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Hydrogen Production by the Solar-powered Hybrid Sulfur Process: Analysis of the Integration of the CSP and Chemical Plants in Selected Scenarios

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Abstract. The Hybrid Sulfur (HyS) is a water splitting process for hydrogen production powered with high temperature nuclear heat and electric power; among the numerous thermo-chemical and thermo-electro-chemical cycles proposed in the literature, such cycle is considered to have a particularly high potential also if powered by renewable energy. SOL2HY2 (Solar to Hydrogen Hybrid Cycles) is a 3 year research project, co-funded by the Fuel Cells and Hydrogen Joint Undertaking (FCH JU). A significant part of the project activities are devoted to the analysis and optimization of the integration of the solar power plant with the chemical, hydrogen production plant. This work reports a part of the results obtained in such research activity. The analysis presented in this work builds on previous process simulations used to determine the energy requirements of the hydrogen production plant in terms of electric power, medium (<550°C) and high (>550°C) temperature heat. For the supply of medium temperature (MT) heat, a parabolic trough CSP plant using molten salts as heat transfer and storage medium is considered. A central receiver CSP (Concentrated Solar Power) plant is considered to provide high temperature (HT) heat, which is only needed for sulfuric acid decomposition. Finally, electric power is provided by a power block included in the MT solar plant and/or drawn from the grid, depending on the scenario considered. In particular, the analysis presented here focuses on the medium temperature CSP plant, possibly combined with a power block. Different scenarios were analysed by considering plants with different combinations of geographical location and sizing criteria .

INTRODUCTION

The Hybrid Sulfur (HyS) or Westinghouse cycle was proposed during the 1970s as a water splitting process for hydrogen production powered with high temperature nuclear heat and electric power [1]; among the numerous thermo-chemical and thermo-electro-chemical cycles proposed in the literature, such cycle is considered to have a particularly high potential [2]. As for all water splitting cycles, HyS could lead to the production of completely renewable and carbon-free hydrogen, if the nuclear energy source could be replaced with a renewable one, such as solar power. However, in order to attain such a challenging goal several additional technological and process issues, mainly related to the intermittent nature of the solar source, must be resolved.

SOL2HY2 (Solar to Hydrogen Hybrid Cycles) is a 3 year research project, co-funded by the Fuel Cells and Hydrogen Joint Undertaking (FCH JU) within the Seventh Framework Programme for Research and Technological Development (FP7) [3]. The project focuses in particular on applied bottle-neck solving, materials research, development and demonstration of the relevant key components of the solar-powered HyS water splitting cycle: i.e. the sulfur depolarized electrolyzer (SDE) and the catalytic reactor for solar-powered SO3 decomposition. A significant part of the research carried out within the SOL2HY2 project is devoted to the analysis and optimization of the integration of the solar power plant with the chemical, hydrogen production plant. This work reports a part of the results obtained in such research activity and builds on previous flowsheeting activity which allowed to determine the energy requirements of the hydrogen production plant in terms of electric power, medium (<550°C)
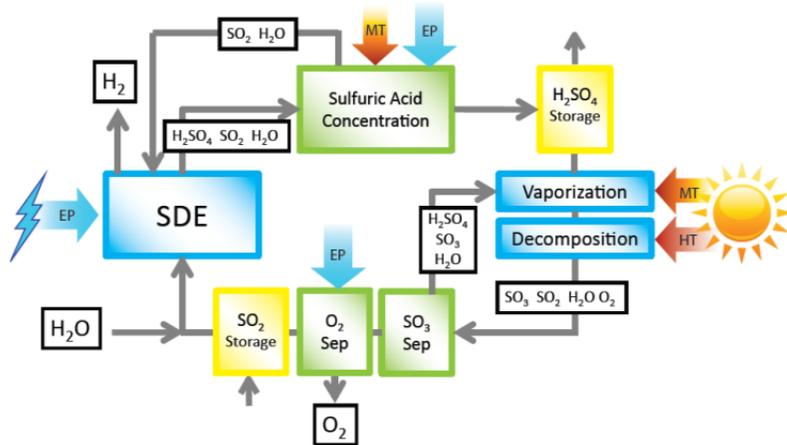
FIGURE 1. Simplified block diagram of the HyS process considered here. The main energy input type required by the different process blocks is highlighted (MT: medium temperature heat; HT: high temperature heat; EP: electric power; SDE: sulfur depolarized electrolyzer).

and high (>550°C) temperature heat, which provide the basis for the design of the solar plant. In particular, the analysis presented here focuses on the medium temperature CSP plant, possibly combined with a power block.

Different scenarios were analyzed by considering plants with different combinations of geographical locations and sizing criteria; furthermore, the possibility of obtaining electricity and/or sulfuric acid (SA) as co-products of the process was also considered.
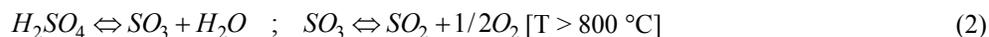
Among the different criteria used to assess each scenario, a special attention was given to the percentage of renewable energy used for hydrogen production, for which a target value of 50% was assumed.

MAIN PLANT CONCEPTS

Chemical Plant

The main objective of the SOL2HY2 project is the production of hydrogen through the use of a HyS-type thermochemical cycle. The possibility of using a partially or completely open version of the cycle, such as the new Outotec Open Cycle® (OOC) process [4], is also envisaged.

The original HyS cycle makes use of SO_2 and H_2SO_4 in a closed cycle starting from water and generating H_2 and O_2 according to the following reactions:

$$SO_2 + 2H_2O \Leftrightarrow H_2SO_4 + H_2 \text{ [T< 100 °C]} \tag{1}$$

$$H_2SO_4 \Leftrightarrow SO_3 + H_2O \quad ; \quad SO_3 \Leftrightarrow SO_2 + 1/2O_2 \text{ [T > 800 °C]} \tag{2}$$

OOC involves only the low temperature reaction (1), without SA decomposition (2). The SO_2 feed required by OOC can be obtained from waste streams of flash smelting, sulfide roasting, sulfur combustion or any other similar operation. Compared to conventional alkaline water electrolysis (standard cell potential E^0=1.23 V; operating voltage 1.8-2.0 V [5]) SO_2 depolarized electrolysis (E^0=0.16 V) can potentially operate with a 40-75% lower power input; indeed, in laboratory-scale hydrogen production tests, SDE could be operated in the range 0.5-1.2 V, depending on the current density and other operational parameters [6-8].

Figure 1 presents a simplified block diagram of the process considered, which highlights the main energy input types required by the different process blocks. The effluent anolyte SA solution from the SDE is concentrated before being evaporated and heated at 1000 °C; here, concentration from 20% to 75% (weight basis) is assumed. The gas stream at 1000 °C, which is composed almost only of SO_3 and H_2O, is fed to an adiabatic reactor where SO_3 is decomposed in SO_2 and O_2. The conversion of such reaction is thermodynamically limited so that separation and recycling of unreacted SO_3 to the reactor's feed is required. Finally, the produced SO_2 is separated from O_2 by refrigerated compression and recycled to SDE.

TABLE 1. Specific energy consumption of the chemical plant divided by plant block and energy input type

Process block	MT heat [kJ/mol]	HT heat [kJ/mol]	Electric Power [kJ/mol]
SA concentration	99.9	-	75
SA evaporation + decomposition	206.1	196.4	-
SO_2/O_2 separation	-	-	20.0
SDE	-	-	273.4
Total	**306.0**	**196.4**	**368.4**

A previous flowsheeting activity based on AspenPlus® (Aspen Technology Inc., Bedford, MA, USA) simulations allowed to determine the type and amount of specific energy consumption of each block of the process shortly described above. The details of such analysis are beyond the scope of this paper and not reported here; however, the specific energy consumption data provide the basis for designing the CSP plant and are reported in Tab. 1.

For several self-evident reasons, if possible, the chemical plant should be operated continuously; however, the use of the intermittent solar source to power the process requires a part of the plant to work discontinuously 8 h per day, when the solar radiation is available. SA and SO_2 storage tanks are used as a buffer to decouple the operating regimes of the continuous and discontinuous part of the chemical plant. Details on operating regimes of the different blocks of the process and coupling with the CSP plant are provided in the following subsection.

CSP Plant

For the supply of medium temperature (MT) heat, a parabolic trough CSP (Concentrated Solar Power) plant using solar salt (i.e. 60:40 w/w $NaNO_3/KNO_3$ mixture) as heat transfer and storage medium was considered; 8 h of daily operation are assumed with 16 h of heat storage in order to allow for continuous operation (in nominal conditions) for the process units that rely on this type of energy input. A set of trough loops connected in parallel with 6 collectors per loop is considered for the MT solar field. A central receiver CSP plant was considered to provide high temperature (HT) heat, which is only needed for SA decomposition; 8 h of daily operation and no heat storage are considered in this case, so that SA decomposition and, consequently, SA vaporization and unreacted SO_3 separation are assumed to operate discontinuously, only at daytime.

The CSP plant is sized by fixing the solar power collected at the mirror's surface under specified conditions and accounting for the heat requirements of the chemical plant. A solar-to-heat collection efficiency of 52% and 40% is assumed for the MT and HT CSP plant, respectively.

As for the operating regime and heat input fed to each process block, the following choices were made:

- SA decomposition requires high temperatures which can be obtained with a CSP system such as a Solar Central Receiver. Since currently consolidated technologies ensure just a few hours of heat storage at this temperature level, this process block is assumed to operate discontinuously (8 h per day).
- SA vaporization is also operated only at daytime, but requires MT heat, which can be provided by the solar trough plant.
- SA concentration is operated continuously, due to the cost of equipment, amortization optimization and, most of all, to avoid daily start-up and shutdown operations, which this type of plant can hardly afford. Also in consideration of the temperature level required (< 200°C), this block is powered with MT heat production by the Solar Troughs CSP plants supplied with proper thermal storage and backup systems, in order to ensure the continuity of operation.
- SDE and gas separation units require an electric energy supply and are assumed to work continuously.

Therefore, the CSP plant provides the chemical plant with 3 types of thermal energy input: continuous MT heat, discontinuous MT heat and discontinuous HT heat.

As for electric power, the easiest option is the use of the electric grid. Nevertheless, in order to increase the fraction of renewables in the energy input, also the installation of a power block coupled with the MT solar plant was considered.
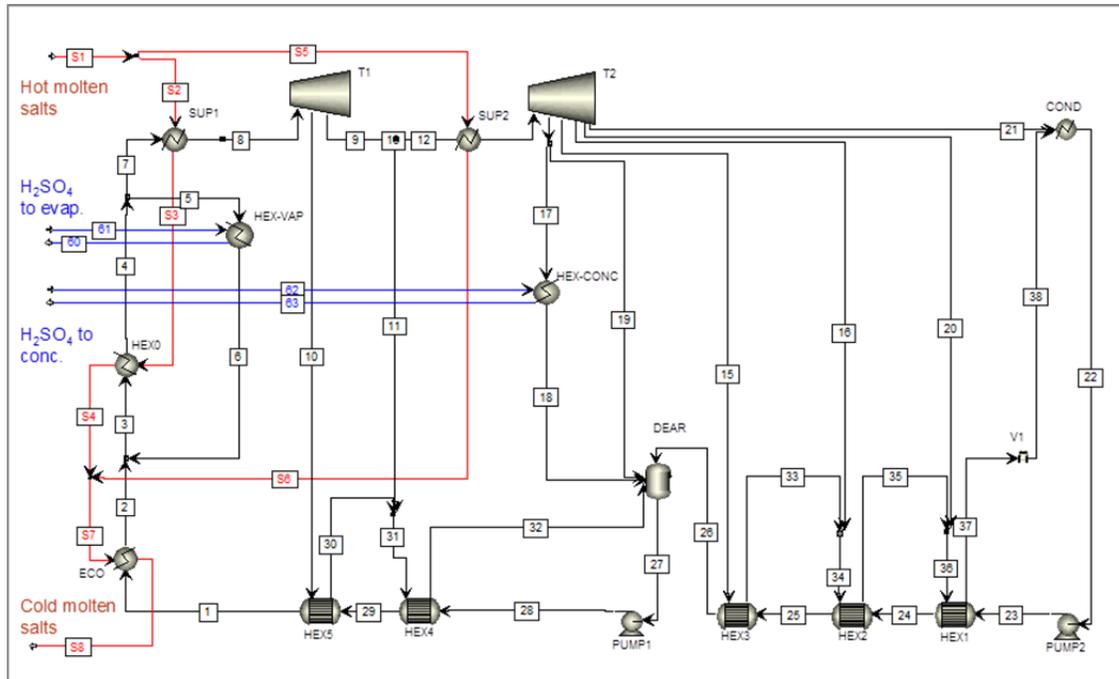
FIGURE 2. Process scheme of the Rankine cycle powered by molten salts sensible heat. In Case 1a (8 hours solar operation) both the heat exchangers HEX-VAP and HEX-CONC work, while in Case 1b (16 hours operation) only the HEX-CONC is in operation. In Case 2 the heat exchangers HEX-VAP and HEX-CONC are not present. HEX: exchangers; HEX-VAP: evaporator for the H2SO4 evaporation in the discontinuous step of the cycle; HEX-CONC: evaporator for the H2SO4 concentration in the continuous step; DEAR: degasifier; COND: condenser; T1, T2: steam turbines; ECO: economizer; SUP: super-heater; V: valve.

Power Block

Depending on the specific scenario considered, a power block was also included in the MT CSP plant; if present, the power block can reduce or avoid the use of grid power or even allow for a net export of power to the grid (i.e co-production of H_2 and power).

Power generation is assumed to be carried out by a steam cycle since coupling of this technology with molten salt CSP plants is already demonstrated and used in existing power plants. Furthermore, this choice allows part of the steam produced with the MS steam generator to be used as heat transfer fluid for the chemical plant and provide heat for SA concentration and vaporization. Figure 2 shows a scheme of the Rankine cycle considered for the power block. In more detail, two different process configurations were considered: 1) the molten salt sensible heat is partly transferred to the Rankine cycle and partly used to produce high pressure steam as thermal fluid for the chemical process (SA vaporization and concentration units), through the heat exchangers HEX-VAP and HEX CONC; 2) the molten salt heat is totally used to produce high pressure steam for generating electricity through the steam turbines. In this second process configuration the heat demand of the SA evaporation and concentration units is directly satisfied by the heat exchange with hot molten salts, without the intermediate exchange with high pressure steam. The first process option can be split in two operation modes: during the daily 8 hours of operation of the CSP, both the SA vaporization and concentration units work and are powered by the high and medium pressure steam (Case 1a), while in the remaining 16 hours operation only the SA concentration unit is active and its energy need is fulfilled by the medium pressure steam (Case 1b). In the present work some common improvements to the Rankine cycle (reheating and regenerative steps) have been introduced with the aim of increasing the cycle thermal efficiency. In particular in this reheating variation, the steam turbine is split in two stages, working in series, and the steam, after the first expansion stage, is re-heated up to the maximum temperature (540°C), removing the moisture produced at the final stages of the expansion process. Furthermore, according to the regenerative cycle, the working fluid, on its way from the condenser to the boiler, is pre-heated by indirect contact with the inter-stage steam bled from the turbine.
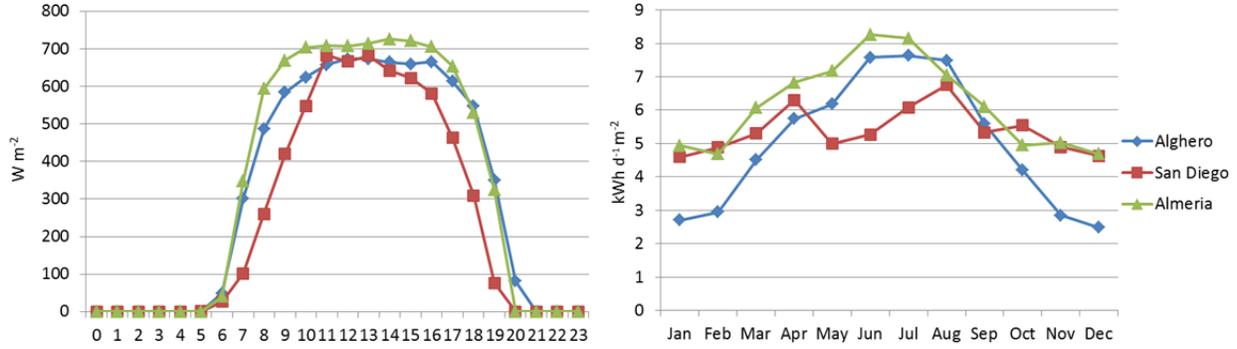
FIGURE 3. DNI at the three reference plant locations: hourly values during the average July day (left) and monthly average during the year (right).

METHODOLOGY

In order to study the integration between the chemical and CSP plants, different scenarios were analysed. Such scenarios differed for:

- Plant location: Alghero (Italy, 40.56 N 8.32 E), San Diego (CA, USA, 32.43N 117.09 W) and Almeria (Spain, 36.9 N 2.36 W) were considered. Alghero and San Diego were chosen as representative of locations with uneven and even irradiation during the year, respectively. Almeria, more specifically the Tabernas site, is a standard reference location since it hosts one of the most important CSP facilities worldwide (Plataforma Solar de Almeria, PSA). The METEONORM database was used to account for the hourly direct normal irradiation (DNI) expected in each location throughout the year. DNI of these sites are shown in Fig. 3. For the sake of simplicity, an average day was considered for each month (Fig. 3 shows July as an example).

- MT CSP plant design criterion: the MT CSP plant was designed to collect a given solar power at the mirror's surface according to the local *maximum*, *average* or *minimum* monthly average irradiation. Clearly, this design criterion affects the size of the solar field: a design based on peak irradiation leads to the smallest plant size (and associated investment costs), which ensures the requested energy collection only for a limited period of the year; on the other hand, the minimum irradiation design criterion fulfils (and, during the summer, exceeds) the heat requirement of the chemical plant at the price of higher investment costs.

- Extent of cycle opening: if a SO_2 source is available, the SDE can be oversized to process both the externally provided SO_2 (*open cycle*, OC, H_2 production) and the SO_2 coming from SA decomposition (*closed cycle*, CC, H_2 production). The extent of cycle opening was defined as

$$OC\% = \frac{\text{Energy required for OC}}{\text{Energy required for OC} + \text{Energy required for CC}} \quad (3)$$

Clearly, when OC% = 0, the cycle is completely closed (pure HyS), while OC% = 100% corresponds to a completely open configuration, such as in the OOC process.

- Presence of a power block (PB): either the grid or a PB coupled with the MT CSP plant were considered as power supply for the chemical plant. Furthermore, when present the PB could be sized to fulfil the power demand of the chemical plant only (*dedicated* PB) or also to export power into the grid (*non-dedicated* PB).

For all the scenarios considered, the plants were sized as follows:

- A CC H_2 production capacity of about 2.7 t/d (15.44 mol/s) was considered. Such capacity roughly requires 400 MWh/d of total solar energy collected on the mirrors of the MT and HT solar plants or 113.4 MWh/d of MT heat produced in the solar trough plant.

- The mirror surface of the solar trough field was sized to fulfil the heat requirements of the chemical plant according to the peak/average/minimum criterion.

- Additional trough loops were added to sustain a PB, if present. A nominal size of 40 MW was chosen for the PB. A lower size was excluded in order to avoid too low heat-to-power conversion efficiencies.

- In partially open cycles, the CC H_2 production was increased by increasing the size and power supplied to the SDE (the capacity of the other blocks of the chemical plant was left unchanged).

TABLE 2. Comparison of different plant scenarios not including a power block (OC% = 0)

Plant location	Alghero			San Diego			Almeria		
MT CSP plant design criterion	Peak	Av.	Min.	Peak	Av.	Min.	Peak	Av.	Min.
MT heat yearly aver. production [MWh/d]	73.5	115.4	398.8	92.5	115.7	127.2	85.5	114.0	170.9
Number of loops	7	11	38	8	10	11	6	8	12
Mirror surface [ha]	2.4	3.7	12.9	2.7	3.4	3.7	2.0	2.7	4.1
Volume of heat storage [m^3]	617	970	3350	777	972	1069	718	95	1436
H$_2$ production with solar heat only [%]	61.7	78.4	100	80.4	95.1	100	73.6	89.8	100
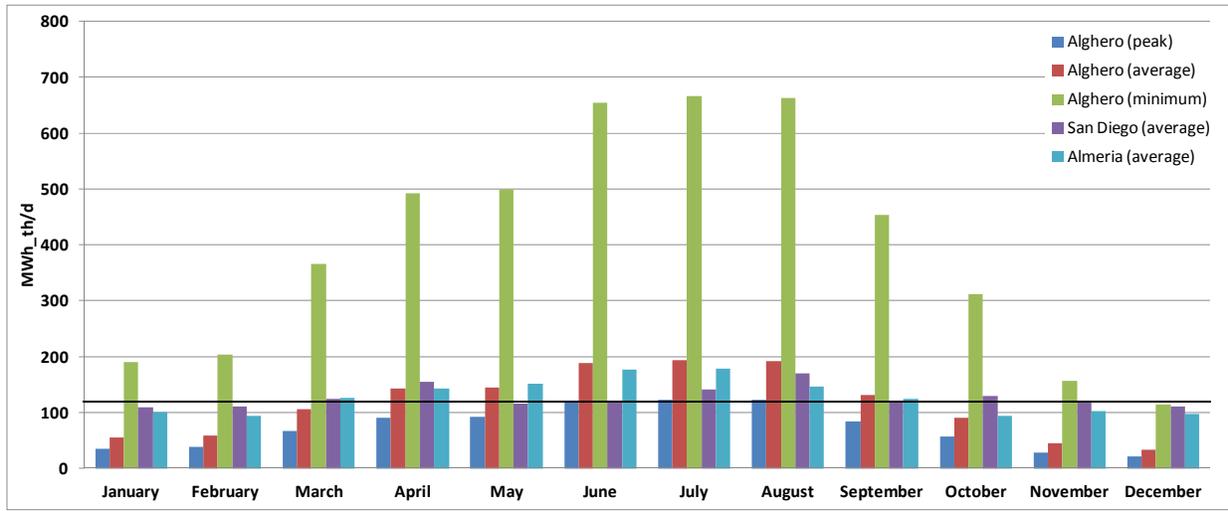
FIGURE 4. MT heat production (kWh/d) in different locations and with different solar trough plant sizing criteria (no PB, OC%=0).

RESULTS

Several scenarios not including a PB were firstly compared in order to analyze the effect of the MT CSP plant design criterion. The results are summarized in Tab. 2. It can be seen that the design criterion has a strong effect on the plant size and yearly average MT heat production for the plant located in Alghero, which exhibit the most uneven DNI distribution throughout the year among the three locations considered, while such effect is much less important when San Diego or Almeria are chosen for the plant site.

As a further consequence of the uneven time distribution of the DNI, it is difficult to efficiently size the MT solar plant in Alghero to meet the heat requirements of the chemical plant. This can be clearly seen in Fig. 4, where the monthly MT heat production distribution along the year is detailed and compared with the MT heat requirement of the chemical plant for the nominal production of 2.7 t/d (113 MWh/day, horizontal black line in the figure). Indeed, if the minimum DNI criterion is applied for Alghero, the MT heat production largely exceeds the plant requirements for a significant part of the year; on the other hand, if the peak DNI criterion is applied, during the winter months the MT solar plant provides only a small fraction of heat required for H$_2$ production.

A similar problem is not observed for locations such as San Diego and Almeria, where it is possible to meet the heat requirements of the chemical plant fairly well throughout the year by sizing the MT solar plant based on the average DNI criterion (see Fig. 4). The slight over- or underproduction of heat occurring during summer and winter respectively can be handled by defocusing a small part of the solar field or using a backup heat source to a reasonable extent. Table 2 also reports the yearly average H$_2$ production that can be sustained by the solar heat collected as a fraction of the chemical plant capacity (2.7 t/d). Besides the use of a backup heat source, it should be considered that when the solar heat production is insufficient, a capacity reduction up to 10-15% of the operating value should be tolerated by the chemical process equipment.

TABLE 3. Comparison of different plant scenarios including a power block).

Location		Almeria		San Diego		Alghero	
Dedicated MT solar plant		No	Yes	No	Yes	No	Yes
OC%	%	0	61	0	61	0	61
MT yearly average heat production	MWh /d	2507	2504	2510	2510	2508	2508
Number of loops		176	176	217	217	239	239
Mirror surface	ha	60	85	74	74	81	81
Volume of heat storage	m^3	21064	21064	21089	21089	21073	21073
H_2 production by OC	mol/s	0	124.74	0	124.74	0	124.74
Thermal energy fraction for H_2 production	%	58	16	58	16	58	16
Grid export	GWh/y	284.0	1.0	283.6	0.4	258.8	2.6
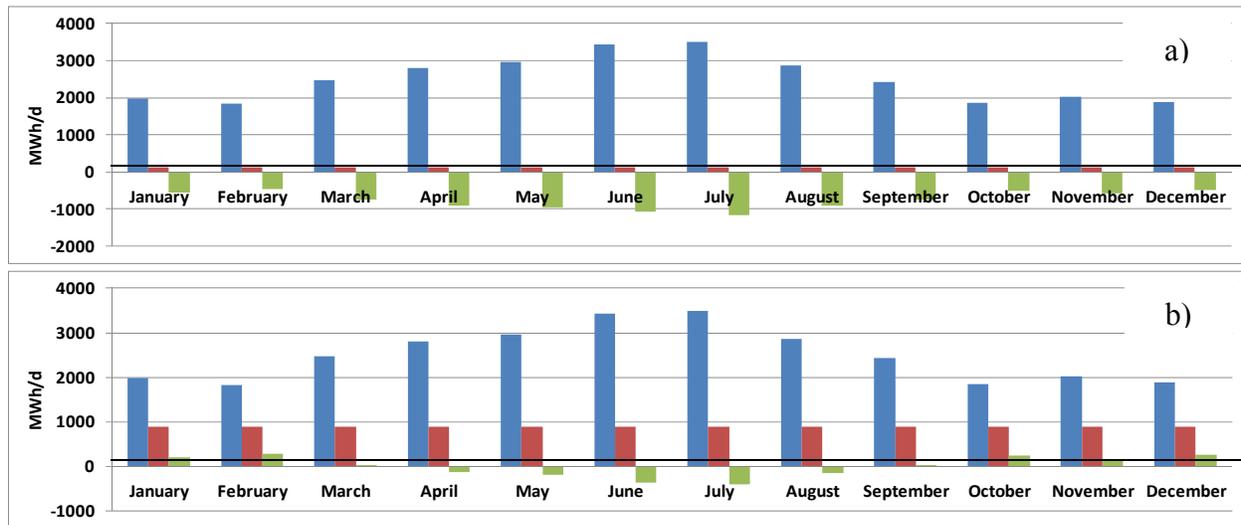
FIGURE 5. MT heat production (blue), power consumption (magenta) and grid export (green) for a plant located in Almeria and equipped with PB: (a) OC% = 0, non-dedicated 40 MW PB; (b) OC% = 61%, dedicated 40 MW PB.

According to the specific energy consumption reported in Tab. 1, when electric power is drawn from the grid the share of renewable energy used for H_2 production can still attain 58% (with the conservative assumption that grid energy comes entirely from non-renewable energy sources). In order to push this value to 100%, a power block can be coupled with the MT solar plant.

Closed cycle H_2 production with a dedicated 40 MW PB is possible for a plant with a capacity of about 18 t/d, which is much higher than the CC plant capacity considered here; therefore, this case was not considered. Rather two other scenarios, both leading to the production of H_2 from 100% renewable energy, were analyzed: CC production with a non-dedicated PB and partially open cycle with dedicated PB. The results obtained for these scenarios are reported in Tab. 3 for all three locations; furthermore, Fig. 5 details the MT heat production, power consumption of the chemical plant and power imported from the grid (a negative grid import represents a net power export to the grid) during the year for the plant in Almeria. In the scenarios with non-dedicated PB, the MT solar plant not only allows to attain the target CC H_2 production, but also significant power export to the grid. The co-production of H_2 and power may be a good solution, because it allows to achieve economies of scale in the solar plant and PB, also for relatively small H_2 production capacities. This is especially important in the early stages of development and diffusion of H_2 production plants based on the solar HyS process. In the scenarios with dedicated PB, the CC H_2 production was kept to the reference value of 2.7 t/d, while the OC production was adjusted in order to entirely devote the 40 MW PB to H_2 production. It can be seen from Tab. 3 and Fig. 5 that, under the conditions considered here, this target is achieved with a cycle opening of 61%, which leads to a negligible yearly net grid export.

CONCLUSIONS

Coupling of a HyS-type H_2 production plant with a CSP plant was studied. Due to the temperature levels associated with the chemical process, the CSP plant considered included both the solar trough and central receiver technologies. Several plant scenarios were analyzed with a specific focus on the solar trough section. The monthly heat production was assessed also with regards to the possibility of ensuring a uniform H_2 production throughout the year. The results show that when the average irradiation design criterion is applied to a plant installed in a location where solar irradiance is not only high, but also uniformly distributed during the year, this target can be successfully achieved with a reasonable use of a backup heat source, without oversizing the CSP plant.

Even when the solar field is only used for process heat, while power is drawn from the grid, H_2 production by the process considered here can be sustained with renewable energy sources up to 58% of the total energy consumption. In order to increase this share up to 100%, a power block can be included in the MT solar plant; however, such power block may be too small to be cost and energy efficient if it is wholly dedicated to fulfilling the power demand of the chemical plant operating in closed cycle with a capacity below 18 t/d: in this case, co-production of H_2 and power could be considered. On the other hand, a dedicated power block may be a viable solution when an external SO_2 source is available and H_2 production can be carried out with a partially open cycle. The analysis presented here is currently being extended in order to consider other plant locations and include a multi objective optimization of the whole plant (CSP and chemical). This will pave the way to a thorough techno-economic analysis and optimization of the solar-powered HyS process.

ACKNOWLEDGMENTS

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