impact of staged combustion on the formation of gaseous pollutants. The facility was operated at over pressure conditions with the flue gas fan (9) turned off in the case of the oxy-fuel combustion to prevent an air ingress and flue gas dilution.

The composition of the flue gas was continuously analyzed. The volumetric fractions of CO_2, O_2, CO, SO_2, and NO_X (the sum of $NO + NO_2$) were measured. The flue gas was sampled downstream the cyclone separator and upstream the flue gas fan. The flue gas analysis consisted of a sampling probe with heated ceramic filter, heated sampling line, secondary sample filtration, cooling to 5 °C, pump, and a set of online gas analyzers.

500 kW$_{th}$ pilot-scale BFB facility

Additional experiments were performed using a pilot-scale 500 kW$_{th}$ BFB combustor to verify the shares of NO, NO_2, and N_2O in nitrogen oxides formed in oxy-fuel combustion in a BFB. This facility was equipped with multiple analyzers for on-line measurement of the flue gas composition (including NO NO_2, and N_2O separately).

The scheme of the pilot-scale BFB combustor is given in Figure 3. The facility consists of three main sections: the BFB combustion chamber (dense bed and freeboard section), the crossover pass, and the heat exchanger. The fluidization gas, formed by primary air (or oxygen) and recirculated flue gas (FGR), enters the bed trough distributor (1). The combustion chamber (3) has a cylindrical cross section and is insulated with a fireclay lining with a water-cooled surface. Secondary air (or pure oxygen) is supplied to the freeboard section (5) by 4 distributors (4) placed evenly on the perimeter. Each distributor can provide the secondary air inlet at 4 different heights. For the experiments, secondary oxygen inlets were used at a height of 550 mm
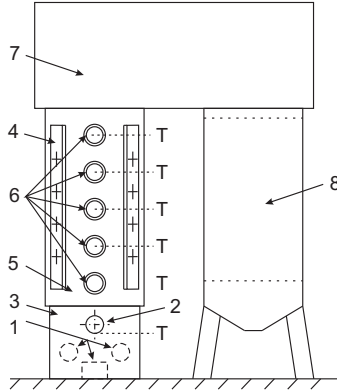
Figure 3: Scheme of the $500\,\mathrm{kW_{th}}$ pilot-scale BFB facility.

above the fluidized bed. From the freeboard section, the flue gas continues to an empty crossover pass (7) with water-cooled surface and then enters a heat exchanger (8). Downstream of the heat exchanger, the fly ash is separated from the flue gas in a cyclone particle separator and in a subsequent fabric filter. The cleaned flue gas is driven by a flue gas fan into a stack or is recirculated into the primary gas by a primary fan. This facility has been used for a number of studies on air-combustion, for example [40]–[43].

Fuels

The experiments were carried out with two fuels, a Czech lignite Bílina HP1 135 and pellets of A1 quality from spruce wood. The proximate and ultimate analysis of these fuels is given in Table 2.

Table 2: Proximate and ultimate analysis of the Czech lignite (Bílina HP1 135) and pellets from spruce wood of A1 quality.

	as received			dry ash free				
	LHV $[\mathrm{MJ}\cdot\mathrm{kg}^{-1}]$	water [wt. %]	ash [wt. %]	C [wt. %]	H [wt. %]	N [wt. %]	S [wt. %]	volatiles [wt. %]
lignite	17.6	21.1	9.9	72.3	6.3	1.1	1.3	47.0
wooden pellets	16.4	7.8	1.5	51.0	6.9	0.3	0.003	84.6

Numerical and experimental analysis

Within the numerical and experimental parts of this thesis, the impacts of

- oxygen stoichiometry (expressed as vol. fraction of O_2 in dry flue gas),
- fluidized bed temperature, and
- staged supply of oxygen

on nitrogen oxides formation in oxy-fuel combustion in a BFB were studied. In the cases of variable oxygen stoichiometry and fluidized bed temperature, only primary oxygen was introduced into the BFB. In the case of staged oxygen supply, the ratio of secondary to primary oxygen ψ (defined in Equation 1) was variable.

$$\psi = \frac{\dot{V}_{O_2,sec}}{\dot{V}_{O_2,prim}}, \tag{1}$$

where $\dot{V}_{O_2,prim}$ and $\dot{V}_{O_2,sec}$ are the volumetric flows of primary and secondary oxygen. Other than the variable parameters were always kept constant. The matrix of parameters of the tests is given in Table 3.

Table 3: Matrix of parameters of the combustion process applied in the experimental tests.

Parameter	Unit	Oxygen stoichiometry	BFB temperature	Oxygen staging at const. t_{BFB}	Oxygen staging at const. $(O_2/CO_2)_{prim}$
$\phi_{O_2}^{DFG}$	[% vol.]	3–9	6	6, 9	6
t_{BFB}	[°C]	880	840–960	880	variable
$(O_2/CO_2)_{prim}$	[−]	variable	variable	variable	0.4
ψ	[−]	0	0	0–1.25	

5   Results

5.1   Analysis of mechanisms of reaction kinetics

The performance of the kinetic mechanisms published by Glarborg et al. [14], Hashemi et al.[16], Miller and Bowman [21], and of GRI-Mech 3.0 [20] mechanism within the proposed model was analyzed. The application of different mechanisms of chemical kinetics led to significant difference in the results calculated at otherwise identical conditions. In the case of lignite combustion, the dominant nitrogen oxide was NO for all four mechanisms. The shares of NO_2 and N_2O were lower and reached from 0 to 75 % of the concentration of NO depending on the parameters of the combustion process. In the case of the combustion of spruce wood, the only mechanism that predicted the dominant formation of NO was that of Hashemi et al. [16]. According to the other mechanism, the final concentrations of NO at the end of the reactor were the same (or even lower) as those of NO_2 and N_2O. The GRI-Mech 3.0 [20] and the Miller and Bowman [21] mechanisms also unrealistically predicted concentrations of NO near zero for low fluidized bed temperatures. The presence of NO_2 in the flue gas from fluidized bed combustors should be limited by low equilibrium concentrations of NO oxidation to NO_2 [2]. Within the laboratory-scale oxy-fuel experiments, NO_2 was detected only in a very low volumetric fractions (in units of ppmv) [12], [13], [24], or was not detected at all [25]. Therefore, the mechanism of Hashemi et al. [16], which predicted the lowest shares of NO_2 in the total amount of formed nitrogen oxides, was selected for a more detailed study.

5.2   Comparison of numerical and experimental results of NO_X formation

5.2.1   Effect of oxygen stoichiometry

NO_X is formed mainly by the oxidation of fuel-bound nitrogen in oxy-fuel combustion in a BFB, hence the O_2 stoichiometry is clearly of importance when examining the key parameters affecting NO_X formation.

The obvious impact of the O_2 stoichiometry can be seen for both fuels (Figure 4). The numerical model predicts a positive dependence of the NO_X formation on the O_2 stoichiometry, which is strongest at the lowest

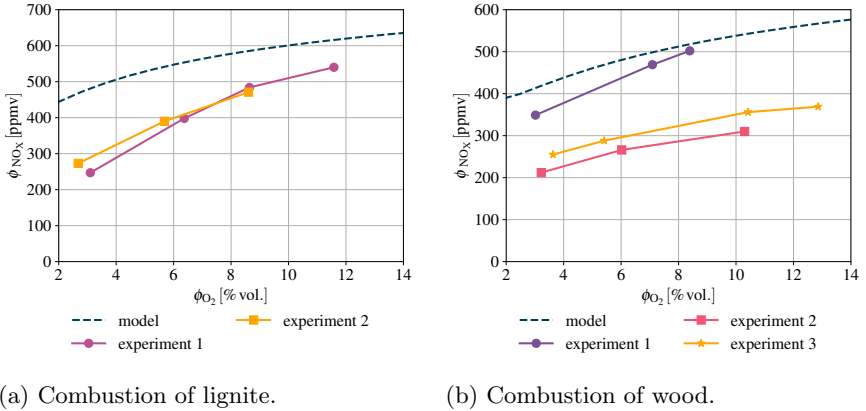(a) Combustion of lignite.   (b) Combustion of wood.

Figure 4: Comparison of num. and exp. results: Vol. fraction of NO_X in dry flue gas in dependence on the O_2 stoichiometry.

volumetric fraction of O_2 in dry flue gas and weakens with increasing ϕ_{O_2}. The experimental results showed the same trends in the studied range of $\phi_{O_2} \in \langle 3 - 9\,(12)\rangle\,\%$, although only a weak decrease in the gradient was observed for higher ϕ_{O_2} in the case of experimental series No 1 of spruce wood oxy-fuel combustion (Figure 4b). The gradients of the studied dependence were always slightly higher in the case of experimental results compared to numerical results. An offset of about 100–200 ppmv can be observed in the comparison of the numerical and experimental results of lignite oxy-fuel combustion (Figure 4a). The observed differences can be explained by the low dimensionality of the numerical approach and by the possibly inaccurate composition of volatiles, which was determined using data published for a different type of lignite. Although the numerical results do not match the experimental results exactly, they are still in very good agreement.

A positive effect of O_2 stoichiometry on NO_X formation was observed also by Lupiáñez et al. [26], who studied the oxy-fuel combustion of different types of coal in a laboratory-scale $90\,kW_{th}$ BFB with simulated FGR. They reached values of NO_X emission factors from 60 to $110\,mg \cdot MJ^{-1}$ for ϕ_{O_2} from 13 to 19 % in the case of lignite combustion. The values of emission factors presented within this thesis are similar, however, the range of ϕ_{O_2} measured by Lupiáñez et al. is significantly higher.

5.2.2   Effect of fluidized bed temperature

The comparison of numerical and experimental results of the effect of fluidized bed temperature on NO_X formation is given in Figure 5.

The results did not show as clear agreement as in the case of the effect of O_2 stoichiometry. In the case of lignite combustion (Figure 5a), all experimental series showed a positive dependence of the NO_X concentration on the fluidized bed temperature in the studied temperature range at least for temperatures up to 920 °C. Similar effect was observed also by de las Obras-Loscertales et al. [12] and de Diego et al. [13] who studied the oxy-fuel combustion of anthracite in a $3\,kW_{th}$ BFB with simulated FGR, by de las Obras-Loscertales et al. [24] who studied oxy-fuel combsution of anthracite, lignite, and bituminous coal in the same device, or by Lupiáñez et al. [26].

The negative effect of the fluidized bed temperature apparent in the numerical results is caused particularly by the temperature sensitivity of the modeled NO_2 formation. The model did not predict any strong temperature sensitivity of NO formation in the case of lignite. De las Obras-Loscertales et al. [12], [24] and de Diego et al. [13] did not detect any NO_2 fractions higher than 10 ppmv. Therefore, the NO_2 formation predicted by the numerical model seems slightly over-rated. The reason for the high for-
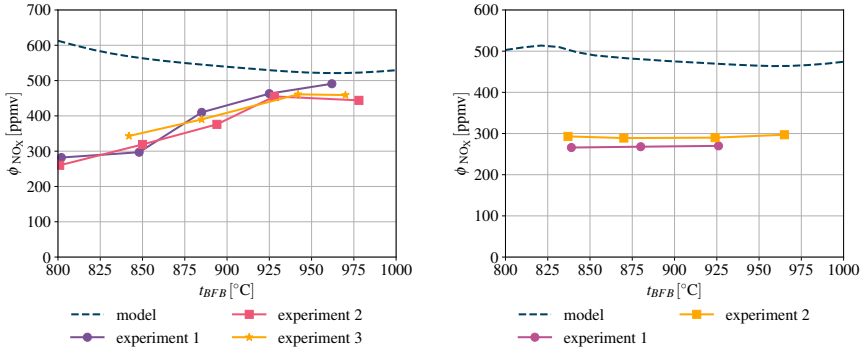
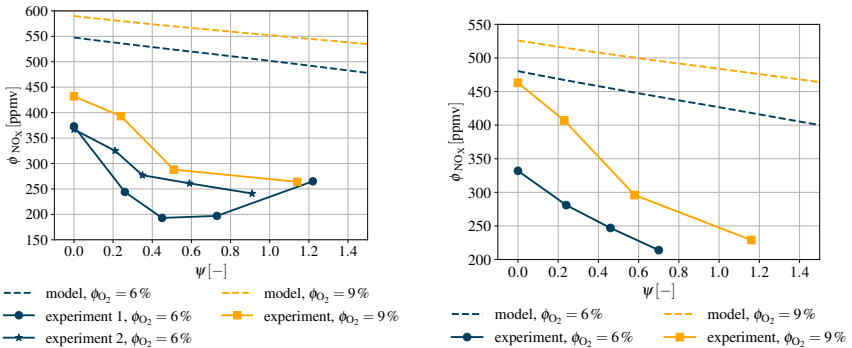(a) Combustion of lignite.   (b) Combustion of wood.

Figure 5: Comparison of num. and exp. results: Vol. fraction of NO_X in dry flue gas in dependence on the fluidized bed temperature.

mation of NO_2 could be the possibly inaccurate composition of volatiles and chars used within the numerical model.

In the case of spruce wood combustion, no effect of the fluidized bed temperature on the formation of NO_X was observed within the studied range (Figure 5b). The NO_X volumetric fraction provided by the numerical model also does not show any strong temperature sensitivity. The impacts of the fluidized bed temperature on the formation of NO and NO_2 were opposite and equalized in the overall volumetric fraction of NO_X. There is no reference in the published literature on oxy-fuel combustion of biomass in a BFB with which the results could be compared.

5.2.3   Effect of staged supply of oxygen

The comparison of numerical and experimental results of the impact of the staged supply of O_2 (Figure 6) shows good agreement in terms of trends. The ϕ_{O_2} of $9\,\%$ vol. led to higher NO_X concentrations compared to $\phi_{O_2} = 6\,\%$ vol. in each case. In all series except for lignite combustion at $\phi_{O_2} = 6\,\%$ vol., every increase of the ratio ψ led to a decrease in the NO_X vol. fraction. In the case of lignite combustion at $\phi_{O_2} = 6\,\%$ vol., the NO_X reduction had an optimum at $\psi = 0.5$ for the experimental results. For higher ratios ψ,

(a) Combustion of lignite.   (b) Combustion of wood.

Figure 6: Comparison of numerical and experimental results: Volumetric fraction of NO_X in dry flue gas in dependence on the staged supply of O_2.

the NO_X vol. fraction was raised again. The numerical model predicted a still decreasing concentration of NO in the flue gas at an increasing ratio ψ for all conditions. It can be seen in Figure 6 that gradients of the curves that describe the experimental results are steeper than those of numerical results. In addition, the numerical model predicted volumetric fractions of NO_X about 300 ppmv higher than were measured within the experiments.

The effect of staged supply of O_2 on NO_X formation in oxy-fuel combustion in a BFB was studied by Lupiáñez et al. [27], Díez et al. [28], or Jankowska et al. [25]. Lupiáñez et al. observed a strong positive effect on the reduction of NO in the case of lignite combustion, but a small to no effect in the case of anthracite combustion. They used two artificial mixtures of O_2 and CO_2 (27/78 and 45/55 %, respectively) for both the primary and secondary oxidizer. Using the mixture of 28/72 % O_2/CO_2 they achieved a reduction of about 25 % in the case of anthracite and about 38 % in the case of lignite for the ratio of secondary to primary oxidizer 0.2. With the mixture of 45/55 % O_2/CO_2 they achieved almost no reduction in the case of anthracite and about 45 % in the case of lignite. Almost identical results for anthracite combustion were reached by Díez et al. [28] using the same experimental facility. Jankowska et al. [25] studied the impact of the staged supply of oxidizer on nitrogen chemistry in oxy-fuel combustion of bituminous coal in a $0.1\,MW_{th}$ CFB. They used a constant ratio of volumetric flows of the secondary and primary oxidizer of 0.43 and changed the volumetric fraction of O_2 in the artificial mixtures of the secondary oxidizer from 21 to 35 % vol. The primary gas was a mixture of 21/79 % O_2/CO_2. They observed that an increase in the concentration of O_2 in secondary gas results in a significant decrease in N_2O concentrations and an increased conversion of fuel-N to NO.

5.3   Pilot-scale experimental results of the NO_X formation and speciation

These supplementary experiments were conducted to study the shares of NO, NO_2, and N_2O in the nitrogen oxides formed in the oxy-fuel combustion in a BFB using the pilot-scale $500\,kW_{th}$ BFB combustor equipped with analyzers, which are able to measure concentrations of these oxides separately. The operation of the pilot-scale combustor was accompanied by significant air ingress, which caused that the volumetric fraction of CO_2 in the dry flue gas was reached in the range from only 60 to 70 % vol. This ingress was

caused by a still unaddressed leakage in the flue gas duct or in the sealing of the shaft of the primary or flue gas fan. The graphic results of the pilot-scale experiments showing the impacts of O_2 stoichiometry, fluidized bed temperature, and staged supply of O_2 on the formation of NO_X are given in Figures 7a, 7b, and 7c, respectively.

Despite the low concentration of CO_2 in the flue gas from the pilot-scale combustor within the experiments, the results give valuable insight into the speciation of nitrogen oxides in the oxy-fuel combustion in a BFB.
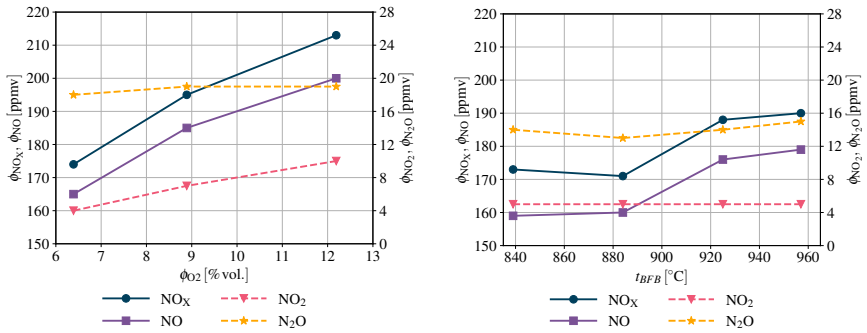
(a) Effect of O_2 stoichiometry.
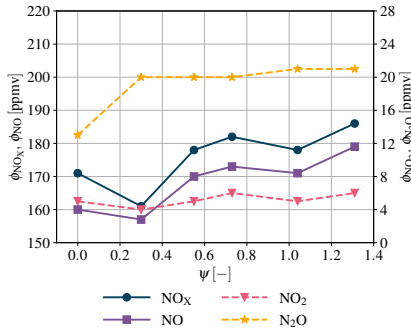

(b) Effect of fluidized bed temperature.

(c) Effect of staged supply of O_2.

Figure 7: Pilot-scale experimental results: Volumetric fractions of NO, NO_2, N_2O, and NO_X in dry flue gas in dependence on operating parameters.

The volumetric fraction of NO in dry flue gas varied in the range from 160 to 200 ppmv in all experimental cases, while the volumetric fraction of NO_2 was in the range from 4 to 10 ppmv, and the volumetric fraction of N_2O was in the range from 13 to 21 ppmv. On average, the shares of the volumetric fractions of NO, NO_2, and N_2O in the total sum of nitrogen oxides were about 88.4 %, 2.8 %, and 8.8 %, respectively.

The pilot-scale experimental results of NO_X (sum of NO and NO_2) agree well with the laboratory-scale experimental results of oxy-fuel combustion of spruce wood, which reported similar trends in the cases of dependence on oxygen stoichiometry and fluidized bed temperature. Only the staged supply of oxygen did not lead to a reduction of NO_X in the case of pilot-scale experiments. This could probably be due to the short residence time in the reduction zone, since the secondary oxygen inlets are placed very near above the dense bed section (only 550 mm above the distributor of fluidizing gas).

6   Conclusions

In this thesis, the characterization of NO_X formation in oxy-fuel combustion of two fuels (a Czech lignite and spruce wood pellets) in a BFB combustor was presented. The main goals of this study were: creation of a numerical model describing the formation of nitrogen oxides in oxy-fuel combustion in a BFB using chemical kinetics; design and preparation of a lab-scale BFB combustor operating under oxy-fuel conditions with real flue gas recirculation; an experimental evaluation of the nitrogen oxides formation in the laboratory-scale BFB facility; and validation of the numerical model. These goals were fully achieved.

A 1-D plug flow reactor was used to model the oxy-fuel combustion in a BFB. Four different kinetic mechanisms were used to calculate the progress of homogeneous gaseous reactions and the results were compared. There were significant differences in the formation of nitrogen oxides predicted by these mechanisms, particularly in the shares of NO, NO_2, and N_2O. Using all mechanisms except one, the model calculated unrealistically high final concentrations of NO_2. Nitrogen dioxide should not be formed in significant amounts at temperatures typical for BFBs, therefore, the mechanism that led to the lowest formation of NO_2 was selected for further analysis. The

results obtained using this mechanism were analyzed in detail and compared with the experimental results.

The experimental part was carried out using a $30\,\mathrm{kW_{th}}$ BFB combustor with real flue gas recirculation. The effects of key operating parameters, oxygen stoichiometry, fluidized bed temperature, and the staged supply of oxygen on NO_X (sum of NO and NO_2) formation were studied. The results showed that the formation of NO_X is highly sensitive to oxygen stoichiometry for both fuels, since oxygen availability is essential for the oxidation of fuel-N. The sensitivity of NO_X formation to fluidized bed temperature was observed only in the case of lignite combustion, where increasing temperature promoted NO_X formation. The results of the staged supply of oxygen showed that a significant NO_X reduction can be achieved (about $40-50\,\%$) deploying the sub-stoichiometric conditions of oxygen in the dense bed and subsequent oxidation conditions in the freeboard section. However, it was possible to reach the volumetric fraction of NO_X in the dry flue gas of only about $200\,\mathrm{ppmv}$ at minimum within the experiments, which is still about $100\,\mathrm{ppmv}$ higher than is required in CO_2 processing and transport processes. This shows the limits of NO_X reduction achievable by adjusting the parameters of the combustion process and applying primary measures.

It can be concluded that the numerical and experimental results show quite good agreement in the overall production of NO_X. The sensitivity of the formation of NO_X to the oxygen stoichiometry observed within the experimental part was confirmed by the numerical model, as was the extension of this sensitivity within the reduction of NO_X by the staged supply of oxygen. The effect of the fluidized bed temperature observed in the case of lignite combustion was not confirmed within the studied temperature range, where the numerical model predicted the negative effect of the fluidized bed temperature on the formation of NO_X. On the contrary, there was an agreement of the numerical and experimental results in the case of the oxy-fuel combustion of wood, where no effect of the fludized bed temperature on the formation of NO_X was observed. It appeared that the numerical model predicted slightly higher NO_2 formation than was expected and was also observed within competitive studies. The concentration of NO_2 could not be measured separately within the experimental part of this thesis performed using the laboratory-scale combustor. Therefore, additional pilot-scale experimental tests were performed using a $500\,\mathrm{kW_{th}}$ BFB combustor equipped with analyzers to measure the concentrations of NO, NO_2, and N_2O sepa-

rately to verify the accuracy of the model. These experimental tests were carried out with only one fuel, spruce wood pellets. The results were in good agreement with the laboratory-scale experimental test (in terms of concentrations of NO_X) except for the effect of the staged supply of oxygen, which did not lead to a reduction of NO_X in the case of pilot-scale experiments, probably due to the very short residence time of the flue gas in the primary reduction zone. Within pilot-scale experiments, the average volumetric shares of NO, NO_2, and N_2O in the flue gas were 88.4 %, 2.8 %, and 8.8 %, respectively. These results confirmed that the formation of NO_2 calculated by the numerical model with all studied kinetic mechanisms except for the Hashemi et al. [16] mechanism is unrealistically high. In the case of the Hashemi et al. [16] mechanism, the shares of the volumetric fractions of NO, NO_2, and N_2O in the total sum of nitrogen oxides were in the ranges 79.1–94.1 %, 1.7–13.5 %, and 3.1–8.5 %, respectively, in dependence on the parameters of the combustion process. In this case, the numerical results correspond well to the pilot-scale experiments.

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Summary

This thesis presents a numerical and experimental study of the formation of nitrogen oxides (NO_X) in the oxy-fuel combustion in a bubbling fluidized bed (BFB). A one-dimensional numerical model based on the principle of a plug flow reactor (PFR) with calculation of flue gas composition using chemical kinetics was developed. Four mechanisms describing the kinetics of the formation of nitrogen oxides were adapted and tested within the model. The most convenient mechanism was then applied for detailed analysis. The numerical results were experimentally verified using a $30\,kW_{th}$ BFB combustor operating in full oxy-fuel combustion with real flue gas recirculation (FGR). Since BFBs are facilities typical for their ability to combust different types of fuel, two fuels were used in the numerical and experimental tests, Czech lignite and spruce wood pellets. The sensitivity of the formation of NO_X to the most important parameters of the combustion process was studied. These were the oxygen stoichiometry, the temperature of the fluidized bed, and the staged supply of oxygen. The formation of NO_X in the oxy-fuel and air-combustion was also compared within the experiments.

The numerical and experimental results showed in agreement that the formation of NO_X is strongly dependent on the oxygen stoichiometry for both fuels. On the contrary, the effect of fluidized bed temperature on the formation of NO_X was not so clear. There was a good agreement in the numerical and experimental results in the study of the effect of staged supply of oxygen. The experimental comparison of the formation of NO_X in the oxy-fuel and air-combustion regime showed that despite the relative concentrations of NO_X being higher in the oxy-fuel combustion (because of the lower volume of the formed flue gas), the absolute amount of formed NO_X is significantly lower.

To verify the results and to validate the numerical model, additional experiments of the oxy-fuel fuel combustion were carried out in a pilot-scale $500\,kW_{th}$ combustor. These tests showed the speciation of NO, NO_2, and even of N_2O, since their concentrations in the flue gas were measured separately. The results showed that the average shares of NO, NO_2, and N_2O in the formed nitrogen oxides were $88.4\,\%$, $2.8\,\%$, and $8.8\,\%$, respectively. That was in good agreement with the numerical results obtained with the selected kinetic mechanism.

Anotace

Tato práce obsahuje numerickou a experimentální studiji tvorby oxidů dusíku (NO_X) při oxy-fuel spalování v kotlích s bublinkovou fluidní vrstvou (BFB). V této práci je představen jednorozměrný numerický model oxy-fuel spalování v ohništi s bublinkovou fluidní vrstvou založený na principu plug-flow reaktoru (PFR) s výpočtem složení spalin pomocí reakční kinetiky. V rámci modelu byly testovány čtyři mechanismy popisující reakční kinetiku tvorby oxidů dusíku. Nejvhodnější mechanismus byl poté použit pro podrobnou analýzu. Numerické výsledky byly experimentálně ověřeny pomocí laboratorního spalovacího zařízení s bublinkovou fluidní vrstvou o výkonu $30\,kW_{th}$ pracujícího v úplném oxy-fuel režimu spalování se skutečnou recirkulací spalin. Vzhledem k tomu, že kotle s bublinkovou fluidní vrstvou jsou zařízení typická svou schopností spalovat různé druhy paliv, byla při numerických i experimentálních testech použita dvě paliva, české hnědé uhlí a pelety ze smrkového dřeva. Byla studována citlivost tvorby NO_X na nejdůležitější parametry spalovacího procesu. Těmi byly stechiometrie kyslíku, teplota fluidní vrstvy a stupňovitý přívod kyslíku. V rámci experimentů byla rovněž porovnána tvorba NO_X při oxy-fuel spalování a při běžném spalování se vzduchem.

Numerické a experimentální výsledky shodně ukázaly, že tvorba NO_X je u obou paliv silně závislá na stechiometrii kyslíku. Naopak vliv teploty fluidní vrstvy na tvorbu NO_X nebyl tak jednoznačný. Při studiu vlivu stupňovitého přívodu kyslíku byla zjištěna dobrá shoda numerických a experimentálních výsledků. Experimentální porovnání tvorby NO_X v oxy-fuel a vzduchovém spalovacím režimu ukázalo, že přestože relativní koncentrace NO_X jsou vyšší při oxy-fuel spalování (z důvodu menšího objemu vznikajících spalin), absolutní množství vzniklých NO_X je výrazně nižší.

Pro ověření výsledků a validaci numerického modelu byly provedeny další experimenty oxy-fuel spalování v pilotním spalovacím zařízení s bublinkovou fluidní vrstvou o výkonu $500\,kW_{th}$. Tyto testy ukázaly speciaci NO, NO_2 a dokonce i N_2O, protože jejich koncentrace ve spalinách byly měřeny odděleně. Výsledky ukázaly, že průměrné podíly NO, NO_2 a N_2O ve vznikajících oxidech dusíku byly 88,4 %, 2,8 % a 8,8 %. To bylo v dobrém souladu s numerickými výsledky získanými pomocí zvoleného mechanismu reakční kinetiky.