

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Multi-scale analyses of cycled industrial-scale packed-bed adsorbers

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to my wife

Abstract

Separations processes account for 10%–15% of the total energy consumed in process industries worldwide. In such separation processes, it is common to use activated carbon in packed-bed adsorbers, to remove undesired substances from a process stream. This is particularly useful for the removal of harmful volatile organic compounds (VOCs) in a multitude of settings and in an ever-growing, billion-dollar industry. Much research effort has been expended in understanding and improving the use of activated carbon for VOC removal. In this context, numerical modeling has become an increasingly useful tool as computers become more powerful and faster. Most of the currently used numerical models describe laboratory-scale environments, where the circumstances regarding the state and operation of the adsorbers are well-controlled. However, very little work has been done on this topic for industrial scale, with real-world operational cycles and bed states. Since there are major differences between the industrial operation of packed-bed units and laboratory-scale controlled environments, the applicability and performance of numerical models for real-world industrial settings need to be investigated.

In this work, a one-dimensional (1D) numerical model is formulated for an industrial-size adsorber and compared with real-world, industrial temperature data from a biomass gasification plant operated in Gothenburg, Sweden. The end-goal of the model is an improved understanding of the requirements for a successful numerical model of real-world, industrial conditions. This is done to facilitate the design and optimization of packed-bed setups for industrial conditions before construction of the actual facilities, as well as to characterize and improve units that are already operational. The model is also used to study how best to simulate industrial conditions and how to use steam as a regeneration medium for temperature-swing adsorption (TSA) operation.

To improve packed-bed adsorbers, a detailed three-dimensional (3D) numerical study is also performed on the material packing structure. Here, the flow through a bed section is studied and packings with different particle shapes are compared using the Lattice Boltzmann Method (LBM).

The results show that major trends in the industrial data are captured, while some aspects of the dynamics of the real process are not well-described. This is due to the complex composition of the product gas from biomass gasification, and limitations associated with the adopted modeling for steam and water. The results also show that in order to simulate industrial cases, the cycling procedure used in industry should be incorporated into the model, so as to account for the different adsorption

mechanisms that emerge during cycling. Finally, it is shown that packing the bed with spherical (rather than cylindrical) particles reduces the pressure drop across the bed.

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Adam Jareteg
Göteborg, May 2021

List of Publications

This thesis is based on the following appended papers:

Paper I. Adam Jareteg, Dario Maggiolo, Anton Larsson, Henrik Thunman, Srdjan Sasic and Henrik Ström. *Industrial-scale benzene adsorption: assessment of a baseline one-dimensional temperature swing model against online industrial data* Ind. Eng. Chem. Res. (2020), 59: 12239–12249.

Paper II. Adam Jareteg, Dario Maggiolo, Srdjan Sasic and Henrik Ström. *Finite-volume method for industrial-scale temperature-swing adsorption simulations* Comput. Chem. Eng. (2020), 138:106852.

Paper III. Adam Jareteg, Dario Maggiolo, Henrik Thunman, Srdjan Sasic and Henrik Ström. *Investigation of steam regeneration strategies for industrial-scale temperature-swing adsorption of benzene on activated carbon* Submitted to Chemical Engineering and Processing: Process Intensification.

Paper IV. Adam Jareteg, Dario Maggiolo, Anton Larsson, Henrik Thunman, Srdjan Sasic and Henrik Ström. *Effects of bed aging on temperature signals from fixed-bed adsorbers during industrial operation* Res. Eng. (2020) 8:100156

Paper V. Adam Jareteg, Dario Maggiolo, Srdjan Sasic and Henrik Ström. *On the roles of interstitial liquid and particle shape in modulating microstructural effects in packed-bed reactors* To be submitted to a scientific journal.

Other relevant publications:

Adam Jareteg, Dario Maggiolo, Henrik Thunman, Srdjan Sasic and Henrik Ström. *The influence of particle shape on the capacity of packed beds - a numerical investigation using the Lattice Boltzmann Method*. Proceedings of the International Conference on Multiphase Flow (ICMF2019). Rio de Janeiro, Brazil, 2019.

Adam Jareteg, Dario Maggiolo, Henrik Thunman, Srdjan Sasic and Henrik Ström. *Detailed simulations of heterogeneous reactions in porous media using the Lattice Boltzmann Method*. EFMC12 – 12th European Fluid Mechanics Conference. Vienna, Austria, 2018.

Adam Jareteg, Dario Maggiolo, Henrik Thunman, Srdjan Sasic and Henrik Ström.
Finely resolved numerical simulations of reactive flow in porous media. 8th
International Energy Conference & Workshop REMOO. Venice, Italy, 2018

Adam Jareteg, Mikael Israelsson, Henrik Thunman, Srdjan Sasic and Henrik Ström.
*Packed-Bed Reactor Characterization of Steam-Regenerated Solvent Adsorbers
for Raw-Gas Cleaning.* 14th International Conference on Multiphase Flow in
Industrial Plant. Desenzano del Garda, Italy, 2017

List of Acronyms

BGK	–	Bhatnagar-Gross-Krook
DFB	–	Dual Fluidized Bed
FVM	–	Finite Volume Method
LBE	–	Lattice Boltzmann Equation
LBM	–	Lattice Boltzmann Method
LDF	–	Linear Driving Force
PSA	–	Pressure-Swing Adsorption
SNG	–	Synthetic Natural Gas
TSA	–	Temperature-Swing Adsorption
VOC	–	Volatile Organic Compound

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Part I

Introductory chapters

Chapter 1

Introduction

Separation processes represent an important technology branch within the chemical industry, accounting for 10%–15% of the energy consumption of process industries (Rossi et al. 2019). Efforts to optimize energy use in this sector are a high priority. A prevailing technology, used to separate low concentrations of undesired substances from large-scale gaseous or liquid streams, is packed-bed adsorbers (Schweiger 1996; Yang et al. 2019a). They are often applied for air and water purification (March and Rodríguez-Reinoso 2006), for solid fuel gasification (Larsson et al. 2019), and in the chemical industry (Kolade et al. 2009), where beds packed with activated carbon have been shown to remove efficiently volatile organic compounds (VOCs) in particular (Brosillon et al. 2001).

Packed-bed adsorbers utilize adsorption to remove undesired substances from a stream of either gas or liquid. The stream is passed through a container filled with a material to which the undesired substances adsorb. Adsorption is the process wherein a substance, or adsorbate, sticks to the surface of a solid state, or an adsorbent, for which activated carbon is commonly used.

The removal of VOCs from either water or gas is in increasing demand. In China alone, VOC emissions in 2015 were estimated to be around 31 million tonnes (Yang et al. 2019b) and increasing. Moreover, the negative effects of VOCs are well-documented, both on the climate (Zhang et al. 2018) and human health (Pui et al. 2019). Therefore, there is an urgent need to reduce VOC emissions. Using activated carbon for cleaning purposes is a mature, cheap, and often accessible method (Shah et al. 2013) that is used worldwide. The market for activated carbon was in 2017 reported to be around 3 billion USD (Hagemann et al. 2018), with approximately 30% of the market comprising granular activated carbon for VOCs and chlorine removal (Hagemann et al. 2018). In addition, steadily increasing demand for activated carbon is projected for the future.

With the large demand for activated carbon for VOC removal, it is no surprise that there exists a large body of research on this subject. To date, investigations in this area have covered the more-fundamental issues, such as carbon generation and

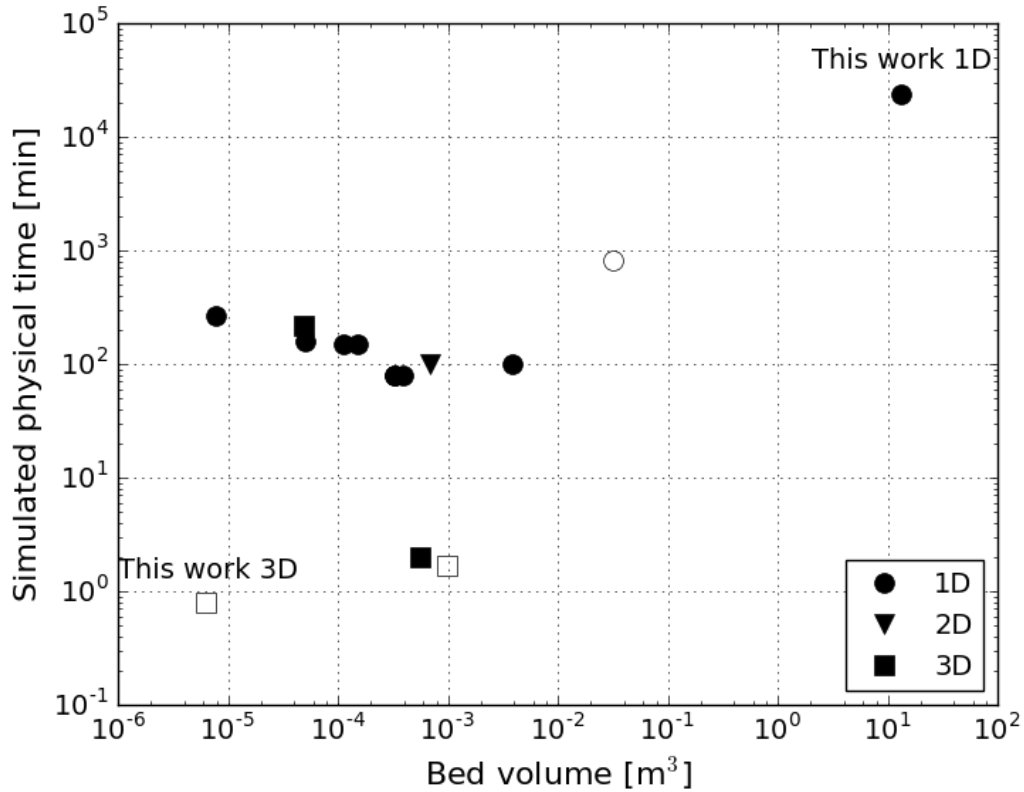


Figure 1.1: Compilation of temporal and spatial scales of this work in relation to studies in the literature on fixed-bed adsorption modeling. The empty symbols indicate simulations without any experimental data for comparison. Included are studies involving: 1D-modeling (Giraudet et al. 2009; Hwang et al. 1997; Kim et al. 2007; Delage et al. 2000; Dobre et al. 2016; Yun et al. 2000; Bonjour, Clausse, et al. 2005; Talmoudi et al. 2018); 2D-modeling:(Xiao et al. 2013); and 3D-modeling (Gautier et al. 2018; Nouh et al. 2010; Rambabu et al. 2014)

activation methods (Heidarinejad et al. 2020), isotherm determination for different carbons and substances (Kim et al. 2007; Dobre et al. 2016) and competitive adsorption (Cal et al. 1996; Schideman et al. 2006), as well as research into modeling (Joss et al. 2015; Chuang et al. 2003; Nouh et al. 2010; Webley and He 2000) and regeneration (Bonjour, Clausse, et al. 2005; Salvador et al. 2015a; Salvador et al. 2015b; Talmoudi et al. 2018). Studies involving modeling have ranged from detailed studies of specific phenomena (Das et al. 2017) to full systems and complete processes (Bonjour, Clausse, et al. 2005; Delage et al. 2000). However, when one is modeling processes, whether for optimization or design purposes, it is important to note that the research is performed mainly in laboratories in which the experiments are substantially smaller in scale and shorter in duration than real-world industrial problems. Figure 1.1 shows some of the typical scales found in the literature, where experiments are normally of the order of minutes and centimeters (Gautier et al. 2018; Das et al. 2017; Delage et al. 2000; Chuang et al. 2003), whereas the corresponding parameters in industry are in the order of days and meters (Thunman, Seemann, et al. 2018).

In industry, regeneration of the activated carbon used in the process often makes both economic and operational sense (Shah et al. 2013). To regenerate the activated carbon used in industry, thermal regeneration is the most commonly used technique (Salvador et al. 2015a). It is based on the fact that the equilibrium of the gaseous concentration and adsorbate attached to the adsorbent shifts with temperature. In this situation, a higher-temperature adsorbent cannot hold as much adsorbate as a lower-temperature adsorbent. This causes the release of adsorbate back to the gaseous phase when the temperature is raised. To accomplish this in industry, steam is usually used (Gu and Bart 2005), as it is cheap and accessible. Here, steam is used both to heat the adsorbent and to flush out the gaseous concentration of the adsorbate from the system.

Even though activated carbon is widely used and steam is an important medium for the regeneration of activated carbon, research on the effect of steaming in industrial plants is quite limited (Gu and Bart 2005), and the reports on modeling related to these processes are scarce. The same is true for simulations of complete industrial processes, where we have not found any comparisons with real-world industrial data. With modeling, there are several aspects of the industrial processes that can be studied, with process efficiency optimization being probably the one that has received the greatest attention. However, breakthrough behavior, operational control, and energy efficiency are the topics that numerical models can investigate. Naturally, questions about the difference between modeling laboratory experiments and modeling real-world industrial processes arise; more-detailed discussions on this can be found in Section 2.3.

Irrespective of the scale, models can be a useful tool when the goals are to understand and improve a process. For small scales, detailed 3D simulations of the flow and energy can be used to understand better and describe the bed transfer rates (Mahmoudi et al. 2014; Gautier et al. 2018; Das et al. 2017; Lu et al. 2019). This can be used to, for example, provide information to system models or to understand how changes in microstructures can affect macroscopic objectives. This is an important approach when considering bed optimization, since microstructural changes can be implemented relatively independently of bed operation.

For descriptions of larger-scale systems, it is common to revert from a 3D description of the problem to lower-dimensional models in which 1D models commonly feature (Delage et al. 2000; Dobre et al. 2016; Ortiz et al. 2019). 1D models provide the foundation whereupon process parameter optimizations can be performed, both prior to building the reactor beds and during live operation of the reactor (Cruz et al. 2003). However, the lack of comparisons between industrial data and modeling results causes uncertainty as to the applicability to real-world processes, in terms of both the accuracy and potential benefits of such models.

Research questions and thesis aim

This thesis aims to connect real-world industrial processes and the process modeling, discussed in the previous section. The following key research questions have been identified.

- To what extent can state-of-the-art models of steam-regenerated packed-bed adsorbers predict the behavior of a complex process for an industrial application?
- What is required of the solution methodology in order to ensure the quality of the predictions obtained through numerical simulations using such models?
- What are the possible improvements in macroscopic bed performance that can be achieved by changing the microstructure of the bed?

With these questions in focus, the overall aim of this thesis is to elucidate:

The general guidelines with respect to the choice of regeneration protocol that can be derived on the basis of numerical simulations of steam-regenerated, packed-bed adsorbers.

To study the difference between industrial data and the data obtained through typical modeling of such processes, a 1D model has been formulated for this thesis. The model results are compared with industrial data from the GoBiGas facility, which was a gasification plant in Gothenburg, Sweden that was designed to transform forest residues into bio-methane (Thunman 2018) in an effort to reduce carbon emissions by replacing fossil products with bio-based alternatives.

Both the numerical and methodological aspects of the 1D model are studied to understand better the issues specific to the modeling of cyclic, industrial-scale operation. This model is also used to study the optimization of the regeneration of packed beds using steam, with the focus on the effect of the state of the steam.

In order to identify bed improvements linked to the microstructures of the packed beds, we carried out 3D fully resolved simulations of the flows through beds that were packed with particles of different shapes. This was accomplished using the Lattice Boltzmann Method (LBM) with a multi-physics strategy, to identify those aspects of the physics in a bed cycle that are influenced by the bed microstructure and where improvements can be achieved.

This thesis highlights selected results from the appended papers, which provide insights into and clarity regarding the research questions and aim of this research program. A short discussion about the significance of the results is included, and the reader is referred to the appended papers for details of the in-depth analyses.

Chapter 2

Process

This chapter introduces the fundamental concepts that are needed to address adsorption in packed beds at industrial scale.

2.1 Adsorption and packed beds for gas cleaning

This section contains details as to how adsorption works in the context of packed-bed gas cleaning.

The concept of using packed beds of activated carbon to remove substances from a process stream is based on the fact that the targeted substance adsorbs to the activated carbon. If that is not the case, the beds cannot remove the substance. Adsorption is the phenomenon in which molecules, the adsorbate, attach or adhere to a solid surface, the adsorbent (Knaebel 2008). In the case of benzene removal, benzene molecules adhere to the surface of the activated carbon. Adsorption is a consequence of surface energy, and relies on the fact that the adsorbate is in a lower energy state when attached to the adsorbent (Knaebel 2008). This means that adsorption is an exothermic process and releases heat. The reverse process, desorption, in which molecules move from the surface back to the fluid or gas phase, is endothermic.

Adsorption is not a process that continues indefinitely. To describe the basics of the process, it is convenient to introduce the concept of adsorption sites (Marsh and Reinoso 2006). A site is a place where a molecule can attach and it is a feature of the microscopic surface properties of the adsorbent. There are sites of different sizes and strengths, such that molecules of different sizes may adhere to different sites, and there is only a finite number of these sites available (Marsh and Reinoso 2006). In addition, several different interactions occur between molecules and sites, e.g., molecules can stack upon each other (Pandit et al. 1982). The fundamental restriction of a finite number of locations at which molecules can stick is, ultimately, limiting. When there are no more sites available, the adsorbent is saturated and,

under the prevailing conditions, equilibrium is achieved.

However, whether a molecule actually adheres to a site is not only a function of the type of molecule and site, but is also a function of both the number of molecules in the surrounding fluid that are eligible for adherence and the energy of those molecules (Knaebel 2008). In macroscopic terms, this would correspond to the concentration of molecules and temperature in the fluid. A higher concentration of adsorbates in the fluid leads to more substance being adsorbed, whereas a higher temperature leads to a lower amount of adsorbed substance. The system tends towards an equilibrium point between the adsorbed concentration of substance and the concentration of substance in the gas phase.

The use of activated carbon for the removal of a substance from a stream in industrial applications is heavily dependent upon the ability to remove the adsorbed substance from the adsorbent (Salvador et al. 2015a). Otherwise, any activated carbon would have to be replaced after saturation occurred. While this might be acceptable for consumer goods, such as face masks, for industrial use it is often preferable to regenerate the adsorbent to a state where it can once again adsorb new substance. This regeneration is achieved by: (i) increasing the temperature of the bed, while simultaneously flushing it with a purge gas, often referred to as temperature-swing adsorption (TSA); or (ii) decreasing the pressure in the bed, often referred to as pressure-swing adsorption (PSA). With either TSA or PSA, the equilibrium shifts so that the adsorbed substance desorbs from the adsorbent and is released into the purge gas, which transports the substance out of the bed.

For a TSA process that uses steam, most of the energy comes from the latent heat in the phase change to water, and the steam flow itself acts as the carrier gas. However, steam can be provided to the system as saturated or superheated steam, as well as under different superheated or saturation conditions. Paper III delves deeper into these issues.

2.2 GoBiGas and the industrial data

The industrial data used in this thesis are from the Gothenburg Biomass Gasification Project (GoBiGas) gasification plant situated in Gothenburg, Sweden, which was designed to transform forest residue streams into bio-methane of a quality that was sufficiently high that it could be directly distributed through the high-pressure gas infrastructure already existing in the region. The plant produced 20 MW of product gas with a gasification capacity of 32 MW. The main purpose of the plant was to demonstrate that the technology could indeed be used, with success, to produce bio-methane on a commercial basis while simultaneously maturing the technology sufficiently to be able to build a second plant, in the 200-MW scale (Thunman, Gustavsson, et al. 2019).

In the facility, forest residue was gasified in a dual fluidized bed (DFB) gasifier. The product gas was, thereafter, run through a series of cleaning steps and finally synthesized into methane (Larsson et al. 2019). The final step in the gas cleaning chain involved the gas being run through packed-bed adsorbers. The goal was to remove the final tar components from the product gas, mainly benzene, which could not be removed by the scrubbers. Some residual larger compounds were also removed, most notably naphthalene. This was achieved in a two-step process in which three out of four available beds were used in a TSA rotation to remove the residual tars. The first bed served as a pre-adsorber that trapped scarce heavier tars and was always online.

Certain circumstances surrounding the adsorbers, either specific to biomass gasification or to this plant specifically, are pertinent to the modeling. The foremost of these is the complexity of the product gas. Paper I provides details of the gas composition. However, it is important to note that the product gas itself contains several species, in large quantities, that are known to adsorb to activated carbon. Two other important, albeit less so for the modeling choices, circumstances related to limitations as to how much pressure drop the system could handle from the adsorbers and the amount of regeneration steam that the plant could handle. The steam was limited in terms of production and in how the steam mixture could be handled after regeneration. These two aspects do not influence how the industry adsorbers are modeled, but rather what operational limitations there are and how eventual improvements must be made.

2.3 Simulation of industrial-sized packed-bed adsorbers

This section discusses the differences between industrial conditions and traditional laboratory conditions.

Industrial adsorbers show distinct differences from the more-common laboratory-scale adsorbers that need to be taken into consideration when performing numerical simulations. Noteworthy for this case is that the gas composition is far more complex, the beds are continuously cycled and, due to the larger sizes of the beds, the mass ratio of the activated carbon to the actual container is significantly different (Bonjour, Clausse, et al. 2005). With this comes also uncertainty about the state of the beds and the flow through them at any given time.

The increased complexity of the product gas in industrial units, as compared to controlled laboratory-scale experiments, has several implications. First, the product gas contains several species that, as is the case for the target substance benzene, adsorb to the activated carbon. In contrast, laboratory-scale experiments, and also their numerical simulation counterparts, deal with a single adsorbing species (Giraudet et al. 2009; Bonjour, Chalfen, et al. 2002; Kim et al. 2007). Second, complex

interactions can occur between the different species during the adsorption process, e.g., competitive adsorption (a phenomenon in which different substances that can adsorb to the same site compete for that site) and different site interactions (which can include layering, hysteresis effects, pore filling, etc.) (Kim et al. 2007).

That the beds are of industrial size and used in an industrial setting also has impacts. First, the beds will never be in a fresh state, instead being always be in some form of inter-cyclic steady state condition. This imposes requirements on the numerical simulations to be able to handle real-world cycling times. Thus, the simulations must be able to handle simulated physical times in the order of days, and possibly weeks. Second, the physical sizes of the beds will shift the main thermal mass more towards the activated carbon itself. In laboratory-scale, the container itself may, in several cases, have significantly more thermal mass than the carbon. Incidentally, the shift of the main thermal mass towards the carbon simplifies the numerical simulations, since the inclusion of support systems, such as the containing geometry, loses significance (Bonjour, Clausse, et al. 2005).

Chapter 3

Methodology

3.1 Governing equations

The state of a packed bed is determined by the mass, the momentum, and the energy flows through it. To determine the state for any given time and place, the governing equations for these flows have to be solved. Depending on the type of information that is sought, the method used to solve the equations will differ greatly. For this thesis, two different approaches have been adopted. One approach is to solve the balances through the entire beds by reducing the equations to a single spatial dimension and carefully selecting the terms that are included. The other approach is to solve the flow only through a small part of a bed, so as to identify possibilities with the internal bed structure itself. For this, all dimensions are solved and all terms are present to reduce the number of assumptions and limitations associated with the involved physics.

The equation that is always present in any of the simulations is the conservation of mass,

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_j}{\partial x_j} = S_m, \quad (3.1)$$

where $\rho = \rho(\mathbf{x}, t)$ is the density, $u_j = u_j(\mathbf{x}, t)$, $j = x, y, z$ is the velocity in the x-, y- and z-direction, respectively, and S_m represents any mass source terms present in the domain, e.g., adsorption. The flow of momentum is described by the following equations,

$$\frac{\partial \rho u_i}{\partial t} + \frac{\partial \rho u_i u_j}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j} \left(\mu \frac{\partial u_i}{\partial x_j} \right) + S_u \quad (3.2)$$

where $p = p(\mathbf{x}, t)$ is pressure, μ is viscosity, and S_u is any momentum source term, where gravity is a common term. Besides the mass continuity and momentum flow, solving for individual species in the system requires a separate equation for each species. The transport of such a species is determined by the mass flow, as,

$$\frac{\partial \rho \omega}{\partial t} + \frac{\partial \rho \omega u_j}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D_m \frac{\partial \rho \omega}{\partial x_j} \right) + S_c, \quad (3.3)$$

where $\omega = \omega(\mathbf{x}, t)$ is the mass fraction of the transported species, D_m is molecular diffusivity and S_c represents any mass sources, such as adsorption. The final equation details the transport of energy,

$$\frac{\partial \rho C_p T}{\partial t} + \frac{\partial \rho C_p T u_j}{\partial x_j} = \frac{\partial}{\partial x_j} \left(K \frac{\partial T}{\partial x_j} \right) + S_T \quad (3.4)$$

where C_p is the specific heat, $T = T(\mathbf{x}, t)$ is the temperature, K is the heat conductivity, and S_T is any energy sources, e.g., heat of adsorption.

3.2 System level model

To model the entire bed system, a 1D model is an excellent tool for numerical studies. It provides opportunities to simulate large-scale units for extended durations. However, due to the complex multi-scale and multi-physics nature of the packed bed system, the modeling choices naturally entail assumptions as to what are and are not the important phenomena to include. The choices made here are based on the most common model choices listed in the literature. The choices made when simulating and comparing to the GoBiGas setup also align with the design considerations for the GoBiGas plant.

First, there are some general assumptions regarding the flow and the bed. More specifically, any radial or tangential variations are assumed to be small compared to the main direction, which means that the transport is only solved in the axial direction. As the bed is considered to be homogeneously packed, it can be characterized by a single scalar porosity. This corresponds well with the situation of industrial beds, where care is also taken to ensure that the flow through the bed is as homogeneous as possible in the two off-directions. Inert particles are spread below and above the activated carbon, to disperse any flow heterogeneity, and the activated carbon is itself raked to level.

Assumptions are also made with regards to the active species in the model, whereby the major ones are: a restriction linked to the gas composition, the species do not interact (e.g., no competitive adsorption), there are no homogeneous reactions, and there is no diffusive gas transport. The restriction related to the modeled gas composition is a modeling choice that is limited to include only benzene. The reason for this is that benzene is the substance that is targeted for removal and the substance for which the beds are designed. The exclusion of the diffusive term is due to a normally limited axial dispersion, which is here even more restricted due to the dominant source terms in the equations, representing the adsorption/desorption phenomena. These phenomena completely dominate the dynamics of the bed, such that the substance will be transported by the gas to an adsorption front and thereafter

adsorbed abruptly, thereby effectively limiting the effect of diffusion (see Paper III).

Finally, assumptions are made regarding the steam and condensed water. It is assumed that steam does not adsorb to the activated carbon but only condenses. The condensed water will remain condensed at the same location or be evaporated once again; it will, however, not flow anywhere. As with the previously described assumptions, these are made despite the knowledge that there are some linked phenomena that likely have significance. For instance, it is known that steam will adsorb to the carbon and that it might affect the isotherm for the other species (Cal et al. 1996). However, it makes little sense to include competition between steam and benzene while disregarding both the full gas complexity and the competition between all of these gas components. It is, for GoBiGas, also known that some of the condensed water flows out of the bed. However, calculations of the theoretical water content of the carbon, if all the water is absorbed (i.e., the process of liquid water penetrating into the carbon particles) by the carbon, reveal that the carbon is more than capable of simply absorbing all of the condensed water. This makes predictions of the actual level of liquid water drainage troublesome, and the assumption that no water drains out of the bed becomes a more conservative option.

Taking the assumptions and model choices into consideration, the governing equations (3.1) - (3.4) are reduced significantly in complexity and the source terms take the relevant forms. Thus, the gas phase total continuity (Eq. (3.1)) is reduced to,

$$\frac{\partial \varepsilon \rho_g}{\partial t} + \frac{\partial \rho_g u}{\partial x} = \sum \frac{\partial \rho_b q_x}{\partial t} \quad (3.5)$$

where, ε is the bed porosity (-), ρ_g is the gas phase density (kg/m^3), u is the linear gas velocity (m/s), ρ_b is the bed density (kg/m^3) and q_x is the mass fraction of a species x in the bed (-).

The mass transport in the gas phase for species x , or equation (3.3), is simplified to,

$$\frac{\partial \varepsilon \rho_g \omega_x}{\partial t} + \frac{\partial}{\partial x} (\rho_g u \omega_x) = \frac{\partial}{\partial t} (\rho_b q_x) \quad (3.6)$$

where ω_x is the mass fraction of species x in gas phase (-) and the source term on the right-hand side represents transport to, or from, the bed.

The mass transport from the fluid to the solid phase is described by the conventional linear driving force (LDF) model (Bonjour, Clausse, et al. 2005; Ramalingam et al. 2012; Kim et al. 2007; Yun et al. 2000), the equation for the solid phase mass is then,

$$\frac{\partial}{\partial t} (\rho_b q_x) = a k (c_{x,eq} - \rho_g \omega_x) \quad (3.7)$$

where a is the specific surface area of the carbon (m^2/m^3), k is the mass transfer rate (m/s), and $c_{x,eq}$ is the equilibrium concentration (kg/m^3).

When reduced, the energy equation (Eq. (3.4)) becomes for the gas phase,

$$\frac{\partial}{\partial t} (\varepsilon \rho_g C_{p,g} T_g) + \frac{\partial}{\partial x} (\rho_g u C_{p,g} T_g) = ah (T_b - T_g) \quad (3.8)$$

while the solid phase energy balance becomes,

$$\frac{\partial}{\partial t} (\rho_b C_{p,b} T_b) = -ah (T_b - T_g) + \sum \left(\Delta H_x \frac{\partial}{\partial t} (\rho_b q_x) \right) \quad (3.9)$$

where $C_{p,g}$ and $C_{p,b}$ are the specific heat capacities for the gas mixture and solid phase respectively (J/kg,K). T_g and T_b are the gas and bed temperatures respectively (K), and h is convective heat transfer coefficient (W/m,K). ΔH_x is the heat release associated with the mass transport to/from the bed (J/kg).

The formulated equations (Eqs. (3.5) - (3.9)) are solved with the Finite Volume Method (FVM), which discretizes the system into a finite number of computational cells. Each partial differential equation turns into a system of algebraic equations, one for each cell, which are then assembled into a matrix formulation. In this thesis, all the equations are assembled into the same matrix, often referred to as a coupled system, and simultaneously solved. One important aspect of this process is the method used for transforming a mathematical equation into a numerical one, termed discretization. In particular, the advection term requires special consideration, as the problem is dominated by advective transport and adsorption is a strongly frontal phenomenon. The species move through the bed with a sharp front and adsorption occurs over a relatively narrow width. Classical, lower-order advection discretizations in the FVM are known to be problematic in such systems, as the number of cells required to describe a sharp interface is significantly higher compared to modern higher-order front-tracking schemes (Van Leer 1974).

3.3 Microstructure model

To investigate the properties of the different microstructures based on particle shape, the flow through that bed was fully resolved using the Lattice Boltzmann Method (LBM). This method is highly suitable for solving slow flows through complex structures (Succi 2001), such as packed beds, due to the relative ease of mesh generation, the stability of solving the equations on that mesh, and the inherent parallelizability. The LBM in its purest form, used also in this thesis, is solved on a uniform hexahedral mesh where the required mesh description relates to size and binary information on which cells are solid and which are fluid.

The LBM solves the transport equations (Eq. (3.1) - (3.4)) just as the FVM would. However, rather than solving them directly, as in the FVM approach, the LBM instead discretizes and solves the Boltzmann equation (Liu et al. 2016),

$$(\partial_t + \mathbf{v} \cdot \nabla) f = \Omega[f] \quad (3.10)$$

The equation describes the evolution of the single-particle distribution function $f(\mathbf{x}, \mathbf{v}, t)$. The left-hand side describes the free advection of f , while on the right-hand side, Ω describes pairwise particle collisions. This operator is commonly simplified to the linear Bhatnagar-Gross-Krook (BGK) form of,

$$\Omega[f] = -\frac{1}{\tau_\nu} (f - f^{eq}) \quad (3.11)$$

where f^{eq} is the Maxwell-Boltzmann equilibrium distribution and τ_ν is a characteristic relaxation time. This equation obeys the governing transport equations in the limits of small Mach and Knudsen numbers. The Boltzmann equation (3.10) is discretized in space and time to obtain the Lattice Boltzmann Equation (LBE),

$$f_i(\mathbf{x} + \mathbf{c}_i \Delta t, t + \Delta t) - f_i(\mathbf{x}, t) = -\frac{1}{\tau_\nu} (f_i(\mathbf{x}, t) - f_i^{eq}(\mathbf{x}, t)) \quad (3.12)$$

where f_i is the discrete particle distribution for the i -th discrete velocity, $\mathbf{c}_i$, at a lattice node. The exact definition of how many f_i exist at each node is sometimes referred to as the 'stencil'; in this thesis, the popular D3Q19 stencil is used. The latter is a 3-dimensional stencil with 19 possible velocities. This equation is, similar to the FVM equations, solved at specific nodes in a connected node mesh.

The macroscopic properties can be calculated from the particle distributions as,

$$\rho(\mathbf{x}, t) = \sum_i f_i(\mathbf{x}, t) \quad (3.13)$$

$$\rho(\mathbf{x}, t) \mathbf{u}(\mathbf{x}, t) = \sum_i \mathbf{c}_i f_i(\mathbf{x}, t) \quad (3.14)$$

Apart from the bare-bone LBM described above, a few models are used in the work to simulate pressure drop, gravity, multiphase flow and passive scalar transport. A pressure drop and gravity are modeled through an additional source term on the right-hand side of equation (3.12) according to Guo et al. (2002). The multiphase setup is based on the Shan-Chen model (Shan and Chen 1993), with a complete description given by Maggiolo et al. (2019). The passive scalar is modeled through an additional particle distribution g_i , which is solved using the same equation as for f_i (Eq. (3.12)) where the scalar is evaluated as,

$$c(\mathbf{x}, t) = \sum_i g_i(\mathbf{x}, t) \quad (3.15)$$

Chapter 4

Case Setup

The results presented in this thesis are based upon several different run cases. This section introduces the basic setups of the cases. For detailed descriptions of the parameters used, the reader is referred to the corresponding papers.

4.1 Case setup for the industrial comparison

For this thesis, a large industrial dataset was compiled from a first-of-its-kind wood-based bio-methane production plant (comprising a 32-MW th DFB gasifier (150 dry tonnes of biomass/day), complemented by synthetic natural gas (SNG) synthesis, producing up to 20 MW of bio-methane and located in Gothenburg, Sweden (Thunman, Seemann, et al. 2018)). This plant has in total four adsorber beds for the removal of mainly benzene, but also naphthalene, toluene, xylene, hydrochloric acid, ammonia and hydrogen sulfide.

As mentioned in the *Introduction*, a packed-bed adsorber is a large container that holds the active material and allows the stream to pass through it. Figure 4.1 shows a representation of a bed at the GoBiGas facility, and the main characteristics of the bed are summarized in Table 4.1. Inert particles were used to homogenize the flow as much as possible before entering the bed, and each bed in the plant had four temperature sensors mounted inside the bed to monitor its current state. The sensors were positioned at distances of 0.40, 0.80, 1.15 and 1.55 m from the bottom of the bed, which corresponded to 20%, 40%, 60% and 80% of the bed height, respectively. Since adsorption is an exothermic process and desorption is an endothermic one, the temperature of the bed increases in the region where adsorption takes place and decreases where desorption occurs. Thus, the temperature data measured inside the beds make it possible to acquire continuous on-line information about the state of the bed and how that state changes. However, it is not a trivial task to relate the temperature information definitively to the internal immeasurable state of the bed. A major ambition of this work is to assess the extent to which the temperature information can be used together with 1D numerical simulations to facilitate the

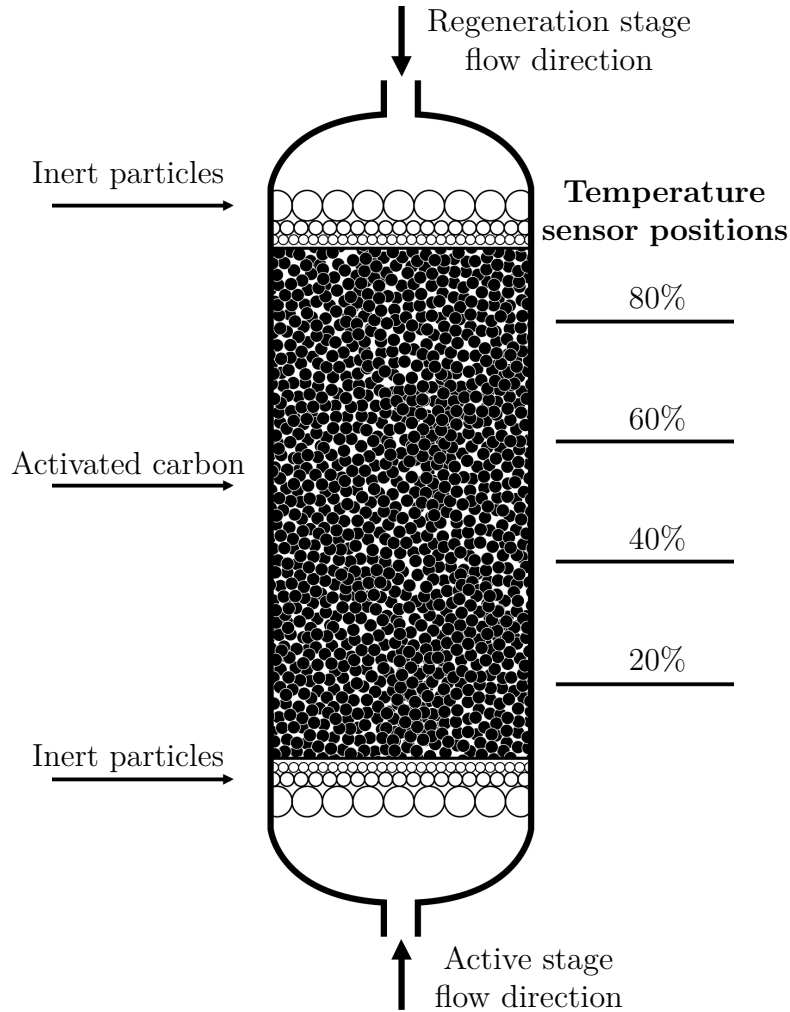


Figure 4.1: Illustration of a packed-bed at the GoBiGas facility.

design and operation of adsorber beds such as these.

For the industrial comparison, real industrial conditions were used as much as possible in the simulation. The boundary conditions were taken from best-knowledge operation, and the same numbers / types of operational cycles were followed. This included three subsequent stages that were continuously cycled. These are represented in Figure 4.2 and include an active stage, a regeneration stage, and a final cooling stage. During the active stage, the bed acted as a benzene separator, removing benzene from the product gas and storing it, through adsorption, in the bed. The flow entered the bed from below and streamed upwards through the bed. The subsequent stage regenerated the bed after it was filled with benzene. During this stage, steam flowed from the top downwards, i.e., in a counter-current to the gas flow. The last stage was an intermediate stage, designed to revert the temperature of the newly generated bed to the active stage state. This was done by directing a part of the product gas flow from the bottom upwards through the newly generated bed before the product gas flow entered the bed that was at that time in the active stage. Details of the

Table 4.1: Bed size and carbon amount

Bed radius, r	1.375 m
Bed height, L	1.9425 m
Total amount of carbon, m_c	4500 kg
Bed density, ρ_b	390 kg/m^3
Bed porosity, ε	0.5
Carbon type	WS-490, Chemivron
Characteristic particle size	6 mm
Specific surface area, a	500 m^2/m^3

conditions used are given in Paper I.

4.2 Case setup for other numerical studies with the 1D model

With the existing models, a study on how the steam state affects regeneration performance and a study on the numerical aspects of the cyclical nature of the problem are presented. Since no comparisons to industrial data were made, the operational scheme was altered to allow for a simpler analysis of the data. This included a two-stage cycle (Figure 4.3), established through alternation of the active and regeneration stages. While the industrial comparison used boundary conditions that replicated the industrial conditions, the results presented from the study of the steam state instead involved boundary conditions that connected the regeneration stage to a fixed energy amount and energy flow rate while running a variable active stage that proceeded until breakthrough. The total mass-flow rate was also fixed to the same value as for the studied cases, and the geometry was the same as that for the industrial study (Table 4.1). For the numerical study, both the flow rate and the time spent in each stage were locked for all the cases. In addition, the geometry was much simpler, with a unit length and radii but with the same carbon properties as the other studies.

4.3 Case setup for the microstructure studies

The study of the microporous bed properties and possible optimization routes involves two different packed beds. One was packed with cylinders (a simplified pellet shape), much like the ones used in GoBiGas, while the other was packed with perfect spheres. These particles were chosen because one shape is common in industry (cylinders) while the other is common in the literature (spheres). To generate the virtual bed samples, the particles were randomly packed, using a physics engine, by dropping them from a distance and letting them fall into a large container (Figure 4.4a). From there, a smaller sample size was extracted (Figures 4.4b, 4.4c) from the middle of

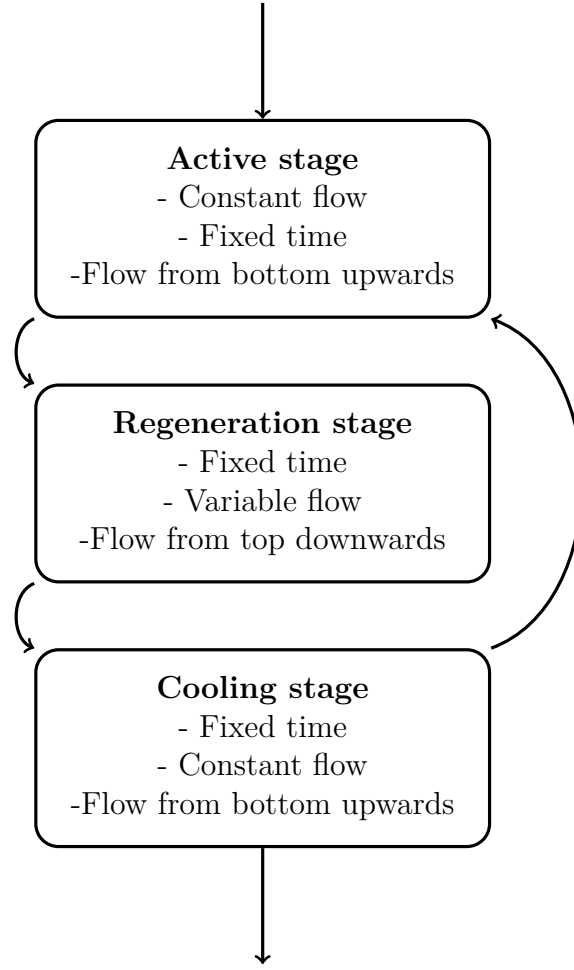


Figure 4.2: Operational scheme for the GoBiGas plant

the virtually packed bed. The resulting geometries are depicted in Figure 4.5. The samples were then voxelized into the required binary matrix for the LBM simulation.

Two different simulation setups of these beds are presented. One has a single-phase gas flow through the beds, and one has a two-phase setup. In the two-phase simulation, a liquid is introduced and it is held within the structure by surface tension. This is done to study the effects on the flow of the condensate from regeneration. A gas flow, much like that in the first case, is then run through the bed and the effects of the interstitial liquid are studied.

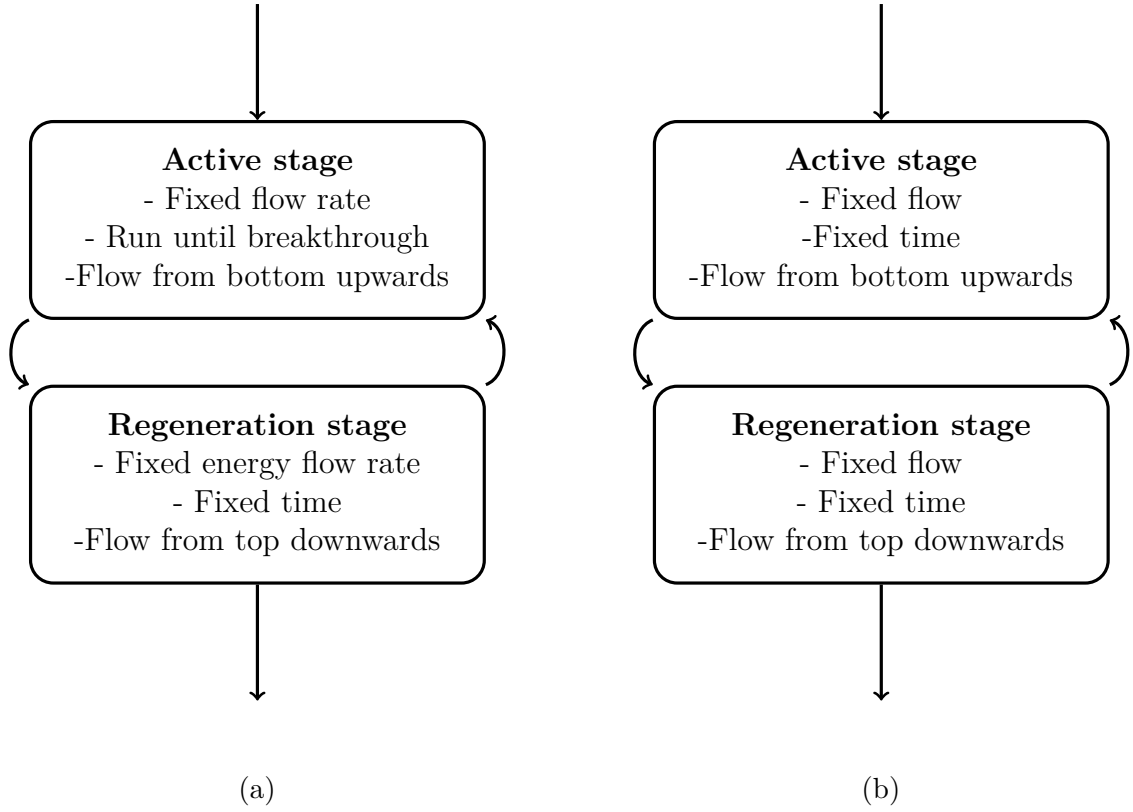


Figure 4.3: Operational schemes for a) the regeneration study; b) the numerical study.

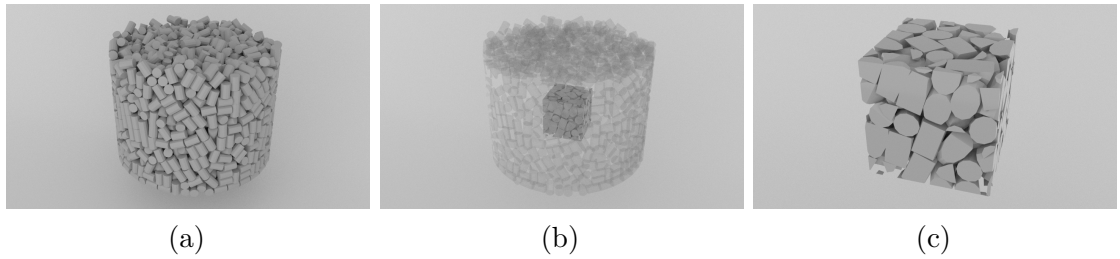


Figure 4.4: Illustration of the bed generation procedure. a) A container packed with particles; b) a square box located far away from the container walls is chosen as the representative geometry; and c) the resulting cut-out of the bed to be used in the subsequent simulations.

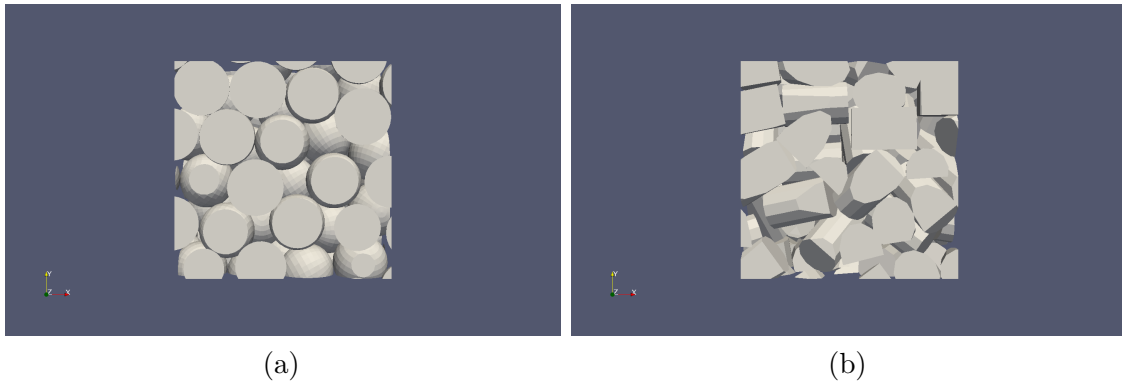


Figure 4.5: Illustration of the two computational geometries for the microstructure studies: a) packed bed of spheres; b) packed bed of cylinders.

Chapter 5

Results and Discussion

This collated results from the appended papers are highlighted here in terms of the most important and noteworthy conclusions.

5.1 Industrial data comparison with 1D model

Figure 5.1 shows the comparison of the industrial application and the numerical simulation. The upper panel in the figure shows the temperature signals for a given position in the bed, for both the simulation and industrial data, while the lower panel shows the in-bed difference between the top-most and the bottom-most positions. A direct comparison of the temperature data (upper figure) reveals that while major trends are well-represented, the dynamics of the temperature are still missing from the modeling. There is a major difference during the cooling stage, when the industrial data show significantly higher temperatures. Furthermore, in a section of the regeneration stage, the industrial bed data indicate a lower temperature than in the simulation. In addition to these two major differences, there is a discrepancy in the cooling rate between the beds. The industrial data indicate slower cooling during the cooling stage and noticeable cooling during the active stage, while the simulation indicates that cooling occurs rapidly during the cooling stage and is not seen during active operation.

For a better understanding of what happens in the bed according to the two different datasets, the lower panel in Figure 5.1 offers a useful visualization. Comparing the two most-extreme points in the bed gives a different perspective as to what happens within the bed. The active region is, again, rather well-captured. During the regeneration step, there is a greater change in the temperature intra-bed for the simulation during the initial bed warming. The industrial data are not as frontal, with the data being more similar between the bed positions. During the initial cooling period, there is a substantial peak in temperature, as seen in the upper figure, which indicates that the bed is cooler at the bottom than at the top for a period of time. This is not captured in the model, which only shows a steadily warmer bottom bed position. In other words, in the simulation, cooling occurs between the

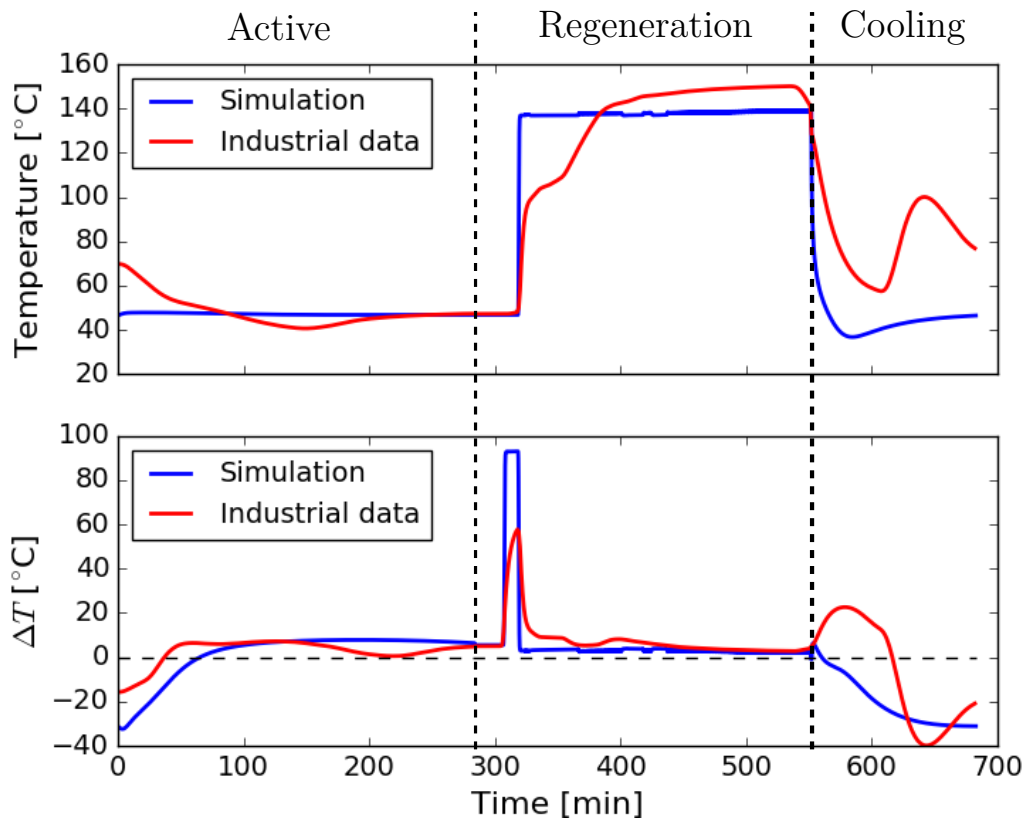


Figure 5.1: Upper panel: Temperature signal for a full cycle for both the industrial data and simulation cases. Lower panel: Differences noted between the top-most and bottom-most temperature bed sensors, using data from both the simulation and industrial cases.

bed positions, whereas in reality the bed is being warmed.

The lack of dynamics in the simulation data is somewhat expected, given that the model represents a substantial reduction in terms of the process physics compared to the full complexity of the industrial process. There are two main things in the industrial data that the model does not capture. The first one is the major differences seen both during the regeneration stage and in the subsequent cooling stage with regards to the strong interactions from additional species. In the regeneration stage, this takes the form of a heat sink that is present during desorption and that delays heating to the steam temperature. During the cooling stage, these additional substances instead have the opposite effect, in that they heat the bed during a severe adsorption event in the newly regenerated bed. Compared to the heat demand and heat release from benzene (which are included in the simulation data), the additional species contribute significantly to the dynamics within the bed (and much more so than does benzene, which is the targeted substance for removal). The second difference is the bed cooling rate and amount. In terms of cooling, the simulation is

substantially quicker. This is due to the steam/water modeling, where steam only condenses and does not adsorb such that all the water stays in the bed, as per the assumptions.

The best way to overcome the aforementioned shortcomings is not obvious. Inclusion of additional species in the simulation could, of course, produce a stronger thermal response. However, there are several problems that need to be addressed first. Given the violent reaction, and the fact that the bed still functions well as a benzene filter, there is likely to exist a substance that fills the bed rapidly during the cooling stage and thereafter either does not stop the benzene from adsorbing to the bed or it is replaced by benzene at the surface. In other words, competitive adsorption must be considered, and since the gas contains a multitude of species that are known to adsorb to activated carbon, sorting the process out will be demanding and involve experiments with specific compositions of compounds. The potential advantages of completing such a task will be diminished with every tailored experiment and model required, as the strengths of 1D system models reside in their *a priori* design capabilities, particularly at times in the design process when everything is unknown and the design space is being examined.

The issue with the steam/water modeling involves a number of aspects, with some aspects being easier to handle in the modeling than others. The physics not included in the model encompasses mainly steam/water adsorption to the carbon, the variability of the surface area of the liquid water, liquid water transport in the bed, and intra-particle processes, such as water absorption by the particles. The addition of water adsorption requires resolution of the competitive adsorption and the balance between adsorption and condensation. Water is reported to influence the adsorption of VOCs (Cal et al. 1996). However, given the complexity of the gas composition, a possible strategy is to disregard any competition and simply include it as an independent adsorbing species. This would act to slow the cooling rates without requiring too much additional experimental work. Introducing variable surface coverage of liquid water, for the rate calculations, would also serve this purpose. This should be quite straightforward to implement, providing that accurate and reliable correlations can be determined. Addressing the liquid water transport through the bed is a much more complicated task that poses complex multi-physics questions. The transport of liquid water will affect the energy balance in the bed mainly in two ways. First, water transported through the bed will bring heat from the condensation front to cooler areas. Second, water that exits the bed will not partake in any re-evaporation, thereby limiting cooling effects. While the first point concerns where energy is distributed in the intra-bed energy balance, the second point is more important because it shifts the energy balance for the entire bed. When water leaves the system by flowing out, rather than evaporating and being transported by the gaseous phase, the entire latent heat requirement for drying that volume of water vanishes. Predictions as to when and how water flows out of the bed during regeneration are, therefore, a crucial issues to resolve.

5.2 Numerical performance studies with the 1D model

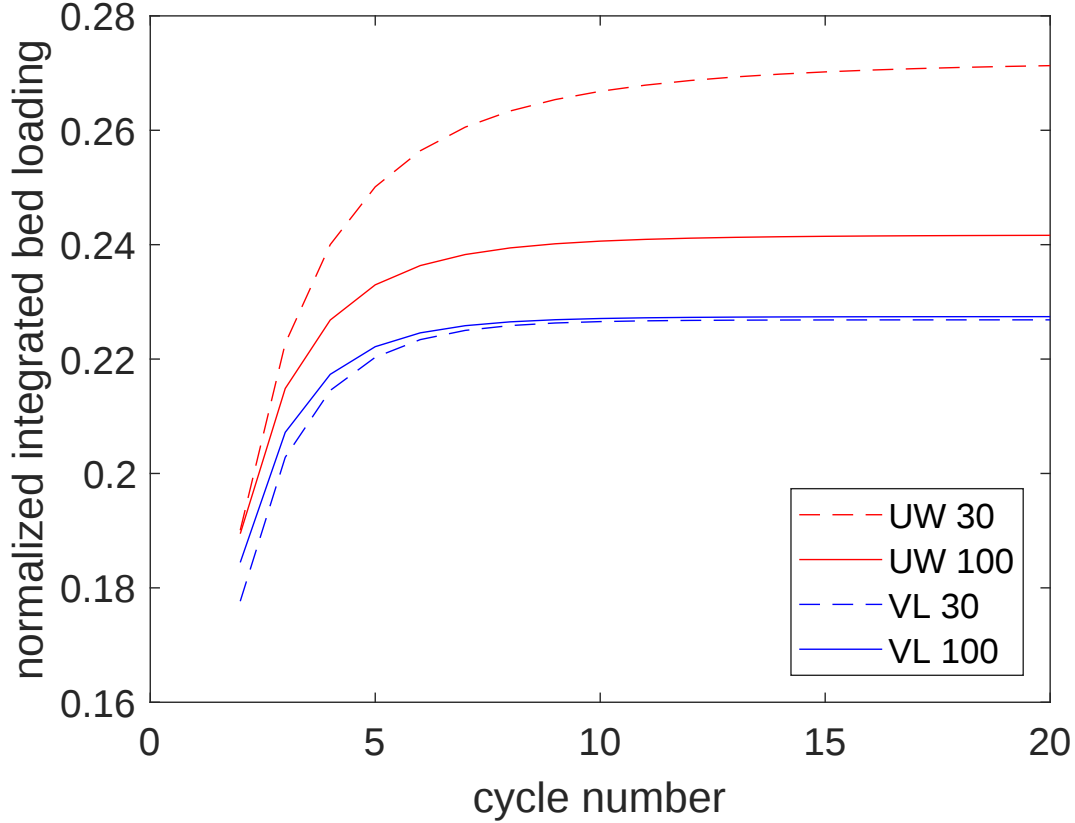


Figure 5.2: Total load depending on cycle. (UW = first-order upwind scheme, VL = van Leer scheme, 30/100 = number of computational cells)

Figure 5.2 shows the amount of adsorbed substance in the bed for two different discretization schemes, a first-order upwind (UW) scheme and a third-order van Leer (VL) scheme, and at two different cell counts (30 and 100) as a function of the cycle number. All the cases require more than 5 cycles for the bed load to stabilize, and the low-resolution upwind scheme is not stable even at 20 cycles. In contrast to the van Leer scheme, the upwind scheme does not converge on the same final bed load when the resolution changes.

In Figure 5.2, it is evident that it is not sufficient to use lower-order (upwind) schemes, at least not with the given cell counts. The higher-order scheme is required to capture accurately the adsorption behavior, and at least the species advection needs to be discretized with front-capturing schemes.

Figure 5.2 shows the importance of cycling the beds so as to capture accurately the load in the bed. Figure 5.3a shows an example of the rate of adsorption in the

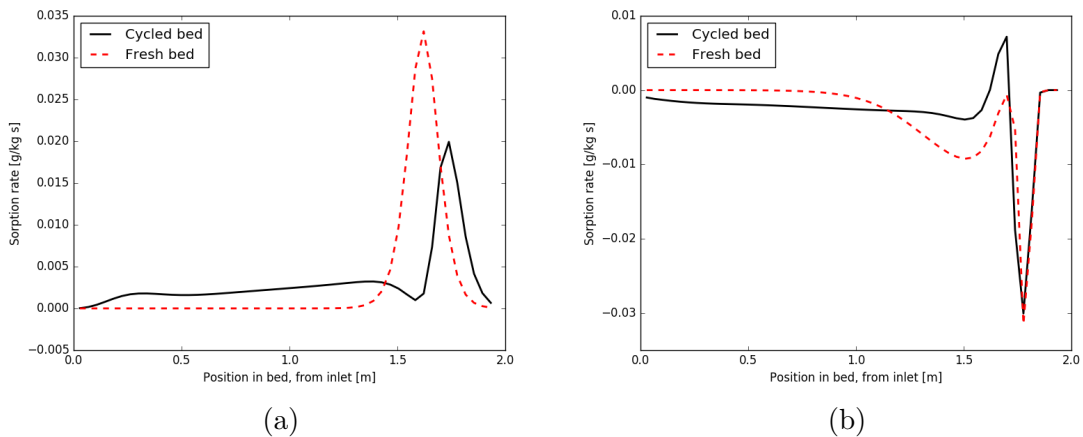


Figure 5.3: Sorption rates in the middle of a) the active stage, or b) the regeneration stage. Positive rates indicate adsorption and negative rates indicate desorption.

bed from Paper III, and compares a fresh bed with one that has undergone cycling. The data are for the middle of the active stage and show that cycling produces a significantly more complex loading mechanism. It is clear that the majority of the regenerated bed section is active during the active stage, and that there is a local minimum rate close to the outlet. Similar conclusions can be drawn from the rate of desorption during regeneration of the bed (Figure 5.3b). The cycled bed once again exhibits activity in a larger part of the bed.

The observed spread of activity in the bed is an important phenomenon, as it gives indications as to where heat will be released and consumed in the bed. Localized heat release can cause too-high temperatures, which can be problematic for certain types of processes. However, from the modeling perspective, it is more important that artefacts from the previous stage persist for long periods in the bed. For example, the local minimum during adsorption in Figure 5.3a is a direct effect of the regeneration. That the influence of the previous stage continues long into the new stage highlights the importance of correct cycling.

Table 5.1: Amount of steam required for desorbing a fixed amount of benzene from the bed.

Case	Steam required [kg]	Steam consumption vs. <i>Baseline</i>	Energy required vs. <i>Baseline</i>
Baseline, atmospheric conditions	2460	—	—
Superheated steam (+60°C)	2424	-1.5%	+3.0%
Saturated steam (+60°C)	2167	-11.9%	-18.7%

As mentioned previously, one of the benefits of numerical simulations is that they allow design-space investigations. Table 5.1 shows the energy and mass required for regeneration using steam in three different states. Higher-temperature steam

decreases the required mass, whereas for superheated steam the energy requirement increases. For saturated steam, both the required mass and energy decrease.

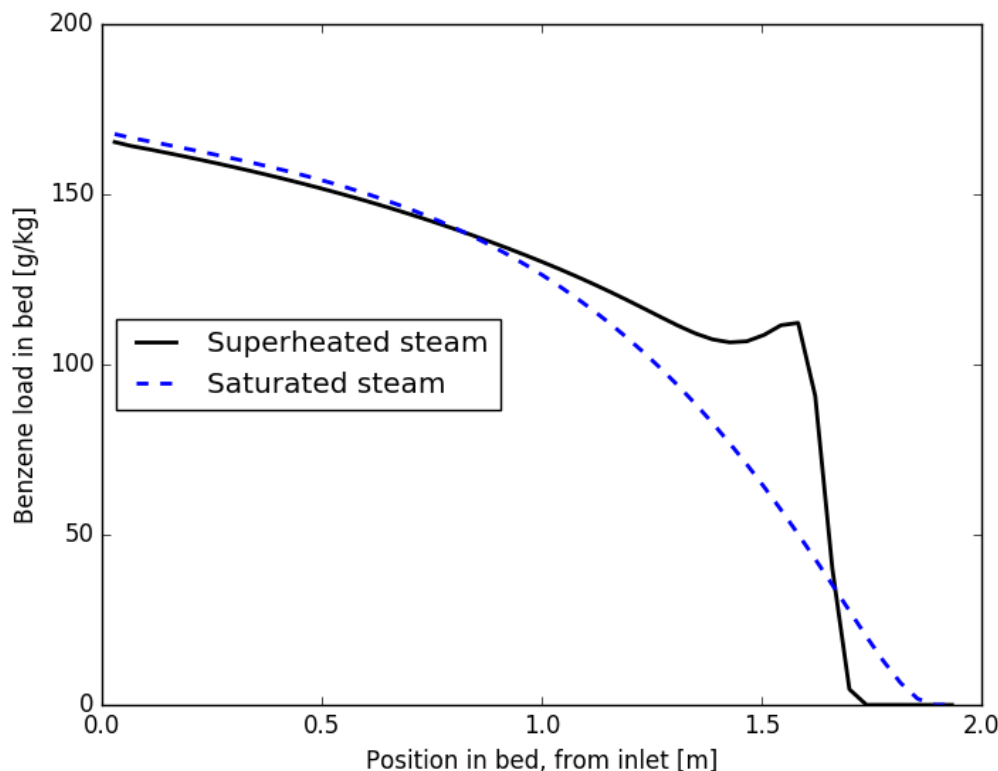


Figure 5.4: Benzene loads in bed after regeneration with superheated or saturated steam.

Figure 5.4 shows the amount of benzene that remains in the bed after regeneration. Most noteworthy is that superheated steam produces a region in the bed that is more fully regenerated and that has a much sharper front. The profile also reflects that benzene desorbs from the entire bed during regeneration, as evident from the sloped profile through the entire bed.

As mentioned above, superheated steam is not as efficient as saturated steam when it comes to energy and mass consumption. This is because superheated steam can, and will, dry itself, whereas saturated cannot do this. However, this also comes with some benefits regarding the completely regenerated region of the bed loading profile. This region appears because the temperature can increase beyond the saturation temperature after any condensed water is evaporated back to the gas. However, as shown in Figure 5.5, the increased desorption rate that comes with increased temperature is offset when the gas encounters regions that contain liquid water. In that scenario, the temperature is once again reduced to the saturation condition. This causes re-adsorption to occur, such that preciously desorbed benzene is transported

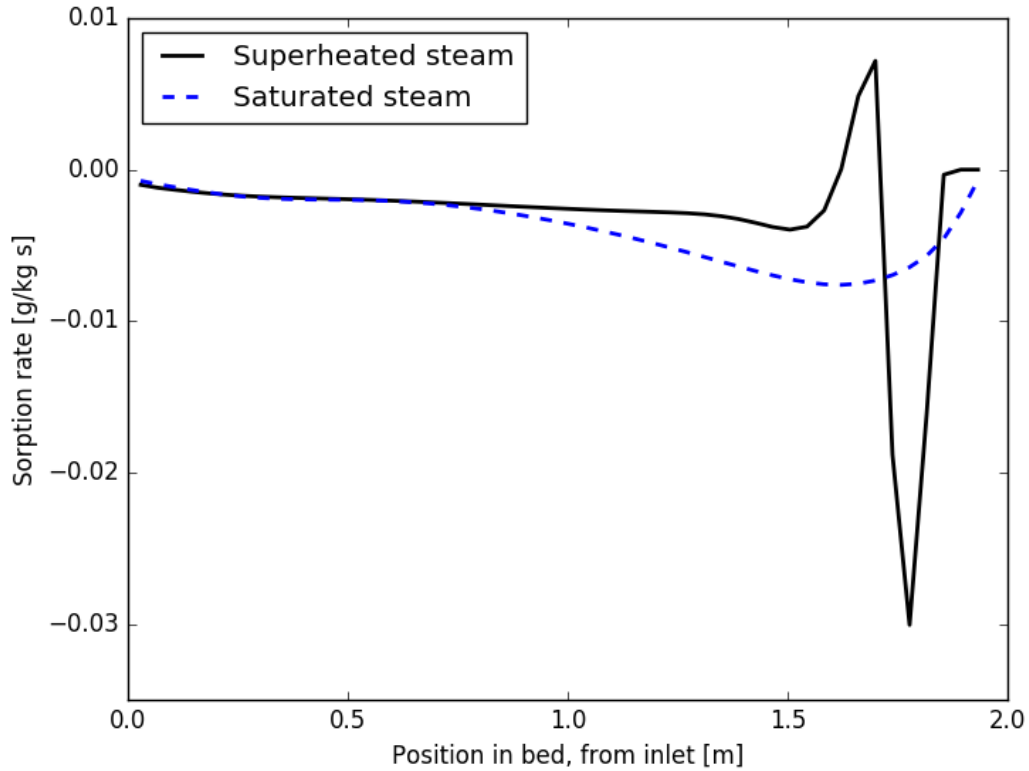


Figure 5.5: Sorption rate of superheated and saturated steam, extracted from a time step in the regeneration stage. Positive values indicate adsorption and negative values indicate desorption.

back into the bed. This explains the higher bed loading at the observed front (Figure 5.4), effectively limiting the derivation of any energy benefits from the increased temperature at the steam inlet.

5.3 3D Simulations

Besides optimizing operational factors, such as the steam state discussed above, changing the microstructure of the bed can have significant impacts on the macroscopic performance of the bed. In packed beds, this translates into how the particle shape might influence macroscopic measurable parameters, e.g., pressure drop, flow uniformity, liquid transport and reactive properties.

When comparing the microstructures generated by packing cylinder-shaped particles to those created by packing perfectly spherical particles, a significant difference in permeability is noted (Table 5.2) between the two cases when only a gas is present. However, this difference is reduced when an interstitial liquid is introduced into the system as a consequence of condensation during the regeneration stage.

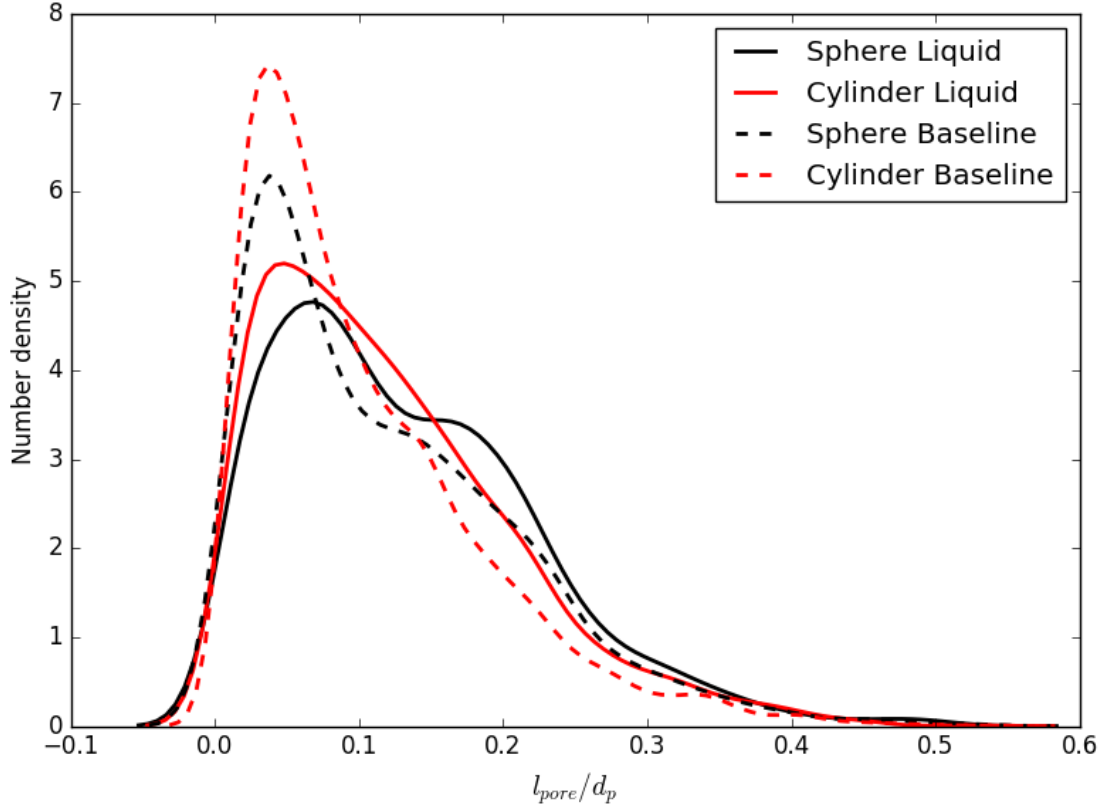


Figure 5.6: Pore size distribution for LBM simulations with ("Liquid") and without ("Baseline") interstitial liquid.

The permeability of the packed bed is strongly connected to the pore networks of the structures. When analyzing the pore size distributions in Figure 5.6 for the two bed geometries, it is found that a bed packed with cylinder-shaped particles has a higher degree of smaller pores. However, when an interstitial liquid is introduced to the domain, the pore size distribution shifts slightly towards larger pores, and there is a clear reduction in the amount of smaller pores. The difference between the two geometries decreases when an interstitial liquid is introduced.

Permeability is an important characteristic of the bed, since pressure is often related to the work that has to go into the system. Thus, a pressure drop is often considered as a loss, and for industry this might translate into a cost. Applying a higher

Table 5.2: Permeability comparisons for the two microstructures. Permeability K is compared to the permeability of the cylinder base case K_c for the cases with and without an interstitial liquid.

Case	Sphere	Cylinder
K/K_c [-]	1.69	1
K/K_c liquid [-]	1.18	1

permeability in the bed is, thus, an avenue towards cost reductions. However, for some applications in which the pressure drop cannot be compensated for arbitrarily, it is instead an important limiting factor in the system. For those cases, packing a bed with spherical particles rather than cylindrical particles could allow for a higher total mass of carbon to be packed without overstepping the limits. Increased total mass would allow for longer operational times and greater operational flexibility, such that the effectiveness of the bed would be increased.

Chapter 6

Conclusions

This thesis includes the results from studies conducted on both the full-system scale and detailed pore-size scales. The main findings from the appended papers have been summarized in the previous chapters. In this chapter, conclusions are drawn regarding industrial simulations and operations, as well as phenomenological details.

This thesis shows that state-of-the-art models for simulating real-world industrial packed-bed adsorbers capture the main trends well while still lacking information on the dynamics. However, the data can together with the theoretical model provide on-line information about, amongst other things, benzene loading and the residual liquid.

The results presented in this thesis also show that in order to predict the behaviors of industrial-scale, cyclically regenerated adsorption beds, simulations of the beds must use the appropriate cycling procedures and interface-capturing schemes are required to resolve the species concentration front. Otherwise, the effective bed capacity will be misrepresented and the active regions, together with the loading mechanisms, will be erroneously predicted.

When steam condenses during regeneration of the adsorption bed, the residual liquid in the beds exerts strong influences on, and complex interactions with both the energy and momentum transport. The modeling of condensed water represents one of the strongest reasons for the observed disparity between the performed simulations and the industrial data. It is also observed that flow differences between different beds are reduced by the presence of an interstitial liquid.

Improvements to the macroscopic performance of packed beds can be achieved by choosing the appropriate bed particle shape. Changing the shape of the particles in the bed packing can increase bed permeability, allowing more mass to be packed for a given pressure drop.

Not only the amount of energy in the steam, but also the state of the steam used for regeneration is important for the performance of industrial cyclically generated adsorption beds. Overall, the use of saturated steam requires less energy and mass.

There are potential advantages associated with the use of superheated steam, the foremost being that superheated steam locally cleans the beds to a higher degree. However, before this effect can be satisfactorily used to benefit the operation, the main steaming state should involve saturated steam at high temperatures.

Chapter 7

Future Work

The next steps towards modeling and improving industrial steam-regenerated adsorbers should aim to improve the steam/water modeling. This is necessary to define correctly the rate of the process, as well as the behavior and transport of condensed water. The quantity of water that is drained from the bed is unknown, and it is also an unknown parameter in the energy balance. This is a problem for the regeneration part of the cycle. The regeneration stage is the stage in which there is scope for changes and improvements. In the main active stage, the adsorbers are tightly coupled to the product that they clean and to the process that generates that product. Making changes to the product gas is likely to be difficult, whereas implementing changes to the regeneration process, which is a support system for the adsorbers, is more likely to be feasible. Therefore, it seems likely that modeling efforts can be directly useful in this context. There are several promising methods to simulate and model water transport in porous media, and the LBM is definitely one of these. Even though this problem is far from easy to resolve, any progress away from neglecting the problem would be beneficial.

When it comes to adsorbers in applications such as GoBiGas, where there are several other substances that can bind to the adsorbers, efforts should be made to include all the effects of the full gas complexity. For this, there is a balance between the level of usefulness of the solution and the level of effort that needs to be expended to reach that solution. Simulating the actual gas complexity necessitates the inclusion of many complex interactions between active species, and would likely not give much more useful information than would be provided by the use of an aggregated representative theoretical substance. While formulating such a lumped representation is not a simple task, the outcomes would be valuable.

An additional effect seen in the industrial beds is aging, which occurs on a much longer time scale than the cycling itself. In Paper IV, two beds of different ages were compared and differences were noted in the temperature response in the bed. Further work needs to be carried out to define appropriate ways to model this aging process. The outcome might be a useful tool to predict the lifespans of packed beds and to indicate when they need to be changed.

Chapter 8

Division of Work

Paper I

Besides being main author, I developed the code, did the simulations and analyzed the results. The industrial data was provided by GoBiGas and the co-authors supervised the work, contributed with feedback and ideas.

Paper II

I developed the code, did the simulations and analyzed the results. I wrote the first draft, together with Henrik Ström. The other co-authors supervised the work and contributed with feedback and ideas.

Paper III

Besides being main author, I developed the code, did the simulations and analyzed the results. The co-authors supervised the work, contributed with feedback and ideas.

Paper IV

I was the main author and did the analysis. The industrial data was provided by GoBiGas. The co-authors supervised the work, contributed with feedback and ideas.

Paper V

Besides being main author, I did the simulations and analyzed the results. The code was developed by Dario Maggiolo and all co-authors supervised the work, contributed with feedback and ideas.

Bibliography

- Bonjour, J., J.-B. Chalfen, and F. Meunier (2002). “Temperature Swing Adsorption Process with Indirect Cooling and Heating”. In: *Ind. Eng. Chem. Res.* 41.23, pp. 5802–5811 (cit. on p. 9).
- Bonjour, J., M. Clausse, and F. Meunier (2005). “A TSA Process with Indirect Heating and Cooling: Parametric Analysis and Scaling-up to Practical Sizes”. In: *Chem. Eng. Process. Process Intensif.* 44.9, pp. 969–977 (cit. on pp. 4, 9, 10, 13).
- Brosillon, S., M.-H. Manero, and J.-N. Foussard (2001). “Mass Transfer in VOC Adsorption on Zeolite: Experimental and Theoretical Breakthrough Curves”. In: *Environ. Sci. Technol.* 35.17, pp. 3571–3575 (cit. on p. 3).
- Cal, M.P., M.J. Rood, and S.M. Larson (1996). “Removal of VOCs from humidified gas streams using activated carbon cloth”. In: *Gas Sep. Purif.* 10.2, pp. 117–121 (cit. on pp. 4, 13, 25).
- Chuang, CL, PC Chiang, and EE Chang (2003). “Modeling VOCs Adsorption onto Activated Carbon”. In: *Chemosphere* 53.1, pp. 17–27 (cit. on p. 4).
- Cruz, P., J.C. Santos, F.D. Magalhaes, and A. Mendes (2003). “Cyclic adsorption separation processes: analysis strategy and optimization procedure”. In: *Chem. Eng. Sci.* 58.14, pp. 3143–3158 (cit. on p. 5).
- Das, S., N.G. Deen, and J.A.M. Kuipers (2017). “A DNS Study of Flow and Heat Transfer through Slender Fixed-Bed Reactors Randomly Packed with Spherical Particles”. In: *Chem. Eng. Sci.* 160, pp. 1–19 (cit. on pp. 4, 5).
- Delage, F., P. Pré, and P. Le Cloirec (2000). “Mass Transfer and Warming during Adsorption of High Concentrations of VOCs on an Activated Carbon Bed: Experimental and Theoretical Analysis”. In: *Environ. Sci. Technol.* 34.22, pp. 4816–4821 (cit. on pp. 4, 5).
- Dobre, T., O.C. Parvulescu, A. Jacquemet, and V.A. Ion (2016). “Adsorption and Thermal Desorption of Volatile Organic Compounds in a Fixed Bed – Experimental and Modeling”. In: *Chem. Eng. Commun.* 203.12, pp. 1554–1561 (cit. on pp. 4, 5).
- Gautier, R., T. Dbouk, J.-L. Harion, L. Hamon, and P. Pré (2018). “Pressure-Swing-Adsorption of Gaseous Mixture in Isotropic Porous Medium: Numerical Sensitivity Analysis in CFD”. In: *Chem. Eng. Res. Des.* 129, pp. 314–326 (cit. on pp. 4, 5).
- Giraudet, S., P. Pré, and P. Le Cloirec (2009). “Modeling the Heat and Mass Transfers in Temperature-Swing Adsorption of Volatile Organic Compounds onto Activated Carbons”. In: *Environ. Sci. Technol.* 43.4, pp. 1173–1179 (cit. on pp. 4, 9).

- Gu, J. and H.-J. Bart (2005). “Heat and Mass Transfer in Steam Desorption of an Activated Carbon Adsorber”. In: *Int. Commun. Heat Mass Transfer* 32.3-4, pp. 296–304 (cit. on p. 5).
- Guo, Z., C. Zheng, and B. Shi (2002). “Discrete lattice effects on the forcing term in the lattice Boltzmann method”. In: *Phys. Rev. E* 65.4, p. 046308 (cit. on p. 15).
- Hagemann, N., K. Spokas, H.-P. Schmidt, R. Kägi, M.A. Böhler, and T.D. Bucheli (2018). “Activated carbon, biochar and charcoal: linkages and synergies across pyrogenic carbon’s ABCs”. In: *Water* 10.2, p. 182 (cit. on p. 3).
- Heidarinejad, Z., M.H. Dehghani, M. Heidari, G. Javedan, I. Ali, and M. Sillanpää (2020). “Methods for preparation and activation of activated carbon: a review”. In: *Environ.l Chem. Lett.* 18.2, pp. 393–415 (cit. on p. 4).
- Hwang, K.S., D.K. Choi, S.Y. Gong, and S.Y. Cho (1997). “Adsorption and Thermal Regeneration of Methylene Chloride Vapor on an Activated Carbon Bed”. In: *Chem. Eng. Sci.* 52.7, pp. 1111–1123 (cit. on p. 4).
- Joss, L., M. Gazzani, M. Hefti, D. Marx, and M. Mazzotti (2015). “Temperature Swing Adsorption for the Recovery of the Heavy Component: an Equilibrium-Based Shortcut Model”. In: *Ind. Eng. Chem. Res.* 54.11, pp. 3027–3038 (cit. on p. 4).
- Kim, J.-H., S.-J. Lee, M.-B. Kim, J.-J. Lee, and C.-H. Lee (2007). “Sorption Equilibrium and Thermal Regeneration of Acetone and Toluene Vapors on an Activated Carbon”. In: *Ind. Eng. Chem. Res.* 46.13, pp. 4584–4594 (cit. on pp. 4, 9, 10, 13).
- Knaebel, K. S. (2008). *Adsorption*. Ed. by Lyle F. Albright. Vol. 1. CRC Press: Boca Raton, pp. 1119–1170 (cit. on pp. 7, 8).
- Kolade, M.A., A. Kogelbauer, and E. Alpay (2009). “Adsorptive Reactor Technology for VOC Abatement”. In: *Chem. Eng. Sci.* 64, pp. 1167–1177 (cit. on p. 3).
- Larsson, A., I. Gunnarsson, and F. Tengberg (2019). “The GoBiGas Project - Demonstration of the Production of Biomethane from Biomass via Gasification”. In: *Göteborg Energi AB Project Report*. Pp. 1–101 (cit. on pp. 3, 9).
- Liu, H., Q. Kang, C.R. Leonardi, S. Schmieschek, A. Narváez, B.D. Jones, J.R. Williams, A.J. Valocchi, and J. Harting (2016). “Multiphase lattice Boltzmann simulations for porous media applications”. In: *Comput. Geosci.* 20.4, pp. 777–805 (cit. on p. 14).
- Lu, J., E.A.J.F. Peters, and J.A.M. Kuipers (2019). “Direct Numerical Simulation of Fluid Flow and Dependently Coupled Heat and Mass Transfer in Fluid-Particle Systems”. In: *Chem. Eng. Sci.* 204, pp. 203–219 (cit. on p. 5).
- Maggiolo, D., M. Seemann, H. Thunman, O. Santos, A. Larsson, S. Sasic, and H. Ström (2019). “Self-Cleaning Surfaces for Heat Recovery During Industrial Hydrocarbon-Rich Gas Cooling: An Experimental and Numerical Study”. In: *AIChE J.* 65.1, pp. 317–325 (cit. on p. 15).
- Mahmoudi, A.H., F. Hoffman, and B. Peters (2014). “Application of XDEM as a Novel Approach to Predict Drying of a Packed Bed”. In: *Int. J. Therm. Sci.* 75, pp. 65–75 (cit. on p. 5).
- March, H. and F. Rodríguez-Reinoso (2006). *Activated Carbon*. Vol. 1. Elsevier Science: Amsterdam, pp. 1–12 (cit. on p. 3).

- Marsh, H. and F.R. Reinoso (2006). *Activated Carbon*. Ed. by Harry Marsh. Elsevier Science & Technology (cit. on p. 7).
- Nouh, S.A., K.K. Lau, and A.M. Shariff (2010). “Modeling and Simulation of Fixed Bed Adsorption Column using Integrated CFD Approach”. In: *J. Appl. Sci.* 10.24, pp. 3229–3235 (cit. on p. 4).
- Ortiz, F.J.G., M.B. Rodríguez, and R.T. Yang (2019). “Modeling of Fixed-Bed Columns for Gas Physical Adsorption”. In: *Chem. Eng. J.* 378, p. 121985 (cit. on p. 5).
- Pandit, R., M. Schick, and M. Wortis (1982). “Systematics of multilayer adsorption phenomena on attractive substrates”. In: *Phys. Rev. B: Condens. Matter* 26.9, p. 5112 (cit. on p. 7).
- Pui, W.K., R. Yusoff, and M.K. Aroua (2019). “A review on activated carbon adsorption for volatile organic compounds (VOCs)”. In: *Rev. Chem. Eng.* 35.5, pp. 649–668 (cit. on p. 3).
- Ramalingam, S.G., P. Pré, S. Giraudet, L. Le Coq, P. Le Cloirec, O. Baudouin, and S. Déchelotte (2012). “Recovery Comparisons — Hot Nitrogen Vs Steam Regeneration of Toxic Dichloromethane from Activated Carbon Beds in Oil Sands Process”. In: *J. Hazard. Mater.* 205, pp. 222–228 (cit. on p. 13).
- Rambabu, K., L. Muruganandam, and S.C.F.D. Velu (2014). “CFD Simulation for Separation of Carbon Dioxide-Methane Mixture by Pressure Swing Adsorption”. In: *Int. J. Chem. Eng.* 2014, p. 402756 (cit. on p. 4).
- Rossi, E., M. Paloni, G. Storti, and R. Rota (2019). “Modeling dual reflux-pressure swing adsorption processes: Numerical solution based on the finite volume method”. In: *Chem. Eng. Sci.* 203, pp. 173–185 (cit. on p. 3).
- Salvador, F., N. Martin-Sanchez, R. Sanchez-Hernandez, M.J. Sanchez-Montero, and C. Izquierdo (2015a). “Regeneration of Carbonaceous Adsorbents. Part I: Thermal Regeneration”. In: *Microporous Mesoporous Mater.* 202, pp. 259–276 (cit. on pp. 4, 5, 8).
- Salvador, F., N. Martin-Sanchez, R. Sanchez-Hernandez, M.J. Sanchez-Montero, and C. Izquierdo (2015b). “Regeneration of carbonaceous adsorbents. Part II: chemical, microbiological and vacuum regeneration”. In: *Microporous Mesoporous Mater.* 202, pp. 277–296 (cit. on p. 4).
- Schideman, L.C., B.J. Marinas, V.L. Snoeyink, and C. Campos (2006). “Three-component competitive adsorption model for fixed-bed and moving-bed granular activated carbon adsorbers. Part I. Model development”. In: *Environ. Sci. Technol.* 40.21, pp. 6805–6811 (cit. on p. 4).
- Schweiger, T.A.J. (1996). “A Design Method for Adsorption Bed Capacity: Steam-Regenerated Adsorbents”. In: *Ind. Eng. Chem. Res.* 35.6, pp. 1929–1934 (cit. on p. 3).
- Shah, I.K., P. Pré, and B.J. Alappat (2013). “Steam regeneration of adsorbents: an experimental and technical review”. In: *Chem. Sci. Trans* 2.4, pp. 1078–1088 (cit. on pp. 3, 5).
- Shan, X. and H. Chen (1993). “Lattice Boltzmann model for simulating flows with multiple phases and components”. In: *Phys. Rev. E* 47.3, p. 1815 (cit. on p. 15).

- Succi, Sauro (2001). *The lattice Boltzmann equation: for fluid dynamics and beyond*. Oxford university press (cit. on p. 14).
- Talmoudi, R., A. AbdelJaoued, and M.H. Chahbani (2018). “Dynamic Study of VSA and TSA Processes for VOCs Removal from Air”. In: *Int. J. Chem. Eng.* 2018 (cit. on p. 4).
- Thunman, H. (2018). “GoBiGas demonstration—a vital step for a large-scale transition from fossil fuels to advanced biofuels and electrofuels”. In: *Chalmers University of Technology, Gothenburg, Sweden* (cit. on p. 6).
- Thunman, H., C. Gustavsson, A. Larsson, I. Gunnarsson, and F. Tengberg (2019). “Economic Assessment of Advanced Biofuel Production via Gasification using Cost Data from the GoBiGas Plant”. In: *Energy Sci. Eng.* 7.1, pp. 217–229 (cit. on p. 8).
- Thunman, H., M. Seemann, et al. (2018). “Advanced Biofuel Production via Gasification – Lessons Learned from 200 Man-years of Research Activity with Chalmers’ Research Gasifier and the GoBiGas Demonstration Plant”. In: *Energy Sci. Eng.* 6.1, pp. 6–34 (cit. on pp. 4, 17).
- Van Leer, B. (1974). “Towards the ultimate conservative difference scheme. II. Monotonicity and conservation combined in a second-order scheme”. In: *J. Comput. Phys.* 14.4, pp. 361–370 (cit. on p. 14).
- Webley, P.A. and J. He (2000). “Fast Solution-Adaptive Finite Volume Method for PSA/VSA Cycle Simulation; 1 Single Step Simulation”. In: *Comput. Chem. Eng.* 23.11-12, pp. 1701–1712 (cit. on p. 4).
- Xiao, J., R. Peng, D. Cossement, P. Bénard, and R. Chahine (2013). “CFD Model for Charge and Discharge Cycle of Adsorptive Hydrogen Storage on Activated Carbon”. In: *Int. J. Hydrogen Energy* 38.3, pp. 1450–1459 (cit. on p. 4).
- Yang, C., G. Miao, Y. Pi, Q. Xia, J. Wu, Z. Li, and J. Xiao (2019a). “Abatement of Various Types of VOCs by Adsorption/Catalytic Oxidation: A Review”. In: *Chem. Eng. J.* 370, pp. 1128–1153 (cit. on p. 3).
- Yang, C., G. Miao, Y. Pi, Q. Xia, J. Wu, Z. Li, and J. Xiao (2019b). “Abatement of various types of VOCs by adsorption/catalytic oxidation: A review”. In: *Chem. Eng. J.* 370, pp. 1128–1153 (cit. on p. 3).
- Yun, J.-H., D.-K. Choi, and H. Moon (2000). “Benzene Adsorption and Hot Purge Regeneration in Activated Carbon Beds”. In: *Chem. Eng. Sci.* 55.23, pp. 5857–5872 (cit. on pp. 4, 13).
- Zhang, S., J. You, C. Kennes, Z. Cheng, J. Ye, D. Chen, J. Chen, and L. Wang (2018). “Current advances of VOCs degradation by bioelectrochemical systems: a review”. In: *Chem. Eng. J.* 334, pp. 2625–2637 (cit. on p. 3).