



Comparison of closed and open thermochemical processes, for long-term thermal energy storage applications



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ABSTRACT

This paper focuses on the study of a solid/gas thermochemical reaction between a porous reactive bed and vapor. The objective is to determine the operating mode, either closed or open system, that best suits the requirements of a thermochemical seasonal storage applied to house heating. These two working modes have been compared thanks to two validated 2D models. This study shows that for the chosen set of parameters, the two operating modes lead to close global performances (the average specific power is 0.96 and 1.13 W/kg respectively for open and closed operating mode). Thus, the open thermochemical reactor, which presents technical advantages (easier conception and management, lower cost, ...), is a promising way to implement a thermochemical process as long-term heat storage. Moreover, simulations allow identifying the main limitations for each working mode and the ways to reduce them.

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1. Introduction/objectives

To limit the global warming and reach the Kyoto objectives, it is necessary to reduce the energy consumption and the greenhouse gas emissions. The residential sector is a key issue. For example, in France, this sector represents 43% of the national energy consumption and 25% of greenhouse gas emissions [1]. The use of renewable energies and in particular solar energy for household applications is a relevant mean to reach this target. In order to maximize the use of solar energy for house heating, it is interesting to utilize the solar energy excess in summer using a long-term storage (3–6 months).

Several studies deal with seasonal storage for residential applications [2–4]. Such storage systems must have on one hand the lowest heat losses between summer and winter, and on the other hand, the smaller volume i.e. the highest energy density. Among available processes, a thermochemical storage takes advantage of its high storage density (about 200–500 kWh m⁻³), and negligible heat losses between the storage and the recovery periods because the energy is stored as a chemical potential and the heat capacity of the components is weak [3]. Therefore, this kind of storage is relevant for seasonal storage for house heating. For comparison

purpose, the energy density of latent storage is about 90 kWh m⁻³, and about 54 kWh m⁻³ for sensible storage (water for a ΔT of 70 °C and heat losses of 25%) [5].

Such a thermochemical storage process involves a reversible chemical reaction between a solid and a gas. This paper focuses on a hydrate/water pair. The synthesis (or hydration) of the solid is exothermic (heating stage), while its decomposition (or dehydration) requires a heat input (storage stage).

Beside the high storage density criteria, a seasonal storage system has also to fulfill requirements about thermal power production for the heat recovery step. Previous works have defined a target value for this thermal power, for an acceptable range of mass of salt (5–10 tons), a typical French climate and an efficient house (Single Family House SFH100 used in IEA (Internal Energy Agency) works) [6,7]. Thus, the average thermal power required for heating is about: 3.5 kW and, the thermal specific power of the salt ranges between 0.3 and 0.7 W kg⁻¹. These values are weak compared to those of classical sorption systems (about 10–100 time lower), but a long-term storage system is based on a high amount of reactive salt and a low reaction rate.

For such large thermal storages, the simplest and efficient reactor configuration has to be designed. Several configurations have been proposed for thermochemical storage reactors [8]. According to Processes, materials and solar energy (PROMES) laboratory knowledge [9–11], a fixed bed configuration is chosen and a modular reactor is designed.

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Nomenclature

| | |
|------------------|--|
| c | molar heat capacity, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ |
| c_m | heat capacity, $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ |
| D | thickness of the heat collector, m |
| D' | thickness of the mass diffuser, m |
| D_h | hydraulic diameter, m |
| Dec | energy density of the reactive bed, $\text{J} \cdot \text{m}^{-3}$ |
| Dec _m | mass energy density of the salt, $\text{J} \cdot \text{kg}^{-3}$ |
| Der | energy density of the reactor, $\text{J} \cdot \text{m}^{-3}$ |
| h | molar enthalpy, $\text{J} \cdot \text{mol}^{-1}$ |
| h_{ech} | thermal losses coefficient, $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ |
| j | molar flow, $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ |
| k | permeability, m^2 |
| K | equilibrium constant |
| k_{cin} | kinetic constant, s^{-1} |
| L | length of the reactor, m |
| M | molar weight, $\text{kg} \cdot \text{mol}^{-1}$ |
| m | mass, kg |
| n | molar density, $\text{mol} \cdot \text{m}^{-3}$ |
| \mathbf{n} | unitary vector normal to the boundaries |
| N | mole quantity of salt, mol |
| \dot{n} | sink or source of gas, $\text{mol} \cdot \text{s}^{-1}$ |
| p | pressure, Pa |
| P_m | specific power, $\text{W} \cdot \text{kg}^{-1}$ |
| Δp | pressure drop across the salt bed, Pa |
| \dot{q} | sink or source of heat, $\text{J} \cdot \text{s}^{-1}$ |
| Q | power, W |
| \dot{Q}_m | specific power, $\text{W} \cdot \text{kg}^{-1}$ |
| R | gas constant, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ |
| \dot{S} | total entropy production, $\text{W} \cdot \text{K}^{-1}$ |
| T | temperature, K |
| T_c | constraint temperature, K |
| \mathbf{u} | velocity vector, $\text{m} \cdot \text{s}^{-1}$ |
| \dot{V} | flow rate, $\text{m}^3 \cdot \text{h}^{-1}$ |
| V | volume, m^3 |
| X | reaction advancement |
| y_v | molar water content in the moist air, $\text{mol}_v \cdot \text{mol}_h^{-1}$ |
| Z | thickness, m |

Greek symbols

| | |
|----------------|--|
| ΔG_r | free Gibbs energy, $\text{J} \cdot \text{mol}^{-1}_s$ |
| Δh_r^0 | standard enthalpy of reaction, $\text{J} \cdot \text{mol}^{-1}_s$ |
| Δs_r^0 | standard entropy of reaction, $\text{J} \cdot \text{mol}^{-1}_s \cdot \text{K}^{-1}$ |
| ϵ | porosity |
| μ | air viscosity, $\text{Pa} \cdot \text{s}$ |
| ν | stoichiometric coefficient, $\text{mol}_G/\text{mol}_S$ |
| ρ | density, $\text{kg} \cdot \text{m}^{-3}$ |
| Ω | cross section of the salt bed, m^2 |
| ρ | density, $\text{kg} \cdot \text{m}^{-3}$ |
| λ | thermal conductivity, $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ |
| $\dot{\sigma}$ | local entropy production, $\text{W} \cdot \text{m}^{-3} \cdot \text{K}^{-1}$ |

Indices

| | |
|------|--------------------------|
| 0 | dehydrated salt |
| 1 | hydrated salt |
| a | dry air |
| atm | atmospheric |
| c | heat collector |
| dif | diffuser |
| eff | effective |
| eqLG | liquid/gas equilibrium |
| eqSG | solid/gas equilibrium |
| f | at the reaction front |
| G | gas |
| h | moist air |
| i | inlet of the porous bed |
| ini | initial |
| j | outlet of the porous bed |
| out | outdoor |
| s | salt |
| t | total |
| v | water vapor |
| X | reaction advancement |
| x | x direction |
| y | y direction |
| z | z direction |

Exponents

| | |
|---|-----------|
| 0 | reference |
|---|-----------|

Moreover, for a hydrate/water pair, two operating modes of the thermochemical reactor can be used: closed and open system. In a closed thermochemical system, the salt reacts with pure water vapor at vacuum pressure, while in an open system, the reactive solid bed is crossed by a moist air flow at atmospheric pressure. Many thermochemical systems operate with pure vapor [12–16]. Nevertheless, this kind of working under atmospheric pressure generates strong technological constraints for the thermochemical system design. The open operating mode, at atmospheric pressure, allows to avoid these constraints and it is free of the evaporator/condenser and the water storage reservoir. Thus it could lead to a simpler and cheaper reactor conception [17].

The feasibility of open thermochemical storage system is currently investigated [11,18–23], and seems promising [24]. However, up to date there is no completed seasonal storage based on a thermochemical process [3,17].

Therefore, the objective of this work is to determine the operating mode, either closed or open, that best suits to thermochemical seasonal storage applied to house heating. These two working modes have been compared due to two 2D models described in this paper. A sensitivity study and a second law analysis allow identifying the main limitations for each working mode and the ways to reduce them. The

objective of this paper is to evaluate the performance and limitations of each working mode before setting an experimental bench and performing an experimental study and a thorough validation.

2. Principle of solid/gas sorption processes for seasonal heat storage

2.1. Solid/gas reaction for seasonal thermochemical storage

A thermochemical system is based on the thermal effect of a monovariant reversible reaction between a solid and a gas:



The equilibrium conditions (p_{eqSG} , T_{eqSG}) of the solid/gas reaction follow the Clausius–Clapeyron relation. This relation is obtained by stating that the free Gibbs energy of this transformation is equal to zero at the thermodynamic equilibrium:

$$\Delta G_r = \Delta G_r^0 + RT_{\text{eqSG}} \ln K = \Delta h_r^0 - T_{\text{eqSG}} \Delta s_r^0 + RT_{\text{eqSG}} \ln K = 0 \quad (2)$$

K is the equilibrium constant for the solid/gas reaction. Assuming that the reactive gas behaves as a perfect gas, K becomes:

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