



Review of Doctoral Dissertation

Title: **Low-temperature adsorption for post-combustion CO₂ capture from fossil fuel combustion**

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Study program: Energy and Process Engineering (CTU)

The present doctoral thesis is focused on the technical and economic aspects of the application of low-temperature adsorption for CO₂ separation in post-combustion CO₂ capture (PCC) applications. The thesis contains the original results of the author's work, which are documented in papers in 1 impact journal, in 3 scientific journals of the Jsc type, and several papers at international conferences.

The following points should be commented on in the review:

- ***The recency of the doctoral thesis theme***

Ongoing climate change is often associated with a strong reliance on the fossil fuel industry. Today, most of the energy is generated from carbon-containing fossil fuels. Therefore, the development of CO₂ capture technologies is still challenging. In this work, decentralized energy systems with CO₂-lean emissions were selected for such an assessment. These systems are often overlooked at the expense of large-scale coal power generation and lack CO₂ capture solutions.

The work aimed to develop the mathematical model in MATLAB to predict various breakthrough experiments at elevated pressure and continuous operation of vacuum-swing adsorption (VSA) cycle, and to assess the design and economics of PCC in urban-scale cogeneration and heat plant (CHP). Due to the global effort to reduce CO₂ emissions, the chosen doctoral thesis theme is up to date.

- ***Fulfillment of the objectives of the dissertation***

The objectives of the dissertation are formulated in chapter 2.5. Their fulfillment is summarized in chapter 5.1 of the thesis. I state that the formulated goals were met.

- ***Theoretical and practical contributions of the dissertation***

The present doctoral thesis is focused on the design and modeling of the PCC technology suitable for decentralized energy systems with CO₂-lean emissions. Based on the review, the 4-

step VSA technology was chosen and simulated for post-combustion CO₂ capture. The theoretical concept was designed alongside other flue gas-treating sub-systems and auxiliary components, forming a ready-to-operate PCC process downstream from the CHP.

1. The simplified non-linear dynamic mathematical model predicting high-pressure CO₂ breakthrough curves in a fixed-bed column was developed. This model was validated against these data, measured at two pressures (2 and 5 bar) and four temperatures (283 - 313 K). Model reliability and robustness were demonstrated by an accurate prediction of all CO₂ breakthrough curves and by fitting the missing adsorption isotherm parameters, respectively.

2. A 4-step VSA process model incorporating PDEs of mass, enthalpy, and momentum transfers was developed and validated using various literature data. The model was applied for the theoretical design of a PCC adsorption process.

3. The PCC system integrated into an urban-scale energy system was proposed including main subsystems such as SCR-deNO_x, and two-step flue gas dehydration. The resulting ready-to-operate process with adsorption PCC process was considered downstream from a 4.3 MW natural gas-fired CHP, representing an industrial point emission source. The simulated 4-step VSA achieved a CO₂ purity and recovery of 90.4 % and 15.6 %. The economic analysis was also included.

It should also be noted that the obtained results were obtained within two Czech grants, the Ministry of Education, Youth and Sports of the Czech Republic (OP RDE) and CTU.

- **Methodology**

- *Analysis of the state-of-the-art*

The analysis of the state of the art is presented in Chapter 2. The analysis is processed regarding the objectives of the work and is therefore focused on: 1) low-temperature adsorption technologies, 2) adsorbents for CO₂ capture, 3) adsorption process modeling, and 4) adsorption process economy. I have no comments on the quality of the analysis.

- *Methodology – used approach*

The approach combining experimental measurement and numerical simulation was used for Investigation.

- *Methodology – application of used methods*

I state that the application of methods to achieve the goal was at an excellent level. The author proved that he has theoretical and practical knowledge in the field of numerical simulation of processes, preparation, and implementation of experiments.

I have the following comments on this section:

- o Figure 12 (page 70) and Table 5 (page 71) – the steepness of breakthrough curves at various temperature changes (Figure 12a). It indicates the different values of π_1 criterion. The rules for volume flow determination (Table 5) are not presented. It is not clear by which way the volume flow was determined.
- o Page 88, Table 9 – output ammonia concentration is not presented. It is not clear whether the effect of output ammonia on VSA should be taken into account or not.
- o Page 92, Table 11 - output water concentration is not presented. It is not clear whether the effect of output water on VSA should be taken into account or not. Complete dehydration was assumed (page 98).
- o Table 12 (page 94) and Table 13 (page 96) - the mass transfer coefficient used for simulation should be also presented. The desorption performance should be also discussed.

- o Economy assessment - the results are presented in the relative scale. The mass transfer coefficient used for simulation should be also presented. The desorption performance should be also discussed.

- *Expertise*

Based on the submitted dissertation, I state that the author proved that he has adequate knowledge both in mechanical and process engineering in the field of adsorption processes and gas treatment.

- **Formal and language level**

The quality of the manuscript is adequate. The manuscript is well-structured and written in scientific language. The formal issues are fulfilled.

I have the following comments on this section:

- o Page 16 W-work (W or J) - The use of the one symbol for different properties is confusing.
- o Page 16 β_{mass} – dimensionless parameter in Equations (27) and (29) - the numbering of equations was probably changed and not corrected somewhere. Figure numbering similarly (e. g. page 59, figure 4)
- o Page 81 equation (35), β_{mass} is a dimensionless parameter– the equation is not correct, the β_{mass} in Eq. 35 is a dimensional quantity with a unit of m/s.
- o Page 92, Table 11 – Energy consumption (kW_{th}) – consumption (kWh_{th}) or duty (kW_{th})?
- o Page 100, Figure 21 Process flow diagram – the complete stream parameters should be presented.

Comments and questions for the defense

- o *Figure 12 (page 70) and Table 5 (page 71) – volumetric flow determination*

How were the volumetric flow rates determined? Could you present the values of π_1 criterion for presented experimental data?

- o *Competitive adsorption isotherms of CO₂ and N₂ on zeolite 13X - Figure 16*

Figure 16, page 80 – Could you also present adsorption isotherms of oxygen and water vapors for comparison?

- o *CO₂ capture plant design*

The following parameters should be presented: output ammonia concentration from SCR, output water concentration from TSA dehydrator, composition of “Purified gas” stream (Figure 21), energy consumption for CO₂ captured ($\text{kWh}/\text{t}_{\text{CO}_2}$), CO₂ capture cost ($\text{EUR}/\text{t}_{\text{CO}_2}$).

- o *CO₂ purity and recovery*

The simulated 4-step VSA achieved a CO₂ purity and recovery of 90.4 % and 15.6 %. The VSA technologies presented in Appendix A show higher values of purity and recovery. Could you comment on these differences?

I state that the dissertation meets the conditions specified in § 47, paragraph 4 of the Act on Higher Education Institutions, and therefore I recommend submitting it for defense. I propose to award the academic title “Ph.D.”.

Prague, October 11, 2023

Assoc. prof. Ing. Radek Šulc, Ph.D.