

HYDROGEN PRODUCED BY SOLAR ENERGY AND THEIR USE AS CLEAN FUEL FOR POWER GENERATION IN A COMBINED CYCLE POWER PLANT

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ABSTRACT

The solar energy is one of the most promising energy sources expected for the future, due at their huge potential and the wide availability around the world. However, nowadays this important source of energy is not being harnessed or even addressed in their full potential. According to the last statements, it is important to develop solar energy conversion systems of high efficiency, as well as spreading its use in other forms besides the traditional systems of electric power generation or heating systems. For this reason, in this paper, it is explored the production of hydrogen through solar energy utilization, and the later electrical energy production by burning the produced hydrogen in a combined cycle power plant. The process was modelled for 3 MWe of electricity generation, and using the organic Rankine cycle. The main process for producing hydrogen from water using solar energy is based on a two steps redox thermochemical cycle, which has a theoretical conversion efficiencies of 54% at 1600 K. It is expected that this paper could contributed to the development of ways to enable a better integration of the solar energy with the current electricity generation technologies, as well as to incentive the use of the hydrogen as a clean fuel.

Keywords: solar fuel, hydrogen production, ORC, combined cycle, renewable power generation

NOMENCLATURE

C= Water concentration at the inlet, moles of gas/m³.

F = molar production rate per gram of redox material, moles/minute.

K= Temperature-dependent reaction rate constant in oxidation stage, m³/moles/min.

Q= Heat Flux kW.

t= time (s).

Greek symbols

Ψ = Instantaneous concentration of adsorbed oxygen, molesO₂ /g_{redox}.

Φ = Instantaneous capacity of water splitting of the redox material, molesH₂ /g_{redox}.

η = Efficiency.

Subscripts

Att = Attenuation.

Cosine = Cosine.

Reflec = Reflectance.

Shadowing = Shadowing.

tr = Thermal Reduction.

ws = Water splitting.

INTRODUCTION

With the imminent changes in the world

weather and environment, mainly associated with the human activities and the fossil fuels consumption. In an addition to this phenomena, one can observe an increase in energy consumption related with the grow up of the human population and the higher energetic demand in the developing countries. This scenario is leading to the rise of the generation of global warming gases and a higher dependence to the fossil fuels.

Due the last statement it is important to achieve the optimal use of the renewable energy, looking for minimize the cost and effort to have its integration with the current infrastructure, and offering to the society several energetic carriers such as fuels, heat, electricity, etc.

One of the more promissory renewable resources is the solar energy, due the wide accessibility around the world and the infinity availability in human time lapse. Two different ways for taking advantage of the solar energy have been traditionally developed; the first one is transform the solar energy into heat, using the radiation heat transfer as the conversion path. The second one is the photovoltaic cell, which converts the incident solar radiation directly in electric energy using the photoelectric phenomena.

According with the last statement it would be extremely useful to have an energy source that it easily transformed into another. In this way, the best option to satisfy these constrains is use the thermal solar energy, because with different processes, it is

possible obtain different energy carriers (e.g.). Using heat with heat machines one can obtain mechanical energy, and with the arrangement of electrical generator it is obtained electrical energy. In addition, it is possible the direct electrical energy generation using the thermoelectric effect. Beyond the last exposed technologies, is possible achieve a more valuable resource, as the concept of solar fuels, which is the use of the solar energy to convert a raw material (mainly water and/or carbon dioxide) into a fuel (pure hydrogen, or a syngas) being the hydrogen production the main focus. Many articles have been published about this topic, one of the principles is the paper published by Kodama (2003) and Martin *et al.* (2006).

HYDROGEN PRODUCTION PATHS BY SOLAR ENERGY

Several paths for solar hydrogen production have been developed; four different mechanism was used to produce hydrogen, as follows:

- Photoelectric effect.
- Photovoltaic panel with electrolysis.
- Heat with thermochemical cycles.
- Heat with thermal dissociation of water.

In the following it is shown the main paths for the hydrogen production, using the water as raw material, and using different technologies to achieve the solar energy such as, photovoltaic panel, photoelectrolysis cell and solar collectors.

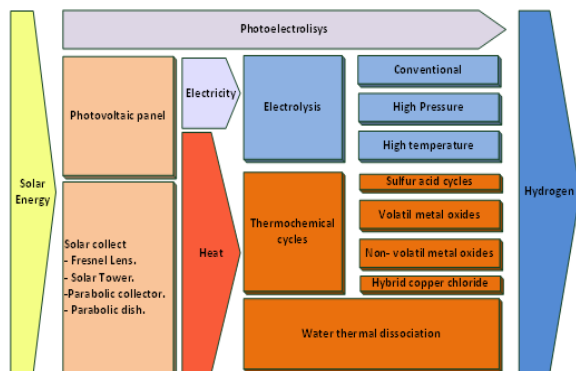


Figure 1. Mains paths for solar hydrogen production using water as raw material.

According with the research of Pregger *et al.* (2009), the more efficient process for the hydrogen production using solar energy is the thermochemical cycles using metal oxides as shown in the figure 2. Therefore, the process that will be used for the hydrogen production in this work is the metal oxide thermochemical cycle.

Many investigations have been done in this topic, but the more advanced is the project developed by Hydrosol, which test, in 2008, a pilot plant of 100

kW_{th} for hydrogen production Roeb *et al.* (2011); the modelling of the use of SIC monolith reactors for hydrogen production Agrafiotis *et al.* (2007) and the characterization of different material and synthesis of the materials Martin *et al.* (2006).

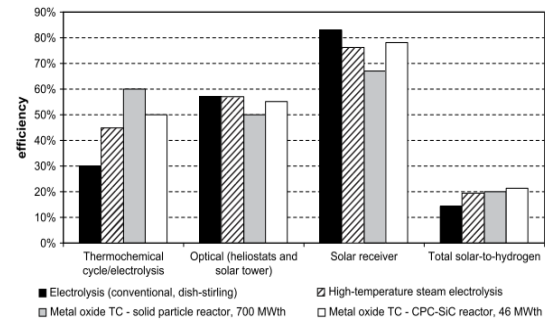


Figure 2. Efficiencies of solar hydrogen production under different process (Pregger *et al.*, 2009).

The metal oxides thermochemical cycle is composed by just two stages. The first stage for the oxygen release, using an inert gas or vacuum for remove the oxygen from the metal oxide matrix, generally this stage occurs at the higher temperature and is endothermic. As result of this reaction, the metal oxide is free of oxygen or with lower valence level, and ready for the oxidation and initiate the hydrogen production stage. In this stage, steam and nitrogen enter in the matrix and the process begins. The metal oxide matrix is oxidized by the steam, allowing the hydrogen production (liberation).

The integration of the hydrogen with the current technologies is possible in different ways such as, power generation, hydrogen supply for different process and carbon recycling. The objective of this paper is to show the use of the hydrogen for power generation in a combined cycle for a power generation of 3 MWe, using as bottoming cycle the organic Rankine cycle, and as top cycle the Bryton cycle. Other remarkable concept beyond of the scope of this article is the possibility of using the hydrogen produced to recycle the carbon dioxide taken from another process and convert both of them, by means of a methanation reaction, into synthetic methane. Which can be supplied for the gas natural network or directly used as energy storage method, these topics have been deeply researched by Sterner (2009) and Giglio *et al.* (2015).

It will be considered two scenarios for the hydrogen burning in the gas turbines, this according the technical limitations of burning the hydrogen in the actual equipment. The first scenario will be the co-firing of the hydrogen with methane by 30% volume described by Wind, Güthe and Syed (2014). And one for long term scenario, according the research done by Siemens Bradley and Marra (2014), of co-firing up to 70% hydrogen by volume.

This paper will be developed in various sections, the first one related with the important

parameters for the heliostat field and their energetic behaviour, the second section related with the hydrogen production in a solar reactor, and the third section related with the power generation.

SOLAR ENERGY

For the solar thermal only two solar thermal technologies are capable of reaching the high temperatures (above 1200 K) required for the hydrogen production via thermochemical cycles s: which are parabolic dish (reach temperatures of 1500 °C Malagueta *et al.*, (2014)) and solar tower (reach temperatures of 2000°C Kalogirou (2004)). Due to the high amount of energy required and the solar reactor layout, it was considered the solar tower technology. As reference was taken the following values as the average year efficiency for a heliostat solar field.

Table 1. Annual average efficiencies for a solar heliostat field, adapted from Stine and Harrigan, (1985).

Solar field efficiencies - Annual average			
Cosine loss	77%	Reflectance	90%
Shadowing	94%	Attenuation	94%
Total field efficiency			61%

$$\eta_f = \eta_{\text{Cosine}} \eta_{\text{shadow}} \eta_{\text{reflec}} \eta_{\text{Att}}, \quad (1)$$

With the values presented on Table 1 it is possible to have a general view of the different losses of a heliostat field, allowing one to calculate the total field efficiency, according to Eq. (1).

Beyond the use of the solar collectors as energy concentrator, in the Hydrosol project the heliostat was used also as a way for controlling the process. Due to the different energy requirements during the reduction and oxidation stages, the energy input for the reactor is controlled by the number of heliostat focused on it. In this way, the better arrangement for a quasi-continuous hydrogen production is synchronizing two reactors, in such form that while the first is in the reduction stage the second one is in oxidation stage, switching the stages when the process finish.

SOLAR HYDROGEN REACTOR.

For the reactor model it was used the experimental information about the behavior of thermal reduction and oxidation process based in the NiFe₂O₄ metal oxide Agrafioti *et al.*, (2009), supported in a SIC matrix. The equation was developed considering the experimental behavior of the hydrogen production and the release of oxygen, also taking in account the degradation of the matrix

across different cycle numbers.

$$F_{H_2} = k_{ws} \phi C_{H_2O} e^{-k_{ws} C_{H_2O} t}, \quad (2)$$

$$F_{O_2} = k_{tr} \psi e^{-k_{tr} \psi t}, \quad (3)$$

Using equations (2) and (3) it is possible to describe the production of hydrogen and oxygen, and to dimension the required reactors for the hydrogen production. For the develop of this paper is required the design of solar reactor composed by matrix based in NiFe₂O₄ metal oxide, this due the necessity to know the behavior of the solar reactor under different solar fluxes and this implication in the hydrogen production. Therefore will be used as reference information, the reactors developed for the Hydrosol project, since this is the first plant in the world for metal oxides thermochemical cycles Roeb *et al.*, (2009). The information took from the reference, is the matrix material properties and their geometry. For this paper, it was considered an arrangement of nine matrix materials in SIC with 146mmX146mmX60mm, being the same arrangement used in the Hydrosol 100 kWth plant Roeb *et al.*, (2011).

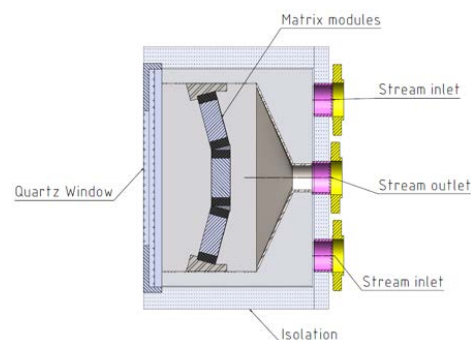


Figure 3. Predesign of solar reactor.

One of the most important parameters during the oxidation and reduction cycles is keep the temperature for each stage, for this reason and having in consideration the complexity of the phenomena and the diverse heat transfer forms involved in the reactor (conduction, convection and radiation). Was simulated the thermal response of the reactor, with a 3D CFD code floworks, being this code part of the CAD suite Solidworks. The main objective of this simulation is find the working temperature for each stage in the matrix, under different solar powers, as boundary conditions was used the incoming solar flux and the mass flow inside the reactor, considering the different temperatures and streams for each cycle stage. Was used k-epsilon as turbulence model.

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In the figure 4, it is represented the simulation result for the temperature distribution inside the reactor for a solar power of 40 kW, showing the average temperature of the matrix and the inlet temperature. For understand the behaviour of the reactor under different values of solar power and the response of the temperatures under this change, it was made two plots showing the variation of the temperature related with the sun power for the two stages of the cycle, oxidation and reduction described in the figure 5. Where the solar power consumption are concordant with the field behaviour tested by the 100 kWth solar hydrogen production plant Roeb et al, (2011).

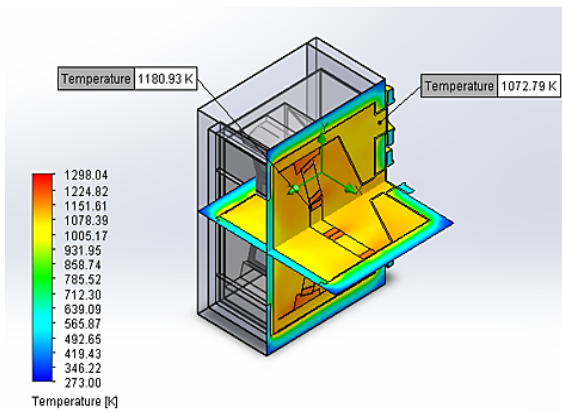


Figure 4. Temperature distribution for a solar power of 40 kW in oxidation stage.

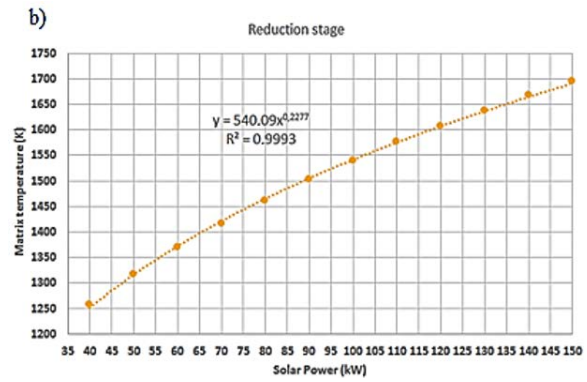
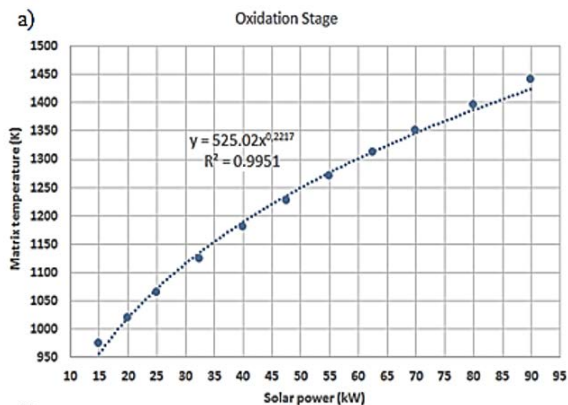


Figure 5. Matrix Temperature vs Solar Power, a) Oxidation stage, b) Reduction stage.

Knowing the solar energy input and the hydrogen yield described by the equations (2) and (3), it is possible to calculate the behavior of the cycle as showed in the figure 6. It is interesting to notice the deviation of the hydrogen production between the first and the second oxygen cycle, due the degradation of the matrix and the irreversibility in the process.

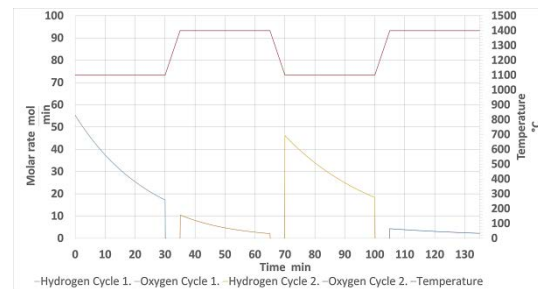


Figure 6. Hydrogen and oxygen production.

Therefore, the global mass of hydrogen production per cycle, i.e., the hydrogen production yield, is showed on Figure 6. The temperature of the reduction stage is fixed, because at higher temperatures of 1400 K the nickel enclose starts to degrade. For this reason, the plot is in function only of the oxidation stage temperature.

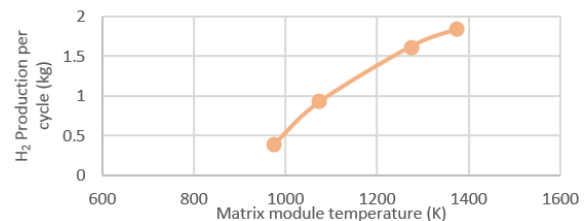


Figure 6. Mass production in function of the oxidation stage temperature.

$$\eta_{reator} = \frac{m_{H_2} LHV_{H_2}}{\dot{Q}_{Oxidation} t_{stage} + \dot{Q}_{reduction} t_{stage}}, \quad (4)$$

$$\eta_{STH2} = \frac{m_{H2} LHV_{H2}}{\dot{Q}_{Oxidation} t_{stage} + \dot{Q}_{reduction} t_{stage}} \eta_f, \quad (5)$$

The efficiency of the solar reactor and the whole process was described in the Eq. (4) and Eq. (5), relating the solar energy input and the energy stored in the hydrogen and the efficiency of the solar field.

The efficiencies obtained for the different reduction temperatures is shown in the next figure, describing the efficiencies for the solar reactor and for the whole process.

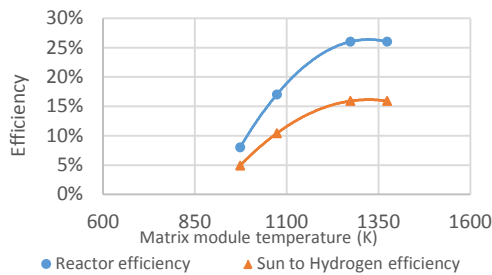


Figure 7. Efficiencies of the processes.

POWER GENERATION

To achieve a good thermal efficiency at lower power, it was used a combined cycle composed of a gas turbine and an Organic Rankine Cycle. To have a common frame with the currents technologies it was chosen the best gas turbines in terms of efficiency from the Gas turbine World 2010 GTW Handbook Farmer (2010), listed below.

Table 2. Commercial gas turbines bellow of 3 MW adapted from Farmer (2010).

Brand	Pratt & Whitney	OPRA Turbine	ZM Turbine	Mitsui Engineering
Model	ST18A	OP16-3A	UGT 2500	SB15
Power kW	1961	1910	2670	2720
Efficiency	30.4%	26.9%	26.7%	25.6%
Pressure ratio	14	6,7	12	10
Mass flow kg/sec	8	8.7	16.5	14.5
Speed RPM	18900	26000	3000	13070
Exhaust temperature °C	532.2	555.6	460	491.1

These turbines are designed to burn natural gas. The strategies and changes in operation and design for burn hydrogen is discussed by Chiesa, et al (2005). In the combined cycle proposed these turbines will be arranged as the top cycle for the combined cycle, and for the bottoming cycle it will

be used an ORC with the following working fluids and parameters.

Table 3. Power generation under different co-firing scenario.

Working Fluid	Toluene	Cyclopentane	Decane
Max Pressure (Bar)	35.76	40	18
Max temperature (°C)	300	230	300
Sat. Pressure (kPa)	5	40	5
$\eta_{turbine}$ (%)	85	85	85
η_{pump} (%)	75	75	75

Hence with this values it was calculated the power generated by the combined cycle and their efficiency, what is shown in the Figure (8).

With these results it is possible to calculate the amount of hydrogen required for the combined cycle and the number of solar reactors required for suppling this hydrogen. The power plant was conceived for the peak energy hours, when the solar power is not available and therefore the hydrogen produced for one day must be enough for the power plant operation during the estimated time, in this case, a period of 3 hours was considerate. Due to the limitation of burning pure hydrogen in gas turbines, it will be considered its burning with natural gas as explained in the previous section.

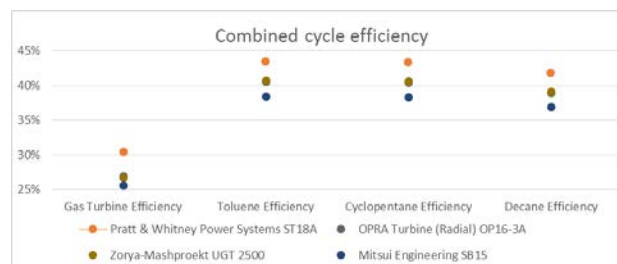


Figure 8. Combined cycle efficiencies for different working fluids.

The table 4 summarizes all the information of the hydrogen production and the power generated for the combined cycle. Where was calculated the hydrogen mass rate required for the two scenarios (hydrogen and methane co-firing in 30% and 70% by volume), and their necessary number of solar reactors to produce this amount of hydrogen according with the behavior seeing in the figure 4. For the hydrogen production was taken a period of 8 hours, based in the average solar hours in Brazil, according with the Brazilian solar atlas ANEEL (2005).

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Brand	Pratt & Whitney	OPRA Turbine	ZM Turbines	Mitsui Engineering
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Model	ST18A	OP16-3A	UGT 2500	SB15
Power Turbine kW	1961	1910	2670	2720
H ₂ mass rate kg/s -30%	0.0103	0,0113	0.016	0.017
H ₂ mass rate kg/s -70%	0.0518	0,057	0.0803	0.0853
Solar reactors for 30% co-firing	10	12	16	18
Solar reactors for 70% of co-firing	52	56	80	84
Cyclopentane Power kW	2791.4	2871	4064.4	4068.2

These values were calculated under the best scenario for the hydrogen yield as seen in the figure 5 and 6, which is 1673 K for the reduction stage and 1373 K for the oxidation stage. For the Organic Rankine cycle was chosen the Cyclopentane as working fluid due at good performance and the higher safety compared with the toluene.

CONCLUSIONS

Using the solar production of hydrogen is possible to have an integration between the solar energy and the current technologies of power generation and use it in co-firing with fossil fuels, allowing the decrease of the generation global warming gases and the dependence for the fossil fuels. Beyond this, the paper explores the concept of solar fuels and the thermochemical cycles, one of the most promissory technologies for the thermal solar power.

In the figure 6 is possible see a strongly dependence of the hydrogen yield with the temperature. With higher temperatures is possible to obtain higher disassociate rates, improving the hydrogen yield. However, the increase of this temperature produces some problems related with the degradation of the matrix, and thermal losses in the reactor. Therefore, more research must be done looking for improving the water splitting in the reactor through better matrix materials and improve the thermal performance of the solar reactor.

One of the advantages of use this technology is the elimination of the requirement of heat storage and burners for the solar thermal plants, where these technologies were required for the electrical energy generation without solar resource. Looking for reduce the plant cost the use of these technologies must be avoided. Therefore, in this works the energy storage was done through the hydrogen production, which can be used at any part of the day.

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