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Review of the doctoral dissertation of Mr. Matěj Vodička

This review was written in response to letter No. 246/12921/O/2023 of March 27, 2023. Mr. Matěj Vodička's doctoral dissertation submitted for evaluation is entitled "formation of NO_x in oxy-fuel combustion in a bubbling fluidized bed". The supervisor of the doctoral thesis is prof. Jan Hrdlička.

1. Formal issues of the PhD thesis

From the formal side, the dissertation is written in English and it's presented on 165 pages and contains 8 chapters, which are preceded by abstracts in English and Czech, a table of contents, a list of figures, tables and a list of nomenclature used in the dissertation. The thesis ends with a bibliography (172 items) and 3 appendices. There are 35 tables and 41 figures. The structure of the dissertation is typical for doctoral theses. Therefore, the dissertation is complete and can be subject to substantive and formal evaluation.

2. Overview/characteristics of the content of the work

Mr. Matěj Vodička's doctoral dissertation consists of two basic parts, namely the theoretical part based on current literature related to the subject of the dissertation and the research part presenting the author's own research. The thesis is preceded by a four-page introduction and a "motivation and scope of the thesis". From the technical side, the work is divided into eight chapters. The first contains an introduction and "motivation and scope of the thesis". The next two chapters (2 and 3) contain a description of the literature review in the field of oxy-combustion in bubbling fluidized bed and nitrogen oxides formation in combustion processes. The fourth chapter describes the goals and novelty of the thesis. Chapters 5, 6 and 7 constitute the essential, original, part of the research work. In chapter 5, the author described the materials, methods of numerical modeling and included a description of the test stand (experimental set-up). In chapter 7, the PhD student included the results of numerical modeling analyses, and in chapter 8, he presented the experimental results and validated the numerical model. The summary, future prospects for the development of research, as well as the possibility of using the results of work in oxy-fuel combustion were included by the PhD student in chapter 8. The work ends with a bibliography of literature, which includes 172 items from peer-reviewed scientific journals.

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3. Substantive characteristics (evaluation) of the work

3.1 Achievement of the aims of the thesis:

The aims of the thesis:
Matěj Vodička's thesis was focused on the formation of nitrogen oxides in oxy-fuel combustion in a bubbling fluidized bed (BFB).
The goals of this thesis were: development of a numerical model describing the formation of nitrogen oxides in oxy-fuel combustion in a bubbling fluidized bed (BFB) using chemical kinetics; simulation of the formation of nitrogen oxides in the oxy-fuel combustion; design and construction of the experimental facility and experimental verification of the numerical results.

Description and evaluation of the presented work:
The aim of the numerical model was to explain the effects of the operational parameters of the combustion process and their significance in the formation of nitrogen oxides; rather than precisely predict their concentrations in flue gas from various types of combustors. Regarding numerical work, Matěj Vodička's idea was not to create such a mechanism, but rather to use an existing one and apply it to a model under specific conditions of oxy-fuel combustion in a BFB.
To achieve this goal, Mr. Vodička used four different kinetic mechanisms to calculate the progress of homogenous gaseous reactions and then compared achieved results. There were significant differences between these mechanisms of nitrogen oxide formation. After a thorough analysis, Matěj Vodička selected the mechanism, with the most realistic data for further examination. It was mechanism for modelling the chemistry of nitrogen in the oxy-fuel combustion of pulverised coal developed by Hashemi et al. It was one-dimensional plug flow reactor (PFR) model which describes a chemical or physical processes with a large number of subsequent steps. He carefully analyzed obtained results and compared them to experimental ones.

The first part of experimental work was performed in the 30 kWth laboratory-scale BFB combustor. The experiments and numerical studies were done for two types of fuels (lignite and wooden biomass). The aim was to examine at the effects of oxygen stoichiometry, fluidized bed temperature, and staged oxygen supply on nitrogen oxide formation in BFB oxy-fuel combustion. The significance of the experimental results is increased by the fact that the oxy-fuel combustion process was carried out in a facility equipped with a real flue gas recirculation system.
Additional studies were carried out in a pilot-scale 500 kWth BFB combustor equipped with various gas analyzers to validate the shares of NO, NO_2, and N_2O in the nitrogen oxides generated during oxy-fuel combustion in a BFB. Only pellets made from spruce wood were investigated in this case. Comparable to laboratory-scale experiments, the effects of oxygen stoichiometry, fluidized bed temperature, and staged oxygen supply on nitrogen oxide formation were investigated.

Mr. Matěj Vodička proved that the production of NO_x is significantly influenced by the oxygen stoichiometry of the fuels and the presence of oxygen is crucial for the oxidation of fuel-N. The impact of fluidized bed temperature on NO_x formation was found to be significant solely in the context of lignite combustion, as elevated temperatures were observed to facilitate the production of NOx. The results of a

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staged oxygen supply indicated that a significant reduction in NOx (approximately 40-50%) can be achieved by utilizing sub-stoichiometric oxygen conditions within the dense bed, followed by oxidation conditions in the freeboard section.
The overall formation of NO_x showed a satisfactory correlation between the numerical model and laboratory-scale experimental findings. The numerical model generated a slightly higher level of NO_2 formation, which aligned with the findings of comparable studies.
In order to verify the precision of the model, a pilot-scale testing was also conducted. The findings indicated a high level of consistency between the findings and the laboratory-scale experiments, specifically in relation to NO_x concentrations. However, the staged supply of oxygen did not result in NO_x reduction in the pilot experiments, potentially due to the flue gas having a very short residence time in the primary reduction zone. The average volumetric percentages of NO, NO_2, and N_2O in flue gas during pilot-scale experiments were 88.4%, 2.8%, and 8.8%, respectively. Matěj Vodička's results confirmed that the formation of NO_2 calculated by the numerical model with all studied kinetic mechanisms, with the exception of the Hashemi et al. mechanism, is unreasonably high. In the Hashemi et al. mechanism, the volumetric fractions of NO, NO_2, and N_2O in the total sum of nitrogen oxides varied from 79.1 to 94.1%, 1.7% to 13.5%, and 3.1% to 8.5%, depending on the combustion process parameters. The numerical results in this case corresponded well with the pilot-scale experiments what proves that Matěj Vodička has proposed a simplified model that offers valuable insights and is reasonably consistent with experimental findings.
In conclusion, all assumed goals were successfully achieved.

Despite the importance of the topic, there are issues in the work, phrases that raise questions and doubts:

Critical/discussion/editorial comments (specific comments):

1. The doctoral thesis concerns the formation mechanisms of nitrogen oxides in oxy-combustion conditions in fluidized beds. Therefore, the reader would expect a proposed chemical mechanism for the formation of nitrogen oxides under such conditions. This is missing in the dissertation. However, in the introduction part of dissertation, the known mechanisms of nitrogen oxides formation in the conditions of classical combustion are discussed in detail. The process conditions in oxy-combustion vary significantly, and so do the reaction mechanisms. The Author focused mainly on shares of the volumetric fractions of NO, NO_2 and N_2O, without a deeper understanding of the chemical mechanisms themselves. Please explain this approach.

2.The PRF model is a simple one-dimensional mathematical model for describing chemical mechanisms based on reaction kinetics in a continuous system. In the reactor, only forward flow is considered, there is no reverse flow or mixing. Perfect mixing and uniform conditions are considered at each stage. In addition, fluidized bed hydrodynamics and heterogeneous reactions have been omitted. In BFB, solids flow and move dynamically, but this cannot be accounted for in a 1-D PFR model.

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However, the obtained results were very good, consistent with the experimental trial. Please explain how this can be done and what assumptions need to be made.

3. A lot of simplifications have been introduced in the numerical model, e.g., instead of the parameters of the combusted solid fuel, a mixture of gaseous products of the fuel devitalization have been introduced. This is a very big simplification, because the whole combustion path is omitted. Please explain this approach.

4. Chemistry in the model: The numerical model, presented in the dissertation, was based on the calculation of homogenous combustion reaction kinetics. The GRI-mech 3.0 mechanism was used within the proposed model. This mechanism was initially designed to model natural gas combustion, including NO formation and reburning, and contains 325 reactions and 53 species. Model showed very high, unrealistic high concentrations of NO2. Therefore, Matěj Vodička compared the performance of the model with the four most cited mechanisms of nitrogen chemistry in combustion processes. On the basis of his results, mechanism presented by Hashemi et al. was found as a most suitable for application on oxy-fuel combustion in a BFB and was further used in the model. The question is, what was the motivation of applying nitrogen chemistry mechanisms used in conventional combustion techniques to oxyfuel conditions? Why did you not use any chemical mechanism, even if it was imperfect but designed specifically for oxy-combustion?

5. The chapter entitled "the goals and the novelty of the thesis" does not contain information, not even two sentences, about the research carried out on a pilot scale at the 500 kWth pilot-scale BFB facility. Writing in this chapter about the experimental part of the work, the Author does not mention anything about pilot-scale studies, and in turn a lot of space is devoted to them in the later part of the work. The pilot installation, unlike the laboratory tests, was very richly equipped with a number of "multiple analyzers for on-line measurements" and independently measured: NO, NO_2 and NO_2, NH_3, which helped to verify the model. What's more, research on a larger scale than a laboratory one is always very valuable, because it is closer to real conditions. It is even more a pity that this research is not mentioned in such an important place of the dissertation.

3.2 Level of the analysis of state-of-the art done on the issues dealt with the dissertation and contribution of the PhD thesis to the theory of the subject elaborated

The doctoral thesis contains a wide (172 items) and current review of literature from peer-reviewed scientific journals. 15 cited works are co-authored works of the author. The description of the state of the literature is presented in two chapters and mainly concerns oxy-combustion and the formation of nitrogen oxides during combustion and oxy-combustion processes. The literature review may not be the widest (37 pages), but it contains the most important aspects that are the subject of the doctoral dissertation.
The present doctoral dissertation makes a significant contribution to the advancement of research on the generation of nitrogen oxides during oxy-fuel combustion in a

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bubbling fluidized bed. Both the scientific papers dealing with numerical modelling and the experimental part have substantial worth in this context. Several studies have been conducted on the modelling of oxy-fuel processes, especially in relation to the generation of various gaseous pollutants. However, there is a lack of research on the oxy-fuel combustion bubbling fluidized beds environment. The author's contribution in this field is undoubtedly valuable.

3.3 Contribution of the PhD thesis to the engineering practice

Oxy-fuel combustion is currently a hot topic due to the need for economy decarbonization. Therefore, presented research is very valuable for engineering practice. Presented research, on the formation of nitrogen oxides in oxy-fuel combustion in a bubbling fluidized bed (BFB), can be useful in future designing flue gas cleaning technology under oxy-combustion. Understanding chemistry is fundamental to all technologies because it helps to avoid costly errors in process design (such as reactor size). Therefore, I do not have doubts that Matěj Vodička's research are contributing to the engineering practice.

3.4 Relevance of the applied methods and Relevance and the approach to the method application

In order to complete the research, Matěj Vodička used existing and validated numerical-analytical methods and conducted a series of empirical experiments on a laboratory and pilot scale. He divided his research into four stages:
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 30kWth laboratory-scale BFB combustor, which could be operated under full oxy-fuel conditions with real wet flue gas recirculation (FGR) and with various fuels,
4. Experimental verification of the nitrogen oxides formation in the 30 kWth BFB facility operating under full oxy-combustion conditions with real flue gas recirculation, and experimental validation of the numerical model Mr. Matěj Vodička's carefully performed each of these stages using available and reliable tools and methods.

3.5 Adequacy of student's knowledge in special field as demonstrated by the dissertiation contents

Mr. Matěj Vodička mastered the research technique very well and showed knowledge in the subject, because he performed all the above tasks correctly, in accordance with applicable standards and norms. His research was also reviewed and published in prestigious international journals.

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4. **Explicit statement whether you recommend or do not recommend the dissertation to the final defense presentation**

I state with conviction, that the topic of the dissertation is up to date, important from a scientific and practical point of view. The obtained results will significantly contribute to the development of the research area in the field of in oxy-fuel combustion and flue gas chemistry. I would like to point out, that most of the comments are of a debatable nature and do not diminish the value of the dissertation. Mr. Matěj Vodička demonstrated the acquisition of planning skills, conducting an experiment and analyzing the results of research. All the tasks were planned carefully. Taking into account the above, and the selection of methods, research tools and the synthesis of the results achieved, it can be concluded that Mr. Matěj Vodička has demonstrated knowledge and research skills necessary to conduct research in the field of technical sciences and meets the conditions for applying for the degree of doctor of technical sciences. In view of the above, **I strongly recommend allowing the dissertation to the final defense presentation**

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