CAVITY RECEIVER CONCEPTION FOR CHEMICAL REACTORS USING SOLAR ENERGY

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Abstract. *The purpose of this work is to study a cavity receptor for chemical and metallurgical reactions. Solar energy is concentrated in such device, which absorbs thermal radiation, transforming it in thermal energy, used to activate chemical reactions. Therefore, the cavity receiver can be used to convert solar energy into chemical energy. The main chemical product is hydrogen gas. The first step of this work was an assessment of metal/oxides pairs studied in literature, which can be used to activate thermochemical cycles for hydrogen production. These pairs were compared based in four parameters essentials to cavity receptor design: reaction temperature, physical state of the reactants and products, material resistance to several cycles; hydrolysis reaction rate and other aspects. The chosen pair, rated as the higher average in all parameters, was the pair tungsten and tungsten trioxide (W/WO$_3$). A standard reactor was defined, which was studied regarding cavity reactor performance. By such analysis, it was possible to determine the main design parameters, which are: cavity window aperture, window transmittance, and the cavity geometric dimensions. Moreover, an efficiency assessment was described. The results allowed establishing a mathematical model in which solar energy can be converted in useful energy for chemical processes, inside a cavity receptor. Given a profile of solar energy concentration, it was calculated absorption and energy lost efficiencies, related to a solar concentration field and radiation available. This method can be used in tandem with available methodologies and data of solar energy predictions, allowing estimations of hydrogen production via solar powered thermochemical cycles.*

Keywords: *solar fuels, cavity receiver, hydrogen gas*

1. NOMENCLATURE

E_a - aperture emissive power
E_{co} - aperture black body emissive power
J_a - aperture radiosity
J_c - cavity radiosity
E_c - cavity emissive power
A_a - cavity aperture area
A_c - cavity internal surface area
$F_{a\text{-}c}$ - cavity aperture to surface shape factor
ϵ_c - cavity surface emissivity
T_{cav} maximum cavity equilibrium temperature
Q_{ap} - inner solar energy
α_{ef} - cavity effective absorptivity
σ - Stefan-Boltzmann constant
T_{amb} - ambient temperature
μ - energy utilization ratio
q_i – amount of heat of each type of flow
C - concentration ratio
I - normal direct solar irradiation
M - metallic element
MO_x - metallic oxide
Q_{abs} - energy used for chemical reaction
Q_{cond} - energy loss by conduction
Q_{gas} - energy loss by inert gas flow
Q_{rad} – energy loss by radiation
η_{abs} - cavity absorption efficiency
η_{loss} - cavity conduction and inert gas flow efficiency
A_{ap} - cavity aperture area
η_{global} - global efficiency

2. INTRODUCTION

The debate regarding renewable energies is constant. Among all the technologies, solar energy is definitely the one of the most promising. The industry of this sector have been developing mainly because of the acceptance of solar water heating and photovoltaics. There are other applications that are less known, but not less explored, such as biomass gasification, electric generation by thermal power cycles, among many others.

However, solar energy have one major problem associated with its intermittence. Often, the timing that thermal or electrical energy is used is not the same as the energy is produced. Such case can occur by day cycle reasons or cloud interference over the solar collector field. In this way, some form of energy storage is necessary to make solar energy more useful.

Many researches have been carried out to develop technology capable to transform solar energy into chemical fuel. There are several technologies based on chemical cycles, some of them already in use driven by other energy sources than solar. Among all possibilities, there is a class of chemical cycles which have been studied in many parts of the world, with interesting results. It is based on thermochemical cycles of metal oxidation and reduction.

The principle consist in initiate a high temperature endothermic reaction through concentrated solar energy. This is achievable by building a proper reactor. It must be a reliable mechanical device which support heat transfer and chemical reaction at high temperatures between 1200 to 2500 K, depending on the process.

The best device achievable so far is a cavity type apparatus, which behaves as a black body. The characteristic shape can trap and hold the inner solar radiation. It effect allows the interior chamber to reach temperatures high enough to activate the metal reduction. The reduced material can follow the process and generate hydrogen gas or other chemical fuels. Fuels produced by such technology have been named *solar fuels*.

3. CAVITY

A cavity is defined as a closed surface, with a small opening, where concentrated solar radiation can enter through and it behaves as a black body. By multiple radiation reflection and absorption inside, there occurs an enhanced radiation absortivity compared to a similar surface area of absorption corresponding to the cavity opening area. Following this concept, it is possible to build cavity devices for solar thermal energy absorption. This kind of device is called cavity receptor.

The cavity effective absortivity, without transparent cover, is function of the internal surfaces absortivity and the ratio of aperture area to the internal surface area. Fig. 1 shows the equivalent electrical circuit of a cavity receptor. Eq. (1) shows the cavity effective absortivity.

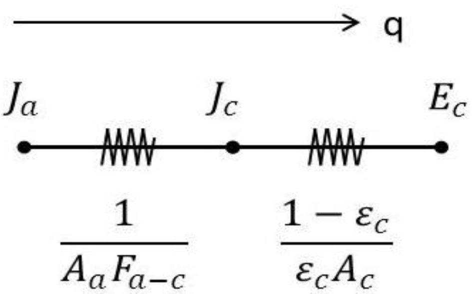

Figure 1. *Equivalent electrical circuit for a cavity receiver.*

By solving the circuit from Fig. 1, one can define the effective cavity absortivity, as given by Eq. (1).

$$\alpha_{ef} = \frac{1}{1 + \frac{A_a}{A_c} \cdot \left(\frac{1-\alpha_c}{\alpha_c} \right)} \tag{1}$$

Inside an adiabatic cavity, as all incident energy flux is equal to the energy flux that exits it, leading the cavity temperature to a high level. The cavity equilibrium adiabatic temperature is given by Eq. (2).

$$T_{cav} = \sqrt[4]{\frac{Q_{ap}}{\alpha_{ef} . \sigma} + T_{amb}^4} \tag{2}$$

The equilibrium cavity temperature is predicted considering that part of incident heat is lost by conduction and convection. Some energy flux is used to activate and maintain the chemical reactions. According to Eq. (3), μ is defined as the fraction of the income energy flux that is used for the chemical reactions. Therefore, the cavity temperature becomes Eq. (4).

$$\mu = 1 - \left(\frac{\sum_{i=1}^{n} q_i}{Q_{ap}} \right) \tag{3}$$

$$T_{cav} = \sqrt[4]{\mu . \frac{C.I}{\alpha_{ef} . \sigma} + T_{amb}^4} \tag{4}$$

When all heat fluxes losses are zero (μ=1), the cavity is adiabatic and there are no reactions, then Eq. (4) becomes Eq. (2) and determines the maximum equilibrium temperature. When the sum of all heat fluxes is equal to the incident energy flux, μ is zero and, therefore, the equilibrium temperature is the same as the ambient temperature.

Figure 2 shows cavity temperature relation to solar concentration, for some μ values. The curves indicate values from which one can start the design of a cavity receiver, using concentration information available.

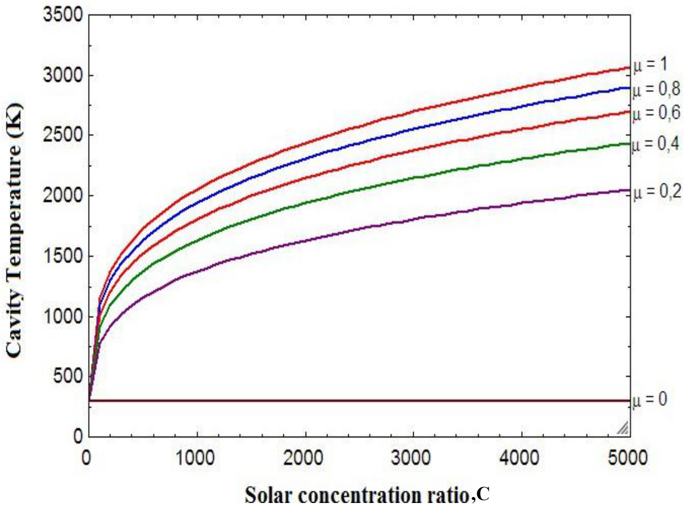

Figure 2. *Equilibrium temperature as a function of solar concentration, for some values of energy utilization.*

4. THERMOCHEMICAL CYCLE

Thermochemical cycle studies were based on reduction and oxidation pairs. The first reaction is the endothermic oxide reduction, resulting in metallic material and oxygen. The second step combines the resulting metal with water (hydrolysis) producing metal oxide and hydrogen. That oxide returns to the first step. Eq. (5) and (6) represent the cycle.

$$MO_X \rightarrow MO_{X-Y} + 0{,}5yO_2 \tag{5}$$

$$MO_{X-Y} + yH_2O \rightarrow MO_X + yH_2 \tag{6}$$

This cycle was originally proposed by Nakamura (1977), using the reduction pair Fe_3O_4/FeO. Many other pairs were developed, and the most developed one is the pair ZnO/Zn (XIAO et al, 2012). As part of this work, an alternative pair was determined considering the set of criteria shown in Tab.1. The first criteria is the *reaction temperature*. It is the most important because it determines all dimensions and characteristics of the reaction itself. The other criteria are also important regarding material usage, and have consequences on the process sequence. They are *reactant and products physical state*, *material recycling* and *other relevant aspects*. The results determined that the pair W/WO_3 comply with the criteria regarding utilization in new concept of cavity receiver.

Table 1 – *Evaluation criteria for reduction-oxidation pairs.*

Redox Pair	Parameter (a)	Parameter (b)	Parameter (c)	Parameter (d)
GeO_2-GeO	1673 – 2073 K	Solid	Limited cycles	Formation of passive layer
ZnO-Zn	2300 – 2433 K	Gas	Unlimited recycling	Formation of passive layer
SnO_2-SnO	1900 – 2328 K	Solid	Limited cycles	Low exothermic heat to feed hydrolysis
Fe_3O_4-FeO	2500 – 3103 K	Solid	Limited cycles	Necessary milling
CeO_2-Ce_2O_3	1677 – 2709 K	Liquid	Limited cycles	Necessary milling
W-WO_3	1173 – 1643 K	Solid	Limited cycles	Greater kinetics. Tungsten volatilization.
Best choice	W-WO_3	GeO_2-GeO SnO_2-SnO Fe_3O_4-FeO W-WO_3	ZnO-Zn	

(a) Reaction temperature. (b) Reactants and products physical state. (c) Material recycling. (d) Other relevant aspect.

Milshtein et al (2013) introduced a new thermochemical cycle based in the pair W/WO_3 aiming production of fuel. The cycle's reactions are those shown on Eq. (7) and (8).

$$2WO_{3(s)} \rightarrow 2W_{(s)} + 3O_{2(g)} \tag{7}$$

$$W_{(s)} + 3H_2O_{(g)} \rightarrow WO_{3(s)} + 3H_{2(g)} \tag{8}$$

If the conditions allow temperatures under WO_3 melting point, the cycles can be physically assembled as a pebble bed configuration. This can be advantageous because the material can be always in solid state. The reactions kinetics are improved on this porous configuration, comparing to liquid form. It is necessary to maintain oxygen partial pressure under the critical level of solid tungsten formation, in order to reduce the oxide in metal material. Therefore, the process must inject inert gas into the control volume to achieve right levels of partial pressure. Figure 3 shows the studied process, with special attention to the solar reactor, which was designed as cavity receiver.

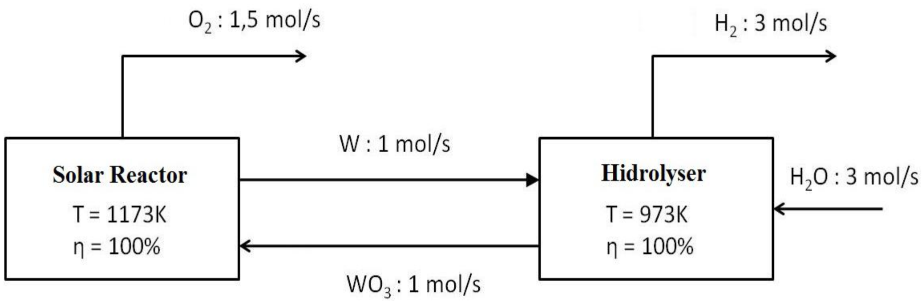

Figure 3. *Thermochemical process.*

5. REACTOR DESIGN

The reactor is a cylindrical body, in which there is a cylindrical cavity. There is also insulation material surrounding the cavity. All energetic relation happen inside the reactor's cavity. Hence, in order to initiate the design, an energy balance was considered in steady state within the control volume, as shown in Fig. 4. The energy flux that enters control volume through the aperture is driven by solar concentration apparatus. This radiation is equivalent to the absorption of a surface with the same perpendicular area as the aperture, with absortivity equal to the effective cavity absortivity, as defined in Eq. (1).

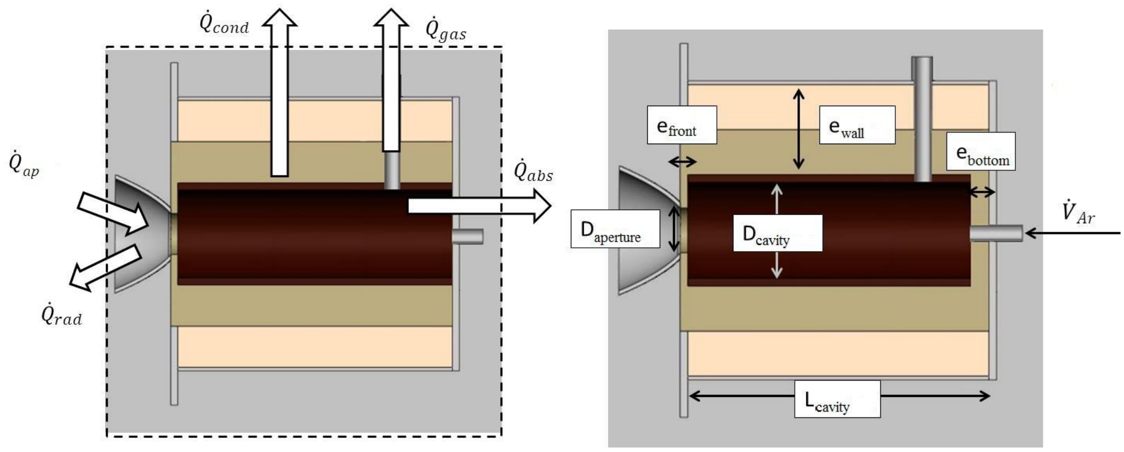

Figure 4. (a) *Control volume and energy balance*. (b) *Cavity receiver geometric parameters*.

Once determined the geometry, the design process evaluated the variable impacts on the energy system balance. The initial parameters and considerations can be found in Tab. 2 and Fig. 4. The methodology used was varying a parameter from its initial value observing the energy output. To be possible to compare different parameters, the variation ranged from -50% to 100% increase.

Table 2. *Initial parameters and assumptions*.

Parameter	**Value**	**Parameter**	**Value**
Equilibrium temperature	T_{high} = 1173 K	Reduced tungsten production	$\dot{m}_w$= 1,838 g/s
Reaction efficiency	$\eta_{reaction}$= 1	Cavity surface absortivity	$\alpha_{surface}$ = 0,73
Inert gas flow rate (Argonium)	V_{ar}= 20 NL/min	Aperture diameter	$D_{aperture}$ = 0,1 m
Window transmittance (visible)	$\tau_{visible}$= 0,95	Cavity cylindrical diameter	D_{cavity} = 0,3 m
Window transmittance (infrared)	$\tau_{infrared}$= 0,3	Cavity cylindrical long	L_{cavity} = 0,5 m
External surface temperature	T_{sup} = 303 K	Insulation wall thickness	e_{wall} = 0,3 m
Insulation	$k_{insulation}$ = 0,05 W/m*C	Insulation wall thickness (bottom)	e_{bottom} = 0,3 m
Solar irradiance	1000 W/m^2	Insulation wall thickness (front)	e_{front} = 0,1 m

Comparing the results, the aperture diameter is the most important aspect, as shown in Fig. 5. By increasing it, there is more useful energy flux loss. It is more relevant than the other parameters altogether. That result is important because the aperture diameter do not depend only the designer choice, but also the concentration capacity of the heliostat field. If the heliostats cannot reflect radiation on a plane in which the reflection area is smaller than the aperture, it is useless to restrict the aperture diameter to minimize energy flux loss. The second most important aspect is the window transmittance. Its interference is also notable relating to others parameters studied. In fact, the results show that in cavity receivers most energy flux is lost due to reirradiation.

5. CAVITY RECEPTOR EFFICIENCY

From Eq. (5) it is possible to obtain cavity temperature variation in function of solar radiation concentration, shown in Fig. 6. It is also visible the value for minimal concentration of 133 to obtain the maximum temperature required by reaction W/WO_3, which value is 1173 K. That concentration is enough to keep adiabatic equilibrium temperature at 1173 K. However, in an actual equipment, there should be losses and also should be energy used to drive the chemical reaction. Hence, regarding the real operation, solar concentration must be higher than 133.

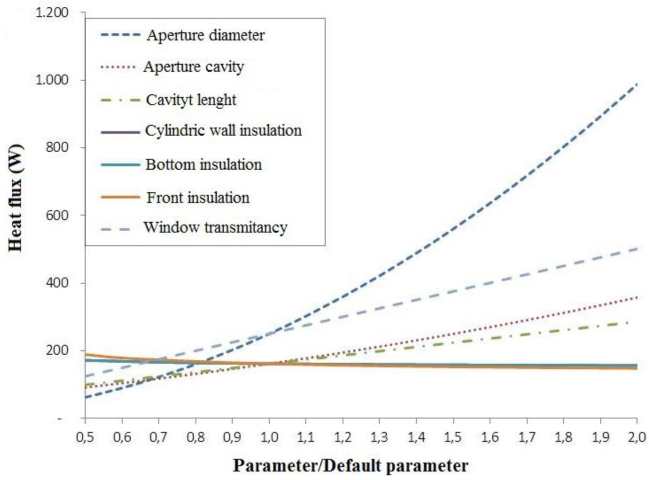

Figure 5. *Energy flux loss evaluation related to cavity receiver parameters study.*

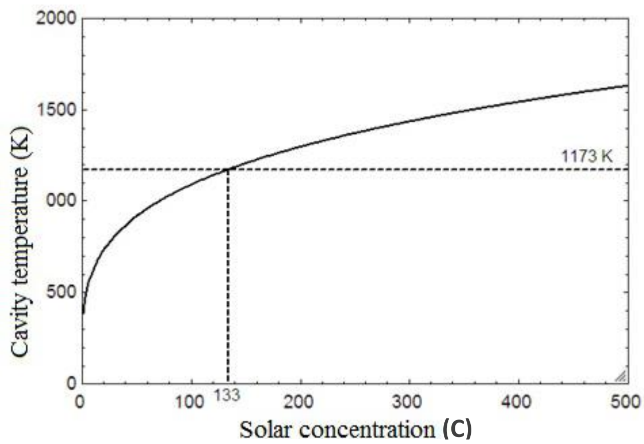

Figure 6. *Temperature variation as a function of solar concentration.*

Regarding to energy flux loss by wall conduction and gas flow, Fig 7 shows the behavior of receptor efficiency. For a fixed temperature at *T*= 1173K the efficiency is 0,943.

It was also considered the effect of cavity absorption, which is how much energy flux is useful after radiation losses. Figure 8 shows the overall efficiency, that is the sum of all kinds of efficiency effects, in relation to cavity temperature.

High temperatures can only be achieved by higher concentrations and higher concentrations result in less efficiency. This is particularly important because it is not the best solution to increase the cavity temperature in order to improve reaction kinetics. Instead, it is more important do increase the concentration ratio.

Figure 8 also shows the base reaction temperature for the cycle analysis. It can be seen that there is an increase on cavity efficiency to deliver energy flux to the reaction when there is an increase in concentration values from 250 to 2000. By this point, efficiency increase is not significant, which justify limit concentration elevation.

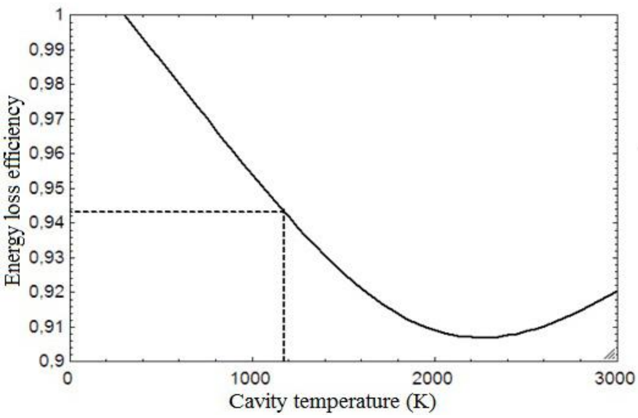

Figure 7. *Cavity losses efficiency as a function of cavity temperature*.

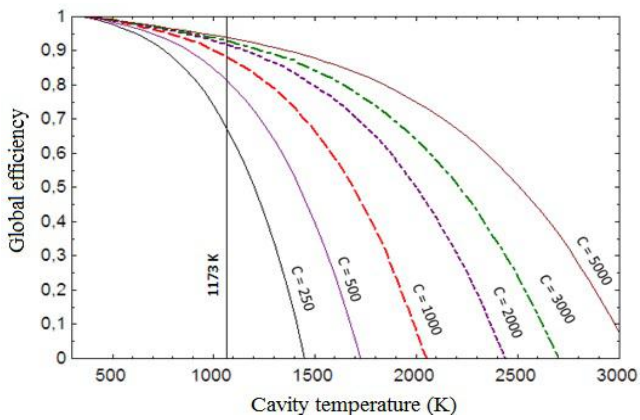

Figure 8. *Global cavity efficiency as a function of cavity temperature, for selected concentration values.*

6. USEFUL ENERGY IN CAVITY RECEIVER

Hereafter it will be described a methodology. It is suggested for cavity receptor design, at dimension phase. It takes into account the solar availability and a given available concentration distribution. Figure 9 shows an hypothetical distribution used on this study in order to determine a cavity reactor. The distribution is supposed to be symmetrical on focal plane area, differing from real profiles. On the *x* axis, there is the radial distance from the center. The *y* axis is the percentage of total solar power on that specific distance from center.

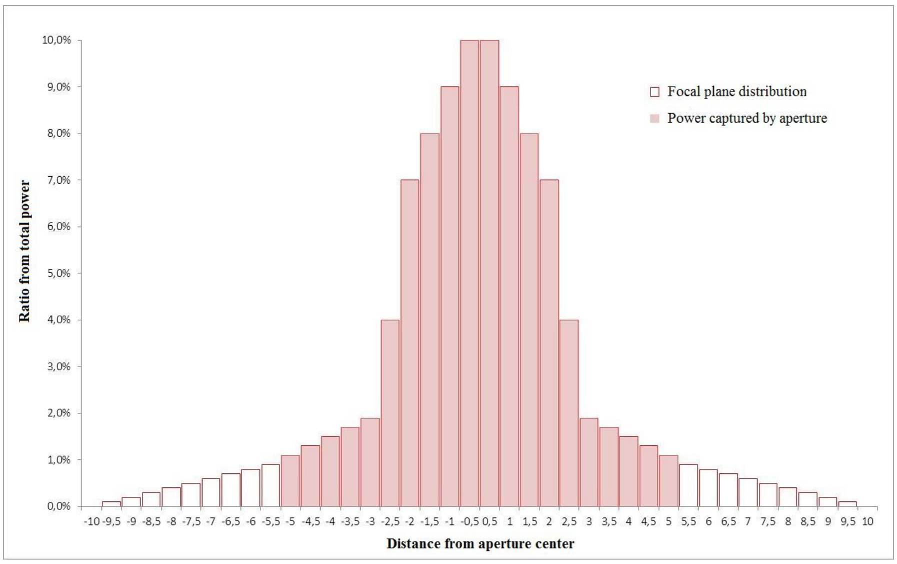

Figure 9. *Solar power distribution on focal plane of studied concentration system*.

The aperture radius of this receptor is 5 cm, which means that not all solar radiation is absorbed by the cavity. In Fig. 9, columns between -5 and 5 cm indicate the portion of radiation intercepted by the aperture area. The sum of each portion corresponds to the total energy flux available to the receptor for utilization.

The energy balance (Eq. 4) gives the solar radiation necessary to maintain operational thermocycle in steady state. That energy flux is equal to the reaction enthalpy and losses. Therefore, the useful energy in cavity reactor is the energy reflected by the heliostat field, concentrated on cavity aperture, and discounted all efficiencies of the subsystems. This relation is given by Eq. 9.

$$\dot{Q}_{ut} = \eta_{abs} . \eta_{abs} . \dot{Q}_{ap} \qquad (9)$$

The absorption efficiency is defined in Eq. 11. It is the ratio between radiation absorbed on the aperture and available energy flux on cavity, discounted emitted radiation by aperture.

The global efficiency is the product of all defined efficiencies. In this study, considering the concentration system of Fig. 9, the global efficiency relates to the reflectors area as can be seen in Fig. 10. Below 10 m^2, the cavity receptor efficiency's variation is more acute than above area values. It is important because reflector field is most part of capital expenditure in thermal solar projects.

The previous analysis concluded that aperture cavity is the most important geometric parameter. Thus, Fig. 11 summarizes the study of receptor efficiency behavior related to aperture variation. Each curve represents different reflector field area. The influence of aperture on reflector area decreases for smaller aperture area. This implicates less cost with reflector installation.

In addition, the efficiency is greater for smaller apertures. Even if less energy flux is captured by the cavity, less energy losses compensate it. However, it should be considered that, in this study, the power distribution of Fig. 11 concentrates 91% of total power in an area less or equal to 10 cm diameter. In this way, it is necessary to consider solar energy concentration potential of the reflector field before conclude if a receptor is adequate to a specific process.

Another important aspect to evaluate is the intermittent nature of solar energy. Until this point, the study detailed the cavity receiver itself and its dependency on concentration. However, solar availability is determinant for any device, which transforms solar radiation on useful energy. It is also important to remember that cavity receivers can only utilize direct radiation from the sun.

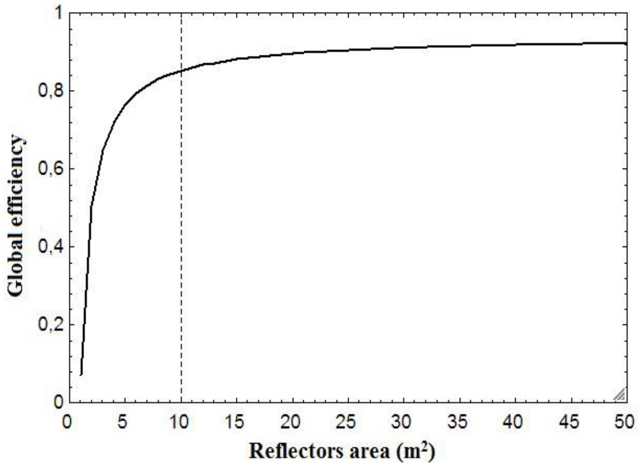

Figure 10. *Global cavity efficiency in function of reflectors area.*

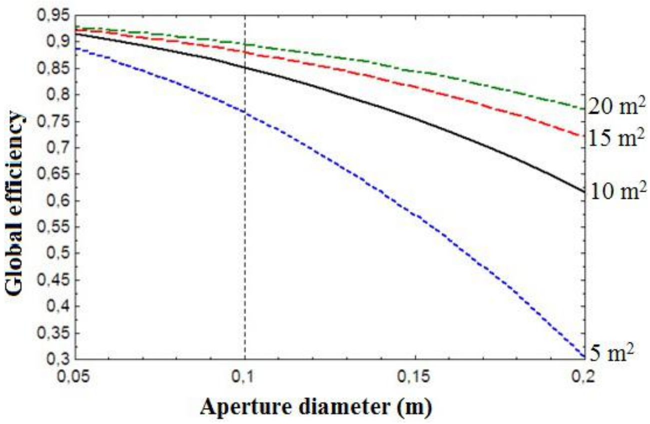

Figure 11. *Global cavity efficiency in function of aperture diameter, for selected reflectors area.*

Figure 12 shows the efficiency behavior related to the aperture diameter, considering some values of direct radiation. The concentration area of 10 m^2 was chosen for this case. Smaller values of available radiation causes larger efficiency drop. At a low level of direct radiation, as the case of 200 and 300 W/m^2, the cavity receiver cannot deliver useful energy flux to the reaction, considering diameters larger than 15 and 19 cm, respectively.

It is also important do evaluate the efficiency as a function of available solar radiation, considering the reflector area. It can be seen in Fig. 13, which considered a 10 cm aperture. Enhancing the value of reflector area contributes to higher efficiency, but its proportional increase is smaller as larger the area becomes. In other words, for 400 W/m^2, 10 m^2 area reflectors have efficiencies higher that 5 m^2 area reflectors (70% and 50% respectively). However, increasing the area from 10 to 15 m^2, despite the same 5 m^2 increase, results in only 8% larger efficiency, from 70% to 78% approximately.

Available solar radiation can be found in solar information database. The previous methodology can be used together with the utilizability method (Duffie and Beckman, 2006) using available solar radiation found on solar information database. It consists in calculating the amount of available solar energy above a critical level, at an one hour mean interval. This approximation determines the amount of available energy a cavity receptor can supply to the process, which determines a daily production profile.

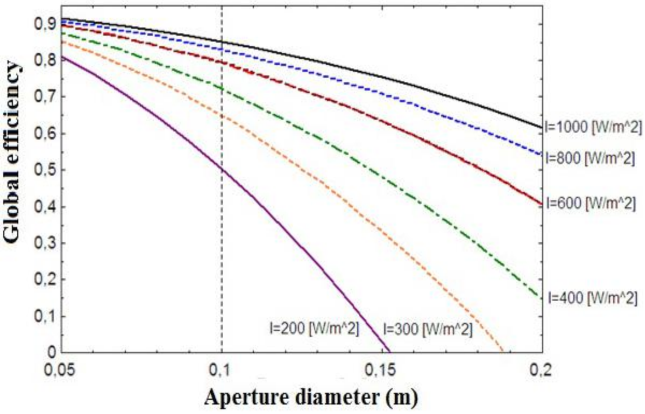

Figure 12. *Global cavity efficiency as a function of aperture diameter, for selected direct radiation values.*

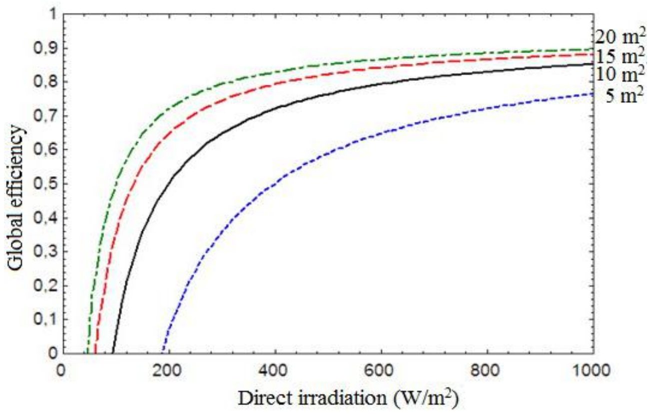

Figure 13. *Global cavity efficiency in function of direct radiation, for selected reflectors area.*

6. ACKNOLEDGMENTS

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