Adsorption energy systems library - Modeling adsorption based chillers, heat pumps, thermal storages and desiccant systems

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Abstract

A library for dynamic modeling adsorption based thermal systems like chillers, heat pumps, thermal storages or desiccant units is presented. Adsorption devices can serve a wide range of applications but usually consist of the same basic components. By modeling these basic components, the presented model library allows to investigate any interesting topology. Thereby this adsorption library gives the user the opportunity to design and optimize adsorption systems quickly and efficiently. To demonstrate the flexibility of the library and the accuracy of the simulations, three validated examples are presented: A desiccant unit; a thermal storage; and an adsorption chiller.

Keywords: adsorption; simulation; validation; modular; chiller; thermal storage; heat pump; desiccant

1 Introduction

Physical adsorption of a fluid on a solid surface is a reversible exothermic process which can be efficiently employed in energy systems. Adsorption phenomena can be used to build a wide variety of thermal devices: e.g. heat driven chillers and heat pumps; high density storages; or desiccant units [1, 2]. Since all these devices enable the use of waste heat or solar heat, they can provide heating and cooling demand more efficiently than conventional devices, and thereby help to reduce CO_2 emissions. To exploit this CO_2 reduction potential, adsorption based thermal devices have to be well designed. The design of adsorption systems is challenging due to their intrinsic dynamic nature: During operation, adsorption devices switch between ad- and desorption phases, meaning they work discontinuously. In addition, they have a characteristic energy output peak at the beginning. Besides, adsorption devices consist of several components, all being influencing the performance. In an optimal design, these components need to be balanced avoiding oversized components on the one hand and bottlenecks on the other. To meet this optimal design challenge, time-dependent models have been developed to describe and improve adsorption based devices (see e.g. [3, 4, 5]). These models have been developed mainly to study the performance of one specific configuration. To enable the library presented here to describe all kinds of adsorption based thermal devices, a generic modular approach is taken to model the adsorption process. To the best knowledge of the authors only the model of Schicktanz and Núñez describes an adsorption chiller by using a modular approach [6]. By dividing the chiller in its basic components, this approach allows components to be exchanged. Joos et al. presented a modular Modelica library for separation processes including adsorption [7], that can be used to model separation processes, but is not designed for thermal applications, in contrast to the presented library in this paper.

In Section 2, the adsorption phenomenon is described briefly. In Section 3, the library structure and both its basic and enhanced models are described. To illustrate the library, Section 4 contains three examples of validated adsorption systems.

2 Adsorption

Adsorption describes the process of attaching fluid molecules to the surface of a (porous) solid, so called sorbent. For a detailed introduction, the reader is referred to Kärger, Ruthven and Theodorou [8]. The internal energy u of the adsorbed fluid is lower than of the liquid phase and the vapor phase, leading to an exothermic process:

$$u_{ad} < u_l < u_v \, . \tag{1}$$

This difference between the energies of the liquid and the adsorbed phase is called bond energy. The amount of fluid (adsorbate) adsorbed by the sorbent is described by the loading:

$$w = \frac{m_{ad}}{m_{sor}} \, , \tag{2}$$

and depends on both the system temperature T and pressure p. The relation between loading, temperature, and pressure is described by the thermodynamic equilibrium, which is specific for every working pair. Working pairs (solid / fluid) often used for thermal applications are for example zeolite / water, silica gel / water, and active carbon / methanol. Equilibrium data is used to determine start and end points of adsorption processes. The system dynamics are determined by heat and mass transfer which occur simultaneously: the fluid has to reach a free surface location where it can be adsorbed, while heat has to be transported within the porous solid at the same time. Mass transfer takes place by convective and diffusive processes. Heat transfer can usually be modeled by a mixture of heat conduction in the materials and contact resistances between them.

To control and use the adsorption process in thermal devices, sorbent material and working fluid are heated or cooled in a defined way. For this purpose, either sorbent or working fluid are connected to heat exchangers, building key components of an adsorption device: evaporator; condenser; or adsorber. By connecting the different components in the right way, it is possible to build chillers or heat pumps, thermal storages, as well as air drying units. For more information regarding the design of specific devices see also [9] and [10].

3 Library structure

The presented model library follows a modular approach. By coupling a reusable model (working pair is exchangeable) of the adsorption process to heat exchangers, it enables the user to model a wide range of adsorption based devices.

The presentation in this section follows the library structure shown in Figure 1, by classifying the models as media, basic components, and enhanced components.
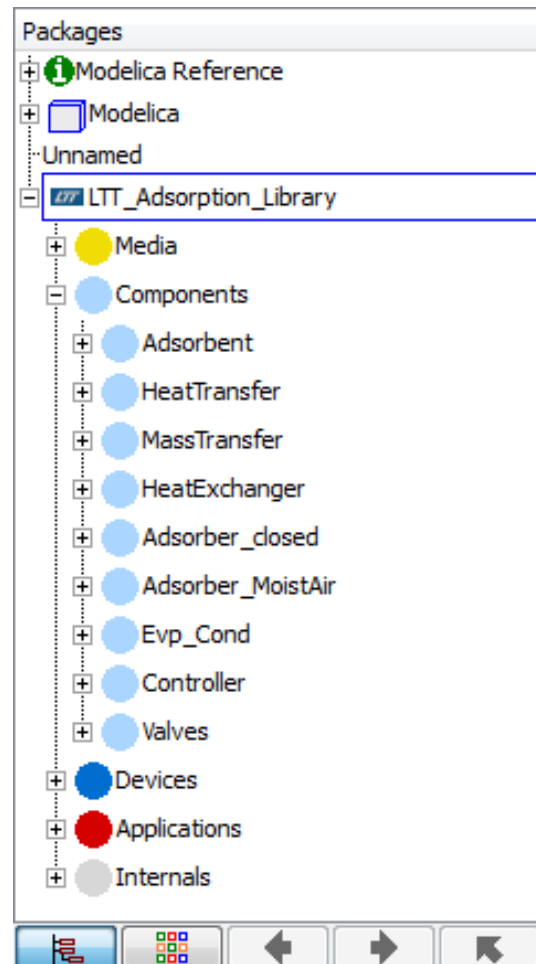

Figure 1: Structure of adsorption library

3.1 Media

As described in Section 2, the core of every adsorption based device is the working pair. The media model describes the working pairs characteristic properties: equilibrium data; internal energy of the adsorbed fluid (u_{ad}); and specific heat capacity of both sorbent (c_{sor}) and adsorbate (c_{ad}).

In literature, many approaches describing adsorption equilibria can be found, e.g. the model of Langmuir [11], assuming adsorption only in one layer, the Brunauer, Emmet and Teller model (BET) [12], allowing adsorption in more layers, or the Dubinin model

[13], which is based on Polanyi's potential theory [14]. Which approach is used is not important for the media model as long as adsorbate pressure p_{ad} at equilibrium state can be described as a function of temperature T and loading w:

$$p_{ad} = f(T, w) . \qquad (3)$$

The specific energy in the adsorbed state (u_{ad}) is derived from the used adsorption model.

The total heat capacity of sorbent and adsorbate c_{tot} is the sum of the individual heat capacities:

$$c_{tot} = c_{sor} + w\, c_{ad} . \qquad (4)$$

In the present library, most equilibrium data are described using the Dubinin model.

The properties of the fluid are based on TILMedia [15], a library provided by TLK-Thermo GmbH.

3.2 Basic components

The following components are the smallest units the library consists of. All extended components and device models are based on these basic components.

Adsorbent

In the adsorbent model, equilibrium data, provided by a media model, and mass and energy balances for sorbent and working fluid are combined. The adsorbent is described by a lumped model; i.e., with a homogeneous temperature, loading and pressure distribution. State variables of the model are temperature T and loading w. Mass of fluid vapor within the adsorbent can be neglected, in other words, all working fluid within the adsorber is assumed to be in adsorbed state. The adsorbent model contains heat and fluid ports, allowing for heat and mass transfer (see Figure 2).
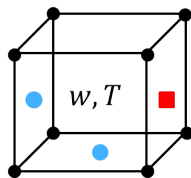

Figure 2: Scheme of adsorbent including the state variables: loading w; and temperature T, as well as the connection ports: fluid (blue); and heat (red)

The mass balance of the working fluid is given by:

$$\frac{\mathrm{d}m_{ad}}{\mathrm{d}t} = m_{sor}\frac{\mathrm{d}w}{\mathrm{d}t} = \dot{m}_{fluid,in} - \dot{m}_{fluid,out} . \qquad (5)$$

The energy balance is given by:

$$c_{tot}\frac{\partial T}{\partial t} + u_{ad}\frac{\partial w}{\partial t} =$$
$$\frac{1}{m_{sor}}\left(\dot{m}_{fluid,in}\, h_{in} - \dot{m}_{fluid,out}\, h_{out} + \dot{Q}\right) . \qquad (6)$$

The fluid is leaving the adsorber as vapor with adsorber temperature T and equilibrium pressure of adsorbent p_{ad}. The media model used can be changed easily, allowing for a high flexibility. For example, it is possible to investigate the influence on system performance of a changed working pair.

Heat transfer

The heat transfer model connects the adsorbent to a heat exchanger or to the environment. The heat flux is described by:

$$\dot{Q} = \alpha A \cdot \Delta T . \qquad (7)$$

The implemented heat transfer coefficient α can be changed. For example, it can be chosen to be a constant parameter or to be dependent on the flow velocity as in the air drying unit described (Section 4).

Mass transfer

Mass transfer to or from the adsorbent is described similarly to the heat flow as a linear function of a driving potential (LDF approach). As driving force, either the pressure difference between the pressure on the outside and adsorbate pressure (p and p_{ad}), or the difference between actual and equilibrium loading (w_{ad} and w_{eq}) can be used:

$$\dot{m} = \beta_p\left(p - p_{ad}\right) ; \qquad (8)$$

or

$$\dot{m} = \beta_w\left(w_{ad} - w_{eq}\right) . \qquad (9)$$

In this library, both equations are implemented. Since fluid entering the adsorbent is assumed to be adsorbed instantaneously, the mass transfer coefficient β includes not only convective flow resistances but also diffusive resistances occurring within the adsorbent. It is also modeled modular, allowing the user to choose between different models to determine mass transfer coefficient β, similar to the heat transfer coefficient (see also Section 4).

Tube (heat exchanger)

Heat exchangers for closed adsorption systems are represented by a tube model based on TIL library [15]. The tube model is discretized in flow direction. Heat transfer on the inside is described similarly to equation (7) also using a changeable α. For liquids, e.g Dittus-Boelter [16] or Sieder-Tate [17] correlations can be used. Also heat conduction within the tube wall is modeled.

Gas volume (heat exchanger)

An open adsorption system is a system which is not sealed and therefore allows mass transfer between adsorption system and ambient. The ambient, more specifically the surrounding moist air, fulfills two tasks simultaneously: it allows for heat and for mass transfer. Therefore the ambient can be regarded as both, a form of heat exchanger as well as a form of evaporator or condenser. The surrounding air is modeled by a gas volume (see Figure 3). The state variables of the gas volume are gas temperature T, water mass fraction X, and air density ρ. To allow for a gas flow through the volume, the model has two gas ports. It also contains a heat port and a fluid port which are connected to the adsorbent to exchange water (working fluid for open systems) and heat.
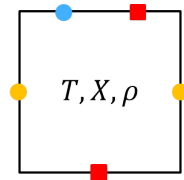
Figure 3: Scheme of gas volume including the state variables: temperature T; water mass fraction X; and density ρ, as well as the connection ports: fluid (blue); heat (red); and gas (yellow)

The mass balance of the inert gas component (dry air) is:

$$\frac{\mathrm{d}m_{\mathrm{dryair}}}{\mathrm{d}t} = \dot{m}_{\mathrm{dryair,in}} - \dot{m}_{\mathrm{dryair,out}} \,. \qquad (10)$$

The mass balance of water is correspondingly:

$$\frac{\mathrm{d}m_{\mathrm{water}}}{\mathrm{d}t} = \dot{m}_{\mathrm{water,in}} - \dot{m}_{\mathrm{water,out}} + \dot{m}_{\mathrm{water,ads}} \,, \qquad (11)$$

which can also be written as:

$$m_{\mathrm{air}}\frac{\mathrm{d}X}{\mathrm{d}t} = \dot{m}_{\mathrm{air,in}}X_{\mathrm{in}} - \dot{m}_{\mathrm{air,out}}X + \dot{m}_{\mathrm{water,ads}} \,, \qquad (12)$$

with the water mass fraction:

$$X = \frac{m_{\mathrm{water}}}{m_{\mathrm{air}}} \,. \qquad (13)$$

The energy balance of the gas volume is given by:

$$\frac{\mathrm{d}U_{\mathrm{air}}}{\mathrm{d}t} = \dot{H}_{\mathrm{air,in}} - \dot{H}_{\mathrm{air,out}} + \dot{H}_{\mathrm{water,ads}} + \dot{Q} \,. \qquad (14)$$

Water is assumed to leave the gas volume as vapor with gas temperature T_{gas} and partial pressure p_{water}.

3.3 Enhanced components

The main component of an adsorption system is the adsorber. For closed adsorption systems, also the evaporator and condenser are of major importance. The library already includes prebuild enhanced components, consisting of basic components. By parameter choice these enhanced components can be adapted for many applications.

Closed Adsorber

The closed adsorber model consists of an adsorbent model, a heat exchanger model, as well as models for heat and mass transfer (see Figure 4).
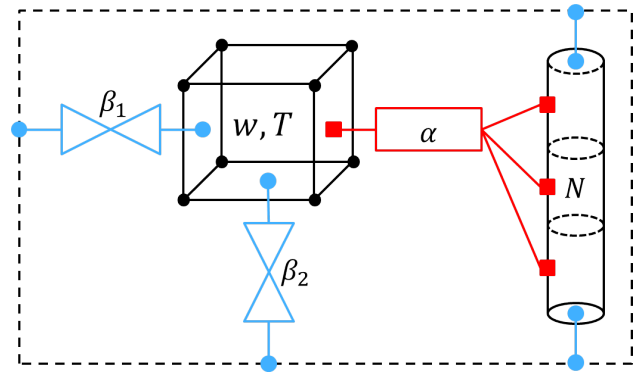
Figure 4: Scheme of closed adsorber model consisting of adsorbent (see Figure 2), heat exchanger (right), mass resistances (β_1 and β_2), and heat resistance (α)

Moist Air Adsorber

The moist air adsorber model consists of an adsorbent volume, a gas volume and a wall volume. These volumes are again connected by models for heat and mass transfer (see Figure 5). The moist air adsorber model can be discretized in flow direction.
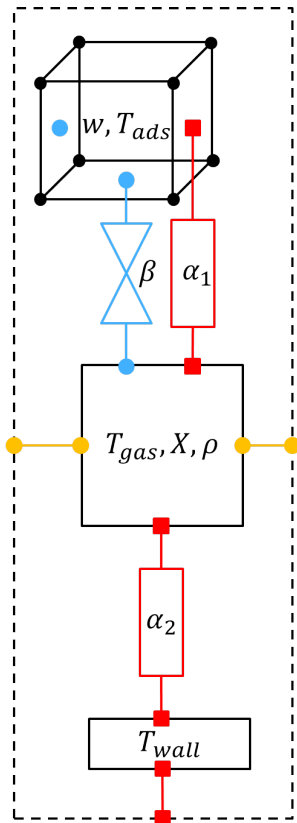
Figure 5: Scheme of moist air adsorber model consisting of an adsorbent (see Figure 2), a gas volume (see Figure 3), a mass resistance (β), heat resistances (α_1 and α_2), and a wall model

Evaporator / Condenser

The evaporator / condenser model consists of a vapor-liquid-equilibrium (VLE) fluid volume and a heat exchanger. The fluid volume is thermally connected to the heat exchanger and is assumed to be in the two-phase region. The model has a liquid and a vapor port. At the vapor port, the fluid leaves as saturated vapor; at the liquid port it leaves as saturated liquid.

4 Validated examples

The library presented in Section 3 is used to model several adsorption based devices. To demonstrate model accuracy, three validated examples are presented: an air drying unit; an adsorption thermal storage; and an adsorption chiller.

4.1 Adsorption dryer

An adsorption dryer or desiccant unit is used to simultaneously reduce air humidity and preheat the air. During adsorption, cold humid air enters the dry adsorber.

Until equilibrium state is reached water is adsorbed and the adsorption enthalpy is released. For regeneration of the unit by desorption, hot dry air flows through the adsorber. The air leaves the adsorber with a higher water loading and decreased temperature.

The adsorber model is validated using experimental data by Pesaran and Mills [18]. The used adsorber has a cylindrical shape and is filled with silica gel (Equilibrium data of silica gel is given in [19]).

The driving potential used for mass transfer is pressure difference Δp (equation (8)). Coefficients for mass and heat transfer are modeled by correlations dependent on the Reynolds number based on Hougen and Marshall [20]. Since the model determines the outlet temperature and mass fraction from the inlet values, geometries and input parameters, the model is predictive.

Figure 6 and 7 show temperature and water mass fraction during an adsorption process at adsorber inlet and outlet.
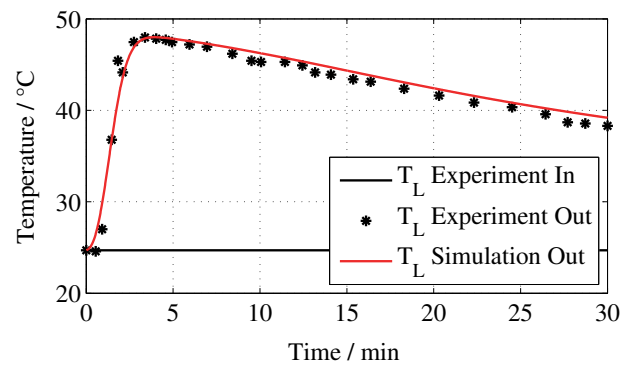

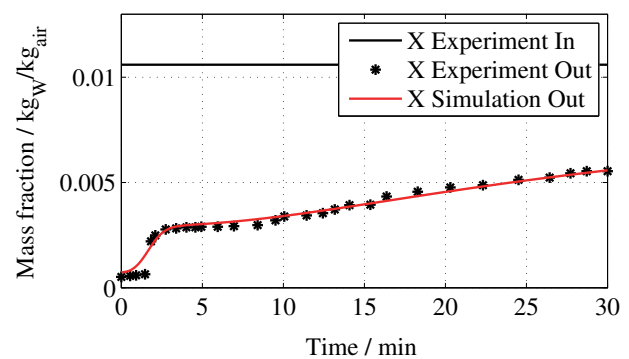Figure 6: Air temperature T at inlet and outlet during adsorption

Figure 7: Water mass fraction X at inlet and outlet during adsorption

Validation shows good agreement in both, temperature T and mass fraction X. The input conditions are

changed suddenly at $t = 0\,\mathrm{s}$, resulting in a step function. The output is reacting by an increase in outlet temperature due to adsorption heat emitted. Around 5 min after start, temperature peaks at $46.9\,°\mathrm{C}$ and afterwards declines only slightly. By reaching a temperature of $45.4\,°\mathrm{C}$, simulation corresponds well to the measured peak after around 5 min. Water mass fraction between inlet and outlet is reduced by about 0.01 $\mathrm{kg_{water}/kg_{air}}$ with nearly dry air at the outlet. Measured and simulated water loading fit almost perfectly. Pesaran and Mills [18] have experimentally varied input parameters, adsorber length, and particle size of adsorbent grains in their experiments. For all six tested input variations simulation and the experiments agreed well (not shown).

4.2 Thermal adsorption storage

Thermal energy, stored in an adsorption storage, can be divided into a sensible and a latent part. Sensible heat increases with system temperature, while at the same time, latent heat is stored by desorption of water. The desorbed water leaves the adsorber as vapor and is condensed afterwards in the condenser. During condensation, low grade heat is emitted at medium or low temperature level, that can be either used or emitted to the ambient. When using the stored heat (discharging the storage), water is evaporated using low grade heat. The evaporated water flows to the adsorber where it is adsorbed and heat at process temperature is released.

The storage model is validated using experimental data from a storage prototype at our institute [21]. Figure 8 illustrates the thermal adsorption storage model. Since temperature difference between adsorber and evaporator is high and there is no insulation between these components, they are thermally connected in the model. For further details regarding the experimental setup see Binkert [22].

The working pair used in the experiments is zeolite 13X / water. Equilibrium data for this pair can be found in Núñez [23]. Heat and mass transfer coefficients were fitting experimental and simulation data. Optimization criterion used to determine fit accuracy is the root mean square deviation (RMSD) of adsorber heat. Figure 9 shows the adsorber heat flow during desorption, Figure 10 during adsorption. Desorption temperature increases to almost $200\,°\mathrm{C}$, with a condensation temperature of $90\,°\mathrm{C}$. After around 3 hours, the operation mode is switched from desorption to adsorption (loading to unloading). Adsorption takes about 30 min with adsorption temperature falling from $200\,°\mathrm{C}$ to $120\,°\mathrm{C}$. Evaporation is kept at $60\,°\mathrm{C}$ during
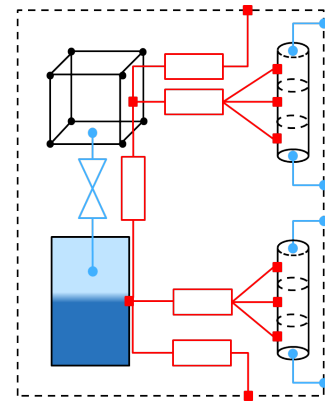

Figure 8: Scheme of thermal adsorption storage consisting of an adsorbent (see Figure 2), two heat exchangers (right), mass resistances, heat resistances, and an evaporator / condenser model

adsorption. Although time varies by factor 6 and heat flow even by factor 10, comparison between experimental data and simulations shows good agreement for both, desorption and adsorption. During desorption, the peak in heat flow at 15 min is slightly overestimated by the simulation, for adsorption it can be observed that the trend fits well. At the end of adsorption phase, slight differences between experiment and simulation occur, but they are still in a tolerable range.
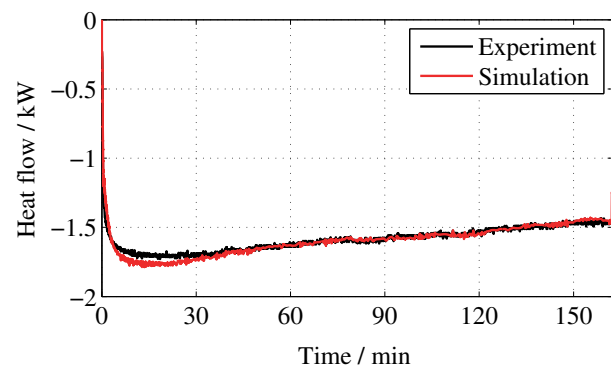

Figure 9: Heat flow $\dot{Q}$ of adsorber during desorption

4.3 Adsorption Chiller

The investigated adsorption chiller consists of an adsorber, an evaporator, and a condenser. These components are separated by valves, allowing to disconnect the adsorber from the evaporator and condenser separately. Because adsorption and desorption phases take place successively (Section 1), an adsorption chiller with only one adsorber bed operates discontinuously. During the adsorption phase, water is evaporated at a low temperature level (cooling output). The water
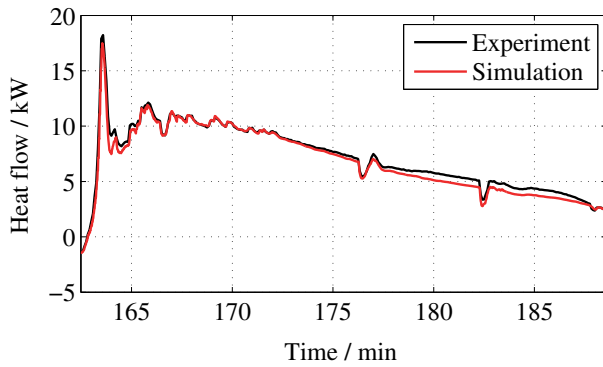
Figure 10: Heat flow $\dot{Q}$ of adsorber during adsorption

flows to the adsorber where it is adsorbed and heat is emitted. Thus, the adsorber has to be cooled, which occurs at a medium temperature level. During the desorption phase, the adsorber bed is regenerated. By using the heat exchanger, heat is passed into the adsorber at a high temperature level. The desorbed water vapor flows to the condenser, where it is condensed at a medium temperature level again. The high temperature level is determined by the heat source available: mostly waste or solar heat. The medium temperature level is usually determined by the ambient temperature; and the low temperature level by the cooling application. An experimental setup of the described adsorption chiller at our institute is used for model validation. Figure 11 shows a schematic picture of the model, representing the experimental setup.
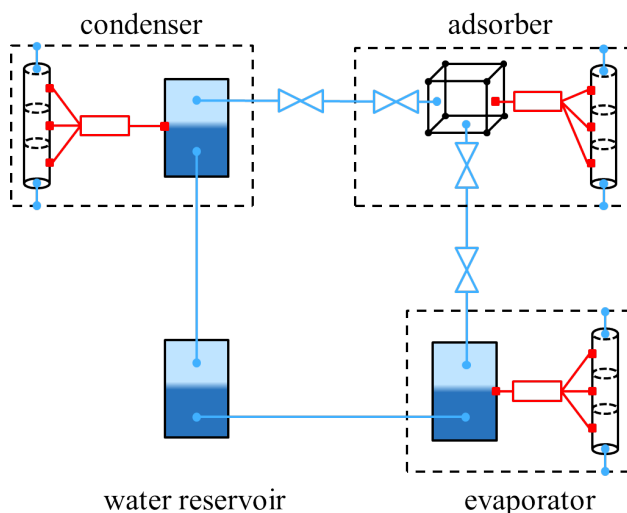

Figure 11: Scheme of adsorption chiller consisting of an adsorbent (see Figure 2), evaporator, condenser, mass resistances, heat resistances, and a water reservoir model

The model was investigated for both silica gel and zeolite 13X. In this paper we show validation for silica gel. A more in-depth validation can be found in Lanzerath [24], discussing the effects of varying input parameters and changed adsorbent materials. Equilibrium data for silica gel are implemented using the Dubinin approach from Schawe [25].

Coefficients for heat and mass transfer are used as fitting parameters. They are determined by using the experimental data of a complete cycle (adsorption and desorption) and minimizing the RMSD of heat flows between experimental and simulation data. The fitted heat and mass transfer parameters were kept constant for all variations of experimental settings and proved to be robust [24]. Figure 12 shows the adsorber heat flow, Figure 13 the heat flows of evaporator and condenser. Although only lumped models are used for adsorber, evaporator and condenser, it can be observed, that system dynamics, as well as steady state conditions, are predicted well.
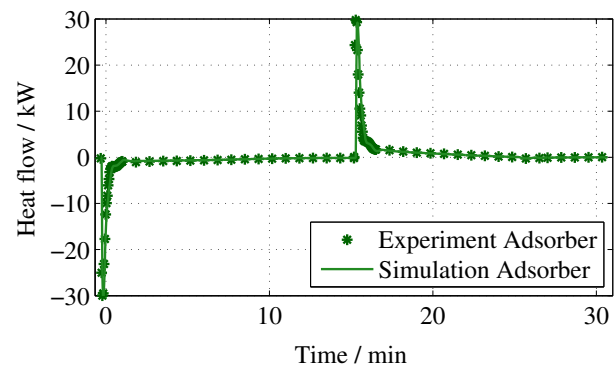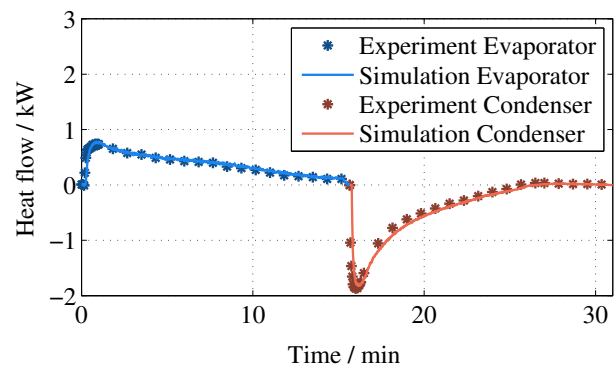

Figure 12: Heat flow of adsorber

Figure 13: Heat flows of evaporator and condenser

5 Conclusion

An adsorption library, capable of modeling a wide variety of adsorption devices is presented. The models were validated using three examples: a desiccant system; an adsorption thermal storage; and an adsorption chiller. All examples show very good agreement of simulation results with experimental data. Thereby, the library is shown to be a valuable toolbox for research purposes, allowing to describe, analyze and improve the design and topology of adsorption based devices.

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