COUPLING HEAT AND ELECTRICITY SOURCES TO INTERMEDIATE TEMPERATURE STEAM ELECTROLYSIS

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Abstract

The use of CO_2-free energy sources for running Solid-Oxide Electrolysis Cell technologies (SOEC) has a great potential of reducing the carbon dioxide emissions compared to fossil fuel based technologies for hydrogen production. This paper is related to the work of the JU-FCH project ADEL, which investigates different carbon-free energy sources with respect to potential coupling schemes to Intermediate Temperature Steam Electrolyser (ITSE). A predominant focus of the analysis is put on on solar concentrating energy systems (Solar tower) and nuclear energy as energy sources to provide the required electricity and heat for the ITSE.

An overview of the main considerations, boundary conditions and results is presented concerning the development of coupling schemes of the energy conversion technologies to the electrolyser.

Keywords: Intermediate temperature electrolysis, electrolyser, hydrogen, solar, flow chart

1. Introduction

Hydrogen is mainly produced from fossil fuels through steam reforming of natural gas. Unfortunately, the fossil fuel based hydrogen generation does not contribute to the reduction of greenhouse gas emissions. Hydrogen can be generated instead by carbon-free energy sources via water electrolysis in order to avoid the emissions of carbon dioxide. There are three main types of water electrolysers: the alkaline electrolyser, polymer electrolyte membrane (PEM) electrolysers, and the Solid-Oxide Electrolysis Cell (SOEC)[1] [2].The two first technologies normally work at temperatures below 100 ºC; while SOEC technologies operates with steam. SOEC systems are normally divided into two temperature ranges, a low range between 600-800 ºC called intermediate temperature systems, and high temperature systems which operate in the range of 800-1000ºC. SOEC uses a combination of thermal energy and electricity and the water is fed to the electrolyser in vapor phase. The advantage of the operation at higher temperature consists of reducing the electricity demand of the electrolyser. In addition to that, the reaction kinetics is increasing at higher temperatures. The overall thermal-to-hydrogen efficiency for high temperature electrolysis can be as high as 50%, which is about double the overall efficiency of the conventional alkaline electrolysis[3].

Within ADEL project, the integration of the ITSE system with different carbon-free energy sources has been done. Some of these energy sources are: CSP systems (Tower systems, parabolic trough collectors, dish

Stirling and linear Fresnel reflector), nuclear plants, geothermal, energy, wind energy etc. In this work, the integration with central receiver systems using air, water/steam, and molten salt cooled receivers, and nuclear pressurized water reactor (PWR) are analyzed.

2. Thermodynamics of the intermediate temperature electrolysis

2. 1. Principle

ITSE aims to operate at temperatures below 700°C. This process integrates a ceramic electrolyte conducting ions O^{2-}. The advantage of this process is that its electricity consumption is lower than the one of a low temperature electrolyser (PEM or alkaline), as seen in the thermodynamic diagram (Figure 1). On top of that, the improvement of reaction kinetics at high temperature enhances the process efficiency. This type of process could enable a large scale hydrogen production in the future[4].

The reactions that take place in the electrolyser are:

Cathode: $$H_2O_{(g)} + 2e^- \rightarrow O^{2-} + H_{2(g)}$$

Anode: $$O^{2-} \rightarrow \frac{1}{2} O_{2(g)} + 2e^-$$

At the cathode (hydrogen electrode), the water molecule is dissociated because of the electrical current and the heat provision, in order to form a molecule of hydrogen and an oxygen ion O^{2-}. Under the effect of the electrical field, the ion O^{2-} goes through the electrolyte and migrates to the anode (oxygen electrode) where its oxidation produces an oxygen molecule O_2.

2.2. Operation modes

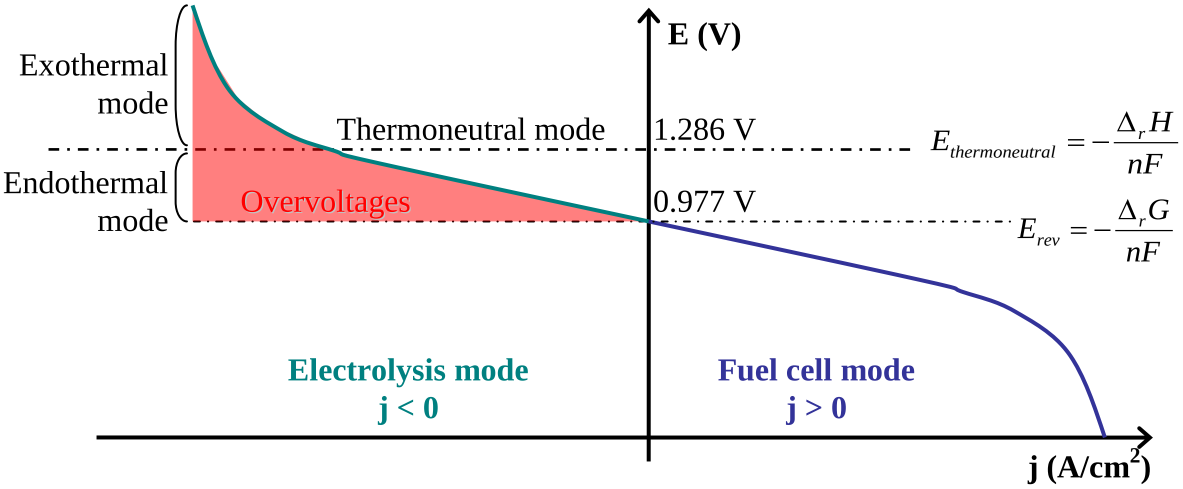

Fig. 1 Scheme of different HTSE operating modes at 1073K

Thermoneutral mode

The thermoneutral voltage ($E_{thermoneutral}$) of an electrolyser corresponds to an operation where electrolysis-needed heat is brought by all the overvoltages present in the cell. This voltage is given by the following equation:

$$E_{thermoneutral} = -\frac{\Delta_r H}{nF}$$

$E_{thermoneutral}$	Thermoneutral voltage in V.
$\Delta_r H$	Enthalpy change of reaction in J/mol.

F	Faraday constant in C/mol.
n	Number of exchanged electrons in the water electrolysis reaction.

At 298 K and 1 bar, the thermoneutral voltage is 1.481 V. It decreases to 1.286 V at 1073 K and 1 bar. At this particular voltage, the heat absorbed by the endothermic electrolysis reaction is compensated by overvoltages. In this mode, outlet gases (H_2/H_2O and O_2) have the same temperature as the inlet gases (H_2O/H_2).

Exothermal mode

In this operating mode, the cell voltage is above the thermoneutral voltage. Current densities imposed on the cell are higher, so that overvoltages are also higher. Heat production in the cell is higher than heat absorbed by the endothermic electrolysis reaction. Thus, exhaust gases (H_2/H_2O and O_2) have higher temperature than inlet gases (H_2O/H_2). Therefore, low temperature steam can be heated up to the electrolyser operational temperature just by the exhaust gases. As a part of the electricity is used to overheat the streams, the voltage efficiency of this mode is lower than 100%.

Endothermic mode

If the cells' voltage is lower than the thermoneutral voltage, overvoltages are also lower. Heat production in the cell is lower than heat absorbed by the endothermic electrolysis reaction. Therefore, outlet streams (H_2/H_2O and O_2) have lower temperature than the inlet gases (H_2O/H_2). Heat to reach the operational stack temperature should be provided by external heat.

As a part of the heat needed by the endothermic reaction is supplied by external heat sources, the voltage efficiency of this mode is higher than 100%. This operating mode is particularly adapted for coupling a high temperature electrolyser with an available external high temperature heat source.

2.3. System performance

Theses electrolysers can operate at high current densities (up to 1.4 A/cm^2 with 1.1 V at 800°C [5] and up to 3.6 A/cm^2 with 1.48 V at 950°C[6]). Because they are at research state, most tests have been carried out only at atmospheric pressure on planar cells so far. Tubular cells operate better at higher pressure, but research is currently focuses on planar cells, whose production capacity can be higher. The operating temperature is commonly 600-800°C. The system can reach 70% efficiency based on primary energy (considering that the production of electricity has an average efficiency of less than 40%), or 90% efficiency based on total energy input into the electrolyser[7]. The ITSE operating temperature enables ionic conductivity of the electrolyte to be high enough, and ensures high electrode reaction kinetics, so that electrode overvoltages are low compared to low temperature electrolysis.

These different elements have a notable impact on the total electricity consumption of electrolysis. Indeed, the electricity consumption is around 4.6 kWhe/Nm^3 of hydrogen with low temperature electrolysis, whereas it is 3.2 kWhe/Nm^3 of hydrogen with high temperature electrolysis in the thermoneutral mode. The consumption can even be reduced to 2.6 kWhe/Nm^3 of hydrogen in the endothermic mode according to the results of Dornier et al[8].

3. Energy conversion technologies

3.1. Solar air cooled tower

3.1.1. Description of the technology

Some current European designs use air as heat transfer medium because of its high temperature and its good handiness [9]. Another advantage of air as heat transfer medium is his freely availability, his non-toxicity, and the fact that it does not require freeze protection during times of non-operation. That is why we will use air as transfer fluid in our concept.

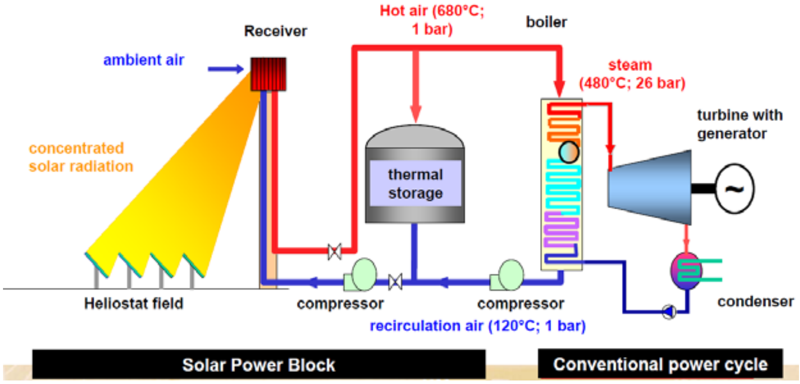

Fig. 2 Air solar power tower

3.1.2. Process design basis

In this study, a solar tower with nominal capacity between 1 and 50 MW is considered. We proposed to design two plants: one with nominal power of 10 MWe and other with nominal power of 40 MWe. The time-dependant performance for the solar collector field and the solar transients and fluctuations can be resolved by using an oversized heliostat field and making use of the excess energy to load a thermal storage system. The electricity for the electrolyser will be generated with a steam turbine for which the steam will be produced with concentrating solar energy. Power tower plants use a conventional power block and can easily dispatch power when storage is available. The thermal source of the steam generator is hot air stream at 680 ºC.

Thermal-energy storage in the power tower allows electricity to be dispatched to the grid when demand for power is the highest, thus increasing the monetary value of the electricity. Besides making the power dispatchable, thermal storage also gives the power-plant designer freedom to develop power plants with a wide range of capacity factors to meet the needs of the utility grid.

In parallel to the steam generator and receiver, the heat storage is integrated into the power cycle and implemented as an air-cooled regenerator storage. This technology stores in concrete some of the thermal energy collected by the solar field for conversion to electricity later in the day. Storage can adapt the profile of power produced throughout the day to demand and can increase the total power output of a plant with given maximum turbine capacity. With this storage type, air is in direct contact with the solid storage medium and exchanges heat as it flows along a flow-path through the storage medium.

3.1.3. Flow chart

The solar power tower consists of the following components:

- An heliostat field
- An open volumetric receiver (RECEIVER) for air heating and sweep gas generation.

The electrolyser consists of two components:

- a steam splitter (STEAMSPL), where the water splitting reaction will take place
- a membrane (MEM), where the product is split into a stream containing H_2 and H_2O and a stream containing O_2 and N_2.

Finally, the heat recovery system aims to the overheating of water steam up to the operating temperature of the electrolyser. It consists of two heat exchangers (SUPERHX3, SUPERHX 2).

The following figure shows the flow chart of the plant.

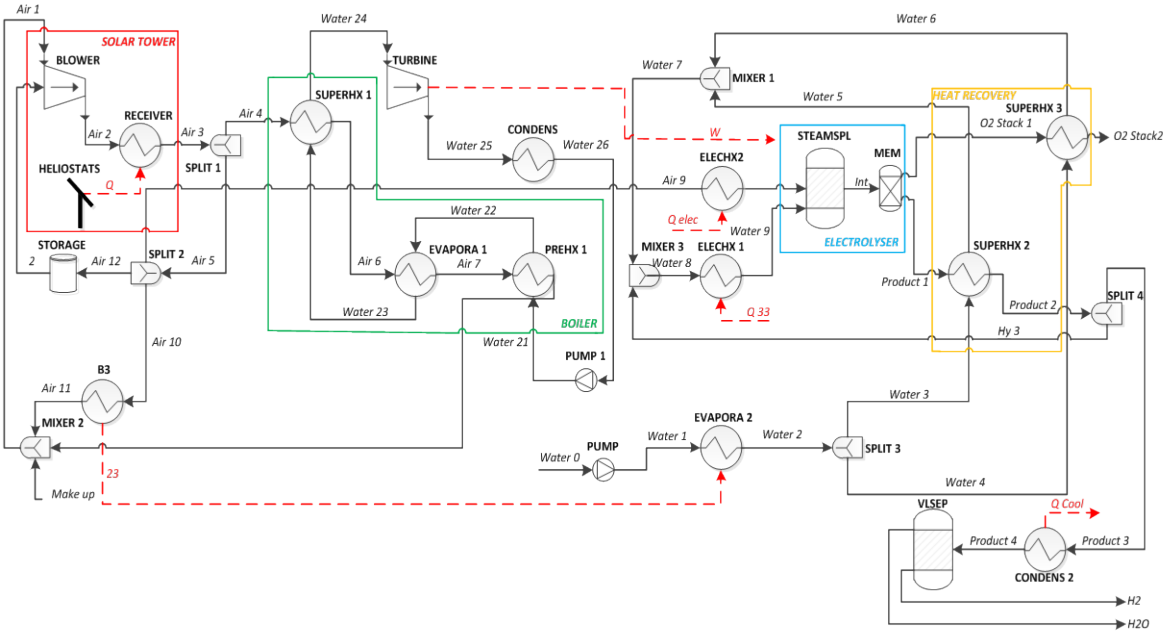

Fig. 3 Flow chart of the air cooled solar tower coupled to the ITSE

High concentrated solar radiation is used in the open volumetric receiver (RECEIVER) to produce hot air at 700 °C (*Air 3*) to generate high temperature steam in a heat boiler (BOILER). This steam is used as feed for a steam Rankine cycle (TURBINE) to generate electricity for the electrolyser.

A part of the hot air is directly sent to the electrolyser and used as sweep gas (*Air 9*) while another part (*Air 12*) is sent to the storage system (STORAGE) which is connected parallel to the boiler.

Another part of the hot air production (*Air 10*) is used to heat the water for the electrolysis water evaporation. The evaporator has been simulated as a single heat exchanger (EVAPORA2), which is connected to B3 by the read heat stream (*23*) in the flow diagram.

After the evaporation of the electrolysis water, the steam (*Water 2*) is split in the splitter (SPLIT3) into two sub-streams (*Water 3* and *Water 4*); the first sub-stream (*Water 3*) is overheated in the heat exchanger (SUPERHX2) up to 680°C by the stream (HY1) leaving the electrolyser. The second sub-stream (*Water 4*) is overheated in the heat exchanger (SUPERHX3) up to 525°C by the stream (*O2 Stack 1*). Then, both sub-streams are mixed in the mixer (MIXER 1) and the mixture is introduced to another mixer (MIXER 3), where it will be mixed with the stream (*HY 3*) in order to maintain reducing conditions at the cathode side, since it was assumed by the ADEL project-partner that the stream (*Water 8*) has to contain 10mol%H_2.

An electrical heater (ELECHX) is necessary in order to rich the operating temperature of the electrolyser. A second electrical heater is added to heat the sweep gas up to 700°C if it is necessary for the transient conditions. Thus it enables to control the sweep gas temperature and to guarantee fixed conditions for the sweep gas in the electrolyser. The electrical air and steam heaters are modelled as heaters receiving heat, which is considered to be a realistic representation since virtually all electric power supplied will be dissipated as heat.

The first simulation results show that the quantity of sweep gas and the ratio sweep gas: steam is a very important factor for the process efficiency. In an optimized case, an efficiency of 62% for a 10 MWel plant was reached.

3.2. Direct Steam Generation Central Receiver System, DSG-CRS

Different integration schemes for water/steam cooled receiver system have been analyzed within ADEL project. The variables analyzed in the study were the electrolyser steam generation system, thermal energy storage, and steam conditions and design of the Rankine cycle.

As can be seen in the Figure 4, thanks to the heat recovery system of the exhaust gases, the feed water stream required by the ITSE can be preheated, and superheated up to 660 ºC. Thus, external heat input is limited to the evaporation step, and a last superheated step to increase the stream inlet temperature to the nominal operational temperature of the electrolyser. On the other hand, the sweep gas stream, air in this case, is heated by the exhaust sweep stream up to 680 ºC, requiring a last heater to overcome the driven temperature difference of the heat recovery system. Both streams include an electrical heater to carry out the last heating step. To evaporate the water stream two options were proposed, direct evaporation into the receiver at the top of the tower, and using steam extracted from the power block as heat source of a heat exchanger. A low fraction of steam is extracted from the low pressure turbine, and sent to a thermal Phase Change Material (PCM) storage tank. Steam is there condensed, and the PCM melted. Through a secondary line, the electrolyser water stream is fed at 90 ºC, and evaporated by the solidification of the PCM. Through this system a higher temperature difference between steam and water is required, but heat is stored at the same time. Thereby the hydrogen production plant is able to work even when the DSG-CRS plant is shut down, running with power from the Grid. Thus, the power/hydrogen production plant can be used as an active Grid buffer.

Seven different Rankine cycles have been compared for DSG-CRS plants which capacities are 10 and 50 MWe. Steam conditions have been varied from saturated to superheated condition; and reheat and no-reheat turbine have been analyzed. In every case, the reduction of the DSG-CRS performance when integrating the ITSE Unit has been lower than 4 %.

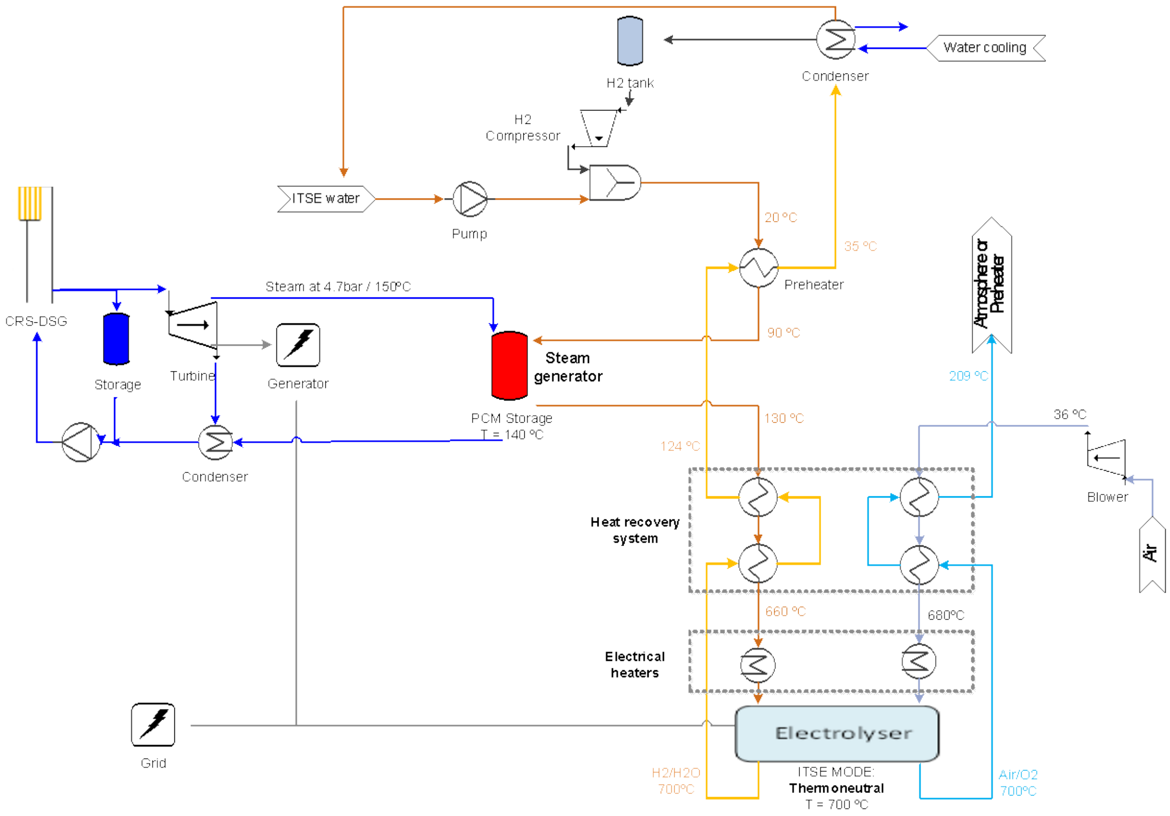

Fig. 1 Flow diagram of the integration of ITSE into a DSG-CRS

3.3. Molten salt tower system

The third option analyzed was the integration of the ITSE Unit with a molten salt tower plant. Molten salt-cooled central receiver plant has two heat transfer fluid loops, which decouples the steam generation from the collector subsystem and makes possible the integration of high capacity thermal energy storage. Therefore, the ITSE can operate under high stable steam and electricity conditions. Thanks to long-term thermal storage system, which normally is integrated in these kinds of plants, it is possible to operate round-the-clock in summertime, leading to an annual capacity factor of 74%. Therefore, these plants can be designed easily for both cases: stand-alone hydrogen production plants or grid stabilizer as a power sink at low demand periods.

The temperature range of this kind of plants is between 565 ºC in the hot tank, and 290 ºC in the cold tank. The cold tank is kept 70-40 ºC above the salt mixture freezing point, 220-250 ºC. Steam temperature at the inlet of the electrolyser system must be at 130 ºC. Therefore, it could be possible to feed the ITSE steam generator with cold molten salt. In this way, temperature difference between hot and cold streams of the steam generator is reduced, maximizing the exergy efficiency of the process. However, it should be kept in mind that solidification must be avoided and therefore, molten salt cannot be cooled down below a limited temperature, higher than freezing temperature. The temperature reduction achieved by the cold molten salt through the steam generator depends on the salt mixture quality, its design cold temperature, and the required steam mass flow. The proposed scheme for the integration of the ITSE into a molten salt power plant is shown below.

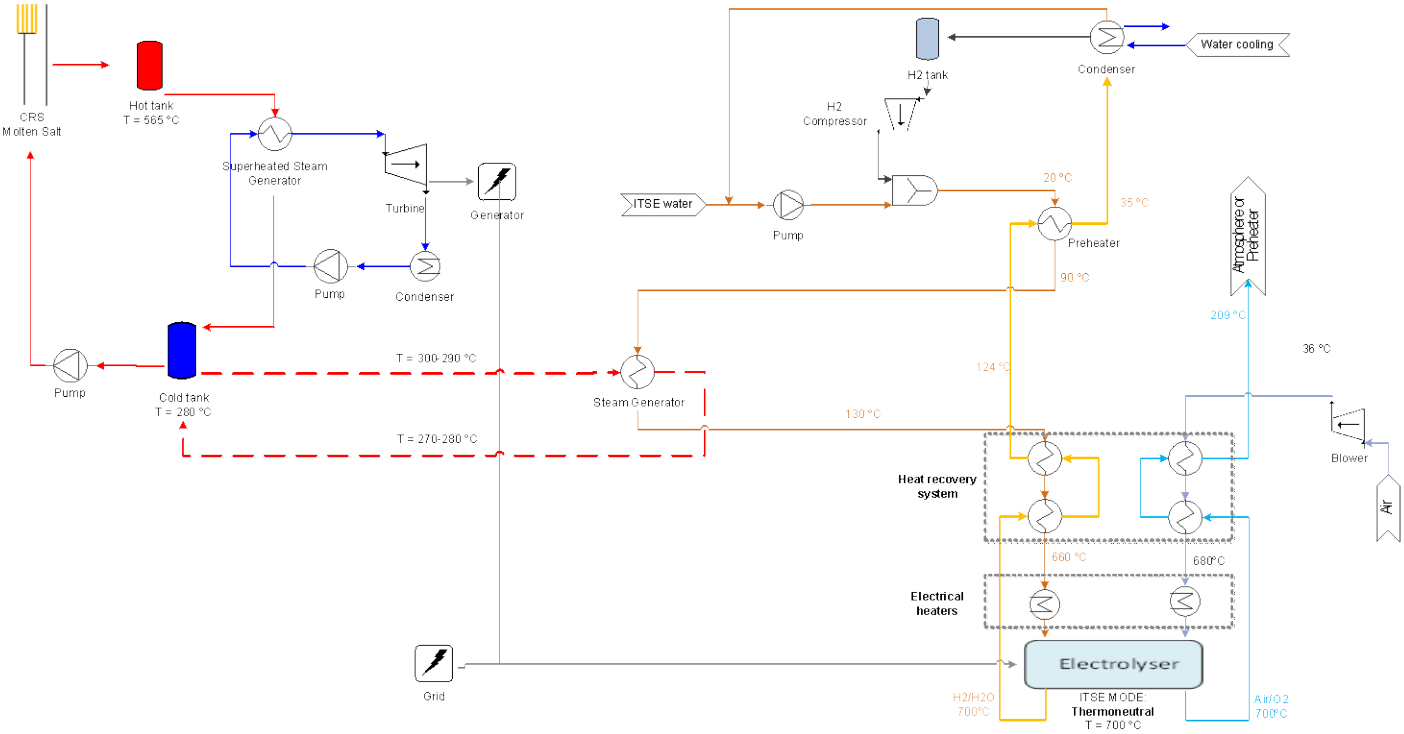

Fig. 5. Flow diagram of the integration of ITSE into a DSG-CRS

3.4. Nuclear Pressurized Water Reactor, PWR

Another energy source selected consists of a nuclear reactor, which has a high degree of availability and is a reliable source of energy. Coupling a reactor and an electrolyser, without any other power source, also requires installing a power block that uses part of the heat from the reactor to generate the electric power needed for the electrolyser. How to produce this electricity involves choosing the proper power block, and this decision is mainly restricted by the reactor technology chosen and how it is coupled with the electrolyser system.

Choosing a Pressurized Water Reactor (PWR) makes it impossible to take the heat directly from the reactor to the electrolyser, due to the outlet temperature from the reactor. That way, a typical steam cycle is considered for a PWR reactor that will extract the electricity demanded by the electrolyser. Furthermore, in this case, the only feasible option is to transfer heat to the electrolyser system from one of the extractions of the low pressure turbine in that cycle, and choosing a suitable pressure for it accordingly. It will therefore be necessary to have an electrolyser system that includes regeneration and electric heating in order to reach the 700ºC as required.

It would be a steam cycle saturated at 70 bar at the inlet to the high pressure turbine, where it would expand up to 12 bar. This would also be the pressure of the deaerator fed from the outlet of that HP turbine. In addition, the discharged steam would go to the required moisture separator (the steam would exit the high pressure turbine at too low a quality to keep it expanding in the low pressure turbine), and then undergo double heating with steam taken from the high pressure turbine and with main steam. The reheated steam then goes to the low pressure turbine and condenses. A pump pumps the condensate through the train of low pressure pre-heaters and on to the deaerator. The deaerator drainage is pumped by the feedwater pump to the train of feedwater pre-heaters and finally enters the reactor steam generator. To do this, a configuration was chosen consisting of two extractions from the high pressure turbine (two high pressure pre-heats) and three extractions from the low pressure turbine to do three low pressure pre-heats. In addition, there is also a first extraction just at the inlet to the turbine for the thermal demand of the electrolyser system.

The most efficient way to produce H_2 using a constant power source, as a nuclear reactor, to feed a variable sink of energy is to connect the power cycle to the grid, which will absorb the surplus of energy. At the electrolyser operation temperature (700ºC), the ratio heat to electricity demanded is 20 to 80. The content of hydrogen obtained is 63 % at the electrolyser outlet, which means, 694.5 kg / h of hydrogen produced at the chemical plant.

The proposed scheme for the integration of the ITSE into a nuclear pressurized water reactor is shown below.

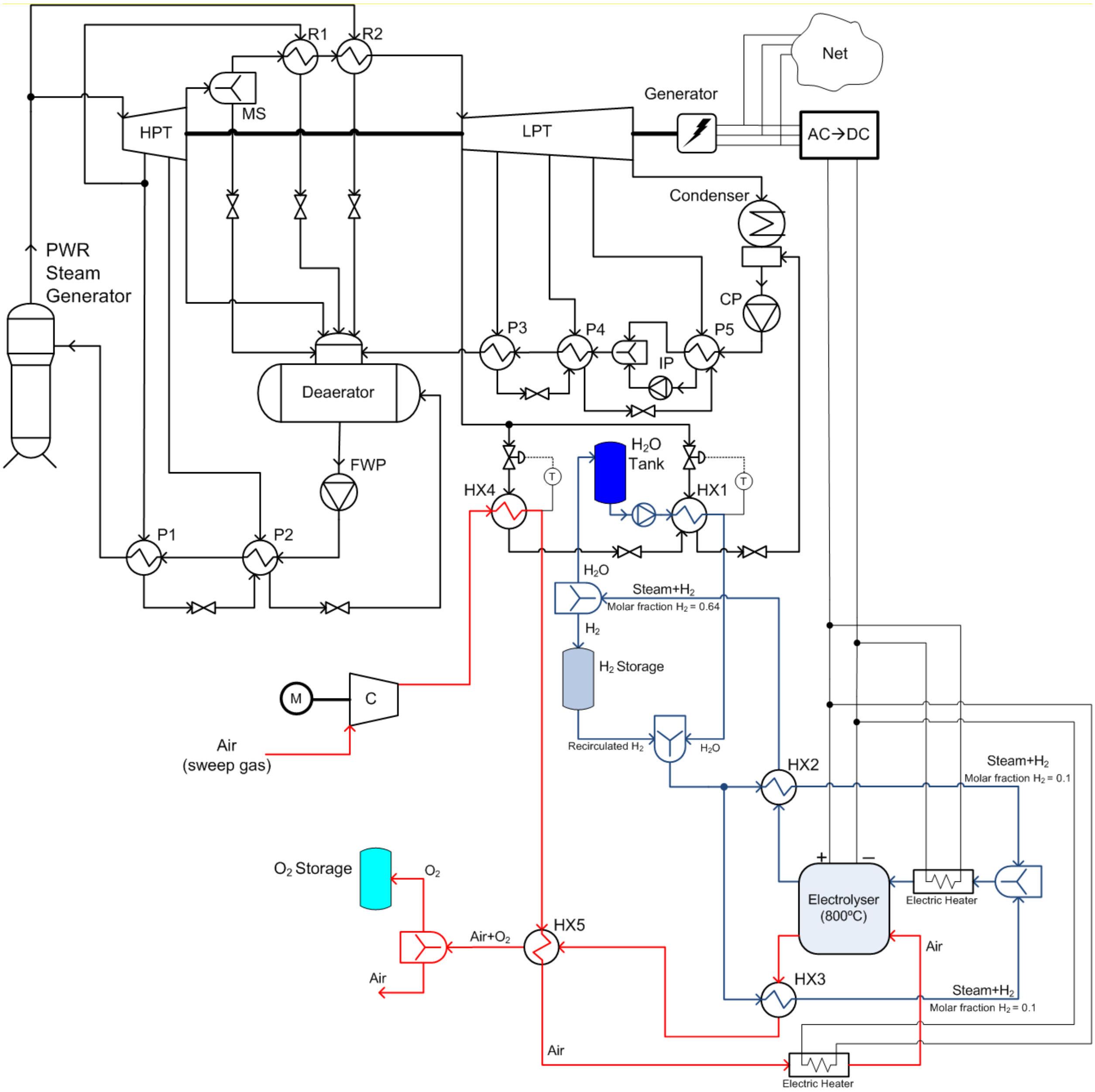

Fig. 6 Flow diagram of the integration of ITSE into a PWR reactor coupled with the steam cycle

4. Conclusion

The coupling of the solar central receiver systems and the nuclear pressurized water reactor with an ITSE Unit has been analysed.

The solar tower technology with ambient air as heat transfer fluid has been analyzed. As the air is heated in the receiver up to similar temperature than the ITSE operational temperature, 700 ºC, it can be used directly as sweep gas in the electrolyser.

Central receiver systems with direct steam generation have been investigated. Seven different Rankine cycles have been analyzed. The integration of the ITSE into the solar power plant has a low influence, reducing less than 4% the performance of the DSG-CRS.

In relation with nuclear energy, a conventional light water reactor (PWR) has been studied. It is concluded that the most effective way to produce hydrogen using a constant power source, as a nuclear reactor, is providing energy to the grid and the hydrogen plant at the same time. With this design, it would be possible to regulate the output to the grid varying the production of hydrogen.

In following phase of the project the influence of transients on process performance and on operational strategies will be analyzed by dynamic simulation. For some representative scenarios a site and its boundaries will be selected. For such cases the set-up of the real plant and the evaluation of energy efficiencies and performance under transient conditions will be analyzed to get a refined view on the future potential of the technology.

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