

Completion and Operation of the thermo-chemical water splitting sulfur iodine process in a lab scale plant for a continuous hydrogen production.

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ABSTRACT

In the hydrogen production framework, ENEA (Italian National Agency for New Technologies, Energy and Environment), collaborating with some Italian University, is involved in a study of the water splitting through thermochemical cycles powered by solar energy. As main objective of the TEPSI project, a plant, made mainly of glass and PTFE, for the production of 10 NL/h of hydrogen by sulphur-iodine cycle has been operated with the aim to demonstrate the scientific feasibility of the sulphur-iodine cycle and the collection of all data necessary to design a pilot plant.

In the experiment, hydrogen production at the rate of 10NL/h for 48 h was successfully accomplished.

Keywords: hydrogen, water splitting, thermo-chemical sulfur-iodine cycle.

1 INTRODUCTION

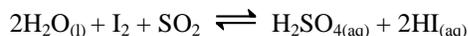
This article deals with the realization of this laboratory plant for the sulphur-iodine cycle and concerns the experimental performances of all the equipments constituting the plant.

The Sulphur-Iodine thermochemical is one of most promising cycle for the production of hydrogen by splitting water using energy and chemical processes. This cycle has been investigated by ENEA over the last five years, focusing on chemical aspects, reactions, total efficiency, technical feasibility and cost analysis. The majors goals for futures applications are providing the energy demand with free carbon energy, rise as much possible the total efficiency and solve some technical matter. Efforts at the ENEA laboratories are focused also on materials vs corrosion, due almost the entire cycle involves strong acids and oxidant in extreme environmental conditions such high temperatures and pressures.

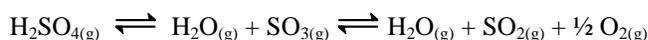
2 OVERVIEW OF THE IS PROCESS

The IS cycle consists of the following reactions:

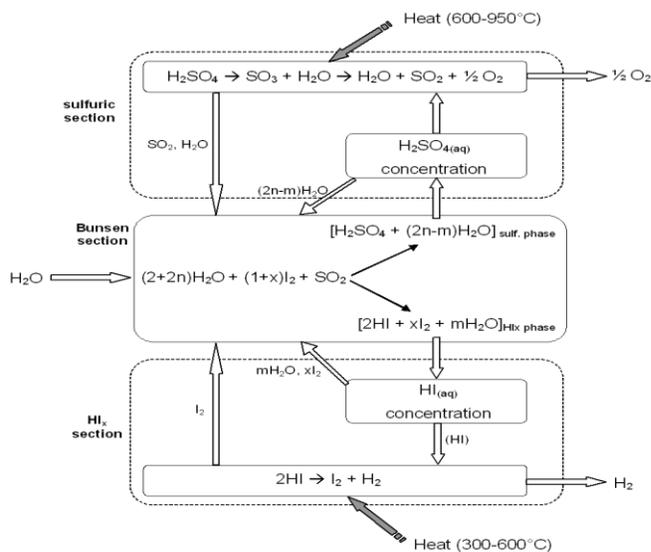
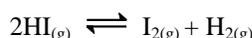
- 1) Bunsen reaction
($T = 20^{\circ}\text{--}120^{\circ}\text{C}$; $\Delta H = -75 \pm 15 \text{ kJ mol}^{-1}$)



- 2) H_2SO_4 decomposition
($T = 600\text{--}900^{\circ}\text{C}$; $\Delta H = 186 \pm 3 \text{ kJ mol}^{-1}$)



- 3) HI decomposition
($T = 300\text{--}500^{\circ}\text{C}$; $\Delta H \sim 12 \text{ kJ mol}^{-1}$)



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]: one containing mainly a mixture of upper and water to H_2SO_4 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 - 95)% 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.

Thermal efficiency η of the IS process is defined by:

$$\eta = \frac{H_{HHV}}{H_{heat}}$$

where HHHV is the higher heat value of hydrogen per 1 mol (285.8 kJ), and Hheat is the total heat used in the process for hydrogen production of 1 mol.

3 CLOSED CYCLE OPERATION FOR HYDROGEN PRODUCTION

3.1 Experimental facilities

In advance of the construction of the plant the tree main sections have been widely independently investigated in order determine all the equipments materials, dimensions, and procedures and executed with the aim to collect scientific data and finally the governmental chemistry.

3.2 Bunsen reaction

The Bunsen reactor with downstream purification units for the two produced acids (HI and H2SO4) represents a fundamental process stage. A large excess of iodine and water is required to drive the Bunsen reaction, to avoid side reactions, and to separate the two produced acids by segregation in two immiscible liquid phases, namely the Sulfuric phase and the HIx phase. Such residual amount of iodine and water in the produced streams enhances the removal of sulfur contaminants (sulfates and SO2) from the HIx phase, but has a negative impact the efficiency and the technological feasibility of the SI cycle. A continuous counter-current glass-made (1300mm toll, 70mm OD) Bunsen reactor with SO2 feed flow rates in the range of 5-10 L/h has been run alone and its performances deeply investigated and then mounted in the plant. This reactor geometry and configuration allows simultaneous reaction and phase separation: the heavier HIx phase will settle and removed at the column bottom, whereas the lighter sulfuric phase will float in the upper section where it is continuously drained out. The column is packed with inert solid (pyrex and tantalum rings).

Temp.	120°C
Pressure	1 atm
SO2	5 - 10 NmL/h
H2O	40-60 mL/h
I2	200-600 gr/h
H2SO4 prod. rate	21 mL/h @ 46-52 %wt.
HIx phase/Sulfuric phase	3.1-6.1 vol/vol
HI/(HI+H2O)	57-67 %wt.
I2 in HIx phase	80-85 %wt.

3.3 HI decomposition section

Iodidric phase is 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 (H3PO4) 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.

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 $[HI] / ([HI] + [H2O])$ of the feed from the Bunsen reaction.

We have seen, however, by the last experiments at ENEA Casaccia, that even if we operate at 393 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 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 are forced to work with mixtures with high content of iodine, even 84 wt% leading to a over-sizing of certain equipment, particularly the Bunsen reactor by iodine and especially, create problems of mobility to the mixture, which should always be kept warm (373-383 K) to avoid the iodine solidification.

After careful experimentation, it was considered useful for this plant to operate under these conditions anyway, since the H2SO4 content in the HI phase is < 0.2% wt.

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 200-500°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. At end we focused on carbon materials and 7 grams of commercial activated carbon (Norit) are used in the HI decomposition plant reactor. The temperature of the reactor, a quartz tube (1000mm, OD 40mm), is 773 K. The reactor fed at the rate of 10ml/min with pseudo-azeotropic HI produce 10 NL/h of H₂ at the conversion rate of 21.4 %.

The stream leaving this reactor, removed from H₂, is essentially composed by H₂O, HI, and I₂, formed by the HI decomposition it has to be purified from the iodine and returned in pseudo-azeotropic conditions, since the HI decomposition produced a mixture more diluted.

Consequently, this stream is sent to another distillation column, that will produce H₂O as distillate and a pseudo azeotropic mixture as residue. The residue will be sent at the purification column, another time, in order to eliminate the iodine.

3.4 H₂SO₄ decomposition section

The stream leaving the upper part of Bunsen reactor after an appropriate distillation (92% w/w) in a flash column (where the water and iodine traces are removed) is pumped and metered by a diaphragm pump into a quartz tube (1000mm, 17mm OD) by the mean of a quartz injector. The top of the tube is filled by quartz raching rings package that works as evaporator than the stream encounter the catalytic bed constituted by 15 grams of iron oxide (Fe₂O₃) in pellets (homemade: size 1.2mm). The conversion rate is 87% at 1123 K. The stream leaving this reactor is essentially composed by H₂O, SO₂ O₂ and H₂SO₄ not decomposed. The slightly acid water (< 10% w/w) is treat as water and recirculated into the Bunsen. The incondensables was sent to the Bunsen reactor too, SO₂ forms new H₂SO₄ and O₂ evolves from the top of the reactor as product of process.

4 PROCEDURE

We start with solutions which had been prepared for the initial contents and were placed into each equipment, then into each section. Then a long period warming up all the equipments is required especially to ensure not cold point on traced iodine lines and pumps. After this we commenced

starting on pumps and controlling flow rates and levels in the vessels. Next, the sections were combined to get the process working in the closed-cycle. From there, the process conditions were controlled to be maintained at a stable state until shut down of the experiment. In addition, fine adjustments made manually and frequently were essential during the experiment. The water as raw material was fed into the process at the regular flow rate. The principle test conditions were as follows: for the temperatures of the chemical reactors, the Bunsen reactor was maintained at about 120°C by heating-cooling the glass jacket of the reactor, the H₂SO₄ decomposer was maintained at about 850 °C and the HI decomposer was maintained at about 500 °C. All equipment was operated at atmospheric pressure. The plant, whose scheme is depicted in Figure 1, consists of equipment in Pyrex and quartz, and Teflon tubing and will have an output of about 10 NL / h of H₂.



5 CONCLUSIONS

The experiment lasted for 48 h in the closed-cycle. Temperatures and liquid levels of each equipment were almost constant. The amounts of H₂ and O₂ production is almost stable at a rate of 10 l/h, and the production ratio of oxygen to hydrogen almost agrees to 0.5:1. The experiment duration ensures a complete replacement of the starting solutions in tanks so the entire HI and H₂SO₄ inside the facilities has been consumed and replaced by acids produced by the plant itself. After this, automation and control of the process, the improvement of efficiency and the selection of materials are good issues for future challenges.

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