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Article

황-요오드 수소 제조 공정에서 초음파 조사를 이용한 분젠 반응의 특성

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Characteristics of Bunsen Reaction using Ultrasonic Irradiation in Sulfur-iodine Hydrogen Production Process

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초 록

황-요오드(SI) 공정의 통합 운전을 위한 분젠 반응 단계에서, I_2 및 H_2O 반응물들은 HI_x 용액 내 용해된 성분들로써 공급된다. HI_x 용액과 SO_2 공급을 이용하여 분젠 반응이 수행될 때 HI_x 상 내 대부분의 H_2SO_4 생성물이 존재하며, 이에 따라 HI_x 상에 대한 H_2SO_4 상의 부피 비가 매우 낮다. 본 연구에서 우리는 상 분리 성능을 향상시키기 위해 HI_x 용액을 이용한 분젠 반응에 대한 초음파 조사의 효과들을 연구하였다. 분젠 반응과 함께 초음파가 조사될 때 HI_x 상으로부터 H_2SO_4 상으로 이동된 H_2SO_4의 양은 최대 58.0 mol%까지 증가하였으며, H_2SO_4 상의 부피 또한 최대 13.1 vol%까지 증가하였다. 특히, 상 분리에 대한 초음파 조사의 효과는 온도, I_2 및 H_2O 공급 농도가 감소함에 따라 향상되었다. 초음파 조사는 HI_x 상 내 반응 평형을 미시적으로 이동시킴으로써 추가적인 H_2O 분자들의 형성을 유도하였다. 이로부터 추가적으로 생성된 H_2O 및 분리된 H_2SO_4 분자들이 H_2SO_4 상으로 이동할 수 있는 더 많은 $H_2SO_4 \cdot xH_2O$ (x = 5-6) 착물들을 형성하였다.

Abstract

In Bunsen reaction section for the integrated operation of sulfur-iodine (SI) process, I_2 and H_2O reactants are supplied as dissolved species in an HI_x solution. Most of the H_2SO_4 product is found in the HI_x phase when Bunsen reaction is performed using the HI_x solution and SO_2 feed, so that the volume ratio of the H_2SO_4 phase to the HI_x phase is very low. In this study, we investigated the effects of ultrasound irradiation on Bunsen reaction using the HI_x solution to improve its phase separation performance. With ultrasound irradiation, the amount of H_2SO_4 moved to the H_2SO_4 phase from the HI_x phase increased by up to 58.0 mol% and the volume of H_2SO_4 phase also increased by up to 13.1 vol%. In particular, the effect of ultrasound irradiation on the phase separation was improved with decreasing operating temperature, I_2 and H_2O feed concentrations. The ultrasound irradiation induces the formation of additional H_2O molecules by shifting microscopically the reaction equilibrium in the HI_x phase. Afterward, the additionally generated H_2O and isolated H_2SO_4 molecules form more $H_2SO_4 \cdot xH_2O$ (x = 5-6) clusters that can be moved to the H_2SO_4 phase.

***Keywords**: sulfur-iodine process, hydrogen production, bunsen reaction, HIx solution, ultrasonic irradiation*

1. Introduction

Hydrogen can be utilized as an energy carrier in various industrial applications. When it is produced from water, no environmental pollutants are emitted. Therefore, technologies for producing hydrogen from water have been investigated worldwide[1-3]. The thermochemical hydrogen production method proposed by Funk and Reinstrom can be

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performed at lower temperatures than that required to split water directly by combining several chemical reactions[4]. General Atomics (GA) proposed and investigated a thermochemical hydrogen production method known as the sulfur-iodine (SI) process[5]. The Japan Atomic Energy Agency (JAEA) demonstrated the continuous operation of the SI process at the bench scale with an output of 32 L/h[6]. It was reported that approximately 45-50% of the theoretical thermal efficiency of the SI process can be achieved under optimal operating conditions using the heat generated by a nuclear energy source[7-9]. The SI process is composed of the following three chemical reactions:

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

$$H_2SO_4 \rightleftarrows H_2O + SO_2 + 0.5O_2 \quad (2)$$

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

Sulfur dioxide (SO_2) reacts with water (H_2O) and iodine (I_2) to produce sulfuric acid (H_2SO_4) and hydrogen iodide (HI) in the Bunsen reaction (Eq. (1)). The Bunsen product solution spontaneously separates into two immiscible liquid phases (the H_2SO_4-rich phase is referred to as the SA phase, and the HI-rich phase is referred to as the HI_x phase) because the use of excess I_2 results in a density difference between the two phases. The H_2SO_4 and HI phases decompose as shown in eq. (2) and (3), respectively. The overall reaction leads to the decomposition of H_2O into H_2 and O_2, and SO_2, I_2 and H_2O are recycled to the Bunsen reaction.

Side reactions in the Bunsen section should be minimized for the steady-state operation of the integrated SI process. It is also important to reduce the amount of impurities in each phase (HI and I_2 in the SA phase and H_2SO_4 in the HI_x phase). In previous study for characteristics of Bunsen products (quaternary mixture including H_2SO_4, HI, I_2 and H_2O), increasing the I_2 feed concentration enhances separation characteristics and reduces side reactions occurrence[10]. Since HI/H_2SO_4 molar ratio was fixed and continuous feeding of SO_2 was not considered, the study for quaternary mixture were insufficient to demonstrate Bunsen reaction system which carried out simultaneously Bunsen reaction, side reactions and phase separation. Therefore, we performed the Bunsen reaction with continuous SO_2 feeding and investigated the effects of I_2 feed concentration and temperature on the phase separation characteristics of Bunsen reaction and side reactions. The operating temperature was also varied because the I_2 feed concentration can be increased further with increasing temperature. Increasing the I_2 feed concentration results in a decrease in the impurities contents and inhibition of the side reactions occurrence[11-13].

In a typical SI process, all Bunsen reactants are recycled from the H_2SO_4 and HI decomposition sections. Specifically, I_2 and H_2O including HI are recycled to the Bunsen reactor as an HI_x solution ($HI-I_2-H_2O$)[14,15]. Therefore, we investigated the phase separation characteristics of the Bunsen reaction using the HI_x solution. The products separation was difficult due to the very low volume fraction of the SA phase. In our previous study, we suggested that the phase separation of the Bunsen reaction could be enhanced when extra water was added to the Bunsen products[16]. We found that each mole of H_2SO_4 in the HI_x phase should be in contact with approximately 5-6 mol of H_2O to aid its transfer to the SA phase.

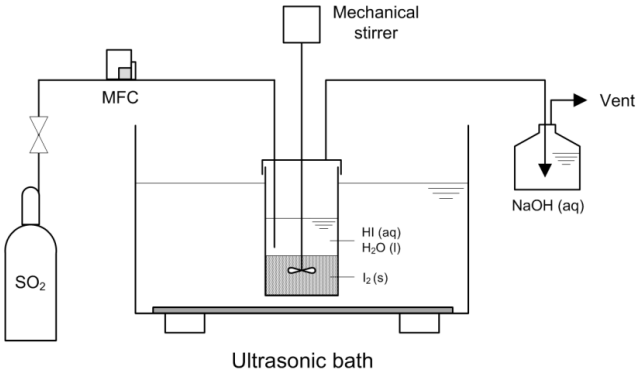


Figure 1. Schematic diagram of the Bunsen reaction equipment with ultrasound irradiation.

On the other hand, ultrasound irradiation can enhance the chemical and physical effects and increase the kinetic rates by inducing cavitation, which is the phenomenon of small bubbles expanding and contracting[17-19]. In this work, therefore, we performed the Bunsen reaction using the HI_x solution and ultrasound irradiation to improve its phase separation performance. The volume and composition of the Bunsen products were measured. The effects of ultrasound irradiation on the Bunsen reaction were investigated at various temperatures and I_2 and H_2O feed concentrations.

2. Experimental

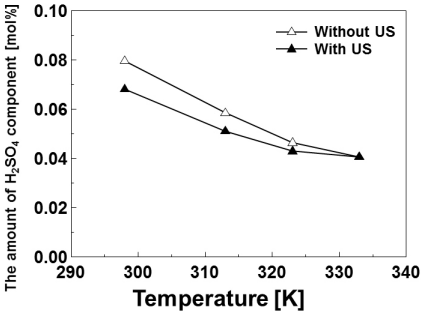
Figure 1 shows the experimental apparatus for the Bunsen reaction with ultrasound irradiation. A mechanical stirrer was employed to dissolve the iodine quickly. The ultrasonic frequency was 28 kHz. The operating temperature was controlled by regulating the temperature of the water in the ultrasonic bath. A vent line was connected to a scrubber, which was filled with an aqueous NaOH solution, to trap unreacted SO_2 gas.

The concentration of HI was measured by chemical titration before use. The amounts of I_2 and H_2O were controlled within an I_2/HI molar ratio of 2.0-3.8 and a H_2O/HI molar ratio of 6.17 based on 0.5 mol of HI. The operating temperature was varied from 298 to 333 K. To prepare the HI_x solution, the reactants (HI, I_2 and H_2O) were introduced into the reactor and were mixed for 30 min at the desired temperature. Subsequently, the reaction began when SO_2 gas was fed at 110 mL/min with or without ultrasonic irradiation. The reaction proceeded until a quasi-steady state was achieved (i.e., 340 min). The Bunsen products were transferred to the liquid-liquid separator. Afterward, the amount and composition of the Bunsen products were measured.

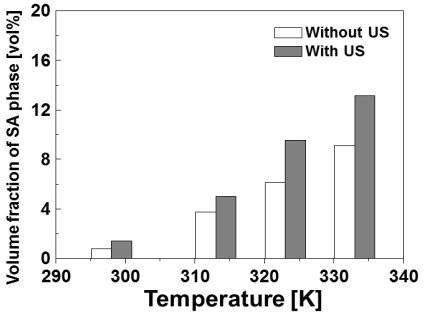
The HI and I_2 concentrations were measured by titrating I^- and I_2 with 0.1 N $AgNO_3$ and 0.1 N $Na_2S_2O_3$ standard solutions (Samchun Chemical), respectively. The H_2SO_4 concentration was calculated by

Table 1. The H_2SO_4 Distribution Ratio in Each Phase with or without Ultrasound (US) Irradiation; $HI/I_2/H_2O$ = 1/2.0/6.17

Temp. (K)	The H_2SO_4 distribution ratio (mol%)			
	Without US		With US	
	SA phase	HI_x phase	SA phase	HI_x phase
298	2.2	97.8	5.1	94.9
313	14.7	85.3	18.4	81.6
323	30.0	70.0	39.4	60.6
333	47.8	52.2	58.0	42.0

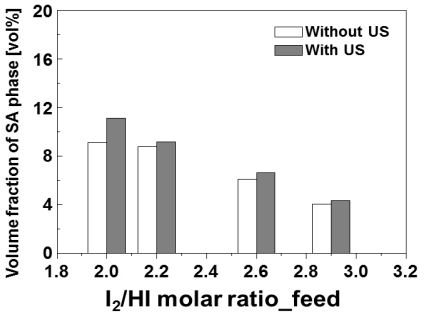


(a)

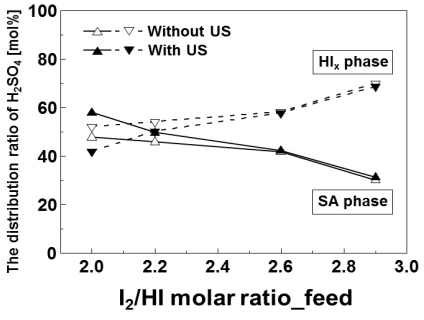


(b)

Figure 2. Effects of the temperature on the (a) amount of H_2SO_4 component and (b) volume fraction of the SA phase with or without ultrasound (US) irradiation; $HI/I_2/H_2O$ = 1/2.0/6.17.



(a)



(b)

Figure 3. Effects of the I_2/HI feed molar ratio on (a) the volume fraction of the SA phase and (b) H_2SO_4 distribution ratio with or without ultrasound (US) irradiation; H_2O/HI = 6.17, temperature : 333 K.

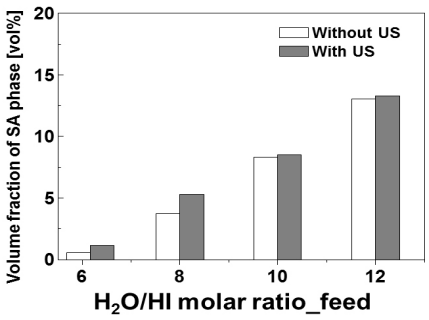
subtracting the amount of HI from the amount of H^+ titrated with a 0.1 N NaOH standard solution (DC Chemical). The water concentration was calculated using a mass balance equation. The chemical titrations were performed using a potentiometric titrator (KEM, AT-510) and electrodes (acid-base titration electrode: KEM C-171, redox titration electrode: KEM C-272 and precipitation titration electrode: KEM C-373). Three samples for each ion were measured to minimize the errors resulted from sampling and analysis processes, and then the average concentration values were determined.

3. Results and Discussion

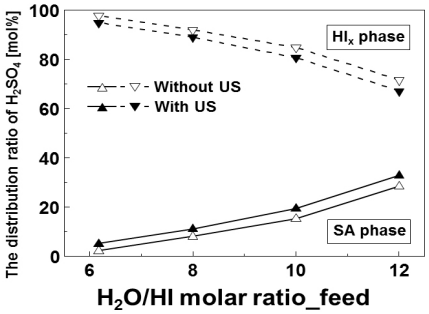
3.1. Effects of the temperature and I_2 concentration

The Bunsen reaction was performed using the HI_x solution with a 1/2/6.17 of $HI/I_2/H_2O$ molar ratio at various temperatures between 298 and 333 K with or without ultrasound irradiation. As the temperature increased, the H_2SO_4 content (mol%) in the total product decreased (Figure 2a). This result was attributed to the decrease in the SO_2 conversion due to the increase in temperature[20]. The amount (vol%) of the SA phase increased gradually (Figure 2b), and the H_2SO_4 distribution ratio in the SA phase increased (Table 1) with increasing temperature. The total H_2SO_4 content decreased, and the amount of the SA phase increased when ultrasound was irradiated. Additionally, the H_2SO_4 distribution ratio in the SA phase increased under ultrasound irradiation. When ultrasound was irradiated, the increase in the amount of the SA phase was correlated to the H_2SO_4 distribution ratio in each phase. The effect of ultrasound irradiation on the Bunsen reaction was significant when temperature decreased.

A series of experiments were performed at 333 K with various I_2 concentrations with or without ultrasound irradiation. The H_2O/HI molar ratio was set to 6.17, and the I_2/HI molar ratio was varied from 2.0 to 2.9. The amount of the SA phase decreased from 9.1 to 3.9



(a)



(b)

Figure 4. Effects of the H_2O/HI feed molar ratio on the (a) volume fraction of the SA phase and (b) H_2SO_4 distribution ratio with or without ultrasound (US) irradiation; I_2/HI = 2.0, temperature : 298 K.

vol% as the I_2 feed concentration increased (Figure 3a). In addition, the H_2SO_4 content distributed to the SA phase decreased from 47.8 to 30.0 mol%, whereas H_2SO_4 content distributed to the HI_x phase increased as the I_2 feed concentration increased (Figure 3b). The amount (vol%) of the SA phase was greater for the reaction with ultrasound irradiation than for the reaction without ultrasound irradiation. The use of ultrasound irradiation led to a slight increase in the H_2SO_4 content distributed to the SA phase. The effect of ultrasound irradiation on the phase separation of the Bunsen reaction was more significant for the lower I_2/HI molar ratios than for the I_2/HI molar ratio of 2.9 at 333 K.

Consequently, the H_2SO_4 content distributed to the SA phase increased when ultrasound was irradiated so that the amount of the SA phase increased. It was concluded that ultrasound irradiation improves the phase separation performance of Bunsen reaction products.

3.2. Effects of the H_2O concentrations

We proposed increasing the H_2O feed concentration to improve the poor phase separation due to a low volume ratio of the H_2SO_4 phase to the HI_x phase obtained from Bunsen reaction using the HI_x solution. We performed the Bunsen reaction at 298 K with various H_2O feed concentrations with or without ultrasound irradiation. The I_2/HI molar ratio was set to 2.0, and the H_2O/HI molar ratio was varied from 6.17 to 12.

The amount of the SA phase increased from 0.6 to 13.0 vol% as the H_2O feed concentration increased (Figure 4a) so that it was easier to separate the Bunsen products. The H_2SO_4 distribution ratio in the SA phase increased gradually with increasing H_2O feed concentration

Table 2. Molar fractions of the components in the Bunsen products using ultrasound (US) irradiation without the SO_2 feed; temperature : 298 K; HI/I_2/H_2O = 1/1.6/6.17

	Molar fraction (mol%)			
	X_{I2}[a]	X_{H2SO4}	X_{HI}	X_{H2O}
$X_{i,\ before\ US}$	0.08	0.09	0.30	0.52
$X_{i,\ after\ US}$	0.11	0.07	0.24	0.58
ΔX_i[b]	0.03	-0.03	-0.06	0.06

[a] X_i : Molar fraction of component i in the Bunsen products
[b] ΔX_i : $X_{i,\ after\ US}$ - $X_{i,\ before\ US}$.

(Figure 4b). The amount of the SA phase increased when ultrasound was irradiated. The ultrasound irradiation led to an increase in the H_2SO_4 distribution ratio in the SA phase. Therefore, it was concluded that the amount of the SA phase increased as the H_2O feed concentration increased due to increasing the H_2SO_4 distribution ratio in the SA phase. In other words, ultrasound irradiation and a higher H_2O feed concentration led to better phase separation performance of the Bunsen products.

3.3. The specific role of ultrasound irradiation

The H_2SO_4 and HI content decreased, and the I_2 content in the Bunsen products increased after ultrasound irradiation. It was assumed that the H_2O generated by the microscopic shift in the reaction equilibrium formed a complex with the isolated H_2SO_4, and therefore, the volume of the SA phase increased when ultrasound was irradiated. The variation in the composition of products by ultrasound irradiation was investigated to clearly identify the effects of ultrasound irradiation on the Bunsen reaction. The Bunsen reaction was performed at 298 K using the HI_x solution with a 1/1.6/6.17 of HI/I_2/H_2O molar ratio, which resulted in a single-phase product (mainly the HI_x phase). After the Bunsen reaction was completed, the ultrasound was irradiated for 180 min with or without the SO_2 gas feed.

The molar fractions (mol%) of the product components before and after ultrasound irradiation and their variations are listed in Table 2. The I_2 and H_2O contents increased by approximately 0.03 and 0.06 mol%, and the H_2SO_4 and HI contents decreased by approximately 0.03 and 0.06 mol% when ultrasound was irradiated without the SO_2 feed. Here, the ratios of the variations in the I_2, HI and H_2O content to the variation in the H_2SO_4 content were approximately 1.1, 2.1 and 2.0, respectively. When the reverse Bunsen reaction (Eq. 4) occurs, these ratios are 1, 2 and 2 for I_2, HI and H_2O, respectively. Therefore, it appeared that the Bunsen reaction equilibrium shifted microscopically toward the SO_2, I_2 and H_2O when ultrasound was irradiated. This phenomenon is due to the creation of hot spots due to a localized high temperature associated with the transient collapse of cavitation voids[21,22].

$$H_2SO_4 + 2HI \rightleftarrows SO_2 + I_2 + 2H_2O \quad (4)$$

Interestingly, the single-phase product was separated by producing the SA phase (approximately 3.7 vol%) during ultrasound irradiation.

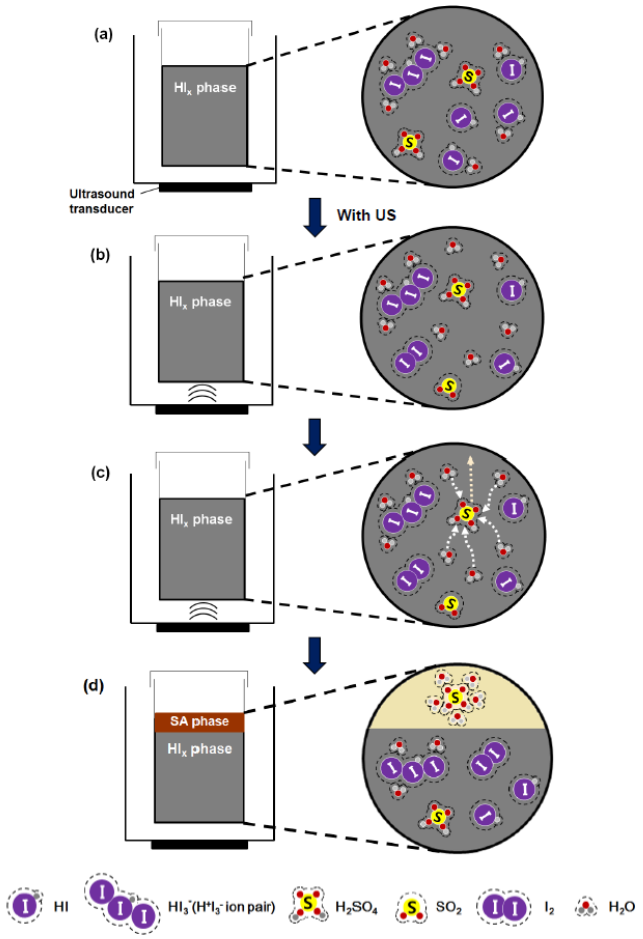


Figure 5. Conceptual illustration of the behavior of the Bunsen products during ultrasound (US) irradiation; (a) the single-phase product, (b) the SO_2, I_2 and H_2O formed by ultrasound irradiation, (c) the complexation of H_2SO_4 and H_2O and (d) the formation of SA phase.

When SO_2 gas was fed into the product solution during ultrasound irradiation, approximately 6.3 vol% of the SA phase was formed, and the H_2SO_4 distribution ratio in the SA phase increased to 17.0 mol%. The following steps were assumed to lead to these results: (a) The isolated H_2SO_4 formed a complex with the H_2O generated by the microscopic shift in the reaction equilibrium in the single-phase product, (b) When H_2SO_4 combined with a sufficient amount of H_2O, the SA phase formed due to the density differences.

Based on these results, a conceptual illustration of the effects of ultrasound irradiation on the behavior of the Bunsen products is depicted in Figure 5. Figure 5(a) shows the single-phase HI_x solution product. At low I_2 concentrations, the solution contains HI and HI_3^* ($H^+I_3^-$ ion pair) complexes and a small amount of H_2SO_4. The Bunsen products were not separated because the isolated H_2SO_4 molecules are not in contact with a sufficient amount of water (H_2O/H_2SO_4 molar ratio of approximately 5-6)[16]. When ultrasound was irradiated, the reaction equilibrium microscopically shifts toward the SO_2, I_2 and H_2O (Figure 5b). The generated H_2O forms a complex with the isolated H_2SO_4 molecules in the HI_x phase (Figure 5c). Consequently, the SA phase forms due to the number of $H_2SO_4 \cdot xH_2O$ (x = 5-6) clusters that can be moved to the SA phase increases (Figure 5d).

4. Conclusions

To improve the phase separation performance of the Bunsen reaction using the HI_x solution, the Bunsen reaction was performed under ultrasound irradiation. The ultrasound irradiation increased the H_2SO_4 distribution ratio in the SA phase and the amount of the SA phase. The effect of ultrasound irradiation on the Bunsen reaction was significant when the operating temperature, I_2 and H_2O feed concentrations were decreased. It was assumed that ultrasound irradiation microscopically shifts the equilibrium toward the SO_2, I_2 and H_2O in the Bunsen reaction system. The H_2O which generated by ultrasound irradiation forms complex with the isolated H_2SO_4 in the HI_x phase, and the SA phase forms because the number of $H_2SO_4 \cdot xH_2O$ (x = 5-6) clusters that can be moved to the SA phase increases. Therefore, the ultrasound irradiation effectively improves the phase separation performance of the Bunsen products.

Acknowledgments

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