

Bunsen Reaction using a HI_x Solution ($HI-I_2-H_2O$) with Countercurrent Flow for Sulfur-Iodine Hydrogen Production Process

Hyo-Sub Kim^{1,a}, Hyun-Kyu Park^{1,b}, Chu-Sik Park^{2,c}, Ki-Kwang Bae^{2,d} and Young-Ho Kim^{1,e,*}

¹Department of Chemical Engineering and Applied Chemistry, Chungnam National University, 220 Gung-dong, Yuseong-gu, Daejeon 34134, Republic of Korea

²Hydrogen Energy Research Center, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 34129, Republic of Korea

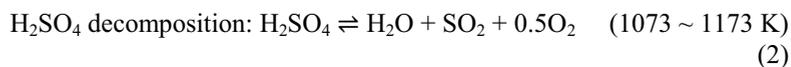
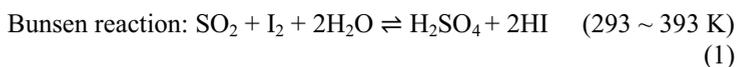
^ahskim05@cnu.ac.kr, ^bphk955@cnu.ac.kr, ^ccspark@kier.re.kr, ^dkkbae@kier.re.kr, ^{e,*}yh_kim@cnu.ac.kr

Abstract. In the sulfur-iodine hydrogen production process, the Bunsen reaction is a crucial section because of the linkage with the H_2SO_4 and HI decomposition sections. The HI_x solution ($HI-I_2-H_2O$ mixture) was fed to the Bunsen reaction section as a reactant from the HI decomposition section. In this study, the Bunsen reaction using the HI_x solution with countercurrent flow was performed. The production rate of HI_x phase solution increased while that of H_2SO_4 phase solution was maintained constant when increasing the flow rate of HI_x solution. As the SO_2 flow rate increased, the production rates of H_2SO_4 and HI_x phase solutions increased. The amount of resultant H_2SO_4 phase was very lower than that of resultant HI_x phase under the conditions examined in this study.

1 Introduction

The industrial system based on fossil fuels induces various environmental problems. The development of alternative energy is required to resolve the environmental problems. Hydrogen is regarded as an energy carrier that can substitute for fossil fuels. The thermochemical water splitting process produces the hydrogen from water at a lower temperature than operating condition of the direct water splitting process [1]. Among the thermochemical water splitting process, the sulfur-iodine hydrogen production process (SI process) can produce a large amount of hydrogen from water [2]. This process consisted of the following three reactions:

* Corresponding author: yh_kim@cnu.ac.kr



H₂SO₄ and HI that produced by the Bunsen reaction (Eq. (1)) were separated spontaneously by a density difference under an excess of iodine. The resultant H₂SO₄ and HI were decomposed at each decomposition section (Eqs. (2) and (3)). This process was operated in a closed-cycle by recycling the decomposition products except for O₂ and H₂. Consequently, H₂O was decomposed into H₂ and O₂ via this process.

Meanwhile, a HI_x solution consisting of HI, I₂ and H₂O was fed to the Bunsen reaction section as a reactant from the HI decomposition section [3]. We performed the Bunsen reaction in a semi-batch mode using the HI_x solution in a previous study [4]. However, these results had limitations to use for the integrated operation of the SI process. Therefore, the Bunsen reaction was conducted in a counter-current mode using the HI_x solution to provide the operating data for SI process. The flow rates of HI_x solution and SO₂ gas were changed as the operating variables.

2 Experimental

A 460 mL glass reactor was used for the Bunsen reaction using HI_x solution with counter-current flow (Fig. 1). The ceramic packing materials of Raschig ring type were introduced to the reactor to avoid the channeling of SO₂ gas and increase the contact area of reactants. The operating temperature was maintained at 333 K by a thermostatic water bath.

Before the reaction, the H₂SO₄ phase and HI_x phase solutions were prepared for a smooth operation. For the HI_x phase solution, I₂ (99 wt%, Junsei) and H₂O (ultrapure water) to achieve a 1/2/6.17 of HI/I₂/H₂O molar ratio based on 1.27 mol of HI were fed to the reactor. The HI_x phase solution was prepared by feeding N₂ gas at a constant rate of 20 mL/min for 1 h. Afterwards, the H₂SO₄ phase solution with the H₂O/H₂SO₄ molar ratio of 4.04 based on 0.4 mol of H₂SO₄ was introduced above the HI_x phase solution. I₂ and H₂O were fed to the HI_x solution reservoir to prepare the HI_x solution with the HI/I₂/H₂O molar ratio of 1/2/6.17 based on 1.75 mol of HI. The reaction was performed with feeding of the SO₂ (99.595 vol%), HI_x solution and H₂O. Flow rates of the HI_x solution and SO₂ were controlled by using metering pump (QG 50, Fluid Metering, Inc.) and MFC (MKS Instruments Inc.), respectively. The additional H₂O was fed to be 7.8 of H₂O/HI molar ratio of the HI_x solution to increase the amount of H₂SO₄ phase. The reaction proceeded by maintaining a constant interface between H₂SO₄ phase and HI_x phase in the reactor.

HI and I₂ concentrations were measured by titrating I⁻ and I₂ with 0.1 N AgNO₃ and 0.1 N Na₂S₂O₃ standard solutions (Samchun Chemical), respectively. H₂SO₄ concentration was calculated by subtracting the amount of HI from the amount of H⁺ titrated with 0.1 N NaOH standard solution (DC Chemical). H₂O concentration was calculated using a mass balance equation. The titrations were performed using a potentiometric titrator (AT-510, KEM) and electrodes (acid-base titration electrode: KEM C-171, redox titration electrode: KEM C-272 and precipitation titration electrode: KEM C-373). To minimize the error resulting from the sampling and analysis processes, three samples were measured for each ion and the average concentration values were calculated.

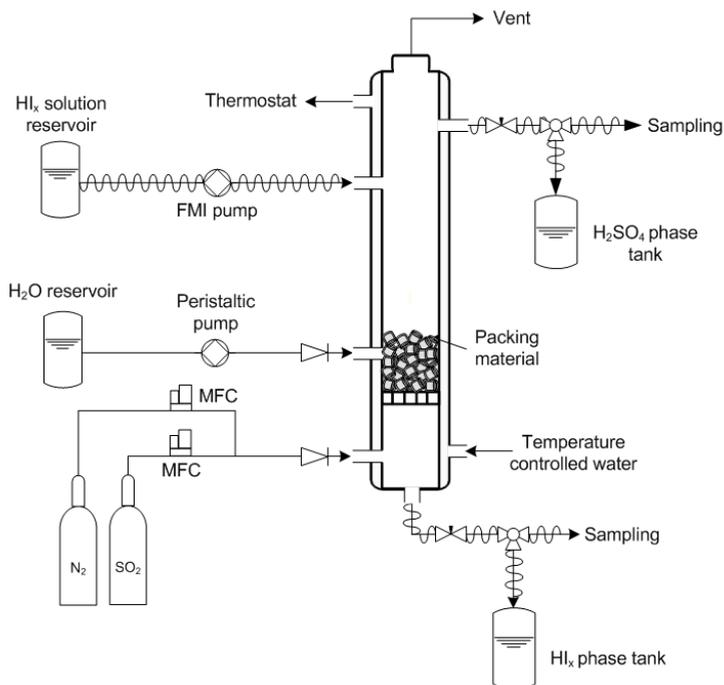


Fig. 1. Schematic diagram of experimental apparatus for the Bunsen reaction using the HI_x solution with countercurrent flow.

3 Results and Discussion

It was found that the feed pipe for the HI_x solution was clogged with solid I_2 when the HI_x solution was fed to the reactor that filled the H_2SO_4 phase and HI_x phase solutions. This result can be explained by the occurrence of the reverse Bunsen reaction (Eq. (4)) due to a direct contact between the HI_x feed solution and the H_2SO_4 phase solution. Therefore, the HI_x feed solution should be introduced to the HI_x phase in the reactor to avoid the solidification of I_2 .

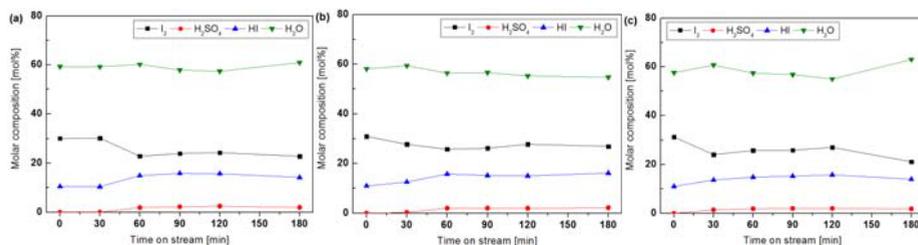


Fig. 2. The composition change in HI_x phase with different the HI_x solution flow rate; (a) 2.8 g/min, (b) 4.9 g/min and (c) 7.7 g/min.

Flow rate of the HI_x solution was changed to confirm the effect of the HI_x solution flow rate on the composition of Bunsen products. Flow rate of SO_2 was controlled at 110 mL/min. Fig. 2(a) shows the composition change in HI_x phase at 2.8 g/min of HI_x solution flow rate. The composition of HI_x phase was maintained constant after 60 min and the

HI/H₂SO₄/I₂/H₂O molar ratio was 1/0.14/1.61/4.28 at 180 min. For the H₂SO₄ phase, the H₂SO₄/HI/H₂O molar ratio was 1/0.09/5.55. The production rates of H₂SO₄ and HI_x phase solution were 0.26 and 3.09 g/min, respectively. Fig. 2(b) shows the composition change in HI_x phase at 4.9 g/min of HI_x solution flow rate. The composition of HI_x phase was maintained constant after 60 min and the HI/H₂SO₄/I₂/H₂O molar ratio was 1/0.13/1.67/3.39 at 180 min. The H₂SO₄/HI/H₂O molar ratio in H₂SO₄ phase was 1/0.09/5.55 at 180 min. The production rates of H₂SO₄ and HI_x phase solution were 0.16 and 5.32 g/min, respectively. The composition change in HI_x phase at 7.7 g/min of HI_x solution flow rate was shown in Fig. 2(c). The composition of HI and H₂SO₄ was maintained constant after 60 min while the composition of I₂ and H₂O were changed significantly. The HI/H₂SO₄/I₂/H₂O molar ratio in HI_x phase was 1/0.13/1.51/4.50 and the H₂SO₄/HI/H₂O molar ratio in H₂SO₄ phase was 1/0.07/6.19 at 180 min. The production rates of H₂SO₄ and HI_x phase solution were 0.22 and 8.55 g/min, respectively. As the flow rate of HI_x solution increased, the production rate of HI_x phase solution increased while that of H₂SO₄ phase solution did not change significantly. In addition, the HI content in H₂SO₄ phase and the I₂ and HI contents in HI_x phase were increased by increasing the flow rate of HI_x solution. This result was because the amounts of HI, I₂ and H₂O in feed increased relatively compared with the supplied amount of SO₂.

Flow rate of SO₂ gas was controlled to identify the effect of SO₂ flow rate on the characteristics of Bunsen reaction in a counter-current flow mode. The HI_x solution was fed at approximately 7.7 g/min. The composition and production rates of HI_x phase and H₂SO₄ phase at 180 min with different SO₂ flow rate were listed in Table 1. Regardless of the variation in the SO₂ flow rate, the compositions of HI and H₂SO₄ in HI_x phase were maintained constant after 60 min. The amount of H₂SO₄ corresponding to an impurity in HI_x phase increased by increasing the SO₂ flow rate. In addition, the production rates of H₂SO₄ phase and HI_x phase solutions increased when increasing the SO₂ flow rate. This result can be explained by an increase in the amount of SO₂ used as a reactant.

Table 1. The Composition And Production Rate Of HI_x Phase And H₂SO₄ Phase At 180 Min With Different The SO₂ Flow Rate

SO ₂ flow rate [mL/min]	Composition [molar ratio]								Production rate [g/min]	
	H ₂ SO ₄ phase			HI _x phase					H ₂ SO ₄ phase	HI _x phase
	H ₂ SO ₄	HI	H ₂ O	HI	H ₂ SO ₄	I ₂	H ₂ O			
80	1	0.07	6.19	1	0.10	1.72	6.22	0.21	8.51	
110	1	0.09	6.06	1	0.13	1.51	4.50	0.22	8.55	
200	1	0.13	6.21	1	0.17	1.36	4.17	0.23	8.62	

On the other hand, the composition of products obtained in the counter-current flow mode was similar to the results obtained in a semi-batch mode [4]. The amount of H₂SO₄ phase was lower than that of HI_x phase, which was in accordance with the results obtained in a semi-batch mode [4]. A method to increase the amount of H₂SO₄ phase solution for the continuous operation of Bunsen reaction with countercurrent flow should be further investigated.

4 Conclusions

In this study, the effects of the flow rates of HI_x solution and SO_2 on the Bunsen reaction using the HI_x solution with counter-current flow were investigated. Major results were summarized as follows.

1) When the HI_x solution was fed to the H_2SO_4 phase solution in the reactor, the solidification of I_2 occurred by the reverse Bunsen reaction. The HI_x solution should be introduced to the HI_x phase in the reactor for a continuous operation of Bunsen reaction.

2) The composition of HI_x phase was maintained constant after 60 min regardless of the variation in the HI_x solution flow rate. The production rate of HI_x phase solution increased while that of H_2SO_4 phase solution did not change significantly as the flow rate of HI_x solution increased.

3) The compositions of HI and H_2SO_4 were maintained constant after 60 min regardless of the variation in the SO_2 flow rate. The impurity content in HI_x phase was increased by increasing the SO_2 flow rate. The production rates of H_2SO_4 phase and HI_x phase solutions also increased as the SO_2 flow rate increased. The amount of resultant H_2SO_4 phase was very lower than that of HI_x phase under all experimental conditions.

5 Acknowledgments

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