Bunsen reaction and hydriodic phase purification in the sulfur–iodine process: An experimental investigation

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ABSTRACT

This paper reports an investigation on the Bunsen reaction. An experimental campaign was conducted by means of a stirred reactor. Runs were carried out at a constant temperature in the 30–120 °C range, following a semi-batch procedure by feeding gaseous sulfur dioxide in an iodine/hydriodic acid/water solution. A specific analytical procedure to measure the hydriodic phase composition was implemented. It was observed that both the amount of absorbed SO_2 and its conversion lowered as the temperature increased. Secondary reactions were beyond the detection limit in the reactor, even at low temperature and low iodine content. The purification of the produced hydriodic phase was also investigated. It was possible to satisfactorily reduce the impurities content without the occurrence of secondary reactions only when high temperature and high iodine content were applied.

1. Introduction

The Italian National Agency for New technologies, Energy and Sustainable Economic Development (ENEA) with the co-operation of the University of Rome "La Sapienza" is involved in a research investigation on thermochemical hydrogen production by means of the Sulfur–Iodine water splitting cycle (S–I). This process was originally developed by General Atomics in the late seventies[1,2]; since then, many research works were focused on it [3,4] and, nowadays, it is considered as one of the most promising long term routes for massive hydrogen production [5,6]. ENEA aims to demonstrate the feasibility of the hydro S–I cycle using solar energy supplied by parabolic trough technology [7] in order to produce hydrogen with a higher yield and a reduced cost when compared with the more traditional process consisting of water electrolysis connected to a photovoltaic device.

The present study reports and discusses the results obtained in an experimental campaign conducted over the Bunsen reaction (1), consisting of the reaction between sulfur dioxide, iodine and water to produce sulfuric and hydriodic acids:

$$2H_2O + SO_2 + I_2 \leftrightarrow H_2SO_4 + 2HI \qquad (1)$$

Sulfuric and hydriodic acids are afterwards purified and vaporized to enhance oxygen and hydrogen production, respectively, by vapor phase decomposition.

According with the commonly adopted recipe [8], reaction (1) is carried out in liquid media under a certain excess of both water (n) and iodine (x) with respect to the stoichiometric values. In this way it is possible to thermodynamically drive the reaction and enhance separation of the two products into two corresponding liquid phases, namely a sulfuric acid rich phase and a "HI_x phase". Therefore, almost all excess iodine is
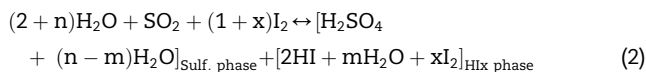
finally dissolved in the heavier HI_x phase, while water will split between the two contacted liquid phases. Accordingly, the process can be schematized as follows:

$$(2 + n)H_2O + SO_2 + (1 + x)I_2 \leftrightarrow [H_2SO_4$$
$$+ (n - m)H_2O]_{Sulf.\ phase} + [2HI + mH_2O + xI_2]_{HIx\ phase} \quad (2)$$

However, along with the reaction (2), the two side reactions (3) and (4) have been found to occur producing elemental sulfur S and hydrogen sulfide H_2S [9]:

$$6HI + H_2SO_4 \leftrightarrow S + 3I_2 + 4H_2O \quad (3)$$

$$8HI + H_2SO_4 \leftrightarrow H_2S + 4I_2 + 4H_2O \quad (4)$$
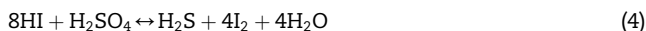
It has been recently highlighted that a non-negligible amount of sulfur-containing compounds are finally dissolved in the HI_x phase [10]: sulfates (and residual SO_2) must be quantitatively removed in a downstream purification unit [11,12] before subsequent operations prior HI decomposition.

In the framework of the S–I process optimization, the study of the Bunsen section has got wide concern, considering that the economic and technical sustainability of the whole process is very sensitive to several factors involved in this section, such as the composition of the above mentioned phases, the side reactions, and the excess of iodine and water in the feed.

Most works focused on the Bunsen section investigated the liquid–liquid equilibrium (LLE) phase separation performance [10–16]. The effects of the HI and I_2 concentration in a quaternary system $H_2SO_4/HI/I_2/H_2O$ were investigated in a temperature range of 25–120 °C. It was found that the LLE phase separation improved with a decrease of water and an increase of iodine content in the mixture [15], but was not sensitive to the HI concentration. Additionally, it was observed that the allowable range of iodine content for phase separation, i.e. between the lower limit for liquid–liquid phase splitting and the upper one related with iodine precipitation, became wider at higher temperatures. Recently, all the experimental data presented by Sakurai et al. [4], Giaconia et al. [10], and Lee et al. [16] have been collected together and common trends were examined through a series of parametric studies [13] in order to identify the optimal operating window for Bunsen process. It was concluded that the optimal point is represented by 4 mol of excess iodine and 11 mol of excess water in the stoichiometry at temperature of about 60 °C, while the allowable window ranges between 4 and 6 mol for the excess iodine (x), 11–13 mol for the excess water (n), and 50–80 °C for the temperature.

In addition, an attempt to relate the chemo-physical behavior of the Bunsen reaction system and the chemical equilibrium involving iodine and sulfur compounds have been made: a thermodynamic model has been proposed [17] and validated through Sakurai et al. [4] and Giaconia et al. [10] experimental data. Thus, an important contribution has been provided to the knowledge of the existing equilibriums in and between the two phases.

However, for the time being, there is a lack of data on the effect of the reaction temperature on the efficiency of SO_2 conversion into sulfuric acid. The aim of this study is to provide new experimental data on the efficiency of SO_2 conversion in the Bunsen reaction by varying temperature and iodine content. Operation temperatures have been varied from 30 °C up to 120 °C by saturating $HI–I_2–H_2O$ solutions with gaseous SO_2, whereas the iodine content has been changed between 0.22 and 0.57 mole fraction. At 30 and 45 °C tests have been performed at unsaturated conditions too. The subsequent purification step of the obtained HI_x phase was also investigated adopting a stripping procedure with nitrogen flowstream at constant temperature.

2. Experimental setup and procedures

The experimental setup, shown in Fig. 1, consists of a 500 mL jacketed stirred reactor. The reactor is connected to an acid gas trap, filled with a small amount of sodium hydroxide solution, to absorb the unreacted sulfur dioxide. A SO_2 sensor, placed on the trap exit line, detects the saturation of the alkaline solution. A thermostatic bath, connected to the reactor jacket, allows the regulation of the reactor temperature. The stirrer is connected to an electrical engine rotating at about 500 rpm.

The reaction was carried out following a semi-batch procedure. The reactor was initially filled with iodine, hydriodic acid and water, and the thermostatic bath and the stirrer were switched on. The HI/water ratio was always kept at about 57% (weight percentage) that is the azeotropic composition. Considering that the driving force of the Bunsen reaction is mainly due to the high value of the free Gibbs energy for the sulfuric acid hydration, it was not useful to drop the water content. Once the desired temperature was attained, and iodine dissolved, gaseous SO_2 was fed at a constant rate of 83 NmL/min, until the SO_2 sensor detected the saturation of both the reactor and the alkaline trap. According with this experimental procedure, only a very small amount of upper phase (sulfuric acid) was produced; hence, it was not possible to perform any sampling and analysis on the sulfuric phase. However, a qualitative (visual) detection of this phase was always necessary to ascertain a situation of chemical and physical equilibrium. Afterwards the stirrer was stopped and the mixture was kept motionless for 30 min to allow the stratification of the sulfuric and HI_x phases: then, the two phases were separated, and the hydriodic one was sampled and analysed. The trap was weighted before and after the experiment in order to exactly determine the quantity of SO_2
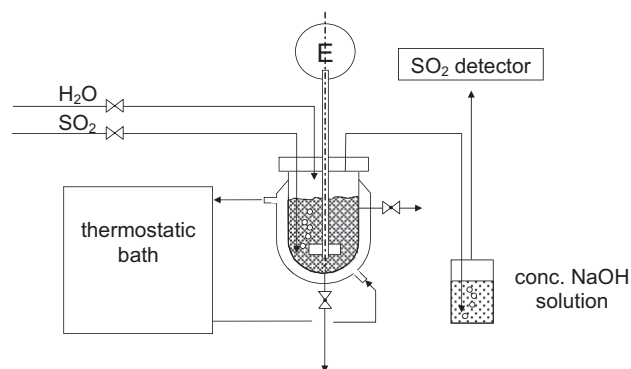

Fig. 1 – Bunsen reactor setup.