Characteristic of the Pressurized Continuous Bunsen Reaction using HIx Solution

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Abstract. The Sulfur-Iodine thermochemical hydrogen production process (SI process) consists of the Bunsen reaction section, the H2SO4 decomposition section and the HI decomposition section. The HIx solution (HI-I2-H2O) could be recycled to Bunsen reaction section from the HI decomposition section in the operation of the integrated SI process. The phase separation characteristic of the Bunsen reaction using the HIx solution was similar to that of SO2-I2-H2O system. However, the amount of produced H2SO4 phase was too small. To solve this problem, the study was carried out by the pressurized continuous Bunsen reaction. Bunsen reactions were performed at variation of feed rate of SO2/O2 gas in 3 bar of atmosphere. Also, it was performed to check the effects of the residence time in the reservoir on the characteristics of Bunsen products. As the results, the concentration of H2SO4 and HI in Bunsen products was increased with increasing the amounts of SO2. When the residence time in the reservoir increased, the concentration of H2SO4 and HI in HIx phase was decreased by reverse Bunsen reaction.

Keywords: Hydrogen production, Sulfur-Iodine process, Bunsen reaction, HIx solution, Continuous reaction, Pressurized reaction

1 Introduction

The SI process, which is one of methods for the hydrogen production by splitting water, consists of three reaction steps as follows; the Bunsen reaction (Eq. 1), the H2SO4 decomposition (Eq. 2), and the HI decomposition (Eq. 3).

\[ \text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI} \]  

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\[
\begin{align*}
\text{H}_2\text{SO}_4 & \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 0.5\text{O}_2 \quad (2) \\
2\text{HI} & \rightarrow \text{H}_2 + \text{I}_2 \quad (3)
\end{align*}
\]

H\(_2\)O is decomposed into H\(_2\) and O\(_2\) by the overall reaction and the decomposition products (SO\(_2\), I\(_2\) and H\(_2\)O) are recycled to the Bunsen reaction. According to the previous works proposed for the SI process, the decomposition products in the HI decomposition section could be recycled as the form of the HI\(_x\) (HI-I\(_2\)-H\(_2\)O) solution to the Bunsen reaction section [1,2]. Kim et al. investigated the phase separation characteristics of the Bunsen reaction using the HI\(_x\) solution. Although the phase separation characteristics were similar with the Bunsen reaction using the I\(_2\) and H\(_2\)O, the low volume of the H\(_2\)SO\(_4\) phase solution was formed [3]. Therefore, the method for improving the performance of the Bunsen reaction using the HI\(_x\) solution was required.

According to Henry’s law, the solubility of gas increases in aqueous solution when temperature decreases. On the other hands, the solubility of gas increases in aqueous solution when pressure of atmosphere increases [4]. However, Bunsen reaction couldn’t be carried out with low temperature, because the precipitation of iodine has occurred. For the solubility of SO\(_2\) gas, pressure in Bunsen reaction was increased. In this study, the pressurized continuous Bunsen reaction using HI\(_x\) solution was carried out to identify the characteristic at 3 bar and 333 K.

### 2 Materials and Methods

The experimental apparatuses were composed of the PFA tubular reactor, water bath, HI\(_x\) solution container, syringe pump (PHD 4400, Harvard apparatus), mass-flow controller (MFC 5850E, Brooks), sampling pot, and reservoir. The reactor was placed in the water bath in which the temperature was kept constant. The HI\(_x\) solution container was made up of 500 mL water jacketed beaker, and the temperature was controlled at 333 K. Temperature of syringe pump and HI\(_x\) solution was controlled at 333 K. On the other hand, feeding line of SO\(_2\) gas was controlled at 323 K.

HI (55-58 wt%, Yakuri), I\(_2\) (99 wt%, Junsei), and H\(_2\)O (ultra-pure water) were used to prepare HI\(_x\) solution. HI\(_x\) solution was prepared in HI\(_x\) solution container. The molar ratio of HI/I\(_2\)/H\(_2\)O was fixed as 1.0/2.5/8.0. HI, H\(_2\)O, and I\(_2\) were fed into the HI\(_x\) solution container. The magnetic stirrer was applied to dissolve the I\(_2\) quickly. The prepared HI\(_x\) solution was measured by titration before the usage of HI\(_x\) solution. SO\(_2\) (99.95%) and O\(_2\) (99.999%) gas were used as a feeding gas in this reaction.

The prepared HI\(_x\) solution was supplied at a constant feed rate of 2 mL/min using syringe pump. Feed rate of SO\(_2\) and O\(_2\) gas were controlled by the mass-flow controller. The reaction product was collected at a sampling pot and reservoir, respectively.

The composition of Bunsen products in sampling pot and reservoir was measured by following methods. The HI and I\(_2\) concentrations were measured through titration of I\(^-\) and I\(_2\) using an AgNO\(_3\) solution and a Na\(_2\)S\(_2\)O\(_3\) solution, respectively. The H\(_2\)SO\(_4\) concentration was measured by subtracting the amount of HI from the amount of H\(^+\) titrated with NaOH. The H\(_2\)O content was calculated using a mass balance equation. Titration was conducted with a potentiometric titrator (AT-510, KEM) and electrode (acid-base titration electrode: KEM C-171, redox titration electrode: KEM C-272, precipitation titration electrode: KEM C-373).

### 3 Results and Discussion

Experimental was performed with HI\(_x\) solution at various SO\(_2\)/O\(_2\) gas feed rate. Partial pressure ratio of SO\(_2\)/O\(_2\) was 2. The result of this experimental is shown in the Table 1. The
composition by titration analysis of HI\textsubscript{x} solution is 1/2.49/10.5 of HI/I\textsubscript{2}/H\textsubscript{2}O molar ratio. H\textsubscript{2}SO\textsubscript{4}/HI molar ratio is increased from ca. 0.06 to 0.12, but I\textsubscript{2}/HI molar ratio is decreased from ca. 1.72 to 1.47 with increasing the feed rate of SO\textsubscript{2}/O\textsubscript{2} gas. The concentration of H\textsubscript{2}SO\textsubscript{4} and HI in the reaction products is increased with increasing the feed rate of SO\textsubscript{2} gas (Fig. 1).

Table 1. the effects of SO\textsubscript{2}/O\textsubscript{2} feed rate on the pressurized continuous Bunsen reaction using HI\textsubscript{x} solution.

| Sample          | Molar ratio | Feed rate (mL/min) |
|-----------------|-------------|--------------------|
|                 | I\textsubscript{2} | H\textsubscript{2}SO\textsubscript{4} | HI | H\textsubscript{2}O | SO\textsubscript{2}/O\textsubscript{2} |
| HI\textsubscript{x} solution | 2.4896 | 0.0000 | 1 | 10.508 | - |
| 16-1            | 1.6212 | 0.0900 | 1 | 5.2933 | 40/20 |
| 16-2            | 1.4659 | 0.1160 | 1 | 4.8058 | 50/25 |
| 16-3            | 1.7432 | 0.0641 | 1 | 5.8098 | 30/15 |
| 16-4            | 1.7204 | 0.0667 | 1 | 5.6857 | 20/10 |

In this result, the products of H\textsubscript{2}SO\textsubscript{4} and HI are increased as SO\textsubscript{2} gas is increased. It is expected that the characteristic of Bunsen reaction is improved in accordance with increasing residence time. However, the opposite result is derived. Irrespective of residence time in reactor, the conversion of I\textsubscript{2} is increased with the amounts of SO\textsubscript{2}. As a result, the characteristic of the pressurized continuous Bunsen reaction is improved with increasing the amounts of SO\textsubscript{2} gas.

![Figure 1. The effects of SO\textsubscript{2}/O\textsubscript{2} feed rate on the concentration of H\textsubscript{2}SO\textsubscript{4} and HI in Bunsen products.](image-url)
Also, the different physical properties of Bunsen products are shown in the reservoir (Fig. 2). The products of Bunsen reaction separated into two immiscible liquid phases (H$_2$SO$_4$-rich phase is referred to as H$_2$SO$_4$ phase, and HI-rich phase is referred to as HI$_x$ phase) because the use of I$_2$ results in a density difference between the two phase [5]. The density of H$_2$SO$_4$ phase is lower than density of HI$_x$ phase. For this reason, H$_2$SO$_4$ phase is upper phase. The shape of H$_2$SO$_4$ phase is ring (Fig. 2). This is due to the adhesive force of H$_2$SO$_4$.

![Figure 2](image-url)  
**Figure 2.** Plane photograph of reservoir with Bunsen products. [A] Cored HI$_x$ phase and H$_2$SO$_4$ phase attached inner wall of reservoir. [B] H$_2$SO$_4$ phase after removing HI$_x$ phase.

The effects of residence time in reservoir on the variation of Bunsen products were investigated. Bunsen reaction was carried out at 40/20 mL/min of the SO$_2$/O$_2$ feed rate. Bunsen products were brought into reservoir. HI$_x$ phase solution in reservoir was collected every hour. The result of this experimental is shown in the Table 2. The composition of HI$_x$ solution is 1/2.48/10.1 of HI/I$_2$/H$_2$O molar ratio. Then the composition of Bunsen product is 1/1.69/6.93/0.057 of HI/I$_2$/H$_2$O/H$_2$SO$_4$ molar ratio. Table 2 shows that the H$_2$SO$_4$/HI molar ratio is decreased from 0.057 to 0.042, while the I$_2$/HI molar ratio is increased from ca. 1.69 to 1.95 with residence time in reservoir.

**TABLE 2.** THE EFFECTS OF THE RESIDENCE TIME IN RESERVOIR ON THE COMPOSITION OF BUNSEN PRODUCTS.

| Sample    | I$_2$  | H$_2$SO$_4$ | HI  | H$_2$O | Residence time in reservoir |
|-----------|--------|-------------|-----|--------|----------------------------|
| HI$_x$ solution | 2.4817 | 0.0000 | 1   | 10.103 | -                           |
| Product   | 1.69   | 0.0570      | 1   | 6.93   | -                           |
| 10-1      | 1.7183 | 0.0688      | 1   | 6.6275 | 1 h                         |
| 10-2      | 1.8031 | 0.0590      | 1   | 5.7712 | 2 h                         |
| 10-3      | 1.8309 | 0.0548      | 1   | 5.8949 | 3 h                         |
| 10-4      | 1.9917 | 0.0453      | 1   | 6.2781 | 4 h                         |
| 10-5      | 1.9545 | 0.042       | 1   | 6.0505 | 5 h                         |
Also, the concentration of H\textsubscript{2}SO\textsubscript{4} and HI in HI\textsubscript{x} phase is decreased (Fig. 3). It is that the reverse Bunsen reaction (Eq. 4) occurred in the reservoir. The concentration of I\textsubscript{2} in HI\textsubscript{x} phase is increased due to reverse Bunsen reaction. On the other hands, H\textsubscript{2}O/HI molar ratio in HI\textsubscript{x} phase fluctuates because of moving of H\textsubscript{2}O into H\textsubscript{2}SO\textsubscript{4} phase.

\begin{equation}
\text{H}_2\text{SO}_4 + 2\text{HI} \rightleftharpoons \text{SO}_2 + \text{I}_2 + \text{H}_2\text{O}
\end{equation}

![Figure 3](image)

**Figure 3.** The effects of residence time in reservoir on the concentration of Bunsen products in the HI\textsubscript{x} phase.

4 Conclusion

The results provide that the characteristic of the pressurized continuous Bunsen reaction using HI\textsubscript{x} solution improves when the feed rate of SO\textsubscript{2} gas was increased. Bunsen products are separated into the H\textsubscript{2}SO\textsubscript{4} and HI\textsubscript{x} phase. The composition of Bunsen products in reservoir is changed due to reverse Bunsen reaction. The composition of the Bunsen products may be controlled by using the reverse Bunsen reaction.

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