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Reaction parameters of the Bunsen reaction under simulated recycling conditions

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ABSTRACT

The iodine–sulfur (IS) thermochemical process is one of the most prospective, efficient, CO_2-free, massive hydrogen production approaches that use nuclear or solar energies. Among the three reactions composed of the IS cycle, the Bunsen reaction is crucial to the smooth operation of the continuous closed cycle. In the Bunsen reaction, sulfuric and hydriodic acids are produced by the reaction of recycled products of the decomposition of these two acids, In this work, a Bunsen reaction under simulated closed-cycle conditions, i.e., reaction between $I_2/HI/H_2O$ solution and SO_2, was investigated. The effects of reaction conditions such as SO_2 flow rate, HI acid concentration, I_2/HI molar ratio, and temperature on the characteristics of the Bunsen products were examined. These characteristics were phase separation, phase volume ratio, and compositions of HI_x and H_2SO_4 phases. The concentration of HI acid and the I_2/HI molar ratio of the initial solution, but not the flow rate of SO_2, were found to affect the phase states and compositions of Bunsen reaction products. The phase states and compositions of the products were predicted or calculated with self-built empirical models. Results well agreed with the experimental results for phase states and HI_x composition. All these findings validated the reliability of the models and offered crucial reference and guidance for the operation of the closed-cycle IS process.

Introduction

The iodine–sulfur (IS) thermochemical water-splitting process is one of the most promising, efficient, CO_2-free, and massive hydrogen production approaches that uses solar or nuclear energies. The IS process, which was initially proposed by the General Atomics company [1], has been extensively studied by many institutions since the 1970s [2]. Closed-cycle and continuous operation were achieved by the Japan Atomic Energy Agency [3] and the Institute on Nuclear and New Energy Technology of Tsinghua University [4].

The IS process consists of the following three reactions:

Bunsen reaction (exothermic at 293 K–393 K):

$$SO_2 + I_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \quad (1)$$

Sulfuric acid decomposition (endothermic at 1073 K–1173 K):

$$H_2SO_4 \rightarrow SO_2 + H_2O + 1/2O_2 \quad (2)$$

Hydriodic acid decomposition (endothermic at 573 K–773 K):

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$$2HI \rightarrow H_2 + I_2 \tag{3}$$

The efficiency of the IS process is predicted to exceed 40% when coupled with the use of a high temperature gas-cooled reactor (HTGR) or solar plant [5].

In the IS process, H_2SO_4 and HI acids are produced by the reaction of I_2, H_2O, and SO_2, after which the two acids are separated, purified, concentrated, and decomposed. Except for H_2 and O_2, the decomposition products of the two acids are recycled to the Bunsen reaction unit as reactants. Thus, the cycle is completed, and water decomposes to H_2 and O_2. A typical flow chart showing the main operations of the process is shown in Fig. 1.

The Bunsen reaction cannot be spontaneously conducted with its positive thermodynamic free-energy change ($\Delta G^0_{400\ K} = +82$ kJ/mol) [6]. Hence, excessive water and iodine are used to make ΔG become negative by the negative hydrated energy of the two acids. A research of General Atomics revealed that H_2SO_4 and HI_x could be spontaneously separated into two aqueous phases with excessive I_2, although the two phases are slightly cross contaminated. Therefore, the Bunsen reaction under actual conditions is usually expressed as [7]

$$xI_2 + SO_2 + (n+2)H_2O \Leftrightarrow [H_2SO_4 + (n-m)H_2O] + [2HI + (x-1)I_2 + mH_2O] \tag{4}$$

The amounts of water and iodine affect the thermodynamics, phase separation characteristics, and impurities of the separated acids. Thus, many studies have focused on the optimization of the reaction conditions and phase-separation characteristics. We summarized the primary objectives of studies on the Bunsen reaction as follows: to spontaneously carry out the reaction and phase separation, and to minimize cross-contamination. To meet these requirements, the amount of excess water and iodine must be minimized because excess water and iodine decrease the efficiency of the process. Given the complexity of the Bunsen reaction, numerous studies have focused on the reaction and phase-separation behavior of the $HI–H_2SO_4–I_2–H_2O$ quaternary mixture. Giaconia et al. [8] studied the effects of temperature, iodine, and water on the phase separation of the $HI/H_2SO_4/I_2/H_2O$ quaternary from 353 K to 393 K. They pointed out that temperature does not significantly affect the compositions of the two phases and that the impurities in both phases can be reduced by increasing iodine concentration. Sakurai et al. [9,10] investigated the effect of iodine concentrations on the phase-separation behavior at 273 K–368 K, with initial molar ratios of 0.07, 0.048, and 0.882 for HI, H_2SO_4, and H_2O, respectively. The separation performance was better at 273 K, as indicated by the increase in I_2 concentration in the raw material. The molar ratios of I_2/HI for phase splitting and saturation were 0.791 and 1.292, respectively. Colette et al. [11,12] studied the miscibility gap of the solution comprising $H_2SO_4/HI/I_2/H_2O = 1/2/m/14$ (molar ratio) at 293 and 308 K. The iodine soluble range expanded with increased temperature, and phase separation improved with decreased water and increased iodine in the mixtures. Lee et al. [13,14] and Yoon et al. [15] performed a series of experiments to study the characteristics of phase separation at different temperatures. They found that phase-separation performance is impaired with increased water content when the water concentration is below 0.88 mol fraction. Zhu et al. [16] studied the effects of iodine content on the separation characteristics of the liquid–liquid phase at 291 K–358 K. The increases in both the iodine concentration and solution temperature promoted phase separation, and the effect of solution temperature was less significant than that of iodine concentration.

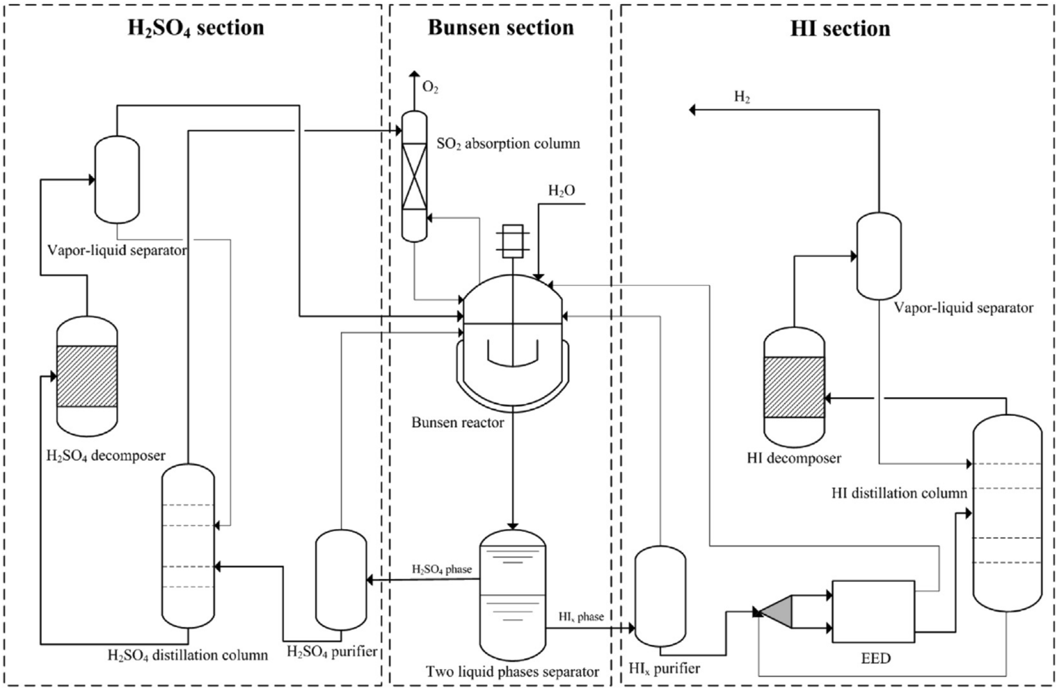

Fig. 1 – Flow sheet of the I–S process with an EED cell.