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Phase separation characteristics of HI–I_2–H_2SO_4–H_2O mixture at elevated temperatures

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ABSTRACT

The iodine–sulfur (IS) thermochemical water splitting cycle is one of the most promising massive hydrogen production approaches using nuclear or solar energy. Bunsen reaction is a crucial reaction of the process by which sulfuric and hydriodic acids form. The simultaneously phase separation of the Bunsen production products, composed of HI, I_2, H_2SO_4, and H_2O are essential for the smooth operation of the process. In this work, the phase separation characteristics of the quaternary mixtures were studied at elevated temperatures of 40–80 °C to clarify the phase separation characteristics. The critical conditions of the phase separation and iodine solubility in the mixture, as well as the effects of the composition and temperature on the purity of the two phases, were investigated. Favorable concentration range of each component in the quaternary solutions at various temperatures was obtained and presented in a tetrahedron diagram. The solution separates into two liquid phases spontaneously without iodine precipitation within the range. The amount of I_2 should be as high as possible, with no I_2 precipitation, to keep impurities at minimum content in the two phases. The results of this study offer technical basis for the design and operation of the IS process.

1. Introduction

Hydrogen is one of the most promising and potential alternatives of energy carriers with its apparent merits. Among the various hydrogen production methods, the iodine–sulfur (IS) thermochemical water-splitting cycle is one of the highly efficient, massive, and CO_2-free approaches. Over the past decades, the IS cycle, initially proposed by the General Atomics Corporation (GA) in the 1970s, has been intensively studied worldwide [1–4]. The IS process primarily consists of the following three reactions:

Bunsen reaction (exothermic at 20–120 °C):

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

Sulfuric acid (H_2SO_4) decomposition (endothermic at 800–900 °C):

$$H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2}O_2 \quad (2)$$

Hydriodic acid (HI) decomposition (endothermic at 300–500 °C):

$$2HI \rightarrow H_2 + I_2 \quad (3)$$

The efficiency of the IS process is expected to exceed 40% when coupled with a nuclear reactor, more specifically, a high temperature gas cooled reactor [5,6] or a solar plant [7,8].

In Bunsen reaction, H_2SO_4 and HI are produced by the reaction among iodine, water, and sulfur dioxide. The produced HI and H_2SO_4 are then separated and sent to the concentration and decomposition sections for conversion to H_2 and O_2 by reactions (2) and (3), respectively. Decomposition products, except hydrogen and oxygen, are recycled to the Bunsen reaction unit as reactant materials. Therefore, by processing these three reactions, water is decomposed to hydrogen and oxygen, and the other elements are circulated. The concept and the main unit operation of the IS process are shown in Fig. 1.

On the condition of excess iodine concentration and the concentration of each component is within an appropriate range, the Bunsen products can be separated into two immiscible liquid phases spontaneously, i.e., H_2SO_4 phase (the lighter phase) and poly-HI phase (HI_x, the heavier phase) [9,10]. The lighter phase contains a large amount of sulfuric acid and a small amount of HI and iodine, whereas the heavier phase is rich in HI, I_2, and a small amount of H_2SO_4. The compositions of the two phases from the liquid–liquid phase separator should be kept constant to ensure continuous and stable running of the closed cycle operation. However, keeping the Bunsen reaction products always separated and maintain the compositions of the two phases stable are very

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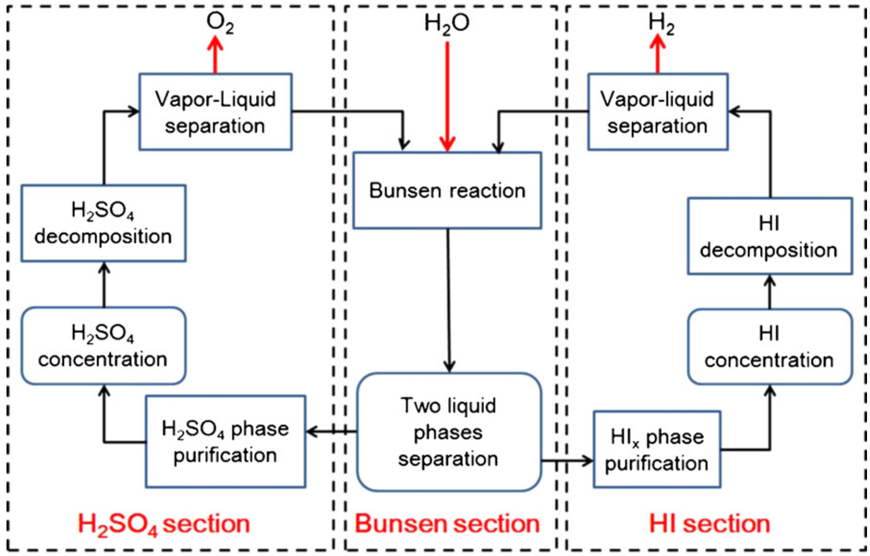

Fig. 1. Schematic diagram of the sulfur-iodine thermochemical water-splitting cycle.

difficult. The compositions of the recycled streams from the other two sections are liable to change under the recycling conditions, leading to the failure of the phase separation. The compositions of the two phases, or more specifically, the amount of the impurities in each phase, affects the purification steps and process efficiency. An effective way to decrease impurities in each phase is to operate the Bunsen reaction and the two liquid phase separation at high iodine concentration and higher temperatures [11]. Therefore, knowing the phase separation characteristics of the H_2SO_4–HI–I_2–H_2O solution at elevated temperatures is crucial to obtain the appropriate concentration range of each component at various temperatures. Under these conditions, the two phases can be easily formed without iodine precipitation, whereas the impurities in each phase were kept as low as possible.

Studies have been conducted on the phase separation behaviors of the HI–H_2SO_4–I_2–H_2O quaternary mixture in the Bunsen process. Giaconia et al. [11] studied the effect 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. [11,12] investigated the effect of iodine concentrations on the phase separation behavior in the range of 273–368 K, with an initial molar ratio of 0.07/0.048/0.882 for HI, H_2SO_4, and H_2O, respectively. The separation performance was better at 273 K, as the I_2 concentration increased in the raw material. The molar ratio of I_2/HI for phase splitting and saturation was 0.791 and 1.292, respectively. Colette et al. [13,14] studied the miscibility gap of the solution comprising H_2SO_4/HI/I_2/H_2O = 1/2/m/14 (molar ratio) at 293 K and 308 K. The iodine soluble range expanded with increasing temperature, and the phase separation improved by decreasing water and increasing iodine in the mixtures. Lee et al. [15,16] and Yoon et al. [17] performed a series of experiments to study the characteristics of phase separation at different temperatures. They indicated that phase separation performance was impaired with increasing water content when water concentration was below 0.88 in mole fraction. Zhu et al. [18] studied the effects of iodine content on the separation characteristics of the liquid–liquid phase in the temperature range of 291–358 K. The increase in both the iodine concentration and solution temperature promoted phase separation; the effect of solution temperature was less significant than that of iodine concentration. A number of studies on the phase separation characteristics of Bunsen products have been reported. However, most of these studies focused on the effect of iodine and water concentration on phase separation; only few have studied the quaternary mixtures as a whole. The influences of other components on phase separation have not yet been fully elucidated, and the published results show some disagreements. In our previous study [19], the phase separation characteristics of the HI–I_2–H_2SO_4–H_2O mixture at 20 °C were experimentally studied. The critical conditions of phase separation, iodine solubility, and intermiscibility of the mixture were determined and depicted in a tetrahedron figure. In addition, a program was developed to easily determine the phase state of the mixture. However, Bunsen reactions and phase separation are usually conducted at higher temperatures; thus, phase separation behavior at various temperatures must be investigated. In this study, the phase states of the HI–I_2–H_2SO_4–H_2O mixture at elevated temperatures and the effect of temperature on the phase splitting condition and liquid–liquid phase equilibrium are investigated.

2. Experiment

2.1. Experimental method

HI (57 wt%), H_2SO_4 (97 wt%), and I_2 (99.5 wt%) were of analytical grade. Deionized water was used all throughout the experiment. The HI–I_2–H_2SO_4–H_2O solution was prepared in a 100 mL jacket glass vessel, and the temperature of the solution was maintained at given temperatures using a thermostatic water bath. The critical phase separation conditions, iodine saturation conditions, and compositions of the two phases after separation were analyzed.

First, the relationship of the feed solution composition and its equilibrium state at various temperatures was investigated. A given amount of I_2 was added into the HI–H_2O solution, the temperature was raised to the desired level, and then the H_2SO_4 solution was added. The mixture was energetically stirred for 10 min, and the solution was allowed settle for more than 1 h to achieve phase equilibrium. The mass, density, and composition of each phase were determined and the total composition was calculated if the solution was separated into two phases. If the solution still kept a homogenous phase, its composition was also measured. Second, the solubility of I_2 in H_2SO_4–HI–H_2O is measured by adding enough