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Research Paper

# Kinetic analysis of Bunsen reaction with HI existence in the thermochemical sulfur–iodine cycle for hydrogen production

Zhi Ying, Xiaoyuan Zheng *, Yao Zhang, Guomin Cui

*School of Energy and Power Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China*

## HIGHLIGHTS

- The detailed kinetics of Bunsen reaction with HI recycled was studied.
- Effects of temperature and initial HI on the overall reaction rate were explored.
- A $SO_4^{2-}$ production rate model for the Bunsen reaction was proposed.
- The activation energy for kinetics-controlled reactions (4) and (5) were determined.

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## ABSTRACT

The sulfur–iodine (SI) cycle is considered as a promising method for large-scale and high-efficiency hydrogen production. The Bunsen reaction in the cycle dominates the following HI and $H_2SO_4$ decomposition section and even the whole SI flowsheet. In this work, the detailed kinetics of the Bunsen reaction at practical condition with HI recycled was studied. The effects of operating temperature and initial HI concentration on the overall reaction rate were explored. A $SO_4^{2-}$ production rate model was proposed based on three elementary reactions, and well described the kinetic process of Bunsen reaction. Both theoretical and experimental results indicated that increasing the initial HI concentration (0–3.08 mol/$kg_{H2O}$) or operating temperature (303–358 K) enhanced the reaction rate, including the earlier appearance of liquid separation and thermodynamic equilibrium. But the recycled HI should be controlled within 6.17 mol/$kg_{H2O}$, so as to make the separation of $H_2SO_4$ and HIx phase possible. The calculated apparent activation energy for kinetics-controlled reactions (4) and (5) were 8.536 and 21.516 kJ/mol, respectively. These results may contribute to the further optimization and reactor design of the Bunsen reaction in the SI cycle.

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## 1. Introduction

Hydrogen demand, as a high-quality energy currency, is expected to rise dramatically in the next few decades [1–3]. The utilization of hydrogen relates to direct combustion, power generation, transportation, etc. The fuel cell technology using hydrogen for power generation is especially concerned at present. The key component for hydrogen economy is hydrogen production via coal/biomass gasification, natural gas reforming, water electrolysis, etc. Economics, environmental effect, and other factors should be considered when choosing the method for producing hydrogen. Water is generally used to produce hydrogen because of its clear, plentiful and convenient feature. Direct splitting of water to produce hydrogen and oxygen requires high temperature (more than 2500 K) with low decomposition rate (4%). However, water splitting via thermochemical cycles [4] allow appreciable amounts of hydrogen and oxygen to be obtained at a much lower temperature (almost below 1272 K), and achieve thermal efficiency up to 50%. Thermochemical cycles for hydrogen production apply a series of reactions between intermediates and water. The net reaction is the splitting of water to hydrogen and oxygen, with intermediates regenerated.

One of the most representative thermochemical water splitting methods is the thermochemical sulfur–iodine (SI) cycle [5,6], as shown in Fig. 1, which can be driven by solar or nuclear energy [7,8], exhibiting high thermal efficiency and low environmental pollution. The SI cycle mainly consists of following three reactions:

$$SO_2 + I_2 + 2H_2O \overset{293-393K}{\rightarrow} H_2SO_4 + 2HI \quad (1)$$

* Corresponding author.
*E-mail address:* xyzheng@usst.edu.cn (X. Zheng).

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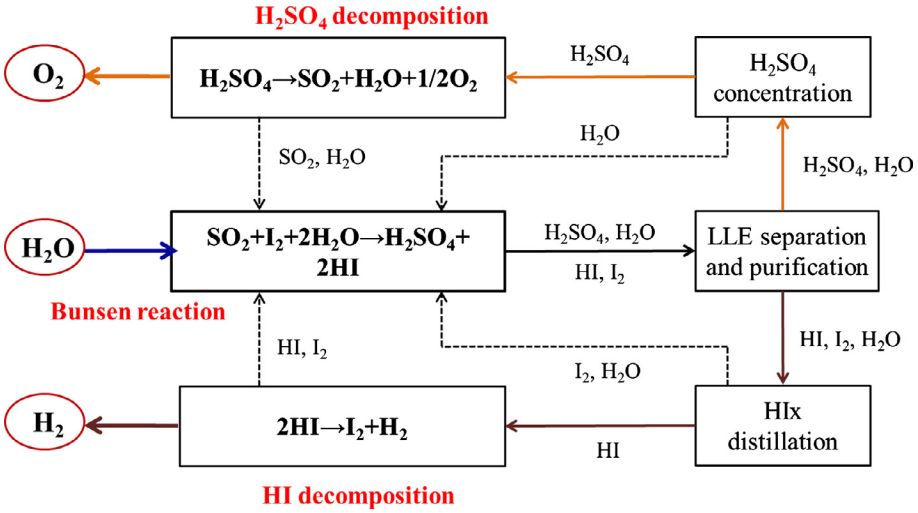


**Fig. 1.** Schematic diagram of the sulfur–iodine cycle.

$$H_2SO_4 \overset{1073-1273K}{\rightarrow} SO_2 + H_2O + 0.5O_2 \quad (2)$$

$$2HI \overset{573-773K}{\rightarrow} H_2 + I_2 \quad (3)$$

In brief, the net reaction for Bunsen reaction (1), $H_2SO_4$ and HI decomposition (2) and (3) is the splitting of $H_2O$ into $H_2$ and $O_2$. The intermedium, $SO_2$ and $I_2$, are recycled in the SI cycle. For Bunsen reaction, excessive water is required to make the reaction thermodynamically favorable [9]. Moreover, excess iodine with respect to its stoichiometric value is always applied to separate the produced $H_2SO_4$ and HI [10]. The complexation between excess iodine and the produced iodide forms polyiodides [11], and increases the HI solution density, which leads to the spontaneous separation of produced acids into the lighter $H_2SO_4$ phase ($H_2SO_4$–$H_2O$) and the heavier HIx phase (HI–$I_2$–$H_2O$) [12,13]. Meanwhile, some of the unexpected impurities in each phase always require further purification [14] and two acids require concentrating [15] before the subsequent decomposition of $H_2SO_4$ and HI [16–18].

The multiphase Bunsen reaction is a complex gas-solid-liquid reaction between $SO_2$, $I_2$, and $H_2O$. Most work has been focused on its thermodynamic feature, such as the liquid–liquid equilibrium (LLE) phase separation and side reactions [9,12,13,19,20]. However, the kinetics of Bunsen reaction, which stands for the practical operation, is dominant for the development of reactor design, material selection, and even scale up of the SI cycle in the future. But less effort has been made in this field.

Parisi et al. [21] explored the effects of operating temperature on the $SO_2$ conversion for Bunsen reaction, and found its conversion lowered with increasing temperature. Zhu et al. [22] investigated the kinetic process of the Bunsen reaction, and determined the effects of operating temperature, $SO_2$ flow rate, $I_2$ content, and $H_2O$ content. A kinetic model was also proposed and verified. Rao et al. [23] studied the Bunsen reaction through semi-batch experiments, and observed that increase in pressure or decrease in temperature increases the reaction rate. Wang et al. [24] carried out Bunsen reaction in a gas-liquid-liquid multiphase system with the existence of toluene, and studied the apparent reaction rate using the initial rate analysis method. The variation of toluene/water volume ratio, agitation speed, and temperature confirmed that the rate-limited step is the $SO_2$ absorption. To overcome the disadvantages in Bunsen reaction using excess iodine and water, three alternative routes, including electrochemical [25–27], reaction solvents [28], and precipitate methods [29], have been proposed. However, the traditional mode for Bunsen reaction is still the dominant one.

In the practical SI cycle, undecomposed HI is usually recycled to the Bunsen reaction, that is, the practical Bunsen reaction under recycling condition is among four compositions, $SO_2/I_2/HI/H_2O$ [30]. However, less information on the actual Bunsen reaction kinetics between $SO_2$, $I_2$, HI and $H_2O$ is available in literature. The definite kinetic model and sufficient kinetic data are important for operating parameters optimization, practical reactor design, material selection, flowsheet control, and even SI cycle scale-up. Hence, in this work, the detailed kinetics of practical Bunsen reaction at recycled condition was explored using a continuous operating reactor. A definite kinetic model was developed and verified by experimental results. The effects of operating temperature and initial HI concentration on the reaction rate were determined, and the activation energy and pre-exponential factor were finally obtained. The study will contribute to the further optimization and reactor design of the Bunsen reaction in the SI cycle.

## 2. Experimental

The Bunsen reaction was carried out in the experimental setup shown in Fig. 2. The initial reactants, iodine (>99.9%), hydriodic acid (approximately 56 wt%), and deionized water, were poured in a double-jacketed stirred reactor, which was temperature-controlled by a thermostatic water bath. An electrical engine driven stirrer mixed solution uniformly. Gaseous $SO_2$ and $N_2$ were continually fed into solution at a constant flow rate of 60 and 357 N mL/min until the $SO_2$ saturation was detected by $SO_2/H_2S$ analyzer. The exhaust was finally scrubbed using NaOH solution.

At atmospheric pressure, four typical operating temperatures, 303 K, 323 K, 345 K and 358 K, were chosen for determining the relationship between reaction rate and temperature and making further kinetic analysis. The initial water amount of 4.2 mol was fixed, while the initial $I_2$ and HI concentration changed. To induce the separation of produced $H_2SO_4$ and HI, the initial $I_2$ content should be within the range for liquid-liquid phase separation without iodine saturation at different temperatures [12]. The excess iodine with respect to its stoichiometric value dissolves in iodide and increases the HI solution density [11], leading to the spontaneous separation of produced acids into the immiscible lighter $H_2SO_4$ phase and the heavier HIx phase [12,13]. The $I_2/H_2O$ molar ratio was 0.78/4.2 and 1.362/4.2 at 303–323 K and 345–358 K, respectively. Four initial HI concentrations, 0, 1.55, 3.08, and

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