REACTOR DESIGN AND PROCESS SIMULATION OF A TWO-STEP THERMOCHEMICAL CYCLE FOR SOLAR HYDROGEN PRODUCTION FROM WATER

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Abstract

This present study is related to the European research project HYDROSOL 3D and aims to design a new reactor with 1 MW_{th} thermal input based on the experimental experiences with a reactor developed and tested in the previous projects HYDROSOL I and II. The first part of this study aims at the design of the overall process by taking into account all process units such as heat exchangers, compressors, hydrogen separation unit etc. Once the whole process is defined, the simulation of the process is carried out in order to calculate the efficiencies of the components and the overall efficiency of the system based on an exergy analysis. The results of the simulation will be the basis to identify possible improvements and serve as input for the components sizing and cost estimation of the solar hydrogen production. The second part of this study consists of the design of a new reactor for the HYDROSOL 3D process in order to increase the efficiency by minimizing the re-radiation losses.

Keywords: solar, hydrogen, thermochemical, two-step cycle, process simulation, exergy analysis

1. Introduction

A very promising pathway for the solar production of hydrogen is solar water splitting via a two-step thermochemical cycle using a metal oxide redox system. The main advantages of this process are the avoiding of electrochemical steps requiring expensive electrical power and the avoiding of the H_2/O_2 separation problem since the oxygen is being fixed by the metal oxide. Furthermore, lower temperatures are required for the reaction and the regeneration step as compared to the direct water thermolysis. Thermochemical cycles aim to decompose water into its main parts, hydrogen and oxygen. A benefit of the thermochemical cycles is the moderate operating temperature, which is much lower than the direct water splitting.

The process heat for the thermochemical cycle can be provided by solar concentrating systems [1, 2]. Temperatures of up to 2000°C can be achieved. The usage of solar heat to run a two-step cycle has been proposed by Nakamura [3]. The considered redox system was Fe_3O_4/FeO, which allows hydrogen generation through a redox reaction according the following equations:

$$H_2O + MO_{red} \longrightarrow MO_{ox} + H_2$$

$$MO_{ox} \longrightarrow MO_{red} + \frac{1}{2}O_2$$

The water decomposition occurs at a low temperature in the range of 500 to 800°C by reacting with the reduced form of the oxide MO_{red} and leads to the formation of the oxide MO_{ox} and H_2. The reduction of the oxidised form of the oxide MO_{ox} , which is highly endothermic, proceeds at temperatures above 1400°C. The list of redox pairs, which can be used, is long consisting of oxide pairs of multivalent metal oxides. Prominent examples are iron oxide Fe_3O_4/FeO [3, 4], manganese oxide Mn_3O_4/MnO [5], cerium oxide CeO_2/Ce_2O_3 [6] or metal oxide/metal pairs like zinc oxide/zinc ZnO/Zn [7, 8].

1. Plant design

A first design concept of the solar thermochemical process for the water splitting has been performed. Figure 1 shows the plant designed for a thermal input of 1MW. The designed plant includes the solar hydrogen reactor and all necessary upstream and downstream units needed to feed in the reactants and separate the products. Figure 3 shows the assembly and the piping of the reactor chambers on the solar tower platform and the peripheral components. By passing a pipe, water flows into the preheater (1), where it is heated from about 35 °C to about 80 °C by heat recovery from the returned product gas. After this, the preheated water is divided and streams into two separate vaporizers. The heat demand of one of the vaporizers (2) is covered by the heat content of the product, the other one (3) by hot air from the volumetric thermal receiver (7). The two streams of steam are merged and led into the super heater (4). At this point, the water steam is overheated by hot air from the volumetric receiver (7).
A 4/2-way valve, upstream the reactor inlet piping (5), ensures that the regenerating reactor group is fed with nitrogen during the injection of the overheated steam in the other reactor group (8/9). The outlet piping converges in another 4/2-way valve (6). The gas mixture, built up of water steam and hydrogen that was generated during the water splitting process, is led through the vaporizer 2 and the preheater. The gas from the regenerating reactor group is released into the environment, because separation into the components oxygen and nitrogen is considered too expensive.

The product gas consists of hydrogen, nitrogen and water steam. A condenser liquefies the water steam. By that means the water is separated from the remaining components. The condensate is returned to the water tank, which feeds the reactors. The cooling water has an own circuit. The nitrogen is separated by a PSA unit (Pressure Swing Adsorption) from the hydrogen. Two floors below the reactor chamber two buffer containers are located, which compensate pressure surges in pumping fluids and to ensure a continuous flowing (see Figure 2).

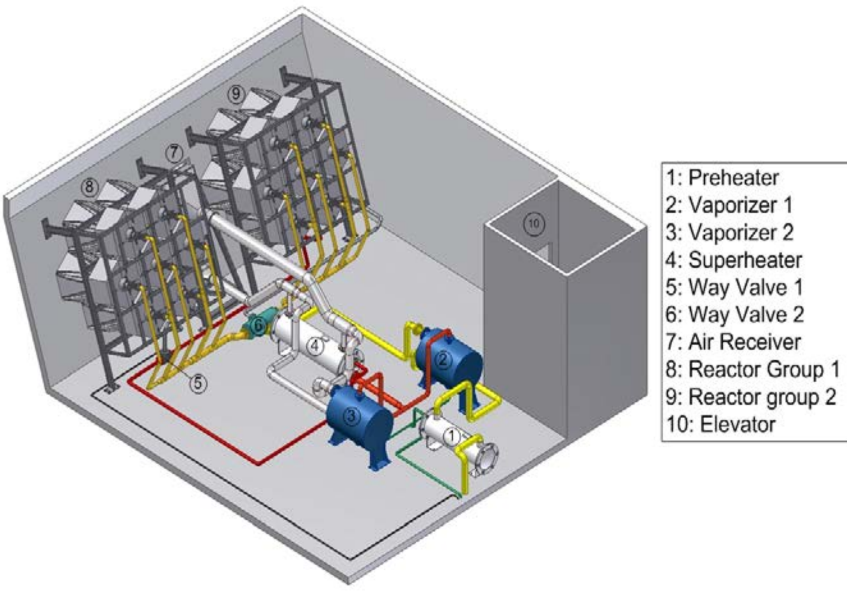

Figure 1: Plant design inside the tower platform

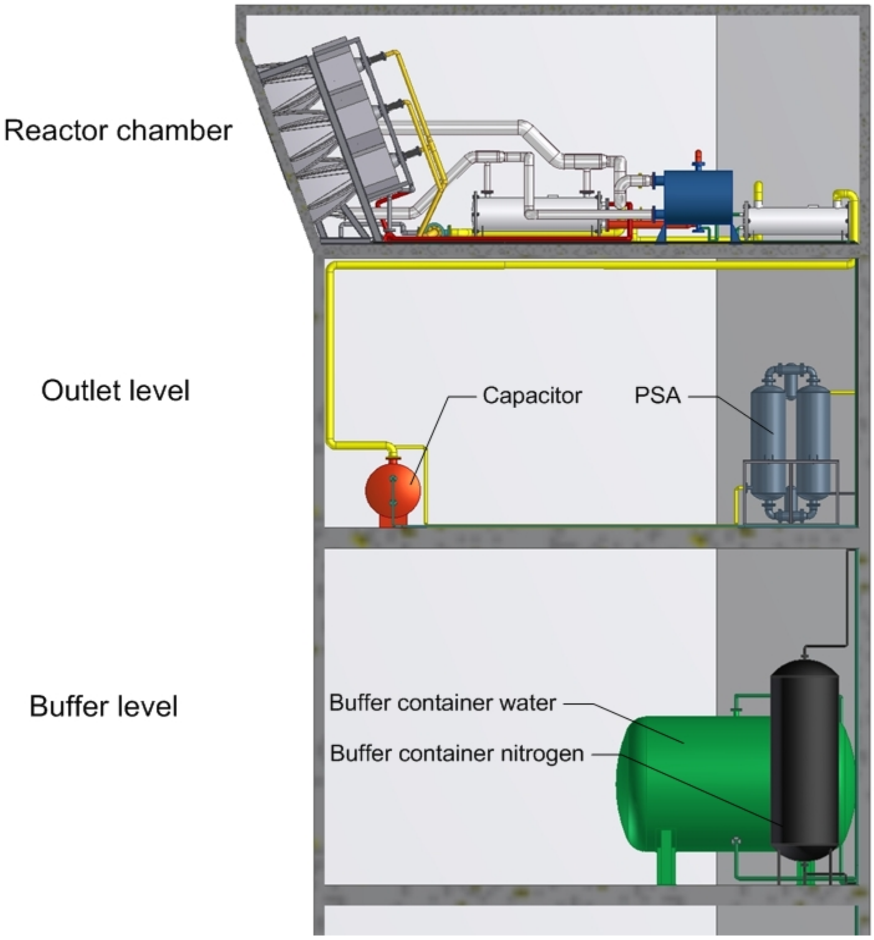

Figure 2: Sectional view of the greenfield plant

2. Process simulation and exergy analysis

2.1. Process simulation

The steady-state simulation of the processes has been carried out by using the commercial simulation tool Aspen Plus, which is a well-known environment for flow charts of chemical processes. The following Figure 3 shows the flow sheet of the process.

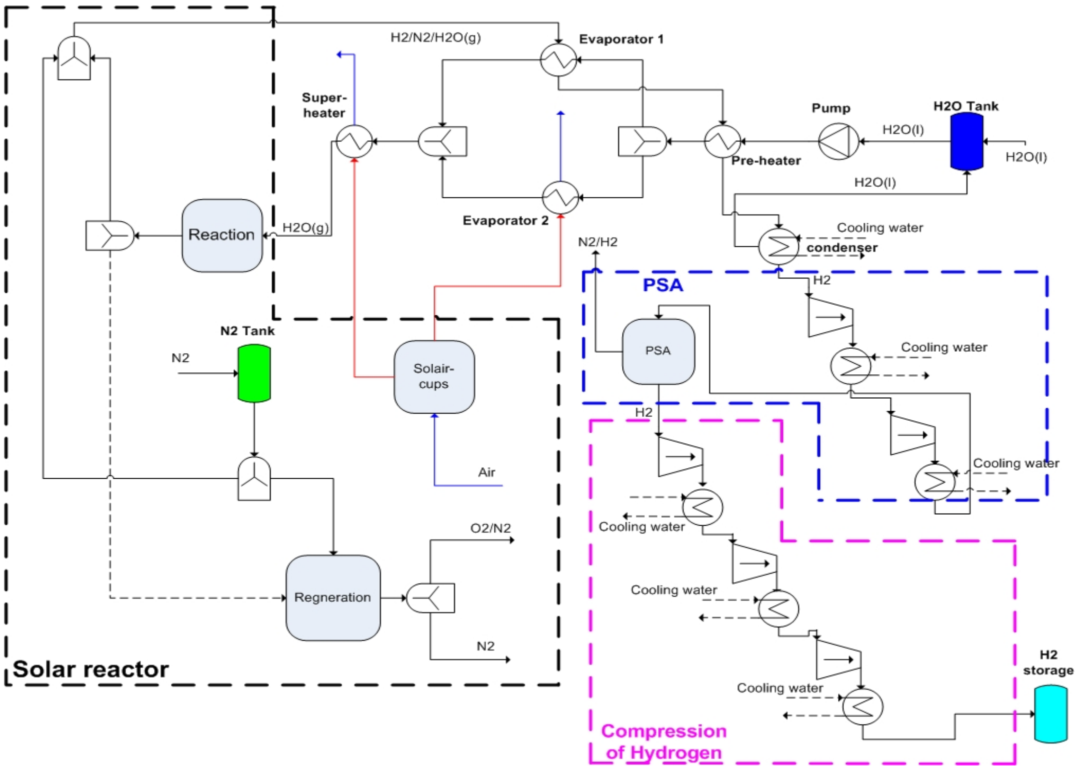

Figure 3: Flow sheet of the process

Demineralized water is fed to the pre-heater at 25°C and is heated up to 76°C. The H_2O stream is split into two sub-streams for evaporation: the first sub-stream will be evaporated by heat recovered from the product gas, which leaves the solar reactor and the second sub-stream will be evaporated by heat from the heat transfer medium air, which is heat in the solar cups of the receiver. Overheating of the water stream is required. Therefore a part of the air heated in the solar cups is led to the super-heater. The product gas contains water steam, which has to be removed in the condenser. After condensation of water, the product gas mainly contains hydrogen and nitrogen. Since the operating pressure of the PSA is 15 bar, the compression of the H_2/N_2 mixture from 1 up to 15 bar is required. The compression takes place in a 2-stage compressor with inter-cooling. The compression ratio of each compressor is 3.89 with an isentropic efficiency of 0.69. The hydrogen will be stored in a tank at 350 bar. In order to achieve this goal, a compression in a 3-stage compressor with inter-cooling is required. Each compressor has a pressure ratio of 3.08 and an isentropic efficiency of 0.69.

3.1. Exergy analysis

Exergy analysis is commonly used to quantify and localize the thermodynamic losses in industrial processes. The process components, which exhibit the most important influence on the heat balance, can be identified so that potential measures can be taken in order to improve the efficiency of the overall process. Based on the simulation results carried out with ASPEN Plus, an exergy analysis of the process has been performed. The exergy analysis identifies the location, the magnitude and the sources of thermodynamic inefficiencies in a thermal system[9] . This information cannot be provided by other means (e.g. an energy analysis). The exergy efficiency of each component has been calculated according to the next equation [10]:

$$\varepsilon_k = \frac{\dot{E}_{P,k}}{\dot{E}_{F.k}} \qquad \text{Eq. 1}$$

Here, $\dot{E}_{P.k}$ and $\dot{E}_{F,k}$ denote the exergy streams of the product and the exergy stream, of the fuel. The rate of exergy destruction in the *k*th component is given by:

$$\dot{E}_D = \dot{E}_{F,k} - \dot{E}_{P,k} - \dot{E}_{L,k} \qquad \text{Eq. 2}$$

Here $\dot{E}_{L,k}$ represents the exergy loss in the k^{th} component, which is usually zero when the component boundaries are at T_0. For the overall system, the exergy loss includes the exergy flow rates of all streams leaving the system. In addition to ε_k and $\dot{E}_{D,k}$ **,** the thermodynamic evaluation of a system component is based on the exergy destruction ratio $y_{D,k}$ **,** which compares the exergy destruction in the *k*th component with the fuel supplied to the overall system $\dot{E}_{F,tot}$ **:**

$$y_{D,k} = \frac{\dot{E}_{D,k}}{\dot{E}_{F,tot}} \qquad \text{Eq.3}$$

The percentage of the decrease in the overall exergetic efficiency due to the exergy destruction in the *k*h system component is given by the following equation:

$$\varepsilon_{tot} = \frac{\dot{E}_{P,tot}}{\dot{E}_{F,tot}} \qquad \text{Eq.4}$$

The following Table 1 shows the results of the exergy analysis.

Process unit	$\dot{E}_F$ **[kW]**	$\dot{E}_P$ **[kW]**	$\dot{E}_D$ **[kW]**	ε_K **[%]**	y_k **[%]**
Solar reactor	896	283.05	612.95	31.59	60.51
Preheater	3.26	1.26	2	38.65	0.19
Evaporator 1	35.89	14.02	21.87	39.06	2.15
Evaporator 2	41.03	20.59	20.44	50.18	2.01
Super-heater	4.69	3.97	0.7	84.64	0.001
PSA	16	3.84	12	23.92	1.18
Hydrogen compression	16.04	7.06	8.98	44.01	0.88
Overall system	1012.95	333.79	679.16	32.95	

Table 1: Results of the exergy analysis

With the aid of the exergy analysis, the thermodynamic inefficiencies of the process and the amount of the exergy destruction in the system have been determined. The result shows that the solar reactor is responsible for almost 60% of the exergy destruction within the process. Other components such as heat exchangers, compressors and hydrogen separation unit contribute to a very small extent to the overall thermodynamic inefficiencies of the process. Therefore, the solar reactor is selected as the first improvement option.

3. Solar reactor

The solar reactor, which has been considered in this study, has been developed within the projects HYDROSOL I and HYDROSOL II. The reactor contains neither moving parts nor moving solid particles as compared to other reactor configurations, but the issue of continuous production of solar hydrogen has been resolved with a modular dual-chamber fixed honeycomb absorber design and implementation (so-called Conti reactor). This modular set-up allows for a continuous provision of solar hydrogen, because one part of modules splits water while the other is being regenerated. After completion of the reactions, the regenerated modules are switched to the splitting process and vice versa by switching the feed gas.
Within HYDROSOL II, the “Conti” reactor was chosen as a starting point and a sound base for the design of the pilot reactor. The 100 kW_{th}-scale reactor consists of two adjacent but separated reaction chambers that represent the minimum array of modules suitable for continuous hydrogen production. Scale up to 100 kW_{th} was implemented mainly by increase of absorber surface realized by setting up the absorber of individual pieces of square-shaped monoliths.
In order to decrease the exergy destruction in the solar reactor, modifications of the design of the solar reactor have to be carried out. A key issue is to decrease the radiations losses in the reactor since the exergy destruction is related to the thermodynamic losses, which occurs in the solar reactor.
The new reactor concept consists of the following main parts:

- The outer hull, which holds the insulation material;
- The reactor body shall be the outer part of the reactor, hence holding the parts together. In addition, it shall be the boundary between the feed fluid and the environment.
- The middle hemisphere separates the feed from the outgoing fluid. In this part, there is an additional heat exchange between the feed and the outlet.
- The inner part is the holding structure for the coated honeycombs. It consists of one hemisphere, which holds the structures and carries out a good distribution for the outlet gas stream.
- The front plate of the reactor, whereupon the inlet absorber cup holding structure is welded on. In this part, the quartz window is located, too. Furthermore, this is the bearing part of the reactor.

A sectional view of the reactor body is shown in Figure 4.

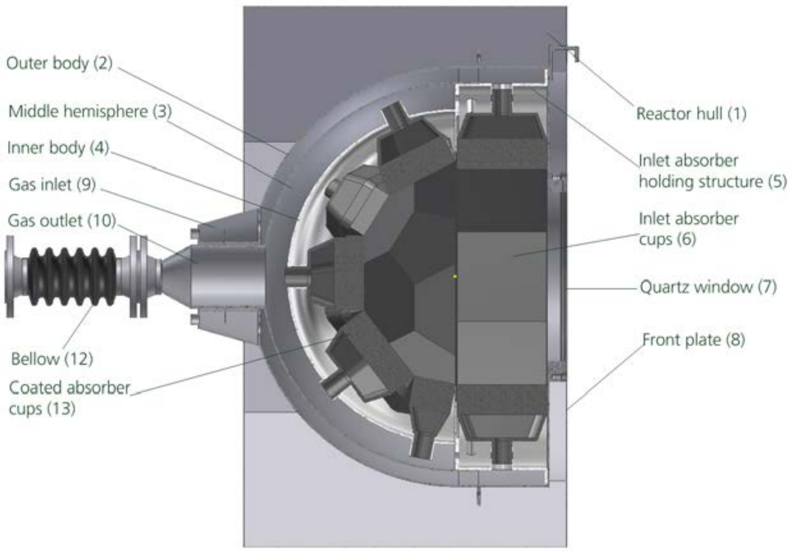

Figure 4: Sectional view of the solar reactor model

The fluid flows through the inlet ring (9), which surrounds the outlet pipe. For a most homogeneous current inside the gas lead, there are baffle plates installed. The gas stream is led through the outer body (2) and the middle hemisphere (3) towards the inlet absorber (5&6). In this streaming, a first heat exchange is taking place between the outgoing and the incoming fluid. Furthermore, the inlet fluid acts as a heat shielding between the hot inner part and the outer part. So the 800 °C (or 1200 °C) are not wasting their energy in heating up unneeded parts. After this, the fluid is further heated up in the inlet absorber, because some irradiation hits these cups. The fluid streams inside the chamber between the quartz window (7) and the coated absorber cups (13). At this place the irradiation hits the gas directly before it streams inside the coated absorber cups. At this point the reaction takes place. This means that the water steam will be split into Hydrogen, which streams to the outlet and into the oxygen, which is bonded in the metal oxide coating. The Hydrogen streams together with the unreacted water steam between the inner body (4) and the middle hemisphere (3), where it is the hot part of the heat exchange to the inlet gas. After this process the product gas leaves the reactor at the outlet (10) through a pipeline to the periphery. The bellow (10) is used to compensate thermal expansion of the reactor and the pipeline.
The separate parts are almost all assembled by screw-fixation. This means that they are able to move while the thermal expansion takes place, but the parts are generally immobile. This is needed to make sure that an easy disassembling can be carried out. The insulation hull consists of three different parts. One is the front plate, which is directly fixed on the reactor front plate by screws, only a quite small space is left for the insulation material. The hull itself is divided into two equal parts, which are fixed by screwing and clip collars to each other and to the front plate. The reactor main body is assembled to the front plate by a flange connection. The inlet holding structure is welded onto the front plate and has the shape of a Z-profile, because of the high stability. The inlet absorber cups are fixed with a spring ring to stainless steel tubes in the holding structure. On top of the holding structure, the middle hemisphere is radially connected with screws.

The coated absorber cups are equally fixed onto the inner body by spring rings. This fixation has been proofed within the HitRec concept.[11] The outlet pipe is flanged at the middle hemisphere and has a breakthrough through the outer body, where the inlet pipe composes the outer ring. Afterwards, the bellow is flanged alike.
The inlet absorber cups have a square shape to assemble a good ring structure. The coated absorber cups are of three different shapes for having a most spherical structure, the so-called “football shape”. The three shapes are pentagonal, hexagonal and half hexagonal. The football shape counts to the Archimedean solids and is calculated based on these functions for assembling.
A main objective of this new design was to lower the heat radiation losses through the window. In the earlier versions of the reactor[12] the window had the same size as the absorber. Due to the relative large surface of the absorber the radiation losses were very high. Therefore, calculations with MATLAB were carried out to determine the preferable ratio between absorber size and window size. Furthermore, the absorber shape has been changed from rather flat to a distinct bowl-shape. By this the reactor rather forms a cavity. Both changes lead to a strong decrease of thermal radiation to the environment. To realise a smaller inlet aperture, a secondary concentrator is needed. This device is not only used for narrowing the aperture but also for homogenization of the solar flux impinging on the absorber. Some results of this calculation are shown in Figure 5.

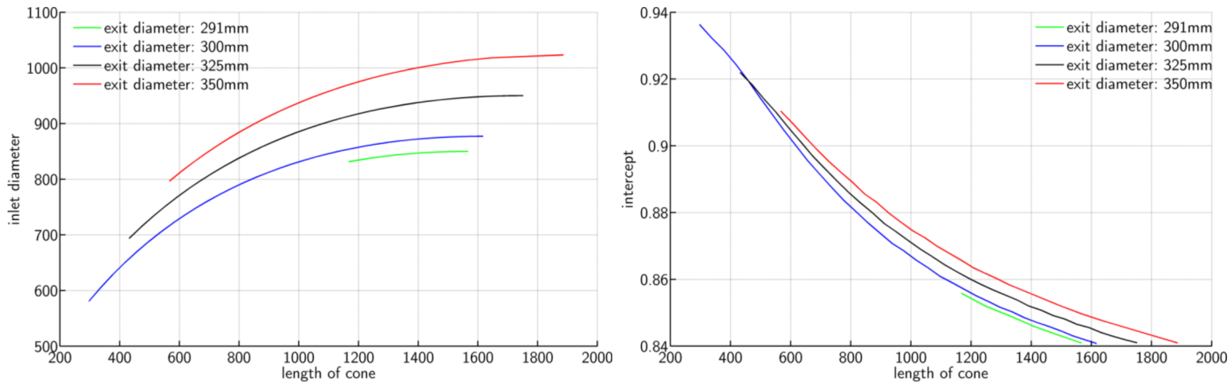

Figure 5: Calculation of the inlet and outlet diameter

As the curves in Figure 5 suggest, the exit diameter of about 290 mm provides a suitable ratio between the intercept and the length of the cone. The inlet diameter was set to 800 mm because of limitations concerning the size of the reactor hull. Consequently, the length of cone was determined to be about 1200 mm.

4. Conclusion

Tthe whole plant was laid out. That means the storage tank and their shape, the power supply by open volumetric receiver, the piping, the evaporation process and the secondary concentrators combined with the solar receiver-reactor modules have been integrated in a flow sheet. The power and/or heat for preheating, evaporation and superheating have been calculated. The piping, storage tanks, the heat exchanger, the reactor modules, the separation and storage of the product gas have been laid out.

In a further step, an exergy analysis has been carried out. The analysis shows that the solar reactor has the highest exergy destruction value (~60%) due to high operational temperature and due to the nature of two-step process (water splitting and regeneration). The evaporators are ranked in the second place according to their contribution to the exergy destruction of the overall system due to the heat transfer on a low temperature level. In comparison the super heater has very small contribution due to the heat transfer on higher temperature level.

Based on the original concept of the EU-founded HYDROSOL project series, a new reactor has been designed in order to decrease the exergy destruction. An optimization of the reactor shape has been carried out such that the heat losses are much lower than in earlier versions of the reactor. This is mainly because of the smaller ratio between the quartz window and the absorber surface. Another point for the reduced radiation losses is the cavity design. The spherical shape of the absorber and a suitable secondary reflector ensure a more homogenously distributed solar flux and there therefore a more homogeneous temperature distribution than in previous version which exhibited a flat design of the absorber. Furthermore, the whole reactor set-up and all components were designed in a way allowing easy maintenance and replacement of parts, in particular of the individual absorber monoliths. To ensure the reliability of the design it was supported by calculating the thermo-structural behaviour of the reactor and heat losses by conduction, irradiation and convection.

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