Study of Reaction Temperature and Sulfur Dioxide Feed Rate in the Sulfur Iodine Production Cycle Reactions

Warunee Chankerd, Paisan Kittisupakorn and Iqbal Mohammed Mujtaba

Abstract—**The Bunsen reaction is one of the sulfur iodine production cycle (SI or IS) reactions in the thermochemical process that involves in the production of HI which is one of the most important intermediate chemicals in the hydrogen energy. In this work, the Bunsen reaction in a designed plug flow reactor (1 inch diameter x 12 inches length) equipped with a cooling jacket for the production of hydroiodicacid and sulfuric acid is studied. The Bunsen reaction is simulated by commercial simulation software based on the kinetic data from literatures with the temperature of 330 K, excess iodine, water feed rate and the feed rate of sulfur dioxide of 50 kg/hr. In order to validate the model, the amount of iodine, sulfur dioxide, water, sulfuric acid and hydroiodic acid are compared with experimental data; the relative discrepancies are 0.22 %, 1.43%, 0.17%, 2.85% and 2.88%, respectively. These simulation results guarantee that the model is reliable to be used to study the effects of reaction temperature and sulfur dioxide feed rate on the amounts of products. In the effect of reaction temperature, the amounts of products (hydroiodic acid and sulfuric acid) increase when the reaction temperature is raised from 293 to 373 K but they decrease when the temperature is higher than 373 K. These results indicate that the reaction temperature of higher than 373 K promotes the side reaction and inverse the Bunsen reaction. Moreover, the amounts of products increase when the sulfur dioxide feed rate increase. These results show that the amount of products are directly depended on the sulfur dioxide feed rate. In contrast, the amounts of iodine and water decrease when the feed rate of sulfur dioxide increases.**

Keywords—**simulation, Bunsen reaction, plug flow reactor, hydroiodic acid, sulfur iodine**

I. INTRODUCTION

During the last decade, the demand of the energy has been suddenly increased while the rate of energy production from fossil fuel to supply that demand are still the same. To avoid the lack of energy supply in the future, there are many researches about the alternative energy resources which have the properties as good as to fossil fuel such as hydrogen and sulfur iodine [1].

Manuscript received January 10, 2015; revised February 05, 2015.
Warunee Chankerd Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand. (corresponding author to provide e-mail: warunee.cha@student.chula.ac.th).
Paisan Kittisupakorn Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand. (corresponding author to provide e-mail: paisan.k@chula.ac.th).
Iqbal Mohammed Mujtaba School of Engineering, Design & Technology, University of Bradford, Bradford BD7 1DP, UK. (corresponding author to provide e-mail: I.M.Mujtaba@bradford.ac.uk).

The sulfur iodine (SI or IS) is the thermochemical process that increases the potential of overall efficiency and the operating cost is lower than the fossil fuel production process [2].

The cycle of sulfur iodine production consists of three chemical reactions. A scheme of a reference process is proposed by General Atomics (GA) [3].

Bunsen reaction:

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

Decomposition reaction of hydroiodic acid:

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

Decomposition reaction of Sulfuric acid:

$$H_2SO_4 \quad \rightarrow \quad SO_2 + H_2O + 1/2O_2 \qquad (3)$$

The Bunsen reaction (Eq.1) is an exothermic reaction at the temperature 293-393 K [1]. The reaction of sulfur dioxide (SO_2), the excess of water (H_2O) and iodine (I_2) generates hydroiodic acid (HI) and sulfuric acid (H_2SO_4) as the products [3]. The excess of iodine and water provide for avoiding the reversible Bunsen reaction. The products in this process always separate into two liquid phases because hydroiodic acid and sulfuric acid are immiscible liquids. The separation between two phases takes place under gravity. The upper phase consists of sulfuric acid, sulfur dioxide as well as water and–the lower phase consists of hydroiodic acid, iodine, sulfur dioxide and water. After separation section, hydroiodic acid decomposes into iodine and hydrogen. The decomposition of hydroiodic acid (Eq.2) is an endothermic reaction at the temperature 673-773 K [1]. In addition, Sulfuric acid is decomposed to sulfur dioxide, water and oxygen. The decomposition of sulfuric acid (Eq.3) is an endothermic reaction at the temperature 1073-1273 K [4]. The net of reactions is a dissociation of water into hydrogen and oxygen. The other chemicals are recycled in the closed cycle process.

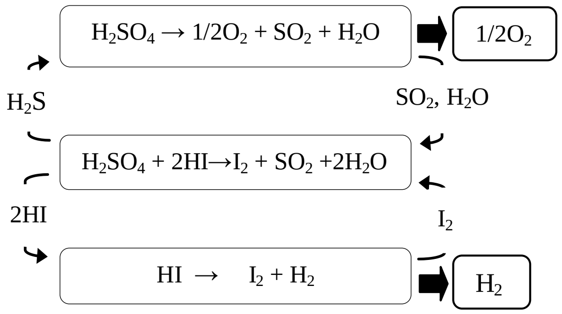

Fig. 1 Schematic diagram of the sulfur-iodine thermochemical cycle for hydrogen production.

Establishing the closed-cycle operation technology and improving the thermal efficiency of the process are both highly sensitive to several factors involved in the Bunsen reaction [4] such as reaction temperature, the amount of sulfur dioxide in the feed and the composition of process solution.

In this work, the Bunsen reaction is simulated by using commercial simulation software. In addition, the effect of reaction temperature is investigated by changing the reaction temperature in range of 293 – 393 K and the effect of sulfur dioxide feed rate is investigated by varying the sulfur dioxide feed rate from 40 to 60 kg/hr.

II. EXPERIMENTAL METHODS

A. Plug flow reactor simulation

A plug flow reactor is selected to use in this work because it is a better choice over a CSTR [5].This process based on the low feed rate of sulfur dioxide (SO_2) to the Bunsen reactor that is designed by Matt Channon. The reactor's specification for this work is shown in Fig. 2. The simulation flow model in commercial simulation software is shown in Fig. 3.

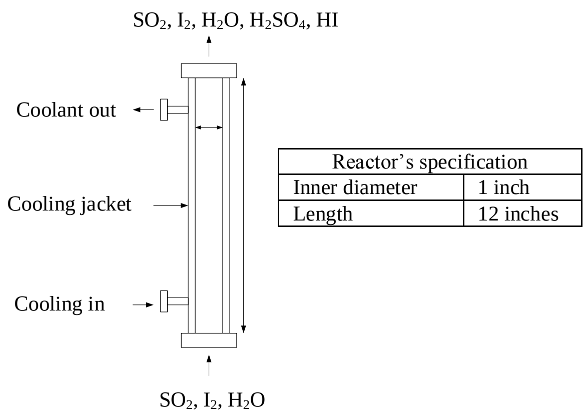

Fig. 2.The design of plug flow reactor.

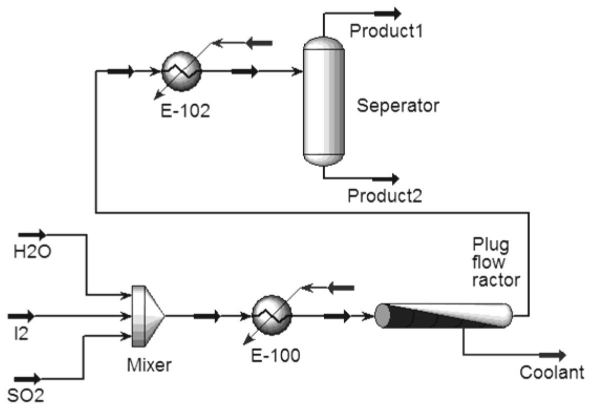

Fig. 3.The simulation model of Bunsen reaction in plug flow reactor.

This reactor is produced from a glass lined pipe and equipped with a cooling jacket. The materials for producing the cooling jacket depend on the section of coolant [5]. For this work, the cooling jacket is made by glass and water use as a coolant.

In the simulation section, the temperature in a Bunsen reaction operates at 330 K with excess iodine and water feed rate [7]. The feed rate of sulfur dioxide to the Bunsen reactor is 50 kg/hr.

TABLE I
FEED RATE AND VALUES RECOMMENDED BY Lee et al. (2008)

Species	**Feed in to reactor (kg/hr)**
Iodine	991.4
Sulfur dioxide	50
Water	182.8

In this work, the simulation results of Bunsen reaction by commercial simulation software are compared with experimental data [5]. In addition, the effects of reaction temperature and sulfur dioxide feed rate are studied.

III. RESULTS AND DISCUSSION

In order to validate the model, the amount of iodine, sulfur dioxide, water, sulfuric acid and hydroiodic acid are compared with experimental data; the relative discrepancies are 0.22 %, 1.43%, 0.17%, 2.85% and 2.88%, respectively. The simulation results are slightly different from the experimental data as presented in Table II. Therefore, the model is reliable to be used to study the effects of reaction temperature and sulfur dioxide feed rate.

ISBN: 978-988-19253-2-9
ISSN: 2078-0958 (Print); ISSN: 2078-0966 (Online)

TABLE II
SIMULATION RESULTS

Species	Feed in to reactor (kg/hr)	Output from reactor (kg/hr)		Relative discrepancy (%)
		experimental data	Simulation	
I_2	991.40	925.90	927.91	0.22
SO_2	50.00	33.50	33.98	1.43
H_2O	182.80	173.50	173.80	0.17
H_2SO_4	-	25.26	24.54	2.85
HI	-	65.90	64.00	2.88

A. Effect of reaction temperature on the Bunsen reaction

To investigate the influence of reaction temperature, the reactants such as iodine (I_2), sulfur dioxide (SO_2) and water (H_2O) are fed into the reactor with flow rate equal to 991.4, 50 and 182.8 kg/hr, respectively. The reaction temperature that use in this work is in range of 293 K to 393 K.

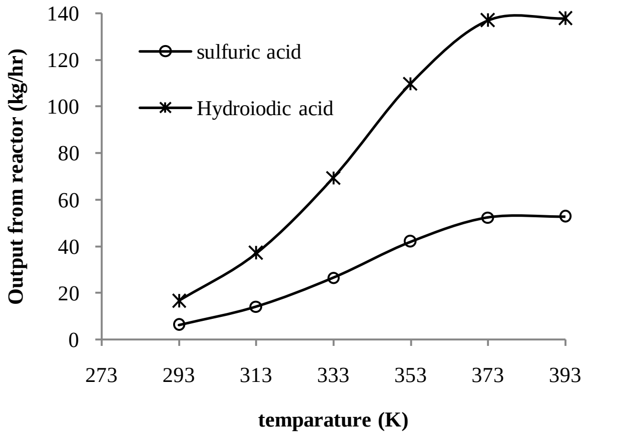

Fig. 4.The effect of temperature on the amount of products (sulfuric acid and hydroiodic acid).

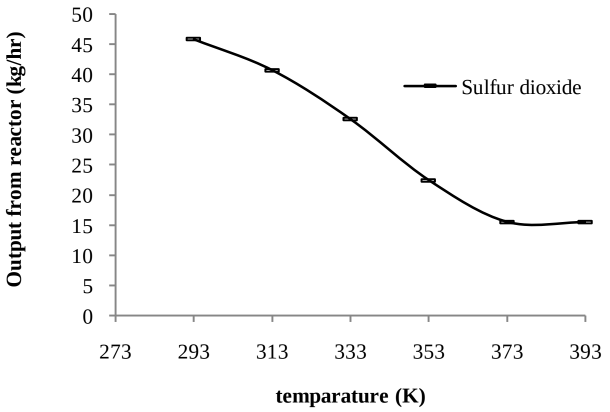

Fig. 5a.The effect of temperature on the amount of sulfur dioxide.

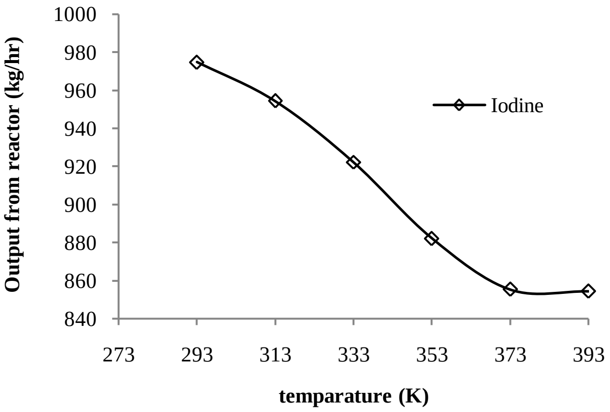

Fig.5b.The effect of temperature on the amount of iodine.

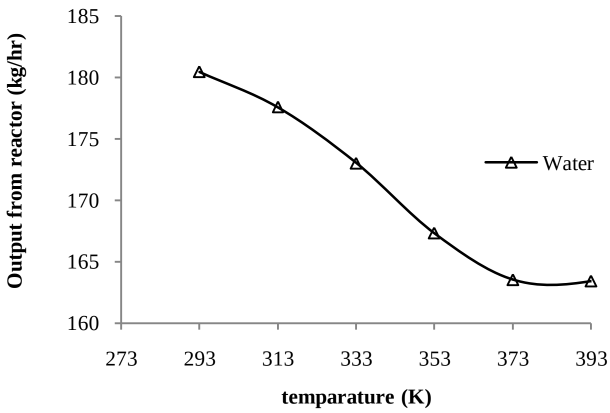

Fig.5c.The effect of temperature on the amount of water.

From Fig.4., the trends of the amounts of sulfuric acid (H_2SO_4) and hydroiodic acid (HI) are increased when the reaction temperature is increased from 293 K to 373 K. However, the amounts of products start to decrease when the reaction temperature is higher than 373 K. These results indicate that the reaction temperature higher than 373 K promotes the side reaction and inverse Bunsen reaction.

In the other hand, the amount of reactants (sulfur dioxide, iodine and water) are decreased when the reaction temperature is increased from 293 K to 393 K but it increases when the reaction temperature is higher than 373 K as shown in Fig. 5a-5c.

These phenomena can be explained by the endothermic property of the Bunsen reaction and the active kinetic of the compositions in both of two acid phases at the higher reaction temperature [1, 8, and 10].

B. Effect of the sulfur dioxide feed rate on the Bunsen reaction

To study the effect of the sulfur dioxide feed rate on the Bunsen reaction, the experiment are performed by varying the sulfur dioxide feed rate from 40 to 60 kg/hr and operated at 293 K. The water and iodine feed rate are set as constant at 182.8, 991.4 kg/hr, respectively.

ISBN: 978-988-19253-2-9
ISSN: 2078-0958 (Print); ISSN: 2078-0966 (Online)

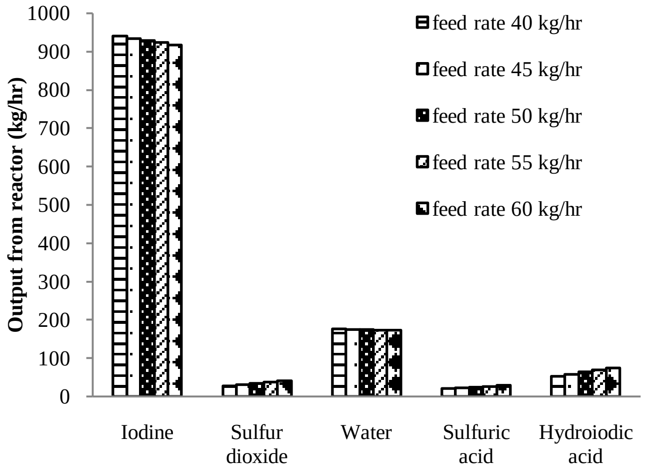

Fig.6.The effect of sulfur dioxidefeed rate on the amount of products and reactants.

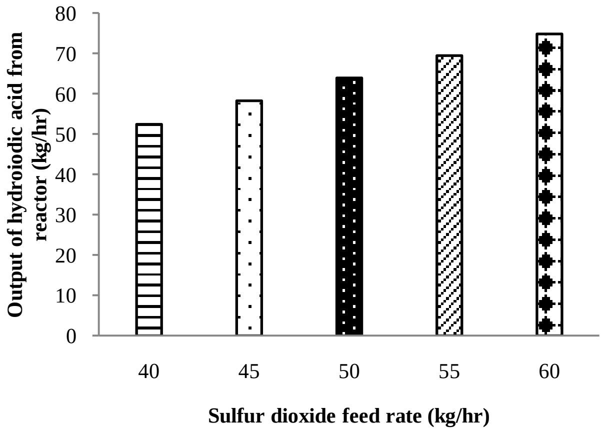

Fig.7a.The effect of sulfur dioxidefeed rate on the amount of hydroiodic acid.

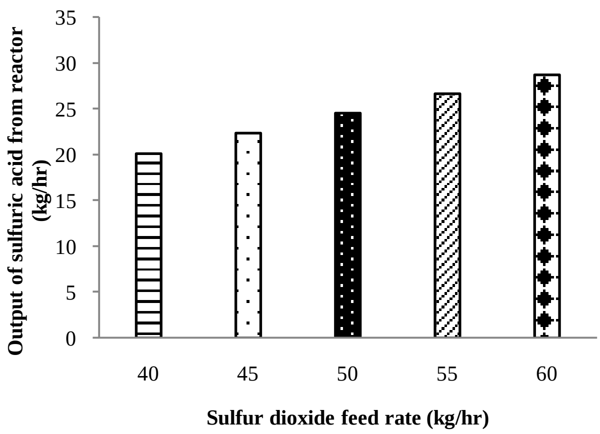

Fig.7b.The effect of sulfur dioxidefeed rate on the amount of sulfuric acid.

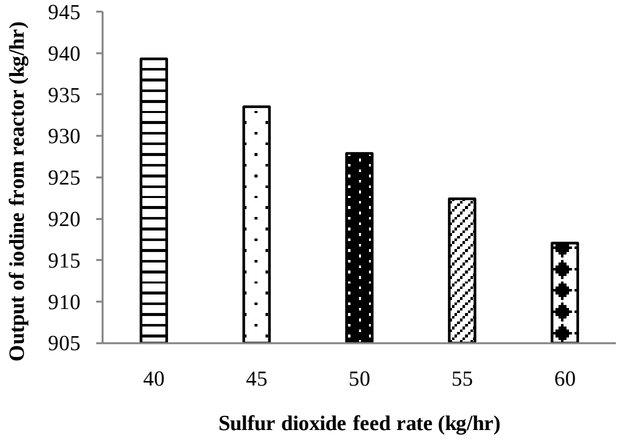

Fig.7c.The effect of sulfur dioxidefeed rate on the amount of iodine.

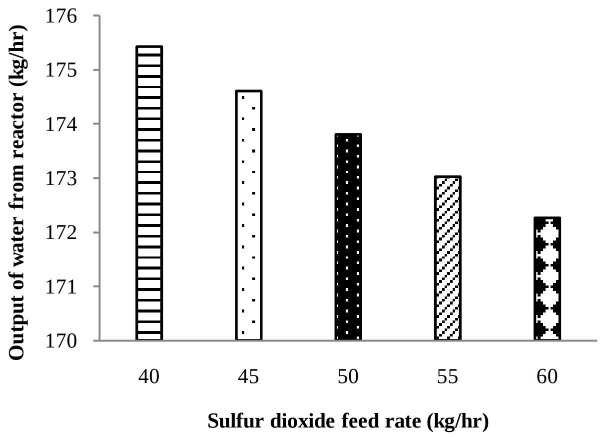

Fig.7d.The effect of sulfur dioxidefeed rate on the amount of water.

From Fig. 7a and 7b., the amounts of sulfuric acid (H_2SO_4) and hydroiodic acid (HI) are increased when the sulfur dioxide feed rate is increased. These results show that the amount of products are directly depended on sulfur dioxide feed rate. In contrast, the amount of iodine and water are decreased when increasing the feed rate of sulfur dioxide as shown in Fig. 7c-7d.

IV. CONCLUSION

The Bunsen reaction in a plug flow reactor is simulated by commercial simulation software. In order to validate the model, the amount of iodine, sulfur dioxide, water, sulfuric acid and hydroiodic acid are compared with experimental data. The simulation results show a slightly different trend from the experimental data and there are guarantee that this model is reliable to study the effects of reaction temperature and sulfur dioxide feed rate in the sulfur iodine production cycle (IS) reactions.

In the effect of reaction temperature, the amounts of products (hydroiodic acid and sulfuric acid) increase when the reaction temperature is raised from 293 to 373 K but they decrease when the temperature is higher than 373 K. These results indicate that the reaction temperature of higher than 373 K produce elemental sulfur or hydrogen sulfide (H_2S) [8] and inverse the Bunsen reaction. Moreover, the amounts of products (hydroiodic acid and sulfuric acid) are directly increased when the feed rate of sulfur dioxide increase.

ACKNOWLEDGMENT

The authors would like to acknowledge financial support of the Research Grant No. PHD/0335/2552 from the Royal Golden Jubilee Ph.D.Program and Chulalongkornuniversity.

REFERENCES

[1] Q. Zhu, Y. Zhang, Z. Ying, J. Zhou, Z. Wang and K. Cen, "Occurrence of the Bunsen side reaction in the sulfur-iodine thermochemical cycle for hydrogen production", *Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)*, vol.14(4), pp. 300-306, 2013.

[2] M. E. Davis and W. L. Conger, "An entropy production and efficiency analysis of the Bunsen reaction in the general atomic sulfur-iodine thermochemical hydrogen production cycle", *International Journal of Hydrogen Energy*, vol.5, pp.475-485, 1980.

[3] Norman, J., Besenbruch, G., Brown, L., O'Keefe, D. and Allen, C., 1981. "Thermochemical Water-Spitting Cycle, Bench-Scale Investigations, and Process Engineering. Final Report, February 1977 – December 31, 1981" General Atomics-Report GA-A16713, DOE Report DOE/ET/26225-1.

[4] Q. Zhu, Y. Zhang, C. Zhao, Z. Wang, J. Zhouand K. Cen "Optimization of Liquid-Liquid Phase Separation Characteristics in the Bunsen Section of the Sulfur-Iodine Hydrogen Production Process", *International Journal of Hydrogen Energy*, vol. 37, pp. 6407-6414, 2012.

[5] R. C. Moore, "Design options for a Bunsen reactor", Sandia National Laboratories, October 2012.

[6] Y. Zhang, P. Peng, Z. Ying, Q. Zhu, J. Zhou, Z. Wang, J. Liu and K. Cen, "Experimental investigation on multiphase Bunsen reaction in the thermochemical Sulfur-iodine cycle" *Industrial & Engineering Chemistry Research*, vol.53, pp. 3021-3028, February 2014.

[7] B. J. Lee, H. C. NO, H. J. Yoon, S. J. Kim and E. S. Kim, "An optimal operating window for the Bunsen process in the I-S thermochemical cycle", *International Journal of Hydrogen Energy*, vol.33, pp.2200-2210, 2008.

[8] M. Sakurai, H. Nakajima, R. Amir, K. Onuki and S. Shimizu, "Experimental study on side-reaction occurrence condition in the iodine-sulfur thermochemical hydrogen production process",*International Journal of Hydrogen Energy*, vol.25, pp.613-619, 2000.

[9] H. S. Kim, Y. H. Kim, S. J. Han, C. S. Park, K. K. Bae and J. G. Lee, "Continuous Bunsen reaction and simultaneous separation using a counter-current flow reactor for the sulfur-iodine hydrogen production process", *International Journal of Hydrogen Energy*, vol.38, pp.6190-6196, 2013.

[10] M. Parisi, A. Giaconia, S. Sau, A. Spadoni, G. Caputo and P.Tarquini, "Bunsen reaction and hydriodic phase purification in the sulfur-iodine process: An experimental investigation", *International Journal of Hydrogen Energy*, vol.36, pp.2007-2013, 2011.