Transferts de chaleur dans un réacteur thermochimique solaire muni d'un récepteur volumique poreux

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Résumé- Un réacteur thermochimique solaire de 1 kW muni d'une structure céramique poreuse en céramique est modélisé pour simuler les transferts thermiques a l'intérieur du récepteur volumétrique. Le modèle développé a été utilisé pour prévoir le comportement thermique du réacteur en fonction des différentes conditions opératoires qui concernent le débit de gaz inerte, le flux solaire incident, la porosité, la longueur du récepteur, et la prise en compte de réactions chimiques. Les résultats montrent que la température maximale est de 1850K pour une concentration solaire de 1000 soleils. La température diminue de manière significative lorsque le débit de gaz augmente. Un débit de 6 L/min permet d'avoir une température optimale dans le récepteur afin d'effectuer la réduction de l'oxyde.

1.Introduction

The conversion of concentrated solar energy into a sustainable energy carrier such as hydrogen is an attractive option to produce a long-term storable and transportable fuel without green house gas emissions. One of the most promising options to obtain "solar hydrogen" relies on the solar thermochemical cycles that present satisfactory energy efficiency due to the direct conversion of heat to hydrogen [1]. Several of these cycles were analyzed and demonstrated experimentally [2-6] and recently, special interest was paid in the use of the Fe_3O_4/FeO redox pair and mixed metal ferrites [7-11]. This iron-based process was first proposed by Nakamura [12] and it is realized in two steps: the first one consists of a highly endothermic reduction reaction that needs temperatures above 1800 K to produce the FeO (wüstite phase) (thermal-reduction step). In the second step (hydrolysis step), hydrogen and Fe_3O_4 are obtained from the reaction of wüstite with water at about 800 K [12-13].

$$Fe_3O_4 \rightarrow 3FeO + \tfrac{1}{2}O_2 \qquad \text{(Thermal-reduction Step)}$$
$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \qquad \text{(Hydrolysis Step)}$$

Mixed oxide materials such as ferrites (like nickel ferrites) were proposed to lower the temperature of the thermal reduction step below 1600 K while the reduced phase was still reactive with water to produce hydrogen at about 1200 K [7]. Due to the lower reduction temperature of the ferrites, a few solar reactor concepts have been developed and tested [7,10,14].

In order to implement this chemical process in the solar furnace of PROMES-CNRS, a volumetric solar receptor/reactor based on low cost ceramic structures is proposed. This reactor consists of a porous ceramic foam made of silicon carbide impregnated with the reactive material (e.g., $M_xFe_{3-x}O_4$) deposited as a coated layer. This structure is directly irradiated by concentrated solar energy with the aim of obtaining the necessary reaction temperatures. With such a reactor configuration, several advantages can be expected, some of them are [15]: (I) The solid transport (reactants feeding and products collection) is avoided

because of the use of a reactive solid fixed in the receiver; (II) the whole chemical process (hydrolysis and reduction reactions) can be achieved in the same reactor; (III) there is a high geometric surface area and therefore good gas-solid interface contact, low pressure drop and a high mass transfer performance because of using a porous media.

The modeling of reactors is a tool that allows the reactor design improvement. In the field of volumetric solar receivers, a few previous studies have been done [7,14,16]. Therefore, a model for a solar volumetric reactor devoted to the thermochemical hydrogen production is developed in this study. The model includes mass, momentum and energy equations as well as both the reduction and hydrolysis reactions. The commercial software ANSYS FLUENT was used to solve the transport equations in the fluid phase. For the solid phase, the radiative transfer and kinetics of the chemical reactions were computed using the UDFs (User Defined Functions). The aim of this study is to perform a parametric study and to predict the system performances as a function of operational conditions.

2. Solar reactor description

The reactor consists of a horizontal cylindrical chamber (0.035 m i.d. and 0.044 m long) that contains the porous ceramic structure (Fig. 1). The front of the device is directly irradiated by concentrated solar energy supplied by a solar furnace consisting of a sun-tracking heliostat and a 2 m-diameter parabolic concentrator (maximal flux density of 1600 W/cm^2, Gaussian distribution).The lateral walls of the foam are surrounded by an insulator and a hemispherical glass window separates the system from the ambient air to provide a controlled atmosphere inside the chamber. A flow of inert gas (nitrogen) enters by the front of the receiver, flows inside the porous foam and sweeps the gaseous product species out of the chamber.
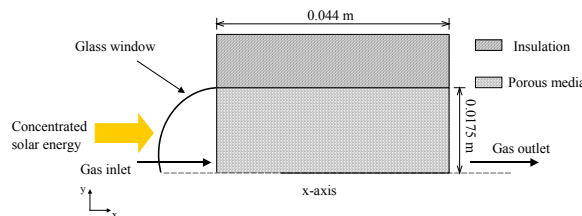

Fig. 1: Cross-section sketch of the solar reactor

3. Methodology

The receiver was simulated with ANSYS Computational Fluid Dynamics (ANSYS CFD) and User-Defined Functions (UDFs). The UDFs are programmed functions that are coupled with the ANSYS-FLUENT solver for enhancing the standard features of the code. The developed model solves the 2D steady state continuity, momentum and energy equations for an axi-symmetrical flow (see Fig.1).

Simulations were first conducted for a non-reactive flow in order to determine the thermal behavior of the reactor in different operational conditions; then both reduction and hydrolysis reactions were included separately into the model for studying their impact on the temperature distribution. The model convergence criterion was set to 1 x 10^{-10}. The model assumes that the

flow within the monolith pore channels is laminar and that the lateral walls are well insulated (adiabatic). The radiation entering the receptor is collimated with a Gaussian distribution, and the foam is considered as a gray, optically thick, absorbing, emitting and isotropic scattering media. The reaction rate expressions include all the possible mechanisms involved in the conversion of gas and solid species (e.g., adsorption, desorption). The properties of the monolith materials correspond to those of silicon carbide, and the influence of the coating on the physical properties is neglected.

4. Results and discussion

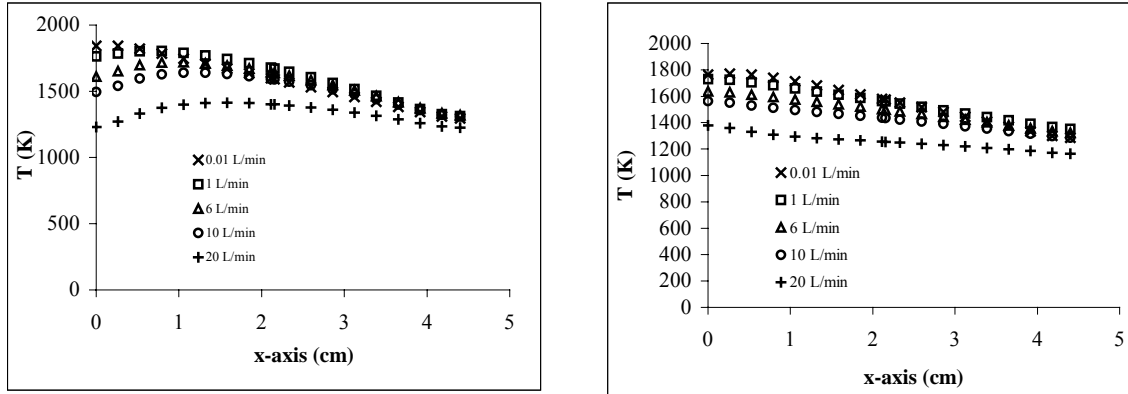### 4.1 Simulations in the case of a non-reactive flow

Regarding a non-reactive flow, the inert gas (N_2) is assumed to enter the cavity at 300K and 1 atm. The nitrogen was injected by the front of the reactor and several gas flow rates were considered. The front of the foam is subjected to concentrated solar radiation (total incident power of 1 kW, mean concentration of 1000 suns), which is represented either by a constant solar flux density or by a Gaussian distribution.

The temperature of the foam along the symmetry axis is represented in Fig 2. The gas flow rate has a strong impact on the temperature of the foam. The higher the gas flow rate, the lower the temperature. A flow rate lower than 20 L/min permits to reach temperatures above 1400K in the major part of the foam. Such temperatures are suitable to carry out the thermal-reduction step, which suggests that the reaction can occur in the whole material. The maximal temperature is 1850 K and corresponds to the lowest gas flow rate (0.01 L/min).

The temperature of the foam along the symmetry axis for a uniform incident solar flux density of 1004 kW/m^2 is shown in Fig. 2B. In this case, the temperature decreases almost linearly along the receiver and, similarly to the previous case (Fig. 2A), the flow rates lower than 20 L/min are necessary to reach the temperatures required in the endothermic thermal reduction reaction (over 1400K).

The model was then applied to investigate the effect of the foam length on the temperature distribution. Three different lengths of the receptor were analyzed in figure 3: L1=2.2 cm, L2=4.4 cm, and L3=6.6 cm. The diameter of the foam was kept unchanged (3.5 cm). The results show that the shorter the receptor, the lower the solid temperatures in the first 60% of the foam length. At the end of the foam (last 40%), the inverse tendency is obtained: the solid temperatures decrease when increasing the receiver length. The temperature difference along the receiver x-axis is not very large (50-80 K) and so, the receiver length does not affect significantly the temperature distribution.

Another parametric study was related to the porosity of the material. In the simulations, several porosities of the foam were considered with the aim of analyzing their impact on the solid and fluid temperatures. The results of the study shows that the porosity impacts slightly the temperature of the solid. The fluid temperature remains almost unchanged whatever the different porosities considered.

(A)   **(B)**

Fig 2. Temperature of the foam along the symmetry axis for several inert gas flow rates and for an (A)incident Gaussian flux distribution (B) uniform incident flux density of 1004 kW/m^2
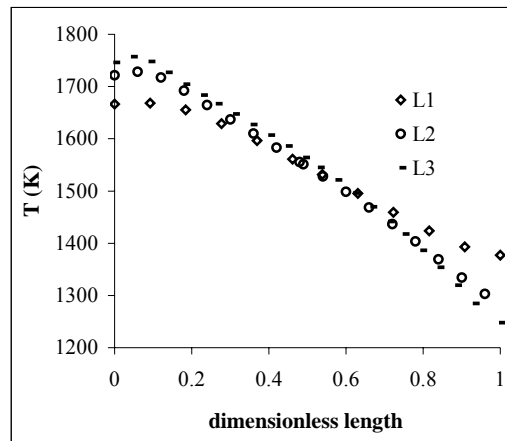

Fig 3. Temperature of the foam as a function of the foam length for an incident Gaussian flux distribution and an inlet gas flow rate of 6 L/min

4.2 Simulations in the case of a reactive flow

In the next simulations, a reactive flow was modeled in order to study the effect of the chemical reaction on the temperature distribution in the gas and solid phases. Both the reduction and hydrolysis reactions were analyzed (Fig. 4 and 5). In the reduction step, nitrogen was supposed to enter within the receptor at a flow rate of 6 L/min and an incident solar irradiation characterized by a Gaussian flux distribution was considered. An inlet gas mixture composed of nitrogen and water was considered in the hydrolysis step.

4.2.1 Reduction Step

The solid and fluid temperature distributions along the x-axis with and without the reduction reaction are compared in figure 4. As expected, both temperatures decrease when accounting for the reduction reaction. However, the impact of the reduction reaction on the temperatures is weak (maximum temperature difference below 50 K) although the reaction is

highly endothermic. This is due to the fact that the energy required by the chemical reaction is lower than the energy losses by radiation and convection.

4.2.2 Hydrolysis Step

The required reaction temperature in the hydrolysis step is lower than the temperature of the reduction reaction to avoid competition between reactions. It is thus necessary to reach temperatures around 1200 K. In order to adjust the temperature of the receiver, the influence of the incident solar power on the temperature of the solid is studied (Fig. 5). As a result, the optimal solar power to conduct the hydrolysis step at the desired temperature of 1200 K is in the range 500-700 W.
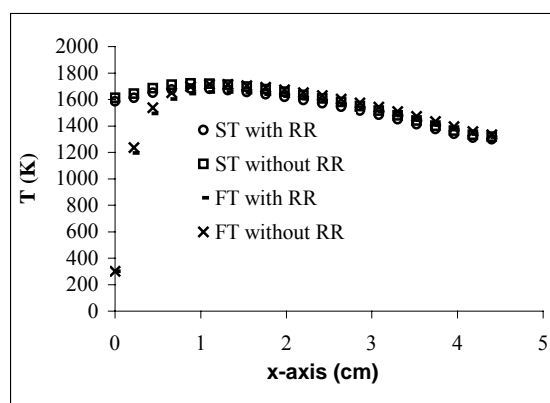

Fig. 4. Fluid (FT) and solid (ST) temperature distributions with and without the reduction reaction (RR)
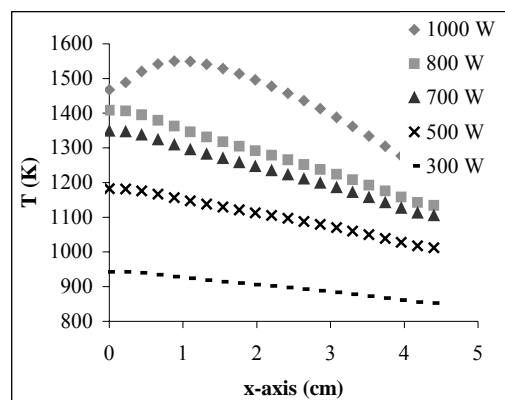
Fig. 5. Temperature of the solid along the x-axis for several incident solar powers

5. Conclusions

A 2D - computational fluid dynamic model was developed to predict the reactor performances at different operational conditions. Simulations were first carried out for a non-reactive flow and then chemical reactions were implemented. For a non-reactive flow, the influence of different inert gas flow rates for either a uniform or a Gaussian incident solar flux distribution was analyzed. The results showed that gas flow rates lower than 20 L/min were necessary to reach high enough temperatures required by the thermal-reduction reaction (above 1400 K). Another parametric study was related to the length of the porous ceramic receiver. Numerical simulations revealed that the receiver length does not affect significantly the temperature distribution of the solid phase. Likewise, changing the medium porosity leads to negligible change in the foam temperature distribution.

Regarding simulations accounting for a reactive flow, the impact of the endothermic reduction reaction on temperature distributions was first analyzed, and a temperature decrease reaching about 50 K was evidenced due to the endothermic reaction. In the case of the hydrolysis reaction producing hydrogen, a parametric study regarding the incident solar power was performed to adjust the reaction temperature. As a result, an incident solar power of 500-700 W is necessary to reach reaction temperatures of about 1200 K in the porous foam receiver.

On the basis of these numerical simulations, the solar reactor designed to carry out the two chemical steps of the process in a semi-continuous mode will be developed for the production of hydrogen.

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