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Demonstration of Hydrogen Production by the Sulphur-Iodine Cycle: Realization of a 10 NL/h Plant

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In the hydrogen production framework, ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) is involved in a study of the thermolysis through thermochemical cycles powered by solar energy. The TEPSI project, in this regard, has as its main objective, the construction of a plant for the production of 10 NL/h of hydrogen by sulphur-iodine cycle, for the demonstration of scientific feasibility of the sulphur-iodine cycle and the collection of all data necessary to design a pilot plant.

TEPSI is a project funded by the Italian Ministry of Research and consists of 3 lines:

1. Hydrogen production from water by thermochemical cycles.
2. New materials for H₂ storage.
3. Hydrogen and electrical power production by hydro –gasification.

Line 1, in particular, has endeavoured to study and develop the sulphur-iodine and the mixed ferrites thermochemical cycles. It saw also the participation of several Italian Universities: Roma 1, Roma 3, Cagliari, Milan and Trento.

This paper deals with the realization of this laboratory plant for the sulphur-iodine cycle and concerns the experimental performances of all the equipments constituting the plant.

The tests of the equipment related to this cycle, executed in the ENEA laboratories, are described in order to analyze the reasons behind the choices of equipment, compositions, temperatures, pressures and devices, with particular emphasis on the ones concerning iodine purification. The equipment, indeed, consumes the most energy and, if not optimized, can invalidate the efficiency of all the cycles.

Since the objective of the laboratory plant is to verify the feasibility of the reactions and processes involved and to test their integrability and cyclicity, the heat source used, for simplicity, was provided by electrical devices. However, an evaluation concerning the realization of an industrial plant is possible starting from the acquired data.

Among all the thermochemical cycles proposed in literature over the last 30 years [1], the Sulphur-Iodine cycle [2] is widely considered one of the most promising, and it has been studied by several important research groups in the world [2–5]. The process, starting from water through a closed cycle of reactions that generate and consume iodine, hydriodic acid, sulphuric acid and sulphur dioxide, produces hydrogen and oxygen at a temperature compatible with current solar collectors technology.

The sulphur-iodine thermochemical cycle is based on three main reactions carried out at three different temperature levels (low, medium and high temperature):

- Reaction of acid production (called Bunsen, exothermic at 293 ÷ 393 K):
$$2\text{H}_2\text{O} + \text{I}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI} \quad (1)$$

- Decomposition of HI (endothermic at 573 ÷ 773 K):



- Sulphuric acid decomposition (endothermic at 1073 K ÷ 1173 K):



In the section of Bunsen [6], water, iodine and SO_2 at a temperature between 293 K and 393 K, produce two immiscible liquid phases [7]: the upper one containing mainly a mixture of water and H_2SO_4 at 50% by weight, and the other containing HI, I_2 and water.

The sulphuric acid from the top section of the Bunsen reaction is concentrated up to (90 - 98)% by weight and then sent to the decomposition reactor where it produces water, oxygen and SO_2 . The latter is re-sent in the Bunsen section.

The lower phase of the Bunsen reaction, however, is sent to the section of decomposition of HI, which is decomposed into hydrogen and iodine. The lower phase of the Bunsen reaction, however, consists of HI, water and H_2SO_4 residue and a high iodine content (~ 80-90% wt), since the reaction itself is conducted with an excess of iodine, to promote separation of the two phases.

The Iodidric phase is then subjected to a series of separation operations in order to obtain a binary azeotropic mixture HI-H₂O at 57 wt% of HI content in order to be sent to the decomposition reactor. This is one of more energy-cycle phases and requires considerable work on optimizing. To this end several techniques for purification-separation have been proposed. General Atomics has proposed the use of phosphoric acid (H_3PO_4) to obtain concentrated HI [8, 9] and the separation of iodine. Roth and Knoche [10] have proposed and studied the reactive distillation, which involves replacing the stills and decomposition in an integrated process. Further improvements in this technique were reported by Goldstein [11], Hong [12] and Kasahara [13] who studied an electro-electrodialysis as a method of concentration.

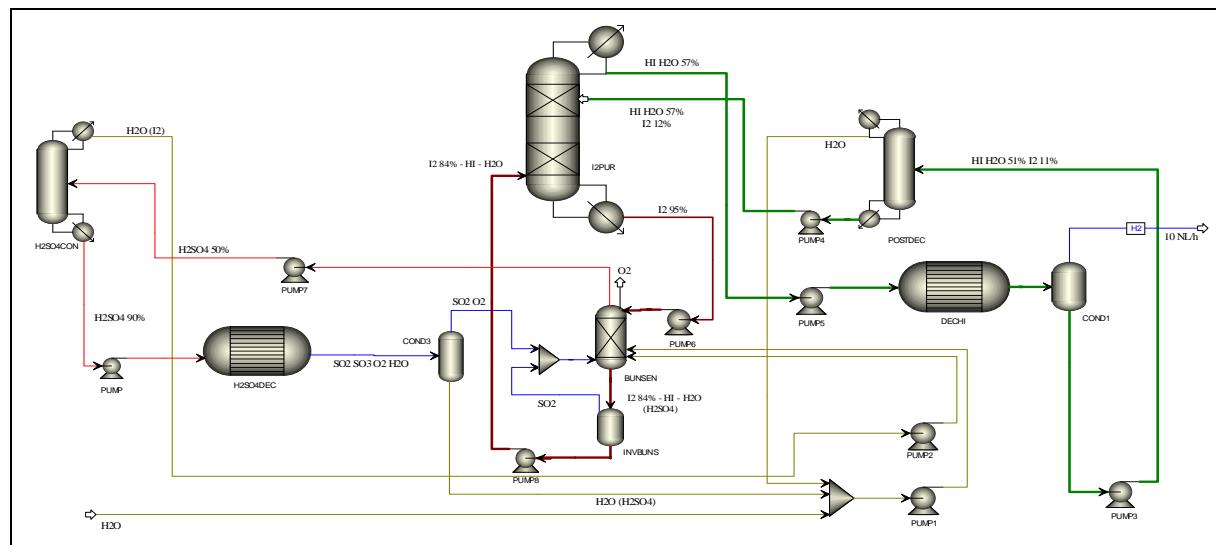


Figure 1: ENEA Laboratory Sulphur-Iodine plant schema, $\text{HI}^* = \text{HI}/(\text{HI} + \text{H}_2\text{O})$.

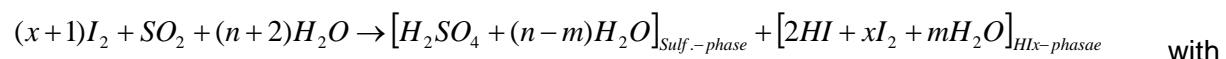
In order to achieve a sulphur-iodine system for small-scale hydrogen production (Figure 1), ENEA proposed the separation of iodine from HI-H₂O mixture in a distillation plant at atmospheric pressure after the reaction of Bunsen, in order to send to the HI decomposition reactor an HI-H₂O azeotropic mixture devoid of I₂. This technique is a classic way to separate from I₂ in HI-HI-H₂O ternary mixture, considering the large difference in boiling point among the three components (at atmospheric pressure: 238 K for HI, 373 K for H₂O, 457 K for I₂). The distillate, however, is highly dependent on the composition of the [HI] / ([HI] + [H₂O]). Depending on the concentration of the feed from the Bunsen reaction, two possible patterns of plant are possible. If the content of HI is greater than the pseudo-azeotrope (with pseudo-azeotrope [14], meaning the ternary mixtures HI-H₂O-I₂ with minimum vapour pressures in isothermal conditions, at varying concentrations of iodine), these mixtures have a ratio of concentration ([HI] / ([HI] + [H₂O])) close to 57% wt) and the distillate is enriched in HI, if the contents of HI is lower than the pseudo-azeotropic point, the distillate is instead enriched in water.

For this reason it was necessary to determine the most appropriate composition of the lower phase of the Bunsen reaction and the quantities of reagents to be introduced.

It is true that reaction (1) is entrusted with the production of acid phases: the hydriodic and the sulphuric one, but the two phases do not contain exclusively H₂SO₄ and HI, but also significant amounts of water, which has to be included in excess.

To obtain a good separation of phases and having no amount of H₂SO₄ in the hydriodic phase and / or sulphuric acid in the HI phase it is necessary to work with a large excess of iodine, which will go into the hydriodic phase.

In this way the Bunsen reaction appears to be:



n and m depending by temperature at constant pressure. We have seen, however, by the last experiments at ENEA Casaccia, that even if we operate at 353 K [11], a content of about 1%wt in H₂SO₄ is being and the iodine content is about 82%wt. Because of this, a purification of this phase is necessary: a way is the reversing of the Bunsen reaction at a temperature of about 403 K. This reaction, however, consumes 2 moles of HI for every mole of H₂SO₄ and forms 2 moles of H₂O, further diluting the HI phase. Since this phase will be purified by iodine and sent to the decomposition reactor for the production of the H₂ at an appropriate concentration (at least 57% wt), we can understand that if this phase is more dilute more problems of distillation and recirculation will happen. Furthermore it was noted that high concentrations of iodine in the Bunsen reactor produce, in the HI phase, more content of HI against water, which further facilitates the distillation itself.

It could be preferred, at this point, to get even greater excesses of I₂ and higher temperatures (393 K) in the Bunsen reactor, but in this case, we would be forced to work with mixtures with high content of iodine, even 84 wt% leading to an over-sizing of certain equipment, particularly the Bunsen reactor. Furthermore we would have problems handling the mixture, which should always be kept warm (373-383 K) to avoid iodine precipitation. This would make it necessary to track and control the temperatures in the lines and the pumps. After careful experimentation, it was considered useful for this plant to operate under these conditions anyway.

Concerning the sulphuric acid decomposition, the temperature of reaction was 1123 K with an iron oxide based catalyst and with a feed mixture composed of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ with 90 %wt in H_2SO_4 . This stream is the one leaving the Bunsen reactor after an appropriate distillation in $\text{H}_2\text{SO}_4\text{CONC}$.

Concerning the HI decomposition, it has been widely investigated in ENEA laboratories, usually feeding the reactor with HI-water azeotropic solution as starting reactant, since this is the expected composition coming from the other sections of the cycle; recently, some experimental test with pure gaseous HI has been executed too. Various catalysts have been investigated in order to enhance the kinetics of this reaction in the range of temperature 400-500°C, searching for efficiency (high conversions), time stability (no deactivation), low pressure drop and low cost. Ni-based catalysts using alumina as support, Pt-based catalysts supported over different carbon materials and carbon materials catalysts are used. The first ones provided starting conversion values at 500°C almost agree with the theoretical one (about 22%), but in any case a slow but gradual deactivation was evident. The second ones gave, in contrast, good results in terms of efficiency and stability, but we didn't consider them interesting for a large scale application because of their high cost. We focused therefore on carbon material ones, and they were used in the HI decomposition reactor of the lab plant. The temperature of reaction was fixed at 773 K and the obtained conversion was about 21.4 %. The stream leaving this reactor is essentially composed of H_2O , HI and the I_2 formed by the HI decomposition. It has to be purified from the iodine and reconcentrated to pseudo-azeotropic conditions, since the HI decomposition produced a more diluted mixture.

Consequently, this stream is sent to another distillation column (POSTDEC), that will produce H_2O as distillate and a pseudo azeotropic mixture as residue. The residue will be sent at the purification column (I_2PUR), another time, in order to eliminate the iodine.



Figure 2: ENEA Sulphur-Iodine laboratory plant picture.

As stated before, the goal is to construct a facility at ENEA Casaccia laboratories to experiment and develop a thermochemical cycle that, starting from water, produces hydrogen and oxygen continuously.

The plant, whose scheme is depicted in Figure 1, consists of equipment in Pyrex and quartz, PTFE tubing and it has an output of about 10 NL / h of H₂.

Before the plant realization (figure 2), all the equipment was tested.

As well as the authors of this paper, the ENEA equipment which realised this laboratory plant was constructed by Mauro Vignolini (Project Manager), Pietro Tarquini (Technical Manager), Antonio Ceroli, Paolo Favuzza, Alberto Giaconia, Michela Lanchi and Salvatore Sau.

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