

**CZECH TECHNICAL
UNIVERSITY
IN PRAGUE**

**FACULTY
OF MECHANICAL
ENGINEERING**



**DOCTORAL
THESIS
STATEMENT**

CZECH TECHNICAL UNIVERSITY IN PRAGUE
FACULTY OF MECHANICAL ENGINEERING
DEPARTMENT OF ENERGY ENGINEERING

THESIS STATEMENT

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

Ing. Marek Nedoma

Doctoral study programme: Energy and Process Engineering

Supervisor: *prof. Ing. Jan Hrdlička, Ph.D.*

Co-supervisor: *Ing. Matěj Vodička, Ph.D.*

Dissertation thesis statement for obtaining the academic title of
"Doctor", abbreviated as "Ph.D."

Prague

August, 2023

Title in Czech language:

Nízkoteplotní adsorpce pro záchyt CO₂ ze spalování fosilních paliv

This dissertation is an outcome of a full-time doctoral study programme at the Department of Energy Engineering, Faculty of Mechanical Engineering, Czech Technical University in Prague.

Author: Ing. Marek Nedoma
Department of Energy Engineering, Faculty of Mechanical, CTU
Technická 4, Prague, 160 00, Czech Republic

Supervisor: Professor Jan Hrdlička
Department of Energy Engineering, Faculty of Mechanical, CTU
Technická 4, Prague, 160 00, Czech Republic

Reviewers:

The thesis statement was sent out on:

The defence of the dissertation thesis will take place on
at in the meeting room number 17 (ground floor Faculty of
Mechanical Engineering, CTU in Prague, Technická 4, Praha 6 before the
commission for the defence of the dissertation in the study field of Energy and
Process Engineering.

The thesis is available in the Department of Science and Research of the
Faculty of Mechanical Engineering, CTU in Prague, Technická 4, Praha 6.

Professor František Hrdlička
Head of Doctoral Study Field Energy and Process Engineering
Faculty of Mechanical Engineering, CTU in Prague

List of contents

1 Introduction	6
2 Low-temperature adsorption technologies	7
2.1 Fundamentals of adsorption phenomena	7
2.2 Adsorption cycle principle and technology overview	7
2.2.1 Adsorption cycle steps	8
2.2.2 Adsorbents for CO ₂ capture: selection importance	8
2.2.3 Adsorption cycle technologies and their performance	8
2.2.4 Adsorption cycle technologies in the context of power plant retrofitting	9
2.3 Adsorption process modelling	9
2.4 Adsorption process economy	9
2.5 Aims of the thesis	10
3 Modelling of adsorption experiments	10
3.1 Materials	10
3.2 Experimental breakthrough apparatus	10
3.2.1 Main components	11
3.2.2 Measurement protocol	11
3.3 Constitution of simplified mathematical model	12
3.4 Evaluation of experimental data	13
3.5 Evaluation of breakthrough curve modelling	14
3.6 Evaluation of breakthrough curve modelling	15
4 Simulation, design, and evaluation of a 4-step VSA process for retrofitting urban-scale CHP	17
4.1 PCC plant design	17
4.1.1 Process flow diagram	17
4.1.2 NO _x reduction – SCR	18
4.1.3 Dehydration – Condenser and TSA	18
4.1.4 CO ₂ removal – VSA	19
4.2 Summary of PCC chain design for CHP	21
4.3 Process economy assessment	22
5 Conclusions	23
5.1 Accomplishment of individual goals	23
5.2 Future perspectives	24
References	25
Publications of the author	27
Anotace	28
Annotation	29

1 Introduction

Addressing climate change and carbon neutrality requires a rapid but smooth transition to renewable energy. "Smoothness" makes immediate diversion from fossil fuels difficult and implies the urgent need to develop CO₂ capture technologies. This led to the *Paris Climate Agreement* and gave rise to the *European Green Deal*, which aims to make Europe the first climate-neutral continent by 2050 by reducing carbon footprints in various sectors [1, 2].

In industrial combustion processes, CO₂ capture technologies can be divided into three categories:

- **Post-combustion technologies** (PCC) capture CO₂ downstream of the combustion process. It is the most mature technology suitable for retrofitting existing power plants, approaching large-scale deployment.
- **Pre-combustion technologies** capture CO₂ upstream of the combustion process via fuel pre-treatment. These technologies show continuous progress, but are ill-suited for retrofitting power plants.
- **Oxy-fuel combustion** uses high-purity oxygen as an oxidiser, producing pure and easy-to-separate CO₂. The expensive and energy-intensive oxygen production slows down the deployment.

The technical advancements and ease of integration into existing power plants of PCC techniques motivated me to further explore this topic [3]. Prevalent and emerging PCC technologies include:

- Chemical absorption
- Physical adsorption
- Membrane separation
- Cryogenic distillation
- Gas hydrates
- Calcium looping

Of these, the first three offer the widest range of applications.

Post-combustion technologies: *A state of the art*

At present, chemical absorption is the cornerstone of PCC processes tested for commerce in several coal-fired power plants, with monoethanolamine-based aqueous amines at Technology Readiness Levels (TRL) 9. The main drawbacks include high toxicity, corrosiveness, and energy-intensive regeneration [4]. Membranes are at TRL 6-7 threshold; therefore, no advanced pilot projects exist. Their effectiveness in treating CO₂-rich flue gases is not met in PCC. The main characteristics include excellent selectivity and stability;

however, propensity to clogging, mediocre permeability, and costly development. Low-temperature adsorption is at TRL 7 with the most advanced PCC pilot system from *Svante Inc.* [5] labelled almost TRL 8. It offers several advantages, *e.g.* high selectivity and adsorbent regenerability, but the treated gas must be free of impurities and, for most adsorbents, water, which is costly [6, 7]. High-temperature adsorption (*i.e.* calcium looping) is at TRL 7, but its applicability is limited to cement plants [8].

Considering CO₂ separation efficiency, all technologies can produce high purity CO₂, despite economic and technical considerations. As absorption progress may have reached a plateau in many areas, other separation techniques warrant exploration. Adsorption is a promising candidate for PCC in fossil fuel emission sources, which I decided to examine further.

2 Low-temperature adsorption technologies

2.1 Fundamentals of adsorption phenomena

Adsorption is a separation process taking place in a multicomponent system at the interface of two phases, where the concentration of one or more components in the gas phase changes by a transition to a solid phase (adsorbent) where it is physically or chemically bound. In this thesis, I focus exclusively on physical adsorption, which requires low temperatures, is reversible, and driven by *van der Waals* forces [9].

Physical adsorption can be controlled by equilibrium or kinetics. Equilibrium-controlled processes are typical for gases, where the adsorption isotherm bears quantitative information about the gas species retaining in adsorbent at a given temperature. For CO₂ capture, *Type I* isotherm (*IUPAC* classification [10]) is the most common due to the use of highly microporous adsorbents. Typical theories are *Langmuir*, *Freundlich*, *Sips*, and *Tóth* adsorption isotherms [9].

Adsorption processes are typically found in a fixed bed columns filled with adsorbent, although moving or fluidised beds are gaining attention. These processes employ adsorption cycles, which are classified according to the desorption principle (the reverse adsorption process), which can be carried out by varying temperature, pressure or introducing an inert gas stream [9].

2.2 Adsorption cycle principle and technology overview

Adsorption processes are non-stationary, reach equilibrium quickly, and operate at cyclic steady state (CSS). In PCC, they concentrate CO₂ from a low concentration in flue gas to a high concentration as a product of desorption. Traditional examples are pressure- and vacuum-swing adsorptions (PSA and

VSA, respectively), using the effect of alternating pressure, and temperature swing adsorption (TSA), relying on temperature changes.

2.2.1 Adsorption cycle steps

A variety of steps placed in a logical sequence form a continuously operating adsorption process. Individual steps differ in duration, gas flow direction, column interconnection, and initial and final states that are shared among two subsequent steps. A typical PCC VSA cycle comprises four steps, namely pressurisation, adsorption, blowdown, and evacuation [11].

2.2.2 Adsorbents for CO₂ capture: selection importance

Adsorbents are highly porous solids with pores of nanometre size. Both non-carbonaceous and carbonaceous adsorbents can be used in PCC, with the latter exceeding the former. Their selection is important and can be made through evaluation criteria or by meeting properties such as fast kinetics, low adsorption heat, low adsorption hysteresis, cyclic and chemical stabilities, impurity tolerance, and low cost. All properties are impossible to meet, thus the rapid development. Most adsorbents are available for laboratory use at a high price or are synthesised by scientists; in PCC, zeolites currently provide an attractive combination of performance, availability, and cost [12, 13].

2.2.3 Adsorption cycle technologies and their performance

Since pioneering work on CO₂ capture by adsorption in the 1990s [14], various pressure- and temperature-swing based processes have been tested. Process performance indicators (PIs): CO₂ purity, CO₂ recovery, productivity, and energy consumption often measure their performance in PCC [15].

A detailed literature review (thesis, Appendices A and B) indicated that zeolite 13X is the most widely used adsorbent, especially for VSA cycles, which prevail over PSA or TSA cycles. Fixed-bed columns are a rational choice except for TSA because of their low heat transfer rate. Theoretical studies using mathematical models or simulation software outnumber experimental studies, without overly compromising the accuracy of experiments. Comparison of PIs of CO₂ purity and energy consumption for PSA, VSA, and TSA processes using zeolite 13X revealed that TSA cycles tend to be more energy-intensive, although conclusions should be approached with caution, as explained in more detail in my thesis. Their comparison is shown in Figure 1.

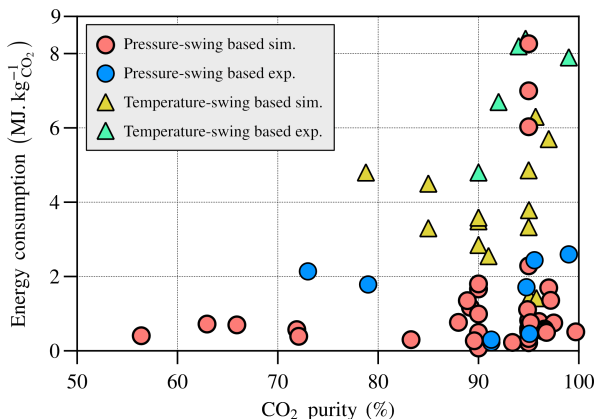


Figure 1. CO₂ purity and energy consumption reported in the existing literature for pressure-swing based (PSA, VSA, VPSA) and TSA cycles using zeolite 13X.

Red circles: theoretical studies of pressure-swing based cycles; **blue circles:** experimental studies of pressure-swing based cycles; **yellow triangles:** theoretical studies of temperature-swing based cycles; **light green triangles:** experimental studies of temperature-swing based cycles.

2.2.4 Adsorption cycle technologies in the context of PCC power plants

Overall, some studies have assessed adsorption PCC in the context of fossil fuel power plants. These studies used process modelling and favoured basic 4-step cycles with zeolite 13X, achieving 90 % CO₂ purity. They focused on large-scale coal power plants at the expense of small-scale plants with CO₂-lean emissions. However, a multi-column adsorption systems required for the former may be economically-inefficient compared to alternative PCC technologies.

2.3 Adsorption process modelling

Mathematical models are essential and play a vital role in evaluating and optimising adsorption PCC processes. They are based on thermodynamic behaviour, considering mass, energy, and momentum transport mechanisms between gas and solid phases, which produce a system of coupled non-linear partial differential equations (PDEs), necessitating numerical methods to obtain a solution. But first, a proper discretisation, the definition of boundary and initial conditions, and their effective implementation must be carried [16].

2.4 Adsorption process economy

The economic aspect is crucial from the point of views of the energy sector, the commercialisation, and the investors themselves. Economy analysis follows technical design and uses cost measures either per mass unit of CO₂ captured or per annual operating cost. Consequently, the PCC process chain must be

established beforehand, considering power plant operation, emissions, and mechanical design of all sub-systems. The final assessment includes capital and operating expenses [17].

2.5 Aims of the thesis

The main objective of this thesis was to investigate low-temperature adsorption for small-scale PCC, given its potential advantages over other processes at this scale. A 4-step VSA process using zeolite 13X was chosen to be assessed through mathematical modelling, as it appeared to be a promising candidate for examining operation of this process and analysing its feasibility for integration into a PCC power plant, including basic economics.

The following steps had to be carried out:

1. Development of a simplified non-linear dynamic mathematical model of adsorption phenomena. The reliability of the model will be verified using high-pressure breakthrough experimental data, and its robustness assessed through analysis of the numerical approach and balance equations, and application for process design.
2. Development of a complex non-linear dynamic mathematical model of 4-step VSA process, enabling simulation of various scenarios for different process parameters and configurations, and its application to experimental and theoretical studies.
3. Design of adsorption PCC system integrated into an urban-scale energy system, including general economic assessment.

3 Adsorption experiments and modelling

This chapter discusses the design of a simplified mathematical model for predicting experimental CO₂ breakthrough measurements using zeolite 13X [MN3]. The capabilities of mathematical modelling are further examined through sensitivity analysis and initial PCC adsorption process design [MN1].

3.1 Materials

A commercial sample of zeolite 13X beads (Figure 2d) with physical properties described in Table 1.

3.2 Experimental breakthrough apparatus

The main components include gas distribution and flow control systems, adsorption column and humidifier, climate chamber with programmable temperature controller, and analytical terminal as shown in Figures 2a-b.

Table 1. Adsorption column geometry, physical properties of the adsorbent packing, and of the adsorbent particles (zeolite 13X).

Adsorption column: geometry	
Bed type, material	<i>Fixed-bed, stainless steel</i>
Inner column, empty space, inert and adsorbent bed lengths	$L_{col} = 0.26$ m, $L_{emp} = 0.08$ m, 0.019 – 0.025 m, 0.155 – 0.161 m
Inner diameter, wall thickness	$d_{in} = 0.04$ m, $t_w = 0.002$ m
Adsorption column: packing (zeolite 13X)	
Material, manufacturer	<i>Molecular sieve 13X, Sigma Aldrich</i>
Total material volume	$V_m = 195 - 202$ cm ³
Material weight	$m_m = 0.1425 - 0.1435$ kg
Bulk density, bed voidage	$\rho_b = 710 - 730$ kg.m ⁻³ , $\varepsilon_b = 0.373$
Particles shape	<i>Homogenous spheres</i>
Particle diameter, volume	$d_p = 1.90 - 2.10$ mm, $V_p = 2.84 - 3.46$ mm ³

3.2.1 Main components

The entire apparatus is shown in Figure 2 with adsorption column geometry (no. 21 in Figures 2b-c) summarised in Table 1. It processes a gas mixture of 13 vol% CO₂ balanced by synthetic air, *i.e.* a pre-purified PCC flue gas.

3.2.2 Measurement protocol

The validity and reproducibility of experiments was ensured by following the same procedure with blank volume correction before each measurement at 2 and 5 bar and 283, 293, 303, and 313 K with a gas mixture of known composition and a constant flow rate. The procedure consisted of three steps:

1. **Regeneration** of the adsorbent and column.
2. **Breakthrough experiment** under eight different conditions.
3. **Desorption** using high temperature.

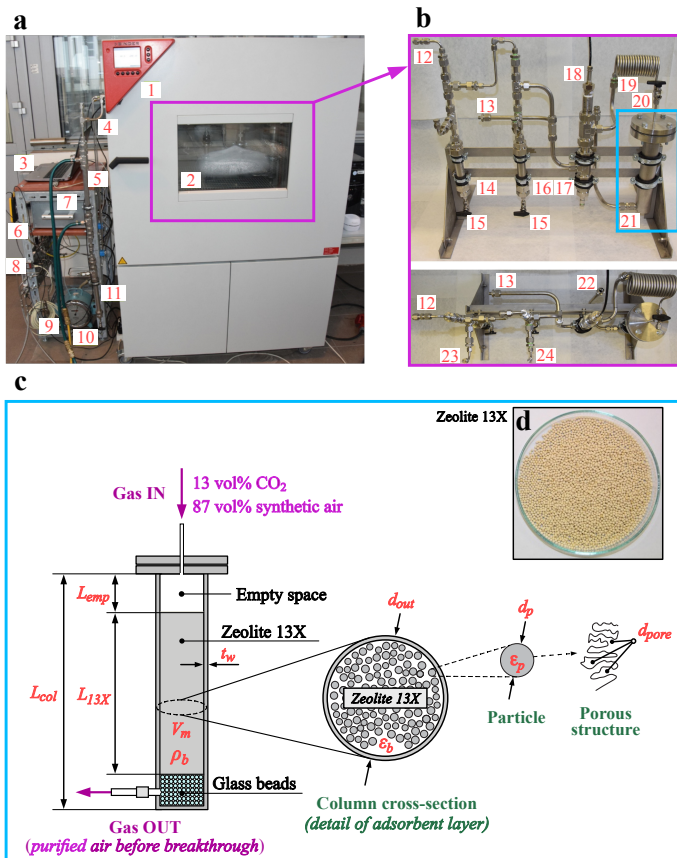


Figure 2. The breakthrough apparatus: **(a) Outside view:** 1 - glazed chamber, 2 - climate chamber, 3 PC (data collection and process control), 4 - side chamber passage of pipes and cables, 5 - liquid cooler, 6 - thermometer with data-logger, 7 - IR spectrometer, 8 - mass flow meter, 9 - safety valve, 10 drum-type gas meter, 11 - condensate sump; **(b) Climate chamber:** 12 - humidifier gas inlet, 13 - dry gas path inlet, 14 - first humidifier chamber, 15 - water discharge, 16 - second humidifier chamber, 17 - hygrometer pressure sump, 18 - hygrometer probe, 19 - heat exchanger, 20 - three-way valve (adsorber column bypass), 21 - adsorber column, 22 - adsorber column outlet, 23 and 24 - water inlet regulators (humidifier wetting); **(c) Adsorption column detail:** no. 21 in (b); **(d) Zeolite molecular sieve 13X.**

3.3 Constitution of simplified mathematical model

The breakthrough experiment was described by a one-dimensional plug-flow model for the CO₂/N₂ gas mixture. It implements PDEs of mass transport (Eqs.

(1-2)) and parameter estimates (Eqs. (4-7)), arising from the assumptions made [18].

$$\text{Mass balance in gas phase: } \frac{\partial c_i}{\partial t} = \frac{\partial}{\partial z} \left(D_{ax} \frac{\partial c_i}{\partial z} \right) - v \frac{\partial (c_i)}{\partial z} - \rho_p \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \frac{\partial q_i}{\partial t} \quad (1)$$

$$\text{Mass balance in solid phase: } \frac{\partial q_i}{\partial t} = \frac{15 D_{p,eff}}{r_p^2} \frac{c_i}{\rho_p q_i^*} (q_i^* - q_i) \quad (2)$$

$$\text{Adsorption isotherm (single-site Langmuir): } q_i^* = \frac{q_s b_i c_i}{\rho_p (1 + b_{CO_2} c_{CO_2} + b_{N_2} c_{N_2})} \quad (3)$$

$$\text{Axial dispersion: } D_{ax} = \gamma D_{m,CO_2-N_2} + \frac{P e_{\infty}^{-1} v d_p}{1 + \beta \gamma D_{m,CO_2-N_2} / (v d_p)} \quad (4)$$

$$\text{Molecular diffusion: } D_{m,CO_2-N_2} = \frac{0.00143 T^{1.75}}{P M_{CO_2-N_2} \left[(\sum v_{CO_2})^{1/3} + (\sum v_{N_2})^{1/3} \right]^2} \quad (5)$$

$$\text{Knudsen diffusion: } D_{K,i} = \frac{9}{13} \left(\frac{d_{pore}}{3} \sqrt{\frac{8 R_g T}{\pi M_i}} \right), \text{ where } d_{pore} = \frac{4 V_{pore}}{S_{BET}} \quad (6)$$

$$\text{Macropore diffusion: } D_{p,eff} = \frac{\varepsilon_p}{\tau_p} \left(\frac{1}{D_{m,CO_2-N_2}} + \frac{1}{D_K} \right)^{-1}, \text{ where } \varepsilon_p = \rho_p V_{pore} \quad (7)$$

The adsorption isotherm parameters (Eq. (3)) parameters were fitted, as they were not measured. A second-order total variation diminishing explicit finite volume (FVM) with van-Leer flux limiter scheme was used. The discretised PDEs were solved in *MATLAB* using the *ode23s* solver.

3.4 Evaluation of experimental data

Textural properties of zeolite 13X

Textural properties were characterised by N_2 physisorption at 77 K. The BET area of $511.65 \text{ m}^2 \cdot \text{g}^{-1}$ and pore volume of $3.317 \times 10^{-4} \text{ m}^3 \cdot \text{kg}^{-1}$ were measured at $P/P_0 \approx 1$, while average pore size of $3.33 \times 10^{-8} \text{ m}$ was estimated.

CO_2 sorption properties of zeolite 13X: breakthrough experiments

The breakthrough experiments were carried out over five adsorption and desorption cycles after 24 h of degassing at 423 K. The results at 2 and 5 bar at four temperatures (283, 293, 303, and 313 K) were averaged for each cycle.

The highest CO_2 capacity was achieved at 283 K for both pressures, with a noticeable difference between 293 and 303 K. The experiments indicated fast CO_2 kinetics by steep breakthrough curves, showing more pronounced steepness decay at 2 bar and 313 K (Figure 3). A less noticeable decrease in adsorption capacity with increasing temperatures at 5 bar could be considered for processing CO_2 -rich wet flue gases above dew point to avoid energy-intensive dehydration.

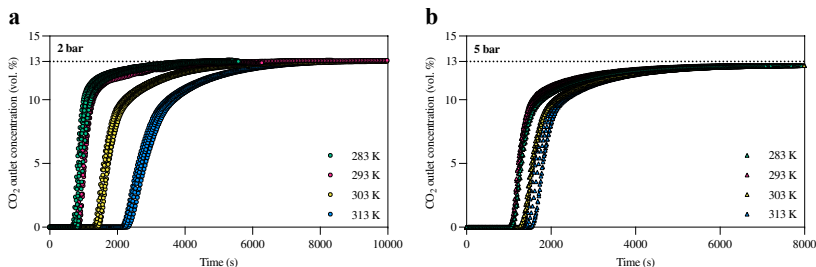


Figure 3. Experimentally measured breakthrough curves at 283 K (green), 293 K (red), 303 K (yellow), and 313 K (blue) at (a) 2 bar and (b) 5 bar.

3.5 Evaluation of breakthrough curve modelling

The necessary adsorption isotherm fitting paradoxically allowed further examination of mathematical modelling. The single-site Langmuir isotherm model (Eq. (3)) was indirectly fitted to predict the breakthrough onset time at 283 K and 2 bar, using parameters within the typical range for zeolite 13X [19]. The best fit obtained was verified for other temperatures at 2 bar (Figure 4). Overall, the results can be generalised as follows:

- The mathematical model is flexible for various parameter inputs.
- The breakthrough onset time prediction achieved a maximum deviation of 2 % from experimental values across all temperatures.
- The breakthrough curve trend of slowly reaching its plateau is difficult to predict accurately, despite being less relevant in swing processes.
- The isothermal model seemed adequate for low flue gas velocities, yet including energy balance in the future may bring further improvements.

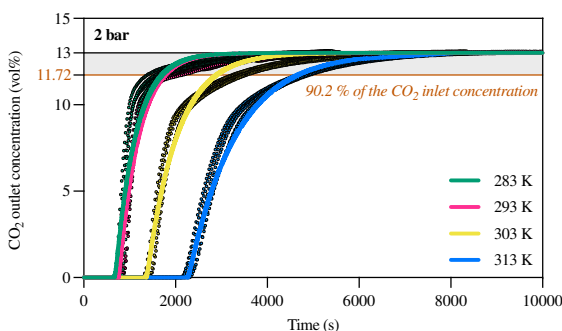


Figure 4. Comparison between the experimentally measured breakthrough curves (dotted lines) and simulation results (solid lines) at 283 K (green), 293 K (red), 303 K (yellow), and 313 K (blue) and 2 bar. The grey-shaded area represents the highest deviation between simulation and experimental data.

Sensitivity analysis

Sensitivity analysis on a breakthrough curve onset time prediction at 2 bar and 293 K assessed four key parameters and numerical scheme (the effects of column size, adsorbent amount, and volumetric flow rate would be obvious):

- **Axial dispersion coefficient:** less sensitive with correlations tested falling within a 1.62 % onset time prediction range.
- **Bed voidage:** the most sensitive parameter changing gas throughput, yet is difficult to obtain experimentally. Using another correlation changed bed porosity by 14 % and reduced the prediction error to 0.8%.
- **Mass transfer coefficient:** including external (surface) mass transfer showed an insignificant effect with a 0.3 % deviation.
- **Molecular diffusion coefficient:** less sensitive, with different empirical formulas yielding almost identical results.
- **Flux limiters:** superbee and Koren flux limiters achieved the highest accuracy of about 4 %; van Leer (error of 5 %) provided the best fit for the upper end of the curve. No single limiter was found to be universal.

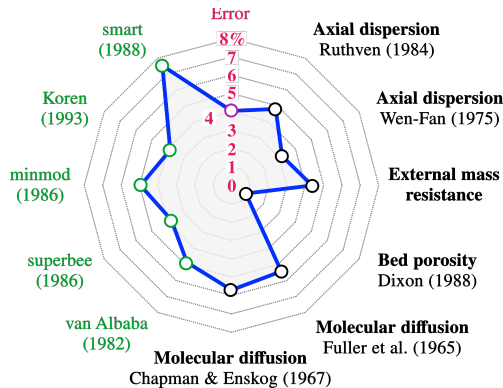


Figure 5. A deviation from the breakthrough curve onset time at 293 K and 2 bar performed for various parameters (black) and flux limiters (green). The original error is shown in purple.

3.6 Numerical model-based adsorption process design

An empirical approach was used to propose an initial VSA design for a small-scale natural gas combined heat and power (CHP) plant, taken as a case study. An abbreviated emission protocol is provided in Table 2.

Table 2. Abbreviated emission protocol for CHP *TEDOM Quanto D2000*, block "KJ1".

Parameter	Value
CHP plant	<i>TEDOM Quanto D2000</i>
Dimensions (height × width × length) (m)	3 × 3 × 15
Average fuel consumption (natural gas) (m ³ .h ⁻¹)	553
Nominal electric power, nominal heat power (kW)	2000, 2238
Electric efficiency, thermal efficiency (%)	43.7, 43.2
Flue gas	
Wet / dry flue gas flow rates (m _N ³ .h ⁻¹) ¹	9850, 8740
Pressure (Pa), temperature (K)	98310, 355.2
NO _x mass flow (kg.h ⁻¹) ²	2.851
CO mass flow (kg.h ⁻¹) ²	0.294
CO ₂ concentration (vol%) ³	6.4

The empirical approach combined a mathematical model, empirical process-design criteria [20], and literature-based recommendations. The CO₂/N₂ adsorption isotherm was taken from existing literature along with the physical properties of the pelletised zeolite 13X [11]. The model refinements included new assumptions, controlling the empirical ranges (Eqs. (8-10)) and outlet CO₂ concentration, axial dispersion coefficient estimate, and setting the interstitial velocity to 85 % of the fluidisation velocity threshold [9].

$$\text{Biot number: } Bi = \frac{\beta_{mass} d_p}{2D_{p,eff}} = \frac{\text{Transfer to the particle surface}}{\text{Difussion into the particle}} > \mathbf{10} \quad (8)$$

$$\pi_1 - \text{criterion: } \pi_1 = \frac{v d_p^2 \varepsilon_b}{LD_{p,eff}(1 - \varepsilon_b)} = \frac{\text{Convection through the column}}{\text{Difussion into the particle}} < \mathbf{0.1} \quad (9)$$

$$\pi_2 - \text{criterion: } \pi_2 = \frac{D_{ax}}{v_0 L} \approx \frac{\beta_{mass} d_p}{2L} = \frac{\text{Axial dispersion}}{\text{Convection in the column}} < \mathbf{0.001} \quad (10)$$

The initial adsorption process design produced the following results:

- **Column sizing:** dimensions of 2 × 1 m (about 1.1 t of zeolite 13X) met the empirical criteria ranges for a steep breakthrough profile and corresponded to the recommended length-to-diameter ratios [21, 22]. The interstitial gas of 1.9 m.s⁻¹ and a theoretical evacuation pressure of 0.13 bar were proposed.
- **Train sizing:** CO₂ outlet concentration of 15% was estimated to occur after about 274 s (Figure 6). Under the optimistic assumption that the adsorption step time is comparable to the residual step times, the VSA system requires eight columns to continuously process 9000 m_N³.h⁻¹ of dry flue gas at 1 bar and 303 K containing 6 vol% of CO₂.

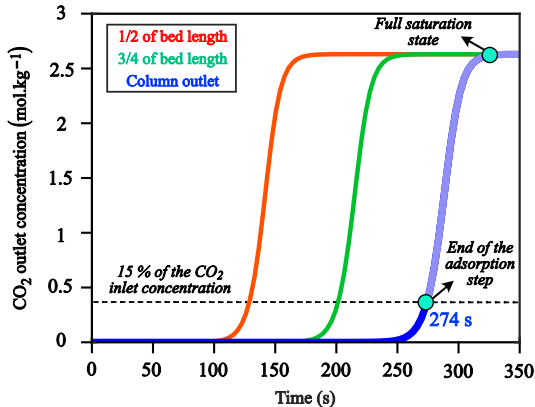


Figure 6. Theoretical CO₂ breakthrough curves at different positions in the column obtained by the mathematical model with an estimate of adsorption step length of 274 s, highlighted by a turquoise circle. The black dashed line corresponds to 15 % of the CO₂ outlet concentration relative to its inlet concentration.

The empirical approach was faster to perform, but limited in assessing the entire cycle and introduced inaccuracies due to the neglect of temperature and momentum variations. Hence, it is crucial to (1) simulate all cycle steps; (2) implement energy and momentum balances; and (3) determine process performance. Additionally, for rigorous VSA integration study, designing necessary sub-systems to remove impurities and auxiliary components is needed to verify the properties of flue gas at the VSA inlet.

4 Simulation, design, and evaluation of a 4-step VSA process for CO₂ capture in urban-scale CHP

In this chapter, a flue gas pre-treatment system is first proposed to determine the flue gas properties for the tail-end VSA process (zeolite 13X), designed by rigorous mathematical modelling. Following is the constitution of complete PCC process for retrofitting CHP [MN4] and basic economic assessment.

4.1 CO₂ capture plant design

The emphasis was placed on proposing a ready-to-operate process by considering real operating conditions without simplifications, including the climate of the Czech Republic to search for cost-efficient solutions. CO₂ conditioning was included to illustrate the CCS process; however, it was not examined in detail due to the case-specific requirements.

4.1.1 Process flow diagram

The design procedure involved eight successive steps to produce the process flow diagram and considered operation under nominal conditions. The main sub-systems are SCR for NO_x removal, two-step dehydration, and VSA for CO₂ removal.

4.1.2 NO_x reduction – SCR

The SCR was selected for favourable operating conditions and high efficiency at low temperatures. It has a modular V₂O₅/TiO₂ catalyst based on the laboratory setup at *Juliska laboratory* [23]. Its size was determined by scaling this setup to accommodate the CHP flue gas and NO_x flow rates of 9634 m_N³.h⁻¹ and 2.85 kg.h⁻¹, respectively. As a result, eight catalyst blocks (0.46 m) within a single carbon steel module (1.94 × 0.97 × 1.00 m) remove NO_x with a 90 % efficiency at 533 K, consuming 1.2 kg.h⁻¹ of NH₃.

4.1.3 Dehydration – Condenser and TSA

Dehydration is a two-step process consisting of a water-cooled condenser and a TSA system due to the high moisture content in the flue gas and the necessity of removing even the last bits of water.

Condenser

The proposed condenser is a baffled shell-and-tube carbon steel heat exchanger (4.29 × 1.44 × 0.73 m) with heat transfer area of 98.9 m² and heat transfer rate of 512 W. m⁻².K⁻¹ (turbulent regime). The use of natural cooling water with an annual average temperature of 284 K at a flow rate of 75 kg.s⁻¹ allows for 87 vol% of water vapour removal. Seasonal temperature variations were addressed by scaling up the TSA system for a worst-case scenario of 300 K (water removal drops to 67 vol%). All calculations were performed in *Aspen Plus v12.2* in accordance with the *TEMA* standard.

TSA

The TSA removes residual water vapour, which is determined by the condenser performance (*i.e.* the cooling water temperature, 284 - 300 K). It operates in three steps and consists of two fixed-bed CS columns (2.08 × 1.15 × 0.01 m) packed with commercial-grade zeolite 5A (0.9 t). Adsorbent regeneration uses direct heating with 390 K purified gas (2000 m_N³.h⁻¹) from the downstream VSA. Cooling after desorption as well as constant adsorption temperature are achieved by external water cooling. For the worst-case scenario of condenser performance, the column height more than doubles (for the same diameter), and energy consumption increases from 92 kW_{th} to 170 kW_{th} (comparison in Figure 7). All calculations were carried out in *MS Excel*, using an empirical approach [24-26].

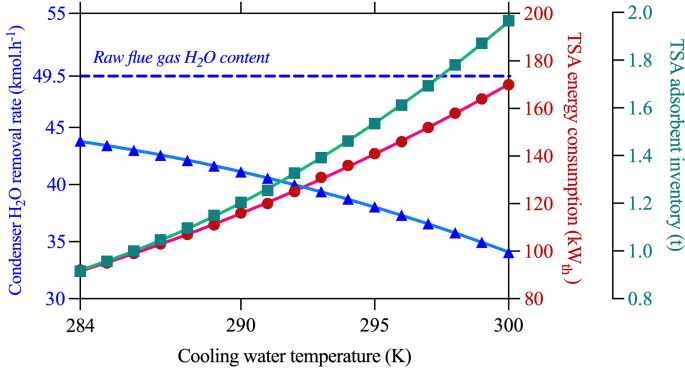


Figure 7. The influence of cooling water temperature on condenser performance expressed as H₂O removal rate (blue curve), TSA energy consumption (red curve), and amount of adsorbent needed to fill both columns (green curve). The blue dashed line at 49.5 kmol.h⁻¹ indicates the H₂O content in the unprocessed (*i.e.* raw) flue gas.

4.1.4 CO₂ removal – VSA

The VSA design initially kept the column sizing, the pressure boundaries, and the interstitial gas velocity consistent with Section 3.6; however, considered an updated flue gas parameters downstream from the TSA. The redefined mathematical model implemented WENO flux limiter, the total mass, energy and momentum balances - model PDEs are in Eqs. (11-16), with adsorption isotherm in Eq. (17)., the remaining VSA steps, and Pls of CO₂ purity and recovery. It was verified against various literature data (Appendix D).

$$\text{Mass balance in gas phase: } \frac{\partial c_i}{\partial t} = \frac{\partial}{\partial z} \left(D_{ax} \frac{\partial c_i}{\partial z} \right) - v \frac{\partial (c_i)}{\partial z} - \rho_p \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \frac{\partial q_i}{\partial t} \quad (11)$$

$$\text{Total mass balance: } \frac{\partial P}{\partial t} - \frac{P}{T} \frac{\partial T}{\partial t} = -T \frac{\partial}{\partial z} \left(\frac{vP}{T} \right) - R_g T \rho_b \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \sum_{i=1}^{n_{comp}} \frac{\partial q_i}{\partial t} \quad (12)$$

$$\text{Mass balance in solid phase: } \frac{\partial q_i}{\partial t} = \frac{15 D_{p,eff}}{r_p^2} \frac{c_i}{\rho_p q_i^*} (q_i^* - q_i) \quad (13)$$

$$\text{Energy balance of gas and solid pseudo-phase: } \left[\rho_p \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \cdot \left(C_{p,s} + C_{p,a} \sum_{i=1}^{n_{comp}} q_i \right) \right] \frac{\partial T}{\partial t} = \frac{K_{ax}}{\varepsilon_b} \frac{\partial^2 T}{\partial z^2} - \frac{C_{p,g}}{R_g} \frac{\partial P}{\partial t} - \quad (14)$$

$$\frac{C_{p,g}}{R_g} \frac{\partial}{\partial z} (vP) + \rho_p \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \sum_{i=1}^{n_{comp}} \left[(-\Delta H_i - C_{p,a} T) \left(\frac{\partial q_i}{\partial t} \right) \right] - \frac{2h_{in}}{\varepsilon_b r_{in}} (T - T_w)$$

$$\text{Energy balance of column wall: } \rho_w C_{p,w} \frac{\partial T_w}{\partial t} = K_w \frac{\partial^2 T_w}{\partial z^2} + \frac{2r_{in} h_{in}}{r_{out}^2 - r_{in}^2} (T - T_w) - \frac{2r_{out} h_{out}}{r_{out}^2 - r_{in}^2} (T_w - T_a) \quad (15)$$

$$\text{Momentum balance: } -\frac{\partial P}{\partial z} = \frac{150}{4r_p^2} \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right)^2 \mu_g v \quad (16)$$

$$\text{Adsorption isotherm (DSL): } q_i^* = \frac{q_{sb,i} b_i c_i}{1 + \sum_{i=1}^{n_{comp}} b_i c_i} + \frac{q_{sa,i} d_i c_i}{1 + \sum_{i=1}^{n_{comp}} d_i c_i} \quad (17)$$

Simulating a single continuously operating column allowed for overall design updates and the determination of scheduling, process parameters, process sizing and PIs. The final results were obtained in a CSS, which occurred after 103 cycles. The 4-step VSA with pelletised zeolite 13X (16.8 t in total) consisted of three columns (2 × 1 m) placed in five parallel trains. The desired CO₂ purity over 90 % (90.4 %) was achieved upon reducing the evacuation and intermediate pressures to 0.061 and 0.081 bar, respectively. Without pre-pressurising the flue gas, achieving such purity is not possible at higher evacuation pressures. The CO₂ purity was estimated at 15.6 %. The continuity of operation was ensured by incorporating an additional idle step (25 s). The total cycle time was 360 s. The selected model outputs are shown in Figure 8.

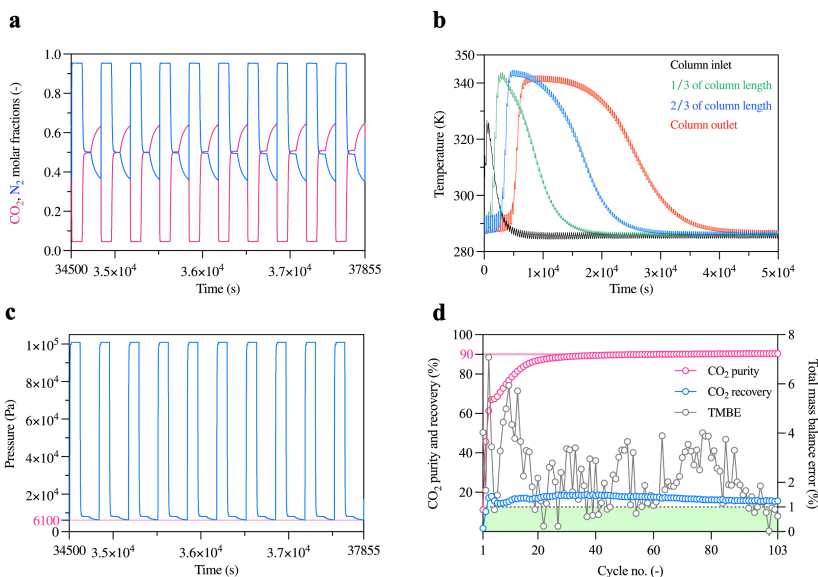


Figure 8. The results of 4-step VSA cycle simulation: **(a)** concentration profiles of CO₂ (red) and N₂ (blue) in the gas phase under CSS for 10 consecutive cycles; **(b)** temperature profiles at the column inlet (black), and the column outlet (red), along with internal temperature profiles at 1/3 (green) and 2/3 (blue) of the column length, until the point where the outlet flue gas temperature stabilizes (it occurs after reaching CSS). The red line indicates the cessation of flue gas outlet temperature fluctuations after about 50000 s of VSA operation; **(c)** pressure profile of 10 consecutive cycles under CSS with the evacuation pressure (red) highlighted at 0.061 bar, as required by the CO₂ purity constraint; **(d)** progression of TMBE (grey), along with the CO₂ purity (red) and recovery (blue) values. The green-shaded area indicates the desirable TMBE below 1 %, and the solid red line represents the target CO₂ purity of 90 %. The total number of 103 cycles were required to reach CSS, where CO₂ recovery and purity values are 90.4 % and 15.6 %, respectively.

4.2 Summary of CO₂ capture plant design

Figure 9 illustrates the process flow diagram of the proposed flue gas cleaning process downstream from the CHP. It consists of: (1) core sub-systems: SCR-deNO_x for NO_x removal, two-step dehydration for water vapour removal, and 4-step VSA for CO₂ removal; and (2) auxiliary components: fans, heat-exchangers, and pumps. Moreover, it includes CO₂ storage and transport to illustrate CCS. The latter part was not analysed in detail, as the final purpose of CO₂ utilisation was unspecified and difficult to implement within the Czech Republic infrastructure.

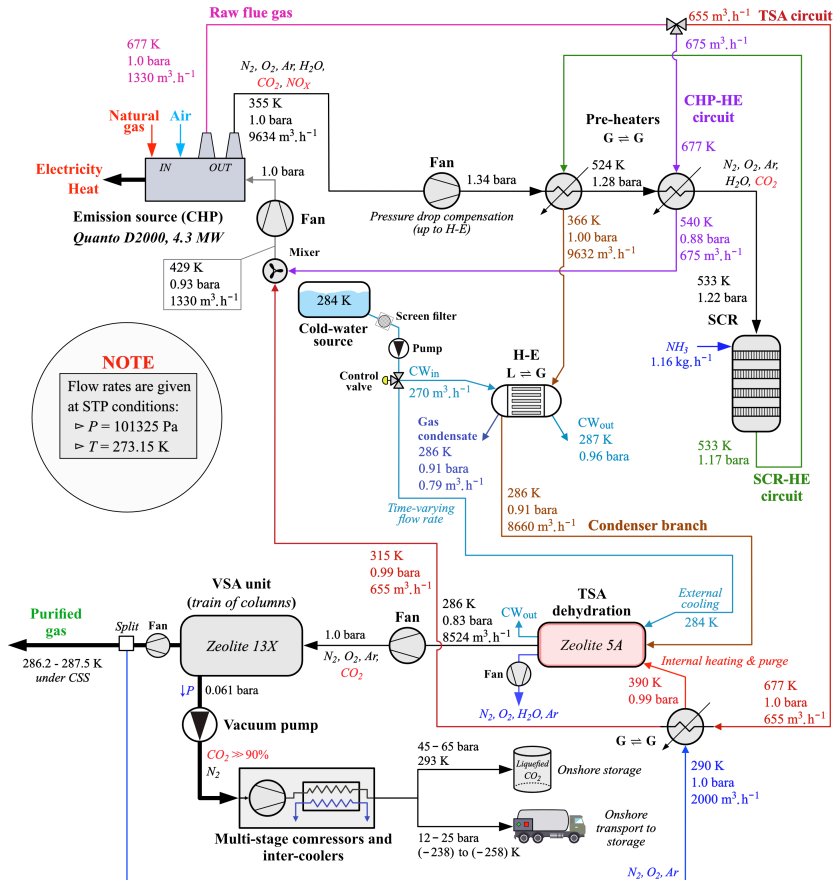


Figure 9. Process flow diagram for CHP flue gas cleaning with CO₂ capture operating in nominal mode.

4.3 CO₂ capture plant economy assessment

The direct (purchase) costs of components and sub-systems in PCC process flow diagram (Figure 9) compared the non-commercial 4-step VSA with well-established commercial technologies. Four processes compared:

- **Drying:** TSA columns, switching valves, heat-exchanger, and adsorbent.
- **NO_x removal:** SCR module, catalyst, and NH₃ supply.
- **PCC:** VSA columns, switching valves, vacuum pumps, and adsorbent.
- **Pipeline transport:** flue gas fans.

Direct costs were obtained from the existing literature [21, 22, 27-33], converted to Euros, and adjusted to 2021 using *Chemical Engineering Plant Cost Index* ratios [34]. The following assumptions were made:

- Exclusion of electricity and operating costs.
- Freely-available cooling and makeup waters and no water storage tank.
- CHP lifetime of 25 years.
- Purchase and replenishment costs of zeolites 13X and 5A were retrieved from the literature and estimated from manufacturer surveys, respectively.
- The SCR direct cost is expressed as a function of catalyst cost, based on the available literature data and our laboratory SCR cost.

The PCC was found to be the most expensive sub-system, accounting for about 70 % of the total direct costs (Figure 10a). Drying followed by accounting for almost 20 % and demonstrated the drawback of using water-sensitive adsorbents. Conversely, NO_x removal appeared to be cost-effective (9 %), as did the residual components compensating for pressure drop occurrences and covering heat demand. Individual component costs are shown in Figure 10b.

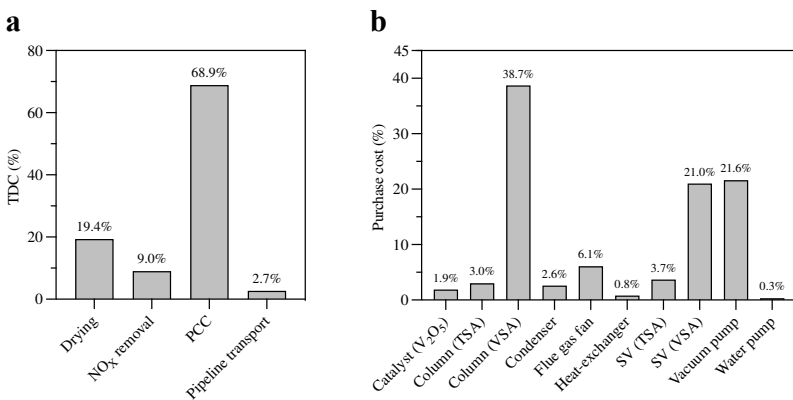


Figure 10. Results of economic assessment: **(a)** TDC of four sub-systems over 25 years of the CHP lifetime. **(b)** Basic purchase costs (without process contingency) of individual components forming the CHP PCC chain. *Note:* SV = switching valve.

5 Conclusions

This thesis dealt with the feasibility of low-temperature adsorption technology for PCC in point emission sources by simulating the continuous operation of a 4-step VSA cycle. For this purpose, a mathematical model was developed in *MATLAB*. Its first simplified version, used for predicting breakthrough curve experiments and initial process design, was subsequently modified, validated, and improved to ultimately examine the performance and economy of 4-step VSA with zeolite 13X within the context of a district-scale CHP. A ready-to-operate flue gas cleaning was proposed as a consequence of the rigorous VSA process assessment. The core sub-systems of this process were subjected to a basic economic analysis.

5.1 Accomplishment of individual goals

The main objectives, specified in Section 2.5, have been addressed as follows:

- 1. Development of a simplified non-linear dynamic mathematical model of adsorption phenomena. The reliability of the model will be verified using high-pressure breakthrough experimental data, and its robustness assessed through analysis of the numerical approach and balance equations, and application for process design.**

I successfully developed a simplified non-linear mathematical model of adsorption phenomena for predicting experimentally measured high-pressure CO₂ breakthrough experiments in a fixed-bed column. 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. Transport PDEs of mass in gas and solid phases were subjected to a sensitivity analysis, involving parameters that often need to be estimated. High-order flux limiters were also incorporated into this sensitivity analysis. Finally, the mathematical model was used in conjunction with process-design criteria and literature recommendations to establish an initial PCC process design.

- 2. Development of a complex non-linear dynamic mathematical model of 4-step VSA process, enabling simulation of various scenarios for different process parameters and configurations, and its application to experimental and theoretical studies.**

I developed a 4-step VSA model based on an experimentally validated model in the literature, incorporating PDEs of mass, enthalpy, and momentum transfers. I drew on previous experience with FVM used in a

simplified mathematical model of adsorption phenomena, which helped to implement more complex system of PDEs. The model was verified against various literature data (Appendix D) and applied for the theoretical design of a PCC adsorption process. The detailed description of model assumptions, PDEs, initial and boundary conditions, non-dimensionless scheme, including the determination of CSS and process performance indicators, is provided in Appendix D.

3. Design of adsorption PCC system integrated into an urban-scale energy system, including general economic assessment.

I approached the designing part in three steps: (1) establishing an initial VSA process design using a simplified model (Section 3.6); (2) proposing essential sub-systems and auxiliary components to define flue gas properties at the VSA inlet; and (3) using a complex mathematical model to verify and revise an initial design. This ready-to-operate process with adsorption PCC process was considered downstream from a 4.3 MW natural gas fired CHP, serving as a case study. The main sub-systems included SCR-deNO_x, two-step dehydration combining condenser and TSA with zeolite 5A, and 4-step VSA with zeolite 13X (Section 4.1). The simulated 4-step VSA achieved a CO₂ purity and recovery of 90.4 % and 15.6 %, respectively, with 15 columns arranged into five h 286 K and 1 bar (Section 4.1.4). Economic assessment was limited to an estimate of the parallel trains continuously processing 8524 m_N³.h⁻¹ of dry flue gas containing 6.4 vol% CO₂ at component purchase costs. PCC was determined to be the largest cost contributor, accounting for about 70 % of the total direct costs throughout the CHP lifetime (Section 4.3).

5.2 Future perspectives

I suggest the following points to be considered for future research:

- Verifying mathematical model through experimental measurements under various conditions.
- Extending the 4-step VSA concept by steps that transfer gas between the columns, which can improve the process performance.
- Including water vapour and trace impurities as a secondary component to CO₂ or in a ternary mixture (experimentally supported).
- Implementation of a process optimiser to determine the optimum process settings and scheduling.
- Performing process optimisation and techno-economic analysis to compare VSA with alternative PCC techniques.
- Exploring possibilities of using neural network models.

References

- [1] DeConto RM, Pollard D, Alley RB, Velicogna I, Gasson E, Gomez N, et al. The Paris Climate Agreement and future sea-level rise from Antarctica. *Nature* 2021;593(7857):83-9. <https://doi.org/10.1038/s41586-021-03427-0>
- [2] United Nations Framework Convention on Climate Change. The Paris Agreement. [cited 2023 16 January]. Available from: <https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement>.
- [3] Gür TM. Carbon Dioxide Emissions, Capture, Storage and Utilization: Review of Materials, Processes and Technologies. *Progress in Energy and Combustion Science* 2022;89. <https://doi.org/10.1016/j.pecs.2021.100965>
- [4] Nessi E, Papadopoulos AI, Seferlis P. A review of research facilities, pilot and commercial plants for solvent-based post-combustion CO₂ capture: Packed bed, phase-change and rotating processes. *International Journal of Greenhouse Gas Control* 2021;111. <https://doi.org/10.1016/j.ijggc.2021.103474>
- [5] Inc. S. Svante Inc. Our Innovative Carbon Capture Technology. [cited 2023 19 January]. Available from: <https://svanteinc.com/carbon-capture-technology/>.
- [6] Romero-García AG, Mora-Morales C, Chargoy-Amador JP, Ramírez-Corona N, Sánchez-Ramírez E, Segovia-Hernández JG. Implementing CO₂ capture process in power plants: Optimization procedure and environmental impact. *Chemical Engineering Research and Design* 2022;180:232-42. <https://doi.org/10.1016/j.cherd.2022.02.023>
- [7] Chao C, Deng Y, Dewil R, Baeyens J, Fan X. Post-combustion carbon capture. *Renewable and Sustainable Energy Reviews* 2021;138. <https://doi.org/10.1016/j.rser.2020.110490>
- [8] Hashemi SM, Sedghkerdar MH, Mahinpey N. Calcium looping carbon capture: Progress and prospects. *The Canadian Journal of Chemical Engineering* 2022;100(9):2140-71. <https://doi.org/10.1002/cjce.24480>
- [9] Ruthven DM. Principles of adsorption and adsorption processes: John Wiley & Sons; 1984.
- [10] Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, Rouquerol J, et al. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry* 2015;87(9-10):1051-69. <https://doi.org/10.1515/pac-2014-1117>
- [11] Haghpanah R, Majumder A, Nilam R, Rajendran A, Farooq S, Karimi IA, et al. Multiobjective Optimization of a Four-Step Adsorption Process for Postcombustion CO₂ Capture Via Finite Volume Simulation. *Industrial & Engineering Chemistry Research* 2013;52(11):4249-65. <https://doi.org/10.1021/ie302658y>
- [12] Hedin N, Andersson L, Bergström L, Yan J. Adsorbents for the post-combustion capture of CO₂ using rapid temperature swing or vacuum swing adsorption. *Applied Energy* 2013;104:418-33. <https://doi.org/10.1016/j.apenergy.2012.11.034>
- [13] Modak A, Jana S. Advancement in porous adsorbents for post-combustion CO₂ capture. *Microporous and Mesoporous Materials* 2019;276:107-32. <https://doi.org/10.1016/j.micromeso.2018.09.018>
- [14] Ishibashi M, Ota H, Akutsu N, Umeda S, Tajika M, Izumi J, et al. Technology for removing carbon dioxide from power plant flue gas by the physical adsorption method. *Energy Conversion and Management* 1996;37(6-8):929-33. [https://doi.org/10.1016/0196-8904\(95\)00279-0](https://doi.org/10.1016/0196-8904(95)00279-0)
- [15] Rajagopalan AK, Avila AM, Rajendran A. Do adsorbent screening metrics predict process performance? A process optimisation based study for post-combustion capture of CO₂. *International Journal of Greenhouse Gas Control* 2016;46:76-85. <https://doi.org/10.1016/j.ijggc.2015.12.033>

- [16] Shafeeyan MS, Wan Daud WMA, Shamiri A. A review of mathematical modeling of fixed-bed columns for carbon dioxide adsorption. *Chemical Engineering Research and Design* 2014;92(5):961-88. <https://doi.org/10.1016/j.cherd.2013.08.018>
- [17] Danaci D, Webley PA, Petit C. Guidelines for Techno-Economic Analysis of Adsorption Processes. *Frontiers in Chemical Engineering* 2021;2. <https://doi.org/10.3389/fceng.2020.602430>
- [18] Wilkins NS, Rajendran A, Farooq S. Dynamic column breakthrough experiments for measurement of adsorption equilibrium and kinetics. *Adsorption* 2020;27(3):397-422. <https://doi.org/10.1007/s10450-020-00269-6>
- [19] Pai KN, Prasad V, Rajendran A. Practically Achievable Process Performance Limits for Pressure-Vacuum Swing Adsorption-Based Postcombustion CO₂ Capture. *ACS Sustainable Chemistry & Engineering* 2021;9(10):3838-49. <https://doi.org/10.1021/acssuschemeng.0c08933>
- [20] Ciahotný K, Vagenknechtová A, Netušil M, Dítl P, Prokopová O. Adsorption Drying of Natural Gas under High Pressure. *Oil Gas European Magazine* 2014;40(2):91-5.
- [21] Ward A, Pini R. Efficient Bayesian Optimization of Industrial-Scale Pressure-Vacuum Swing Adsorption Processes for CO₂ Capture. *Industrial & Engineering Chemistry Research* 2022;61(36):13650-68. <https://doi.org/10.1021/acs.iecr.2c02313>
- [22] Subraveti SG, Roussanaly S, Anantharaman R, Riboldi L, Rajendran A. Techno-economic assessment of optimised vacuum swing adsorption for post-combustion CO₂ capture from steam-methane reformer flue gas. *Separation and Purification Technology* 2021;256. <https://doi.org/10.1016/j.seppur.2020.117832>
- [23] Jeníková J, Michalíková K, Hrdlička F, Hrdlička J, Pilař L, Vodička M, et al. Applicability of Secondary Denitrification Measures on a Fluidized Bed Boiler. *Acta Polytechnica* 2022;62(3):341-51. <https://doi.org/10.14311/ap.2022.62.0341>
- [24] Association GPS. *GPSA engineering data book*. 12th ed. Tulsa, Oklahoma: Gas Processors Suppliers Association; 2004.
- [25] Gandhidasan P. Dehydration of natural gas using solid desiccants. *Energy* 2001;26(9):855-68. [https://doi.org/10.1016/s0360-5442\(01\)00034-2](https://doi.org/10.1016/s0360-5442(01)00034-2)
- [26] Kumar S. *Gas Production Engineering*. Houston: Gulf Publishing Company, Book Division; 1987.
- [27] Zhang G, Yan H, Li T, Zhu Y, Zhou S, Feng Y, et al. Relation analysis on emission control and economic cost of SCR system for marine diesels. *Science of The Total Environment* 2021;788. <https://doi.org/10.1016/j.scitotenv.2021.147856>
- [28] Smith R. *Process Economics. Chemical Process Design and Integration*. 2nd ed: John Wiley & Sons, Ltd; 2016. p. 19-36.
- [29] Guo-Yan Z, En W, Shan-Tung T. Techno-economic study on compact heat exchangers. *International Journal of Energy Research* 2008;32(12):1119-27. <https://doi.org/10.1002/er.1449>
- [30] Turton R, Shaeiwitz J, Bhattacharyya D, Whiting W. *Analysis, Synthesis, and Design of Chemical Processes*. 5th ed. Boston: Pearson Education, Inc.; 2018. 1520 p.
- [31] Kučera J. *Technology to remove nitrogen oxides (NO_x) from flue gases for large combustion plants*. Brno: Vysoké učení technické v Brně; 2020.
- [32] Zhang Q, Wu Y, Yuan H. Recycling strategies of spent V₂O₅-WO₃/TiO₂ catalyst: A review. *Resources, Conservation and Recycling* 2020;161. <https://doi.org/10.1016/j.resconrec.2020.104983>
- [33] Najafi H, Najafi B, Hoseinpoori P. Energy and cost optimization of a plate and fin heat exchanger using genetic algorithm. *Applied Thermal Engineering* 2011;31(10):1839-47. <https://doi.org/10.1016/j.applthermaleng.2011.02.031>
- [34] Engineering C. *Economic Indicators. Chemical Engineering*. 2022;60.

Publications of the author

- [MN1] Nedoma, M., & Netušil, M. (2021). CO₂ Separation from Flue Gases by Adsorption. *Chemical Engineering Transactions*, 88, 421-426. <https://doi.org/10.3303/CET2188070>
- [MN2] Nedoma, M., Netušil, M., & Dítl, P. (2022). Experimental Investigation and Modelling of PSA Oxygen Generator in Context of Oxy-fuel Combustion. *Chemical Engineering Transactions*, 94, 283-288. <https://doi.org/10.3303/CET2294047>
- [MN3] Nedoma, M., Staf, M., & Hrdlička, J. (2022). Experimental and simulation study of CO₂ breakthrough curves in a fixed-bed adsorption process. *Acta Polytechnica*, 62(3), 370-385. <https://doi.org/10.14311/ap.2022.62.0370>
- [MN4] Nedoma, M., Netušil, M., & Hrdlička, J. (2023). Integration of adsorption based post-combustion carbon dioxide capture for a natural gas-fired combined heat and power plant. *Fuel*, 354. <https://doi.org/10.1016/j.fuel.2023.129346>

Conference contributions

- (1) Nedoma, M., & Netušil, M. (2021). CO₂ Separation from Flue Gases by Adsorption. In *24th Conference Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction*, PRES'21 - Brno. [MN1]
- (2) Nedoma, M., Netušil, M., & Dítl, P. (2022). Experimental Investigation and Modelling of PSA Oxygen Generator in Context of Oxy-fuel Combustion. In *25th Conference Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction*, PRES'22 - Croatia. [MN2]
- (3) Nedoma, M., Azzan, H., Yio, M. H. N., Danaci, D., Pini, R., & Petit, C. (2023). The effect of adsorbent shaping on the equilibrium and kinetic CO₂ adsorption properties of ZIF-8. In *6th Annual UKPorMat Conference*, Sheffield.

Anotace

Tato disertační práce se zabývá využitím nízkoteplotní adsorpce pro post-combustion záchyt CO_2 (PCC) se zaměřením na technické a ekonomické aspekty. Cílem bylo studovat alternativu k tradičnímu procesu chemické adsorpce pomocí rozpouštědel na bázi aminů, které jsou nešetrné k životnímu prostředí, vykazují energeticky náročnou regeneraci a malou efektivitu při nízkých koncentracích CO_2 . Adsorpce je dobře zdokumentovaný proces, který je však omezen na laboratorní aplikace, což v rámci studia průmyslových aplikací vyžaduje teoretický přístup. Lokální energetické systémy produkující emise s nízkou koncentrací CO_2 byly vybrány jako potenciálně vhodná průmyslová oblast, která je často přehlížena na úkor velkých uhelných elektráren. Hlavní přínos práce spočívá ve vývoji matematického modelu v prostředí *MATLAB* s cílem predikovat experimentálně změřené průřazové křivky při zvýšeném tlaku a kontinuální provoz vacuum-swing adsorpčního cyklu (VSA) se střídavým tlakem pro návrh a ekonomickou analýzu PCC v malokapacitní kogenerační jednotce (CHP).

Modelování bylo nejprve použito pro simulaci průřazových křivek CO_2 na zeolitu 13X v adsorbéru s pevným ložem, které byly úspěšně predikovány a model validován. Následná citlivostní analýza pomohla lépe porozumět matematickému modelování, numerickým principům a míře vlivu klíčových parametrů na přesnost predikce. Zkombinování modelu s návrhovými empirickými kritérii a poznatky z literatury umožnilo počáteční návrh VSA systému pro záchyt CO_2 ze spalin 4.3 MW kogenerační jednotky na zemní plyn, která byla vybrána jako zástupce průmyslové aplikace. Model byl následně upraven do podoby umožňující simulovat kontinuální 4-krokový VSA proces za neizotermických a neizobarických podmínek, což posunulo počáteční návrh blíže k realitě. Důsledkem byl teoretický procesní návrh záchytu CO_2 v elektrárně, která je schopna získávat CO_2 s vysokou čistotou. Návrhový postup uvažoval reálné provozní podmínky a zahrnoval selektivní katalytickou redukci, dvou stupňovou dehydrataci pomocí kondenzátoru a 3-krokovou adsorpce se střídáním teploty používající zeolit 5A, 4-krokovou VSA se zeolitem 13X a sérii pomocných komponent. Nakonec byla provedena ekonomická analýza všech dílčích systémů a komponent v tomto procesu, což koncovému uživateli poskytuje cenné informace.

Annotation

This thesis investigated the application of low-temperature adsorption for CO₂ separation in post-combustion CO₂ capture (PCC) applications, focusing on both technical and economic aspects. The emphasis was placed at investigating an alternative to traditional amine-based absorption processes using solvents, which are not environmentally friendly, energy-intensive to regenerate, and inefficient at low CO₂ concentrations. Adsorption is a well-documented process that remains limited to laboratory-scale applications and requires a theoretical approach to assess industrial applications. Local energy systems with CO₂-lean emissions were selected as a potentially suitable industrial area, which is often overlooked at the expense of large-scale coal power generation. The key contribution of the thesis is the development of mathematical model in *MATLAB* to predict various breakthrough experiments at elevated pressure and continuous operation of vacuum-swing adsorption (VSA) cycle to assess the design and economics of PCC in urban-scale cogeneration and heat plant (CHP).

The modelling first focused on simulating CO₂ breakthrough curves on zeolite 13X in a fixed-bed adsorber, which were successfully predicted and model validated. The subsequent sensitivity analysis helped to understand the robustness of mathematical modelling, numerical principles, and the impact of key parameters on prediction accuracy. Furthermore, combining the model with empirical process-design criteria and literature review findings allowed for the initial proposal of a VSA system to capture CO₂ from emissions produced by a 4.3 MW natural gas-fired CHP, which was selected as a representative of an industrial application. The model was then refined to simulate a continuous 4-step VSA process under non-isothermal and non-isobaric conditions and bring the initial proposal closer to reality. As a consequence, a ready-to-operate CO₂ capture plant capable of recovering highly pure CO₂ was theoretically designed. The design procedure adhered to the real operating conditions and consisted of selective catalytic reduction, two-step dehydration combining condenser with 3-step temperature-swing adsorption using zeolite 5A, 4-step VSA using zeolite 13X, and a series of auxiliary components. Finally, an economic assessment was carried out for all sub-systems and components found in the CO₂ capture plant, providing valuable end-user insights.