

CHEMICAL STORAGE OF THERMAL SOLAR ENERGY FOR COLD PRODUCTION: A CASE NUMERICAL STUDY OF THE INFLUENCE OF FINS IN TUBULAR PACKED BED REACTORS ON THERMAL AND KINETIC PERFORMANCES OF THE SYSTEM

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ABSTRACT

The key element of thermo-chemical heat pumps is the reactor. Its design should facilitate the heat and mass transfer during both phases of the cycle (absorption and desorption) while ensuring a high energy density.

This study concerns the simulation of heat and mass transfer in the solid/gas tubular packed bed reactor of a solar chemical heat pump. The reactor is located in the flat-plate solar collector of the machine. It is equipped with fins to enhance heat and mass transfer.

A two-dimensional mathematical model was developed for the reactor. This model is based on the energy balance equation coupled with the kinetic equations reflecting the transformations that occur in the reactive medium. The resolution of the model is based on the control volume analysis. The studied case concerns a solar chemical heat pump using $\text{CaCl}_2/\text{CH}_3\text{NH}_2$ couple.

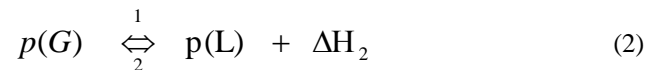
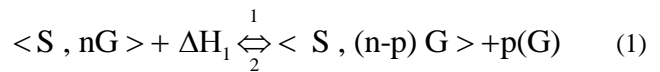
The results show that increasing the number of fins enhances heat transfer in the reactor which leads to improvement of reaction kinetics and results also in mass transfer enhancement.

Key Words: Solid/gas reactor, Chemical Heat Pump, Modelling, Solar

1. INTRODUCTION

A chemical heat pump uses the chemical affinity between a gas and a solid to transfer heat from the cold source to the hot source by mean of a three temperature thermodynamic cycle. The implementation of solar chemical heat pumps based on reversible chemical reactions between a solid and a gas involves the coupling between the reactor placed in a solar collector, a condenser and an evaporator (Figure 1).

The solid/gas reactor is the seat of synthesis and decomposition reactions, whereas the evaporator and the condenser are the seats of the refrigerant phase transitions (liquid/gas). The monovariant equilibriums involved in such a system are of types:



With the notations: S = Solid, G = Gas, L = Liquid.

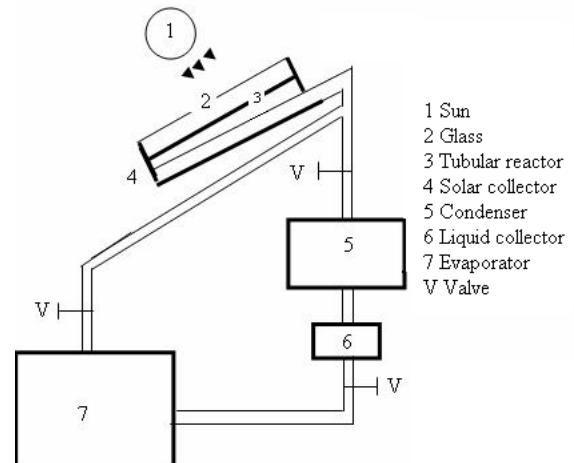


Figure 1. Basic scheme of a solar chemical heat pump

The key element of such a machine is the reactor. Its design should facilitate the heat and mass transfer during both phases of the cycle (absorption and desorption) while ensuring a high energy density.

The poor heat and mass transfer within the solid/gas packed medium limit the development of thermochemical heat pumps. Indeed, the used reactive salts have a weak thermal conductivity and are often used within a particle size range in the order of 100 μm . The reactive environment, since the first cycle, undergoes an irreversible expansion and behaves thereafter like a consolidated porous medium in which heat and mass transfer are very poor [1] thus reducing the machine performances.

The solutions proposed by various authors to improve the heat and mass transfer within the packed bed solid/gas reactors are based on different methods of preparation of the reaction mixture using inert binders [2] or conductive

supports [3]. In this context, the introduction of internal fins in the reactor can be an effective solution that improves heat and mass transfer by minimizing settlement and increasing the overall thermal conductivity of the medium.

This study focuses on the simulation of heat and mass transfer in the solid/gas tubular reactor located in the solar collector of the machine. The reactor is equipped with fins to enhance heat and mass transfer. The studied case concerns a solar chemical heat pump using $\text{CaCl}_2/\text{CH}_3\text{NH}_2$ couple.

2. MATERIALS AND METHODS

2.1. Position of the problem

The modelled system is a solid/gas packed bed tubular reactor equipped with fins and located in the flat-plate solar collector of a chemical heat pump based on the couple $\text{CaCl}_2/\text{CH}_3\text{NH}_2$. The choice of this couple allows the use of a simple flat-plate solar collector with non-selective surface and leads to moderate operating pressures, thus reducing machine sophistications and cost. The solid reaction mixture consists of CaCl_2 salt mixed to a binder (Graphex) in a proportion of 20 % and with a compaction value $N_s = 1542 \text{ moles/m}^3$. The choice of these values is inferred from performed studies aiming to optimize the rate of binder [2] and the compaction in solid/gas packed bed reactors [1]. The scheme in Figure 2 provides details, domains and dimensions of the modelled tubular reactor. The reactor is placed in the flat-plate solar collector of the machine as shown in Figure 1.

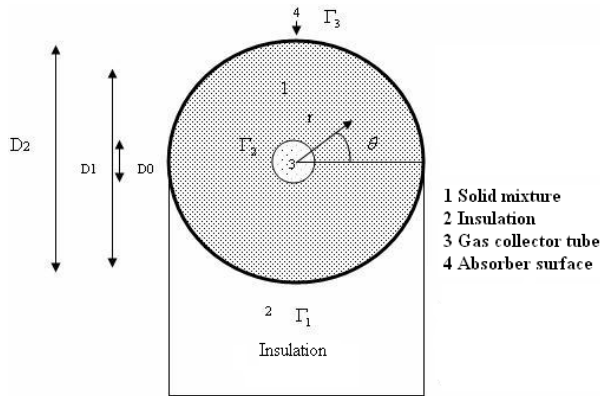
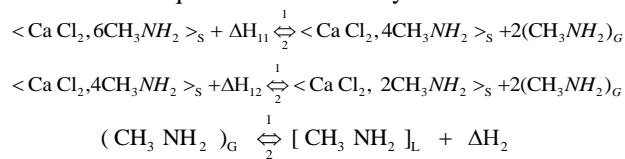


Figure 2. Cross section of the tubular modelled reactor showing the dimensions and the different domains considered.

2.2. Involved equilibriums

The involved equilibriums in such system are:



The conversion rates of the first and second equilibriums are noted respectively X and Y in this text. The enthalpies

ΔH_{11} and ΔH_{12} , accompanying these reactions have a value of 50 kJ/mol and the heat of condensation ΔH_2 has a value of 25.8 kJ/mol.

2.3. Operating cycle

The complete operating cycle of the solar heat pump takes place in two different phases:

- Desorption - condensation phase: in this higher pressure phase which takes place during the day, the heat quantities ΔH_{11} and ΔH_{12} are supplied, at the higher temperature T_{des} , by the hot source (solar collector), and permit the dissociation of the solid reagent. Simultaneously, the heat quantity ΔH_2 delivered by the system at the intermediate temperature T_{con} is released to the environment at the condenser level.
- Evaporation - absorption Phase: in this lower pressure phase which takes place during the night, the amount of heat ΔH_2 is withdrawn from the cold medium at the lower temperature T_{eva} , whereas the amounts of heat ΔH_{11} and ΔH_{12} released by the system at the temperature T_{abs} , during the absorption of gas by the solid reagent, are evacuated to ambient through the solar collector.

2.4. Model hypothesis

To establish the simulation model, the following simplifying assumptions are adopted:

- the gas flow rate is low, and therefore the convective transfer is negligible,
 - the exchange between the solid and the gas is neglected; they are considered to be at the same temperature,
 - the vapour - liquid phase change process of the refrigerant is instantaneous,
 - the accumulation of heat in the vapour phase is neglected.
- The methylamine is constantly under the conditions of vapour-liquid equilibrium. The constraint pressure is imposed by the equilibrium phase change and pressure variations are simply related to the changes in temperature of the evaporator/condenser by the Clausius-Clapeyron relationship.

Given these simplifying assumptions, the behaviour of the reactor can be described by the thermal balance in solid phase including the production or consumption of heat due to chemical reactions and the kinetic equations reflecting the transformations that occur in the reactive medium.

2.5. Energy balance

The heat balance of the solid phase contains a diffusion term, an accumulation term, and a source term proportional to the reaction kinetics. This balance equation writes:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) \pm 2N_s \Delta H \left(\frac{\partial X}{\partial t} + \frac{\partial Y}{\partial t} \right) \quad (3)$$

With $\Delta H = \Delta H_{11} = \Delta H_{22}$

The heat capacity $\rho(X,Y)C_p(X,Y)$ of the mixture may be calculated by simply taking into account the composition and capacities of the components in the mixture. This heat capacity is given by the equation [4]:

$$\rho.Cp(X,Y) = Ns[556.8 - 157(X + Y)] \quad (4)$$

The apparent thermal conductivity of the reaction mixture $\lambda(X,Y)$ varies depending on the composition of the medium. The expression for estimating the conductivity expressed in W/m^2K , during the two phases of absorption and desorption writes as follows [5]:

$$\lambda(X,Y) = 0.48 - 0.22X - 0.02Y \quad (5)$$

2.6. Kinetic equations

The medium considered undergoes two successive reactions with associated rates noted X and Y, each varying in the range 0 – 1. The involved kinetic equations are:

- Desorption phase

$$\frac{\partial X}{\partial t} = C_{1D}(1-X)^{m_{1D}} \exp\left(-\frac{d_{1D}}{T}\right) \left[\frac{\Delta H_{11}}{R} \left(\frac{1}{Teqx} - \frac{1}{T} \right) \right] \quad (6)$$

$$\frac{\partial Y}{\partial t} = C_{2D}(1-Y)^{m_{2D}} X^{nD} \exp\left(-\frac{d_{2D}}{T}\right) \left[\frac{\Delta H_{12}}{R} \left(\frac{1}{Teqy} - \frac{1}{T} \right) \right] \quad (7)$$

- Absorption phase

$$\frac{\partial X}{\partial t} = C_{1A}(1-X)^{m_{1A}} Y^{nA} \exp\left(-\frac{d_{1A}}{T}\right) \left[\frac{\Delta H_{11}}{R} \left(\frac{1}{T} - \frac{1}{Teqx} \right) \right] \quad (8)$$

$$\frac{\partial Y}{\partial t} = C_{2A}(1-Y)^{m_{2A}} \exp\left(-\frac{d_{2A}}{T}\right) \left[\frac{\Delta H_{12}}{R} \left(\frac{1}{T} - \frac{1}{Teqy} \right) \right] \quad (9)$$

All the factors involved in the chemical kinetic model have been identified [5] from experimental results [1]. These values are grouped in Table 1 below.

Table 1. Parameters of Chemical Kinetics

Factor s	C1 (S ⁻¹)	C2 (S ⁻¹)	d1 (K ⁻¹)	d2 (K ⁻¹)	m1	m2	n
Deso.	0.006 2	0.003 7	855	640	1.1 7	1.43 1	1.9 9
Abso.	0.075	0.045	190 0	120 0	0.7 5	1.05	1.5

2.7. Equilibrium state equation

At equilibrium, the Clapeyron relationship is used to express the pressure as a function of temperature:

$$\ln(P) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (10)$$

2.8. Numerical resolution

The simulation model consists of a partial differential equation and two nonlinear differential equations. The resolution of this model is performed using the method of control volumes.

3. RESULTS

The simulation results concern the heat and mass transfer in a solid/gas reactor equipped with internal fins. The reactor is placed in the flat-plate solar collector of a solar chemical heat pump using the couple $CaCl_2/CH_3NH_2$.

Figure 3 shows the evolution of the solar power radiation received by the cylindrical reactor. It is clear that the solar power received is highly dependent on angle θ i.e. on the position of each point on the external surface of the cylindrical tube represented in Figure 2.

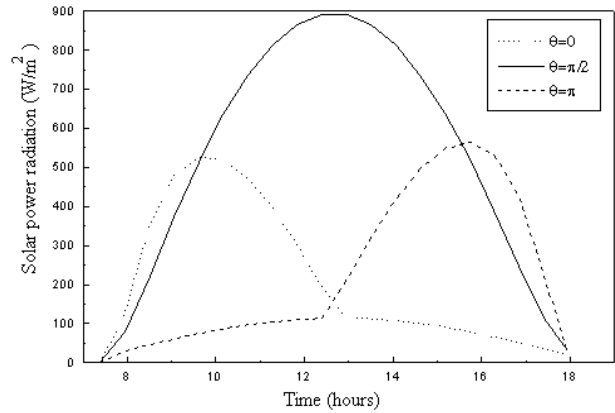


Figure 3. Evolution of the solar radiation power received by the cylindrical reactor, for the typical simulated day, as a function of time and position on the outer surface of the reactor.

3.1. Influence of the number of fins

We are interested by the influence of internal fins on the heat and mass transfer within the reactor. To achieve this objective, the following cases were simulated: reactor without fins, with one fin, two fins and four fins.

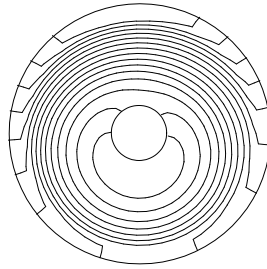
The influence of the number of fins on the performances of the reactor was studied by plotting the iso-values (isotherms and conversion rates) at different instants for both phases of the cycle: absorption and desorption.

The simulation results presented here are the temperature and global conversion rate ($X_g = X + Y$) fields in the reactor during the desorption phase.

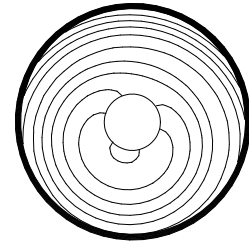
The isotherms are plotted at $t = 13,4$ h (see figure 4). In Table 2, are reported the minimum and maximum temperatures for each configuration.

The iso conversion rates are plotted at $t = 13,4$ h (see figure 5). In Table 3, are reported the minimal and maximal global conversion rates for each configuration.

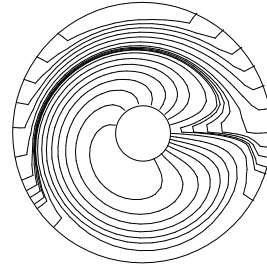
Reactor without fins
Isotherms:
 $321.2 \text{ K} < T < 332.1 \text{ K}$



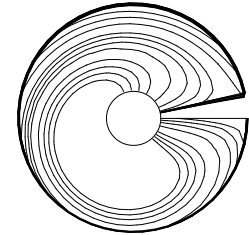
Reactor without fins
Iso - rates:
 $0.276 < X_g < 0.752$



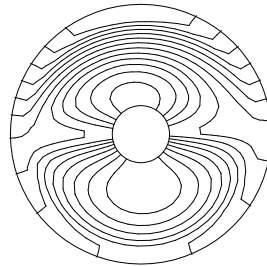
Reactor with one fin
Isotherms:
 $321.3 \text{ K} < T < 331.5 \text{ K}$



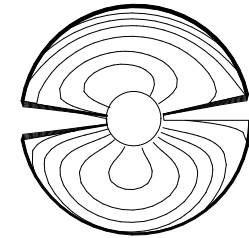
Reactor with one fin
Iso - rates:
 $0.273 < X_g < 0.726$



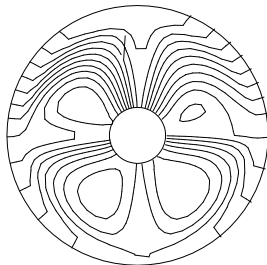
Reactor with 2 fins
Isotherms:
 $321.7 \text{ K} < T < 330.7 \text{ K}$



Reactor with 2 fins
Iso - rates:
 $0.297 < X_g < 0.702$



Reactor with 4 fins
Isotherms:
 $322.4 \text{ K} < T < 329.5 \text{ K}$



Reactor with 4 fins
Iso - rates:
 $0.305 < X_g < 0.650$

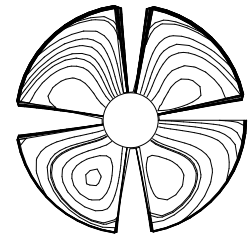


Figure 4. Isotherms within the reactor in desorption phase at $t=13.4$ h. The configurations: reactor without fins, reactor with one, two and four fins are represented.

Table 2. Minimal and maximal temperatures, in desorption phase at $t = 13.4$ h, for different number of fins configurations.

Number of fins	Minimal Temperature (K)	Maximal Temperature (K)	Maximal Difference (K)
0	321.2	332.1	10,9
1	321.3	331.5	10,2
2	321.7	330.7	9
4	322.4	329.5	7,1

Figure 5. Iso - conversion rates ($X_g = X + Y$) within the reactor in desorption phase at $t=13.4$ h. The configurations: reactor without fins, reactor with one, two and four fins are represented.

Table 3. Minimal and maximal global conversion rates, in desorption phase at $t = 13.4$ h, for different number of fins configurations.

Number of fins	Minimal Global reaction Rate X_g	Maximal Global reaction Rate X_g	Maximal Difference
0	0.276	0.752	0,476
1	0.273	0.726	0,453
2	0.297	0.702	0,405
4	0.305	0.650	0,345

3.2. Results Analysis

The analysis of the results obtained for the four configurations studied shows that:

- At the centre of the reactor, the iso values are orthogonal to the border. This fact is due to the condition of zero flux imposed on the central tube. The same remark can be done concerning the outside border at reactor bottom because of the insulation.
- The shape of the iso-values changes with the time considered as each point on the external surface of the reactor receives a different solar radiation power (see Figure 3).
- In the cylindrical reactor without fins, the iso values are almost circular and concentric around the central tube.
- In the case of reactor with two fins, the iso values are almost symmetrical to the axis formed by the two fins.
- In the case of reactor with four fins, isothermal lines are almost radial and the iso conversion rates are almost circular and concentric.

The increase in the number of fins is accompanied by a decrease in the maximal temperature gap in the reactor (Table 2) reflecting a better distribution of heat.

The same observation can be made for iso rates. The increase in the number of fins is accompanied by a decrease in the maximal conversion rate gap in the reactor (Table 3) reflecting an improvement in the mass transfer. This fact may be explained knowing that local reaction kinetics depend on the difference between local temperature and equilibrium temperature as shown in equations 6 – 9. Therefore, improvement in heat transfer enhances mass transfer via improvement of reaction kinetics.

4. CONCLUSION

A two-dimensional model was established for the study of heat and mass transfer in the tubular packed bed reactor of a chemical heat pump driven by solar energy. This model was used to study the influence of the number of fins on the performance of the reactor.

The results of simulated cases show that the increase in the number of fins is accompanied by a decrease in maximal temperature gap in the reactor reflecting a better distribution of heat and heat transfer enhancement. The same observation was made on the conversion rates. The improvement in heat transfer enhances mass transfer via improvement of reaction kinetics.

Thus the increase in the number of fins tends to increase the energy density. However, the volume occupied by the fins will lead to a decrease in the number of moles of reaction mixture per unit volume of the reactor which will cause a decrease in energy density. These two opposing

effects lead to the existence of an optimal number of fins resulting in an optimal energy density.

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6. NOMENCLATURE

D_0	External diameter of the inner reactor tube (m)
D_1	Internal diameter of the outer reactor tube (m)
D_2	External diameter of the outer reactor tube (m)
Γ_1	first physical domain: rear isolation
Γ_2	second physical domain: reactive medium
Γ_3	third physical domain: stainless steel tube jacket
X	Conversion rate for the 1 st reaction (mol/mol)
Y	Conversion rate for the 2 nd reaction (mol/mol)
ΔH	Enthalpy change of reaction (J/mol)
Subscripts	
1D	1 st Desorption reaction
2D	2 nd Desorption reaction
1A	1 st Absorption reaction
2A	2 nd Absorption reaction
Abs	Absorption
con	condensation
des	desorption
eva	evaporation
min	minimal
max	maximal
S	Solid