

Carbon-free Production of Hydrogen via the Solar Powered Hybrid Sulfur Cycle: the SOL2HY2 Project

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This paper presents an overview of the activities carried out during the first half of the SOL2HY2 project. In particular, this paper is focused on the activities carried out by ENEA within the consortium, namely: elaboration of general plant concepts, integration of the hydrogen production plant with a concentrated solar power (CSP) plant, development of the catalyst for SO₃ decomposition and selection and design of balance of plant (BoP) units.

1. Introduction

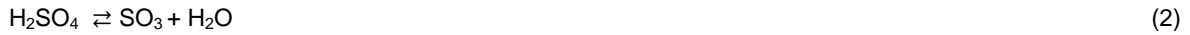
Hydrogen production through water splitting thermochemical cycles powered with renewable energy represents the concrete possibility of obtaining an actually carbon free fuel. While since the 80's several thermochemical cycles have been proposed in the literature, only few of them appear today as industrially feasible. Among these, the Hybrid Sulfur (HyS) cycle is considered to have a particularly high potential, as reported by the Hydrogen Initiative the US Department of Energy (Corgnale and Williams, 2011). However, the HyS cycle was initially conceived to be powered by high temperature nuclear heat and several technological and process challenges must be faced in order to replace the continuous nuclear source with an intermittent renewable one, such as solar power.

SOL2HY2 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). The project focuses 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 and the reactor for solar-powered SO₃ decomposition. The project focus is complemented by the advanced modelling and processes simulation with condition-specific technical-economical assessment, optimization, quantification and evaluation.

This paper reports a summary of the results achieved during the first half of the SOL2HY2 project, which involve general flowsheeting aspects and all the key components of the process. In particular, this paper is focused on the activities carried out by ENEA within the consortium, namely: elaboration of general plant concepts, integration of the hydrogen production plant with a concentrated solar power (CSP) plant, development of the catalyst for SO₃ decomposition and selection and design of balance of plant (BoP) units.

2. General plant concepts and integration with solar energy

Hybrid Sulfur (HyS) is a water splitting cycle proposed for hydrogen production from water. As all cycles of the sulfur family, HyS allows to obtain the decomposition of water into hydrogen and oxygen through the following set of reactions (see Figure 1):



Compared to other purely thermochemical cycles of the sulfur family such as the Sulfur-Iodine cycle, the HyS cycle does not use only heat as energy input, but also electric power. Indeed, in the HyS cycle, reaction (1) is carried out electrochemically in the Sulfur dioxide Depolarized Electrolyzer (SDE). The standard cell potential for reaction (1) is about 85% lower than water electrolysis, which possibly implies a significant reduction of the electrical power required. The sulfuric acid (SA) produced in the SDE is concentrated and sent to the Sulfuric Acid Cracker (SAC) section. Here, the liquid SA solution is firstly completely evaporated and heated at a temperature above 850°C (at which reaction 2 goes to completion) and then fed to the SAC, where reaction 3 is catalytically carried out. At practical SAC operating temperatures, the conversion of reaction 3 is thermodynamically limited; therefore, downstream of the reactor, unreacted SO₃ is separated and recycled into SAC's feed. Furthermore, the produced O₂ is separated from SO₂ in order to close the cycle and recover a valuable co-product. The thermal energy input in the HyS cycle is mainly required for sulfuric acid concentration, evaporation, pre-heating and decomposition.

The HyS cycle was originally conceived to use continuous high temperature waste heat from nuclear plants as thermal input (Gorensek, 2011). The SOL2HY2 process aims at developing a solar-powered version of the HyS cycle, by using concentrated solar power (CSP) to fulfil the heat demand of the chemical hydrogen production plant. The issues related to the use of a discontinuous source such as solar power were addressed by dividing the chemical plant in two sections with different operating regimes: one discontinuous section, which basically includes the SAC block (i.e. SA vaporization, pre-heating and cracking) and SO₃ separation, and a continuous section, which includes the remaining units. The discontinuous section requires high temperature (>550°C) heat, which cannot be efficiently stored with the heat storage technologies currently used in CSP plants; therefore, this section is only operated at daytime, when solar radiation is available. On the other hand, the continuous section requires electric power and medium temperature (<550°C) heat. For this temperature range, several years of investigations on CSP technology proved that molten salt mixtures can be efficiently used as heat transfer/storage media: with proper sizing of the solar field and storage tanks, molten salt based CSP plants can smoothly provide heat also at night-time. Therefore, the continuous section can be coupled with a molten salt system and work continuously without requiring daily start-up and shut-down operations. Indeed, the use of molten salt heating to ensure continuous operation of a solar-powered hydrogen production process was already considered previously (Giaconia et al., 2013).

In order to ensure the highest efficiency for the CSP plant, two different solar collection systems were considered: parabolic solar trough for medium temperature heat and central solar tower (Romero and Steinfeld, 2012) for high temperature heat. The medium temperature CSP plant can also be coupled with a power block to produce electricity in order to completely fulfil the energy requirements of the hydrogen production plant. Thus, the SOL2HY2 plant can potentially produce hydrogen by using only renewable energy.

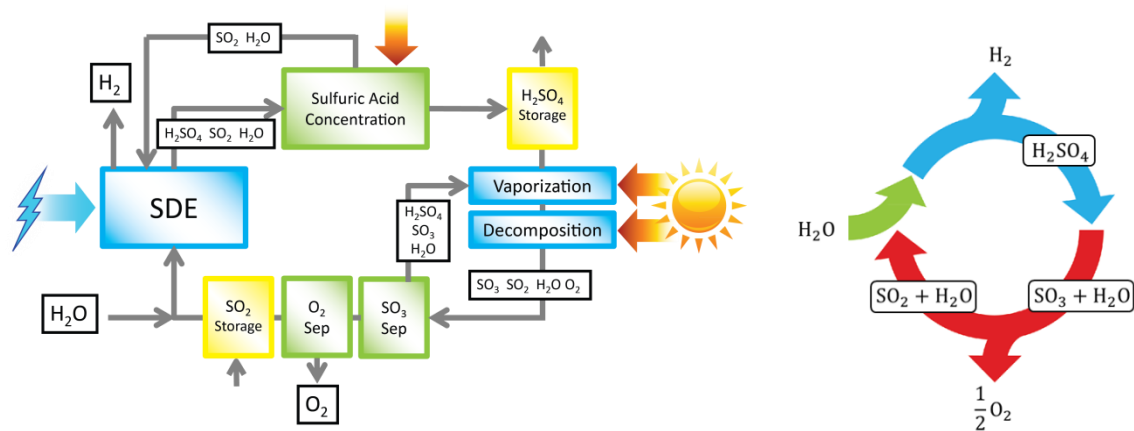


Figure 1: Simplified block diagram of the SOL2HY2 Hybrid Sulfur process (left) and reaction scheme for the sulfur family of thermochemical water-splitting cycles (right).

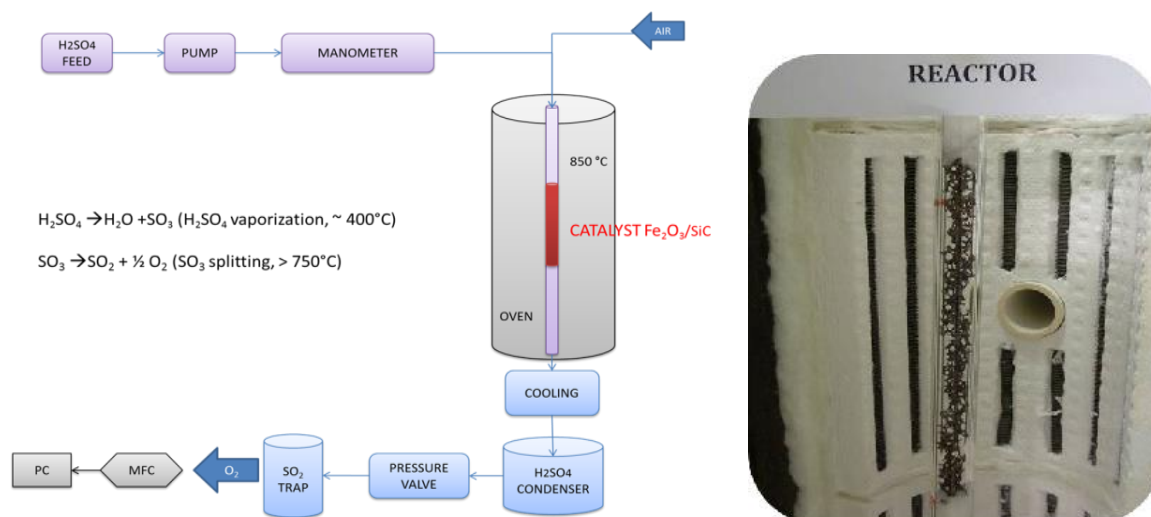


Figure 2: Experimental setup used for catalyst testing. Left: general scheme; right: picture of a catalyst sample placed inside the quartz reactor.

3. Development of the catalyst for SO_3 decomposition

Within SOL2HY2, DLR – German Aerospace Agency is in charge of the design, construction and operation of a SAC pilot plant (higher than 100 kW thermal power) to be installed in the DLR solar tower in Jülich, Germany. ENEA is contributing to the development of the SAC demonstrator by developing the catalyst for SO_3 decomposition. During the first stage of the project, this activity involved the setup of active species deposition techniques on ceramic carriers.

3.1 Experimental apparatus

Catalyst samples were tested in the experimental apparatus schematically represented in Figure 2. A membrane pump was used to feed liquid SA (96% w/w) into a quartz reactor. The reactor was placed inside a ceramic oven equipped with a temperature control system. The upper section of the reactor was filled with inert quartz particles and used as acid evaporator. The catalyst sample was placed in the central section, where the best temperature control is achieved. Downstream of the reactor, unreacted SO_3 and water were condensed as an aqueous SA solution in a room temperature cooler; furthermore, a hydrogen peroxide trap was used to remove SO_2 from the effluent gas. The flowrate of the remaining O_2 stream was measured with a mass flow meter (MFC). The SO_3 conversion was calculated by simple mass balance considerations as the ratio between the produced O_2 and inlet SO_3 molar flow rates.

3.2 Active species deposition and catalyst characterization

Catalyst deposition tests on Silicon-Infiltrated silicon carbide (SI-SiC) solid foam carriers were performed. The tests were aimed at identifying simple preparation methods, still obtaining an acceptable catalytic activity and good stability (higher than 100 hours-on-stream in laboratory tests) under concentrated SA flow at high temperatures and daily thermal cycling. As active catalytic material, Fe_2O_3 was considered because of its low cost and known activity above 750°C ; however, this species deactivates at temperatures below $700/750^\circ\text{C}$. Due to the non-polar characteristics of SI-SiC, the chemical nature of the substrate surface was modified by a preliminary impregnation with an alumina slurry. The effect of high temperatures, which can possibly promote the formation of new bonds and phases between the washcoat and the SI-SiC carrier, was also investigated. As a reference, preliminary tests were carried out on pure SI-SiC, calcined pure SI-SiC, Fe_2O_3 powder and Al_2O_3 powder (washcoat material).

The results reported in this work were obtained by preparing samples in two separate steps: the first one to bind the alumina washcoat to the SI-SiC carrier and the second one to attach Iron (III) oxide to the substrate previously obtained. At this aim, the following procedure was carried out: a slurry made of ethanol (72 wt%), $\alpha\text{-Al}_2\text{O}_3$ (24 wt%) and methyl cellulose (4 wt%) was used to impregnate samples for the first step. SI-SiC samples underwent to 1 min of impregnation into the slurry under stirring, 5 min of centrifugation at 1000 rpm (used as alternative of insufflation of compressed air); the procedure was repeated five times and samples were kept at 120°C for 1 hour. The samples were then calcined at 1500°C , according to a specific temperature program. The active phase was deposited by preparing another slurry, made of ethanol (125 ml)

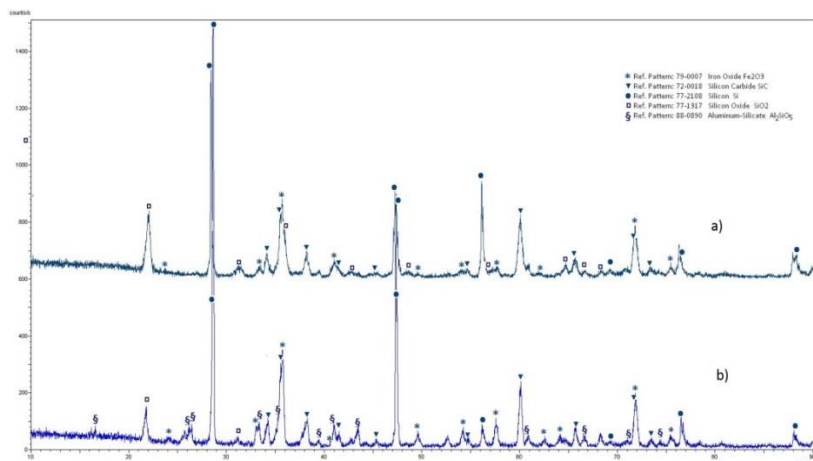


Figure 3: XRD patterns for catalysts obtained with procedure A and B.

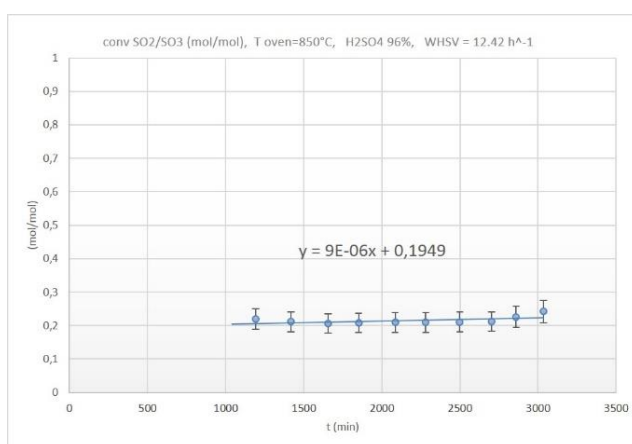


Figure 4: SO_3 conversion during a catalyst stability test.

and $\text{Fe}_2(\text{SO}_4)_3$ (33,3 g), which was used for the second impregnation step. SiC samples underwent to 30 min of impregnation into the second slurry in rotavapor at 50°C , and kept for 1 hour at 120°C . Finally, the samples were calcined again at 1500°C (procedure A) or 1050°C (procedure B).

After the preparation, in order to preliminarily test phase adhesion, each sample was sonicated in ethanol at 80°C for 30 min. Moreover, a visual inspection was preliminarily performed and then samples were analysed by XRD diffraction and SEM. Given the low amount of active phase present on the structured SI-SiC, it was not possible to obtain BET data for the coated materials, because the specific surface was below the detection limit of the instrument.

From XRD and SEM analysis, it was possible to see that SiC does not undergo a change in the lattice shape (hexagonal) if calcined, but is partly oxidized to SiO_2 . The samples calcined at 1500°C showed high coverage with strong bonding, as if the sample was sintered. The formation of a new phase between SI-SiC and the Al_2O_3 washcoat (first step) is evident, but this new phase disappears when the samples are impregnated again with $\text{Fe}_2(\text{SO}_4)_3$ (second step) and calcined at 1500°C (Figure 3 – pattern a). On the contrary, when the second calcination step was carried out at 1050°C , the new phase remained present, with good results of Fe_2O_3 surface deposition (Figure 3 – pattern b). It is important to highlight the presence of Si on the surface, for the "barrier" effect that free silicon can give on the deposition. For stability test, the samples obtained with procedure B were selected.

3.3 Stability

In stability tests, about five grams of catalyst prepared with procedure B were placed inside the reactor and tested on stream. During the experimental run, the outlet O_2 flowrate was recorded and the time course of SO_3

conversion calculated. A typical stability test lasted several days. The feed was always stopped and the reactor cooled at night; the operating conditions were resumed the following morning. In this way, the thermal cycling which characterizes the actual catalyst operation was simulated. Figure 4 shows the results obtained in a test carried out with the following operating conditions: reactor temperature 850°C, inlet SA concentration 96% (weight basis), weight hourly space velocity (WHSV) 12.42 h⁻¹. The WHSV is defined as the ratio of the inlet SA mass flowrate divided by the catalyst mass.

It can be seen that SO₃ conversion is fairly constant throughout the test, which proves that the catalyst prepared is stable.

4. Balance of plant units

Gas separation units, namely SO₃ (downstream of the SAC) and SO₂/O₂ separation units, were identified as the critical BoP components in the SOL2HY2 HyS plant. For each of the above-mentioned components, a comparative analysis of several available processes was carried out, in order to choose the most suitable ones. Only the results obtained for SO₃ separation will be reported here.

For SO₃ separation and recirculation, indirect heat exchange and direct heat and mass transfer with SAC's feed were considered. The former solution was selected because it appeared as more robust and simple. Indeed, these features are of primary importance, considering that the SAC section, which relies on high temperature solar heat for SO₃ cracking, can be operated only at daytime and will require daily start-up and shut-down operations. The direct contact approach seems difficult to handle, especially because it involves the use of a liquid absorption column that cannot easily afford such a discontinuous operating regime. Furthermore, contacting the SO₃ containing gas with diluted liquid SA, can lead to the formation of acid mists which may be hard to separate.

Figure 5 presents the conceptual integrated flowsheet developed with the process simulator Aspen Plus® for the SAC and SO₃ separation sections of the process.

The feed coming from liquid SA storage (FEED) is preheated in heat exchanger E1 with reaction products at the second cooling stage; subsequently, the heated feed (stream 2) is mixed with recycle SA condensed from the product steam (stream 9). Temperature in separator S1 is adjusted in order to obtain a recycle stream with the same SA concentration as the feed. The mixed stream is vaporized and heated to 500 °C (stream 5) before being fed to the solar tower (ST). Heating to 500°C is obtained with two heat sources: heat recovered from the reactor products and heat obtained from the medium temperature CSP plant.

In the ST, the feed stream is heated up 1000°C (the flowsheet developed is flexible respect to this temperature, so that other inlet temperatures could be considered in process optimization) and then fed to an adiabatic reaction chamber (REACTOR). For flowsheets calculations, an adiabatic equilibrium reactor has been assumed. Downstream of the reactor, products are cooled down to ambient temperature in 3 stages, whose temperatures depend on the feed composition. In each cooling step, a liquid stream is separated. Stream 9 is a SA solution with the same composition as the feed, which is recycled and mixed (mixer M1) with SA from storage; stream 12 is SA 30% by weight, which can be stored and used elsewhere in the plant (anolyte preparation for SDE) or recycled upstream of the SA concentration unit; stream 15 is liquid water (saturated with SO₂ and with SA traces) which is directed to a water storage tank and recycled where needed in the plant.

The final effluent of this section (stream 16) contains SO₂ and O₂ (molar ratio 1:0.5, saturated with water vapour) and is directed to the SO₂/O₂ separation block.

Table 1 reports the overall specific energy consumption (per unit mole of SO₂ produced) of the integrated SAC and SO₃ separation block, divided by energy source type. Three possible different concentrations of the liquid SA coming from the storage tank, were considered: 75%, 80% and 90%. The specific energy consumption decreases with increasing inlet SA concentration: this is clearly due to the increasing fraction of (inert) water that has to be heated together with SO₃, which is the actual reactant. However, the concentration will have to be determined by optimization of the whole SOL2HY2 process. Indeed, lower values of this parameter allow to save energy for SA concentration, so that a trade-off between the energy needs of the concentration and SAC section has to be evaluated.

5. Conclusions

An overview of the activities carried out by ENEA during the first half of the SOL2HY2 project was presented. Such activities involved elaboration of general plant concepts, integration of the hydrogen production plant with a concentrated solar power (CSP) plant, development of the catalyst for SO₃ decomposition, selection and design of balance of plant (BoP) units. The above-listed activities have been supported with the development of AspenPlus flowsheets.

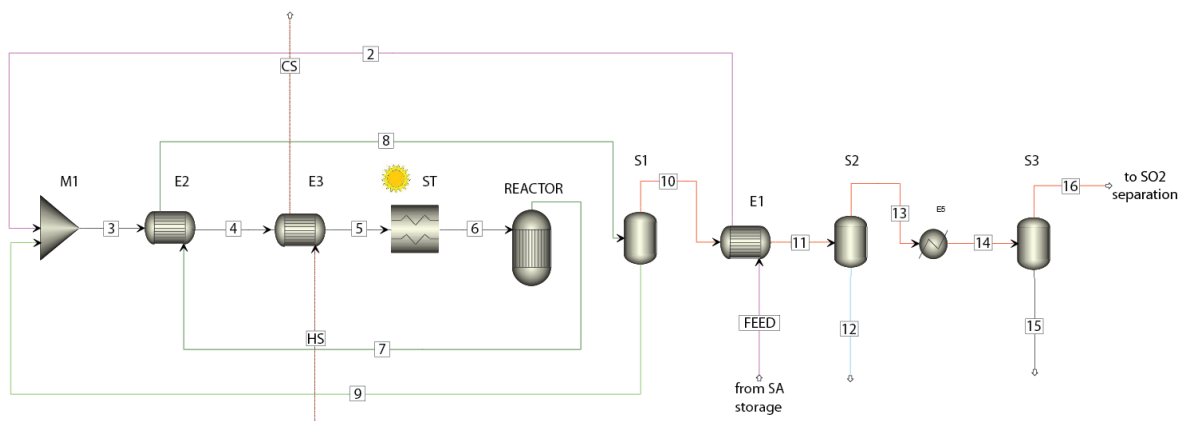


Figure 5: Integrated flowsheet (conceptual) for SAC and unreacted SO₃ separation.

Table 1: Heat input required by the SAC and SO₃ separation sections

Inlet SA concentration	MT heat [kJ/mol SO ₂]	HT heat [kJ/mol SO ₂]	Total [kJ/mol SO ₂]
0.75	234.0	169.5	403.5
0.80	217.5	164.0	381.5
0.90	167.9	155.5	323.4

As for catalyst development, a procedure to deposit Fe₂O₃ on Si-SiC solid foam carriers was defined. Catalysts samples prepared with such procedure were characterised by XRD and SEM, showing good coverage and strong adhesion of the catalytic washcoat on the carrier; furthermore, the catalyst samples showed a stable activity up to 100 h on-stream with daily thermal cycling simulating.

The catalyst development will continue by considering other carrier materials such as alumina; furthermore, activity tests will be carried out to analyse the catalyst performance and determine the reaction kinetics, which is required for the design of the reactor.

Flowsheeting activities will be refined and, together with the experimental results obtained with the demonstrators of the SDE and SAC, will provide the input for the whole plant optimization.

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