

Application of corrosion-resistant Corning advanced-flow reactors for multiphase Bunsen reaction - Part two: Investigation on multiphase reaction

Abstract

Bunsen reaction ($2H_2O + I_2 + SO_2 \rightarrow H_2SO_4 + 2HI$) is a key step for hydrogen production from either the H_2S splitting cycle or the sulfur-iodine (S-I) cycle of water splitting. As pointed out in part one, when engineering this reaction, many challenges such as side reactions and corrosion impede scaling up this process. Using iodine-toluene solution to provide flowing iodine below the melting point of iodine renders the Bunsen reaction to be conducted at ambient temperature such that these challenges can be either overcome or eased. However, using toluene as the iodine solvent makes the Bunsen reaction a multiphase reaction system which includes gas, aqueous, and organic phases. Glass-made Corning® advanced-flow™ reactors (AFRs) can be used for Bunsen reaction because they are claimed to be good at resisting corrosion, improving mixing efficiency of multiphase fluids, and allowing seamless scaling up.

Part one of this work has studied the absorption behavior of SO_2 gas in the liquids used for Bunsen reaction (water, toluene and water-toluene mixture). Part two of mainly studies the Bunsen reaction using the Corning® microscale (LF) and milliscale (G1) AFRs. When I_2 was dissolved in toluene, the Bunsen reaction was conducted by feeding SO_2 gas, water, and I_2 /toluene solution into the AFRs. SO_2 and I_2 were used as the limiting reactants in turn, and the effects of operating conditions such as gas and liquid flow rates, water to toluene ratio, and temperature in the range (22-80 °C) on the absorption rates of SO_2 and the I_2 reaction rate were studied. The results confirm the seamless scaling-up capability of the Corning reactors when the flow rates were increased twenty times from AFR-LF to AFR-G1.

Keywords: Bunsen reaction, H_2S splitting cycle, hydrogen production, Corning® glass advanced-flow™ reactors

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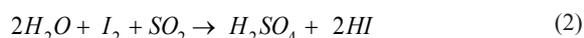
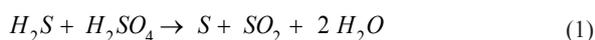
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Introduction

The current global main source of hydrogen (H_2) is from steam methane reforming which process is very energy intensive. Especially in Alberta, Canada, such produced hydrogen is largely consumed for oil sands upgrading and petroleum refining. Along with natural gas processing, the energy-industry there has been leading to the production of a large quantity of hydrogen sulfide (H_2S).¹ It makes more sense that the produced H_2S can be converted to H_2 and this hydrogen can be used back for upgrading and refining than currently being converted into water and elemental sulfur in the Claus process. Wang proposed an H_2S splitting cycle based on the inspiration of the S-I water-splitting cycle.²⁻⁵ According to this process, H_2SO_4 , SO_2 , H_2O , I_2 and, HI are cycled within this process to produce one mole of H_2 and one mole of S from one mole of H_2S .

Similar to the S-I water-splitting cycle, this cycle consists of three chemical reactions:



The overall reaction is:



If elemental sulfur from reaction (1) is to be further oxidized into SO_2 , reaction (5),



the reactions (2) and (3) would occur in doubled scale,⁴ thus giving rise to another new cycle called the H_2S - H_2O splitting cycle. The net reaction is:



the overall reaction (6) shows that one mole of H_2S , two moles of water and one mole oxygen in the feed stream react to produce two moles of hydrogen and one-mole of sulfuric acid, which is economically favored over the basic H_2S splitting reaction (4). Bunsen reaction, reaction (2), is the most critical step in the H_2S splitting cycle as well as in the S-I water-splitting cycle. Unlike S-I water-splitting, the thermal energy consumption has been minimized in our low-temperature H_2S splitting cycle, where toluene was used to dissolve iodine so that the Bunsen reaction could be carried out continuously at room temperature.⁵ This low-temperature process avoids iodine vapor deposition and side reactions, and it eases the corrosion challenge.

The subsequent electrolysis of the Bunsen reaction products relieves the worry about two acid separations as well. However, the use of an I_2 -toluene solution leads to a gas-liquid-liquid multiphase reaction system. Based on our kinetics study,² to increase the reaction yield, improving the contact between reactants in the multiphase

system becomes crucial and the improvement of cross-phase mass transfer becomes the key to the increase of process efficiency. Corning® advanced-flow™ reactors (AFRs) are used in this study because they are able to improve the gas-liquid mass transfer coefficients compared with other gas-liquid contactors, such as bubble columns and spray columns.⁶ They are made of glass or ceramic materials, which are highly corrosion-resistant to aqueous acid solutions. It is claimed that the modulus design of these reactors allows scale-up from the lowest flow rate (10 ML min⁻¹) to highest flow (5000 ML min⁻¹).⁷ In addition these reactors are believed to improve the heat transfer for exothermic reactions, preventing either thermal degradation or explosive evolution.⁷⁻⁹

This work has been divided into two parts. Part one investigates SO₂ absorption and mass transfer for SO₂-water, SO₂-toluene, and SO₂-water-toluene systems using two types of AFRs (AFR-LF and AFR-G1). The purpose is to identify the optimum operating conditions to be used when iodine is involved in the multiphase mixture. The results reveal that the absorption of SO₂ is most likely completed at the contacting (first) fluidic module where the gas-liquid mixture is initially mixed. It is also understood that the absorption efficiency is quite similar in both AFR-LF and AFR-G1 as the K_La is in the same order of magnitude.¹⁰ In this part, the multiphase Bunsen reaction is studied when SO₂ and I₂ are used as the limiting reactants in turn, and the effects of operating conditions such as gas and liquid flow rates, the water to toluene ratio, and the temperature are investigated on the absorption of SO₂ and the consumption rate of I₂.

Experimental

The experiments in this paper were conducted in two different research centers. The initial experiments conducted at the University of Saskatchewan (U of S) utilizing AFR-LF. Then, similar experiments were repeated utilizing next commercially available size of AFRs (AFR-G1) at the Corning Reactor Technology Center (CRTC), China, where the gas and liquid analyses were performed in the Department of Biochemical Engineering, Changzhou University. To avoid duplication, readers are referred to part one for the schematic diagram of the experimental setup which was used for both mass transfer in SO₂ absorption and the reaction.¹⁰

I. Corning AFR-LF

The experiments in this section were carried out at temperatures between 22-70 °C at different gas flow rates ranging from 22 to 85.7 mL min⁻¹ at standard temperature and pressure (STP), and at different liquid flow rates from 1.5 to 4.5 mL min⁻¹.

II. Corning AFR-G1

The second set of experiments was conducted in the AFR-G1 to understand the effects of scaling-up on the Bunsen reaction. Again, the details of AFRs can be found in part one of this research,¹⁰ but to refresh readers' mind, the internal volume of the fluidic module (8 mL) of the AFR-G1 is about 20 times that of the AFR-LF. Therefore the maximum allowable liquid flow rate of that a AFR-G1 module can handle is also 20 times that a AFR-LF module can do, which is 200 ML min⁻¹ for the liquids. The others such as material, geometry, and design operating conditions are the same. For this study only two fluidic modules (1 and 3) were used, modules 1 for mixing the SO₂-N₂ with the I₂-toluene solution and modules 3 for the reaction where water was introduced. The experiments were carried out at temperature range between 22-80 °C at different gas flow rates between 600 and 2000 mL min⁻¹ of STP and different liquid flow rates between 30 and 90 mL min⁻¹.

III. Chemicals

The chemicals used for the experiments with AFR-LF were mostly ACS grade as received: iodine (99.8%, Acros Organics), sulfur dioxide (99.98%, Praxair), nitrogen (99.99 %, Praxair), sodium hydroxide (97 %, EMD), sodium thiosulfate anhydrous (99.5%, Fisher), sodium iodide (99.999 %, Acros Organics), toluene (99.95 %, BDH), sulfuric acid (96 wt%, Fisher) and phenolphthalein and thymol blue as the indicators. The chemicals used for the experiments with AFR-G1 were also ACS grade as received. They are iodine (99.8%, Shanghai Shenbo), sulfur dioxide (99.99%, Shanghai Weichuang Gas), nitrogen (99.999%, Changzhou Wujin Huayang Gas), sodium hydroxide (96%, Sinopharm Chemical Reagent), sodium thiosulfate anhydrous (99%, Shanghai Lingfeng Chemical Reagent), potassium iodide (98.5%, Shanghai Shenbo Chemical), toluene (99.5%, Sinopharm Chemical Reagent), and phenolphthalein and thymol blue as the indicators. All the solutions used in both series of experiments and analyses were prepared by diluting the corresponding chemicals with deionized water.

IV. Measurement techniques and analysis methods

The concentrations of iodine in toluene and iodide in water were measured for the runs in the AFR-LF by a Shimadzu UV mini 1240 UV-Vis spectrophotometer; while the corresponding measurements for the runs in the AFR-G1 were carried out at Changzhou University using a Gold Spectrum lab 53 UV-Vis spectrophotometer of Shanghai Lenguang Technology with Mandel 10 mm path length quartz cuvettes. The proton concentration in the water phase was determined by titration with a standard sodium hydroxide solution using phenolphthalein as the indicator. The iodine concentration in the water phase was determined by titration with standard sodium thiosulfate using thymol blue as the indicator.

Non-reacted SO₂ was analyzed using a Varian CP-3800 gas chromatograph equipped with TCD conducted in the AFR-LF. The internal normalization method was used for the gas calibration in the AFR-LF because this technique corrects for the sample-size error when the sample size is variable.¹¹ Since the volume of gas after either reaction or absorption was drastically decreased in the system, therefore, the amount of sample injected into the GC sample loop would become different each time at the outlet compared to the reactor inlet and the external calibration method might not have given accurate results. However, for the experiments conducted in the AFR-G1, the external calibration method was used. Due to unavailability of the online method, gaseous sulfur dioxide samples were stored in Cole-Parmer Tedlar bags and then were analyzed by a Taizhou Zhonghuan Analysis Instrument Co. RPP-2000S Fluorescence Sulfur instrument at Changzhou University.

Results and Discussion

I. Bunsen reaction in AFR-LF

The Bunsen reaction was studied by feeding SO₂ gas, water, and I₂/toluene solution into the AFR-LF. SO₂ and I₂ were used as the limiting reactant in turn, and the effects of operating conditions on the reaction rate SO₂ and I₂ were studied. SO₂ absorption rate was measured based on the difference of the molar flow rate of SO₂ in the gas phase per unit volume. I₂ reaction rate was measured based on the difference of the molar flow rate of I₂ in I₂-toluene solution at the inlet and outlet of the reactors. Based on our previous work in the batch reactor,⁵ the excessive amount of water was used compared with the amount that stoichiometry required for all the reaction runs.

The effect of increasing water volumetric fraction

Runs were conducted with the LF-AFR at an SO₂ mole fraction of gas (y_{SO₂}=0.909), liquid flow rate (4.0 mL min⁻¹), gas flow rate (22 mL min⁻¹ at STP), room temperature (22 °C), and three water volumetric fraction levels (0.125, 0.25 and 0.38). Table 1 lists the inlet and outlet values of molar flow rates of the reactants and products. The SO₂ flow rate was either lower than or close to that of I₂, rendering SO₂ the limiting reactant with nearly complete conversion because only trace amounts of sulfur dioxide were detected in the effluent gas phase for all the runs. I₂ could not be balanced based on the data listed in Table 1. The 15 to 33% missed iodine/iodide species will be explained later. However, the amount of proton (H⁺) produced could be used to make the charge balance with iodide and sulfate anions, assuming all the converted SO₂ became sulfate.

Table 1 Molar flow rates of reactants and products when varying water volumetric fraction with AFR-LF.

Water fraction in liquid (v/v)	Inlet I ₂ (mmol min ⁻¹)	Inlet SO ₂ (mmol min ⁻¹)	Outlet I ₂ (mmol min ⁻¹)	Outlet I ⁻ (mmol min ⁻¹)	Outlet H ⁺ (mmol min ⁻¹)
0.125	1.4	0.9	0.28	1.33	2.97
0.25	1.2	0.9	0.17	1.53	3.4
0.38	1.0	0.9	0.09	1.52	3.39

Figure 1 shows the effects of increasing the water volumetric fraction in the liquid on the SO₂ absorption and the I₂ reaction rates. An identical SO₂ absorption rate was observed regardless of the varying water fraction in the liquid and the inclusion or exclusion of the Bunsen reaction due to the nearly complete conversion of SO₂. However, the reaction rate with respect to I₂ was greater than that of SO₂ at a smaller water fraction in the liquid, and they became the same when the volumetric fraction of water in the liquid was 0.38. According to the Bunsen reaction stoichiometry (reaction 2), it is expected that two moles of water convert one mole of SO₂ and one mole of I₂ into acid products—sulfuric acid and iodic acid.

Assuming all the SO₂ was consumed in each run, the calculated amount of H⁺ agreed with the measured I⁻ values. However, the

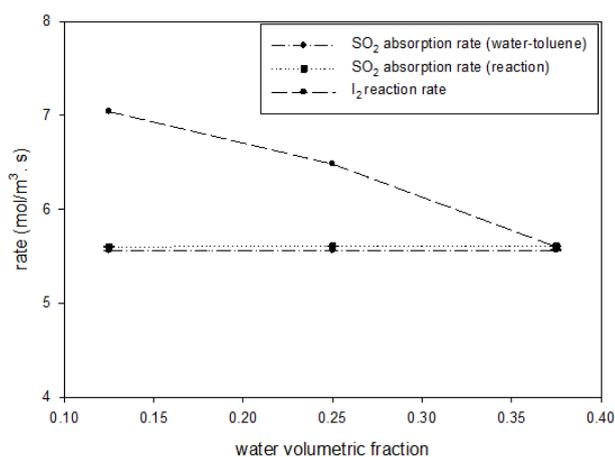
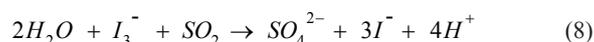


Figure 1 SO₂ absorption rate and I₂ reaction rate versus water volumetric fraction with AFR-LF (mole fraction of SO₂=0.909, liquid flow rate=4.0 mL min⁻¹, [I₂]=0.4 mol L⁻¹, gas flow rate=22 mL min⁻¹, T=22 °C, A₁: toluene (toluene-iodine), A₂: SO₂-N₂ and A₃: water)

converted I₂ was more than stoichiometry predicted for all the runs. The following reaction may have converted some of the iodine to tri-iodide:



Since iodine solubility in the HI solution is substantially higher than in water, the existence of iodide (I⁻) and proton (H⁺) would greatly increase the iodine solubility. The iodine crystals could dissolve rapidly in an iodide aqueous solution by forming soluble tri-iodide ions (I₃⁻). Moreover, poly-iodine species, I_{2x}⁻, where x=1, 2, 3, 4, etc., could also be stabilized by H⁺ in the solution.¹² Zhu et al.,¹³ studied the kinetic and thermodynamic properties of the Bunsen reaction in the sulfur-iodine water-splitting cycle in a stirred reactor. Including reactions (7), they assumed that the produced tri-iodide took part in the following reaction as well.



Therefore, the formation of I₃⁻ may be one of the reasons that led to I₂ being unbalanced. The errors in analytical chemistry may be another reason for I₂ unbalancing. Nonetheless, this experiment showed that the maintenance of equal I₂ and SO₂ feeding rates would lead to their nearly complete conversion into acid products.

The effect of increasing gas flow rate

Runs were conducted with the AFR-LF at an SO₂ mole fraction of gas (y_{SO₂}=0.933), liquid flow rate (1.5 mL min⁻¹), water volumetric fraction (0.15), room temperature (22 °C), and four gas flow rate levels (53.6, 64.3, 75.0 and 85.7 mL min⁻¹). Table 2 lists the inlet and outlet molar flow rates of SO₂ and I₂. The inlet flow rate of SO₂ in this group of runs was 4 to 7 times that of I₂, rendering I₂ the limiting reactant. Under this condition, the conversion of I₂ became constant at about 93%, regardless of the increase in gas flow rate. The difference between the inlet and outlet SO₂, which increased with the gas flow rate, was mainly due to SO₂ absorption.

Table 2 Molar flow rates of reactants and products when varying gas flow rate with AFR-LF.

Gas flow rate (mL min ⁻¹)	Inlet I ₂ (mmol min ⁻¹)	Inlet SO ₂ (mmol min ⁻¹)	Inlet H ₂ O (mmol min ⁻¹)	Outlet I ₂ (mmol min ⁻¹)	Outlet SO ₂ (mmol min ⁻¹)
53.6	0.51	2.23	12.8	0.036	0.096
64.3	0.51	2.67	12.8	0.035	0.15
75	0.51	3.13	12.8	0.035	0.23
85.7	0.51	3.57	12.8	0.035	0.33

Figure 2 confirms this by showing that the SO₂ absorption rate was much greater than the I₂ reaction rate. Figure 2 also compares the SO₂ absorption rates by toluene, toluene-water mixture, and toluene-I₂ solution-water mixture. It can be seen that when the reaction became insignificant, the gas flow rate enhanced the interface mass transfer, which controlled the SO₂ absorption rate. The increase of the gas flow rate did not change the I₂ reaction rate, indicating that mass transfer did not control the reaction. Considering possible errors in the experiment, the constant conversion of 93%, observed with the increasing gas flow, may indicate that the reaction had reached equilibrium conversion.

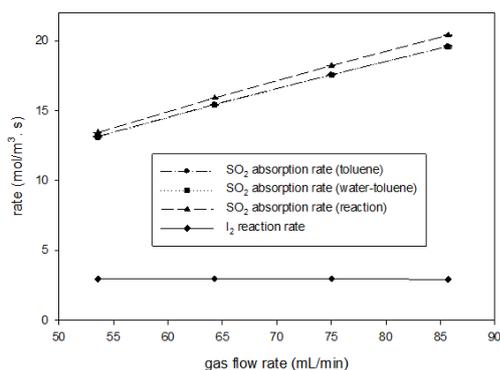


Figure 2 SO₂ absorption and I₂ reaction rates versus gas flow rate in AFR-LF (mole fraction of SO₂=0.933, [I₂]=0.4 mol L⁻¹, liquid flow rate=1.5 mLmin⁻¹, water volumetric fraction=0.15, T=22 °C, A₁: toluene (toluene-iodine), A₂: SO₂-N₂ and A₃: water).

The effect of increasing liquid flow rate

Runs were conducted with the AFR-LF at an SO₂ mole fraction of gas (y_{SO₂}=0.933), gas flow rate (53.57 mL/min at STP), room temperature (22 °C), water volumetric fraction (0.15), and three levels of liquid flow rate (1.5, 3.0, and 4.5 mL min⁻¹). SO₂ was excessive and I₂ was the limiting reactant. Table 3 shows the inlet and outlet molar flow rate of SO₂ and I₂. Figure 3 shows a constant SO₂ absorption rate but an increasing I₂ reaction rate. With a constant SO₂ feeding rate and sufficient liquid flow, the SO₂ was nearly completely absorbed, leading to only trace amounts of SO₂ in the exiting gas. This is why a constant SO₂ absorption rate was observed. On the other hand, the increase in the liquid flow rate increased the feed rate of I₂; thus, it also led to the increase in the I₂ reaction rate. However, data in Table 3 show that the conversion of I₂ was a constant. That means that with excessive SO₂ dissolved in liquid, the reaction of I₂ was still controlled by equilibrium.

Table 3 Inlet and outlet molar flow rate of reactants when varying liquid flow rate with AFR-LF.

Liquid flow rate (mL min ⁻¹)	Inlet I ₂ (mmol min ⁻¹)	Inlet SO ₂ (mmol min ⁻¹)	Inlet H ₂ O (mmol min ⁻¹)	Outlet I ₂ (mmol min ⁻¹)	I ₂ conversion (%)
1.5	0.507	2.23	12.8	0.034	93
3	1.01	2.23	25.6	0.076	92
4.5	1.52	2.23	38.3	0.144	91

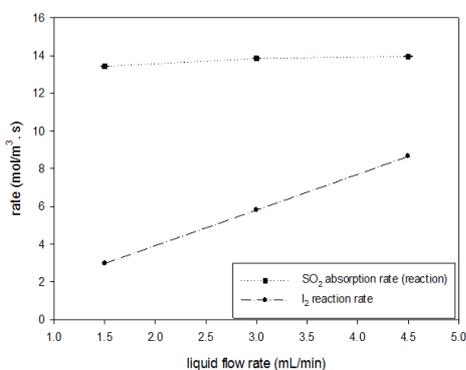


Figure 3 SO₂ absorption and I₂ reaction rates versus liquid flow rate in AFR-LF (mole fraction of SO₂=0.933, water volumetric fraction=0.15, [I₂]=0.4 mol L⁻¹, gas flow rate=53.57 mL min⁻¹, T=22 °C, A₁: (toluene-iodine), A₂: SO₂-N₂ and A₃: water).

The effect of increasing temperature

Runs were conducted with the AFR-LF at an SO₂ mole fraction in gas (y_{SO₂}=0.933), gas flow rate (53.57 mL min⁻¹ at STP), liquid flow rate (1.5 mL min⁻¹), water volumetric fraction (0.15), and four temperature levels where I₂ was the limiting reactant. As can be seen from Figure 4, both SO₂ absorption rates without and with reaction were decreased by increasing the temperature, while enhancement was observed in the reaction, especially at higher temperatures. On the other hand, increasing the temperature did not have obvious impact on the iodine reaction rate, which stayed quite constant at all the temperature levels. Giaconia et al.,¹⁴ also investigated the LLE phase separation behavior of products of the Bunsen reaction and noticed that temperature had little or no effect on the sulfuric acid and HI concentrations in the two phases unless using a large amount of iodine at 120 °C. Therefore, the enhancement may not be due to the reaction with I₂ only. It may also be caused by the absorption improvement with I₂-tolerance solution.

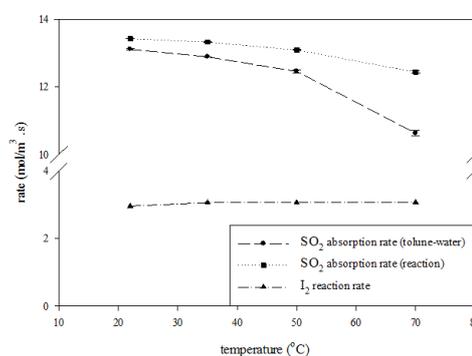


Figure 4 SO₂ absorption and I₂ reaction rates versus temperature with AFR-LF (mole fraction of SO₂=0.933, liquid flow rate=1.5 mL min⁻¹, water volumetric fraction=0.15, [I₂]=0.4 mol L⁻¹, gas flow rate=53.57 mL min⁻¹, A₁: toluene (toluene-iodine), A₂: SO₂-N₂ and A₃: Water).

II. Bunsen reaction in AFR-G1

Experiments were conducted with the AFR-G1 to understand the effects of AFR scaling-up on the Bunsen reaction. For this study only two fluidic modules (1 and 3) were used, modules 1 for mixing the SO₂-N₂ with the I₂-toluene solution and modules 3 for the reaction where water was directly introduced. Reaction just took place in the second module.

Reaction rate in AFR-G1 when SO₂ was the limiting reactant

Runs were conducted with AFR-G1 at an SO₂ mole fraction of gas (y_{SO₂}=0.50), liquid flow rate (80.0 mL min⁻¹), two levels of gas flow rate (600 and 800 mL min⁻¹ at STP), a water volumetric fraction (0.125), and three temperature levels (22, 50 and 80 °C) where SO₂ was as the limiting reactant. Table 4 lists the inlet and outlet molar flow rates of the reactants and products for a gas flow rate of 800 mL min⁻¹. Figure 5 shows the SO₂ absorption rate and I₂ reaction rate versus temperature at both gas flow rate levels (600 and 800 mL min⁻¹ at STP). SO₂ absorption rate was decreased with temperature due to the lower solubility of SO₂ at higher temperatures. SO₂ absorption rate was increased with the gas flow rate because it improved the mass transfer between phases. Since SO₂ is the limiting reactant, the reaction rate with respect to the I₂ conversion took the similar trend.

Assuming total consumption of SO₂, the calculated H⁺ value agreed with the measured I⁻ values. However the I₂ conversion was decreased at higher temperatures from 80% at 22 °C to 73.8 % at 80 °C, resulting in smaller quantities of the H⁺ and I⁻ produced. The converted I₂ was

also more than the values predicted by stoichiometry for all the runs. As discussed earlier, the missed iodine/iodide species could be due to the formation of I_3^- leading to unbalanced I_2 .

Table 4 Molar flow rates of reactants and products when varying temperature with AFR-G1 (gas flow rate=800 mL min⁻¹).

T (°C)	Inlet I ₂ (mmol min ⁻¹)	Inlet SO ₂ (mmol min ⁻¹)	Outlet I ₂ (mmol min ⁻¹)	Inlet I (mmol min ⁻¹)	Outlet H ⁺ (mmol min ⁻¹)
22	28.3	17.9	5.16	30.8	64.8
50	28.6	17.9	7.31	27.5	60.9
80	28.3	17.9	7.35	27.2	59.1

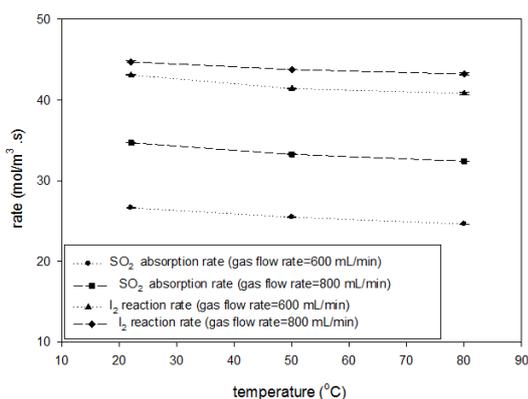


Figure 5 SO₂ absorption and I₂ reaction rates versus temperature in AFR-G1 (liquid flow rate=80 mL min⁻¹, mole fraction of SO₂=0.50, water volumetric fraction=0.125, [I₂]=0.4 mol L⁻¹, A₁: (SO₂-N₂), A₂: (toluene-I₂) and A₃: Water).

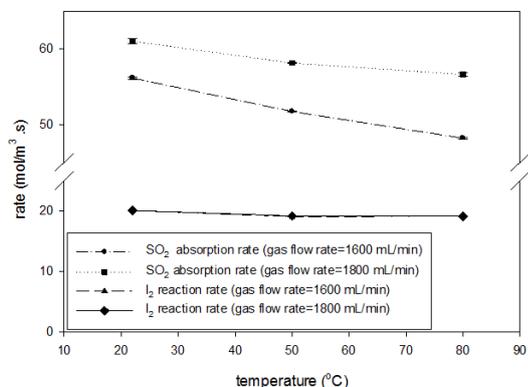


Figure 6 SO₂ absorption rate and I₂ reaction rate versus temperature with AFR-G1 (liquid flow rate=30 mL min⁻¹, mole fraction of SO₂=0.50, water volumetric fraction=0.15, [I₂]=0.4 mol L⁻¹, A₁: (SO₂-N₂), A₂: (toluene-I₂) and A₃: Water).

Reaction rate in AFR-G1 when I₂ was the limiting reactant

Runs were conducted with AFR-G1 at an SO₂ mole fraction in gas ($y_{SO_2}=0.50$), liquid flow rate (30 mL/min), water volumetric fraction (0.15), two gas flow rates (1600 mL/min and 1800 mL/min at STP) and three temperature levels (22, 50 and 80 °C) where I₂ was the limiting reactant. Figure 6 shows the effects of increasing the temperature on the SO₂ absorption and I₂ reaction rates. As can be seen, increasing the temperature reduced the SO₂ absorption rate in liquid at both gas flow rate levels; however, this variation had no significant effect on the I₂ reaction rate. I₂ conversion was also quite constant and no significant

difference was observed when the temperature was increased. These results are completely in agreement with the similar runs performed in the AFR-LF. One may question the reason why conducting the experiments below 80 °C.

The main objective of choosing toluene as the I₂ solvent was to lower the reaction temperature. Although, from thermodynamic point of view, for an exothermic reaction like the Bunsen reaction, lower temperature is in favor of the conversion from reactants to products, three levels of temperatures were selected above the room temperature to see its effect on the reaction rate. It was observed that increasing the temperature decreased the sulfur dioxide absorption rate but did not help the reaction rate with respect to I₂ disappearing.

The effect of increasing liquid flow rate

Runs were conducted with AFR-G1 at six liquid flow rate levels, an SO₂ mole fraction in gas ($y_{SO_2}=0.50$), gas flow rate (1800 mLmin⁻¹ at STP), room temperature (22 °C), and water volumetric fraction (0.15) when SO₂ was excessive and I₂ was the limiting reactant. Table 5 shows the inlet and outlet molar flow rates of SO₂ and I₂. A nearly constant conversion of I₂ regardless of varying the liquid flow rate indicates that the conversion of iodine in the Bunsen reaction was controlled by equilibrium when SO₂ dissolved in liquid was excessive. This observation is the same as that in the AFR-LF. Figure 7 shows the effect of increasing the liquid flow rate on the SO₂ absorption and I₂ reaction rates. Increase in the liquid flow led to the linear increase of the I₂ reaction rate, but it did not significantly increase the SO₂ absorption rate.

Table 5 Inlet and outlet molar flow rate of reactants when varying liquid flow rate with AFR-G1.

Liquid flow rate (mL min ⁻¹)	Inlet I ₂ (mmol min ⁻¹)	Inlet SO ₂ (mmol min ⁻¹)	Inlet H ₂ O (mmol min ⁻¹)	Outlet I ₂ (mmol min ⁻¹)	I ₂ conversion (%)
30	10.3	40.2	250	0.68	93.4
40	13.4	40.2	333	0.97	92.7
45	14.6	40.2	375	1.16	92.1
55	18.9	40.2	458	1.52	91.9
60	20.5	40.2	500	2.19	89.3
90	30.5	40.2	750	3.42	88.8

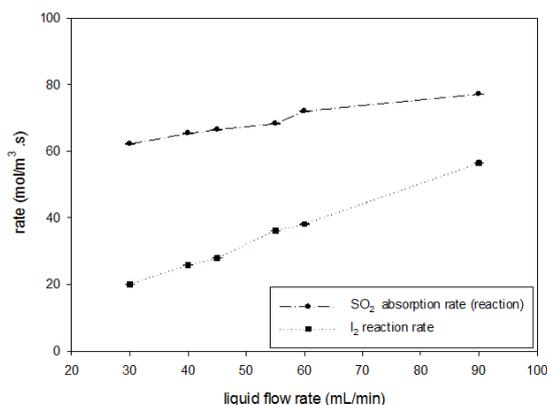


Figure 7 SO₂ absorption and I₂ reaction rates versus liquid flow rate in AFR-G1 (mole fraction of SO₂=0.50, water volumetric fraction=0.15, [I₂]=0.4 mol L⁻¹, gas flow rate=1800 mL min⁻¹, T=22 °C, A₁: (SO₂-N₂), A₂: (toluene-I₂) and A₃: Water).

III. Scalability from AFR-LF to AFR-G1

The scalability from the AFR-LF to the AFR-G1 was evaluated by the iodine conversion rate measured when SO₂ was excessive. The experiment data were chosen from those obtained under the same conditions except the flow rates: the same water volumetric fraction (0.15), the same temperature (ambient), 400 mL min⁻¹ of gas flow rate and 80 mL min⁻¹ of liquid flow rate for the AFR-G1 versus 20 mL min⁻¹ of gas flow rate, and 4 mL min⁻¹ of liquid flow rate for the AFR-LF. The liquid holdup will affect the reaction rate calculated. When multiple fluidic modules were used for the reaction, liquid holdup must be used for the portion where the reaction does take place. It has been observed in the absorption experiment that the absorption has been completed in the first module for both the AFR-LF and AFR-G1.¹⁰ In the reaction experiments, it was also observed by the color change of I₂ (disappearance of the purple color) that the reaction completed after the first module. By dividing the iodine conversion data by the liquid holdup volume of one fluidic module (V_r=0.4 mL for the AFR-LF and V_r=8 mL for the AFR-G1), the reaction rate values of the iodine conversion obtained with both reactors at excessive SO₂ and various liquid flow rates are shown in Table 6.

Table 6 Comparison of the results obtained in AFR-LF and AFR-G1.

Liquid flow rate in AFR-LF (mL min ⁻¹)	I ₂ reaction rate (mol m ⁻³ s ⁻¹)	I ₂ conversion (%)	Liquid flow rate in AFR-G1 (mL min ⁻¹)	I ₂ reaction rate (mol m ⁻³ s ⁻¹)	I ₂ conversion (%)
1.5	19.6	93	30	20	93
3	39.1	92	60	38.1	89
4.5	57.3	91	90	56.5	89

Now, comparing the I₂ conversion data and reaction rate with respective to I₂ disappearance obtained using both AFR's, we can conclude that when the liquid flow rate was increased by 20 times from using the AFR-LF to the AFR-G1, the same performance was achieved even for a range of flow rates. This comparison suggests seamless scale-up between the AFR-LF and AFR-G1 for the Bunsen reaction to be conducted with them. The scalability can be extended to AFR-G4, the largest fluidic module available in market.

Conclusions

After the absorption behavior of SO₂ by toluene, water, toluene-water mixture being studied with Corning AFR-LF and AFR-G1 reactors, the Bunsen reaction with I₂ carried by the I₂-toluene solution was investigated using the same reactors. From the experiments, we can withdraw the following conclusions:

- Continuous operation of the multiphase Bunsen reaction with I₂ provided in the I₂-toluene solution can be fulfilled with the Corning advanced-flow reactors made of glass. This capability provides a corrosion-resistant reactor device for the Bunsen reaction of which the corrosion hazard from its products has been a great concern.
- The reaction rate with respect to SO₂ is controlled by the SO₂ absorption in the toluene-water mixture. The absorption is enhanced by the reaction between dissolved SO₂ and I₂ in the solution. The reaction rate with respect to I₂ is controlled by equilibrium when SO₂ is excessive in the liquid phase. Increasing the reaction temperature higher than the room temperature

decreases the SO₂ absorption rate but does not change much of the I₂ appearance rate in the excessive present of SO₂ in the solution.

- The reaction rate with respect to I₂ and the I₂ conversion show the same magnitude with the AFR-LF and the AFR-G1, indicating the seamless scalability between the two reactors where there is a 20 time throughput increases.
- The two acid products, HI and H₂SO₄, are in the aqueous phase leaving the toluene to become lean of iodine for reuse. No H₂S is detected in gas phase and no elemental sulfur is observed in the liquid.

Nomenclatures and Abbreviations

K _{L,a}	s ⁻¹	Overall mass transfer coefficient in the liquid phase
T	K	Temperature
y _{SO₂}	---	mole fraction of SO ₂ in the gas phase
TCD	---	Thermal conductivity detector
UV-Vis	---	Ultraviolet-visible spectrophotometer
AFR-LF	---	Low flow-Advanced flow reactor
AFR-G1	---	G1 Standard evaluation-Advanced flow reactor

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Conflicts of interest

The author declares that there are no conflicts of interest.

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