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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 a 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.*

1. 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).

The main benefit of generate hydrogen as energy carrier, is the possibility of fulfill all the energy requirements of the society, from the requirements for transport, using it as fuel for a prime mover (fuel cells or combustion engines). Or for the heat requirements for any process (burning the hydrogen). The main challenge of the hydrogen use is the storage, because the lower volumetric heating value in comparison with the conventional fuels, requiring high pressures or very low temperatures to be competitive.

For this purpose in this paper it is explored the concept of hydrogen generation by solar energy, and their posterior burning in a combined cycle, allowing by this way the integration a standard equipment/procedure with the solar energy.

2. 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.

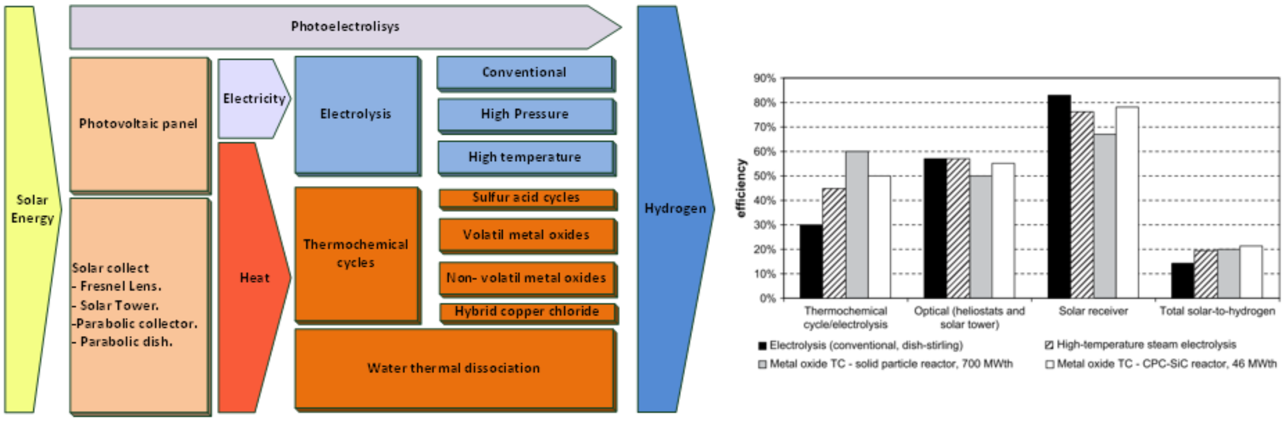


Figure 1. Mains paths for solar hydrogen production using water as raw material and the hydrogen and Efficiencies of solar hydrogen production under different process (Pregger et al., 2009).

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. 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).

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.

3. 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%**

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).

$$\eta_{field} = \eta_{cos}\eta_{shadow}\eta_{ref}\eta_{att} \tag{1}$$

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.

4. 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 $NiFe_2O_4$ 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. The Eq. (2) and Eq. (3) describe the molar rate production of hydrogen and oxygen at any instant of time.

$$F_{H_2} = k_{WS}C_{H_2O}e^{-k_{WS}c_{H_2O}t} \tag{2}$$

$$F_{O_2} = k_{tr}\psi e^{-k_{tr}t} \tag{3}$$

where: F_{H2} = molar hydrogen production rate per gram of redox material, moles/minute.
F_{O2} = molar oxygen production rate per gram of redox material, moles/minute.
K_{ws} = Temperature-dependent reaction rate constant in oxidation stage, m3/moles/min.
Kt_r = Temperature-dependent reaction rate constant in reduction stage, , m3/moles/min.
C_{h20}= Water concentration at the inlet, moles of gas/m3.
Ψ = Instantaneous concentration of adsorbed oxygen, moles of O_2 per g of redox material.
t= time.

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 $NiFe_2O_4$ 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 am arrangement of nine matrix materials in SIC with 146mmX146mmX60mm, being the same arrangement used in the Hydrosol 100 kWth plant Roeb *et al*, (2011).

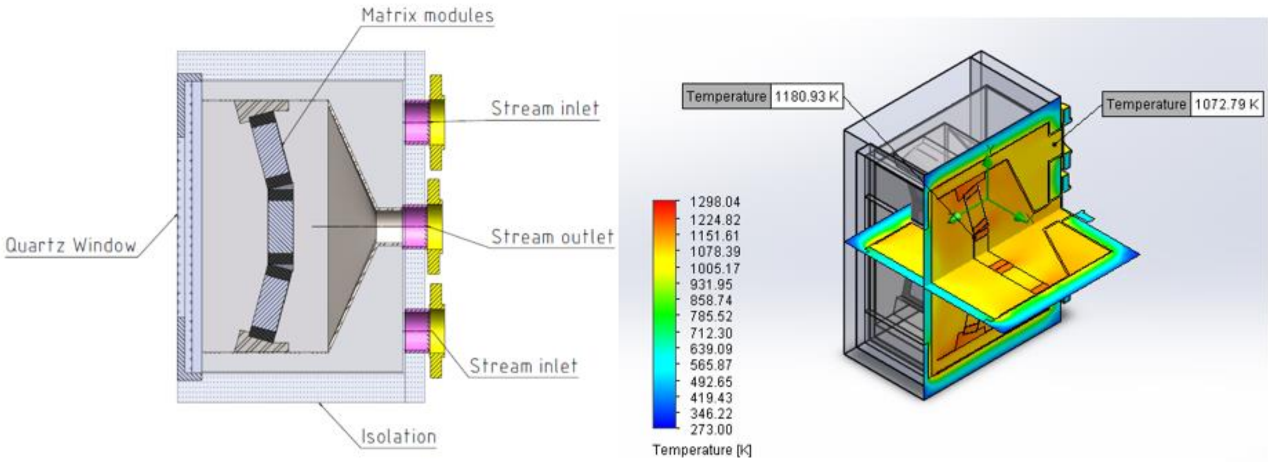
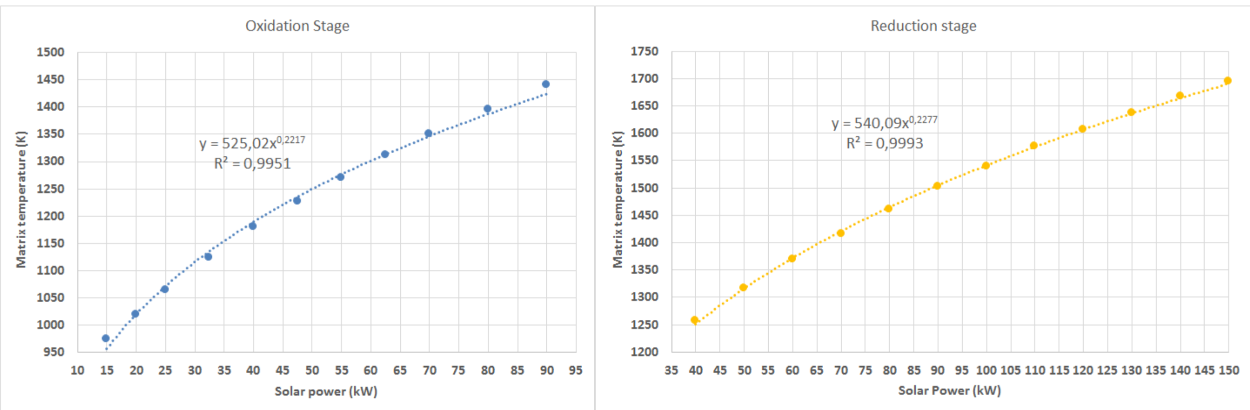


Figure 2. Predesign of solar reactor and temperature distribution for a solar power of 40 kW in oxidation stage.

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.

In the figure 2, 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 behavior 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 3. Where the solar power consumption are concordant with the field behavior tested by the 100 kWth solar hydrogen production plant Roeb *et al*, (2011).



a) b)

Figure 3. 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 4. 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.

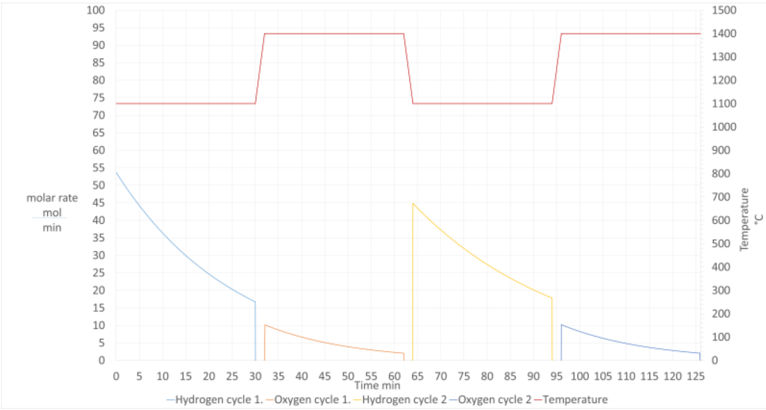


Figure 4. Hydrogen and oxygen production through the cycle.

Therefore, the global mass of hydrogen production per cycle, i.e., the hydrogen production yield, is showed on Figure (5). 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.

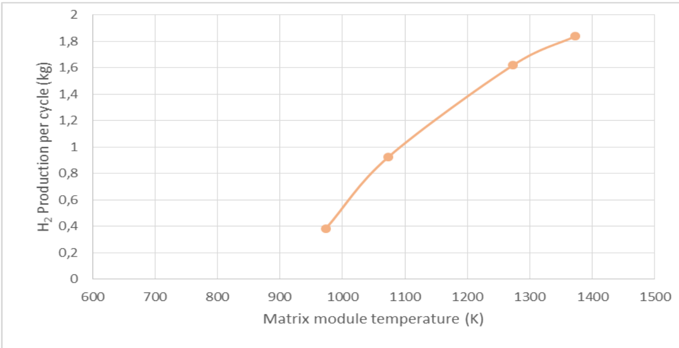


Figure 5. Mass production in function of the oxidation stage temperature.

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.

$$\eta_{reactor} = \frac{m_{produced\,H_2} LHV_{H_2}}{Q_{oxidation} t_{stage} + Q_{reduction} t_{stage}} \tag{4}$$

$$\eta_{sun\ to\ H_2} = \frac{m_{produced\,H_2} LHV_{H_2}}{Q_{oxidation} t_{stage} + Q_{reduction} t_{stage}} \eta_{field} \tag{5}$$

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.

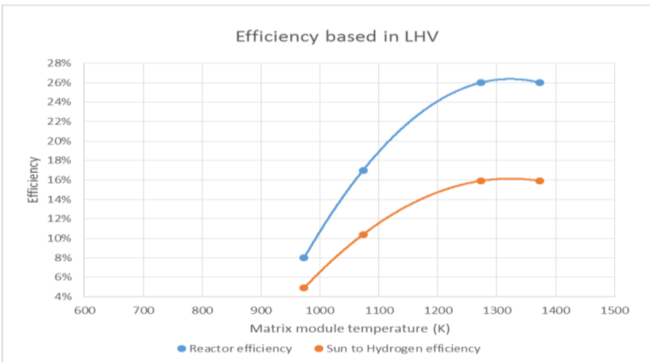


Figure 6. Efficiencies of the reactor and the whole process.

5. 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	Model	Power kW	Efficiency	Pressure ratio	Mass flow kg/sec	Speed RPM	Exhaust temperature °C
Ebara	ST18A	1961	30,40%	14	8,0	18900	498,9
Pratt & Whitney	ST18A	1961	30,40%	14	8,0	18900	532,2
OPRA Turbine	OP16-3A	1910	26,90%	6,7	8,7	26000	555,6
Zorya-Mashproekt	UGT 2500	2670	26,70%	12	16,5	3000	460,0
Mitsui Engineering	SB15	2720	25,60%	10	14,5	13070	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, Lozza and Mazzocchi, (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 a ORC with the following working fluids and parameters.

Table 3. References values for the organic Rankine cycle according to Algieri and Morrone, (2013), and Lai, Wendland and Fischer (2011).

Working Fluid	Max Pressure bar	Max temperature °C	Sat. Pressure kPa	Turbine efficiency	Pump Efficiency
Toluene	35,76	300	5	0,85	0,75
Cyclopentane	40	230	40	0,85	0,75
Decane	18	300	5	0,85	0,75

Hence with this values it was calculated the power generated by the combined cycle and their efficiency, what is shown in the Figure (7).

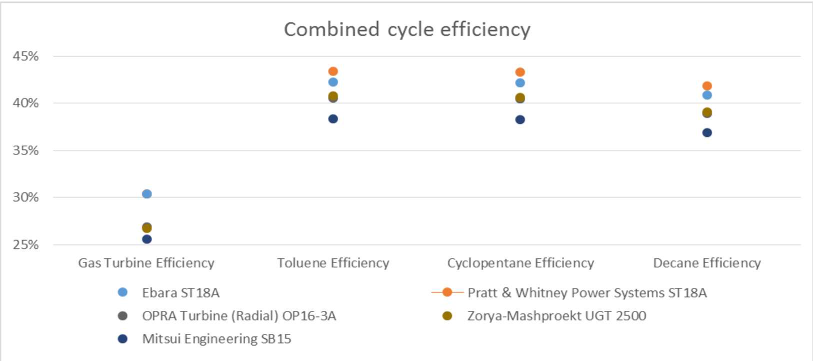


Figure 7. Combined cycle efficiencies for different working fluids.

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.

Table 4. Power generation under different co-firing scenario.

Brand	Model	Power turbine kW	H_2 mass rate kg/s - 30%	H_2 mass rate kg/s - 70%	Solar reactors for 30% co-firing	Solar reactors for 70% of co-firing	Cyclopentane Power kW
Ebara	ST18A	1961	0,0103	0,0518	10,0	52,0	2719,3
Pratt & Whitney	ST18A	1961	0,0103	0,0518	10,0	52,0	2791,4
OPRA Turbine	OP16-3A	1910	0,0113	0,0570	12,0	56,0	2871,0
Zorya-Mashproekt	UGT 2500	2670	0,0160	0,0803	16,0	80,0	4064,4
Mitsui Engineering	SB15	2720	0,0170	0,0853	18,0	84,0	4068,2

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).

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.

6. CONCLUSIONS

Using the solar production of hydrogen is possible to have an integration between the solar energy and the currents 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 5 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 e 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.

7. ACKNOWLEDGEMENTS

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8. REFERENCES.

Agrafioti, C. *et al.* 2009. “Hydrogen Production via Solar-Aided Water Splitting Thermochemical Cycles with Nickel Ferrite: Experiments and Modeling” *IFAC Proceedings Volumes (IFAC-PapersOnline)*, Vol. 7, n. PART 1, p. 405–410.

Agrafioti, C. *et al.* 2007. “Hydrogen production in solar reactors” *Catalysis Today*, Vol. 127, n. 1-4, p. 265–277, 2007.

Algieri, A and Morrone, P. 2013. “Energetic analysis of biomass-fired ORC systems for micro-scale combined heat and power (CHP) generation. A possible application to the Italian residential sector” *Applied Thermal Engineering*, nov. 2013.

ANEEL 2005. “Atlas de Energia Eletrica do Brasil” ANEEL.

Bradley, T and Marra, J. 2014 “Advanced hydrogen turbine development update” *Proceedings of ASME Turbo Expo 2012*, p. 1–9.

Chiesa, P, Lozza, G, and Mazzocchi, L.2005. “Using Hydrogen as Gas Turbine Fuel” *Journal of Engineering for Gas Turbines and Power*, v. 127, n. 1, p. 73.

Farmer, R. 2010 “Gas turbine World 2010 GTW Handbook” Southport: Pequot.

Giglio, E. *et al.* 2015. “Synthetic natural gas via integrated high-temperature electrolysis and methanation: Part I—Energy performance” *Journal of Energy Storage*, Vol. 1, p. 22–37.

Kaloguirou, S. 2004. “Solar thermal collectors and applications” *Progress in Energy and Combustion Science*, Vol. 30,p. 231-295.

Lai, N, Wendland, M and Fischer, J. 2011. “Working fluids for high-temperature organic Rankine cycles” *Energy*, v. 36, n. 1, p. 199–211.

Malagueta, D. *et al.* 2014. “Potential and impacts of Concentrated Solar Power (CSP) integration in the Brazilian electric power system”. *Renewable Energy*, vol. 68, p. 223–235.

Pregger, T. *et al.* 2009. “Prospects of solar thermal hydrogen production processes” *International Journal of Hydrogen Energy*, v. 34, n. 10, p. 4256–4267.

Roeb, M. *et al.* 2009. “Operational strategy of a two-step thermochemical process for solar hydrogen production” *International Journal of Hydrogen Energy*, Vol. 34, n. 10, p. 4537–4545.

Roeb, M. *et al.* 2006 “Solar Hydrogen Production by a Two-Step Cycle Based on Mixed Iron Oxides” *Journal of Solar Energy Engineering*, Vol. 128, n. 2, p. 125.

Roeb, M. *et al.* 2011 “Test operation of a 100kW pilot plant for solar hydrogen production from water on a solar tower” *Solar Energy*, Vol. 85, n. 4, p. 634–644.

Sterner, M. 2009. *Bioenergy and renewable power methane in integrated 100% renewable energy systems*. Ph.D. thesis, Kassel University.

Stine, W and Harrigan, R. 1985, *Solar energy fundamentals and design*. John Wiley & Sons, New Jersey, 1st edition.

Wind, T, Güthe, F and Syed, K. 2014. “Co-firing of hydrogen and natural gases in lean premixed conventional and reheat burners (Alstom GT26)”. *ASME Turbo Expo 2014*, p. 1–9.

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