Modeling and experiments on a finned cylindrical reactor with expanded graphite/activated carbon/lithium chloride-ammonia for chemisorption refrigeration systems

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ARTICLE INFO

Keywords:
Lithium chloride
Ammonia
Chemisorption heat storage
Heat and mass transfer model
Experimental validation

ABSTRACT

This paper presents a transient heat and mass transfer model with experimental validation of a finned cylindrical adsorbent bed for performance analysis in chemisorption refrigeration system. The approximate solution for the mathematical model, including transient heat and mass transfer equations in cylindrical coordinates, was obtained by implementing the Crank-Nicholson approach in a finite difference scheme. Geometrical configuration and physical parameters, including bed material thermal properties and TGA-based kinetic modeling for reaction rate estimation, were used as model data inputs to predict thermal bed distribution, heat flows, and coefficient of performance for a refrigeration system. Results from the model were validated with transient data from a chemical sorption refrigeration test bench. Refrigeration system reactor was made of expanded graphite/activated carbon/lithium chloride (AC/EG/LiCl)-adsorbent (NH3) in solution with a 25% concentration. The model demonstrated excellent agreement and an adequate representation of the physical phenomena, constituting a potential tool for efficiency-enhancing development of adsorption reactors for refrigeration systems.

1. Introduction

Technological development in the field of thermal storage refrigeration systems has shown significant growth in recent years, both sorbate/sorbent pairs and chemical sorption systems. Chemical sorption systems that employ anhydrous salts as sorbent introduce an extended field of research since experimental results related to LiCl/ammonia mixtures has not yet been studied. Recent progress initiates with physical sorption systems development in 1990, when Medini et al. [1] studied a solar ice making machine with a 0.8 m2 collection surface on an intermittent daily cycle that used an active carbon/methanol pair with a 0.4 coefficient of performance. Subsequent advancements set the basis for the development of industrial-scale functional prototypes, such as reported by Delorme & Six [2]. This group published the first operational project at Fribourg University Hospital funded by the CLIMASOL project, in which an activated carbon/methanol pair sorption system coupled to solar collector, and was used for cooling in summer and hot water supply in winter in a cosmetic manufacturing company in Sarantis, Greece.

There have also been relevant technological improvements in the field of the chemical sorption refrigeration systems. Kiplagat et al. [3] tested the sorption/desorption performance of a lab-scale solar-powered ice maker under different temperature conditions. Composite sorbent bed was made from expanded graphite (EG) powder impregnated with LiCl salt, showing higher specific cooling capacity compared to activated carbon/methanol pair. Further developments were reported by Kiplagat et al. [4], were a solid-gas thermochemical sorption heat transformer was developed for integrated thermal energy storage using a lithium bromide/ammonia pair.

Recently, Wu et al. [5] studied a prototype of low-grade heat thermochemical sorption cooling with an EG-SrCl2/NH3 pair, producing a cooling effect with a temperature ranging from −15 to 5 °C, with desorption temperatures below 100 °C and a reactor cooling temperature of 25 °C. Korhammer et al. [6] analyzed the thermodynamics and kinetics of the CaCl2-CH3OH pair, using TGA/DSC. They found that, for applications with evaporator temperatures close to 10 °C, SCP are obtained between 157 W/kg and 366 W/kg and COP between 0.9 and 0.76, for cycles of 60 min. In order to develop kinetic equations and predict the performance of the dynamic cycle for a bed of cylindrical reactor,

https://doi.org/10.1016/j.applthermaleng.2020.116281
Received 15 May 2020; Received in revised form 27 October 2020; Accepted 28 October 2020
Available online 28 November 2020
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Yuan et al. [7] analyzed the performance of the EG-SrCl₂ pair in a chemisorption cooling system, reaching a maximum SCP of 656 W/kg in 2.5 min, and a COP of 0.3 in 60 min. Gao et al. [8] developed a chemisorption system that uses a salt composed of CaCl₂ and MnCl₂, and NH₃ as refrigerant. They analyzed the long-term thermal energy storage, including months of seasonal energy storage and few days of heat storage from exhaust gases in winter. Likewise, Zhu et al. [9] made an experimental analysis with a 13°C/CaCl₂ – water adsorbent pair, using solar thermal energy with 6 single glass flat plate solar collectors with a total area of 12 m².

Modeling of this kind of systems has also been studied, this is the case of numerical approaches on transient state models, that describe physicochemical phenomena in sorption-based refrigeration systems and allow study the dynamical behavior and estimate the operation parameters. Huang et al. [10] reported a thermo-chemical non-stationary model that described the transient response of a sorption-based refrigeration system, that uses a strontium chloride/ammonia pair. The model assumed adiabatic boundary conditions and allowed to include process and sorption reaction kinetic parameters as main inputs, obtaining good agreement between experimental and simulated results. Demir et al. [11] performed a preliminary study that assessed the influence of porosity on temperature distribution on the sorbent bed, assuming adiabatic boundary conditions. Mohammed et al. [12] evaluated numerical methods to determine the performance of adsorption cooling systems using the silica gel-water pair, implementing a detailed coupled heat and mass transfer (CHMT) model and a lumped parameter (LP) model, in order to estimate the specific cooling power (SCP) of the system. It was determined that the difference between the two models lies in the shorter cycles, due to the pressure drop of the evaporator. However, the fact that neglect this pressure drop, the CHMT produces a higher SCP compared to that calculated from the LP model.

Nowadays, some investigations have been focused on the study of composite sorbents. This is the case of Jiang et al. [13], who investigated the non-equilibrium performance of composite adsorbents (calcium chloride-ammonia and ammonium chloride-ammonia) for reabsorption cooling, manganese chloride was used as high temperature salt (HTS) and calcium and ammonium chlorides were used as low temperature salt (LTS) for comparison. The maximum COP and SCP for the proposed experimental conditions in the reabsorption cooling where of 0.272 and 45.6 W/kg, respectively. Moreover, Jiang et al. [14], analyzed the performance of a compact two-stage sorption cooling system with a low-temperature heat source. In this research they used CaCl₂-BaCl₂-NH₃ as a working pair, with a matrix of expanded natural graphite treated with sulfuric acid (ENG-TSA). Authors found that the system adapts to different sources of low temperature heat (<100 °C), between 70 °C and 90 °C and the evaporation temperature between 5 °C and 10 °C.

Noriega et al. [15] assessed the effect of process operation and design parameters on specific cooling power, cooling power density, and COP of a chemisorption refrigeration system, by process simulation based on a two-dimensional heat transfer mathematical model. The authors implemented a central composite design to establish the simulation conditions that included the length and thickness of the sorbent bed, the heat transfer fluid flow, the fins thickness and pitch, the type of the sorbent, the cycle time, and the thermal contact resistance. Findings suggest that bed thickness and cycle time have a significant effect on response variables. Through exploration aided by central composite design, it was possible to find a set of conditions in which these variables were maximized, taking into account that maximizing the COP decreases the SCP.

As indicated by prior art exploration, the advancements in numerical and experimental models for chemical sorption refrigeration systems are focused on pure sorbent materials. In this article, a thermo-chemical transient model to study the mass and transfer phenomena in composite bed materials for chemical sorption-based thermal storage refrigeration systems is developed and experimentally validated. The model included dynamic convection boundary conditions between adsorbent
and adsorbate material. Such an assumption differentiates from the prior art in which adiabatic boundary conditions were considered. Experimental validation was performed with transient data obtained from the operation of a chemical sorption refrigeration system using expanded graphite/activated carbon/lithium chloride (AC/EG/LiCl)-adsorbent (an aqueous mixture of NH$_3$ at 25% H$_2$O v/v). The intention with these results is to improve the reactor design process through numerical modeling of the phenomena to increase the technology readiness level of composite bed materials in chemical sorption refrigeration systems.

2. Chemical sorption heat storage systems

For the development of a solid/gas sorption-based refrigeration system, two different strategies have been studied to improve the performance of the system. The first strategy looks to enhance recovered mass rates during the sorption phase by using new composite materials for the sorbent bed. The second strategy seeks to improve work performance by reducing heat consumption during the desorption phase. Such reduction is achieved by the inclusion of heat recovery devices between different sorption beds and using adsorbent materials that require less reaction activation energy during this phase. The chemical sorption process was selected to decrease energy consumption during the desorption phase, due to high solid-gas specificity. The phenomena is unimolecular and the adsorbent has an exclusively superficial reaction [16]. It is a process in which a substance, whether gas, liquid, or solid, adheres to the surface of a solid in a phenomenon of surface particle accumulation. The material that adsorbs is the adsorbate, and the substance on which it does so is the adsorbent. This reversible process is described with the next equation [17]:

\[
\text{Solid} (n + m) \cdot (\text{Gas}) + \Delta H_{\text{Des}} \xrightarrow{\text{Ads}} \text{Solid} \cdot n \cdot (\text{Gas}) + \text{Gas}
\]

In the previous equation, \( m \) and \( n \) are adsorbate/adsorbent reaction coefficients. Fig. 1 shows a schematic of the adsorption thermal energy storage system. During desorption or “loading” stage, hot water (70 °C) is used to regenerate the adsorbent in the adsorption bed. The adsorbate vapor (refrigerant) is separated from the desorption bed and condensed at room temperature (30 °C) on the condenser coils. Liquid refrigerant flows to the evaporator where it is stored. Finally, the pressure of the bed, condenser and evaporator, reach the saturation pressure of the refrigerant at room temperature. After the charging process ends, all valves in the system are closed to continue the adsorption process [18].

Fig. 1. Energy storage system. a) desorption stage. b) adsorption stage, adapted from Li et al. [18].
Clapeyron equation:

\[ \ln (P_m) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  

(2)

The adsorption bed is cooled to room temperature (pre-discharge process temperature 30 °C). Its pressure drops significantly below the saturation pressure of the refrigerant at room temperature. As the discharge process begins, the valve between the adsorption bed and the evaporator chamber opens, generating a pressure gradient that allows the adsorbate to flow from the evaporator to the bed, leading to the desorption reaction. The pressure reduction in the evaporator chamber causes a decrease in refrigerant temperature at the bottom of the evaporator. The refrigerant absorbs heat through the evaporator coil, producing a cooling effect of the chiller thermal fluid (i.e., cold water) so that the cooling effect is obtained to supply the thermal load of the refrigerated spaces [11].

The supplied energy during the desorption process is proportional to heat transfer rates from the adsorbent bed to the condenser refrigerant flow during the charging process. The supplied energy during the desorption process is proportional to heat transfer rates from the adsorbent bed to the condenser refrigerant flow during the charging process. Therefore, some of the ways to improve the efficiency of the thermodynamic cycle is to maximize the characteristics of the variables involved in the process, such as rate of heat flow from process water to refrigerant, adsorbent mass and refrigerant mass. Fig. 2 shows a heat flux diagram for the adsorption bed.

3. Model development

3.1. Governing equations

The following expression is the non-simplified energy equation that describes the heat transport phenomena in the adsorption bed [19]:

\[ \frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho h \mathbf{v}) = \frac{DP}{Dt} + \nabla \cdot (K \nabla T) + \phi + \dot{Q} \]  

(3)

For solid material, as is the case of the sorption bed, the following assumptions are considered:

- Taking advantage of the geometry of the reactor bed, the domain is considered 2-D axisymmetric
- There is no relative particle motion inside the bed \((\mathbf{v} = 0)\), therefore the effects of viscous dissipation in energy equations are negligible \((\phi = 0)\)

Fig. 2. Heat flux diagram of the adsorption bed.

Where,
- \(\dot{Q}_{\text{in}}\): Input heat transfer to the system
- \(\dot{Q}_{\text{out}}\): Heat transfer from the adsorption bed to the condenser refrigerant.
- \(\dot{Q}_{\text{ext}}\): Heat transfer from high-temperature source to the internal bed surface.

Fig. 3. Domain of the boundary value problem and initial condition.

- The bed material is incompressible \((\frac{\partial \rho}{\partial t} = 0)\)
- Specific heat will be assumed as constant in the temperature interval; for that reason, the following expression will be used \((\Delta h = C_p \Delta T)\).

By defining the product between density and specific heat as \(c\) “specific heat” \((c = \rho C_p, \text{J/m}^3 \text{K})\), then Eq. (3) can be written in cylindrical coordinates as:

\[ \frac{\partial T}{\partial t} = \frac{1}{C_r} \left[ K_r \frac{\partial^2 T}{\partial r^2} + K_z \frac{\partial^2 T}{\partial z^2} + \frac{1}{c} \dot{Q} \right] \]  

(4)

The 2-D axisymmetric, unsteady previous equation is valid for \(r_{\text{int}} < r < r_{\text{ext}}\) and \(0 < Z < L\), as is shown in Fig. 3.

Volumetric heat generation term due to sorption reaction can be evaluated by the following expression [10]:

\[ \dot{Q} = n_s N_s C_p \Delta H_r \frac{d^2 Z}{dt^2} \]  

(5)

The transient-coupled partial differential equation system that describes the mass and heat transport phenomena in the adsorption bed is given by the following equations:

\[ \frac{\partial T}{\partial t} = \frac{1}{C_r} \left[ K_r \frac{\partial^2 T}{\partial r^2} + K_z \frac{\partial^2 T}{\partial z^2} + \frac{1}{c} \dot{Q} \right] \]  

(6)

\[ \frac{d^2 Z}{dt^2} = k_{\text{int}} \exp \left( - \frac{E_{\text{int}}}{RT} \right) \left( 1 - \frac{Z}{Z_{\text{eq}}} \right) \frac{P_{\text{eq}}(t) - P_e}{P_{\text{eq}}(t)} \]  

(7)

\[ \frac{d^2 Z}{dt^2} = k_{\text{ext}} \exp \left( - \frac{E_{\text{ext}}}{RT} \right) \left( 1 - \frac{Z}{Z_{\text{eq}}} \right) \frac{P_{\text{exp}} - P_{\text{eq}}(t)}{P_{\text{eq}}(t)} \]  

(8)

3.2. Auxiliary equations

3.2.1. Efficiency and specific cooling capacity of the reactor

The store and removal efficiency \((\eta)\) in a closed system is defined as the heat removed from the cold reservoir divided by the work done to remove the heat. For chemical sorption refrigeration systems, the coefficient is given by the following equation [4]:

\[ \eta = \frac{Q_{\text{out}}}{Q_{\text{in}}} \]  

(9)

\(Q_{\text{des}}\) is the desorption heat, and it can be calculated according to
reported by [4] using the following expression:

\[ Q_{Des} = \sum_{i=1}^{n/2} \dot{m}_{H_2O, Des} \cdot C_{P_{H_2O}} \left( T_{Des, in} - T_{Des, out} \right) \]  \hspace{1cm} (10)

In Eq. (10), \( \dot{m}_{H_2O, Des} \) and \( C_{P_{H_2O}} \) are the mass flow on desorption stage and specific heat of the thermal fluid (water), \( t_c \) is the cycle time, and \( T_{Des, in} \) and \( T_{Des, out} \) are the inlet and outlet desorption temperature for water in the reactor. Adsorption heat can be calculated by using Eq. (11) as reported by [4]:

\[ Q_{Ads} = \sum_{i=1}^{n/2} \dot{m}_{H_2O, Ads} \cdot C_{P_{H_2O}} \left( T_{Ads, in} - T_{Ads, out} \right) \]  \hspace{1cm} (11)

where \( \dot{m}_{H_2O, Ads} \) is the mass flow on adsorption stage of the thermal fluid (water), and \( T_{Ads, in} \) and \( T_{Ads, out} \) are the inlet and outlet adsorption temperature for water in the reactor.

3.2.2. Specific cooling capacity (SCP)

The specific cooling capacity (SCP) is the parameter that indicates the estimated production capacity for the cooling effect. This calculation is based on the degree to which adsorption takes place represented by the amount of adsorbed material during the cycle adsorption stage. An expression for estimating SCP was reported by [4], and it can be calculated with the following equation:

\[ SCP = \frac{Q_{Ads}}{30 \times t_c} \]  \hspace{1cm} (12)

As stated previously, \( Q_{Ads} \) refers to the adsorption heat in the adsorption process. While, \( t_c \) is the cycle time in seconds.

3.3. Boundary and initial conditions

3.3.1. Initial conditions

\[ T(r, z, 0) = T_w \]  \hspace{1cm} (13)

\[ \xi(0) = 0 \]  \hspace{1cm} (14)

\[ T_r(0) = T_w \]  \hspace{1cm} (15)
3.3.2. Boundary conditions

\[ -K_r \frac{\partial T(x, z, t)}{\partial r} = h_{conv} [T_r - T(x, z, t)] \]  
\[ -K_r \frac{\partial T(r, z, t)}{\partial z} = h_{conv} [T(r, z, t) - T_r] \]  
\[ -K_r \frac{\partial T(r, 0, t)}{\partial z} = h_{conv} [T(r, 0, t) - T_0] \]  
\[ -K_r \frac{\partial T(r, L, t)}{\partial z} = h_{conv} [T(r, L, t) - T_L] \] 

3.4. Solving strategy and numerical method

The solving strategy for the transient-coupled partial differential equation system is shown in Fig. 4. Steps 1 through 7 are followed for a discrete-time interval to calculate the required temperature distribution in step 1 for the next time step.

\[ T_{prev} = \sum_{j=1}^{n+1} T_{j, prev} \] 

\[ \rho_\text{air} = c_{\text{air}} \left( \frac{\text{m}}{\text{n}} \right) \] 

\[ C^{n+1} = \sum_{i=1}^{M} \left( \frac{\text{m}_i}{\text{n}_i} \right) C_n \] 

\[ \frac{\text{d}C}{\text{d}t} = \frac{C^{n+1} - C^n}{\Delta t} \] 

\[ \frac{\text{d}T}{\text{d}t} = \frac{K_r}{\Delta z} \frac{\partial^2 T}{\partial z^2} + \frac{K_t}{\Delta r} \frac{\partial T}{\partial r} + T \frac{\partial (\rho C_p)}{\partial t} + n_{\text{NH}_3} \Delta H_r \frac{\text{d}z}{\text{d}t} \] 

For solving the unsteady, two dimensional PDE with boundary and initial conditions disclosed in Eqs. (6), (13) along (19), an implicit finite difference scheme of the Crank–Nicolson type is performed. After applying the method, the process of estimating the discrete bed temperature distribution is converted into a system of Penta-diagonal equations. The approximate solution for temperature distribution was obtained by performing the conjugate gradient procedure to the Penta-diagonal system of equations.

\[ a_i T_{j, i+1} + a_j T_{j, i-1} - a_k T_{j, i+1} + a_l T_{j, i-1} + a_m T_{j+1, i} + a_n T_{j-1, i} \] 

\[ a_i T_{j, i+1} + a_j T_{j, i-1} - a_k T_{j, i+1} + a_l T_{j, i-1} - a_m T_{j, i+1} - a_n T_{j-1, i} \] 

In this equation, the coefficients are simplified following the next expressions:

\[ a_1 = \frac{C}{2} \left( \frac{K_r}{\Delta z^2} + \frac{K_t}{\Delta r^2} \right) \] 

\[ a_2 = \frac{A}{2} \left( \frac{K_r}{\Delta z^2} + \frac{K_t}{\Delta r^2} \right) \] 

\[ a_3 = \frac{F}{2} \left( \frac{K_r}{\Delta z^2} + \frac{K_t}{\Delta r^2} \right) + \frac{1}{2} \left( \frac{K_r}{\Delta r} + \frac{1}{\Delta t} \right) \] 

\[ a_4 = \frac{G}{2} \left( A + B \right) = \frac{1}{2} \left( \frac{K_r}{\Delta z^2} + \frac{K_t}{\Delta r^2} \right) \] 

\[ a_5 = \frac{F}{2} \left( \frac{K_r}{\Delta z^2} + \frac{K_t}{\Delta r^2} \right) + \frac{1}{2} \left( \frac{K_r}{\Delta r} + \frac{1}{\Delta t} \right) \] 

\[ a_6 = E = \frac{1}{c} \left( \Delta \text{NH}_3 \Delta H_r \right) \frac{\text{d}z}{\text{d}t} \] 

4. Experimental validation

4.1. Kinetic reaction by thermogravimetric analysis

A composite sorbent material simple was prepared according to the parameters indicated in Table 1. The composite sorbent material was dried in a laboratory furnace for 24 h to remove the sample moisture, according to the procedure reported in the work of Carmona et al. [20]. These authors found experimentally that the mixture of activated carbon, lithium chloride and expanded graphite in the indicated proportions, has the potential to generate a great adherence of the bon, lithium chloride and expanded graphite in the indicated proportions, has the potential to generate a great adherence of the system performance. All these features improve the thermal behavior of the adsorbent mixture and contribute to the enhancement of the system performance.

Subsequently, the composite material mixture was impregnated with adsorbate (25% NH₃/H₂O mixture v/v), whose energy density properties are shown in Table 2. Five samples of material with a weight of 2.36, 2.42, 2.51, 2.54, and 2.38 mg were extracted. TGA analysis was performed in a Setsys Evolution TGA-DTA/DSC equipment (SETARAM, France). Mass loss test on saturated adsorbent materials was carried out at different heating rates (5 K/min, 10 K/min, 15 K/min, 20 K/min, 30 K/min).

The model and experimentation included ammonia/water mixture (NH₃ at 25% H₂O v/v) to provide support and allow model validation in the proof of concept stage. This means that, in fact, there is adsorption of water during the loading of the working fluid. However, the DSC/TGA tests allowed to find the kinetic parameters for the mixture used. Furthermore, due to the desorption temperatures (T < 70 °C), it is

---

Table 1

<table>
<thead>
<tr>
<th>Block</th>
<th>mHCL [g]</th>
<th>mAC [g]</th>
<th>mDG [g]</th>
<th>Sieve [No]</th>
<th>Pressure [MPa]</th>
<th>Ks [W/mK]</th>
<th>Kr [W/mK]</th>
<th>Porosity [%]</th>
<th>( \rho_{\text{mix}} ) [kg/m³]</th>
</tr>
</thead>
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<tr>
<td>M1</td>
<td>30</td>
<td>30</td>
<td>40</td>
<td>200</td>
<td>12</td>
<td>76.46</td>
<td>13.83</td>
<td>0.72</td>
<td>1164.32</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Salt</th>
<th>Reaction Enthalpy ( \Delta H ) [J/mol]</th>
<th>Reaction Entropy ( \Delta S ) [J/mol K]</th>
<th>Reaction coefficient ( n )</th>
<th>Reaction coefficient ( m )</th>
<th>Molar mass [g/mol]</th>
<th>Equilibrium temperature @ 30 °C</th>
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</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>36.8</td>
<td>224.6</td>
<td>1.0</td>
<td>3.0</td>
<td>42.3</td>
<td>67.0</td>
</tr>
</tbody>
</table>
assumed that the water stored in the adsorbent is not released in the cycle.

Considering that the adsorption/desorption reaction of NH₃ on LiCl-3NH₃ is given by Eq. (21), and assuming a competitive mechanism with the adsorption of water, a mass fraction-based first-order kinetic model for desorption is proposed:

\[
\frac{-1}{m_a} \frac{dm}{dt} = k_N \theta_N \tag{21}
\]

\[
\frac{-1}{m_w} \frac{dm}{dt} = k_W \theta_W \tag{22}
\]

Where the subscripts \(N\) and \(W\) correspond to ammonia and water, respectively. \(m_a\) is the adsorbent material mass and \(m_i\) is the adsorbed material mass, \(k_i\) are the kinetics constant. \(\theta_i\) is the fractional occupancy of the adsorption sites of the substance \(i\). Assuming initial saturated conditions in the TGA experiment, then \(\theta\) for the adsorbed species can be calculated by the following equations:

\[
\theta_N = \frac{m_N}{m_{N0}} \tag{23}
\]

\[
\theta_W = \frac{m_W}{m_{W0}} \tag{24}
\]

4.1.1. Desorption kinetics

At low heating rates, equilibrium conditions can be assumed. The equilibrium constant for the sorption/desorption process is given by the following expression:

\[
K_e = \frac{r_2}{r_1} = k_i(1 - \theta_N - \theta_W) P_N \tag{25}
\]

where \(K_e\) is the adsorption equilibrium constant, \(r_1\) and \(r_2\) are the desorption and sorption rates, \(k_i\) the kinetic constant, and \(P_N\) the ammonia partial pressure in the vapor phase.

Numerical estimations and experimental reaction kinetics during the desorption phase are shown in Fig. 5. Here it is observed that the global advance of reaction can be described by the numerical model. There is good agreement between thermos-physical parameters evaluated during the experimental phase at proposed conditions to obtain reaction kinetics between the adsorbent/adsorbate pair.

4.2. Thermal properties

The refrigerant pressure is given by the following equation [10]:

\[
ln(P_{eq}) = -\frac{4129}{T} + 27.01 \tag{26}
\]

Thermo-physical reaction parameters for the sorption/desorption reaction such as Arrhenius pre-exponential factor, Arrhenius activation energy, and kinetic coefficient were fitted from experimental TGA data obtained. Radial and axial thermal conductivity were determined by the hot plate method described by Carmona et al. [20]. The number of moles per unit of volume and the reaction enthalpy change were taken from Moren [21]. Thermo-physical properties of the adsorbent material and the adsorbate are shown in Table 3.

4.3. Experimental procedure

4.3.1. Experimental platform

As is shown in Fig. 6, the reactor is a finned concentric tubes heat exchanger, robust enough to bear pressure changes during the sorption and desorption reactions, maximizing the heat transfer area through fins design; compensating low radial thermal conductivity. The reactor is made of stainless steel. It has an inner bed diameter of 22 mm, an outer bed diameter of 42 mm and a length of 700 mm, as well as 63 fins with a thickness equal to 1 mm.

The reactor is integrated in an adsorption cooling system, which

\[
\text{Table 3} \quad \text{Thermo-physical properties of the adsorbent and adsorbate material.}
\]

<table>
<thead>
<tr>
<th>Symbol Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>lnk_{N, Des} Arrenhius pre-exponential factor for desorption</td>
<td>13.8</td>
<td>[1/S]</td>
</tr>
<tr>
<td>lnk_{N, Ads} Arrenhius pre-exponential factor for adsorption</td>
<td>59.7E-7</td>
<td>[1/S]</td>
</tr>
<tr>
<td>lnE_{N, Des} Arrenhius activation energy for desorption</td>
<td>10.9</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>lnE_{N, Ads} Arrenhius activation energy for adsorption</td>
<td>-8.65</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>M_{Des} Kinetic coefficient for desorption</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>M_{Ads} Kinetic coefficient for adsorption</td>
<td>2.96</td>
<td></td>
</tr>
<tr>
<td>K_c Axial thermal conductivity</td>
<td>76.46</td>
<td>[W/mK]</td>
</tr>
<tr>
<td>K_r Radial thermal conductivity</td>
<td>13.83</td>
<td>[W/mK]</td>
</tr>
<tr>
<td>N_i Moles per volume unit</td>
<td>2671E+5</td>
<td>[mol/m³]</td>
</tr>
<tr>
<td>ΔHr Reaction enthalpy change</td>
<td>36,828</td>
<td>[J/kg]</td>
</tr>
</tbody>
</table>

Fig. 5. Experimental and estimated reaction rate during the desorption phase.
delivers a thermal fluid (water) at high temperature for the addition of heat in the reactor. The heat source is an electric heater with a controlled temperature, the water is delivered in a controlled way by means of a pump and the flow is measured with a rotameter. The platform is complemented by an insulated cold box made of expanded polystyrene that houses the condenser. Fig. 7a shows the constructive elements used in the reactor assembly process, while Fig. 7b shows the experimental platform setup.

After finishing the assembly of the reactor, the system was brought to a 30 kPa vacuum condition. Through this process, any humidity trace of the system was removed, and leakage-proof validated. Vacuum pressure was held constant for 24 h, before loading the refrigerant. Next, the system was charged with 300 ml of NH₃/H₂O at 25% v/v. During the experimental phase, thermal fluid, reactor, condenser, and evaporator...
temperature measures were performed. In the adsorption stage, the heat source for the adsorbent bed was water at 67 °C and 1 L/min. For the desorption stage, water at 22 °C and 1 L/min was used to remove the heat from the exothermal desorption reaction. Temperatures were measured at the inlet and outlet of the thermal fluid, additional temperatures were measured at different points of the equipment (see Fig. 6). Detailed information about the experimental platform and protocol are reported by Carmona et al. [22]. These experimental conditions were taken as initial conditions and input variables for numerical simulation.

4.4. Model estimations and experimental data

4.4.1. Temperature distribution in the adsorbent bed estimated by the model

The bed temperature distribution was simulated in 3600-s cycles for both the adsorption and desorption stages. As observed in temperature bed distribution from Fig. 8a and b, generated heat during sorption reaction is successfully removed through inner and lower base surfaces where the fins are arranged, ensuring a fast heat dissipation capacity.

It can be noted from Fig. 8a, that during the first 1800 s of the adsorption cycle, the temperature at the boundary with the convective medium is in the order of 345 K, while the border with the thermal fluid is approximately 336 K, indicating a slow heat dissipation rate at the start of the reaction. In Fig. 8b, it is observed that the heat dissipation rate during the final stage of the adsorption phase is higher. However, homogeneous heat distribution in the bed is not ensured mainly due to the exothermal nature of the adsorption reaction, with a 10 K temperature difference.

Similar to the behavior of simulated temperature bed distribution during the adsorption stage, desorption temperatures are not homogeneously distributed due to the exothermal nature of the reaction represented by the generation term in the energy equation. Bed temperature distribution during desorption stage for 1800 and 3600 s of cycle-time are shown in Fig. 9a and b, respectively. The rise in temperature at the boundary with the convective medium indicates a localized increase in the rate of heat transfer, ensuring a rapid release of the refrigerant due to the contribution of the heat transferred from the inner wall and fin to the adsorbent bed. Heat generation due to desorption reaction produces an additional bed temperature rise, adding up to the transferred heat from the external source. As is observed in Fig. 9a, the bed temperature rise is higher during the first stages of the reaction, showing that a higher adsorbate concentration contributes to the temperature rise due to the desorption reaction. In Fig. 9b, it is shown a more homogeneous bed temperature distribution due to the higher amount of desorbed adsorbate material.

4.4.2. Temperature profile for a complete sorption/desorption cycle

The primary purpose behind the development of the computational model is the possibility of optimizing reactor design through the assessment of different bed geometry configurations and process conditions. For model sensibility testing, inlet and outlet temperatures of the thermal fluid were measured during a complete cycle, and bench reactor geometry configurations were taken as model input variables. Fig. 10 shows the comparison of the measurements with the values estimated by the model, where it was found that the numerical behavior adjusts to the experimental results during the desorption and adsorption stages, in which heat is added and removed to the bed, respectively. The temperatures estimated by the model for the desorption and adsorption processes, have an approximate mean absolute percentage error of 0.38% and 0.53%, respectively.

Additionally, during the experimental stage the temperatures and pressures were measured both in the adsorbent bed and in the cold box. Fig. 11 shows measurements obtained in one operating cycle for each control point (see Fig. 6). According to the results obtained, it is estimated that during the adsorption and desorption stages the ammonia moved from one place to another due to the observed pressure changes.

4.4.3. Efficiency and SCP profiles for a complete sorption/desorption cycle

Fig. 12 shows the simulated and experimental η and SCP profiles for a full refrigeration cycle. A significant onset during the first section of the refrigeration cycle is observed in both the reactor efficiency and the specific cooling power. Although there are no reported experimental studies regarding the use of the expanded graphite/activated carbon/lithium chloride-ammonia pair, it was confirmed the potential of the composite bed material for applications in sorption refrigeration systems coupled to low-grade heat sources. Experimental results show that values between 0.02 and 0.14 for η and 5 to 30 W/kg for SCP are...
Fig. 10. Simulated and measured inlet and outlet temperatures during sorption and desorption phases.

Fig. 11. Operation experimental conditions.
achieved through the use of the expanded graphite/activated carbon/
lithium chloride-ammonia pair. Fig. 12 indicates that the proposed
model presents good-agreement for estimated experimental conditions
in the cycle time interval.

4.5. Parametric analysis

In order to determine the variables that impact on the efficiency
response, a parametric analysis of the design variables was performed
using the validated model. A design of experiment was developed based
on a face-centered response. As factors studied, the following variables
were selected: temperature of the heat source \((T_H)\), reactor cooling
temperature \((T_L)\), the internal radius of the bed \((r_i)\), external radius of
the bed \((r_o)\) and length of the bed \((L)\). Variables and levels of the para-
metric analysis are shown in Table 4.

Results of the parametric analysis showed that the evaluated oper-
ating conditions can obtain values of efficiency between 0.076 and
0.235. These efficiency results involve the experimental factors previ-
ously described in Table 4. Table 5 presents the values obtained in the
parametric analysis of efficiency in each condition.

Table 4
Variables and levels of the parametric analysis.

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Table 5
Results for the response surface of the parametric analysis.

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<th>(T_H)</th>
<th>(T_L)</th>
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Fig. 12. Simulated and experimental efficiency and SCP for a complete sorption/desorption cycle.
Table 6
Results of the analysis of variation (ANOVA).

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<th>Pr(&gt;F)</th>
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Table 7
Significant level of the factors and their interactions.

| Estimate | Std. error | t value | Pr(>|t|) |
|----------|------------|---------|----------|
| (Intercept) | 0.116 | 0.002 | 50.485 | <2.2e-16 |
| A | 0.015 | 0.001 | 11.174 | 1.25e-11 |
| B | -0.105 | 0.001 | -11.122 | 2.86e-11 |
| C | -0.001 | 0.001 | -0.975 | 0.33936 |
| D | 0.028 | 0.001 | 20.034 | <2.2e-16 |
| E | -0.015 | 0.001 | -10.764 | 2.86e-11 |
| A:B | -0.016 | 0.001 | -11.174 | 1.25e-11 |
| A:C | 0.000 | 0.001 | 0.170 | 0.86629 |
| A:D | 0.003 | 0.001 | 2.013 | 0.05416 |
| A:E | -0.002 | 0.001 | -1.199 | 0.24112 |
| B:C | 0.000 | 0.001 | 0.170 | 0.86629 |
| B:D | -0.003 | 0.001 | -2.013 | 0.05417 |
| B:E | 0.002 | 0.001 | 1.199 | 0.24113 |
| C:D | 0.000 | 0.001 | 0.208 | 0.83720 |
| C:E | 0.000 | 0.001 | 0.110 | 0.91301 |
| D:E | -0.003 | 0.001 | -2.304 | 0.02916 |
| A’2 | 0.021 | 0.005 | 4.150 | 0.00029 |
| B’2 | 0.020 | 0.005 | 3.979 | 0.00047 |
| C’2 | -0.011 | 0.005 | -2.046 | 0.05058 |
| D’2 | 0.000 | 0.000 | 0.104 | 0.91301 |
| E’2 | -0.009 | 0.005 | -1.745 | 0.09229 |

Fig. 13 shows the behavior of the efficiency, when the internal radius is 20 mm and the external radius 45 mm, varying the temperature of the heat source and the cooling temperature of the reactor. It is possible to observe that, while temperature $T_H$ increases, the efficiency decreases, which is in agreement with the observed in the analysis of variance.

As can be seen in Fig. 14, the highest efficiency occurs when the difference between the inner radius and the outer radius of the bed is 5 mm, this is due the lower amount of adsorbent mass regardless the length of the bed. This point is detailed in Fig. 14, where it is observed that the efficiency is >0.16 for temperatures $T_H = 67 \degree C$ and $T_L = 22 \degree C$, respectively.

According to Figs. 13 and 14, a higher performance is obtained with an efficiency of 0.2 when the difference between the bed radius is equal to 5 mm. Likewise, for greater radius differences, the efficiency decreases considerably as shown in Fig. 15, which presents the response surface for the efficiency as a function of $T_H$ vs $T_L$, keeping the inner and outer radius in their low (Fig. 15 left) and high levels (Fig. 15 right).

5. Conclusions

An unsteady, two-dimensional, axisymmetric model of the thermo-chemical behavior for a finned adsorbent bed was proposed in this work. Results from the model were validated with transient data from a chemical sorption refrigeration test bench. Experimental results show that values between 0.02 and 0.14 for efficiency and 5 to 30 W/kg for SCP are achieved through the use of the AC/EG/LiCl-25% NH$_3$/H$_2$O mixture, respectively.

A parametric study was accomplished in order to obtain the variability on the efficiency with different operational and constructions conditions.

The model demonstrated good agreement with experimental data and adequate representation of the coupled mass/heat transport thermochromical phenomena in terms of the kinetical parameters, process temperatures, and key performance indicators.

During the sorption stage, the bed heat transfer process is influenced by a rapid onset of temperature due to the exothermic nature of the reaction. This requires higher thermal fluid flow rate in order to remove this amount of heat, achieving a more efficient adsorption reaction in short working cycles that improve the capacity of the system.

The performance of the model to reproduce with relative accuracy the experimental results in the selected process parameter region suggest the potential of a design screening tool for scaling up a sorption bed reactor reducing technology development costs. This screening tool would be particularly useful in systems with low-grade heat sources, such as low-temperature streams recovery, residual heat recovery from industrial processes or use or renewal energies.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to acknowledge to the Ministry of science, technology and Innovation of Colombia for the support given within the framework of the program “Formación de Capital Humano de Alto Nivel” from Norte de Santander department, and the program “Es tiempo de volver”.

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