Doctoral Thesis

Adsorption-based Carbon Dioxide Capture From Multicomponent Gas Mixtures

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Adsorption-based Carbon Dioxide Capture
From Multicomponent Gas Mixtures

A thesis submitted to attain the degree of
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*If I have seen further, it is by standing on the shoulders of giants.* None of the insights gained during my work would have been possible without the foundation laid by those who went before me. For showing me the ropes of the adsorption lab, sparking my interest in this topic, and being a patient teacher, I would like to thank Ronny. Furthermore, a great deal of my work was based on the work done by Nathalie and Johanna; Chapters 3 and 4 of this thesis are a direct continuation of their work on PSA processes. I would like to thank them for many insightful discussions as well as for leaving me excellent experimental setups that made my work easier.

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Zurich, September 2015
The most exciting phrase to hear in science, the one that heralds new discoveries, is not "Eureka!" but "That’s funny..."

Isaac Asimov
Abstract

The phenomenon of adsorption has long been used in the purification of gases such as hydrogen and in the drying of process streams. In most traditional applications the goal is to remove impurities from a valuable gas stream, where the impurities are more strongly adsorbed than the valuable components and are typically of little interest. More recently research work has intensified to explore the potential of adsorption based separation processes for the capture of carbon dioxide from process streams or flue gases within the context of carbon dioxide capture and storage (CCS). In these processes the CO$_2$ to be captured is typically the more adsorbed component, so obtaining a high purity product requires the development of appropriate processes. Depending on the CCS scheme, the conditions present may favor the use of pressure swing adsorption (PSA) or temperature swing adsorption (TSA). The high pressure present in a pre-combustion CO$_2$ capture scenario give PSA an advantage in terms of energy consumption, and its fast operation leads to a high productivity. In the case of post-combustion capture, where the flue gas is typically near atmospheric pressure, TSA shows promise, especially if low-grade heat can be used for the regeneration of the bed. The aim of this thesis is to further the understanding of cyclic fixed bed adsorption processes for the capture of CO$_2$ by either PSA or TSA. For this purpose, the influence of additional components in the gas stream
to be separated was investigated, and the heat transfer within a packed bed that is relevant for TSA processes was studied. This was done by a thorough characterization of the system at hand followed by a rigorous testing of the developed model.

First, gravimetric measurements of the adsorption equilibrium of pure gases and binary mixtures allow the study of the thermodynamics of the adsorption system. The activated carbon that was used in the study of PSA had already been characterized previously; however for the TSA processes investigated for post-combustion capture two additional materials were studied: Zeolites ZSM-5 and 13X. From the equilibrium study it was determined that 13X was the more promising material for the process.

Second, breakthrough experiments were performed to characterize the relevant transport parameters. This was done using binary CO$_2$/N$_2$ feed mixtures with columns packed with either activated carbon or 13X, and allowed the study of the mass transfer of each of the gases on both sorbent materials. Additionally, the heat transfer within the bed under a variety of flow conditions could be characterized. In the case of TSA processes, the heat transfer from the column jacket to the bed is also studied by dedicated heating and cooling experiments.

Third, the model using the equilibrium and transport parameters determined, is tested by using it to predict three types of experiments: Breakthrough experiments using three components, cyclic PSA experiments for the capture of CO$_2$ from CO$_2$/N$_2$ and CO$_2$/N$_2$/H$_2$ mixtures, and cyclic TSA experiments for capture from CO$_2$/N$_2$ mixtures. For the cyclic processes, the separation performance is determined and compared with simulation predictions, for a complete validation of the model.
Zusammenfassung

Das Phänomen der Adsorption wird seit längerer Zeit zur Reinigung von Gasen wie z.B. Wasserstoff oder zur Trocknung von Prozessströmen verwendet. In den meisten Anwendungen ist das Ziel die Abscheidung von Verunreinigungen von einem wertvollen Produkt, wobei die Verunreinigungen häufig stärker zurückgehalten werden als das eigentliche Produkt. Seit einigen Jahren gibt es Entwicklungen dahingehend, das Potenzial von adsorptionsbasierten Trennverfahren für Anwendungen im Bereich der Kohlendioxidabscheidung und -speicherung (CCS) zu ermitteln. In diesem Fall stellt das CO$_2$ meist die stärker adsorbierte Komponente dar, was bedeutet, dass die Verfahren neu daraufhin ausgerichtet werden müssen, diese auch in hoher Reinheit zu produzieren. Je nach den genauen Begebenheiten, unter denen das CO$_2$ abgeschieden werden soll, kann es sich hierbei anbieten, Druckwechseladsorption (PSA) oder Temperaturwechseladsorption (TSA) anzuwenden. In Fällen, bei denen die CO$_2$-Abscheidung zwischen einer Brennstoffvergasung und der Verbrennung erfolgt, führt der hoher Druck des Eingangstroms zu Vorteilen für PSA. Im Fall der Abscheidung nach der Verbrennung ist der Druck üblicherweise nahe des Umgebungsdrucks; in diesem Fall kann TSA von Interesse sein, besonders wenn Abwärme zur Regenerationsprozesse verwendet werden kann.

Das Ziel dieser Doktorarbeit ist die Erweiterung des Verständis von PSA.


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Chapter 1

Introduction

Adsorption refers to the interactions between molecules of a sorbate in a fluid phase and an interface, typically a solid surface, creating a region in space with a composition and density different from that in the surrounding bulk phase. In this region, the sorbate molecules can interact with the surface as well as with other sorbate molecules by forming covalent bonds (referred to as chemisorption) or by weaker interactions such as van-der-Waals forces (referred to as physisorption). Both chemisorption and physisorption have numerous applications in industrial processes in catalysis, separation, storage, or in heat pumps, and are being applied in liquid as well as in gas systems. This work focuses on the study of physisorption as a tool in the separation of gases within the context of CO$_2$ capture and storage technologies. More specifically, a mathematical model is presented that describes the behavior of an adsorption column; it is then calibrated for a pressure swing adsorption and a temperature swing adsorption process, and validated, such that going forward it may be used to simulate and design adsorption-based processes for the capture of CO$_2$ from flue gases and industrial gas streams.
1. Introduction

1.1 Adsorption equilibria, the underlying phenomenon in adsorption-based separation processes

In general, there are three mechanisms by which sorbents are used for separation: steric, kinetic, and equilibrium effects.\(^1\) Steric effects are what lies at the center of the functionality of molecular sieves, as well as some applications using zeolites. In these processes, it is the size or shape of the desired molecule (or the impurity) which discriminates between molecules. An example of this is the separation of normal paraffins from iso-paraffins and cyclic hydrocarbons using 5A zeolite. Meanwhile, kinetic separations exploit differences in molecular diffusion rates between different species. This can be a useful alternative to equilibrium-based separation, and is used e.g. in the separation of \(\text{N}_2\) and \(\text{O}_2\) from air, where \(\text{O}_2\) diffuses into carbon molecular sieve much faster than \(\text{N}_2\).\(^1\) The majority of adsorption separations, however, exploit the adsorption equilibrium.

A sorbent that is useful for an equilibrium separation interacts with the sorbent molecules in a way such that the adsorbed phase not only has a higher density than the bulk phase – it must also have a different composition, similar to how a liquid-vapor equilibrium must have a difference in composition in order to be exploited for separation. This selectivity of the sorbent material for one sorbate over the other(s) and the adsorption capacity are, together with the stability under the conditions of the process, the quantities that first and foremost determine the potential that a sorbent has for any given separation.\(^2\)
1.2 Separations of gas mixtures

The ability of a porous sorbent material to selectively adsorb comparatively large quantities of a sorbate is only the first step of a successful separation process. The adsorption needs to be reversible, preferably returning the solid to its previous state exactly, allowing the sorbent to sustain performance for an extended period of time. A separation process must therefore contain two principal steps: an adsorption step, during which the preferentially adsorbed species is loaded onto the sorbent, and a desorption step, during which said species is removed from the sorbent. The desorption, also frequently referred to as regeneration, is commonly brought about using one of two drivers: a reduction in pressure, or an increase in temperature. Pressure Swing Adsorption (PSA) exploits the difference in equilibrium adsorbed amount at different pressure levels. This can be seen schematically in Figure 1.1. The bed is loaded at $T_{ads}$, $P_{ads}$, typically stopping before the more strongly adsorbed component breaks through; then the pressure is reduced to $P_{des}$, which corresponds to a lower equilibrium adsorbed amount, and the adsorbed gas is recovered. Temperature Swing Adsorption (TSA) exploits the difference in equilibrium adsorbed amount at different temperatures. As illustrated in Figure 1.1, the bed is loaded at $T_{ads}$, $P_{ads}$, and then regenerated by heating in to $T_{des}$, and recovering the more strongly adsorbed species.

One of the main advantages of PSA over TSA is the fact that pressure can often be changed relatively rapidly, making it possible to have much shorter cycle times for PSA than for TSA, and higher productivity for a given bed volume. On the other hand, however, the operating principle of PSA means that either the feed has to be provided at an elevated pressure, or the heavier component has to be recovered under vacuum (VSA, vacuum swing adsorption); both of which can be costly both in
1. Introduction

terms of energy requirement and equipment specifications. However, if
the feed is available at a high pressure, and the valuable product is the
light compound (i.e. least adsorbed), PSA can provide ultra-high purity.
Perhaps the most well-known application for PSA is the purification of
H\textsubscript{2} by way of the Skarstrom cycle.\textsuperscript{4} This process consists of four steps:
pressurization with the feed mixture, increasing the pressure to \( P_{\text{ads}} \); adsorption, during which the light component is produced at high purity;
blowdown, reducing the pressure to \( P_{\text{des}} \); and purge, during which some
of the product from the adsorption step is used to flush the column in
the direction opposite of the adsorption step.

TSA has to contend with the fact that its productivity is often limited
by the heat transfer during the heating and cooling steps of the bed, and
the sorbent material as well as inert parts of the equipment such as the
column wall have to be heated and cooled throughout each cycle, such
that the thermal energy needed can be much larger than just the heat of
adsorption.\textsuperscript{5} Compared to PSA, it does have the advantage that the feed
does not need to be pressurized. Additionally, in some cases low-grade
heat may be used for the regeneration, which can reduce operational
costs.

1.3 Adsorption for carbon dioxide capture
and storage (CCS)

While adsorption separations have been in use for applications in gas
treatment and purification for some time now, their potential for carbon
dioxide capture and storage (CCS) applications has only received inter-
est in more recent years. CCS is a portfolio of technologies that offer
a possible bridging technology during a transitory phase of the global
energy system from one that is heavily reliant on fossil fuels to one that
1.3 Adsorption for carbon dioxide capture and storage (CCS)

Figure 1.1: Conceptual principle of cyclic adsorption processes using either pressure (PSA) or temperature (TSA) to regenerate the bed.

focuses on renewable and nuclear energy. While such a transition is essential in the long-term, the availability of fossil fuels and the increased global demand for energy make fossil fuels indispensable for a long time – according to the Global CCS Institute, fossil fuels currently supply 80% of the global energy. Therefore, this is a shift that will take decades. In the meantime, CCS could offer a path that faces the reality of continued use of fossil fuels while reducing emission of CO₂. The CCS chain includes three main parts:

- Capture of CO₂, preferably at large sources like power plants or industrial plants, where the concentration is relatively high and the capture facility can be tailor-made to the circumstances.

- Transport of the captured CO₂, via pipeline or ship, to a suitable storage site.

- Storage in an adequate site in order to permanently separate it from the atmosphere. If an industrial use is available that permanently binds the CO₂, effectively also keeping it out of the at-
1. Introduction

mosphere, this could provide a revenue stream; however these are typically applications on a smaller scale.

Within these three parts, adsorption bears potential as a separation technology to be used in the capture of CO$_2$. Additionally, some storage facilities exploit adsorption in the subsurface to bind CO$_2$ in coal seams that cannot be mined for coal, in the context of enhanced coal bed methane recovery operations (ECBM).\textsuperscript{8} Operations of this sort might benefit from the competitive adsorption between CO$_2$ and the CH$_4$ present in the coal seams, as the coal often exhibits selectivity for CO$_2$, leading to a release of CH$_4$ upon the injection of CO$_2$.\textsuperscript{9}

This work focuses on the potential of adsorption for the capture of CO$_2$ from large sources. In general, there are three schemes by which CO$_2$ can be captured; they are shown schematically in Figure 1.2. The three schemes differ drastically in the conditions present at the point where the separation takes place. Of these, adsorption shows promise for applications in pre- and post-combustion capture. While adsorption is widely used for air separation, as would be needed for oxyfuel combustion, it is typically used at smaller scale, as cryogenic separation becomes more economical at large scale.\textsuperscript{3}

1.3.1 Pre-combustion CO$_2$ capture

As is seen in Figure 1.2, the CO$_2$ separation in a pre-combustion capture scenario takes place after gasification, water-gas shift, and cleanup such as sulfur removal. At this point, the mixture to be separated consists mainly of H$_2$, CO$_2$, CO, and water vapor and exits the desulfurization unit at a high pressure.\textsuperscript{11} In the case of an air-blown autothermal reforming operation, the waste stream from hydrogen purification by PSA, and other industrial sources, it is also common for the process stream to contain a considerable amount of nitrogen.\textsuperscript{12,13} Due to the high pres-
sure of the feed and the availability of a number of sorbents that exhibit great selectivity for CO$_2$ over H$_2$, PSA has been shown to be a viable option in this context.\textsuperscript{14,15} In this work, the work of Casas and Schell is expanded to consider streams with a significant concentration of N$_2$. In Chapter 3 transport parameters are determined that allow the description of ternary breakthroughs, and in Chapter 4 the model developed by Casas and Schell is tested by using it to simulate the separation of ternary mixtures containing CO$_2$, H$_2$, and N$_2$, which was performed in experiment, and comparing the simulation results to the experiments.
1.3.2 Post-combustion CO$_2$ capture

Post-combustion capture of CO$_2$ is perhaps the most intuitive form of CO$_2$ capture. As seen in Figure 1.2, the CO$_2$ is separated from the flue gas of a combustion. This has the advantage over other CO$_2$ capture strategies that it theoretically allows for a retrofit of an existing plant, by adding a capture unit to the train of flue gas treatment. In this scenario, the conditions under which the separation takes place are quite different from pre-combustion capture: The stream usually consists primarily of N$_2$ with CO$_2$ and water vapor, sometimes also containing some O$_2$. The CO$_2$ content is quite dependent on the fuel that was used in the combustion, and often ranges from 3 to 15 %. As the flue gas is usually near atmospheric pressure, a suitable sorbent would have to have a high capacity and selectivity for CO$_2$ at relatively low partial pressure of CO$_2$. Additionally, the feed entering at low pressure means that in order to use a pressure swing operation, vacuum would be needed. As an alternative, temperature swing adsorption is investigated in this work, calibrating the model that was used for PSA for the simulation of TSA processes that might be of interest in this scenario. The model is then tested similarly to how it was done for PSA by comparing simulated results to experiments in Chapter 5.

1.4 Modeling adsorption processes

The design of adsorption-based processes for the separation of gases has benefited immensely from the development of mathematical models that allow the simulation of these processes, and therefore can be used for model-based process design. In particular, the availability of a large number of possible configurations, cycle schedules, sorbent materials, and recycles make the use of simple heuristics for even the preliminary
design difficult, and motivate the use of simulations at an early stage in process development. In the development of a model that is able to accurately describe the processes that are taking place in an adsorption column, a number of choices needs to be made with regards to the complexity of the model, in particular as added complexity often increases computation time, which is essential in the screening of a large number of possible process configurations. In the following a model is presented that has been developed at the Separation Processes Laboratory (SPL) throughout the past years.

1.4.1 The column model

A one-dimensional model is used to describe all the adsorption columns in this work; it is described in detail in Casas et al., and is summarized in the following. The model incorporates mass- and energy balances along with constitutive equations that are used to describe the pressure drop across the column, the equilibrium adsorption isotherm, the heat capacity of the gas and of the adsorbed phase, and the heat transfer to the column wall. In the development of the model the following assumptions were made:

- Radial gradients of concentration, velocity, and temperature are neglected.
- The gas phase and solid phase are in thermal equilibrium.
- The fluid phase behaves like an ideal gas.
- The column wall and the metal layers that constitute the heating system are described by lumped parameters. This pertains to the work reported in Chapter 3 and Chapter 4, where the columns were surrounded by an electric heating system. For the TSA experiments reported in Chapter 5 the experimental setup was heavily...
modified, and the electric heating system replaced by heating jackets. The modeling considerations that were introduced to describe this system’s behavior are detailed in that chapter.

- The mass transfer resistance for adsorption can be described adequately by a linear-driving-force model.
- Mass transfer coefficients, heat of adsorption, viscosity, heat conductivity, and heat capacities are constant.
- Kinetic and potential energies are neglected in the energy balance, as they are much smaller than the internal energy.

The governing equations are listed in Table 1.1. What boundary conditions apply depends on the current process step and the direction of flow – the BC for the four main steps of a PSA cycle with the flow directions most commonly used in this work are also listed in Table 1.1. During the steps that involve a significant change in pressure (blowdown and pressurization) the pressure at the outlet/inlet is a function of time, which is discussed in more detail in Chapter 4. The partial differential equations that result from the mass and energy balances were discretized using the finite-volume method and implemented in FORTRAN. A commercial solver (DIVPAG) that is part of the IMSL Numerical Libraries was used to integrate in time.

### 1.4.1.1 Constitutive equations

Along with the mass and energy balances, Table 1.1 also lists some of the constitutive equations that are incorporated into the model. Specifically, these are:

**Equation of state:** Throughout this work, the fluid phase was assumed to be described by the ideal gas law, as listed in Table 1.1. This assumption was shown to be reasonable by Casas et al.\textsuperscript{17} by comparison with
1.4 Modeling adsorption processes

Table 1.1: Mathematical model of the column according to Casas et al.\textsuperscript{17}

Component and total mass balances:
\[
\begin{align*}
\epsilon_t \frac{\partial c_i}{\partial t} + \frac{\partial (uc_i)}{\partial x} + \rho_b \frac{\partial q_i}{\partial t} - \epsilon_t \frac{\partial}{\partial x} \left( D_L \frac{\partial c_i}{\partial x} \right) &= 0 \quad i = 1, \ldots, N \\
\epsilon_t \frac{\partial c}{\partial t} + \frac{\partial (uc)}{\partial x} + \rho_b \sum_{j=1}^{N} \frac{\partial q_j}{\partial t} &= 0
\end{align*}
\]

Mass transfer (linear driving force)
\[
\frac{\partial q_i}{\partial t} = k_i(q^e_i - q_i) \quad i = 1, \ldots, N
\]

Energy balance for the fixed-bed:
\[
\begin{align*}
\epsilon_t C_g + \rho_b C_s + \rho_b C_{ads} \frac{\partial T}{\partial t} - \epsilon_t \frac{\partial P}{\partial t} + uC_g \frac{\partial T}{\partial x} \\
- \frac{\rho_b}{\epsilon_b} \sum_{j=1}^{N} (-\Delta H_j) \frac{\partial q_j}{\partial t} + \frac{4h_L}{d_i} (T - T_w) - \epsilon_t \frac{\partial}{\partial x} \left( K_L \frac{\partial T}{\partial x} \right) &= 0
\end{align*}
\]

Energy balance for the wall:
\[
\frac{\partial T_w}{\partial t} = \frac{4}{C_w (d_i^2 - d_o^2)} \left( d_i h_L (T - T_w) + d_o h_w (T_{amb} - T_w) \right)
\]

Momentum balance (Ergun equation):
\[
\frac{\partial P}{\partial x} = -\frac{150 \mu (1 - \epsilon_b)^2}{\epsilon_b d_p^2} u - \frac{1.75 (1 - \epsilon_b) \rho}{\epsilon_b d_p} |u| u
\]

Equation of state (ideal gas law)
\[
c_i = \frac{y_i P}{RT}
\]

Boundary conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Adsorption $\uparrow$</th>
<th>Blowdown $\downarrow$</th>
<th>Purge $\downarrow$</th>
<th>Pressurization $\uparrow$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>$uc = u_{ads} c_{feed}$</td>
<td>$P = P(t)$</td>
<td>$P = P_{des}$</td>
<td>$T = T_{feed}$</td>
</tr>
<tr>
<td>$T = T_{feed}$</td>
<td>$\frac{\partial T}{\partial x} = 0$</td>
<td>$\frac{\partial T}{\partial x} = 0$</td>
<td>$\frac{\partial uc}{\partial x} = 0$</td>
<td>$\frac{\partial uc}{\partial x} = 0$</td>
</tr>
<tr>
<td>$x = L$</td>
<td>$P = P_{ads}$</td>
<td>$\frac{\partial P}{\partial x} = 0$</td>
<td>$uc = u_{purge} c_{feed}$</td>
<td>$\frac{\partial P}{\partial x} = 0$</td>
</tr>
<tr>
<td></td>
<td>$\frac{\partial T}{\partial x} = 0$</td>
<td>$T = T_{feed}$</td>
<td>$\frac{\partial uc}{\partial x} = 0$</td>
<td></td>
</tr>
</tbody>
</table>
the Peng-Robinson EOS under conditions that go beyond those discussed in this work.

**Pressure drop:** The pressure drop across the adsorption column is calculated by the Ergun equation, also listed in Table 1.1.

**Heat capacity of gas mixtures and the adsorbed phase:** The specific heat capacity of the adsorbate depends on the temperature, pressure, composition, and does not have to be the same in the adsorbed phase as it is in the bulk phase. Throughout this work, however, only the dependence on the composition is considered, by way of an average of each of the components’ specific heat, weighted by the concentration of each species in each phase:

\[
C_g = \sum_{i=1}^{N} c_i C_{g,i}^{mol} \quad i = 1, ..., N
\]

\[
C_{ads} = \sum_{i=1}^{N} q_i C_{g,i}^{mol} \quad i = 1, ..., N
\]

where \(C_{g,i}^{mol}\) is the specific heat capacity of species \(i\), which is assumed to be constant with temperature and pressure. An average value over the conditions present is used.

**Adsorption isotherm:** The constitutive equation with the largest impact on the simulated process, choosing the right adsorption isotherm model for both the pure component adsorption as well as for mixtures is crucial for an accurate description of adsorption-based processes. The choice of isotherm equation and the values of the parameters are based on extensive sets of equilibrium adsorption data measured at SPL. The setups and methods used to obtain this data are described in Chapter 2.

**Heat of adsorption:** Adsorption is an exothermic process, and the heat released upon adsorption is in many processes (particularly in gas-phase adsorption) large enough that the process cannot be considered
to be isothermal. The heat of adsorption of each species $i$, $\Delta H_i$ is dependent on a number of quantities, including the sorbent, temperature and loading. Throughout this work, $\Delta H_i$ is considered constant for each sorbate-sorbent pair.

### 1.4.2 Obtaining model parameters

While much can already be learned from a model based on a simplified and idealized system, the applicability to real-world processes and the prediction of key performance indicators depends greatly on accurate determination of model parameters. For a number of these parameters, established methods of measurement and accurate values are available in the literature; these include the column wall material’s density, heat capacity and conductivity, and the sorbent’s material and bed density, among others. For the parameters specific to the adsorption, a commonly used approach is to determine the parameters concerning the adsorption equilibrium and those for the transport processes separately in two sets of experiments$^{17-23}$

#### 1.4.2.1 Equilibrium adsorption isotherms

To establish which isotherm model best describes any given system, as well as to determine the parameters for these models, static adsorption measurements are often taken. For these measurements, the two most common approaches are the volumetric and the gravimetric methods. In volumetric measurements the material to be characterized is placed in one of two chambers of known volume, which is then evacuated. The other chamber is filled with the gas of interest, and the initial gas density determined (usually via a pressure measurement and an equation of state); this value multiplied by the chamber’s volume gives the total amount of gas in the system. The two chambers are then connected and
allowed to reach equilibrium. The resulting equilibrium density is then measured, and multiplied by the total void volume of the two chambers (minus the solid volume of the sorbent) to obtain the amount of gas in the bulk phase. Any difference between the initial and final gas amount must then be adsorbed. The gravimetric method, on the other hand, is based on the change in mass of the sample as it is exposed to the gas at the desired conditions. It should be noted that both methods yield the adsorbed excess, rather than the total amount adsorbed, and assumptions about the adsorbed phase are needed to calculate the total amount adsorbed. The work presented here is based entirely on gravimetric measurements; a more detailed description of the setups and methods used is given in Chapter 2, including the assumptions made to calculate the total adsorbed amount.

1.4.2.2 Transport processes – heat & mass transfer

The transport phenomena affecting adsorption processes are determined by dynamic experiments. Typically, breakthrough experiments are performed using columns packed with the sorbent of interest, and a variety of variables (such as exit composition, bed- and exit temperature, and/or flow rate) are measured and then used in conjunction with the model to fit the heat- and mass transfer coefficients. Despite similarities in many properties across a number of sorbent materials, and a number of studies regarding the heat and mass transfer in packed beds, these phenomena are far from straightforward to study. In addition to the challenges of describing the dynamic aspects of adsorption processes, laboratory scale setups often introduce experimental artifacts that need to be identified and accounted for when calibrating or validating the model. Chapters 3 to 5 discuss how the transport parameters in the systems studied in this work were determined using the laboratory setup built in-house.
1.4 Modeling adsorption processes

1.4.3 Model validation by experiment

As the model is derived from first principles and calibrated using experiments under a range of conditions that resemble those that are encountered during the actual separation process, it should not only be able to predict the behavior of the adsorption in the column during any given individual process step, but should also give accurate predictions about the cyclic steady-state (CSS) behavior of adsorption processes such as temperature or pressure swing adsorption. As there are assumptions made, and the processes of interest can be rather complex, it is important to test the model with regards to its ability to describe PSA and TSA processes at CSS. Only if the model is capable of predicting macroscopic process behavior such as product flow rates and purity on a longer time scale without the need to fit additional parameters can it also be used to design processes and optimize operating conditions with confidence. To this end full cyclic experiments, where it has to be ensured that CSS is reached, need to be performed and compared to simulations. Schell et al. have done this for the model used throughout this work for the separation of CO$_2$ and H$_2$ in the context of pre-combustion CO$_2$ capture.$^{25}$

1.4.4 Model-based design and optimization

Once the model has been adequately calibrated and validated, it becomes a powerful tool to study the behavior of the adsorption process on a larger scale. Different steps constituting a cyclic adsorption process can be simulated in series until a cyclic steady-state is found, and any desired performance indicators can be calculated. This allows for a quick comparison between any set of process configurations, sorbent materials, recycle strategies, and can be used for parametric sensitivity and optimization for continuous variables.
1. Introduction

The model developed at SPL was used to simulate PSA processes using activated carbon (AC) as sorbent material within the scope of pre-combustion CO$_2$ capture in an integrated gasification combined cycle (IGCC) power plant by Casas et al.\textsuperscript{26} By using parameters found through the methods described above, the authors compared the effect that different directions of flow, number of pressure equalization steps, and operating temperatures had on process performance in terms of CO$_2$ capture rate and purity. In addition, the duration of process steps was varied in a parametric sensitivity, allowing the visualization of the trade-off between CO$_2$ capture rate and purity by establishing the pareto-optimal curve in the space of these two quantities.

Further, Casas et al. used the simulation tool to compare the merits of novel materials for the same application.\textsuperscript{27} To this end, the necessary model parameters were determined for the MOF materials USO-2-Ni and a UiO-67/MCM-41 hybrid by the methods described above, and the parametric sensitivity performed for AC was repeated for these new materials, yielding a sound estimate of the promise these materials hold in comparison to the commercially available AC without the need for large quantities up front.

1.5 Objective and structure of this thesis – a comprehensive approach to process model development

The aim of this thesis is the expansion of the previously mentioned model beyond the separation of CO$_2$ and H$_2$ by PSA in the context of pre-combustion capture to allow the simulation of other adsorption-based CO$_2$ capture processes, whether they employ pressure swing or temperature swing as their means of regeneration. Specifically, the applications
of interest were two: First, the added complexity of a third component which adsorbs significantly (N\textsubscript{2}); and second, the study of TSA processes for post-combustion CO\textsubscript{2} capture from a flue gas stream. With this objective in mind, the approach outlined above was followed, investigating the thermodynamic equilibrium adsorption of relevant adsorbate/adsorbent systems, determining the transport parameters by breakthrough experiments, and validating the model for the added component and the heat regeneration. The thesis is structured as follows:

In Chapter 2 the study of the adsorption equilibrium by the gravimetric method is presented. As the adsorption equilibria of CO\textsubscript{2}, N\textsubscript{2}, and H\textsubscript{2} as well as their binary mixtures on activated carbon had previously been characterized thoroughly\textsuperscript{28}, two new materials were chosen for this work which showed promise for post-combustion CO\textsubscript{2} capture: zeolites 13X and ZSM5, both manufactured by ZeoChem (Uetikon, Switzerland). Using a Rubotherm Magnetic Suspension Balance (MSB) (Bochum, Germany), adsorption isotherms for CO\textsubscript{2} and N\textsubscript{2} were measured on each sorbent under a wide range of temperature and pressure. In addition, binary adsorption measurements were performed. This extensive set of data allows the accurate determination of parameters for the Sips isotherm, as well as a comparison between different models for the prediction of binary adsorption equilibria.

Chapter 3 details the results of a study of a non-isothermal fixed bed packed with activated carbon. A previous work using different mixtures of CO\textsubscript{2} and H\textsubscript{2} had resulted in mass transfer parameters for these components as well as heat transfer coefficients for the packed bed under a range of conditions. In this chapter, breakthrough experiments were performed using three different CO\textsubscript{2}/N\textsubscript{2} mixtures at four different pressures (1, 5, 10, and 20 bar) and two different temperatures (25 °C and 45 °C). In addition, experiments were performed using three different feed flow rates. By using the column model to simulate these
binary breakthrough experiments, the mass transfer coefficient for $\text{N}_2$ was determined, and that for $\text{CO}_2$ was confirmed. In a second step, the transport parameters found from binary experiments were used to predict the results of ternary breakthrough experiments, where two different $\text{CO}_2/\text{N}_2/\text{H}_2$ mixtures were fed under the same set of conditions as for the $\text{CO}_2/\text{N}_2$ experiments. The predictive capabilities of the model in describing these experiment served as validation of the expandability of the model to incorporate additional components without the need to conduct experiments with all components. This forms the basis for the simulation of the separation of a ternary $\text{CO}_2/\text{N}_2/\text{H}_2$ mixture via PSA in Chapter 4.

In Chapter 4 the results of the validation experiments for pressure swing adsorption of a binary $\text{CO}_2/\text{N}_2$ mixture and a ternary $\text{CO}_2/\text{N}_2/\text{H}_2$ mixture are presented and discussed. A two-column laboratory setup, packed with the same activated carbon as used by Schell et al.\textsuperscript{25,28} and in Chapter 3, is used to capture $\text{CO}_2$ from a binary mixture representative of a flue gas and a ternary mixture representative of a product stream from an airblown autothermal reformer, at a temperature of 25 $^\circ$C and a feed pressure of 20 bar. In comparison to the previous studies focusing on the $\text{CO}_2/\text{H}_2$ separation, the $\text{N}_2$ provided significant competition for adsorption sites. A thorough analysis of the experimental results and comparison with the simulation results showed that the model is fully capable of handling rather different feed compositions while still predicting satisfactorily the temperatures within the column, the product composition, and the overall process performance for a variety of process configurations and operating conditions.

In Chapter 5 the parameter estimation and validation of the model for the simulation of temperature swing adsorption for post-combustion $\text{CO}_2$ capture is presented. The two column setup presented in Chapter 4 is modified by replacing the two electrically heated columns by jacketed
columns and adding two thermostats along with automatic valves to control the flow of the heat exchange fluid. The columns are packed with zeolite 13X, as the equilibrium data showed it to be the most promising of the materials tested for post-combustion capture. Breakthrough experiments are performed using a CO$_2$/N$_2$ mixture with a CO$_2$ content of 12 % at four temperatures (25°C, 45°C, 65°C, and 100°C) and two flow rates (200 cm$^3$/s and 300 cm$^3$/s), and are used to determine the mass transfer coefficients of CO$_2$ and N$_2$ on 13X as well as the heat transfer within the bed. Then, heating and cooling experiments are performed to characterize the heat transfer from the heating fluid to the column. Finally, three TSA experiments are presented, using three different temperature levels for the regeneration, and the temperatures within the column, product composition, and CO$_2$ capture rate are determined and compared with simulations.

The chapters are written such that they can be read independently. Each chapter introduces the concepts necessary for understanding, and draws conclusions from the data presented. The main conclusions in Chapter 6 tie together results from the individual chapters and provide an outlook for future research directions.

At the end of the thesis some appendices can be found that contain mainly figures with experimental data that, while significant and important to verify the robustness of the findings in the main chapters were not absolutely necessary for the discussion of the general results and were considered too long to be included in the main body of the thesis.

**Notation**

<table>
<thead>
<tr>
<th>Roman</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td>fluid phase concentration</td>
<td>[mol/m$^3$]</td>
</tr>
</tbody>
</table>
1. Introduction

$C$ heat capacity $[\text{J/(K m}^3\text{)]}$

$d_i$ inside column diameter $[\text{m}]$

$d_o$ outside column diameter $[\text{m}]$

$d_p$ particle diameter $[\text{m}]$

$D_L$ axial dispersion coefficient $[\text{m}^2/\text{s}]$

$h_{L}$ heat transfer coefficient (column-wall) $[\text{W/(m}^2\text{ K)}]$ 

$h_{w}$ heat transfer coefficient (wall-ambient) $[\text{W/(m}^2\text{ K)}]$ 

$\Delta H$ heat of adsorption $[\text{J/mol}]$

$k$ overall mass transfer coefficient $[\text{s}^{-1}]$

$K_L$ effective axial thermal conductivity in the fluid $[\text{W/(m K)}]$ 

$N$ number of species $[-]$

$p$ partial pressure $[\text{Pa}]$

$P$ total fluid pressure $[\text{Pa}]$

$q$ solid phase concentration $[\text{mol/kg}]$

$R$ universal gas constant $[\text{J/(mol K)}]$ 

$t$ time $[\text{s}]$

$T$ temperature $[\text{K}]$

$u$ superficial gas velocity $[\text{m/s}]$

$x$ space coordinate in the axial direction $[\text{m}]$

$y$ mole fraction $[-]$

Greek

$\epsilon$ void fraction $[-]$

$\rho$ density $[\text{kg/m}^3]$ 

$\mu$ dynamic viscosity $[\text{Pa s}]$

Sub- and Superscript

amb ambient

$b$ adsorbent bed

eq equilibrium

$g$ gas phase
### 1.5 Objective and structure of this thesis

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i,j$</td>
<td>component $i$</td>
</tr>
<tr>
<td>$p$</td>
<td>adsorbent particle</td>
</tr>
<tr>
<td>$s$</td>
<td>solid</td>
</tr>
<tr>
<td>$t$</td>
<td>total</td>
</tr>
<tr>
<td>$w$</td>
<td>column wall</td>
</tr>
</tbody>
</table>
1. Introduction
Chapter 2

Adsorption Equilibrium Measurement and Modeling

The adsorption equilibrium is what lies at the heart of any adsorption-based separation. It determines the thermodynamic limit to the purity of the heavy component for any given set of operating conditions, and is a significant factor in every key performance indicator from the productivity to the energy consumption. As a result, it is the first tool used in the design of a process, and usually determines the choice of sorbent material. Consequently, a thorough understanding and accurate modeling of the equilibrium between the adsorbed phase and the gas phase is key. It is the first step in the approach used at SPL to design adsorption processes.

In this chapter the methods for the characterization of the adsorption

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1The material presented in this chapter summarizes results reported in the following publication for the sake of completeness:
equilibrium, both single and multicomponent, are presented. Materials that showed promise for application in pre-combustion CO\textsubscript{2} capture via PSA have previously been studied in detail\textsuperscript{28,29}, with pure component isotherms measured for CO\textsubscript{2}, N\textsubscript{2}, and H\textsubscript{2}, and binary adsorption measurements performed for mixtures of CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/H\textsubscript{2}, over a large range of temperature and pressure; of these materials, the AP3-60 activated carbon (AC)(Chemviron, Germany) was used in Chapters 3 and 4. This chapter will summarize the work done to characterize two sorbents that showed promise for application in post-combustion CO\textsubscript{2} capture via temperature swing adsorption (TSA): zeolites 13X and ZSM-5. On both sorbents, the adsorption of CO\textsubscript{2} and N\textsubscript{2} is investigated. First, the single component adsorption of each gas species is measured for temperatures ranging from 25°C to 140°C and pressures up to 10 bar. These data are used to determine the isotherm parameters necessary for an accurate description. Second, binary adsorption equilibrium measurements are performed at two temperatures, 25°C and 45°C, and at three pressures (1, 3, and 10 bar), for a number of different gas compositions. Ideally, a model used for the design of separation processes should be able to predict the binary adsorption equilibrium based only on data obtained from pure gas measurements. The binary equilibrium adsorption data is compared to predictions made by different models: an extended Sips, the application of ideal adsorbed solution theory (IAST) to pure component Sips isotherms, and where necessary also real adsorbed solution theory is used to describe non-ideal behavior.
2.1 Experimental

2.1.1 Materials

In this chapter, two types of zeolites are presented: ZSM-5 and 13X in the form of spherical pellets of diameters ranging from 1.2 to 2 mm and 1.6 to 2 mm, respectively; both manufactured by ZeoChem (Switzerland). The pellets contain a binder content between 15 % and 25 %.

The gases used in this study were obtained from Pangas (Switzerland) with purities greater than 99.9 % for the pure gases, 99.999 % in the case of helium. Gas mixtures had a tolerance of ±1 % relative to the CO\textsubscript{2} content in that mixture. Three different gas mixtures were used for the binary measurement, with compositions of \( y_{\text{feed}}^{\text{CO}_2} = 0.25, 0.5, \text{ and } 0.75 \), with the balance being N\textsubscript{2}.

2.1.2 Interpretation of adsorption data

In practice and for rigorous thermodynamic calculations, it is often desirable to know the absolute amount adsorbed\textsuperscript{30,31}. Using the gravimetric method employed in this study, or any other method, this quantity is not directly accessible. Adsorption is determined as an incremental quantity rather than an absolute one, thus it is associated with a reference state\textsuperscript{32,33}. A set of assumptions is required to convert the raw data to an absolute quantity. There are two frameworks that are commonly used to perform this conversion, namely excess adsorption and net adsorption, that will be briefly presented and compared in the following. The definitions associated to the two approaches are based on the following quantities: the volume of the adsorbent, \( V^s \); the volume of the adsorbed phase, \( V^a \); the bulk density, \( \rho^b \), i.e. the density of the fluid phase far from the adsorbent surface; the total absolute mass adsorbed, \( m^{\text{abs}} \), i.e.
2. Adsorption Equilibrium

the mass of the adsorbate(s) that occupies the volume $V^a$. Within the excess adsorption framework, the excess mass adsorbed, $m^{ex}$, is defined as

$$m^{ex} = m^{abs} - \rho^b V^a$$

which is the difference between the absolute mass adsorbed and the mass that would occupy the same volume $V^a$ at the density of the bulk fluid $\rho^b$.34

Considering net adsorption as the measurable quantity, the net mass adsorbed, $m^{net}$, is defined as:

$$m^{net} = m^{abs} - \rho^b (V^a + V^s)$$

which can be interpreted to be the total amount of sorbate present in the container with the adsorbent minus the amount that would be present in the empty container (without the adsorbent) at the same bulk gas density $\rho^b$.

Both quantities, $m^{ex}$ and $m^{net}$, can be negative, and they are related through the following expression:

$$m^{net} = m^{ex} - \rho^b V^s$$

It is clear from the definitions of these quantities that the absolute adsorbed amount $m^{abs}$ can be calculated if either $m^{ex}$ and $V^a$ or $m^{net}$ and $V^a + V^s$ are obtained. Throughout this study, as in previous studies performed at SPL, the excess adsorbed amount is the measured quantity, and the absolute adsorbed amount is calculated from there.
2.1 Experimental

2.1.3 Single component adsorption equilibrium measurements

All equilibrium adsorption measurements were done with a gravimetric method using a Magnetic Suspension Balance (MSB) by Rubotherm (Germany), as it is described in Ottiger et al. This balance is capable of operating at pressure and temperature levels of up to 250 bar and 400°C, and allows for the direct measurement of the bulk density $\rho^b$ of the gas by way of a calibrated sinker of known mass and volume; by measuring the buoyant force it experiences, the bulk phase density can be deduced – this eliminates the need for an equation of state. In addition, the measurement cell is equipped with an electrical heater that allows regeneration of the sample at temperatures of up to 400°C. The MSB can be seen in the schematic in Figure 2.1 along with the connections and sensors. Note that for the single component measurements, the equipment in the dashed frame is not used. Isotherms were measured at five temperatures for each sample, at 25°C, 45°C, 65°C, 100°C and 140°C, and for pressures up to 10 bar for both CO$_2$ and N$_2$. A number of points on the first isotherm measured (CO$_2$ at 25°C) were repeated after all pure gas measurements were completed to verify that repeated thermal cycling did not alter the equilibrium adsorption characteristics of the sorbent. The measuring principle for pure gases (CO$_2$ and N$_2$) and more information on the measuring principle of a MSB have been described in detail elsewhere$^{30,35}$.

The sample was regenerated before the measurement of each new isotherm by heating it to 400°C for four hours while applying vacuum. This ensures the removal of any moisture that adsorbed during the handling of the sample. Then the system was filled with helium to obtain the volume of the metal parts as well as the sorbent sample. After evacuating the MSB again, it is filled with either CO$_2$ or N$_2$ to the pressure of interest, and the weight is recorded. This
2. Adsorption Equilibrium

technique allows the measurement of the excess mass adsorbed:

\[ q^{\text{ex}} (\rho^b, T) = q^{\text{abs}} - \frac{\rho^b V_a}{M_w m_{\text{zeo}}} = \frac{M_1 (\rho^b, T) - M_1^0 + \rho^b V^0}{M_w m_{\text{zeo}}} \]  \hspace{1cm} (2.4)

where \( q^{\text{ex}} \) is the molar excess adsorbed amount per unit mass and \( q^{\text{abs}} \) is the molar absolute adsorbed amount per unit mass, and the quantities on the right-hand side of Eq. (2.4) are the directly measurable quantities. \( M_1 (\rho^b, T) \) and \( M_1^0 \) are the measured weights under the desired conditions and under vacuum, respectively, and \( \rho^b V^0 \) is the buoyancy experienced by the solids in the MSB, i.e. the zeolite and the metal parts. \( V^0 \) was obtained from the measurement with He at high temperature under the assumption that under those conditions \( q^{\text{ex}} = 0 \), i.e. that the gas density is the same in the pores and in the bulk phase and any buoyancy measured is due to the solid volume. \( M_w \) and \( m_{\text{zeo}} \) are the molecular weight of the gas and the mass of sorbent material, respectively.

To convert the molar excess amount, \( q^{\text{ex}} \), to the molar absolute amount, \( q^{\text{abs}} \), via the excess adsorption framework an additional assumption about the nature of the adsorbed phase is required\(^\text{36}\). A widely used approach is based on the observation that \( q^{\text{ex}} \) decreases linearly with the bulk density once the sorbent has been saturated, i.e. where the change of volume and density in the adsorbed phase can be assumed negligible. Then, a linear regression allows the estimation of the volume of the adsorbed phase and its density \( \rho^a \)\(^\text{30,37,38}\). For the conversion it is then assumed that the estimated value for \( \rho^a \) is valid for the whole isotherm, and thus for the whole pressure range; \( q^{\text{abs}} \) and \( q^{\text{ex}} \) are then related by

\[ q^{\text{abs}} = q^{\text{ex}} \left( 1 - \frac{\rho^b}{\rho^a} \right)^{-1} \]  \hspace{1cm} (2.5)
To determine $\rho^a$ of CO$_2$ on each sample, the CO$_2$ isotherm at a temperature of 45 °C was measured up to approximately 170 bar, which is well into the linear region described above. The temperature of 45 °C was chosen for this as it is above the critical temperature of CO$_2$ (31 °C), thereby avoiding any phase transitions. For N$_2$ the experimental setup does not allow to reach the required conditions so as to determine $\rho^a$ by the method described above. As is common when it is not experimentally accessible, the adsorbed phase density of N$_2$ was assumed to be equal to the liquid density at the boiling point, i.e. $\rho^a = 28.8 \pm 0.4$ mol/L. The same relative error as for the 13X/CO$_2$ system was assumed to allow proper error propagation calculations.


2.1.4 Binary adsorption measurements

The binary adsorption measurements were performed with the same setup as the single component measurements. A schematic of the setup used is shown in Figure 2.1. The core principle of the binary adsorption measurements relies on the fact that the void volume of the system is known. The method of measurement consists of introducing a feed of a known composition and letting the system equilibrate. Once equilibrium is reached, the density and composition of the gas phase are determined (by the MSB and by GC, respectively). The total amount of material is also known, as it is the sum of the gas phase and the excess adsorbed amount, and its composition is that of the feed gas. As the total amounts of each component in the system are known, and the individual amounts in the gas phase, the adsorbed excess amounts of each component can be deduced. The method is described in detail in Ottiger et al.\textsuperscript{30} Key differences to the methods used by Ottiger et al. and Schell et al. are summarized below\textsuperscript{29,30}. The secondary adsorption cell as indicated in Figure 2.1 provides a means to add additional sample to induce a more pronounced compositional change in the gas phase due to adsorption, which is then detected by the GC. That part of the setup, as surrounded by the dashed frame shown in Figure 2.1, is submerged in a Huber Polystat (Renggli, Switzerland)\textsuperscript{9}. It is operable up to 200 °C. To ensure complete regeneration of the sample, we did not make use of the secondary adsorption cell. Instead, to minimize the dead volume in the system a stainless steel cylinder of known volume was used to occupy the secondary adsorption cell. In this way, sorbent is only present in the MSB, and thus can be regenerated at 400 °C. A number of test points were measured to make sure that the compositional change due to adsorption in the gas phase was sufficiently large to be detected by the GC. There is minor leakage present in this setup, which may lead to accumulation of one component in the gas phase. Thus, there is a small penalty
in letting the system equilibrate over an extended period of time. It was observed that a suitable indicator to define equilibrium was when the weight change was less than 0.3 mg per hour. This criterion was used in all binary adsorption experiments in this work. A maximum number of three subsequent equilibrium points were measured before regenerating the system. At every measurement point at least four GC measurements were performed to ensure a representative gas phase composition. Each of the GC measurements requires a minor interference with the system since a small volume is expanded in the sampling loop as shown in Figure 2.1. This was accounted for in the evaluation of the data by a mass balance over the system:

\[
m_i^{\text{eff}} = \sum_{j=1}^{N_m} w_i^{\text{feed}} m_i^{\text{feed}} - \sum_{j=1}^{N_m-1} w_{i,j} \Delta m_j^{\text{sample}}
\]  

(2.6)

This expression yields the corrected amount of component \(i\) in the system, \(m_i^{\text{eff}}\). \(m_i^{\text{feed}}\) is the amount of fluid fed to the system with weight fraction \(w_i^{\text{feed}}\). \(\Delta m_j^{\text{sample}}\) is the mass difference before and after each of the GC measurements and is obtained by the weight response of the MSB. \(w_{i,j}\) is the weight fraction of component \(i\) in the fluid phase sample \(j\) as determined by the GC measurements. Finally, \(N_m\) indicates the number of preceding measurements and ranges in our measurements from 1 to 3. It is worth noting that for the first measurement point \(m_i^{\text{eff}} = m_i^{\text{feed}} w_i^{\text{feed}}\).
2.2 Modeling of the adsorption equilibrium

2.2.1 Single component

The data obtained for pure component adsorption were described with a Sips isotherm\textsuperscript{39,40}. The Sips model expands the standard Langmuir by introducing a third parameter that accounts for a distribution of affinity of the surface sites towards the sorbate molecules as follows

\[ q = \frac{q_i^{\infty} (b_i P)^{c_i}}{1 + (b_i P)^{c_i}} \]  

(2.7)

where \( i \) indicates the component (i.e. CO\textsubscript{2} or N\textsubscript{2}), \( P \) the pressure, \( q_i^{\infty} \) represents the saturation capacity, \( b_i \) the affinity constant, and \( c_i \) the heterogeneity parameter. The larger the deviation of \( c_i \) from unity, the larger is the non-uniformity of the surface for component \( i \). Note that for \( c_i = 1 \) the Langmuir isotherm is obtained.

**Temperature dependence:** Each of the quantities \( q_i^{\infty}, b_i, \) and \( c_i \) vary with temperature; this dependence was described the following way:

\[ q_i^{\infty}(T) = q_{i,\text{ref}}^{\infty} \exp \left( \chi_i \left( \frac{T}{T_{\text{ref}}} - 1 \right) \right) \]  

(2.8)

\[ b_i(T) = b_{0,i} \exp \left( \frac{Q_{b,i}}{RT} \right) \]  

(2.9)

\[ c_i(T) = c_{\text{ref},i} + \alpha_i \left( \frac{T}{T_{\text{ref}}} - 1 \right) \]  

(2.10)

where \( T \) is the temperature, \( R \) is the universal gas constant, \( q_{i,\text{ref}}^{\infty} \) and \( c_{\text{ref},i} \) are reference values at a reference temperature \( T_{\text{ref}} \), and \( \chi_i, b_{0,i}, Q_{b,i}, \) and \( \alpha_i \) are parameters that will be fitted to experimental data.
2.2 Modeling of the adsorption equilibrium

2.2.2 Binary system

To convert the individual excess adsorbed amount $q_{i}^{\text{ex}}$ in the mixture to the absolute quantity $q_{i}^{\text{abs}}$, a similar method as for the pure component case, Eq. (2.5), applies. The relationship between $q_{i}^{\text{ex}}$ and the absolute adsorbed amount is given by

\[
q_{i}^{\text{abs}} = q_{i}^{\text{ex}} \left(1 - \frac{\rho_{i}^{b} y_{i}}{\bar{\rho}_{a} x_{i}}\right)^{-1}
\]

(2.11)

where $y_{i}$ is the mole fraction of component $i$ in the bulk phase, $x_{i}$ is its mole fraction in the adsorbed phase, and $\bar{\rho}_{a}$ is the density of the adsorbed mixture. This relationship is derived from the definition of the adsorbed excess, which as for single component systems is the difference between the amount of species $i$ in the adsorbed phase and the amount that would be present in that same space if the density and composition were equal to the bulk phase. It is worth noting that this expression reduces to Eq. (2.5) for the case of a pure component. While the pure component adsorbed phase densities can be estimated via the method described in Section 2.1.3, an assumption with regard to the mixture adsorbed phase density $\bar{\rho}_{a}$ must be made. Since an inherent assumption of IAST is ideal behavior in the adsorbed phase, an obvious approximation for $\bar{\rho}_{a}$ is provided by applying volume additivity:

\[
\frac{1}{\bar{\rho}_{a}} = \frac{x_{\text{N}_{2}}}{\rho_{\text{N}_{2}}^{a}} + \frac{x_{\text{CO}_{2}}}{\rho_{\text{CO}_{2}}^{a}}
\]

(2.12)

This assumption is made throughout this work.
2.2.3 Extended Sips isotherm

An empirical extension of the pure component Sips isotherm is given by:

\[ q_i = \frac{q_i^\infty (b_i p_i)^{c_i}}{1 + \sum_{j}^{N_C} (b_j p_j)^{c_j}} \]  

(2.13)

where \( N_C \) denotes the number of components (in the following the upper limit for the sum, \( N_C \), is omitted for the sake of clarity). The advantages of this equation are (i) that only pure component parameters are required and (ii) that it is explicit, which is convenient to use in a dynamic process model. When all the heterogeneity parameters are unity, equation (Eq. (2.13)) reduces to the multicomponent Langmuir isotherm.

2.2.4 Adsorbed solution theory

Another way to predict binary adsorption equilibrium from pure component isotherm parameters is the application of a thermodynamically consistent framework introduced by Myers and Prausnitz\textsuperscript{41}; the adsorbed solution theory. At the same chemical potential of the gas and adsorbed phase, the equilibrium relation for mixed-gas adsorption for an ideal gas phase is:

\[ P y_i = P_i^0 (\Pi, T) x_i \gamma_i (\Pi, T, \underline{x}) \]  

(2.14)

where \( P \) is the system pressure and \( y_i \) the mole fraction of component \( i \) in the gas phase. \( P_i^0 (\Pi, T) \) is the hypothetical equilibrium pressure of the pure component at the same \( \Pi \) and \( T \) of the mixture and is obtained
2.2 Modeling of the adsorption equilibrium

from:

\[ z = \frac{\Pi A}{RT} = \int_{0}^{P_i^0} \frac{q_i(P_i)}{P_i} dP_i \] (2.15)

where \( z \) is the reduced surface potential, \( A \) the specific surface area of the sorbent, and \( q_i(P_i) \) is the adsorption isotherm equation for component \( i \). The left-hand side of Eq. (2.15) must be equal for all components. For the Sips isotherm used in this work, the reduced surface potential can be expressed in closed form as:

\[ z = \frac{q_i^\infty \ln \left( 1 + (b_i P_i^0)^{c_i} \right)}{c_i} \] (2.16)

To obtain the total amount adsorbed, \( q_t \), an expression as derived from the definition of the molar area of mixing is used:\(^{41}\)

\[ \frac{1}{q_t} = \sum_i \frac{x_i}{q_i(P_i^0)} + \sum_i x_i \left( \frac{\partial \ln \gamma_i}{\partial z} \right)_{T, \bar{x}} \] (2.17)

This equation complies with the Gibbs-Duhem relation.\(^{42}\) Finally, the number of moles of each component adsorbed is:

\[ q_i = x_i q_t \] (2.18)

If the adsorbed phase behaves ideally, \( \gamma = 1 \) for all components; in this case the ideal adsorbed solution theory is obtained (IAST), and the pure component adsorption data are sufficient to predict the binary adsorption equilibrium. When the activity coefficients are not unity, the real adsorbed solution theory is obtained, and the activity coefficients must be determined in some way. Usually, binary adsorption data is necessary for this. Hefti et al. offered a detailed discussion of the constraints that must be met by the activity coefficients and available models for the
determination of \( \gamma \).\(^{43}\)

### 2.2.5 Parameter estimation

The estimation of the Sips isotherm parameters was carried out by comparing the total adsorbed amounts measured in the single component experiments to values obtained from Eq. (2.7). This was done by finding the maximum likelihood estimate (MLE) of the parameter vector \( \theta = [\theta_1, \theta_2, \ldots, \theta_j, \ldots, \theta_{N_\theta}] \) by minimizing the following objective function

\[
\Phi_p(\theta) = \frac{1}{N_d} \ln \sum_{j=1}^{N_T} \sum_{k=1}^{N_j} \left( q_{\text{exp}}(T_j, p_{jk}) - q(\theta, T_j, p_{jk}) \right)^2
\]

(2.19)

where \( N_d \) is the number of experimental points of all experiments for a given sorbate-sorbent pair, \( N_T \) is the number of temperatures, \( N_j \) the number of experimental points at temperature \( T_j \), and \( q_{\text{exp}}(T_j, p_{jk}) \) and \( q(\theta, T_j, p_{jk}) \) are the experimental and calculated adsorbed amounts. In this way, \( \theta^* \) is obtained as the simultaneous fit of the experimental data sets at all temperatures. The built-in Matlab local optimization routine \texttt{fmincon} using a sequential quadratic programming algorithm was employed in combination with \texttt{GlobalSearch} to cover a large set of initial points in order to find the optimum.\(^{44}\)

In order to reduce the number of parameters, the temperature invariant reference values for the saturation capacity, \( q_{\text{ref},i}^{\infty} \), and for the heterogeneity parameter, \( c_{\text{ref},i} \), were used by setting \( \chi \) and \( \alpha \) in Eqs. (2.8) and (2.10) to zero. The reference values \( q_{\text{ref},i}^{\infty} \) and \( c_{\text{ref},i} \) were defined as the values obtained from a fit to the experiments at \( T_{\text{ref}} = 25^\circ \text{C} \).

The determination of the activity coefficients for the use in RAST is discussed in Hefti et al.\(^{43}\)
2.3 Results and discussion

2.3.1 Pure component isotherms

The pure component (absolute) adsorption data of CO\textsubscript{2} and N\textsubscript{2} on ZSM-5 and on 13X are shown in Figures 2.2 and 2.3, respectively. Isotherms were measured at 25°C, 45°C, 65°C, 100°C and 140°C, a range that was motivated by potential operating conditions in a temperature swing adsorption process for post-combustion capture. Together with the experimental equilibrium data, the corresponding best fits of the Sips isotherm are shown. The estimated parameters are listed in Table 2.1, together with the resulting parameter uncertainty. All of the isotherms are of type I, with a steep initial increase that flattens out as saturation is reached. Furthermore, CO\textsubscript{2} adsorbs more strongly on both sor-
Figure 2.3: Adsorption of pure CO\textsubscript{2} (a) and N\textsubscript{2} (b) on 13X. The symbols are the experimental values; the lines are Sips isotherm fitted to this data. ◦ 25°C, □ 45°C, △ 65°C, × 100°C, ◆ 140°C.

bents and under the whole range of pressure measured in this study. It can also be seen that on 13X, CO\textsubscript{2} has almost reached the saturation capacity at a pressure of 10 bar for the lower temperatures measured, whereas the other systems are still further away from saturation under these conditions. It is clear from the figure that the Sips isotherm describes the experimental data very well, and from the uncertainty intervals for the parameters it is evident that they are well-determined. In order to obtain the absolute amount adsorbed, which is shown in Figures 2.2 and 2.3, the adsorbed phase density $\rho^a$ was assumed to be constant, as discussed in Section 2.1.3. For CO\textsubscript{2} on 13X a density of $\rho^a = 26.58 \pm 0.36$ mol/L was obtained, while for CO\textsubscript{2} on ZSM-5 an adsorbed phase density of $\rho^a = 21.76 \pm 0.71$ mol/L was determined. Because of the smaller pore size of ZSM-5 as compared to 13X a lower $\rho^a$ for CO\textsubscript{2} on ZSM-5 is expected because of the constrained packing of the adsorbed CO\textsubscript{2} molecules. Assuming negligible surface adsorption, an es-
Table 2.1: Pure component parameter estimates for CO\textsubscript{2} and N\textsubscript{2} on ZSM-5 and 13X.

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<thead>
<tr>
<th></th>
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<tr>
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<tr>
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<td>0</td>
</tr>
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</tr>
<tr>
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<td>[bar\textsuperscript{-1}]</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>[kJ/mol]</td>
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</tr>
<tr>
<td>c\textsubscript{i}</td>
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<td>[-]</td>
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</tr>
<tr>
<td>\alpha\textsubscript{i}</td>
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<td>0</td>
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<tr>
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</tr>
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The binary adsorption data for CO\textsubscript{2}/N\textsubscript{2} mixtures on ZSM-5 and 13X at pressures of 1.2 bar, 3 bar and 10 bar and at temperatures of 25°C and 45°C are shown in Figures 2.4 and 2.5. The data shown refers to the absolute adsorbed amount, as it was for the pure component adsorption data. The absolute adsorbed amount was obtained from the estimate of the pore volume of the zeolite may be extracted: For ZSM-5 it is 0.155 ± 0.004 cm\textsuperscript{3}/g and for 13X 0.270 ± 0.003 cm\textsuperscript{3}/g. A comparison of these values with other works is provided by Hefit et al.\textsuperscript{43}
Figure 2.4: Binary adsorption equilibria of the CO$_2$ and N$_2$ mixture on ZSM-5. The symbols are the experimental values; also shown are the predictions according to IAST (dashed lines) and the extended Sips isotherm (dotted lines). Adsorption at the pure component limits $y_{CO_2} = 0$ and $y_{CO_2} = 1$ are indicated with open circles.

excess adsorbed amount under the assumption of volume additivity in the adsorbed phase (see Eq. (2.12)) and by using the pure component adsorbed phase density as reported above. All measurements reported here were performed with three different feed mixtures; their compositions are indicated in the figures at 1.2 bar as vertical dashed lines. The fact that the experimental points are all shifted to the left from the feed composition is due to the selectivity of the sorbent – as CO$_2$ is selectively adsorbed, the gas phase is depleted of CO$_2$. This is especially evident at low pressure; at higher pressures, the relative importance of the ad-
**2.3 Results and discussion**

Figure 2.5: Binary adsorption equilibria of CO$_2$ and N$_2$ on 13X. The symbols are the experimental values; model predictions are lines: Extended sips (dotted), IAST (dashed), RAST (solid). RAST is complemented with the 1-parameter Wilson model fits. In (a) and (d) the feed compositions are shown as vertical dashed lines. Adsorption at the pure component limits $y_{CO_2} = 0$ and $y_{CO_2} = 1$ are indicated with open circles.

The adsorbed phase in the system is reduced, and accordingly the composition shift is lessened. It is clear from the data presented that both sorbents selectively adsorb CO$_2$, and that 13X shows a much higher selectivity, with very little N$_2$ adsorbing in the presence of CO$_2$. Along with the experimental adsorption data, the predictions obtained from the binary adsorption models used is presented.

**Extended Sips** The extended Sips predictions are shown as dotted lines
in Figures 2.4 and 2.5. At both temperature levels, the prediction describe the experimental data rather well for the two lower pressure levels, 1.2 and 3 bar. At 10 bar, however, the extended Sips underpredicts the adsorption of CO$_2$ while overpredicting the adsorption of N$_2$. Thus, this model underpredicts the competition that CO$_2$ represents for N$_2$. Overall the description is still relatively good, particularly considering the simple nature of the model.

**IAST** The predictions of binary adsorption obtained by IAST are shown as dashed lines in Figures 2.4 and 2.5. For ZSM-5, the experimental data are well-described by this model under all conditions tested, even at a pressure of 10 bar, where the extended Sips was not able to correctly predict the data. On 13X, the prediction at low pressure is rather good; but the difference to the extended Sips is not very large. As pressure increases, the difference becomes more significant, but while the extended Sips underestimated the selectivity for CO$_2$, IAST overpredicts it, resulting in higher adsorbed amounts of CO$_2$ and lower amounts of N$_2$ than seen in experiment.

**RAST** The deviations from ideal behavior of the adsorbed phase as predicted by IAST are rather low. Nevertheless, on 13X at elevated pressure they are significant. To obtain a better description, Hefti et al. fitted parameters to a model used to obtain activity coefficients by using the experimental data on 13X. A detailed discussion of the model, and a simplification of the three-parameter model that reduces the number of parameters to one, is presented in that work. In Figure 2.5, the binary adsorption equilibrium calculated using RAST is shown as a solid line.

### 2.4 Conclusions

In this chapter the methods used at SPL to characterize the adsorption equilibrium, both for pure gases and for mixtures, was presented. The
experimental setup and procedure was reported by way of summarizing the work done to study the adsorption equilibrium of CO$_2$ and N$_2$ on zeolites ZSM-5 and 13X.

The pure component adsorption equilibrium of both components on both sorbents could be described well with a Sips isotherm over the entire range of conditions tested. In addition, the estimated parameters were well-defined. To describe the equilibrium of gas mixtures of the two components, three approaches were compared. At low pressure, both the extended Sips and IAST predicted the adsorption equilibrium well using only the pure component data. At higher pressures, IAST showed a much better description of the data on ZSM-5, and a somewhat better prediction on 13X. The data on 13X showed that a better description is possible with RAST, but the determination of the activity coefficients required binary data. In practice, binary data may be difficult to obtain; for cases like this, IAST can be a powerful tool to design processed with gas mixtures where only the pure component isotherm data is known. And in cases that require a large number of evaluations of the adsorption equilibrium, the extended Sips might be the model of choice, as it is an explicit function that is easily implemented and can be calculated quickly. In the following chapters, both the extended Sips and IAST will be used, depending on the sorbent material and the gases used as well as the conditions present.

Regarding the two materials, 13X showed a significantly higher capacity for CO$_2$, as well as higher selectivity than ZSM-5. Indeed, simulations with an equilibrium-based model showed that ZSM-5 would have great difficulty achieving high purity CO$_2$ in a simple TSA process, as would be achievable with 13X. While the adsorption equilibrium is merely one aspect that determines the usefulness of a sorbent for a separation, the results reported here show that 13X is the more promising candidate for post-combustion capture applications. Therefore it is the material that
2. Adsorption Equilibrium

was used in the work presented in Chapter 5.

**Notation**

**Roman**

- $A$: sorbent specific surface area \([\text{m}^1]\)
- $b$: Sips isotherm equilibrium constant \([\text{Pa}^{-1}]\)
- $c$: exponent in Sips isotherm [-]
- $m$: adsorbed mass (specific) \([\text{kg/kg}]\)
- $V$: volume \([\text{m}^3/\text{kg}]\)
- $M$: measured mass (total) \([\text{kg}]\)
- $M_w$: molecular weight \([\text{kg/mol}]\)
- $p$: partial pressure \([\text{Pa}]\)
- $P$: total fluid pressure \([\text{Pa}]\)
- $q$: adsorbed amount \([\text{mol/kg}]\)
- $Q$: exponent for temperature dependence of $b$ [-]
- $R$: universal gas constant \([\text{J}/(\text{mol K})]\)
- $T$: temperature \([\text{K}]\)
- $N_c$: number of species [-]
- $N_m$: number of measurements [-]
- $x$: mole fraction in the adsorbed phase [-]
- $y$: mole fraction in the bulk phase [-]
- $z$: reduced surface potential \([\text{mol/kg}]\)

**Greek**

- $\alpha$: temperature dependence parameter for $c_i$ [-]
- $\gamma$: activity coefficient [-]
- $\rho$: density \([\text{kg/m}^3]\)
- $\chi$: temperature dependence parameter for $q_i^\infty$ [-]
- $\Pi$: spreading pressure \([\text{N/m}]\)
- $\Phi$: objective function \([\text{N/m}]\)
2.4 Conclusions

\[ \theta \] parameter vector

**Sub- and Superscript**

- \( a \): adsorbed phase
- \( \text{abs} \): abolute
- \( b \): bulk phase
- \( \text{ex} \): excess
- \( \text{exp} \): experimental
- \( \text{eff} \): effective
- \( \text{feed} \): feed
- \( i, j \): component \( i, j \)
- \( m \): measurement \( m \)
- \( \text{net} \): net
- \( \text{ref} \): reference
- \( s \): solid
- \( \text{sample} \): sample
- \( t \): total
- \( T \): temperature
- \( \text{zeo} \): zeolite
- \( \infty \): sorbent saturation
2. Adsorption Equilibrium
Chapter 3

Prediction of ternary breakthrough experiments based on binary data

In the context of carbon dioxide capture and storage (CCS) as a mitigation option for increasing emissions of CO₂, pressure swing adsorption (PSA) can be a viable technology for the CO₂/H₂ separation within an integrated gasification combined cycle (IGCC) power plant. In fact, the energy penalty is largely reduced by exploiting the high pressure of the feed (30 bar to 50 bar) and by avoiding any re-compression of recycle streams. Since in such a process the packed columns experience a large range of pressures, temperatures and flow rates due to the different pressure levels and to the heat of adsorption, it is important to consider a broad range of operating conditions when determining the adsorption

specific parameters involved in the mathematical model used process design.

In a previous work, the pure and binary equilibrium adsorption of CO$_2$, H$_2$ and N$_2$ on an activated carbon was studied in a rather large interval of temperatures (25 °C to 140 °C), and pressures (0.1 bar to 200 bar). A follow-up study focused on the estimation of heat and mass transfer parameters for three mixtures of CO$_2$ and H$_2$ in an activated carbon bed. The mathematical model was applied on the one hand for the design and optimization of a PSA process for the CO$_2$/H$_2$ separation under adiabatic conditions in the context of pre-combustion CO$_2$ capture. On the other hand and for the same separation, the same model was used to describe with satisfactory agreement a set of PSA laboratory experiments. In both cases the same competitive adsorption isotherms obtained through static measurements and the same mass transport parameters estimated through fixed-bed experiments were used. The heat transfer coefficients however, while not needed in the optimization study because of the adiabatic conditions (typical of large scale PSA processes), had to be re-estimated for the comparison for experiments; we believe that this was due to the drastically different conditions – in terms of column loading and typical gas phase composition – experienced by the fixed beds during breakthrough experiments and cyclic operations.

Since impurities are generally present within gas streams to be processed, it is important to also validate a mathematical model for multicomponent systems before proceeding to process design calculations. This can be performed by measuring breakthrough responses of pure component data, and combining the obtained heat and mass transfer data for the prediction of multicomponent systems. However, in order to cover a large interval of experimental conditions, this approach requires a substantial amount of experiments.

This is the context of this work, whose goal is to estimate transport pa-
rameters from binary CO$_2$/N$_2$ breakthrough experiments, and to apply the obtained results, together with those of the binary CO$_2$/H$_2$ system$^{17}$ for the prediction of ternary CO$_2$/N$_2$/H$_2$ experiments performed for various compositions, temperatures, pressures and flow rates. This shows that only two independent sets of breakthrough experiments are required for the calibration of the mathematical model, using which ternary experiments can be successfully predicted.

The structure of this work is as follows: in Section 3.1 the experimental setup and procedure are presented. Section 3.2 deals with the estimation of parameters and their uncertainty. Section 3.3 addresses the issue of the need for an accurate measurement of the flow velocity first, and discusses then the results of the binary CO$_2$/N$_2$ experiments; finally the ternary experiments are presented and discussed. In discussing the binary breakthrough experiments, a selection of the experimental data are shown to help highlight certain aspects as needed. The full set of binary experiments is available in the supplementary information, in Figure A.2 to Figure A.7. All ternary experiments are presented and discussed in the main text of the manuscript.

3.1 Experimental

3.1.1 Materials and equilibrium adsorption isotherms

The fixed bed experiments were performed using a stainless steel column packed with a commercial activated carbon (AP3-60 from Chemviron Carbon, Germany) with a pellet size of 3 mm. The adsorption equilibria on this adsorbent have previously been characterized by measuring excess adsorption isotherms of pure CO$_2$, N$_2$, and H$_2$, as well as binary adsorption of the mixtures CO$_2$/N$_2$ and CO$_2$/H$_2$$^{29}$, covering a wide range of pressures from 0.1 bar to 150 bar and temperatures from 25 $^\circ$C
to 140 °C. This allows for the description of the temperature dependence of adsorption as well as the determination of the heat of adsorption, essential features needed to model adsorption processes, where the temperature can vary a lot.

The gases used were obtained from Pangas (Dagmarsellen, Switzerland) with purities higher than 99.9% for the pure gases; the gas mixtures were produced by Pangas with a relative error of ±2%. To calibrate the mass spectrometer, two ternary calibration mixtures were used. They were produced by Pangas, and have a relative error of ±1%.

3.1.2 Experimental setup

The breakthrough experiments were performed using a fixed bed setup, a schematic of which is shown in Figure 3.1 (for more details, see Casas et al, 2012). Concerning the breakthrough experiments, the only significant change made to the setup is that the original back pressure regulator (BPR) was replaced by an electronic BPR from Bronkhorst High-Tech BV (Ruurlo, Netherlands).

The stainless steel column has an inside diameter of 2.5 cm and a length of 1.2 m. An electrical heater (Moser TMT AG, Hombrechtikon, Switzerland) controlled by a thermocouple on the outside wall of the column enables experiments at different temperatures, while a back pressure regulator (BPR) (Bronkhorst High-Tech B.V.) is used to control the pressure in the system. The flow rate of the feed stream is controlled by a mass flow controller (MFC) (Bronkhorst High-Tech B.V.). The BPR, MFC, as well as the automatic valves are operated through LabVIEW software.

During the experiments, the temperature inside the column is recorded by five thermocouples positioned along its central axis, at 10 cm, 35 cm, 60 cm, 85 cm, and 110 cm from the inlet. The pressure is measured by two
3.1 Experimental

Figure 3.1: Flowsheet of the fixed-bed setup used for the breakthrough experiments. The five thermocouples in the column are placed along the center axis, at 10 cm, 35 cm, 60 cm, 85 cm and 110 cm from the inlet of the column. The setup is in principle the same as the one presented in Casas et al. 17

pressure sensors, one before and one after the column. The composition of the product stream is measured on line by a mass spectrometer (MS) (Pfeiffer Vacuum Schweiz AG, Switzerland).

3.1.3 Experimental procedure

In general, the procedure is the same as reported earlier 17. The column is first heated to the desired experimental initial temperature, and then filled with helium (inert) to the desired pressure. Once that is reached, the feed is switched to the binary or ternary feed of interest. The flow rate during the experiment is maintained constant by the MFC. It should
be noted that for the calibration of the MS it is no longer sufficient to use the feed mixture, as both CO$_2$ and N$_2$ produce a signal for a mass of 28. To account for this, two gas mixtures with different molar ratios of CO$_2$ to N$_2$ are used to determine the contribution of each of the components to the signal.

After each experiment the bed is regenerated by applying vacuum for 45 minutes at the temperature of the experiment. Repetition of experiments after this regeneration has shown good reproducibility. After a day of experiments, i.e. after up to four experiments, a more thorough regeneration of the bed is performed, where the column is heated to a temperature of 150°C for 90 minutes while applying vacuum.

In this study, experiments at four different pressures (1 bar, 5 bar, 10 bar and 20 bar) and two different temperatures (25°C and 45°C) were performed for each gas mixture used. Additionally, at 10 bar experiments were performed at three different feed flow rates (10 cm$^3$/s, 20 cm$^3$/s and 30 cm$^3$/s). Five different gas mixtures were used: three binary mix-
3.2 Modeling of fixed fed breakthrough experiments

Table 3.2: Overview of the experiments conducted with ternary mixtures with CO$_2$/N$_2$/H$_2$ molar ratios of 40/30/30 and 15/80/5 at two different temperatures (25 °C and 45 °C) and four different pressures (1 bar, 5 bar, 10 bar and 20 bar)

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<td>30 cm$^3$/s</td>
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tures containing CO$_2$ and N$_2$ at molar ratios of 10/90, 50/50, and 80/20, and two ternary mixtures consisting of H$_2$/N$_2$/CO$_2$ at molar ratios of 5/80/15 and 30/30/40, respectively. A summary of the experiments performed is reported in Tables 3.1 and 3.2.

3.2 Modeling of fixed fed breakthrough experiments

The evaluation of the breakthrough experiments is done by describing them with the 1D non-equilibrium mathematical model described in detail in Casas et al.$^{17}$, and summarized in Section 1.4.1. This model incorporates material and energy balances, as well as constitutive equations that are used to describe the pressure drop across the column, the equilibrium adsorption isotherm, the heat capacity of the gas and of the adsorbed phase, and the heat transfer to the column wall. Additionally
3. Prediction of ternary breakthrough experiments based on binary data

The model also accounts for the effect that the downstream piping has on the measured compositions. The governing equations are listed in Table 1.1 and the used parameters are reported in Tables 3.3 and 3.4. The temperature dependent equilibrium adsorption of the studied system was previously measured with static experiments and described with the Sips isotherm by Schell et al.\textsuperscript{29}:

\[ q_{i,\text{eq}} = q_{i,\text{sat}} \frac{(K_i p_i)^{s_i}}{1 + (K_i p_i)^{s_i}} \]  \hspace{1cm} (3.1)

where \( p_i \) is the partial pressure of component \( i \), \( q_{i,\text{sat}} \) and \( K_i \) are its saturation capacity and adsorption equilibrium constant, respectively. The third parameter \( s_i \) accounts for the surface inhomogeneity. For the description of multicomponent adsorption, two models are considered: the multicomponent Sips equation, and the application of ideal adsorbed solution theory (IAST) to pure component Sips isotherms. Both have previously been compared with regards to their ability to predict binary equilibrium data\textsuperscript{29}.

3.2.1 Parameter estimation

Parameter estimation was carried out by comparing measurements taken during the breakthrough experiments to simulations. The observed variables to be compared were the mole fractions of the two components of interest, i.e. N\textsubscript{2} and CO\textsubscript{2} (but not of the inert He), as well as the temperature inside the bed at five positions along the column. The fitting was done by finding the maximum likelihood estimate (MLE) of each of the fitted parameters. The maximum likelihood estimator \( \mathbf{p}^* \) can be determined by minimizing the objective function \( \Phi(p) \):

\[ \Phi_{\text{MLE}}(\mathbf{p}) = \sum_{k=1}^{N_{\text{meas}}} \ln \left( \sum_{j=1}^{N_{\text{obs}}} \left( y_{j,k} - \hat{y}_{j,k}(\mathbf{p}) \right)^2 \right) \]  \hspace{1cm} (3.2)
Table 3.3: Parameters used in the adsorption column model presented in Table 1.1 to describe the breakthrough experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column length</td>
<td>L</td>
</tr>
<tr>
<td>Column inner diameter</td>
<td>$d_i$</td>
</tr>
<tr>
<td>Column outer diameter</td>
<td>$d_o$</td>
</tr>
<tr>
<td>Bulk density of the packing</td>
<td>$\rho_b$</td>
</tr>
<tr>
<td>Particle density</td>
<td>$\rho_p$</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>$\epsilon_b$</td>
</tr>
<tr>
<td>Total porosity</td>
<td>$\epsilon_t$</td>
</tr>
<tr>
<td>Particle size</td>
<td>$d_p$</td>
</tr>
<tr>
<td>Solid heat capacity</td>
<td>$C_s$</td>
</tr>
<tr>
<td>Heat capacity of the wall</td>
<td>$C_w$</td>
</tr>
<tr>
<td>Fluid viscosity</td>
<td>$\mu$</td>
</tr>
<tr>
<td>Isotherm parameters and heats of adsorption</td>
<td>$h_L, h_w$</td>
</tr>
<tr>
<td>Mass transfer coefficient</td>
<td>$k_i$</td>
</tr>
</tbody>
</table>

where $N_{\text{meas}}$ is the number of measured outputs, $N_{\text{obs}}$ is the number of observations, $y_{j,k}$ is the measured output $k$ at time $j$, and $\hat{y}_{j,k}(\mathbf{p})$ is the corresponding simulated value.

The parameters to be estimated are the mass transfer coefficients $k_{\text{CO}_2}$ and $k_{\text{N}_2}$ and the heat transfer coefficient $h_L$. As described in Casas et al.$^{17}$, the heat transfer coefficient had previously been fitted to experiments carried out with the same packed column and under similar conditions as a function of the initial Reynolds number ($\text{Re}_0 = \rho_0 v d_p / \mu$):

$$\text{Nu} = \frac{h_L d_i}{K_L} = \eta_1 (\text{Re}_0)^{\eta_2} \exp(-6d_p/d_i)$$

(3.3)

where $d_i$ is the inner diameter of the column, $K_L$ the thermal conductivity, and $d_p$ the diameter of the adsorbent particles. The bed-wall heat
3. Prediction of ternary breakthrough experiments based on binary data

Table 3.4: Parameters to describe the temperature dependent Sips isotherm shown in Eq. (3.1)\(^2\)

<table>
<thead>
<tr>
<th></th>
<th>CO(_2)</th>
<th>H(_2)</th>
<th>N(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q_{i,\text{sat}} = a_i \exp\left(\frac{-b_i}{RT}\right))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a_i) [mmol/g]</td>
<td>1.38</td>
<td>6.66</td>
<td>2.82</td>
</tr>
<tr>
<td>(b_i) [J/mol]</td>
<td>-5628</td>
<td>0</td>
<td>-1706</td>
</tr>
<tr>
<td>(K_i = A_i \exp\left(\frac{-B_i}{RT}\right))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_i) [MPa(^{-1})]</td>
<td>1.68 \times 10(^{-2})</td>
<td>6.97 \times 10(^{-4})</td>
<td>1.74 \times 10(^{-3})</td>
</tr>
<tr>
<td>(B_i) [J/mol]</td>
<td>-9159</td>
<td>-9826</td>
<td>-12,661</td>
</tr>
<tr>
<td>(s_i = \alpha_i \text{atan}\left(\beta_i (T - T_{\text{ref},i})\right) + s_{\text{ref},i})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_i) [-]</td>
<td>0.072</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\beta_i) [K(^{-1})]</td>
<td>0.106</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(c_{\text{ref},i}) [-]</td>
<td>0.83</td>
<td>0.96</td>
<td>0.86</td>
</tr>
<tr>
<td>(T_{\text{ref},i}) [K]</td>
<td>329</td>
<td>273</td>
<td>273</td>
</tr>
<tr>
<td>Heat of adsorption (\Delta H) [J/mol]</td>
<td>26,000</td>
<td>9,800</td>
<td>15,600</td>
</tr>
</tbody>
</table>

Heat of adsorption \(\Delta H\) is predicted from this correlation using the parameters \(\eta_1 = 41.13\) and \(\eta_2 = 0.32\)\(^\text{17}\), and the mass transfer coefficients for both CO\(_2\) and N\(_2\) are fitted individually for all binary breakthrough experiments.

For a correct estimation of the transport parameters an accurate prediction of the breakthrough times is crucial. These are determined by the adsorption capacity under the experimental conditions and by the feed velocity. The equilibrium adsorption of the pure components is well known from the extensive measurements carried out previously\(^2\), and has been shown to be well described by the Sips isotherm. For binary N\(_2\)/CO\(_2\) adsorption, IAST provided a somewhat better prediction of the equilibrium adsorbed amount. To gauge the impact of the model uncertainty, the two models are compared with regards to their description of the breakthrough experiments. More significant is the uncertainty in
3.2 Modeling of fixed fed breakthrough experiments

the measured feed flow rate. The mass flow controllers have an accuracy of ±2% of the full scale of the operating range, thus resulting in an uncertainty of under 5% of the set point for most experiments. At low mass flow rates however, as is the case for the experiments at low pressures, the uncertainty can be of the same order of magnitude as the desired flow rate. The feed velocity was therefore regarded as a model parameter to be estimated along with the transport parameters.

For all parameters estimations, a global optimization was carried out by running local optimizations with an interior-point algorithm from several trial points. This was performed with the GlobalSearch routine provided in the optimization toolbox of Matlab together with the fmincon routine.

3.2.2 Parameter uncertainty

The sensitivity of the model to a fitted parameter \( p_i \) was estimated qualitatively by assessing the sharpness of the minimum of the objective function of Eq. (3.2) in the vicinity of the optimal value \( p_i^* \). The interval \( \Delta p_i \) is defined as the range of values of the parameter \( p_i \), for which the objective function lies within a specified range \( \Delta \Phi \):

\[
\Delta p_i = \left\{ p_i : \Phi_{\text{min}} \leq \Phi(p_i, p_j \neq i) \leq \Phi_{\text{min}} \left(1 + \frac{\Delta \Phi}{\Phi_{\text{min}}} \right) \right\} 
\]

(3.4)

where \( \Phi_{\text{min}} = \Phi(p_i^*) \) is the minimum value of the objective function, i.e. its value at the optimal point \( p_i^* \). For a given threshold value \( \Delta \Phi/\Phi_{\text{min}} \) the value \( \Delta p_i \) can be determined from the results of the global optimization as illustrated schematically in Figure 3.2(a). The interval \( \Delta p \) is related to how well the fitted parameter \( p_i^* \) is defined, and therefore to the associated uncertainty on the fitted value: a small interval \( \Delta p_i \) indicates that the optimal value \( p^* \) is well-defined, whereas a large value points to a higher level of uncertainty on the fitted value. The fitting uncertainty
3. Prediction of ternary breakthrough experiments based on binary data

Figure 3.2: (a) Scheme of the region near the minimum of the objective function ($\Phi_{\text{min}} = \Phi(p^*)$). The interval $\Delta p$ is defined as the region of values of the parameter $p$ which satisfy $(\Phi(p) - \Phi_{\text{min}}) \leq \Delta \Phi$. For a given threshold value $\Delta \Phi/\Phi_{\text{min}}$ the value $\Delta p$ can be determined. (b) Distribution of the relative deviation of the fitted feed velocity from the setpoint given by the MFC. The part of the distribution located above the limiting value of 1 are shown in gray. (c) Distribution of the relative fitting uncertainty on the feed velocity $\Delta u_F/u_{F}^*$. The outlier indicated with the triangle in both figures refers to the same simulation (B23)

was evaluated in this work for a fixed threshold $\Delta \Phi/\Phi_{\text{min}} = 0.015$. This arbitrary value was chosen so as to yield an appreciable difference in the fitting uncertainty of the different parameters.

The region in the parameter space, which satisfies Eq. (3.4), is delimited by a hypersurface. The interval $\Delta p_i$ defined by Eq. (3.4) is the projection of this hypersurface onto the parameter axes. Note that for a linear model with normally distributed errors and known parameter covariance matrix $V_p$, the confidence region is given by\textsuperscript{46}:

$$
(p - p^*)^T V_p^{-1} (p - p^*) \leq \chi^2_{N_p}(\alpha)
$$

(3.5)

where $\alpha$ is the confidence level and $\chi^2_{N_p}(\alpha)$ is the chi-squared distribution with $N_p$ degrees of freedom. This region is given by a hyperellipsoid, whose extrema can be used to estimate confidence intervals, as an alter-
native to the univariate $t$-statistics. Hence, the analysis carried out in this work is equivalent to estimating confidence intervals as the width of the box enclosing the projected hyperellipsoid, with the differences that the hypersurface is not restricted to a hyperellipsoid, and that the threshold value $\Delta \Phi$ instead of the confidence level $\alpha$ is the arbitrary parameter defining the hypersurface.

### 3.3 Results and discussion

The aim of this work is to establish whether transport parameters obtained using binary experiments can be applied in the accurate description of experiments with ternary gas mixtures. To this end, the set of breakthrough experiments reported in Casas et al.\textsuperscript{17} was expanded by performing the binary experiments listed in Table 3.1. These experiments are then used to estimate a lumped mass transfer coefficient for nitrogen, as well as to confirm the mass transfer coefficient for carbon dioxide that was previously estimated through the experiments with binary CO$_2$/H$_2$ mixtures.

#### 3.3.1 Feed velocity

As discussed in Section 3.2.1 the estimation of transport parameters by fitting of a mathematical model to experimental data requires an accurate value of the feed velocity. Despite high accuracy flow controllers, some uncertainty is always present. The approach used in this work is to treat the feed velocity as a model parameter to be estimated from the experiments themselves. However, when following such an approach, it is important to confirm that the fitted value of the velocity is consistent with the measured flow rate of the instrument. Let us consider the measured flow by the MFC, and its error $\varepsilon_{\text{MFC}}$ with respect to the setpoint.
value $u_{\text{set}}$ as specified by the manufacturer:

$$u_{\text{set}} \pm \varepsilon_{\text{MFC}}.$$ 

Since the feed velocity is fitted to the experimental profiles, the obtained maximum likelihood estimator of the feed velocity $u_F^*$ will generally deviate from the setpoint of the MFC. This deviation $\varepsilon_{\text{set}}$ is given by:

$$\varepsilon_{\text{set}} = |u_F^* - u_{\text{set}}|.$$ 

The ratio between this deviation and the error on the measurement $\varepsilon_{\text{set}}/\varepsilon_{\text{MFC}}$ is a measure of the accuracy of the fitted velocity relative to the inherent uncertainty of the measurement, i.e. a ratio smaller than or equal to one indicates a fitted value that is within the uncertainty of the instrument.

The distribution of this quantity from the sixty experiments and simulations considered in this work is shown in Figure 3.2(b) in terms of experiment counts. A decreasing distribution is observed, where the large majority of the population is found within the range $0 < \varepsilon_{\text{set}}/\varepsilon_{\text{MFC}} \leq 1$, i.e. the fitted velocity lies within the specified accuracy of the flow meter. The precision of the fitting is another interesting quantity. Figure 3.2(c) shows the distribution of the fitting uncertainty as defined in Section 3.2.2, relative to the fitted value: $\Delta u_F/u_F^*$. A distribution with a log-normal character is observed, with a maximum at a value of about 1% – a clear indication that this parameter is rather well-defined. It is worth noting that the evident outlier is the same experiment appearing as outlier also in Figure 3.2(b).
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3.3.2 Binary breakthrough experiments

Figures 3.3 and 3.4 show a representative selection of all the performed binary experiments. The entire set of experiments performed with the 50/50 CO$_2$/N$_2$ mixture at 25 °C is presented in Figure 3.3 and the experiments performed at a pressure of 10 bar and flow rate of 10 cm$^3$/s for the different mixtures are shown in Figure 3.4. The experimental concentration profiles and three of the recorded temperature profiles (10 cm, 60 cm and 110 cm) are shown for each of the selected experiments (symbols), together with the simulations carried out with the fitted mass transfer coefficients (solid lines). Only three of the measured temperature profiles are shown, for the sake of visualization. Showing several experiments is beneficial for the comprehension of the effect of process conditions such as temperature, flow rate and pressure, and to illustrate the quality of the fitting over the entire range of applied conditions. The full set of experimental data from the binary breakthrough experiments is reported in the available supplementary information.

3.3.2.1 Choice of competitive isotherm

As discussed previously, a meaningful fitting of transport parameters depends on an accurate prediction of the timing of the fronts, which is primarily dependent on the feed velocity (discussed above), on the competitive adsorption and on the associated heat effects. Therefore, the description of the competitive adsorption equilibria requires careful consideration. Previous work by Schell et al.\textsuperscript{29} has shown that the Sips isotherm is capable of describing the single component adsorption equilibrium of H$_2$, N$_2$, and CO$_2$ very well. To describe the adsorption equilibrium in the presence of multiple species, two modeling approaches had been compared, namely the ideal adsorbed solution theory (IAST) and an empirical multicomponent Sips equation. Both delivered similar
3. Prediction of ternary breakthrough experiments based on binary data

Figure 3.3: Concentration and temperature profiles for experiments performed at 25 °C for the 50/50 CO₂/N₂ mixture. Experimental data (symbols) are shown together with the simulations carried out with the mass transfer coefficients fitted to each experiment individually, and the heat transfer coefficient predicted from Eq. (3.3). Only three out of five temperature profiles are shown for the sake visibility.
Figure 3.4: Concentration and temperature profiles for experiments performed at 10 bar and 10 cm$^3$/s for the three binary mixtures, at 25 °C (top) and 45 °C (bottom). Experimental data (symbols) together with the simulations carried out with the mass transfer coefficients fitted to each experiment individually, and the heat transfer coefficient predicted from Eq. (3.3). Solid lines use the multicomponent Sips equation to describe competitive adsorption, while the dashed lines use IAST.
3. Prediction of ternary breakthrough experiments based on binary data

results and were capable of describing binary adsorption data, although IAST provided a somewhat better prediction of adsorption of CO$_2$/N$_2$ mixtures. The impact that the choice of model has on simulated concentration and temperature profiles is illustrated in Figure 3.4. It shows the experimental data from six representative experiments, two with each of the binary CO$_2$/N$_2$ mixtures used, along with two sets of simulations. Depicted by solid lines are the results obtained when using the multicomponent Sips model, while the dashed lines show simulation results obtained by applying the IAST framework to the pure component Sips isotherms. To allow for a fair comparison, the velocity was allowed to be adjusted within the limits specified by the MFC manufacturer as discussed in the previous section, while the transport parameters used were the same for both models. A few remarks can be made on the results illustrated in this figure. Firstly, while IAST provides a somewhat better prediction of the front positions for the 80/20 CO$_2$/N$_2$ mixture, its prediction of the 10/90 CO$_2$/N$_2$ breakthrough experiment is not as good as with the multicomponent Sips model. Secondly, the difference in the position of the fronts is noticeable, but significantly smaller than the uncertainty in the feed velocity; this is the reason why the velocity is extracted from the experiments, while the equilibrium adsorption is described using the relatively well-performing models. Thirdly, the simulations with IAST show that the mass transfer coefficients that were fitted using the multicomponent Sips model maintain their validity. As IAST does not provide an explicit solution in general, it is computationally more intensive. For this reason, and to maintain consistency with the previous work by Casas et al.$^{17}$, it was considered most reasonable to use the multicomponent Sips equation for the description of the adsorption equilibrium in the estimation of the transport parameters and the subsequent prediction of the ternary breakthrough experiments.
3.3.2.2 Energy Balance

In principle a better description of the heat transfer could be achieved by considering a more detailed model. In fact the energy balance used in the model is based on a number of simplifications aimed at reducing the complexity of the necessary computations. The most significant of these are:

- a constant heat of adsorption, $\Delta H$, independent of temperature, gas composition and loading;
- a flat temperature profile in the bed, i.e. no radial gradients;
- a heat transfer coefficient $h_L$ that depends on feed and initial conditions, but not on local conditions.

Moreover, the heat conductivity $K_L$ in Eq. (3.3) depends in principle on composition; however, important changes in composition are present within breakthrough experiments, and if the heat transfer coefficient is assumed to be constant throughout each experiment, it is accordingly reasonable to consider a representative value of the heat conductivity and neglect its dependence on composition. Because the same components are present in the different experiments, this representative value is chosen to be the same for all the experiments.

Since the aim of this work is to describe the behavior of the ternary system based on binary measurements, it is useful to carry out the data analysis in a consistent way with the previous work performed with the binary CO$_2$/H$_2$ mixture by Casas et al.$^{17}$ In order to confirm the applicability of the correlation used to describe heat transfer for the binary CO$_2$/N$_2$ system, the heat transfer coefficient $h_L$ was fitted to selected experiments at different pressures, temperatures, feed velocity and composition so as to cover the entire range of Reynolds numbers of
3. Prediction of ternary breakthrough experiments based on binary data

**Figure 3.5:** Heat transfer coefficients fitted to selected experiments (symbols) as compared to the heat transfer coefficient as a function of the initial Reynolds number using Eq. (3.3) with the parameters $\eta_1$ and $\eta_2$ as reported by Casas et al.\textsuperscript{17} (line)

interest. Figure 3.5 shows the fitted $h_L$ values against $Re_0$ together with the predicted heat transfer coefficient from Eq. (3.3) using $\eta_1 = 41.1$ and $\eta_2 = 0.32$\textsuperscript{17}. Generally, a good agreement is observed between the predicted heat transfer coefficient and the fitted values, and the use of the fitted heat transfer coefficient does not improve the fitting significantly, as shown in Figure S1 of the supplementary material. From the above analysis, we conclude that it is justified to predict the heat transfer coefficients in the same way as for the binary CO$_2$/H$_2$ system in Casas et al.\textsuperscript{17}, i.e. with Eq. (3.3), for the fitting of all the binary experiments and for the description of all the ternary experiments.

Due to the aforementioned simplifications, the validity of the heat transfer model considered in this work is limited to the applied conditions, and the model should not be extrapolated to significantly different conditions, such as during desorption, i.e. either purge or blowdown. As a
3.3 Results and discussion

result, regeneration of the column and cyclic processes need a different
treatment of the heat exchange, as discussed in\textsuperscript{25}.

3.3.2.3 Mass transfer

The fitted mass transfer coefficients for CO\textsubscript{2} are shown in Figure 3.6(a) against CO\textsubscript{2} content in the feed. For the sake of visibility, the values fitted to the experiments at 25\textdegree{}C have been shifted by 1\% to the left (empty circles), and the values fitted at 45\textdegree{}C have been shifted by 1\% to the right (filled circles). It is important to note that the fitted mass transfer coefficients are in agreement with the value suggested by Casas et al.\textsuperscript{17} from the binary CO\textsubscript{2}/H\textsubscript{2} breakthrough experiments (shown as a star). The mass transfer coefficients are higher at the higher temperature for all three feed mixtures. In fact, under these conditions it is reasonable to expect a macro- or micro-pore diffusion limited mass transfer, and since these are temperature activated processes, the observed temperature dependency is expected.

The fitted mass transfer coefficients exhibit a dependence on composition, and are significantly lower for the lower CO\textsubscript{2} content in the feed at both temperatures. Different approaches to interpret the effect of pressure and composition on the lumped LDF mass transfer coefficient for nonlinear systems can be found in the literature. Saleman et al.\textsuperscript{45} extracted kinetic adsorption parameters from pure component breakthrough curves and found a linear dependence of the mass transfer coefficient with the inverse of pressure, which was successfully used to predict multicomponent breakthrough curves. Another approach is to consider the extended Glueckhauf approximation, which is strictly valid for linear systems, modified by replacing the Henry’s constant with the ratio $q_{F,i}^{eq}/c_{F,i}$. This approach has shown to provide reasonable estimates for non-linear systems\textsuperscript{23,47,48}. However, this would predict a strong positive correlation of the mass transfer coefficient with pressure, which is not
3. Prediction of ternary breakthrough experiments based on binary data

Figure 3.6: (a) Fitted CO$_2$ mass transfer coefficients against CO$_2$ content in the feed. For better visibility, the values fitted on the experiments at 25°C (empty circles) are shifted by 1 to the left, whereas the values fitted on the experiments at 45°C (filled circles) are shifted by 1 to the right. The mass transfer coefficient for CO$_2$ obtained from Casas et al.\textsuperscript{17} is shown with a star for comparison. The average mass transfer coefficient for a given temperature and CO$_2$ content are shown with the filled triangles. (b) Distribution of the uncertainty associated to the fitted mass transfer parameters $k_{CO_2}$ (black) and $k_{N_2}$ (gray). The height of the bars indicate the number of experiments leading to different values of $\Delta k_i$ shown on the abscissa (bin width 0.05 s$^{-1}$)

in agreement with the results in Saleman et al.\textsuperscript{45} and is not confirmed from the obtained values of $k_{CO_2}$ from this work.

This lack of concordance is likely due to the complex nature of the underlying physical process. In fact, the true driving force for diffusive transport in porous media is the gradient in chemical potential, rather that the gradient in concentration\textsuperscript{49}, and therefore the mass transfer coefficient depends on composition. However, the simplification that within the pore network it is independent of composition is broadly applied and underlies the linear driving force assumption. It is therefore difficult to predict the dependence on composition of the lumped LDF mass transfer coefficient, and it is not in the scope of this work to carry out such an
3.3 Results and discussion

analysis. These results show that in order to obtain a better description of the breakthrough experiments, a temperature and composition dependent expression for the mass transfer coefficient would be required since large variations in temperature and composition are present throughout the column during each breakthrough experiment.

Regarding the mass transfer coefficient of $\text{N}_2$, the same analysis cannot be carried out. In fact, the fitting of the parameter $k_{\text{N}_2}$ was generally ill-defined as compared to that of $k_{\text{CO}_2}$. This becomes clear when considering the uncertainty on the fitted values $\Delta k_{\text{CO}_2}$ and $\Delta k_{\text{N}_2}$. Figure 3.6(b) shows the distribution of these quantities in terms of simulation counts. As described in Section 3.2.2, this quantity is representative of the uncertainty associated to the fitted parameter. For nitrogen, the distribution is generally located towards higher values as compared to CO$_2$, indicating that the fitted values have a large uncertainty. This shows that the performed experiments are not sensitive to $k_{\text{N}_2}$, making a precise estimation of this parameter difficult. However, from the fitting, a lower boundary for this parameter can be estimated at $k_{\text{N}_2} \geq 0.3 \text{s}^{-1}$, with which a good description of the breakthrough experiments is achieved.

From the fitting of the mass transfer coefficients in the binary experiments, representative values for $k_{\text{CO}_2}$ were chosen as the average value for a given temperature and composition of the feed (marked with triangles in Figure 3.6(a)), and as discussed above, a value of $k_{\text{N}_2} = 0.3 \text{s}^{-1}$ was chosen for nitrogen.

3.3.3 Prediction of ternary breakthrough experiments

The mass transfer coefficients determined in this work are finally combined with the mass transfer coefficient of hydrogen, and the predictive correlation for heat transfer in order to describe the performed ternary breakthrough experiments. While the transport parameters are fixed as
3. Prediction of ternary breakthrough experiments based on binary data

Table 3.5: Overview of the transport parameters used for the prediction of the ternary breakthrough experiments. The different ternary mixtures are referred to as mix $y_{CO_2}/y_{N_2}/y_{H_2}$

<table>
<thead>
<tr>
<th>mix</th>
<th>$k_{CO_2}$ [s$^{-1}$]</th>
<th>$k_{N_2}$ [s$^{-1}$]</th>
<th>$k_{H_2}$ [s$^{-1}$]</th>
<th>$h_L(Re_0)$ (Eq. (3.3))</th>
<th>$h_w$ [W/(m$^2$ K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>mix 15/80/5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T = 25^\circ$C</td>
<td>0.04</td>
<td>0.3</td>
<td>1.0</td>
<td>41.13</td>
<td>0.32</td>
</tr>
<tr>
<td>$T = 45^\circ$C</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mix 40/30/30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T = 25^\circ$C</td>
<td>0.11</td>
<td>0.3</td>
<td>1.0</td>
<td>41.13</td>
<td>0.32</td>
</tr>
<tr>
<td>$T = 45^\circ$C</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

reported in Table 3.5, the velocity of the feed was fitted similarly as for the evaluation of the binary experiments. The experimental profiles of all the performed breakthrough experiments are presented in Figures 3.7 to 3.10 together with the simulations carried out with the transport parameters obtained from the binary experiments done with the CO$_2$/H$_2$ and the CO$_2$/N$_2$ mixtures.

The experiments with the ternary mixtures performed at 25°C are shown in Figures 3.7 and 3.8. Again, only the temperature profiles located at 10 cm, 60 cm and 110 cm are shown. It must be noted that the plotted temperature range was adjusted to each individual experiment, it is therefore not constant throughout the figures. A good agreement is obtained between experimental profiles (symbols) and simulated profiles (solid lines), for both the concentration profiles as well as for the temperature profiles over the entire set of investigated pressure and flow conditions at 25°C.

Figures 3.9 and 3.10 show the ternary experiments carried out at the higher temperature of 45°C, for which the agreement between measured
profiles (symbols) and predictive simulations (solid lines) is somewhat weaker as compared to the lower temperature. This might be explained by the inhomogeneous initial temperature profile of the column. In fact, a closer look at the measured temperatures at time zero reveals that temperature variations of up to $5^\circ C$ are present. The non-monotonic initial temperature profile is likely to be attributed to a non homogeneous heating along the length of the column. However, the predicted simulations assume a homogeneous initial state of the column. Since temperature variations affect both the capacity and the selectivity of the adsorbent, this unavoidable inconsistency between experiments and simulations is most likely responsible for the less satisfactory agreement.

Although the prediction of the experiments at $45^\circ C$ is not as good as at $25^\circ C$, the shape of the breakthrough fronts clearly show that the mass transfer coefficients obtained from the binary experiments are valid.

### 3.4 Concluding Remarks

This work presents binary CO$_2$/N$_2$ breakthrough experiments on activated carbon under a wide range of temperatures, pressures and flow rates. The estimation of transport parameters of the studied adsorption system is carried out by fitting the appropriate parameters of a mathematical model to the experimental profiles.

In order to use an automated fitting procedure, it is crucial to have an accurate measurement of the feed flow rate, since this quantity greatly affects the position of the fronts. To address this issue, in this study the feed velocity was fitted together with the other parameters, and an extensive analysis of the obtained values and their uncertainty was carried out in order to ascertain the legitimacy of this approach.

For the performed experiments, the profiles were shown to be insensitive
3. Prediction of ternary breakthrough experiments based on binary data

Figure 3.7: Concentration and temperature profiles for experiments performed at 25°C for the 15/80/5 CO₂/N₂/H₂ mixture. Experimental data (symbols) are shown together with the predictive simulations carried out with the mass transfer coefficients determined from the binary experiments, and the predicted heat transfer coefficient. Only three out of five temperature profiles are shown for the sake of visibility
3.4 Concluding Remarks

Figure 3.8: Concentration and temperature profiles for experiments performed at 25 °C for the 40/30/30 CO₂/N₂/H₂ mixture. Experimental data (symbols) are shown together with the predictive simulations carried out with the mass transfer coefficients determined from the binary experiments, and the predicted heat transfer coefficient. Only three out of five temperature profiles are shown for the sake of visibility.
3. Prediction of ternary breakthrough experiments based on binary data

Figure 3.9: Concentration and temperature profiles for experiments performed at 45°C for the 15/80/5 CO₂/N₂/H₂ mixture. Experimental data (symbols) are shown together with the predictive simulations carried out with the mass transfer coefficients determined from the binary experiments, and the predicted heat transfer coefficient. Only three out of five temperature profiles are shown for the sake of visibility.
Figure 3.10: Concentration and temperature profiles for experiments performed at 45°C for the 40/30/30 CO₂/N₂/H₂ mixture. Experimental data (symbols) are shown together with the predictive simulations carried out with the mass transfer coefficients determined from the binary experiments, and the predicted heat transfer coefficient. Only three out of five temperature profiles are shown for the sake of visibility.
to mass transfer coefficients larger than 0.3 s\(^{-1}\), which was the case for nitrogen under the investigated conditions. On the other hand, the mass transfer coefficient for carbon dioxide at different temperatures and for different CO\(_2\) contents of the feed could be estimated.

After calibration for CO\(_2\)/N\(_2\) mixtures, the model presented in Casas et al.\(^{17}\) was used to predict ternary breakthrough experiments for two different feed mixtures of CO\(_2\), N\(_2\) and H\(_2\) performed at different temperatures, pressures and flow rates. Comparison of the experimental and predicted profiles showed a good agreement on the entire range of conditions.

This study can be seen as as proof of concept of how two sets of targeted breakthrough experiments with binary mixtures bearing one common component can be used to fully calibrate the transport parameters of a mathematical model for an accurate prediction of the corresponding ternary system.

It is worth noting that this has been possible in a rather large range of temperature, pressure and compositions, which is important when using the model to simulate cyclic adsorption separation processes. For a more thorough test of the model, it is best to perform a cyclic PSA process until it reached cyclic steady state, and compare the experiment with simulation results. This will be the setting for Chapter 4.

**Notation**

**Roman**

- \(a\) temperature dependence parameter for \(q_{i,\text{sat}}\) [mol/m\(^3\)]
- \(A\) temperature dependence parameter for \(K_i\) [MPa\(^{-1}\)]
- \(b\) temperature dependence parameter for \(q_{i,\text{sat}}\) [-]
- \(B\) temperature dependence parameter for \(K_i\) [J/mol]
3.4 Concluding Remarks

\[ c \] fluid phase concentration [mol/m\(^3\)]

\[ C \] heat capacity [J/(K m\(^3\))]  

\[ d_i \] inside column diameter [m]

\[ d_o \] outside column diameter [m]

\[ d_p \] particle diameter [m]

\[ h_L \] heat transfer coefficient (column-wall) [W/(m\(^2\) K)]

\[ h_w \] heat transfer coefficient (wall-ambient) [W/(m\(^2\) K)]

\[ \Delta H \] heat of adsorption [J/mol]

\[ k \] overall mass transfer coefficient [s\(^{-1}\)]

\[ K_L \] effective axial thermal conductivity in the fluid [W/(m K)]

\[ K \] Sips isotherm equilibrium constant [Pa\(^{-1}\)]

\[ L \] column length [m]

\[ N \] number of species, observations, or variables [-]

\[ \text{Nu} \] Nusselt number [-]

\[ p \] partial pressure [Pa]

\[ P \] total fluid pressure [Pa]

\[ p \] parameter vector

\[ \Delta p \] parameter uncertainty interval

\[ \text{Re} \] Reynolds number [-]

\[ q \] solid phase concentration [mol/kg]

\[ s \] exponent in Sips isotherm [-]

\[ t \] time [s]

\[ u \] superficial gas velocity [m/s]

\[ y \] mole fraction [-]

**Greek**

\[ \alpha \] temperature dependence parameter for \( s_i \) [-]

\[ \beta \] temperature dependence parameter for \( s_i \) [K\(^{-1}\)]

\[ \epsilon \] void fraction [-]

\[ \varepsilon \] error in the flow rate [-]

\[ \Phi \] objective function [N/m]

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3. Prediction of ternary breakthrough experiments based on binary data

\[ \mu \quad \text{dynamic viscosity} \quad \text{[Pa s]} \]
\[ \rho \quad \text{density} \quad \text{[kg/m}^3\text{]} \]
\[ \eta \quad \text{parameter in Leva correlation} \]

**Sub- and Superscript**

- 0: feed conditions
- \( amb \): ambient
- \( b \): adsorbent bed
- \( eq \): equilibrium
- \( i, j \): component \( i \)
- \( p \): adsorbent particle
- \( ref \): reference
- \( s \): solid
- \( sat \): saturation
- \( set \): set point
- \( t \): total
- \( w \): column wall
Chapter 4

CO₂ capture from a binary and a ternary mixture by PSA: experiments and predictions

The design of adsorption-based processes for the separation of gas streams has increasingly benefited from the development of mathematical models that allow model-based process design. In particular the availability of many possible configurations, cycle schedules, sorbent materials, and recycles make the optimization of the process very challenging, and the use of a reliable model is required to assess the performance relatively early during process development. The accuracy of such a model is highly dependent on many parameters that are specific to the system being described and the conditions of interest. In a commonly used approach to determine the value of these parameters, the adsorption equilibrium is

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usually measured independently by a gravimetric or volumetric method, while the relevant transport phenomena are studied through the use of fixed bed breakthrough experiments. While these phenomena are a central component of adsorption-based processes and a good description of the breakthrough experiments is a prerequisite for the modeling of full pressure swing adsorption (PSA) cycles, cyclic adsorption processes involve a wide range of conditions in their different steps. In order to use the developed models for process design and optimization with confidence they must be tested rigorously. One way this has been done is by using a lab-scale setup to perform full PSA cycles, separating a binary mixture of H$_2$ and CO$_2$.

The experiments required for the development of such a model are frequently done using synthetic gas mixtures representative of the gas stream of interest, e.g. for a PSA process intended for pre-combustion CO$_2$ capture a mixture of H$_2$ and CO$_2$ might be used, while a process intended for post-combustion CO$_2$ capture might be studied using a binary mixture of N$_2$ and CO$_2$. In reality the feed streams contain multiple components that affect the system behavior; in fact a number of applications such as air-blown autothermal reformers, CO$_2$ pre-combustion capture with membranes, the waste stream from hydrogen purification via PSA, and other industrial sources result in process streams that contain nitrogen in considerable concentration. This can be a challenge due to the fact that on many sorbents, including the activated carbon used in this and previous studies, the adsorption of N$_2$ is significantly higher than that of H$_2$, thus providing competition to CO$_2$. As it is very helpful for a model to be expandable to incorporate this or other additional gas species, one aspect of the model that has been investigated in a previous work is the applicability of transport parameters estimated from binary breakthrough experiments to ternary breakthrough experiments of H$_2$/N$_2$/CO$_2$ mixtures. As with the binary H$_2$/CO$_2$ separation, the ability to describe breakthrough experiments well is prerequisite to using
the model for cyclic processes; however, the PSA processes of interest are not characterized solely by the breakthrough times. Moreover, the goal of the process to be designed may well differ from that of a classical purification in that the desired product stream should contain H\textsubscript{2} in a specified dilution, e.g. for H\textsubscript{2} combustion in a gas turbine\textsuperscript{12}. Therefore, the scope of this work is to verify that the model presented previously by Schell et al.\textsuperscript{25} can predict not only the purity of one particular component, but rather provide the content of all species of interest.

With this scope in mind, two series of PSA experiments were carried out and are presented in this work. The first series of experiments used a binary mixture with 12 mol\% CO\textsubscript{2} and 88 mol\% N\textsubscript{2} as feed, representative of the flue gas from a combustion (on a dry basis). Rather than to present a competitive process for post-combustion CO\textsubscript{2} capture, the objective of this series of experiments is to verify that the effect that the competition for adsorption sites between the two gases has on the separation can be predicted by the model. The second series of experiments used a ternary mixture consisting of 25 mol\% CO\textsubscript{2}, 25 mol\% N\textsubscript{2}, and 50 mol\% H\textsubscript{2}, which is similar to the typical composition found in the applications mentioned above. The PSA cycle performed consists of the steps pressurization, adsorption, blowdown, purge, as well as one pressure equalization, and were run until a cyclic steady state was reached. During the experiments the temperature and pressure inside each column were measured and recorded. The composition of both product streams as well as the flow rate of the light product (N\textsubscript{2} or H\textsubscript{2}/N\textsubscript{2} mix) were measured, allowing the calculation of key process performance indicators such as the overall product purity and component recovery. All quantities measured, those observed directly and those inferred, are compared to simulated results to obtain a complete validation of the model.
4. CO$_2$ capture by PSA: experiments and predictions

4.1 Experimental

4.1.1 Materials and equilibrium adsorption isotherms

Both sets of PSA experiments presented in this work were performed in a two-column lab scale setup packed with commercial activated carbon (AC) (AP3-60 from Chemviron Carbon, Germany) with a pellet size of 3 mm. For each of the gas species used in this work, as well as for binary mixtures of CO$_2$/N$_2$ and CO$_2$/H$_2$, adsorption equilibria have previously been measured for a wide range of temperatures (from 25 $^\circ$C to 140 $^\circ$C) and pressures (from 0.1 bar to 150 bar), and are reported in Schell et al.$^{29}$ Further physical characteristics of the sorbent are listed in Table 4.1. The feed gases were obtained from Pangas (Dagmarsellen, Switzerland) with compositions of 12% CO$_2$, 88% N$_2$ for the binary mixture, and 25% CO$_2$, 25% N$_2$, 50% H$_2$ for the ternary mixture, with a relative error of ±2%.

4.1.2 Setup and Materials

The setup used to perform the experiments has previously been presented by Schell et al.$^{25}$ A schematic of the setup is shown in Figure 4.1. The dimensions of the setup and material characteristics are listed in Table 4.1 along with the physical characteristics of the sorbent material. In the following, the key features of the setup are highlighted. The two stainless steel columns are insulated and are heated electrically (Moser TMT AG, Hombrechtikon, Switzerland), allowing for full regeneration of the sorbent inside the column before each series of experiments. The flow rate of the feed into the columns is measured and controlled by two mass flow controllers (MFC), while the pressure inside the columns is controlled by two back pressure regulators (BPR) (all from Bronkhorst...
Figure 4.1: Flowsheet of the 2-column setup used for the PSA experiments. The five thermocouples in each of the columns are placed along the center axis, at 10 cm, 35 cm, 60 cm, 85 cm and 110 cm from the inlet of the column. The setup is the same as the one presented in Schell et al.\textsuperscript{25}.

High-Tech BV, The Netherlands). All the valves shown in Figure 4.1 are automated and are controlled by LabVIEW (National Instruments Corporation, Texas, USA), which also controls the MFCs and BPRs. Five thermocouples installed in each column measure the temperature along the column axis at 10 cm, 35 cm, 60 cm, 85 cm and 110 cm from the bottom end, and the pressure is measured at both ends of each column.
Table 4.1: Setup dimensions and physical properties of the activated carbon used as adsorbent material.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column length</td>
<td>$L$</td>
<td>[m]</td>
<td>1.2</td>
</tr>
<tr>
<td>Internal radius</td>
<td>$R_i$</td>
<td>[m]</td>
<td>$12.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>External radius</td>
<td>$R_o$</td>
<td>[m]</td>
<td>$20 \times 10^{-3}$</td>
</tr>
<tr>
<td>Heat capacity wall</td>
<td>$C_w$</td>
<td>[J/(K m$^3$)]</td>
<td>$4 \times 10^6$</td>
</tr>
<tr>
<td>Material density</td>
<td>$\rho_M$</td>
<td>[kg/m$^3$]</td>
<td>1965</td>
</tr>
<tr>
<td>Particle density</td>
<td>$\rho_p$</td>
<td>[kg/m$^3$]</td>
<td>850</td>
</tr>
<tr>
<td>Bed density</td>
<td>$\rho_b$</td>
<td>[kg/m$^3$]</td>
<td>480</td>
</tr>
<tr>
<td>Particle diameter</td>
<td>$d_p$</td>
<td>[m]</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>Heat capacity sorbent</td>
<td>$C_s$</td>
<td>[J/(K kg)]</td>
<td>$1 \times 10^3$</td>
</tr>
</tbody>
</table>

\(^a\) at a temperature of 25°C.

The exit composition of the product streams is measured using a mass spectrometer (MS) (Pfeiffer Vacuum Schweiz AG, Switzerland), which can be switched to observe either the light (H$_2$- or N$_2$-rich, depending on the feed) or the heavy (CO$_2$-rich) product. Finally, the flow rate of the light product is measured by a Messglas V-100 rotameter (Vögtlin Instruments, Switzerland) after the BPR and before the MS, as illustrated in Figure 4.1 (labeled “FL”), in conjunction with a webcam and an image analysis script written in MatLab (Mathworks, Massachusetts, USA). For more information on the setup, the reader is referred to the detailed description provided by Schell et al.$^{25}$; the only significant difference is the automation of the flowmeter reading.

In order to determine how meaningful the measured and inferred quantities such as the flow rates, product purities and recovery rates are, great care should be taken to consider the error in each measurement taken, and how it propagates to the quantity of interest. In the determination of the flow rates and the subsequent calculations the following uncertainties were taken into consideration:
4.1 Experimental

- resolution of the camera used in the optical reading of the flow meter;

- manufacturer-supplied accuracy of the MS for the measurement of the gas composition, and by extension the density needed for the interpretation of the flow meter;

- tolerance of the feed gas compositions used for the calibration as well as for the experiments, as given by the supplier;

- error tolerance of the MFC used for calibrations as well as for the experiments, as given by the manufacturer;

- reading accuracy of the manometer attached to the flow meter during calibration to characterize the pressure drop across the flow meter and all downstream piping as a function of the flow rate.

The univariate $t$-statistics\textsuperscript{46} were used to determine the 95\%-confidence interval.

4.1.3 Experimental procedure

In all, eleven PSA experiments were performed in two series: one using the binary CO$_2$/N$_2$ mixture, and one using the ternary CO$_2$/N$_2$/H$_2$ mixture. An overview of the experimental conditions is given in Table 4.2. Before the first experiment in each series the sorbent in the two columns was regenerated by heating the columns to 150°C and applying a vacuum for four hours. Between experiments of the same series, regeneration of the bed would lead to a significant increase of the time necessary to reach cyclic steady state; as a result, regeneration was only done if several days passed between experiments, and when the feed was changed. The two-column lab setup allows for PSA experiments including one pressure equalization step. Both columns underwent the same
4. CO$_2$ capture by PSA: experiments and predictions

**Table 4.2:** Overview of the PSA experiments conducted with two different mixtures: a binary CO$_2$/N$_2$ mixture, and a ternary CO$_2$/N$_2$/H$_2$ mixture. For all experiments, the adsorption was performed at a pressure of 20 bar and a flow rate of 20 cm$^3$/s; desorption was performed at a pressure of 1 bar and a flow rate of 50 cm$^3$/s.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Configuration</th>
<th>$P_{eq}$</th>
<th>$t_{press}$</th>
<th>$t_{ads}$</th>
<th>$t_{peq}$</th>
<th>$t_{blow}$</th>
<th>$t_{purge}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>bottom</td>
<td></td>
<td>27</td>
<td>20</td>
<td>3</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>B2</td>
<td>bottom</td>
<td></td>
<td>26</td>
<td>40</td>
<td>3</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>B3</td>
<td>bottom</td>
<td></td>
<td>25</td>
<td>60</td>
<td>3</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>B4</td>
<td>bottom</td>
<td></td>
<td>25</td>
<td>100</td>
<td>3</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>T1</td>
<td>bottom</td>
<td>CO$_2$/N$_2$ 12/88 (mol %)</td>
<td>24</td>
<td>20</td>
<td>3</td>
<td>55</td>
<td>16</td>
</tr>
<tr>
<td>T2a, T2b</td>
<td>bottom</td>
<td>CO$_2$/N$_2$/H$_2$ 25/25/50 (mol %)</td>
<td>24</td>
<td>47</td>
<td>3</td>
<td>55</td>
<td>16</td>
</tr>
<tr>
<td>T3</td>
<td>bottom</td>
<td></td>
<td>24</td>
<td>80</td>
<td>3</td>
<td>55</td>
<td>16</td>
</tr>
<tr>
<td>T4</td>
<td>bottom</td>
<td></td>
<td>24</td>
<td>100</td>
<td>3</td>
<td>55</td>
<td>16</td>
</tr>
<tr>
<td>T5</td>
<td>top</td>
<td></td>
<td>24</td>
<td>47</td>
<td>3</td>
<td>55</td>
<td>16</td>
</tr>
<tr>
<td>T6</td>
<td>top-to-bottom</td>
<td></td>
<td>24</td>
<td>47</td>
<td>3</td>
<td>55</td>
<td>16</td>
</tr>
</tbody>
</table>

**Cycle:**

- **Pressurization:** The column pressure was raised from $p_{Peq}$ to $p_{high}$, using the feed mixture (flow direction $\uparrow$).
- **Adsorption:** Feeding a constant flow rate at a constant pressure $p_{high} = 20$ bar; production of the high pressure product (N$_2$ in the binary case, H$_2$/N$_2$ mixture in the ternary case) (flow direction $\uparrow$).
- **Pressure Equalization:** The two columns were connected until they

$p_{high} = 20$ bar \hspace{1cm} $V_{feed\,ads} = 20$ cm$^3$/s

$p_{low} = 1$ bar \hspace{1cm} $V_{feed\,purge} = 50$ cm$^3$/s
Figure 4.2: Cyclic sequence of the PSA processes investigated in this work. The sequence follows one column (shown in black) through all steps in the process, showing its pressure level at each step. The columns outlined in gray during the pressure equalization step represent the other column, which is undergoing the same cycle out of phase by half a cycle, as seen in Figure 4.3. In addition, the three configurations used to connect the two columns during pressure equalization are shown: double line is bottom, dashed line is top, and the solid line shows the top-to-bottom configuration.

reached the same intermediate pressure $p_{Peq}$. This recycled a portion of the light product ($H_2/N_2$), raising the $H_2/N_2$ recovery and improving the $CO_2$ purity. In the base case, the flow occurred in the same direction as the blowdown and pressurization steps in the respective columns, however other configurations were also used; see Figure 4.2 and Table 4.2.

**Blowdown:** The column pressure was reduced from $p_{Peq}$ to $p_{low}$; production of the low pressure product ($CO_2$) (flow direction ↓).

**Purge:** Feeding a constant flow rate at a constant pressure $p_{low} = 1$ bar; further production of the low pressure product (flow direction ↓).

The feed entered the column at a temperature of 25 °C. During the pressurization and adsorption steps the feed flow rate was controlled at 20 cm$^3$/s at a pressure of 20 bar. The volumetric flow rate is based on the gas density at 20 bar; as the pressure changes during the pressurization
4. CO₂ capture by PSA: experiments and predictions

Table 2: Overview of the PSA experiments conducted with two different mixtures: a binary CO₂/N₂ mixture, and a ternary CO₂/N₂/H₂ mixture. For all experiments, the adsorption was performed at a pressure of 20 bar and a flow rate of 20 cm³/s; desorption was performed at a pressure of 1 bar and a flow rate of 50 cm³/s.

<table>
<thead>
<tr>
<th>mixture experiment</th>
<th>P₂</th>
<th>step times [s]</th>
<th>(mol%) configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td></td>
<td>27 20 3 50 15</td>
<td>CO₂/N₂</td>
</tr>
<tr>
<td>B2</td>
<td></td>
<td>26 40</td>
<td>12/88</td>
</tr>
<tr>
<td>B3</td>
<td></td>
<td>25 60</td>
<td>12/88</td>
</tr>
<tr>
<td>B4</td>
<td></td>
<td>25 100</td>
<td>12/88</td>
</tr>
<tr>
<td>T1</td>
<td></td>
<td>24 20 3 55 16</td>
<td>CO₂/N₂/H₂</td>
</tr>
<tr>
<td>T2a, T2b</td>
<td></td>
<td>47</td>
<td>25/25/50</td>
</tr>
<tr>
<td>T3</td>
<td></td>
<td>80</td>
<td>25/25/50</td>
</tr>
<tr>
<td>T4</td>
<td></td>
<td>100</td>
<td>50/50/50</td>
</tr>
<tr>
<td>T5</td>
<td></td>
<td>47</td>
<td>25/25/50</td>
</tr>
<tr>
<td>T6</td>
<td></td>
<td>47</td>
<td>25/25/50</td>
</tr>
</tbody>
</table>

All experiments: pₜₕₜₑₜ = 20 bar, ˙Vₜₐₜₛₑₜ = 20 cm³/s, pₜₙₒₜₑ = 1 bar, ˙Vₜₚₑᵦₑ = 50 cm³/s.

Figure 4.3: Schedule of the PSA cycle implemented in this work. Each row qualitatively shows the timing of the steps for one column going from left to right.

<table>
<thead>
<tr>
<th>Column 1</th>
<th>Blowdown</th>
<th>idle</th>
<th>Pressurization</th>
<th>Adsorption</th>
<th>Pₑₑₑₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column 2</td>
<td>idle</td>
<td>Pressurization</td>
<td>idle</td>
<td>Pressurization</td>
<td>Adsorption</td>
</tr>
</tbody>
</table>

At the end of the adsorption step, the gas phase in the column contains a large amount of the lighter component. In reality, pressure equalization steps are commonly performed in order to (i) recover the light component and (ii) reduce compression costs. Therefore, it is very important to validate the model also for these highly dynamic steps, and all PSA experiments performed incorporate one pressure equalization step. In previous work, the flow direction during this step was the same as during the blowdown step in the column being depressurized, and the same as during the pressurization step in the column being pressurized. In this work, this configuration is referred to as the “bottom” configuration, as the gas both exits and enters the columns at the bottom of the setup. However, the bottom of the column is rich in CO₂, which is less beneficial than taking it from the top of the column, which is lean in CO₂. In order to evaluate different cycle configurations, two additional experiments were performed which take the gas to be recycled from the top of the column being depressurized: in the first, the recycled gas is fed into the top of the column being pressurized (“top” configuration), while in the second the recycled gas is fed at the bottom (“top-to-bottom” configuration). All three configurations tested are shown schematically in Figure 4.2. Process design and optimization of PSA processes is mainly concerned with the process performance at cyclic steady-state (CSS);
the simulations needed around 20 cycles to achieve this. Accordingly, all experiments performed ran for at least 20 cycles, during which the MS was switched to record the composition of the light product, thus allowing the interpretation of the flow meter reading. Then the MS was switched to the heavy product for at least 5 cycles, before returning to the light product for another 5 cycles.

4.2 Modeling of pressure swing adsorption experiments

The model used to describe the PSA processes has been described in earlier works and is discussed in Section 1.4.1\textsuperscript{25,26}. It has been validated for the separation of a binary CO\textsubscript{2}/H\textsubscript{2} mixture by PSA. It is a one-dimensional, nonisothermal, nonequilibrium model, which takes into account the characteristics of the experimental setup, e.g. the column wall energy balance and the volume in the piping. The considerations needed to adapt the model for the specific experimental setup are described in detail by Schell et al.\textsuperscript{25}. The mass transfer coefficients for each of the species were established in a previous work by fitting them to an extensive set of fixed bed breakthrough experiments and are reported in Chapter 3\textsuperscript{51}. There, it had been found that for conditions with relatively low CO\textsubscript{2} content and high N\textsubscript{2} content, as is the case in the binary experiments presented here, the mass transfer of CO\textsubscript{2} is particularly slow. This was taken into account by using the appropriate mass transfer coefficient for each mixture (see Table 4.3) as determined earlier. The adsorption equilibrium of multiple species was described by applying the ideal adsorbed solution theory (IAST) to the pure component Sips isotherms as it has been described in Schell et al.\textsuperscript{29}; the isosteric heat of adsorption was assumed to be constant for each component as listed in Table 4.3.
The velocity with which the pressure changes within the column during the pressurization, pressure equalization, and blowdown step has an impact on the state of the column, and thus on the overall process. These transitions depend on a number of factors, including the mass flow controllers used, the feed composition, and the valves and piping used. While it would be possible to characterize the flow of the gas streams through the tubes and valves in the experimental setup, this would involve the determination of a number of parameters that are specific to the setup used; this goes beyond the scope of this work. For our purposes, it is sufficient to describe the pressure as follows: during the pressurization step the pressure at the inlet of the column is described by a linear increase from the intermediate pressure \( p_{\text{peq}} \) to the adsorption pressure \( p_{\text{high}} \) as the MFC used to control the feed provides a constant flow rate: pressurization

\[
p(x = 0; t) = p_{\text{peq}} + (p_{\text{high}} - p_{\text{peq}}) \frac{t}{t_{\text{press}}}. \tag{4.1}
\]

To describe the pressure at the outlet of the column during the blowdown step, an exponential decay with a rate of decay \( \xi \) was used:

**Table 4.3:** Model parameters used for the behavior of the gas phase.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H_{\text{ads},i} ) [J/mol]</th>
<th>( C_{g,i} ) [J/(mol K)]</th>
<th>( k_i ) [s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{H}_2 )</td>
<td>( \text{N}_2 )</td>
<td>( \text{CO}_2 )</td>
</tr>
<tr>
<td>Putative</td>
<td>9800</td>
<td>15600</td>
<td>21000</td>
</tr>
<tr>
<td>Coticuliform</td>
<td>28.9</td>
<td>29.8</td>
<td>42.5</td>
</tr>
<tr>
<td>Hypercystis</td>
<td>1.0</td>
<td>0.3</td>
<td>0.04</td>
</tr>
<tr>
<td>Ternary</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3 Results of PSA experiments

During each experiment a large amount of data is recorded, ranging from local state variables to macroscopic process characteristics. In the following, each of the measured quantities is discussed for a representative experiment (see Table 4.2 for the experimental conditions) while showing values for two nonconsecutive cycles to verify that cyclic steady state was in fact reached.

4.3.1 State of the column

The columns are directly observed through two quantities, the pressure at each end of the column, and the temperature at the five locations described above. All the measured data are shown for one of the columns during two separate cycles of experiment B2 in Figure 4.4; a selection of

\[ p(x = 0; t) = p_{\text{low}} + (p_{\text{Peq}} - p_{\text{low}}) \exp (-\xi t) . \]  

(4.2)

The parameter \( \xi \) depends on the composition of the flowing gas. As a result, two values were used to obtain an adequate description of the pressure during blowdown: for the binary experiments \( \xi = 0.085 \, \text{s}^{-1} \), and for the ternary experiments \( \xi = 0.11 \, \text{s}^{-1} \). Lastly, during the pressure equalization step the pressure at the open end of the column was kept fixed at the intermediate pressure level \( p_{\text{Peq}} \), which was determined iteratively such that the amount of material leaving the column being depressurized is equal to that entering the column being pressurized, as was reported previously by Casas et al.\(^{26}\).
4. \( \text{CO}_2 \) capture by PSA: experiments and predictions

Figure 4.4: Typical experimental temperature a) and pressure b) profiles throughout one full PSA cycle for an experiment with an adsorption step time of 40 s (experiment B2) taken from column 2. The filled and the empty symbols represent experimental data from two separate, nonconsecutive cycles of the experiment to highlight the fact that cyclic steady state has been reached. In a) three sets of data correspond to three positions where temperature was measured: □ 10 cm, ◆ 60 cm, ▽ 110 cm, measured from the bottom of the column. Although five temperatures were measured, only three are shown to improve legibility. The pressure shown in b) was measured at the bottom of the column. The solid lines show the corresponding simulation results.
the same data is also plotted together with the corresponding simulation results.

**Temperature:** Figure 4.4(a) shows the temperature profiles at the positions 10 cm, 60 cm, and 110 cm from the bottom of the column, measured in column 2 during experiment B2. During the first idle step the temperature in the column increases as the column just goes through a pressurization by equalization, and adsorption is still taking place. In the following steps the effect of the adsorption enthalpy can be clearly seen as the bed undergoes ad- and desorption. While five temperatures are measured during the experiment, only three are displayed for the sake of clarity. The temperature near the column entrance, i.e. at 10 cm, is described rather well throughout the whole cycle. Further up the column the model describes the trends in temperature, as well as the overall span of the temperature swing. It also captures phenomena such as the slight temperature drop at the top of the column during the purge step (when the feed is entering at the top of the column). Moreover, the simulations correctly predict that the temperature at the top two positions shown (60 cm and 110 cm) is relatively similar throughout the whole cycle, while that at the bottom end is somewhat lower. Quantitatively, however, there are some differences between the simulations and the experimental data. During the idle time at the beginning of the cycle both simulation and experiment show a rise in temperature along the column, however in the experiment this rise is slower. The pressurization step then sees a relatively steady rise in temperature, both in simulations and experiment. One notable characteristic is the lack of formation of a clear front in the temperature profiles during the adsorption step. During the pressure equalization and blowdown steps, the deviation between experiment and simulation increases due to the rapid changes in conditions (pressure, flow rate) both along the axis of the column and with time.

**Pressure:** Figure 4.4(b) shows the pressure at the column inlet. During
the initial idle step the pressure is almost constant, with only a small
decrease. The following pressurization step sees a linear increase in pres-
sure, as the MFC feeds a constant flow rate into the column. During
the adsorption step the pressure is kept constant by the BPR. The pres-
sure equalization step is marked by a very quick decrease in pressure to
the intermediate pressure $p_{\text{Peq}}$, which is then followed by a somewhat
slower decrease to the desorption pressure $p_{\text{low}}$ during the blowdown
step. During the purge step the pressure is once again controlled by a
BPR, however as all experiments reported in this work purge at ambient
pressure the valve is simply left open. The second idle step shows no
change in pressure, and the final pressure equalization step shows a very
quick increase to $p_{\text{Peq}}$ that mirrors the decrease during the earlier equal-
ization step. Along with the experimental data, the simulation results
are shown. During most of the process the simulations follow a given
pressure profile which is described in Section 4.2, however one aspect
that is predicted by the model is the pressure at the end of the pressure
equalization step and the beginning of the blowdown step, $p_{\text{Peq}}$. For the
cycle shown, this corresponds to the time 0 and 93 s of cycle time. An
arithmetic average of the high and low pressure levels would overesti-
mate its value; in Figure 4.4(b) it can be seen that the true value lies a
little under 10 bar, and is well predicted by the simulations.

4.3.2 Product streams

In addition to the state of the column, the product streams are also
analyzed. As the MS can only measure the composition of one of them
at a time, the results shown for the heavy product are inherently from
a different cycle than those for the light product. Experimental and
simulated composition profiles are shown in Figure 4.5.

*Binary experiments*: The two plots on the left in Figure 4.5 show the
composition of the two product streams for the binary experiments. The
Figure 4.5: Composition of both the light product (top row, a, b) and the heavy product (bottom row, c, d) for all binary experiments performed (left) and of ternary experiment T2 (right). Symbols represent experimental data, while solid lines show the simulation results. The dashed lines indicate the feed composition. Not shown for the sake of legibility is the measurement error of $\pm 0.6\%$ for the binary experiments, and $\pm 1\%$ for the ternary experiment.

profiles are shown for all four experiments performed with the binary mixture to illustrate on the one hand the effect the adsorption step time has on the product composition, and on the other hand the fact that the model captures this effect very well. Concerning the light product composition, shown in Figure 4.5(a), all four experiments exhibited the same characteristics: an initial brief valley, where the $N_2$ purity was up to 2\% lower than during the rest of the adsorption step, followed by a slight crest, and then a long flat portion. The simulation results do not exhibit the initial valley nor the following crest, but match the flat
portion almost exactly. It should be noted that with the exception of the initial valley the measured values are well within the uncertainty of the MS (±0.6%, see Section 4.1.2). The heavy product composition, shown in Figure 4.5(c) for all four binary experiments, is characterized by a gradual increase in the CO$_2$ content throughout the blowdown step, as the CO$_2$ desorbs and dilutes the N$_2$ in the gas phase. During the purge step that follows, the composition is relatively constant, with a small temporary drop in CO$_2$ content about 5 s into the step. This is most likely caused by the onset of the flow during the purge step, delayed a few seconds by the downstream piping. For experiments with longer adsorption steps, the CO$_2$ content is higher throughout both steps producing the CO$_2$. However, the enrichment in CO$_2$ is not very strong. In fact, even if a long adsorption step of 100 s is performed, the CO$_2$ content in this product stream stays well below 50%.

*Ternary experiment:* The two plots on the right in Figure 4.5 show the composition of the two product streams for a ternary experiment (T2). It should be noted that the scale of the vertical axis of the plot is quite different to that of the plot for the binary experiments, showing the full range from 0 to 1. This is in part because the composition varies more strongly throughout the experiment, and in part because the mole fraction of all components is shown. As a result of this, the data for the other ternary experiments would overlay the shown data, and only one experiment is shown here for the sake of clarity – plots showing the other experiments are available in the supporting information (SI). The light product composition, shown in Figure 4.5(b), shares some characteristics with the binary experiments in that it begins with a comparatively low content of the light component (H$_2$ in this case), followed by a slight crest and a fairly smooth tail for the rest of the step. Overall the H$_2$ content of the product is simulated very well, again with the exception of the first few seconds. The breakthrough of the N$_2$, the intermediate component, is clearly visible in both experiment and simulation. The CO$_2$ content
is fairly low throughout the entire adsorption step, as the CO$_2$ front does not reach the end of the column, and is underpredicted slightly by the simulations – this is more evident in the experiments with longer adsorption step times, which are not shown here, but are reported in the SI. The composition of the heavy product exhibits somewhat larger differences between experiment and simulation. Specifically, while the hydrogen content is well-described by the simulations, the simulation results show a lower CO$_2$ content and accordingly higher N$_2$ content during the last part of the blowdown step and during the purge step. It should be noted, however, that a very significant portion of the heavy product is produced during the blowdown step; the composition profile during that step is indeed well-described by the model.

**Product flow rate:** As discussed earlier, only the flow rate of the light product was measured. Results for a binary (B2) and a ternary (T2) experiment are shown in Figure 4.6, along with the contribution of each component to the total flow rate. For the N$_2$ product of experiment B2,
the flow rate is shown in Figure 4.6(a). As the flow rates of the other experiments with the binary mixture overlap and are qualitatively very similar to the one shown, only one is displayed for the sake of clarity. The simulations describe the flow rates remarkably well. In Figure 4.6(b), the results of experiment T2 are shown, along with the simulation results. Compared to the simulations the experimental flow rate is initially a bit lower, before going through a short peak and then settling to values very close to the simulated predictions. This is due to the somewhat delayed reaction of the BPR once the pressurization step is completed. This phenomenon is also present in the binary experiment, but it is far less prominent. Overall, the flow rate is predicted very well, including the breakthrough of N₂. The fact that the mole fraction of CO₂ was somewhat lower in the simulations than in the experiment is reflected here as well.

4.3.3 Separation performance

From the data in Figure 4.6, the total amount and composition of the light product can be determined by integration. Also, as the total amount fed to each column during each cycle is known from the MFC measurement, the amount and composition of the heavy product can be calculated. This allows for the determination of the purity of each product and of the recovery rate of each component (for CO₂ this is also commonly referred to as the CO₂ capture rate, CCR). In Figure 4.7 these quantities are shown for a number of cycles of experiment B2 after cyclic steady state had been reached. In each set of data column 1 is represented by a filled circle, and column 2 by an empty circle, to verify that both columns perform equally well. In addition, the average for the last five cycles (using data from both columns) is shown by a horizontal line. This is also the value that was used for the comparison with simulation results. From cycle 26 to 32 the MS was measuring the
4.3 Results of PSA experiments

composition of the heavy product; as the composition is necessary to
determine the flow rate of the light product, the separation performance
cannot be determined for these cycles. The interpretation of the data
for the experiments using the ternary mixture was done analogously.

The separation performance of the performed binary experiments is
shown in Figure 4.8 in terms of purity of the two product streams and
of the recovery of each component. As with the previously reported
separation of CO$_2$ and H$_2$\textsuperscript{25}, a longer adsorption step time leads to a
lower purity of the lighter component, in this case nitrogen, as the CO$_2$
begins to break through. This also leads to a lower CO$_2$ capture rate.
On the other hand the more complete saturation of the adsorption bed
leads to a higher concentration of CO$_2$ in the heavy product. In this
context the use of the term purity may seem inappropriate, as the CO$_2$
is merely enriched to about 20%; however, for the sake of consistency
it is maintained. The figures show that the model correctly predicts
the calculated performance indicators for the most part, with the CO$_2$
capture rate deviating from the experimentally determined values. It
is also visible from the figure that the uncertainty in the directly mea-
sured quantities translates into a significant error in the calculated CO$_2$
capture rate.

For the ternary experiments, the average product compositions are shown
in Figure 4.9. The composition of the H$_2$ product is shown in Fig-
ure 4.9(a), while that of the CO$_2$ product is shown in Figure 4.9(b). The
experiment with an adsorption step time of 47s was performed twice –
for the sake of visibility, the corresponding data points are shown shifted
slightly to the left and right. The composition of the light product
(shown in Figure 4.9(a)) is predicted remarkably well by the simula-
tions under all conditions tested. Not only is the calculated H$_2$ purity
correct, but the contribution of each of the two impurities is predicted
rather well. Concerning the CO$_2$ product, the results again show that
Figure 4.7: Separation performance for an adsorption step time of 40 s (experiment B2) over a number of cycles after cyclic steady-state has been reached. a) shows the composition of both the heavy (CO$_2$-rich) and the light (CO$_2$-lean) products, as determined by integrating the product flow rate seen in Figure 4.6. b) shows the recovery of CO$_2$ in the heavy product and of N$_2$ in the light product. Filled circles refer to column 1, empty circles to column 2. The symbols are shifted slightly to the left (column 1) and to the right (column 2) for visibility. From cycle 26 to 32 the MS measured the heavy product composition; during this time the flow rate of the light product could not be determined. The horizontal lines represent the average for both columns over the last five cycles.
Figure 4.8: Comparison of the simulated (lines) process performance with experimental results for all experiments with the binary CO$_2$/N$_2$ mixture. a) shows the mole fraction of the enriched component in each product stream, i.e. the N$_2$ in the light product and the CO$_2$ in the heavy product. b) shows the recovery of each component. Symbols: ○ CO$_2$, △ N$_2$.

the measurement errors considered translate to a larger uncertainty in this product’s composition than for the light product.

In addition to varying the duration of the adsorption step, different options for the direction of the gas flow during the pressure equalization step were also investigated. Three configurations were investigated, as illustrated in Figure 4.2 and described in Section 4.1.2. The process performances in terms of product purity and component recovery are listed in Table 4.4, comparing simulations and experiments. The simu-
Figure 4.9: Comparison of simulations (lines) with experimental results (symbols) for all experiments with the ternary CO\textsubscript{2}/N\textsubscript{2}/H\textsubscript{2} mixture. a) shows the composition of the light product, which is rich in H\textsubscript{2}, and b) shows the composition of the heavy product, i.e. the one rich in CO\textsubscript{2}. Subfigure c) shows the recovery of H\textsubscript{2} and CO\textsubscript{2}, the main components in each of the products. Symbols: o CO\textsubscript{2}, Δ N\textsubscript{2}, ◊ H\textsubscript{2}. The experiment using an adsorption step time of 47s was repeated; to distinguish them from each other, experiment T2b is denoted by a ×.
Table 4.4: Comparison of experimental and simulated process performance of the three recycle configurations tested. The experiments listed here all had an adsorption step time of 47 s, and merely differed in the connection during the pressure equalization step.

<table>
<thead>
<tr>
<th>configuration</th>
<th>bottom</th>
<th>top</th>
<th>top-to-bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H\textsubscript{2} purity [%]</strong></td>
<td>simulation</td>
<td>74.7</td>
<td>75.6</td>
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<tr>
<td></td>
<td>experiment</td>
<td>76.1 ± 0.5</td>
<td>78.1 ± 0.4</td>
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<tr>
<td></td>
<td></td>
<td>75.5 ± 0.5</td>
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</tr>
<tr>
<td><strong>CO\textsubscript{2} purity [%]</strong></td>
<td>simulation</td>
<td>49.2</td>
<td>50.1</td>
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<tr>
<td></td>
<td>experiment</td>
<td>50.7 ± 2.5</td>
<td>50.2 ± 2.3</td>
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<tr>
<td></td>
<td></td>
<td>49.4 ± 2.2</td>
<td></td>
</tr>
<tr>
<td><strong>H\textsubscript{2} recovery [%]</strong></td>
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<td>80.5</td>
<td>80.9</td>
</tr>
<tr>
<td></td>
<td>experiment</td>
<td>85.1 ± 2.9</td>
<td>83.2 ± 2.8</td>
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<tr>
<td></td>
<td></td>
<td>82.8 ± 2.7</td>
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</tr>
<tr>
<td><strong>CO\textsubscript{2} recovery [%]</strong></td>
<td>simulation</td>
<td>90.6</td>
<td>92.8</td>
</tr>
<tr>
<td></td>
<td>experiment</td>
<td>89.4 ± 0.7</td>
<td>93.8 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>89.3 ± 0.7</td>
<td></td>
</tr>
</tbody>
</table>

Simulation results show a clear albeit slight increase in performance achieved by taking the high pressure gas from the top of the column (top and top-to-bottom configurations), particularly in the CO\textsubscript{2} recovery, and to a lesser degree in both product purities; the H\textsubscript{2} recovery did not change by much. The choice of feeding point into the low pressure column, on the other hand, seems to have a negligible impact. In general, these trends hold true for the experimental data. However, the results also show the limitations of the experimental setup. While the H\textsubscript{2} purity and the CO\textsubscript{2} recovery are improved by the new recycle configurations, the CO\textsubscript{2} purity and H\textsubscript{2} recovery only change within the experimental error, which is also larger than the performance improvement predicted by simulation.
4. CO₂ capture by PSA: experiments and predictions

4.4 Discussion

In general, the agreement between the simulations and the experiments is satisfactory. It should be kept in mind that most of the model parameters used were the same as in the work of Schell et al.\textsuperscript{25}. New parameters introduced were those pertaining to nitrogen; these were taken from our previous work\textsuperscript{51}. The only tuning needed to describe the experimental data was for the pressure profile during the blowdown step, as the different gas compositions passed through the BPR at different velocities. Regarding the results of the binary experiments, one notable difference to the results presented by Schell et al.\textsuperscript{25} lies in the temperature in the column during the pressurization and adsorption steps, seen in Figure 4.4(a). Specifically, the lack of a formation of a clear temperature front. This is due to the fact that N\textsubscript{2} adsors to a significantly higher degree than H\textsubscript{2}; as a result, the temperature rises throughout the column during the pressurization step. As was seen in the breakthrough experiments under similar conditions\textsuperscript{51}, the mass transfer of CO\textsubscript{2} at low concentrations is rather slow, so the CO\textsubscript{2} is seen at the end of the column from the beginning of the adsorption step on. The adsorption step is then characterized more by the dissipation of the heat to the column wall than by the advancement of the CO\textsubscript{2} front – this is seen in both experiment and simulation. It is clear that the description of the temperature within the bed is complex. The heat transfer to the column wall is affected by the temperature, pressure, composition, and flow rate, and the enthalpy of adsorption is not truly constant as assumed by the model. Nevertheless, the model provides a reasonable description of the column temperature. The low CO\textsubscript{2} content in the heavy product is a result of the competition for adsorption sites and of the cycle performed: During adsorption both the CO\textsubscript{2} and N\textsubscript{2} adsorb – indeed, Schell et al.\textsuperscript{29} have reported data under conditions close to the feed conditions, indicating that at equilibrium the amounts of CO\textsubscript{2} and N\textsubscript{2} adsorbed are of very
similar magnitude. During the blowdown step, the mole fraction of CO$_2$ in the gas phase increases, which hinders its desorption, while the mole fraction of N$_2$ decreases, significantly reducing the competition. As a result, more N$_2$ desorbs during the blowdown step than CO$_2$. According to the simulations for experiment B4 ($t_{ads} = 100$ s, i.e., the conditions with the most completely saturated bed), during the blowdown step the amount of N$_2$ adsorbed in the entire column will decrease from 0.316 mol to 0.041 mol, while that of CO$_2$ goes from 0.481 mol to 0.370 mol. The purge step decreases this further to 0.350 mol CO$_2$, but a much longer purge step would be necessary for a more complete desorption of the CO$_2$. This would, however, lead to breakthrough of the N$_2$ in the purge feed. The CO$_2$ remaining adsorbed at the end of the purge step is also the reason that the purity of the N$_2$ is not higher at the beginning of the adsorption step. Indeed, the longer the adsorption step, and the more completely the bed is saturated with CO$_2$, the higher the concentration of CO$_2$ throughout the entire duration of the adsorption step, as can be seen in Figure 4.5. From a CO$_2$ capture standpoint this indicates that the conventional PSA configuration performed here is not very suited to purify CO$_2$, however it is very useful to assess the ability of the model to predict the behavior of the two adsorbing species competing for adsorption sites. Therefore, this series of experiments is valuable as a tool for model validation.

Considering the results of the ternary experiments, it should be noted that the goal was not to produce high purity H$_2$. This could have been accomplished with short adsorption steps and a H$_2$ purge, as is typically done in H$_2$ purification. Rather, the goal was to test the model’s ability to predict the behavior of an intermediate species within the bed. This could be of great value when a certain stoichiometry of the components is desired for downstream use. As an example, in ammonia production following an air-blown autothermal reformer it would be desirable to have the H$_2$ and N$_2$ present in a 3:1 ratio. As such, it is of great interest
to correctly predict not only the $\text{H}_2$ purity, but also the amount of each of the other component. Figure 4.9 shows clearly that the model is generally capable of doing so, with some deviations. The differences seen in the exit profiles between simulations and experiments are reflected in the Figure, as the experiments with relatively long adsorption step times show a somewhat higher $\text{CO}_2$ content than the simulations. As can be seen in Figure 4.9(c), this “lost” $\text{CO}_2$ is reflected in a $\text{CO}_2$ recovery rate that is lower in the experiments than expected from the simulations. It should be noted, however, that the amount of $\text{CO}_2$ in the feed is half that of $\text{H}_2$, and that inaccuracies are amplified when viewed on a relative scale.

### 4.5 Conclusions

In order to further validate a model developed to describe cyclic adsorption-based gas separation processes, a number of pressure swing adsorption processes have been performed in a two-column lab-scale pilot plant, using a binary $\text{N}_2/\text{CO}_2$ as well as a ternary $\text{H}_2/\text{N}_2/\text{CO}_2$ mixture as feed. The plant had previously been used to separate a binary $\text{H}_2/\text{CO}_2$ mixture. However, the addition of a non-inert compound (nitrogen) is a complication of the system that requires thorough testing to allow the confident use of the model for the development and the design of more complex separations. The experiments presented in this work were performed in two series.

The first used a binary mixture of 12 mol-% $\text{CO}_2$ in $\text{N}_2$, as a mixture representative of flue gas from a combustion process. Binary equilibrium adsorption measurements of $\text{CO}_2/\text{N}_2$ mixtures indicate that the selectivity for $\text{CO}_2$ over $\text{N}_2$ is not very high in the activated carbon used; as a result it should not be expected that the process performance is very high, as was confirmed by the experiments in this work. This se-
ries of experiments was valuable by confirming that the competition for adsorption sites is well-described by the model under a wide range of conditions.

The second series of experiments used a ternary mixture composed of 25% CO$_2$, 25% N$_2$, and 50% H$_2$, similar to what is produced in air-blown autothermal reformers, or to waste streams produced in a number of different applications (refinery, CO$_2$ pre-combustion capture with membranes, PSA waste stream). The main purpose of this series of experiments was to determine whether the model would accurately capture not only the H$_2$ purity, but also the content of each of the three components; this would be valuable in a setting like ammonia production or H$_2$ combustion in a gas turbine, where the desired product is not high-purity hydrogen, but includes a particular stoichiometry of H$_2$ and N$_2$. The model manages to describe the exit profiles of both products as well as the flow rate of the H$_2$ product. Particularly the composition and flow rate of the H$_2$ product are predicted with remarkable accuracy. The effect of a seemingly minor change to the process configuration, taking material for a recycle from the opposite end of the column, was seen in simulations and confirmed in experiment. Longer adsorption step times, which lead to a thorougher saturation of the bed with the adsorbing species, lead to a slight underestimation of the CO$_2$ content in the H$_2$ product, resulting in an overestimated CO$_2$ capture rate under those conditions.

It should further be noted that the simulations of the process are predictions, carried out by building on the work of Schell et al.$^{25}$ and incorporating information obtained in our previous work on the behavior of the ternary H$_2$/N$_2$/CO$_2$ mixture in a fixed bed column.$^{51}$ Particularly in light of the fact that N$_2$ is not inert in this context, but adsorbs significantly and competes with CO$_2$ for adsorption sites, the addition of this intermediate component is not trivial, and the results are therefore
rather satisfying. The experiments have also shown that the description of the temperature inside a fixed bed column is not straightforward. This is not surprising as many factors, such as pressure, temperature, composition, and flow rate, have an impact on the heat transfer and the enthalpy of adsorption, and particularly during parts of the cycle where a significant temperature difference exists between the bed and the surroundings a radial temperature gradient could well form within the bed. Despite some quantitative differences between the simulated and measured temperature along the column, the model described many aspects of the process well. The aim of this work was to show that the model can be used to predict the performance of PSA processes; this work has shown that the model is robust enough to handle the complexity of multicomponent separation, and can be used with confidence in the development of more complex cycles.

### Notation

#### Roman

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<th>Symbol</th>
<th>Description</th>
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<td>heat capacity</td>
<td>[J/(K m³)]</td>
</tr>
<tr>
<td>$d_p$</td>
<td>particle diameter</td>
<td>[m]</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>heat of adsorption</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>$k$</td>
<td>overall mass transfer coefficient</td>
<td>[s⁻¹]</td>
</tr>
<tr>
<td>$L$</td>
<td>column length</td>
<td>[m]</td>
</tr>
<tr>
<td>$p$</td>
<td>operating pressure</td>
<td>[bar]</td>
</tr>
<tr>
<td>$R_i$</td>
<td>inside column radius</td>
<td>[m]</td>
</tr>
<tr>
<td>$R_o$</td>
<td>outside column radius</td>
<td>[m]</td>
</tr>
<tr>
<td>$\dot{V}^{\text{feed}}$</td>
<td>volumetric feed flow rate</td>
<td>[cm³/s]</td>
</tr>
<tr>
<td>$y$</td>
<td>mole fraction</td>
<td>[-]</td>
</tr>
</tbody>
</table>

#### Greek

108
4.5 Conclusions

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho )</td>
<td>density</td>
<td>( \text{kg/m}^3 )</td>
</tr>
<tr>
<td>( \xi )</td>
<td>parameter for blow down rate</td>
<td>( \text{s}^{-1} )</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>void fraction</td>
<td>[-]</td>
</tr>
</tbody>
</table>

**Sub- and Superscript**

- **ads**: adsorption step
- **blowdown**: blowdown step
- **b**: adsorbent bed
- **feed**: feed
- **M**: material
- **s**: solid
- **p**: adsorbent particle
- **peq**: pressure equalization step
- **press**: pressurization step
- **purge**: purge step
- **w**: column wall
4. CO₂ capture by PSA: experiments and predictions
Chapter 5

Temperature Swing Adsorption for post-combustion CO$_2$ capture$^1$

The model for adsorption-based gas separation processes that is presented in Chapter 1 was developed with the pre-combustion capture of CO$_2$ in mind. Due to the high pressure of the feed in this scenario and the relatively high CO$_2$ content, a pressure swing adsorption process using activated carbon was chosen as a basis for comparison$^{17,26,29}$, with novel materials being considered as alternatives.$^{27,28}$ However, the conditions present in the case of post-combustion CO$_2$ capture are quite different – the feed typically contains a lower mole fraction of CO$_2$, and is near atmospheric pressure. In addition, the N$_2$ that makes up the bulk of the flue gas, adsorbs on many sorbents itself, and so provides

competition for adsorption sites. For these conditions, zeolite 13X is a rather promising candidate material, as it is very selective for CO$_2$ over N$_2$, and has a high capacity for CO$_2$; a number of studies are available that use it in a temperature or vacuum swing adsorption process.$^{5,52–55}$ As basic principles in TSA and PSA are the same, the model presented in the previous chapters should be applicable to TSA processes as well. In order to be able to use the model for process design and optimization, a full characterization of the system CO$_2$/N$_2$ on zeolite 13X was performed at SPL. The adsorption equilibrium has been reported by Hefti et al.$^{43}$ and is summarized in Chapter 2. In this chapter, the transport phenomena are characterized using breakthrough experiments to determine mass transfer coefficients for N$_2$ and CO$_2$ as well as the heat transfer coefficient within the bed. Heating and cooling experiments are performed to study the heat transfer between the column wall and the heat exchange fluid that is used to heat and cool the column. Finally, the model is used to design TSA experiments using three different temperature levels for desorption; the experiments are then performed and compared to simulation results.

5.1 Experimental

5.1.1 Sorbent materials and adsorption isotherms

For the experiments presented in this chapter the two columns of the laboratory setup were packed with spherical pellets of zeolite 13X with a diameter between 1.6 and 2 mm, manufactured by ZeoChem (Uetikon, Switzerland), with a binder content between 15% and 25% on a mass basis.$^{43}$ The pure component adsorption equilibria of CO$_2$ and N$_2$ have been measured for temperatures between 25 °C and 140 °C and pressures from 0.05 bar to 10 bar by Hefti et al.$^{43}$ and are summarized in Chap-
ter 2. Based on these data, parameters for the Sips isotherm model were fit that allow accurate calculation of the equilibrium adsorption of each of the components; these parameters are listed in Table 2.1. In addition, binary adsorption measurements of the two gas species at 25 °C and 45 °C showed that the binary adsorption equilibrium can be described reasonably well by using the extended Sips isotherm, but that the application of ideal adsorbed solution theory (IAST) results in a more accurate description of the equilibrium adsorption. Therefore IAST was used throughout this work to describe the adsorption equilibrium.

Before the first experiment, the zeolite was regenerated by heating the columns to 250 °C and maintaining that temperature over night under a constant low flow of helium. This was done primarily to remove any water that might have adsorbed while the sorbent was exposed to the air in the laboratory. In order to avoid adsorption of water after this thorough regeneration, the columns are kept at or above atmospheric pressure whenever possible. In order to regenerate the sorbent between experiments, the columns were kept at 250 °C for two hours under a low flow of helium.

The feed gas was obtained from Pangas (Dagmarsellen, Switzerland) with a CO$_2$ content of 12 % on a mole basis (the remainder being N$_2$) and with a tolerance of ± 2 % relative (i.e. 0.24 % absolute). The helium used for the regeneration of the sorbent and in the transient experiments was also obtained from Pangas and had a purity of 99.999 %.

### 5.1.2 Experimental Setup – changes from PSA setup

The setup used to perform the experiments is based on the setup presented by Schell et al. and shown in Chapter 4, however it has been modified significantly for the work reported here. The gas piping remained the same, including the two MFCs used to measure and control the feed flow rate into the columns, the BPRs used to control the
pressure inside the columns (all Bronkhorst High-Tech BV, The Netherlands), all the automatic gas valves, as well as the thermocouples (at 10, 35, 60, 85, and 110 cm from the bottom end of each column) and pressure sensors used to observe the state of the column. The main difference lies in the temperature control of the columns: The two electrically heated columns were replaced with jacketed columns that allow a heat exchange fluid to externally heat or cool the columns. Tubes passing through both the inside and outside wall of the columns allow the installation of thermocouples for the measurement of the bed temperature without putting them in direct contact with the heat exchange fluid. The columns were constructed at SPL and are made of stainless steel. Both the inside and outside wall are of the same material in order to avoid tensions due to thermal expansion. Automatic valves (GSR Ventiltechnik GmbH&Co, Germany) connected to the inlet and outlet of these jackets allow each column to be connected to one of two thermostats (Huber Kältemashinenbau GmbH, Germany), and thermocouples at each end measure the temperature of the heat exchange fluid entering and exiting each column. During heating, cooling, and TSA experiments one of the thermostats is set to the regeneration temperature (up to 150 °C), while the other one was kept at a set point of 25 °C. The automatic valves are controlled by LabVIEW software (National Instruments, TX, USA), which also controls the gas valves, MFCs, BPRs, and records all temperatures and pressures. The two thermostats, meanwhile, are controlled manually. A schematic of the setup is shown in Figure 5.1. The physical characteristics of the columns and the bed are listed in Table 5.1.

As in Chapter 4, the exit composition of the product stream was measured using a mass spectrometer (MS) (Pfeiffer Vacuum Schweiz AG, Switzerland), which can be switched to observe either the light (N₂-rich) or the heavy (CO₂-rich) product; and the flow rate of the light product was measured by a Messglas V-100 rotameter (Vögtlin Instru-
Figure 5.1: Flowsheet of the 2-column setup used for the TSA experiments. The five thermocouples in each of the columns are placed along the center axis, at 10 cm, 35 cm, 60 cm, 85 cm and 110 cm from the inlet of the column.
Table 5.1: Setup dimensions and physical properties of the adsorbent material.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>column length</td>
<td>m</td>
<td>1.2</td>
</tr>
<tr>
<td>internal radius</td>
<td>m</td>
<td>12.5 x 10^{-3}</td>
</tr>
<tr>
<td>external radius</td>
<td>m</td>
<td>15.0 x 10^{-3}</td>
</tr>
<tr>
<td>heat capacity wall (^a)</td>
<td>J/(K m(^3))</td>
<td>4 x 10^6</td>
</tr>
<tr>
<td>13X material density (\rho_M)</td>
<td>kg/m(^3)</td>
<td>2359</td>
</tr>
<tr>
<td>particle density (\rho_p)</td>
<td>kg/m(^3)</td>
<td>1085</td>
</tr>
<tr>
<td>bed density (\rho_b)</td>
<td>kg/m(^3)</td>
<td>652</td>
</tr>
<tr>
<td>particle diameter (d_p)</td>
<td>m</td>
<td>1.6 - 2.0 x 10^{-3}</td>
</tr>
<tr>
<td>heat capacity sorbent (^a) (C_s)</td>
<td>J/(K kg)</td>
<td>920</td>
</tr>
</tbody>
</table>

\(^a\) at a temperature of 25°C.

...would make it difficult for any flow meter to accurately measure the flow. During the TSA experiments presented here, the flow meter could once again only be used to measure the light product flow rate, albeit for a different reason. The heavy product is produced during the heating step, which is also the longest step of the cycle. Throughout this step the flow out of the column is determined by the heat transfer into the bed and the consequent desorption of CO\(_2\); however it is rather slow, indeed for much of the step it is below the lower threshold of the flow meter. Because of this, once again the light product flow rate was measured, and the heavy product amount was calculated.

### 5.1.3 Breakthrough experiments on 13X

In order to understand the mass transfer of CO\(_2\) and N\(_2\) on zeolite 13X as well as the heat transfer from the bed to the column wall under the condition of reasonably high flow rates, a set of eight breakthrough experiments was performed in one of the columns of the setup. All of
them used the same 12/88 CO$_2$/N$_2$ feed mixture, and were conducted at atmospheric pressure (aside from pressure drop through the piping); they were performed at four initial temperatures (25°C, 45°C, 65°C and 100°C) and using two feed flow rates (200 cm$^3$/s and 300 cm$^3$/s).

In general the procedure for the breakthrough experiments was the same as that outlined in Section 3.1, with differences only in the method of regeneration. The column was heated to the desired experimental initial temperature while filled with helium. Once that was reached, the feed was switched to the 12/88 CO$_2$/N$_2$ mixture. The flow rate during the experiment was maintained constant by the MFC, and the BPR was left in the open position to keep the pressure as close to atmospheric conditions as possible. Throughout the experiment, the temperature and pressure inside the column, as well as the exit composition were recorded.

### 5.1.4 Heating and Cooling Steps

In contrast to the PSA processes of previous works$^{25,56}$, the TSA processes presented here undergo much larger changes in temperature throughout a cycle; this is especially true of the column wall, as the columns are heated and cooled externally. As a result, it is important to understand not only the heat transfer from the bed to the wall, but also the heat transfer on the outside of the column. To this end, experiments are reported that focus on the regeneration and subsequent cooling of one single column. In order to isolate the effects of heat transfer from other phenomena and experimental artifacts, care was taken to start each of the experiments from a homogeneous column state, and maintain atmospheric pressure inside the column. Two sets of experiments were performed, one using helium to exclude the impact of adsorption, and one with the feed CO$_2$/N$_2$ mixture. In each set of experiments, the column was heated from 25°C to 100°C, and then cooled down to 25°C.
5. Temperature Swing Adsorption for post-combustion CO\textsubscript{2} capture

again.

**Preparation:** After regenerating the column as described above, the two thermostats were set such that $T_{\text{cool}} = 25^\circ C$ and $T_{\text{heat}} = 100^\circ C$. With the column connected to the *cool* thermostat, feed was passed through the column until the CO\textsubscript{2} front broke through. The flow was then reduced to $50 \text{ cm}^3/\text{s}$ to reduce the pressure drop along the column and the downstream piping and keep the column near atmospheric pressure, and the column was allowed to cool to $25^\circ C$ along its entire length. This was the initial state for the heating experiment.

**Heating:** This step was performed without a feed, and with the column open at the lower end, as it is during the regeneration step of the TSA cycle investigated. By letting the liquid valves switch such that the column was connected to the *hot* thermostat, hot heat exchange fluid was pumped through the column’s jacket. Temperature and pressure in the column were measured until the column had reached the regeneration temperature. The final state of the column was the initial state for the cooling experiments.

**Cooling:** For these experiments, the liquid valves were switched back to let cold heat exchange fluid through the column jacket. If the column were closed during these experiments, the adsorption of the CO\textsubscript{2} by the cooling bed would create a vacuum, possibly resulting in air (with some humidity) entering the column. In order to avoid that, the column was kept at atmospheric pressure during these experiments by keeping the lower end of the column open and flowing feed past the open valve and through the bypass (see Figure 5.1) at the lowest flow rate possible with the MFC.

### 5.1.5 Cyclic TSA experiments

To validate the parameters found through the transient experiments, three cyclic TSA experiments were performed to cyclic steady state.
The TSA experiments were performed using both columns of the laboratory setup (in contrast to the transient experiments); the columns underwent the same three-step process cycle, out of phase by one-half of one cycle. For all three experiments, the feed flow rate was $300 \text{ cm}^3/\text{s}$, and the pressure was kept near atmospheric. The experiments differed in the temperature used for desorption: 100 °C, 125 °C, and 150 °C, and in the timing of the individual process steps. The three process steps were adsorption, heating, and cooling:

In **adsorption**, feed was passed through the column while it was connected to the *cool* thermostat (flow direction ↑). In this step, the light product was produced (N$_2$-rich).

In **heating**, the column was left open at the lower end while it was connected to the *hot* thermostat (flow direction ↓). In this step, the heavy product was produced (CO$_2$-rich).

In **cooling**, the column was connected to the *cool* thermostat again, and was left open at the lower end while feed passed by the open end at minimal flow rate to maintain atmospheric pressure (flow direction ↑). No product was produced in this step.

As the thermostats’ internal pumps are controlled manually and take some time to start up, it was ensured that they would not be blocked. To achieve this, each of the thermostats was connected to a column at any given time, i.e. there was always one column being heated and one being cooled. As a result, the timing of the process steps is constrained in that $t_{\text{heat}} = t_{\text{ads}} + t_{\text{cool}}$.

Each of the TSA experiments was performed until cyclic steady-state (CSS) was reached. Simulations performed before the experiments used to choose appropriate operating conditions typically converged to CSS in four cycles – as a result, each of the experiments was run for at least five cycles. During the first three, the MS was set to measure the composition of the light product, as that information is necessary in
order to determine the flow rate\textsuperscript{25}. Then the MS was set to record the heavy product composition for at least one cycle, before returning to the light product for a final cycle.

### 5.2 Modeling and parameter estimation

The model is in principle the same as presented in Section 1.4, with the material and energy balance for the bed unchanged. The only difference is in the energy balance for the column wall: In the breakthrough study reported in Chapter 3 as well as the PSA experiments presented in Chapter 4 the outside of the column was insulated and underwent very little temperature variations during the experiments. As a result, the heat transfer coefficient $h_w$ was relatively low and the surrounding temperature $T_{\text{amb}}$ was taken as constant. In the new setup the column is heated and cooled externally, and $T_{\text{amb}}$, the “ambient” temperature, represents the temperature of the heat exchange fluid in the column jacket. This obviously undergoes significant variations during some of the experiments reported here. In addition, it is measured at the inlet and outlet of the jacket, and therefore is known to some degree.

The temperature of the heat exchange fluid at any given time depends on a multitude of factors, from the heating or cooling power of the thermostat used, the pump flow rate, the volume and insulation of the tubing used, to the valves used to control the liquid. Predicting this temperature would be difficult and involve many phenomena that are very specific to the laboratory setup used; this goes beyond the scope of this work. The temperature of the fluid surrounding the column is therefore taken as the measured value, and used as an input into the column model. To determine the value at any given time during an experiment and for any position along the length of the column, the measurements at the inlet...
5.2 Modeling and parameter estimation

and outlet of the column are interpolated linearly in time and position:

\[
T_{\text{amb}}(x, t) = T_{i}^{\text{in}}(t) + \frac{x}{L} \left( T_{i}^{\text{out}}(t) - T_{i}^{\text{in}}(t) \right) \tag{5.1}
\]

\[
T_{i}^{j}(t) = T_{f,j}^{i} + \frac{t - t_{j}}{t_{j+1} - t_{j}} \left( T_{f,j+1}^{i} - T_{f,j}^{i} \right) \quad i = \text{in, out} \tag{5.2}
\]

where \(T_{f,j}^{i}\) refers to the measured temperature of the heat transfer fluid at the inlet or outlet at time \(t_{j}\), which is the time of the last measurement before time \(t\). Accordingly, \(t_{j+1}\) is the time of the next measurement after time \(t\). For the simulation of the breakthrough experiments, where \(T_{i}^{\text{in}}\) and \(T_{i}^{\text{out}}\) are essentially constant and equal, \(T_{\text{amb}}\) is taken as constant and equal to the average of the thermofluid temperature over the duration of the experiment.

5.2.1 Parameter estimation

The estimation of the transport parameters was carried out by comparing measurements taken during the transient experiments (breakthrough, heating, and cooling) to simulations, and using the \textit{fmincon} routine that is part of the optimization toolbox of MATLAB (The MathWorks, Inc., Natick, MA, USA).

\textbf{Breakthrough experiments:} These experiments were used to characterize the mass transfer coefficient for \(\text{CO}_2\) and the heat transfer coefficient from the bed to the column wall \(h_L\) under conditions of flow. The observed variables to be compared were the mole fractions of \(\text{N}_2\) and \(\text{CO}_2\) (but not the inert \(\text{He}\) used to pressurize the column), as well as the temperature inside the bed at five positions along the column, just as was done in Chapter 3\textsuperscript{51}. The objective function was altered to include weighting factors, as it previously placed equal weight on each measured output, which overall emphasizes the temperature measurements. The
objective function to be minimized is now defined as

$$
\Phi_{\text{obj}}(p) = \omega_y \sum_{k=1}^{2} \ln \left( \frac{1}{N_{\text{obs},y}} \sum_{j=1}^{N_{\text{obs},y}} \left( \frac{y_{j,k} - \hat{y}_{j,k}(p)}{y_{j,k} + \gamma} \right)^2 \right) + \omega_T \sum_{k=1}^{5} \ln \left( \frac{1}{N_{\text{obs},T}} \sum_{j=1}^{N_{\text{obs},T}} \left( \frac{T_{j,k} - \hat{T}_{j,k}(p)}{T_{j,k}} \right)^2 \right)
$$

(5.3)

where \(y_{j,k}\) and \(T_{j,k}\) are the measured output (mole fraction or temperature) \(k\) at time \(j\), \(\hat{y}_{j,k}\) and \(\hat{T}_{j,k}\) are the corresponding simulated values, \(N_{\text{obs},y}\) and \(N_{\text{obs},T}\) are the number of observed data points for the composition and temperature, respectively, \(\gamma = 1\) is a constant introduced to avoid dividing by zero when a mole fraction is zero, and \(\omega_y\) and \(\omega_T\) are the weighting factors introduced. As their purpose is to relate the importance of the two measured mole fractions to the five temperatures, an unnecessary degree of freedom was eliminated by constraining the weighting factors to \(2\omega_y + 5\omega_T = 1\). In this work they were chosen to be

$$
\omega_y = 0.25 \quad \omega_T = 0.1
$$

such that the weight given to the mole fractions and the temperatures is the same. The mass transfer of \(N_2\) was sufficiently fast that the data obtained did not allow for an accurate estimate for \(k_{N_2}\), as any value over \(0.5\text{s}^{-1}\) described the data similarly well. Therefore, its value was fixed at \(k_{N_2} = 0.5\text{s}^{-1}\). As is discussed in Chapter 3, a slight shift in the position of temperature and composition fronts can create significant difficulties for the determination of transport parameters. Such a shift can be caused by a small deviation of the flow rate from the set point,
even within the specified accuracy of ±2% of the full scale of the MFC’s operating range. The feed velocity was therefore regarded as a model parameter to be estimated along with the transport parameters $h_L$ and $k_{CO_2}$.\textsuperscript{51}

**Heating and cooling experiments:** These experiments were used to characterize the heat transfer from the thermal fluid in the column jacket to the column wall, and the heat transfer between the bed and the wall under stagnant conditions. Only the five temperatures inside the bed were used for comparison with simulations. As a result, the objective function consists only of the second term in Eq. (5.3). The mass transfer coefficient of CO$_2$ showed almost no impact on the simulated results due to the long duration and lack of sharp transitions in these steps.

### 5.3 Results and discussion

The aim of the work reported in this chapter was to validate the model for adsorption processes developed at SPL and the approach used here to calibrate such a model for temperature swing adsorption processes, such that it may then be used to simulate, design, and optimize such processes for their applications in post-combustion CO$_2$ capture. In the following, the transient experiments performed to determine the transport parameters are presented, followed by a discussion of the phenomena characterized. Finally, the results of the cyclic TSA experiments are presented and compared to simulations.

#### 5.3.1 Breakthrough

In Figure 5.2, the results of one of the breakthrough experiments are shown alongside simulation results. The experiment was performed with an initial column temperature of 25°C and a feed with a CO$_2$ content
5. Temperature Swing Adsorption for post-combustion CO$_2$ capture

Figure 5.2: Concentration (top) and temperature (bottom) profiles for the breakthrough experiment with an initial temperature of 25°C, a feed composition of $y_{CO_2} = 0.12$, and a feed flow rate of 300 cm$^3$/s. Experimental data (symbols) are shown together with the simulations (lines) carried out with the mass transfer coefficients $k_{N_2} = 0.5$ s$^{-1}$, $k_{CO_2} = 0.1$ s$^{-1}$, and the heat transfer coefficient fitted to this experiment, $h_L = 35.3$ W m$^{-1}$K$^{-1}$. The concentration profile is shown with a broken axis to provide better detail on the CO$_2$ concentration.
of 12% and a flow rate of 300 $\text{cm}^3/\text{s}$. It can be seen that the N$_2$ does not adsorb very much, as it breaks through almost immediately; some does adsorb, however, as evidenced by the moderate temperature increase throughout the bed. The CO$_2$, on the other hand, adsorbs significantly more, and breaks through much later. A very notable feature of these results is that the adsorbing CO$_2$ creates a front of very high temperature as it advances through the column, with temperatures in excess of 90 °C.

### 5.3.1.1 Mass transfer

The large amount of heat released as the CO$_2$ adsorbs creates a challenge for the determination of the value of $k_{\text{CO}_2}$, as it hinders adsorption. The rate of uptake is then limited by the rate at which the bed cools, rather than the adsorption kinetics of the CO$_2$. This is consistent with studies found in literature about the mass transfer of CO$_2$ on beads of 13X. Giesy et al. used a combined-technique frequency response apparatus to study the mass transfer of CO$_2$ on 13X at 23 °C and at pressures up to 1 bar, and found that temperature effects played a significant role in the adsorption kinetics$^{57}$. Hu et al. used a zero length column system to study gas mixtures containing between 0.1 and 10 % CO$_2$, and found that for the higher CO$_2$ concentrations the heat transfer was indeed what determined the uptake rate$^{58}$. Some studies have assumed the mass transfer to be controlled by molecular diffusion in the macropores, using approximations for linear systems to describe the mass transfer on 13X$^{52,53}$.

In the experiments reported in this work, the heat transfer limitation was such that the fitting of the mass transfer of CO$_2$ was inconclusive, as the shape of the CO$_2$ front showed very little sensitivity to values of $k_{\text{CO}_2} \geq 0.05 \text{s}^{-1}$. The height of the temperature front exhibited a somewhat stronger dependency to the mass transfer, and it was found that a value of $k_{\text{CO}_2} = 0.1 \text{s}^{-1}$ worked quite well to describe the breakthrough
experiments – this value was used for all simulations. As discussed in Section 5.2.1, the mass transfer coefficient of N\textsubscript{2} was fixed at $k_{N\textsubscript{2}} = 0.5 \text{s}^{-1}$. These are the values used for the simulation shown in Figure 5.2.

5.3.1.2 Heat transfer in the bed

Each of the breakthrough experiments was used to fit a value of $h_L$ individually to that experiment (along with the feed velocity, see Section 5.2.1). The values used for the mass transfer coefficients and the heat transfer on the outside of the column in these simulations were: $k_{CO_2} = 0.1 \text{s}^{-1}$, $k_{N\textsubscript{2}} = 0.5 \text{s}^{-1}$, $h_w = 220 \text{W m}^{-2} \text{k}$. Figure 5.2 shows that this combination of parameters is capable of describing the measured temperatures and compositions rather well. In principle, a better description of the heat transfer could be achieved by considering a more detailed model. The energy balance used in this work is based on a number of simplifications as discussed in Chapter 1:

- A constant heat of adsorption, $\Delta H$, that is independent of temperature, gas composition, and loading;
- A flat temperature profile, i.e. no radial gradients;
- A heat transfer coefficient $h_L$ that depends on the feed conditions and the physical bed dimensions (bed diameter, particle size and shape), but not on local conditions.

Each of these simplifications was made with the intention of reducing the complexity of the model and reducing the computational intensity of the simulations; and they need to be kept in mind when comparing the results. The simulated temperature in the bed, e.g., represents an average temperature across the cross-section of the bed at that position, while the thermocouple measuring the temperature is located at the center of the column axis, where heat dissipation to the column wall takes
somewhat longer than elsewhere. It is therefore not surprising that the simulations do not reach the same temperature peak height, and that the temperature decreases somewhat quicker than what is seen in measurements. Nevertheless, the overall description is good, and adding complexities such as the radial dimensions to the model does not seem to be warranted. The values of $h_L$ resulting from the fitting can be seen in Figure 5.3, plotted as a function of the Reynolds number under the feed conditions.

The problem of heat transfer is not a new one, and a number of studies are available in literature\textsuperscript{59–63}. In Chapter 3, heat transfer coefficients fitted to breakthrough experiments performed with activated carbon were compared to values predicted by an expression by Leva\textsuperscript{51,59}, and it was found that the values were similar. However, this expression goes to zero for $Re = 0$. As the heating and cooling steps take place at very low flow velocities and also the breakthrough experiments have relatively low Reynolds numbers, the correlation developed by Leva is no longer applicable. Instead, the values of $h_L$ fitted to the experiments in this work were compared to a selection of correlations from literature that each also consider a static component to the heat transfer. Three correlations from literature were chosen for this comparison.

DeWasch and Froment found a linear relationship between the Nusselt and Reynolds numbers:\textsuperscript{62,64}

$$Nu = Nu_0 + 0.033PrRe$$

with the dimensionless numbers being

$$Nu = \frac{h_L d_p}{\lambda}, \quad Nu_0 = \frac{h_{L_0} d_p}{\lambda}, \quad Pr = \frac{\rho \nu C_p}{\lambda}, \quad Re = \frac{v d_p}{\nu}$$

Here, $Nu_0$ is the static Nusselt number, a function of the tube diameter, the particle geometry and their physical properties, and the heat conductivity of the gas. For the experiments reported here, its value is
Nu₀ = 1.51, and it is discussed in more detail in Appendix C.3. Dixon as well as Specchia worked with a two-dimensional model, considering separately the effective heat transfer within the packed bed, \( K_R \), and the heat transfer at the column wall, \( \alpha_w \). Dixon used a mechanistic approach wherein he considered the particle geometry and packing density of the bed to find the contribution of conduction through the solid and through the gas phase, as well as convective effects. Specchia et al. used a somewhat more empirical approach, considering for \( \alpha_w \) and \( K_R \) each a static and a convective component. In order to combine the values obtained for \( \alpha_w \) and \( K_R \) into a single heat transfer coefficient, Dixon proposed an equation for the overall heat transfer coefficient in packed beds:

\[
\frac{1}{h_L} = \frac{1}{\alpha_w} + \frac{R_i \text{ Bi} + 3}{3K_R \text{ Bi} + 4}
\] (5.5)

where the Biot number is \( \text{Bi} = \alpha_w R_i / K_R \), and \( R_i \) is the inside column radius. This equation was used for the values obtained using both approaches; they are discussed in more detail in Appendix C.3. The heat transfer coefficients estimated using all three approaches are illustrated in Figure 5.3, together with the values of \( h_L \) fitted individually to each of the breakthrough experiments. All of the correlations obtained values slightly higher than those determined experimentally, but they are quite close in value, and exhibit the same linear increase with \( \text{Re} \) that is seen in each of the correlations shown.

5.3.2 Heating and cooling

In Figure 5.4 the results from the heating and cooling experiment using the same CO₂/N₂ feed as the breakthrough experiments are illustrated. While these two steps were performed in series, they are shown in separate axes, as the individual steps are truncated to make the details more
Figure 5.3: Heat transfer coefficients fitted to each of the experiments performed (symbols), together with a selection of correlations found in literature (lines).\textsuperscript{60,62,63} ○ Breakthrough experiments, △ heating/cooling experiment.

visible. The full length of the steps was 1800 s for the heating step and 1200 s for the cooling step. Along with the temperatures measured in the bed (symbols) and the corresponding simulation results (lines), the measured temperature of the heat exchange fluid at the jacket inlet and outlet is shown using dots (dark and light grey, respectively). These data were not simulated, but rather were treated as an input into the model, as discussed in Section 5.2. From the figure it can be seen that

- The thermofluid temperature initially oscillates a bit, and in both cases overshoots past the set point temperature. This is in part due to back-mixing of the fluid from the heating jacket to the thermostat, e.g. the cold fluid going into the hot thermostat. It is also one of the reasons the fluid temperature was used as the input for the model – predicting this behavior would entail extensive calibration that would be very specific to this laboratory setup.
Figure 5.4: Temperature profiles inside the column during the heating and cooling experiment using the CO$_2$/N$_2$ feed. Symbols are measurements at the five positions: □ 10 cm, ◦ 35 cm, ◇ 60 cm, △ 85 cm, ⋆ 110 cm. The dots are the measured thermofluid temperature at the jacket inlet and outlet. Lines represent simulations. The arrows indicate the axial profile that developed within the column.
and was therefore outside the scope of this work.

- The temperature of the thermofluid entering the column and exiting the column are fairly similar. This is due to the relatively short residence time of the fluid in the column jacket. If the difference were large, the linear interpolation used to calculate the fluid temperature along the length of the column might not be accurate enough, and the energy balance for the thermofluid might have to be included in the model.

- A temperature gradient develops along the length of the bed. As indicated in the Figure by the gray arrow, the temperature measured in the lower part of the bed changes temperature considerably faster than the upper portion of the column. This trend is seen in both the heating and the cooling step.

Initially, the temperature gradient along the length of the column was described by simulations as much smaller than the measurements show. One possible reason is that as the heat transfer fluid enters the jacket at the bottom of the column and exits at the top, there is a gradient in the temperature around the column ($T_{\text{amb}}$); however it is not sufficiently large to explain the rather strong gradient in the bed. Alternatively, if the bed had not been saturated thoroughly enough in the preparation step of the experiment, different adsorbed amounts at different positions in the column could heat up at different rates as the enthalpy needed for desorption delays the heating. If this were the case, however, there would be more CO$_2$ adsorbed in the lower portion of the column, which should delay the heating in that part of the column; the opposite was observed.

Another possibility is that hydrodynamically and thermally developing flow in the entry region of the heating jacket might introduce a dependency on position of the heat transfer, leading to uneven heating of the
bed. While this is specific to the laboratory setup and thus has no bearing on the development and design of TSA processes in general, it may be necessary to account for this in order to accurately describe the experiments performed.

In the jacket around the column, the heat exchange fluid is flowing in an annular tube. The VDI Heat Atlas (Part G2) provides correlations that describe the heat transfer for this kind of geometry under laminar and turbulent flow condition, for the transition region between the two regimes, as well as for the entry region. Many of the physical quantities that are needed to evaluate these expressions are already known or are available from the manufacturer of the thermofluid; however some are more difficult to obtain, such as the thermofluid flow rate, which depends on the pressure drop through the pipes and jacket in addition to the pump power and efficiency. While this makes it difficult to use the Heat Atlas to calculate quantitative values for \( h_w \), the expressions therein make it clear that the Nusselt number, and accordingly the heat transfer coefficient, increase significantly near the entrance. Differences in the temperature and the flow rate of the thermofluid lead to rather different values of \( \text{Nu}_\infty \), the Nusselt number at infinite length (i.e. past any entry region effects); however relative to it the entrance effects behave very similarly along the length of the column. Figure 5.5 shows the entrance effects on the Nusselt number along the length of the column jacket, reduced by \( \text{Nu}_\infty \).

To verify the plausibility of the theory that the entrance effects are causing the axial temperature gradient within the column, the temperature data from the heating and cooling experiment with helium are considered, to exclude any effects from ad- and desorption. The data for this experiments are reported in Appendix C.2, as well as a more detailed report of these considerations. If the system is simplified, the temperature
Figure 5.5: Entry-region effects on the Nusselt number relative to its value at infinite length for temperatures ranging from 25 °C to 150 °C and flow rates from $0.2\frac{kg}{s}$ to $0.6\frac{kg}{s}$ (lines). Symbols show the apparent overall heat transfer coefficient at the position of each of the thermocouples during the heating (□) and the cooling (△) experiment with helium.

The dependence on the position is not quite as strong as for the calculated Nusselt number shown in the same figure, however it has to be kept in mind that the symbols represent the overall heat transfer including the heat transfer within the bed. Overall this
was taken as an indication that the entrance effects on the heat transfer coefficient $h_w$ are worth considering. This was done in the following manner: The heat transfer coefficient $h_w(x)$ at any position along the column was calculated as

$$h_w(x) = h_{w,L} \left( \frac{\text{Nu}(x)}{\text{Nu}(L)} \right)$$  \hspace{1cm} (5.7)

where $\frac{\text{Nu}(x)}{\text{Nu}(L)}$ was calculated for conditions representative of the conditions present throughout a TSA cycle. The value of $h_{w,L}$, the heat transfer coefficient at the end of the column, was fitted to the heating and cooling experiments, along with the heat transfer coefficient within the bed, $h_L$, under the condition of (almost) no flow.

All of the transport parameters that were established via the transient experiments reported above are summarized in Table 5.2. These are the values that are used for all following simulations of TSA processes.

**Table 5.2:** Transport parameters used for the simulation of the TSA experiments.

<table>
<thead>
<tr>
<th>Parameter Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass transfer coefficient CO$_2$</td>
<td>$k_{CO_2}$ [s$^{-1}$]</td>
</tr>
<tr>
<td>Mass transfer coefficient N$_2$</td>
<td>$k_{N_2}$ [s$^{-1}$]</td>
</tr>
<tr>
<td>Heat transfer coefficients</td>
<td></td>
</tr>
<tr>
<td>Internal (flow)</td>
<td>$h_L$ [W mK$^{-1}$]</td>
</tr>
<tr>
<td>Internal (static)</td>
<td>$h^0_L$ [W mK$^{-1}$]</td>
</tr>
<tr>
<td>External (column end)</td>
<td>$h_{w,L}$ [W mK$^{-1}$]</td>
</tr>
</tbody>
</table>
5.3 Results and discussion

5.3.3 Prediction of column behavior during cyclic TSA experiments

Finally, the mass and heat transfer coefficients determined in this work were used to predict the behavior of cyclic TSA processes, and three TSA experiments were performed and compared with simulations. As the desorption temperature, $T_H$, has a large impact on the process performance, three different temperature levels were chosen: 100°C, 125°C, and 150°C. The feed flow rate and the flow direction in each step were kept the same in all three experiments, however the timing of the individual steps was different in each experiment. To determine the timing of the steps, a simple parametric analysis was performed for each $T_H$, varying the duration of the adsorption step between 3 and 12 minutes and the duration of the cooling step between 6 and 20 minutes (the duration of the heating step was fixed as the sum of the other two steps, see Section 5.1.5). As the main objective in a post-combustion CO\textsubscript{2} capture process is the CO\textsubscript{2} product stream, conditions were considered that should yield a CO\textsubscript{2} purity of $\geq 90\%$, according to simulations. Then, a set of conditions was chosen that provided a compromise between CO\textsubscript{2} recovery ($\frac{\text{CO}_2\text{produced}}{\text{CO}_2\text{fed}}$) and productivity ($\frac{\text{kgCO}_2}{t_{\text{zeolite}}}$). The operating conditions chosen for each of the TSA experiments are reported in Table 5.3. In the following, the results of the TSA experiment with a desorption temperature $T_H = 150\, ^\circ\text{C}$ are reported. Each of the measured quantities as well as the calculated quantities such as the product purities and component recoveries are considered and compared with simulation results. The results for the other two TSA experiments performed are reported in Appendix C.5.
Figure 5.6: Temperature profiles inside the column during the TSA experiment with a desorption temperature of 150°C. Symbols are measurements at the five positions: □ 10 cm, ◇ 35 cm, ◇ 60 cm, △ 85 cm, ⋆ 110 cm. The dots are the measured thermofluid temperature at the inlet (dark) and outlet (light). Lines represent simulations. The vertical gray lines indicate the switch times between steps.
Table 5.3: Operating conditions chosen for the TSA experiments performed.

<table>
<thead>
<tr>
<th>$T_H$ (°C)</th>
<th>$y_{\text{CO}_2}^{\text{feed}}$</th>
<th>$\dot{V}_{\text{feed}}$ [cm$^3$/s]</th>
<th>step times [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.12</td>
<td>300</td>
<td>480 1380 900</td>
</tr>
<tr>
<td>125</td>
<td>0.12</td>
<td>300</td>
<td>240 960 720</td>
</tr>
<tr>
<td>150</td>
<td>0.12</td>
<td>300</td>
<td>360 1080 720</td>
</tr>
</tbody>
</table>

5.3.3.1 Temperature profiles

The temperature profiles measured inside column 2 during the TSA experiment are shown in Figure 5.6 along with the simulation results. During the adsorption step the heat released by the adsorption of the advancing CO$_2$ front is clearly visible in both experiment and simulation, and the timing of the temperature front is matched rather well by the simulations. The height of the temperature is not described as well – this might be due to the neglect of the radial gradients in the model. The simulated temperature is a cross-sectional average, while the temperature at the center of the bed might be somewhat higher. During the heating step, the axial gradient seen in the heating and cooling experiments is not quite as evident, as the column does not start out in a homogeneous state, but rather has an initial gradient that runs opposite of what develops during the heating. Nevertheless, the simulations describe the temperature increase well, and by the end of the heating step simulations and measured data are all within a narrow band. During the cooling step that follows, the axial gradient is much more visible in both experiment and simulation.
Figure 5.7: Comparison of simulation (lines) and experimental (symbols) results for the light product. a) shows the composition of the N$_2$ product throughout the adsorption step, as well as the feed composition. b) shows the flow rate of the light product together with the feed flow rate. To show that the two columns operate consistently, data from both columns are shown: ■ column 1, □ column 2.

5.3.3.2 Exit profiles

Figure 5.7 shows the composition and flow rate of the light product (N$_2$) over the duration of the adsorption step. Data from both columns are shown, both to illustrate that the two columns operate the same way, and to verify the reproducibility of the experiment. Along with the data on the product, the feed composition and flow rate are shown. The composition of the N$_2$ product is shown in Figure 5.7a. The measured com-
position is initially very close to the feed compositions of \( y_{\text{CO}_2} = 0.12 \), however this is an artifact that is due to the fact that the preceding step in the TSA cycle is the open cooling step, wherein the feed is passed through the bypass at a low flow rate, and is then analyzed by the MS. The composition then quickly settles on a low concentration of \( \text{CO}_2 \) that slowly decreases throughout the adsorption step until the last few seconds, where it begins to increase again. The level of this plateau is determined by the isotherm, more specifically the partial pressure of \( \text{CO}_2 \) that is in equilibrium with the amount of \( \text{CO}_2 \) adsorbed at the end of the heating step. It slowly decreases between about 30s and 300s of the adsorption step, as the top portion of the column of the bed is still cooling (see the ⋆ in Figure 5.6). Both the level of this plateau and the slow decrease are captured very well by the model. The final increase in \( y_{\text{CO}_2} \) is due to the imminent breakthrough of \( \text{CO}_2 \), which simulations predicted to be a little earlier than seen in experiment.

The flow rate of the \( \text{N}_2 \) product is shown in Figure 5.7b. For this TSA experiment, the step timing was such that the \( \text{CO}_2 \) front did not appreciably break through – as a result the product flow rate is essentially constant for most of the step. The exception is the beginning of the step, where the feed flow rate ramps up over the first few seconds, and the product flow rate lags behind it by about 15 seconds. The relatively high flow rate during this step of the process resulted in a significant pressure drop. In fact, even with the BPR open, the downstream piping and valves provided enough resistance that at the pressure at the end of the column was typically around 1.3 bar during the breakthrough experiment and the adsorption step of the TSA experiments. As the heating and cooling step see much lower flow rates, they are essentially at atmospheric pressure. Until the pressure in the column builds up, the exiting flow rate is lower. In addition, the simulations show a slightly lower flow rate than what was measured. While the difference is not large, it is consistent throughout the entire duration of the adsorption
Figure 5.8: Comparison of simulation (lines) and experimental (symbols) results for the composition of the heavy product. Data from both columns are shown: ■ column 1, □ column 2.

step. It should be noted, however, that it is within the uncertainty of the flow meter.

The composition of the CO$_2$ product can be seen in Figure 5.8. As discussed in Section 5.1, the flow rate of this stream was not measured, so the composition shown here did not figure into the process performance calculations. However, as the course of the composition is very sensitive to both the isotherm and the rate of heating, which in turn depends on the heat transfer into the column, it constitutes a good test of the model and the parameters used. Initially, this product is mostly nitrogen, as it is determined by the (non-selective) gas phase present in the column at the end of the adsorption step. As the column heats, and the CO$_2$ desorbs, it displaces the N$_2$ in the gas phase, until the gas phase consist of pure CO$_2$. In both columns, it took just over two minutes to reach 80% CO$_2$ purity, and about five minutes to reach 95%. The simulations matched this development remarkably well.
5.3.4 Process performance of TSA experiments

From the data presented in Figure 5.7, the total amount and composition of the light product can be determined by integration over the duration of the adsorption step. Similarly, the total amount fed to each column is known from the MFC measurements. This allows the calculation of the purity of each product and the recovery of each component, as has already been reported in Section 4.3.3. Table 5.4 summarizes the calculated performance figures for the TSA experiments performed, together with the results from simulations. The values reported are the mean of the values of both columns during the final cycle performed, while the uncertainties reported are propagated from the uncertainties considered in the measured quantities, as reported in Section 4.1.2. It can be seen that the simulations managed to predict all process performance indicators to within the experimental uncertainties. However, it is quite evident that the numbers calculated for the experimental $N_2$ recovery and $CO_2$ purity require close scrutiny, as both of these quantities were consistently calculated to be over 100\%, and the $CO_2$ purity showed excessively large uncertainty. To understand where these large uncertainties come from, one has to look at how the quantities are obtained, and what numbers go into the calculation:

**$N_2$ purity:** This quantity is calculated directly from the composition and product flow rate measured, and it has an accordingly low uncertainty. In fact, as the product flow rate is present in both the numerator (to determine the amount of each component) and the denominator (to calculate the total amount), the $N_2$ purity is relatively insensitive to the uncertainty in that flow rate.

**$N_2$ and $CO_2$ recovery:** These two quantities are derived from the amounts of each component fed to the column, and the light product composition and flow rate. However, unlike in the case above, the product flow rate is used in the numerator (to determine the amount of each
Table 5.4: Comparison of experimental and simulated process performance figures for the three TSA processes run in experiment. All experiments used the same feed composition and flow rate.

<table>
<thead>
<tr>
<th>desorption temperature $T_H$</th>
<th>100 °C</th>
<th>125 °C</th>
<th>150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$ purity [%]</td>
<td>sim.</td>
<td>92.0</td>
<td>97.4</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>92.1 ± 0.6</td>
<td>97.4 ± 0.6</td>
</tr>
<tr>
<td>$N_2$ recovery [%]</td>
<td>sim.</td>
<td>99.6</td>
<td>99.1</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>100 ± 4.2</td>
<td>103 ± 4.4</td>
</tr>
<tr>
<td>$CO_2$ purity [%]</td>
<td>sim.</td>
<td>90.2</td>
<td>90.1</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>106 ± 101</td>
<td>137 ± 71</td>
</tr>
<tr>
<td>$CO_2$ recovery [%]</td>
<td>sim.</td>
<td>36.5</td>
<td>80.5</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>36.9 ± 4.5</td>
<td>79.6 ± 5.4</td>
</tr>
<tr>
<td>productivity $\left[\frac{kg_{CO_2}}{t_{zeolite} h}\right]$</td>
<td>sim.</td>
<td>37.8</td>
<td>60.4</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>38.0 ± 4.3</td>
<td>58.6 ± 3.1</td>
</tr>
</tbody>
</table>

component), but the feed flow rate (measured by the MFC) is used in the denominator. Each of the flow rates introduces some uncertainty, leading to a larger overall uncertainty. Additionally, the simulations already predicted a $N_2$ recovery of > 99%, so even a relatively small error could result in a value over 100%.

**$CO_2$ purity:** While this quantity is calculated based on the same numbers as the previous ones, it has to contend with the fact that the $CO_2$ product represents a rather small portion of the feed stream. In the case of $T_H = 100$ °C, less than 40% of the $CO_2$ in the feed are recovered, which was only 12% of the feed to begin with. With less than 5% of the feed ending in this stream, and its amount not measured directly, but by measurement of a much larger stream, any error in the flow rate of the light product will be magnified strongly in this quantity.

To illustrate this, Figure 5.9 shows the dependence of the calculated pu-
5.3 Results and discussion

rities and recoveries on the flow rate of the light product. It is clear from this figure that even a small error in the light product flow rate has such an impact on the CO$_2$ purity found that any value determined with this setup has to be taken with great care. There are a number of possibilities to determine the CO$_2$ purity more accurately. One way would be to measure the flow rate of the CO$_2$ stream independently of the light product. As discussed in Section 5.1, this faces the difficulty of a highly variable flow rate along with large changes in the product composition, both of which pose a challenge to any flow meter and introduce uncertainty during the integration. An alternative would be to collect the CO$_2$ product during the experiment, and determine the overall composition after the experiment. However, the container used to hold the product would have to expand in volume and should require minimal pressure, as the process is operated near atmospheric pressure. Under the operating conditions reported here, each column would deliver between 8 and 12 L of CO$_2$ product during each cycle, which means the collection device would need to be rather big. A modification of this magnitude was, for now, not considered.

The quantities that can be determined with some level of certainty, however, show that the model is indeed useful to design cyclic TSA processes. Figure 5.10 shows the results of the parametric analysis performed at the beginning of Section 5.3.3. For each of the desorption temperatures considered, the resulting CO$_2$ recovery and productivity for all of the simulated step time configurations are shown. Small crosses represent configurations that do not meet the $y_{CO_2} \geq 90\%$ specification, while the filled symbols represent those that do. While this is by no means a comprehensive optimization of the TSA process, it shows the trade-off between the CO$_2$ recovery and column productivity for each desorption temperature. Shown in the figure as a red symbol with error bars are the results from the three TSA experiments performed, and in blue are the results from the simulations of the experimental conditions. The only
5. Temperature Swing Adsorption for post-combustion CO$_2$ capture

![Figure 5.9](image)

**Figure 5.9:** Dependence of the calculated product purities and component recoveries on the flow rate of the light product.

The difference between the blue symbols and the corresponding gray symbols is that the simulations shown in gray used temperature profiles for the thermofluid that were estimates based on the heating and cooling experiment performed with the CO$_2$/N$_2$ feed, scaling the temperature for higher values of $T_H$. Once the TSA experiments had been performed, the measured data for $T_{in}^T$ and $T_{out}^T$ were used to repeat the simulations.

### 5.4 Conclusions

In order to validate a model developed to describe cyclic adsorption-based gas separation processes for processes that rely on heat to regenerate the bed (temperature swing adsorption), a number of transient and cyclic experiments have been performed. The model has previously been calibrated and validated for pressure swing adsorption processes using activated carbon to separate binary and ternary gas mixtures in the context of pre-combustion CO$_2$ capture. However the conditions present in
5.4 Conclusions

The low pressure of the feed and the relatively low CO$_2$ content, coupled with the fact that N$_2$ also adsorbs on many sorbents, motivated the use of zeolite 13X in a TSA process. In order to be able to utilize the model for process design and optimization, a full characterization of the system CO$_2$/N$_2$ on zeolite 13X was performed, consisting of the characterization of the adsorption equilibrium and the transport phenomena, and the validation for cyclic processes. The work on the adsorption equilib-
5. Temperature Swing Adsorption for post-combustion CO$_2$ capture

Equilibrium has been reported by Hefti et al.$^{43}$ and is summarized in Chapter 2, while the determination of heat and mass transfer coefficients and the validation by experiment is reported here. Transport parameters were estimated by using two types of experiments: Breakthrough experiments were performed to determine the mass transfer coefficients of the CO$_2$ and N$_2$, however it was found that they could not be determined accurately. For N$_2$ it was the kinetics of adsorption are sufficiently fast that $k_{N_2}$ could not be determined accurately with this setup, while for CO$_2$ the adsorption is limited by the heat transfer. The same breakthrough experiments were then used to characterize the heat transfer within the bed, observing a dependence on the Reynolds number that is also reported in literature$^{60,62,63}$. To study the heat transport from the column wall to the surrounding thermofluid, heating and cooling experiments were performed. A significant effect of the entry region of the heating jacket on the heat transfer at the lower end of the column was observed, and could be modeled accordingly. Finally, the parameters determined were used in the model to choose experimental conditions, and cyclic TSA experiments were performed to validate the process performance indicators calculated by simulation. Although it was found that the laboratory setup in its current form cannot accurately confirm the CO$_2$ purity, the other performance figures show that the model can be used for further process design and optimization with confidence.
Notation

Roman

- $a_w$: specific surface area of the column
- $Bi$: Biot number [-]
- $C$: heat capacity [J/(K m³)]
- $d_p$: particle diameter [m]
- $h_L$: heat transfer coefficient (column-wall) [W/(m² K)]
- $h_w$: heat transfer coefficient (wall-ambient) [W/(m² K)]
- $\Delta H$: heat of adsorption [J/mol]
- $k$: overall mass transfer coefficient [s⁻¹]
- $K_R$: effective heat transfer within the packed bed [W/m K]
- $L$: column length [m]
- $N_{obs}$: number of observations [-]
- $Nu$: Nusselt number [-]
- $p$: parameter vector
- $P$: total fluid pressure [Pa]
- $Pr$: Prandtl number [-]
- $R$: universal gas constant [J/(mol K)]
- $R_i$: inside column radius [m]
- $R_o$: outside column radius [m]
- $Re$: Reynolds number [-]
- $t$: time [s]
- $T$: temperature [°C]
- $U$: overall heat transfer coefficient [W/(m² K)]
- $V_{\text{feed}}$: volumetric feed flow rate [cm³/s]
- $x$: spacial coordinate in the axial direction [m]
- $y$: mole fraction [-]

Greek

- $\alpha_w$: heat transfer coefficient at the column wall [W/(m² K)]
- $\gamma$: constant used in parameter fitting
5. Temperature Swing Adsorption for post-combustion CO$_2$ capture

$\Phi$  objective function [N/m]

$\lambda$  thermal conductivity of the gas [W/(m K)]

$\mu$  dynamic viscosity [Pa s]

$\nu$  kinematic viscosity [m$^2$/s]

$\omega$  weighting factors for parameter fitting

Sub- and Superscript

$^\sim$  calculated value

$^0$  static conditions

amb  ambient

ads  adsorption step

b  adsorbent bed

cool  cooling step

eff  effective

f  heat exchange fluid

feed  feed

heat  heating step

$i, j, k$  component or measurement $i, j, k$

in  inlet

$L$  at the end of the column

M  material

obs  observation

out  outlet

p  adsorbent particle

s  solid

w  column wall
Chapter 6

Conclusions and Outlook

The aim of the work presented in this thesis, as stated in the introduction, was the expansion of the previously mentioned model beyond the separation of CO$_2$ and H$_2$ by PSA in the context of pre-combustion capture of CO$_2$, to allow the simulation of other adsorption-based CO$_2$ capture processes, whether they employ pressure swing or temperature swing as their means of regeneration. Specifically, there were two points that were to be addressed: First, the added complexity of additional components which adsorb significantly; and second, the study of TSA processes for post-combustion CO$_2$ capture from a flue gas stream. With this objective in mind, a comprehensive approach was followed that develops a process model from the bottom up, investigating the thermodynamic equilibrium adsorption of relevant adsorbate/adsorbent systems, determining the transport parameters by breakthrough experiments, and finally validating the model for the added component and the heat regeneration.
6. Conclusions and Outlook

6.1 Results of this work

The two main objectives of this work were addressed separately. Two sets of targeted breakthrough experiments with binary mixtures bearing one common component were used to calibrate the transport parameters of the model for an accurate prediction of the corresponding ternary system. This is important as separation process in real applications almost always have to contend with a multitude of impurities in addition to the bulk species that need to be separated; the model not only needs to be able to simulate their behavior accurately, but any additional parameters needed should be obtainable without excessive effort. The results reported in Chapter 3 show that incorporating additional species is mostly a matter of obtaining the necessary thermodynamic and kinetic parameters, but that those can be obtained independently. Once the necessary mass transfer coefficients and isotherm parameters were used in the model, it was quite capable of predicting the behavior of ternary mixtures in breakthrough experiments accurately.

The results reported in Chapter 4 then more thoroughly test the model in this aspect. The kinetic parameters that were found in Chapter 3 and validated for short, single-step breakthrough experiments were used to predict not only the behavior of the column in a cyclic PSA process that was run until it reached cyclic steady-state, but also the separation performance of a number of experiments that were performed with different operating conditions. This was done for a binary CO$_2$/N$_2$ mixture, and for a ternary CO$_2$/N$_2$/H$_2$ mixture, showing that the addition of another component could be handled well, despite this component having an affinity and adsorption capacity that is intermediate of the two other components in the system.

In the chapters regarding the ternary mixtures, the third component was chosen as nitrogen, on the one hand as it is a well-known and well-
studied species, and adsorption equilibrium data were already available; and on the other, due to its relevance in a number of applications that separate multicomponent gas mixtures such as the process stream from air-blown autothermal reformers.

For the simulation and design of temperature swing processes, an entirely different sorbent/sorbate system was chosen. The conditions for post-combustion CO$_2$ capture via TSA are rather different from those for PSA; as a result, the activated carbon, which proved a useful base case for comparison with novel materials, did not perform particularly well for the separation of CO$_2$ and N$_2$, despite the pressurized feed used for CO$_2$/N$_2$ PSA experiments. At lower pressures, the adsorbed amount would have been much too low to be effective at all. As a result of the work presented in Chapter 2, zeolite 13X was chosen as the sorbent to be used in the work regarding TSA for post-combustion capture. Its high capacity for CO$_2$ along with its high selectivity promised high CO$_2$ purity with even a simple TSA cycle. In general the same approach as for the model development for PSA was followed. Breakthrough experiments were used to determine the mass transfer coefficients for adsorption, as well as to characterize the heat transfer in the modified laboratory setup. The transport parameters found were then used in the model to design experiments, which were then performed. It became evident that unlike for PSA, the heat transfer is a crucial aspect for TSA. Not only does it determine the cycle time, as the heating and cooling represent the majority of the cycle length, it was also seen that the mass transfer of CO$_2$ is heavily influenced by the dissipation of the heat of adsorption. However, while the heat transfer posed a challenge, the quality of the predictions made by simulations about the behavior of the adsorption column during the TSA experiments was very satisfactory. Some of the process performance indicators could not be obtained accurately from the experiment, but those that could be calculated were very much in agreement with the simulations.
It is the combination of the results from both objectives that the model is indeed rather flexible and can be expanded to be used for new circumstances, be they additional components or different operating conditions. Furthermore, the validation for temperature swing adsorption processes has opened up a new dimension which can be exploited in the design of processes.

6.2 Outlook

Research is always a work in progress, and every insight opens new questions and offers new possibilities. The work presented in this thesis built heavily on the work of previous PhD students at SPL, and was inspired to a large degree by the outlook in their theses; and there are a number of challenges that can be addressed that can lead to a better understanding of adsorption-based separations, which can then be used in the design of new processes, whether they are used for the capture of CO\textsubscript{2} or for any number of other applications.

6.2.1 Optimization and process integration

The work reported in this thesis was very experimental in nature. Parameters were determined through experiment, and the model was tested by experiment. This was necessary to get the necessary confidence in the ability of the model to predict the processes that an adsorption column undergoes throughout cyclic adsorption processes. The ultimate purpose of the model, then, is to be used in the design of far more complex process schemes than could be performed in a laboratory setup. Once it is known that a model is robust, expandable, and can be used to simulate a variety of different operating conditions, there are a great number of possibilities. To name an example, the PSA processes studied
for the separation of H₂ and CO₂ could be predicted well, and achieved a reasonable CO₂ purity and recovery. However, the CO₂ product was delivered at atmospheric pressure. In a CCS scenario, this CO₂ would have to be compressed before transport, which can in the end be a major cost factor for the overall operation. It is therefore important to keep the bigger picture in mind. If the PSA process could be operated such that pure CO₂ could be produced at a higher pressure, the productivity of the PSA process might suffer; but a lower cost in recompression might offset that. Additionally, a separation process rarely exists on its own – typically it is a part of a larger operation. Along with that comes the possible availability of other process streams that could be used to purge, units that might benefit from what would otherwise be considered a waste stream, or waste heat that could be used to heat a bed for regeneration. The ability to simulate processes where the column might be heated to aid in desorption at higher pressure is only one aspect of how a fully validated model is a powerful tool in developing new process concepts.

6.2.2 Energy consumption & economic considerations

A separation process needs to meet the specifications provided to even be considered for implementation. The validated simulation tool can aid in the development of processes for a variety of demands, whether for CO₂ capture or in other applications. But once a separation is shown to be feasible, it will only be used if it is also economical. There are many aspects that factor into the cost of an adsorption operation, from the sorbent material cost, to the energy cost which can come from a thermal duty or mechanical power, to capital investment cost that depends greatly on the number of beds needed and the operating conditions that need to be withstood by the equipment. These considerations are no small undertaking, but ultimately necessary to compare the processes
6. Conclusions and Outlook

Finally, this thesis had another very important focal point when it was first conceived. A great number of studies deal with the capture of CO$_2$ from a variety of feeds; many of them consider a dry feed, the work reported here included. While it is easy to dismiss water by assuming it was removed it in a previous drying step, these drying steps are energy-intensive. As drying is frequently achieved by adsorption, it is not so far-fetched to think that an adsorption-based process might be possible that can perform both operations, separating the water along with the CO$_2$, or selectively removing the CO$_2$ while keeping the water vapor in the process stream. The latter would certainly be an acceptable outcome in the case of post-combustion capture, where the water vapor could just be vented along with the N$_2$.

The reason that water vapor is often avoided is that it does not behave like the majority of sorbates. Its polarity and its tendency to condense in pores make virtually every aspect of working with water quite a challenge, from measurements to simulations. As a result, a lot of work has been done at SPL to understand the behavior of water, and it remains a topic of interest. The primary challenges are:

**Equilibrium adsorption:** Measuring the adsorption equilibrium reliably and accurately. This pertains to pure component adsorption as well as multicomponent adsorption. Moreover, the choice of isotherm model is not always straightforward. Water vapor often exhibits a type II or a type V isotherm, with inflection points that make the breakthrough behavior more difficult to predict.

**Transport phenomena:** Throughout the work reported in this thesis, the mass transfer of the different species was described by using the
linear driving force model; whether this remains applicable for water vapor, which may adsorb via a number of different mechanisms, needs to be verified, and the mass transport model adjusted if necessary.

**Hysteresis:** The tendency of water vapor to reach a different equilibrium adsorbed amount depending on whether it’s experiencing *adsorption* or *desorption* is among the causes of the challenges in obtaining reliable data. Understanding, characterizing, and describing the phenomenon of hysteresis in adsorption is an important task if water adsorption processes are to be simulated with any accuracy.

These are just some of the directions possible to go for further research. Most of the ones mentioned here are already underway in some way at SPL, and will continue to be focal topics of research. As the understanding of the phenomena that lie at the base of adsorption grows, so does the number of possible applications, making this an area that should see many interesting developments in the future.
6. Conclusions and Outlook
Appendix A

Supporting Information for Chapter 3

A.1 Validation of the used heat transfer correlation

A comparison of the description of experiment B5 and B22 with the heat transfer coefficient calculated by the correlation as reported by Casas et al. and with the individually fitted heat transfer coefficient.\textsuperscript{17}

A.2 Binary breakthrough experiments

In this section the full set of experimental results for the binary mixtures is presented together with the simulations obtained by fitting the mass transfer coefficients.
**Figure A.1:** Experimental (symbols) and simulated results of breakthrough experiments B5 (a) and B22 (b). Simulations carried out with the predicted heat transfer coefficient from Eq. 2 (solid lines) are compared to the simulated profiles with the individually fitted $h_L$ shown in Figure 2.
Figure A.2: Experimental (○) and simulated (−) results of breakthrough experiments with the binary mixture containing 10/90 CO₂/N₂ at a temperature of 25°C. The top row shows the exit profiles of the experiments performed at various levels of pressure and flow rate, while the bottom row shows the corresponding temperature profiles.
Figure A.3: Experimental (o) and simulated (−) results of breakthrough experiments with the binary mixture containing 10/90 CO$_2$/N$_2$ at a temperature of 45 °C. The top row shows the exit profiles of the experiments performed at various levels of pressure and flow rate, while the bottom row shows the corresponding temperature profiles.
Figure A.4: Experimental (○) and simulated (-) results of breakthrough experiments with the binary mixture containing 50/50 CO$_2$/N$_2$ at a temperature of 25 °C. The top row shows the exit profiles of the experiments performed at various levels of pressure and flow rate, while the bottom row shows the corresponding temperature profiles.
Figure A.5: Experimental (o) and simulated (-) results of breakthrough experiments with the binary mixture containing 50/50 CO$_2$/N$_2$ at a temperature of 45 °C. The top row shows the exit profiles of the experiments performed at various levels of pressure and flow rate, while the bottom row shows the corresponding temperature profiles.
A.2 Binary breakthrough experiments

Figure A.6: Experimental (○) and simulated (-) results of breakthrough experiments with the binary mixture containing 80/20 CO$_2$/$N_2$ at a temperature of 25°C. The top row shows the exit profiles of the experiments performed at various levels of pressure and flow rate, while the bottom row shows the corresponding temperature profiles.
Figure A.7: Experimental (◦) and simulated (-) results of breakthrough experiments with the binary mixture containing 80/20 CO$_2$/N$_2$ at a temperature of 45 ºC. The top row shows the exit profiles of the experiments performed at various levels of pressure and flow rate, while the bottom row shows the corresponding temperature profiles.
Appendix B

Supporting information for Chapter 4

B.1 Experimental and simulation results from binary PSA experiments

In the following pages, the experimental and simulation results from all the PSA experiments using the binary CO$_2$/N$_2$ mixture are reported. For all figures, the subfigures show the following information:

a) Temperature at three location in column 2: 10 cm (green), 60 cm (yellow), and 110 cm (red) from the bottom.

b) Pressure measured at the bottom of column 2.

c) Composition of the light product as measured by the MS.

d) Flow rate of the light product, along with component-specific flow rates.

e) Composition of the heavy product.
Figure B.1: Experiments B1 (top) and B2 (bottom).
B.1 Experimental and simulation results from binary PSA experiments

Figure B.2: Experiments B3 (top) and B4 (bottom).
B. Supporting information for Chapter 4

B.2 Experimental and simulation results from ternary PSA experiments

In the following pages, the experimental and simulation results from all the PSA experiments using the ternary CO\textsubscript{2}/N\textsubscript{2}/H\textsubscript{2} mixture are reported. For all figures, the subfigures show the following information:

a) Temperature at three location in column 2: 10 cm (green), 60 cm (yellow), and 110 cm (red) from the bottom.

b) Pressure measured at the bottom of column 2.

c) Composition of the light product as measured by the MS.

d) Flow rate of the light product, along with component-specific flow rates.

e) Composition of the heavy product.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figureB.3.png}
\caption{Experiment T1.}
\end{figure}
B.2 Experimental and simulation results from ternary PSA experiments

**Figure B.4:** Experiments T2a (top) and T2b (bottom).
Figure B.5: Experiments T3 (top) and T4 (bottom).
B.2 Experimental and simulation results from ternary PSA experiments

Figure B.6: Experiments T5 (top) and T6 (bottom).
B. Supporting information for Chapter 4
Appendix C

Supplementary material for Chapter 5

C.1 Breakthrough experiments on 13X

Figures C.1 and C.2 show the full set of results of the breakthrough experiments with the \( \text{CO}_2/\text{N}_2 \) mixture on 13X together with the simulations obtained by fitting the heat transfer coefficient between the bed and the column wall, \( h_L \).

C.2 Heating and cooling experiments for TSA

Figure C.3 shows the results of the heating/cooling experiments with He along with the simulations obtained by fitting the heat transfer coefficient between the column wall and the heat exchange fluid, \( h_{w,L} \).
Figure C.1: Concentration and temperature profiles for breakthrough experiments performed with a feed flow rate of $200 \text{ cm}^3 \text{s}^{-1}$. Experimental data (symbols) are shown together with the simulations (lines) carried out with the heat transfer coefficient fitted to that experiment. □ $10 \text{ cm}$, ○ $35 \text{ cm}$, ◇ $60 \text{ cm}$, △ $85 \text{ cm}$, ★ $110 \text{ cm}$. 
Figure C.2: Concentration and temperature profiles for breakthrough experiments performed with a feed flow rate of $300 \text{ cm}^3 \text{s}^{-1}$. Experimental data (symbols) are shown together with the simulations (lines) carried out with the heat transfer coefficient fitted to that experiment. □ 10 cm, ◦ 35 cm, ◦ 60 cm, △ 85 cm, ★ 110 cm.
Figure C.3: Temperature profiles inside the column during the heating and cooling experiment using the helium feed. Symbols are measurements at the five positions: □ 10 cm, ◦ 35 cm, □ 60 cm, △ 85 cm, ※ 110 cm. The dots are the measured thermofluid temperature at the jacket inlet and outlet. Lines represent simulations. The arrows indicate the axial profile that developed within the column.
C.3 Heat transfer in the packed bed

C.3.1 According to DeWasch and Froment

DeWasch and Froment found a linear relationship between the Nusselt and Reynolds numbers that is repeated here:\(^4\)

\[
\text{Nu} = \text{Nu}^0 + 0.033\text{PrRe} \tag{C.1}
\]

with the dimensionless numbers being

\[
\text{Nu} = \frac{h_L d_p}{\lambda_g} \quad \text{Nu}^0 = \frac{h_0^0 d_p}{\lambda_g} \quad \text{Pr} = \frac{\rho \nu C_p}{\lambda_g} \quad \text{Re} = \frac{v d_p}{\nu}
\]

where \(h_L^0\) is the static heat transfer coefficient in the bed. In an earlier work Froment had established this to be related to the static contribution of the effective thermal conductivity of the bed, \(\lambda_e^0\), through the following equation:

\[
h_L^0 = 2.583 \frac{\lambda_e^0}{d_t^{4/3}} \tag{C.2}
\]

where \(d_t\) is the tube diameter. To find \(\lambda_e^0\), an approach was followed that is reported by Froment and Bischoff and is based on the work of Kunii and Smith:\(^4,66\)

\[
\frac{\lambda_e^0}{\lambda_g} = \varepsilon \left(1 + \beta \frac{d_p \alpha_r}{\lambda_g}\right) + \frac{\beta (1 - \varepsilon)}{\frac{1}{\varepsilon} + \frac{\alpha_r d_p}{\lambda_g}} + \frac{2 \lambda_s}{3 \lambda_g} \tag{C.3}
\]

under the assumption that the radiative heat exchange is negligible at these relatively low temperatures and that \(\beta = 1\).
C. Supplementary material for Chapter 5

C.3.2 According to Dixon

Lin et al. have collected the correlations necessary to determine the heat transfer coefficient through the bed and at the wall according to the works of Dixon and Cresswell, Dixon, and Derkx and Dixon, in order to calculate the overall heat transfer coefficient which can be used in one-dimensional models. The relevant ones are repeated in Table C.1.

**Table C.1:** Equations used by Dixon et al. to determine heat transfer through the bed and at the wall.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Bi}_s = \frac{\alpha_w R_i}{\chi_s} = 2.41 + 0.156 \left( \frac{2R_i}{d_p} - 1 \right)^2 )</td>
<td>71</td>
</tr>
<tr>
<td>( \frac{\chi_s}{\chi_g} = \sqrt{1 - \frac{\varepsilon_b}{\varepsilon}} \frac{2}{1 - \frac{\chi_s}{\chi_g} B} \times \left[ \frac{(1 - \frac{\chi_s}{\chi_g}) B}{(1 - \frac{\chi_s}{\chi_g} B)^2} \ln \frac{\chi_g}{\chi_g B} - \frac{B + 1}{2} - \frac{B - 1}{1 - \frac{\chi_s}{\chi_g} B} \right] )</td>
<td>68</td>
</tr>
<tr>
<td>( B = 1.25 \left( \frac{1 - \varepsilon_b}{\varepsilon} \right)^{10/9} )</td>
<td>68</td>
</tr>
<tr>
<td>( \beta_f = \frac{(\text{RePr} / \text{Pe}_Rf)}{(8/N_f) + (\text{Bi}_f + 4) / \text{Bi}_f} )</td>
<td>68</td>
</tr>
<tr>
<td>( N_f = \frac{1.5(1 - \varepsilon_b)(2R - i/d_p)^2}{\text{RePr} / \text{Pe}<em>Rf \left[ \frac{1}{N</em>{fs} + 0.1 \frac{\lambda_g}{\chi_g}} \right]} )</td>
<td>68</td>
</tr>
<tr>
<td>( \text{Bi}<em>f = \frac{\alpha_w R_i}{\chi</em>{Rf}} )</td>
<td>68</td>
</tr>
<tr>
<td>( \text{Pe}<em>Rf = \frac{\lambda</em>{Rf}}{2R_i \varepsilon_b \rho g_0 C_p} = \left[ \frac{0.67\varepsilon_b}{\text{RePr} + \frac{1}{7(2 - (1 - d_p / R_i)^2)}} \right]^{-1} )</td>
<td>72</td>
</tr>
<tr>
<td>( \text{Nu}<em>{fs} = \frac{\alpha</em>{fs} d_p}{\chi_g} = 2.0 + 1.1\text{Pr}^{0.33}\text{Re}^{0.6} )</td>
<td>67</td>
</tr>
<tr>
<td>( \text{Nu}<em>{wf} = \frac{\alpha</em>{wf} d_p}{\chi_g} = 0.523 \left( 1 - \frac{d_p}{2R_i} \right) \text{Pr}^{0.33}\text{Re}^{0.738} )</td>
<td>71</td>
</tr>
<tr>
<td>( \text{Nu}_w = \frac{\alpha_w d_p}{\chi_g} = \frac{8\beta_f}{2R_i d_p} + 2\beta_s \frac{\rho g_0 d_p}{2R_i} \left( 1 + \frac{\beta_f}{\chi_v / \chi_g} \right) )</td>
<td>68</td>
</tr>
<tr>
<td>( \frac{\chi_k}{\chi_g} = \frac{\chi_s}{\chi_g} + \beta_f \frac{\text{Bi}_s + 4}{\text{Bi}_s} )</td>
<td>68</td>
</tr>
</tbody>
</table>

The last two equations in Table C.1 are the ones used to obtain \( \alpha_w \) and
$K_R$. These are then combined into the overall heat transfer coefficient by using Eq. (5.5), repeated here

$$\frac{1}{h_L} = \frac{1}{\alpha_w} + \frac{R_i}{3K_R} \frac{Bi + 3}{Bi + 4}$$

(C.4)

where $Bi = \frac{\alpha_w R_i}{K_R}$.

### C.3.3 According to Specchia

Specchia et al. also determined the heat transfer through the bed and at the wall separately, considering for each a static component and a convective contribution. The equations they used are summarized in Table C.2.

Note that the equation used to obtain the static contribution of the effective thermal conductivity of the bed, $\lambda_e^0$, is a simplified version of the one used by DeWasch and Froment. The values obtained for $\alpha_w$ and $K_R$ are then combined in the same manner as the parameters found by Dixon, using Eq. (C.4).
Table C.2: Equations used by Specchia et al. to determine heat transfer through the bed and at the wall.\textsuperscript{60}

**Effective radial thermal conductivity**

\[
K_R = \lambda_e^0 + k_{Rg}
\]

\[
\lambda_e^0 = \lambda_g \left( \varepsilon + \frac{\beta(1-\varepsilon)}{\phi + \frac{\lambda_g}{\lambda_s} \gamma} \right)
\]

\[
\gamma = \frac{2}{3}, \quad \beta = 1, \quad \phi = 0.220\varepsilon^2
\]

\[
k_{Rg} = \frac{Re_g \nu C_p}{Pe_H}
\]

\[
Pe_H = 8.65 \left(1 + 19.4 \frac{d_p}{2R_i} \right)
\]

**Wall heat transfer coefficient**

\[
Nu_w = \frac{\alpha_w d_p}{\lambda_g} = Nu_w^c + Nu_w^0
\]

\[
Nu_w^0 = 2\varepsilon + \frac{\lambda_g}{\lambda_s} \frac{1-\varepsilon}{\gamma_w + \phi_w}
\]

\[
\gamma_w = \frac{1}{3}, \quad \phi_w = 0.00240 \left( \frac{2R_i}{d_p} \right)^{1.58}
\]

\[
Nu_w^c = 0.0835Re^{0.91}
\]
C.4 Heat transfer in the column jacket

C.4.1 Estimating the heat transfer coefficient based on fluid properties

The VDI Heat Atlas (Part G2) provides expressions that describe the heat transfer for annular tubes, as is the case here, under laminar and turbulent flow condition, as well as for the transition region between the two regimes. These expressions estimate the heat transfer coefficient based on the geometry (jacket length, diameter) and the physical properties of the fluid. The manufacturer of the thermofluid used (Therminol 62, Fragol GmbH, Germany) provides physical property data over a range of temperature, shown in Figure C.4. These properties can be approximated by the following equations:

- density: \( \rho(T) = \rho_0 + m_\rho T \)
- heat capacity: \( C_p(T) = C_{p,0} + m_{C_p} T \)
- thermal conductivity: \( \lambda(T) = \lambda_0 + m_{\lambda} T \)
- kinematic viscosity: \( \nu(T) = \nu_0 \exp\left(\frac{K_\nu}{T - T_0}\right) \)

where the necessary parameters were fitted to the available data within the temperature range that is of interest in this work. The results can be seen in Figure C.4 together with the data. Based on these physical properties and the dimensions of the jacket, the relevant dimensionless numbers can be found:

\[
\text{Nu} = \frac{d_h h_w}{\lambda} \quad \text{Re} = \frac{d_h v}{\nu} \quad \text{Pr} = \frac{\rho \nu C_p}{\lambda} \quad d_h = 2(r_w - r_o)
\]
Figure C.4: Physical properties of the thermofluid used in Chapter 5 to control the column temperature. Symbols represent the data provided by the manufacturer, where the circles are the data points used to regress parameters for the models shown here as lines.

where \( r_w \) and \( r_o \) are the radii of the outside and inside wall of the jacket, respectively. For the Nusselt number the VDI Heat Atlas provides the following expressions, depending on the flow regime:

Laminar:

\[
\text{Nu}_{lam} = \left( \text{Nu}_1^3 + \text{Nu}_2^3 \right)^{\frac{1}{3}} \\
\text{Nu}_1 = 3.66 + 1.2a^{-0.8} \\
\text{Nu}_2 = 1.615 \left( 1 + 0.14a^{-0.5} \right) \left( \text{RePr}d_h/L \right)^{\frac{1}{3}}
\]
C.4 Heat transfer in the column jacket

Turbulent:

\[
\begin{align*}
\text{Nu}_{\text{turb}} &= \frac{\xi/8\text{RePr}}{k_1 + 12.7\sqrt{\xi/8\left(\text{Pr}^{2/3} - 1\right)}}f_g \\
f_g &= \left(1 + (d_h/L)^{2/3}\right)0.75a^{-0.17} \\
k_1 &= 1.07 + \frac{900}{\text{Re}} + \frac{0.63}{1 + 10\text{Pr}} \\
\xi &= (1.8\log_{10}(\text{Re}^*) - 1.5)^{-2} \\
\text{Re}^* &= \text{Re}\frac{(1 + a^2)\ln(a) + (1 - a^2)}{(1 - a^2)\ln(a)}
\end{align*}
\]

For the transition region (Re between 2300 and 10000), the Nusselt number is estimated with a linear function between its value at Re=2300 and at Re=10000, i.e.

\[
\begin{align*}
\gamma &= \frac{\text{Re} - 2300}{10^4 - 2300} \\
\text{Nu} &= \text{Nu}_{\text{lam},2300}(1 - \gamma) + \text{Nu}_{\text{turb},10^4}\gamma
\end{align*}
\]

From the data provided by the manufacturer of the thermofluid and of the thermostat (Huber Kältemaschinenbau GmbH, Germany), the value of \(h_w\) can be estimated. However, the flow rate of the fluid depends on the characteristics of the pump used in the thermostat, the thermofluid used, and the resistance of the piping. For a range of flow rates, the estimated Nusselt number therefore varies; its calculated value for a range of flow rates is shown in Figure C.5. From the illustration it can be seen that the value of \(h_w\) for most conditions should be on the order of 200 W/(m\(^2\) K). For a better description of the experiments, the heat transfer coefficient should be fitted to the experiment.
Figure C.5: Heat transfer coefficient $h_w$ calculated according to the VDI Heat Atlas for flow rates ranging from 3 L/min to 40 L/min.

C.4.2 Entrance effects in the heating jacket

for the region of the annular tube that exhibits hydrodynamically and thermally developing laminar flow, the VDI Heat Atlas provides another approximation:

$$\text{Nu}(x) = \left( \text{Nu}_1^3 + \text{Nu}_2^3(x) + \text{Nu}_3^3(x) \right)^{\frac{1}{3}}$$

$$\text{Nu}_1 = 3.66 + 1.2a^{-0.8}$$

$$\text{Nu}_2(x) = 1.615 \left( 1 + 0.14a^{-0.5} \right) \left( \text{RePr}_{dh}/x \right)^{\frac{1}{3}}$$

$$\text{Nu}_3(x) = \left( \frac{2}{1 + 22\text{Pr}} \right)^{1/6} \left( \text{RePr}_{dh}/x \right)^{0.5}$$

It is clear from these equation that the entrance effects diminish with distance from the entrance, and for large ratios of $L/d_h$, Nu is very close to $\text{Nu}_{\text{lam}}$ seen above, as $\text{Nu}_3(x)$ gets small. While the value of $\text{Nu}_{\text{lam}}$ depends on temperature and flow rate, the relationship $\text{Nu}(x)/\text{Nu}_{\text{lam}}$ looks very similar under the whole range of conditions found in this
As discussed in Section 5.3.2, the aim of this analysis was to see if accounting for the entrance effect could yield a significantly better description of the heat transfer in the column jacket. To test this, the column was viewed in a simplified manner, lumping heat capacities and heat transfer coefficients to arrive at Eq. (5.6), restated here:

\[(\rho C_p)_{eff} \frac{dT_{bed}}{dt} = Ua_w (T_f - T_{bed})\]

Figure C.7 shows the development of the temperature within the column as measured by the five thermocouples during the heating and cooling experiment using the helium feed. After an initial lag, the time derivative of the temperature shows a linear relationship with the temperature gradient to the thermofluid temperature. The data with $10 \text{K} < |\nabla T| < 50 \text{K}$ was then used to regress the quantity $\frac{Ua_w}{(\rho C_p)_{eff}}$ at each thermocouple position. The resulting slopes are illustrated in Figure C.8. The trend exhibited by this data along the length of the column is similar to that
found for the estimates of the Nusselt number in Figure C.6, albeit somewhat dampened by the effect of the heat transfer within the bed. It is therefore reasonable to consider entrance effects when simulating the heating and cooling experiments as well as the corresponding steps of the TSA experiments.

C.5 TSA cycle experiments

In the following the experimental and simulation results for the two TSA experiments not reported in Chapter 5 are shown.
Figure C.8: Regressed estimates for $\frac{U_{aw}}{(\rho C_p)_{eff}}$ along the column for the heating (□) and cooling (△) experiment.
Figure C.9: Temperature profiles inside the column during the TSA experiment with a desorption temperature of 100°C. Symbols are measurements at the five positions: □ 10 cm, ○ 35 cm, ◊ 60 cm, △ 85 cm, ⋆ 110 cm. The dots are the measured thermofluid temperature at the inlet (dark) and outlet (light). Lines represent simulations. The vertical gray lines indicate the switch times between steps.
Figure C.10: Comparison of simulation (lines) and experimental (symbols) results for the product streams from the TSA experiment with $T_H = 100$ °C. a) shows the composition of the $N_2$ product throughout the adsorption step, as well as the feed composition. b) shows the flow rate of the light product together with the feed flow rate. c) shows the heavy product composition. To show that the two columns operate consistently, data from both columns are shown: ■ column 1, □ column 2.
C. Supplementary material for Chapter 5

Figure C.11: Temperature profiles inside the column during the TSA experiment with a desorption temperature of 125°C. Symbols are measurements at the five positions: □ 10 cm, ◊ 35 cm, △ 60 cm, ⋄ 85 cm, ⋆ 110 cm. The dots are the measured thermofluid temperature at the inlet (dark) and outlet (light). Lines represent simulations. The vertical gray lines indicate the switch times between steps.
Figure C.12: Comparison of simulation (lines) and experimental (symbols) results for the product streams from the TSA experiment with $T_H = 125$ °C. a) shows the composition of the $N_2$ product throughout the adsorption step, as well as the feed composition. b) shows the flow rate of the light product together with the feed flow rate. c) shows the heavy product composition. To show that the two columns operate consistently, data from both columns are shown: ■ column 1, □ column 2.
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