Analysis and Development of the Bunsen Section in the Sulphur-Iodine Process

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1   Introduction

Thermochemical water-splitting cycles (TWSCs) are a promising carbon-free route for nuclear or solar hydrogen production. Among the hundred cycles proposed yet, the Sulphur-Iodine (S-I) process is one of the most deeply studied: differently from other TWSCs, it basically does not involve either solid management, electrolysis, or membrane exploitation, but it consists of more "conventional" chemical engineering large-scale operations (heat exchange, fixed-bed tubular reactors, distillation column, etc.). The S-I cycle involves the following three reactions [1]:

$$2H_2O + I_2 + SO_2 \rightarrow H_2SO_4 + 2HI \tag{1}$$
$$2HI \rightarrow I_2 + H_2 \tag{2}$$
$$H_2SO_4 \rightarrow H_2O + SO_2 + \tfrac{1}{2}\,O_2 \tag{3}$$

Reaction (1) between SO_2 with I_2 and water to produce H_2SO_4 and HI, called Bunsen reaction, is a fundamental process step. Differently from the acid decomposition sections, this stage proceeds under "mild" temperatures (< 150°C) and requires rather low heat duty (the reaction is slightly exothermic). However, this section must be carefully designed to obtain two concentrated and unpolluted acid streams. This optimization involves some issues like determination of best working conditions, Bunsen reactor design and the separation and purification of the two product streams.

Basic experimental studies have firstly been carried out to characterize the Bunsen reaction, using a jacketed mixed glass reactor at 30-120°C, under different initial compositions. Removal of H_2SO_4 and residual SO_2 from the hydriodic acid phase is also studied, monitoring the possible sulphur or H_2S formation. Also separation of the iodine from the sulphuric acid stream is studied.

A lab-scale continuous apparatus to carry out the Bunsen reaction, together with subsequent purification/concentration of the produced acids, has been tested.

Some experimental results are here presented and discussed. Moreover, the possible application of the Bunsen reactor and separation units to an "open S-I cycle" for sulphur recovery is discussed.

2   Experimental Studies with Batch and Semi-batch Apparatus

A preliminary analysis was carried out to identify the most convenient operation conditions to produce H_2SO_4 and HI as pure and concentrated as possible, in order to enhance downstream operations and maximize the overall S-I cycle efficiency. Thus, several reaction options were initially considered and investigated with batch laboratory experimental tests [2-4]: electrochemical Bunsen reaction, the Bunsen reaction in an organic solvent or liquid (pressurized) SO_2, or the Bunsen reaction with precipitation of insoluble solid salts. Each of these routes proved potential but also showed some important technical/energetic drawbacks. For this reason, subsequent research was mainly focused on the Bunsen reaction in water media, with a large excess of iodine in order to prevent side reactions and allow segregation of the two acids (H_2SO_4 and HI) within two respective immiscible liquid phases, namely the "H_2SO_4 phase" and the "HI_x phase":

$$(x+1)I_2 + SO_2 + (n+2)H_2O \rightarrow [H_2SO_4 + (n-m)H_2O] + [2HI + xI_2 + mH_2O] \qquad (1bis)$$
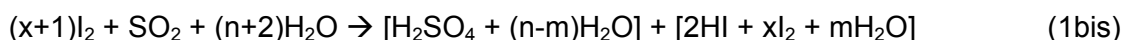
According with reaction (1bis) stoichiometry, iodine excess (x) is almost quantitatively dissolved in the HI_x phase, while water excess (n) splits between the two phases. In this preliminary study this LLE behaviour was characterized too [2], measuring iodine and sulphur impurities and in the H_2SO_4 and HI_x phases, respectively.

The influence of the iodine concentration and the operating temperature on the Bunsen reaction was investigated with a semi-batch procedure in a 500 mL temperature-controlled jacketed stirred reactor (Figure 1). Since the iodine solubility depends on temperature, these two operative parameters are not independent (maximum iodine concentration increases with temperature).
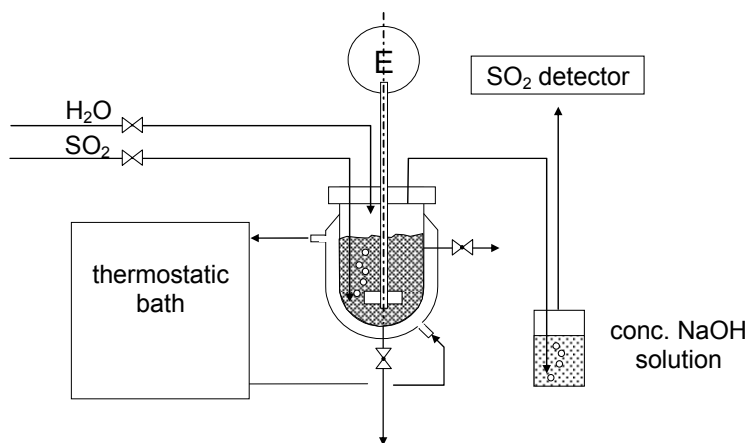

Figure 1:   The mixed semi-batch Bunsen reactor.

The reactor was initially filled with iodine and a liquid azeotropic HI/water mixture (57 %wt. HI), and the thermostatic bath and the stirrer were switched on. Once the desired temperature was attained and after complete iodine dissolution, gaseous SO_2 was fed at a rate of 83 NmL/min, until the SO_2 sensor detected the saturation of both the reactor and the alkaline (NaOH) trap. The upper H_2SO_4 phase was produced only in very small quantity, but always visually detected. Then the stirrer was stopped and the mixture was kept motionless for 30 minutes to allow the stratification of the H_2SO_4 and HI_x phases: afterwards the two

phases were separated, and the HI_x phase sampled and analysed. The NaOH trap was weighted before and after the experiment to exactly determine the quantity of SO_2 absorbed in the reactor. For each run, the temperature was controlled at a constant value within the range of 30-120°C.

We observed that the amount of SO_2 absorbed and reacted in the Bunsen reactor decreases by increasing the temperature due to the exothermicity of Bunsen reaction (equilibrium shifts towards SO_2 by increasing the temperature) and to the lower SO_2 solubility in the liquid.

A representative sample of HI_x phase was bubbled at constant temperature (the same previously adopted for the reaction) with a continuous N_2 flow at (40 NmL/min) for 30 minutes in order to strip the SO_2. After stripping, the residual sulphate content was measured: the stripping should remove all the sulphuric compounds (SO_2 and H_2SO_4) from the HI_x phase by reversing the Bunsen reaction, leading to a dilution of the lower phase:

$$H_2SO_4 + 2HI \rightarrow I_2 + 2H_2O + SO_2\uparrow \tag{1rev}$$
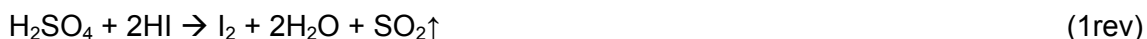
The sulphates content in the HI_x phase before and after the stripping is reported in Figure 2. The measured sulphates contents before stripping are in good agreement with the ones previously measured in the LLE measurement [2]. Clearly, the stripping operation significantly lowered the sulphates content in the produced HI_x phase, but sulphates were completely removed only at the highest temperature of 120°C (Figure 2). On the other hand, when the temperature is increased with an iodine molar fraction not high enough (i.e. < 0.35) secondary reactions took place, as solid sulphur formation was observed in the stripping device. In other words, insufficient iodine excess in the Bunsen reactor results into the formation of solid sulphur (and eventually H_2S) in the required HI_x phase purification stripper to remove sulphates prior HI decomposition.
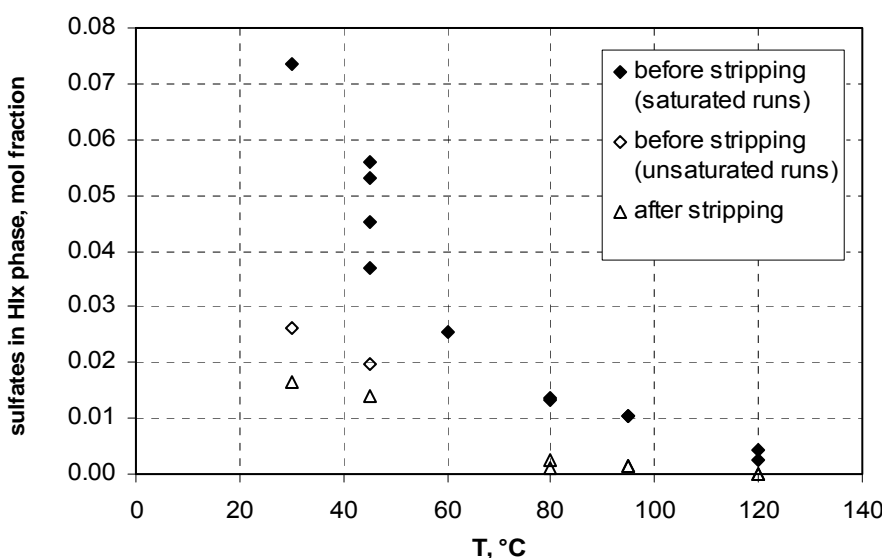

Figure 2: **Sulphates content in the HI_x phase before and after stripping at different temperatures [5].**

3   Continuous Flow Operation of a Counter-current Reactor

Next step of our research program was the set up of a continuous Bunsen reactor to be integrated within a closed S-I bench loop demonstrator. A packed counter-current column was considered, represented in Figure 3, where the selected flow rates of gaseous SO_2 and liquid water are fed from the bottom, and iodine is introduced from the top. Packing made of glass rings is set in the lower region, and tantalum rings in the upper section (to avoid glass rings floating on the heavier phase). Solid iodine pellets are also used as reactive packing in the upper section. Since it was difficult to find a metering pump suitable for liquid iodine, molecular iodine was fed step-by-step as solid powder from the top of the column and the packed bed with iodine pellets continuously restored above the inert glass-tantalum packing; hence a I_2-saturated HI_x phase was ensured throughout the experiment in the upper section of the reactor.
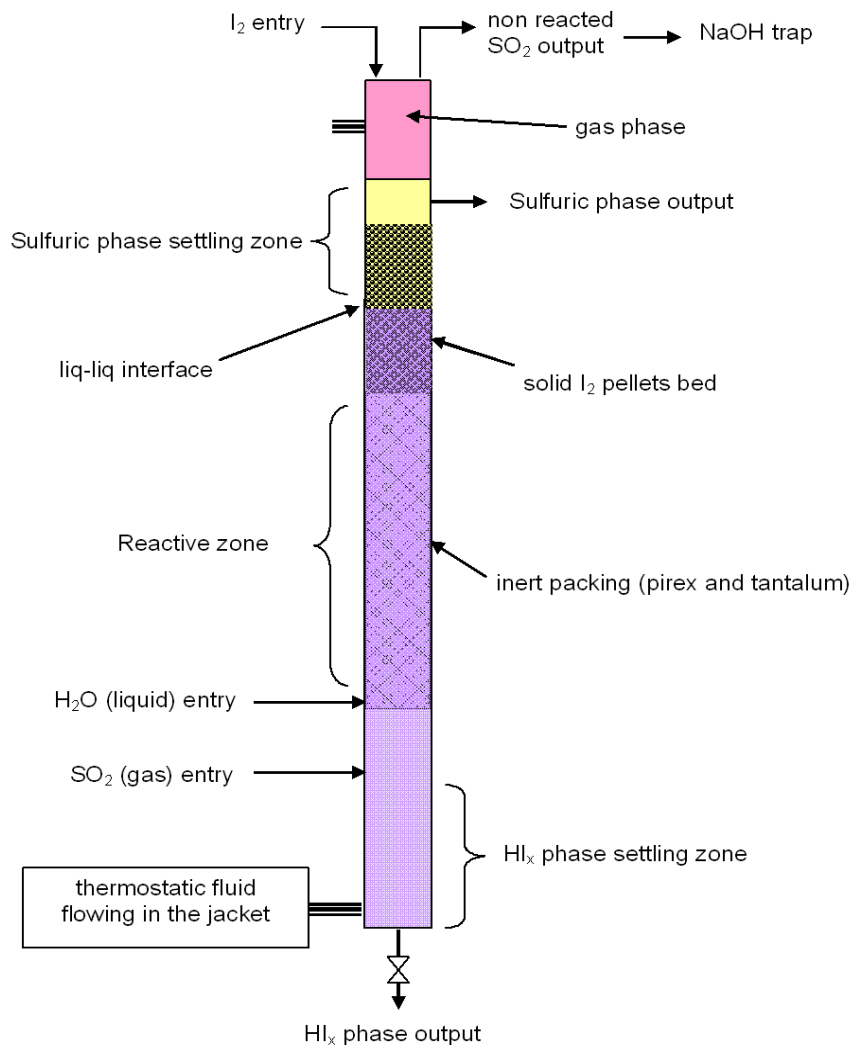

Figure 3:   Counter-current Bunsen reactor scheme.

In the fixed packed bed of reactive zone (Figure 3) the rising SO_2 bubbles are adsorbed in the liquid phase. After adsorption, SO_2 reacts with the dissolved iodine and water according

to the Bunsen reaction stoichiometry (1bis). Hence, droplets of lighter sulphuric phase will nucleate, grow and rise to be collected near the top of the column; simultaneously, the denser HI_x phase will settle near the bottom. In Figure 3 is shown the location of the liq-liq interface between the HI_x phase and the settling sulphuric phase, within the "iodine-packed section".

According with this scheme the sulphuric phase can be continuously drained from the top, while the HI_x phase from the bottom, to be analysed and collected for further treatments like purification and distillation. The experimental reactor is glass made and its temperature controlled by thermostatic liquid (water or ethylene glycol) circulation in the jacket. This apparatus can process about 5-10 Nl/h of SO_2.

This reactor was integrated in a continuous system were the drained HI_x phase was sent into a temperature controlled flash drum at 130°C to eliminate dissolved SO_2 and achieve reverse Bunsen reaction (1rev) without the use of a stripping gas. Moreover, the collected H_2SO_4 phase was separately distilled in a batch apparatus to eliminate I_2/HI impurities. Finally, the collected purified HI_x phase was distilled too in a batch apparatus to remove the I_2 and obtain a HI/H_2O mixture suitable for decomposition. Hence, all units operations involved in a complete Bunsen section were studied, as represented in Figure 4. Each unit is connected with gas traps (NaOH or H_2O_2 solutions) to prevent overpressure and trap non-reacted SO_2.
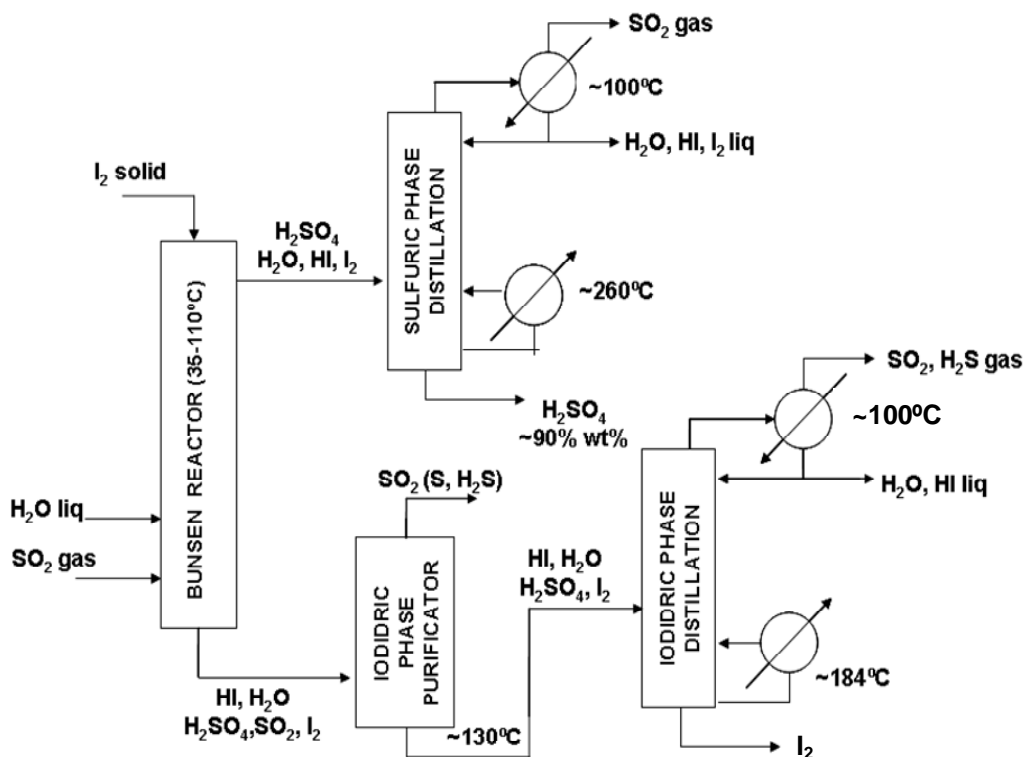

Figure 4:   **Schematic representation of the Bunsen section, with purification and distillation parts, as in the experimental apparatus. In brackets are species expected to be present in traces or present only under certain experimental conditions.**

Bunsen reactor was operated in continuous for 4-6 hours, at constant temperatures in the 35-110°C range, with H_2O-to-SO_2 feed ratio of 12.5-13.7 mol/mol and I_2-to-SO_2 feed ratio of 3.0-8.2 mol/mol (depending on temperature). Recovered phases had similar composition as that one obtained in previous LLE measurements [2]. It was possible to quantitatively purify the H_2SO_4 phase to a iodide content $< 10^{-3}$ %wt. by heating to 270°C, corresponding to simultaneous water vaporization to a final H2SO4 concentration of about 89 %wt. As far as the HI_x phase purification is regarded, the presence of sulphur in the top of the flash drum was observed at the lowest Bunsen reactor temperatures ($< 85°C$), corresponding to the lowest iodine concentration in the outlet HI_x phase; moreover, substantial reduction of sulphates was achieved when the reactor was operated at the highest temperatures ($> 85°C$). These results are in agreement with those discussed in the previous section.

4   Application to Industrial Sulphur Recovery

It is noteworthy that integrated process scheme shown in Figure 4, coupled with a HI decomposition reactor for H_2 production, represents a "open S-I cycle", i.e. a process to convert SO_2 and water to hydrogen and sulphuric acid. This process basically requires heat at temperatures lower than 300°C; the additional low thermal duty at 450-650°C for HI decomposition can be recovered from sulphur or H_2S combustion to SO_2, that is a common industrial process in H_2SO_4 plants. The overall thermal burden of the process can be evaluated to be about 3500 kJ/mol$_{H2}$ at 184°C, that corresponds to a thermal efficiency of about 8 %. This value seems rather low, if compared with the thermal efficiency values reported for many thermochemical water-splitting cycles. On the other hand, it must be recognized that this is obtained with "low-grade" heat, i.e. heat input at $< 200°C$, while most thermochemical cycles require high-temperature heat ($> 800°C$). However, other flowsheets for the S-I cycle have been proposed, especially regarding the HIx section, leading to much lower heat consumption (< 600 kJ/mol$_{H2}$).

5   Summary

The breakthrough of the S-I process still goes by the overcome of some technical issues dealing with the increase of efficiency and management of the HI_x process section, i.e. the treatment of the iodine-rich solution produced in the Bunsen reactor until hydrogen production. These operations have been studied at the ENEA in the framework of a National program on "New Energy Systems", in cooperation with other Italian Academic partners.

Most convenient operative conditions for the Bunsen section operations have been determined and discussed.

Moreover, a possible short-term exploitation of the developed technology in the sulphur recovery field was proposed for industrial sulphuric acid production from sulphur wastes (e.g. sulphur from Clauss plants) with co-production of hydrogen using low-grade heat ($< 300°C$).

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