

Characteristic of the Pressurized Continuous Bunsen Reaction using HI_x 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 HI_x 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 HI_x 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 HI_x phase was decreased by reverse Bunsen reaction.

Keywords: Hydrogen production, Sulfur-Iodine process, Bunsen reaction, HI_x 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).



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H_2O is decomposed into H_2 and O_2 by the overall reaction and the decomposition products (SO_2 , I_2 and H_2O) 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_2O) 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_2O , the low volume of the H_2SO_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_2O (ultra-pure water) were used to prepare HI_x solution. HI_x solution was prepared in HI_x solution container. The molar ratio of $\text{HI}/\text{I}_2/\text{H}_2\text{O}$ was fixed as 1.0/2.5/8.0. HI, H_2O , 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 $\text{Na}_2\text{S}_2\text{O}_3$ solution, respectively. The H_2SO_4 concentration was measured by subtracting the amount of HI from the amount of H^+ titrated with NaOH. The H_2O 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_x solution is 1/2.49/10.5 of $\text{HI}/\text{I}_2/\text{H}_2\text{O}$ molar ratio. $\text{H}_2\text{SO}_4/\text{HI}$ molar ratio is increased from ca. 0.06 to 0.12, but I_2/HI molar ratio is decreased from ca. 1.72 to 1.47 with increasing the feed rate of SO_2/O_2 gas. The concentration of H_2SO_4 and HI in the reaction products is increased with increasing the feed rate of SO_2 gas (Fig. 1).

Table 1. the effects of so_2/o_2 feed rate on the pressurized continuous bunsen reaction using hi_x solution.

Sample	Molar ratio				Feed rate (mL/min)
	I_2	H_2SO_4	HI	H_2O	SO_2/O_2
HI_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_2SO_4 and HI are increased as SO_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_2 is increased with the amounts of SO_2 . As a result, the characteristic of the pressurized continuous Bunsen reaction is improved with increasing the amounts of SO_2 gas.

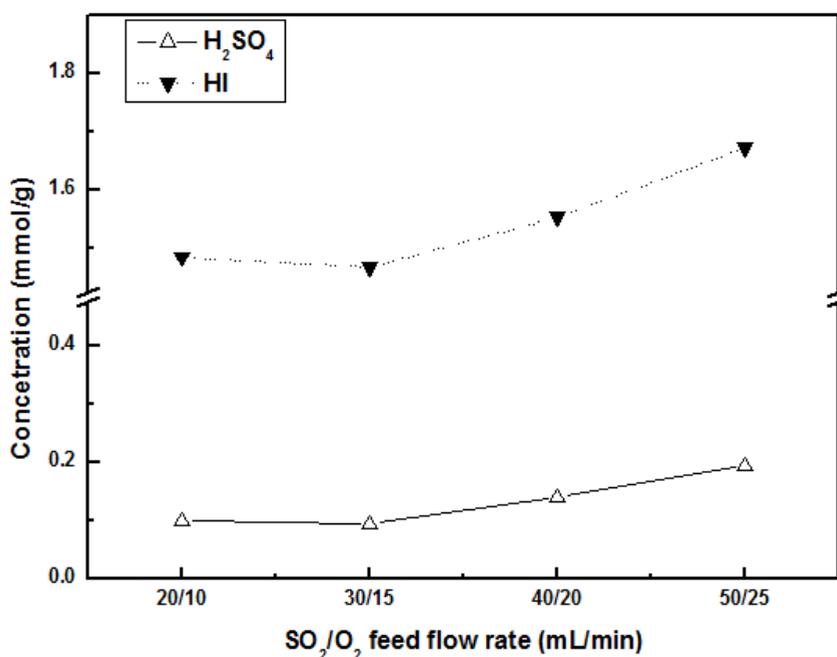


Figure 1. The effects of SO_2/O_2 feed rate on the concentration of H_2SO_4 and HI in Bunsen products.

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_2SO_4 -rich phase is referred to as H_2SO_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_2SO_4 phase is lower than density of HI_x phase. For this reason, H_2SO_4 phase is upper phase. The shape of H_2SO_4 phase is ring (Fig. 2). This is due to the adhesive force of H_2SO_4 .

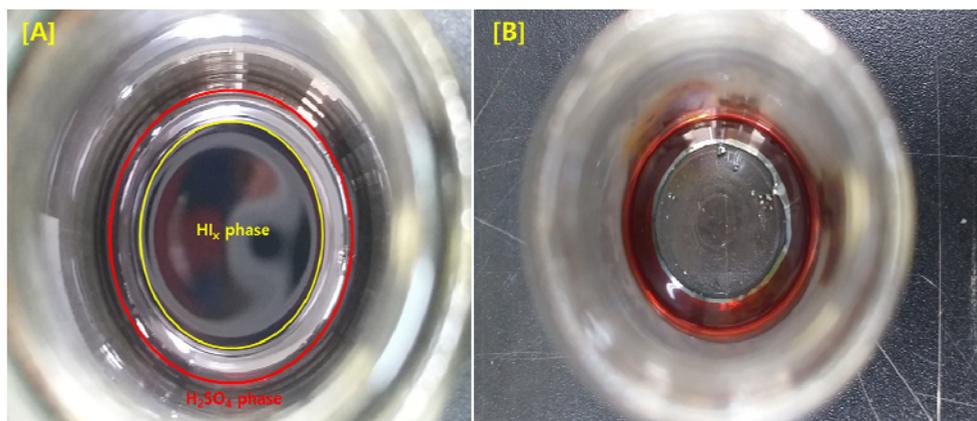


Figure 2. Plane photograph of reservoir with Bunsen products. [A] Cored HI_x phase and H_2SO_4 phase attached inner wall of reservoir. [B] H_2SO_4 phase after removing HI_x phase.

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 $\text{HI}/\text{I}_2/\text{H}_2\text{O}$ molar ratio. Then the composition of Bunsen product is 1/1.69/6.93/0.057 of $\text{HI}/\text{I}_2/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ molar ratio. Table 2 shows that the $\text{H}_2\text{SO}_4/\text{HI}$ 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	Molar ratio				Residence time in reservoir
	I_2	H_2SO_4	HI	H_2O	
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_2SO_4 and HI in HI_x phase is decreased (Fig. 3). It is that the reverse Bunsen reaction (Eq. 4) occurred in the reservoir. The concentration of I_2 in HI_x phase is increased due to reverse Bunsen reaction. On the other hands, $\text{H}_2\text{O}/\text{HI}$ molar ratio in HI_x phase fluctuates because of moving of H_2O into H_2SO_4 phase.

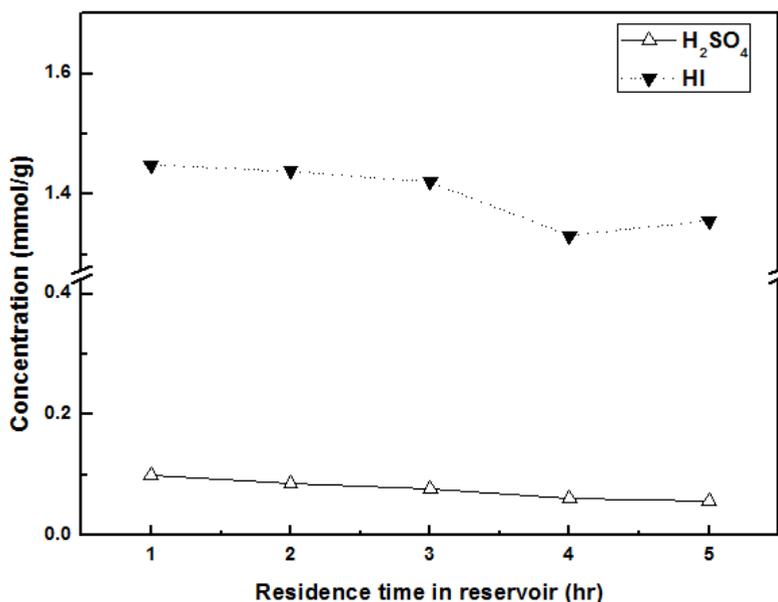


Figure 3. The effects of residence time in reservoir on the concentration of Bunsen products in the HI_x phase.

4 Conclusion

The results provide that the characteristic of the pressurized continuous Bunsen reaction using HI_x solution improves when the feed rate of SO_2 gas was increased. Bunsen products are separated into the H_2SO_4 and HI_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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