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

Abstract

Bunsen reaction \(2 \text{H}_2\text{O} + \text{I}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI}\) is a key step for hydrogen production from either the \(\text{H}_2\text{S}\) 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 good at resisting corrosion, improving mixing efficiency of multiphase fluids, and allowing seamless scaling up.

Part one has studied the absorption behavior of \(\text{SO}_2\) gas in the liquids used for Bunsen reaction (water, toluene and water-toluene mixture). Part two (this work) mainly studies the Bunsen reaction using the Corning® microscale (LF) and milliscale (G1) AFRs. When \(\text{I}_2\) was dissolved in toluene, the Bunsen reaction was conducted by feeding \(\text{SO}_2\) gas, water, and \(\text{I}_2\)-toluene solution into the AFRs. \(\text{SO}_2\) and \(\text{I}_2\) 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 \(\text{SO}_2\) and the \(\text{I}_2\) 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, \(\text{H}_2\text{S}\) splitting cycle, hydrogen production, Corning® glass advanced-flow™ reactors

Introduction

The current global main source of hydrogen (\(\text{H}_2\)) 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 thermal energy consumption has been minimized in our low-temperature \(\text{H}_2\text{S}\) splitting cycle, where toluene was used to dissolve hydrogen sulfide (H(S))\(^1\). It makes more sense that the produced \(\text{H}_2\text{S}\) can be converted to \(\text{H}_2\) 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 \(\text{H}_2\text{S}\) splitting cycle based on the inspiration of the S-I water-splitting cycle.\(^2,5\) According to this process, \(\text{H}_2\text{SO}_4\), \(\text{SO}_2\), \(\text{H}_2\text{O}\), \(\text{I}_2\), and \(\text{HI}\) are cycled within this process to produce one mole of \(\text{H}_2\) and one mole of \(\text{S}\) from one mole of \(\text{H}_2\text{S}\).

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

\[
\begin{align*}
\text{H}_2\text{S} + \text{H}_2\text{SO}_4 & \rightarrow \text{S} + \text{SO}_2 + 2\text{H}_2\text{O} \quad (1) \\
2\text{H}_2\text{O} + \text{I}_2 + \text{SO}_2 & \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI} \quad (2) \\
2\text{HI} & \rightarrow \text{H}_2 + \text{I}_2 \quad (3)
\end{align*}
\]

The overall reaction is:

\[
\text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S} \quad (4)
\]

If elemental sulfur from reaction (1) is to be further oxidized into \(\text{SO}_2\), reaction (5):

\[
\text{O}_2 + \text{S} \rightarrow \text{SO}_2 \quad (5)
\]

The reactions (2) and (3) would occur in doubled scale,\(^4\) thus giving rise to another new cycle called the \(\text{H}_2\text{S}-\text{H}_2\text{O}\) splitting cycle. The net reaction is:

\[
\text{H}_2\text{S} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{H}_2 \quad (6)
\]

The overall reaction (6) shows that one mole of \(\text{H}_2\text{S}\), two moles of water and one mole oxygen in the feed stream react to produce two moles hydrogen and one-mole of sulfuric acid, which is economically favored over the basic \(\text{H}_2\text{S}\) splitting reaction (4). Bunsen reaction, reaction (2), is the most critical step in the \(\text{H}_2\text{S}\) 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 \(\text{H}_2\text{S}\) splitting cycle, where toluene was used to dissolve iodine so that the Bunsen reaction could be carried out continuously at room temperature.\(^3\) 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 \(\text{I}_2\)-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. They are made of glass or ceramic materials, which are highly corrosion-resistance 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) to highest flow (5000 mL/min). In addition these reactors are believed to improve the heat transfer for exothermic reactions, preventing either thermal degradation or explosive evolution.

This work has been divided into two parts. Part one investigates SO\(_2\) absorption and mass transfer for SO\(_2\)-water, SO\(_2\)-toluene, and SO\(_2\)-water-toluene systems using two types of AFRs (AFR-LF and AFR-G1) to identify the optimum operating conditions to be used when iodine is involved in the multiphase mixture. The results reveal that the absorption is most fully completed at 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\(_a\) is in the same order of magnitude. In this part, the multiphase Bunsen reaction is studied when SO\(_2\) and I\(_2\) 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 SO\(_2\) and the consumption rate of I\(_2\).

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 SO\(_2\) absorption and the reaction.

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, but to refresh readers’ mind, the internal volume of each fluidic module (8 mL) of the AFR-G1 is about 20 times that of the AFR-LF, with a maximum allowable flow rate of 200 mL/min for the liquids. The other conditions of both reactors are the same such as material, geometry, and design operating conditions. For this study only two fluidic modules (1 and 3) were used, modules 1 for mixing the SO\(_2\)-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 in the AFR-LF were mostly ACS grade as received: iodine (99.8%, Acros Organics), sulfur dioxide (98.98%, 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 as the indicators. The chemicals used for the experiments in the 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 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 Spectram lab 53 UV-Vis spectrophotometer of Shanghai Lengguang 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 as the indicator.

Non-reacted SO\(_2\) 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. 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 SO\(_2\) gas, water, and I\(_2\)/toluene solution into the AFR-LF. SO\(_2\) and I\(_2\) were used as the limiting reactant in turn, and the effects of operating conditions on the rate of SO\(_2\) and I\(_2\) were studied. SO\(_2\) absorption rate was measured based on the difference of the molar flow rate of SO\(_2\) in the gas phase per unit volume. I\(_2\) reaction rate was measured based on the difference of the molar flow rate of I\(_2\) in I\(_2\)-toluene solution at the inlet and outlet of the reactors. Based on our previous work in the batch reactor, 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 (\(Y_{SO_2}=0.909\)), 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 reactant (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.

<table>
<thead>
<tr>
<th>Water fraction in liquid (v/v)</th>
<th>Inlet I₂ (mmol min⁻¹)</th>
<th>Inlet SO₂ (mmol min⁻¹)</th>
<th>Outlet I₂ (mmol min⁻¹)</th>
<th>Outlet SO₂ (mmol min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>1.4</td>
<td>0.9</td>
<td>0.28</td>
<td>1.33</td>
</tr>
<tr>
<td>0.25</td>
<td>1.2</td>
<td>0.9</td>
<td>0.17</td>
<td>1.53</td>
</tr>
<tr>
<td>0.38</td>
<td>1</td>
<td>0.9</td>
<td>0.09</td>
<td>1.52</td>
</tr>
</tbody>
</table>

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.

![Figure 1 SO₂ absorption rate and I₂ reaction rate versus water volumetric fraction with AFR-LF](image)

Assuming all the SO₂ was consumed in each run, the calculated amount of H⁺ agreed with the measured I⁻ values. However, the converted I₂ was more than stoichiometry predicted for all the runs. The following reaction may have converted some of the iodine to tri-iodide:

\[
I_2 + I^- \rightarrow I_3^-
\]

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, Iₓ⁻, where x=1, 2, 3, 4, etc., could also be stabilized by H⁺ in the solution. Zhu et al., 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.

\[
2H_2O + I^- + SO_2 \rightarrow SO_4^{2-} + 3I^- + 4H^+
\]

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 (\(Y_{SO_2}=0.933\)), 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.

<table>
<thead>
<tr>
<th>Gas flow rate (mL min⁻¹)</th>
<th>Inlet I₂ (mmol min⁻¹)</th>
<th>Inlet SO₂ (mmol min⁻¹)</th>
<th>Outlet I₂ (mmol min⁻¹)</th>
<th>Outlet SO₂ (mmol min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.6</td>
<td>0.51</td>
<td>2.23</td>
<td>12.8</td>
<td>0.036</td>
</tr>
<tr>
<td>64.3</td>
<td>0.51</td>
<td>2.67</td>
<td>12.8</td>
<td>0.035</td>
</tr>
<tr>
<td>75</td>
<td>0.51</td>
<td>3.13</td>
<td>12.8</td>
<td>0.035</td>
</tr>
<tr>
<td>85.7</td>
<td>0.51</td>
<td>3.57</td>
<td>12.8</td>
<td>0.035</td>
</tr>
</tbody>
</table>

(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 rate 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.
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⁻¹ 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 I⁻ was the limiting reactant. Table 3 shows the inlet and outlet molar flow rate of SO₂ and I⁻. Figure 3 shows a constant SO₂ absorption rate but an increasing I⁻ 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 I⁻; thus, it also led to the increase in the I⁻ reaction rate. However, data in Table 3 show that the conversion of I⁻ was a constant. That means that with excessive SO₂ dissolved in liquid, the reaction of I⁻ was controlled by equilibrium.

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

<table>
<thead>
<tr>
<th>Liquid flow rate (mL min⁻¹)</th>
<th>Inlet I⁻ (mmol min⁻¹)</th>
<th>Inlet SO₂ (mmol min⁻¹)</th>
<th>Inlet H₂O (mmol min⁻¹)</th>
<th>Outlet I⁻ (mmol min⁻¹)</th>
<th>I⁻ conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.507</td>
<td>2.23</td>
<td>12.8</td>
<td>0.034</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>1.01</td>
<td>2.23</td>
<td>25.6</td>
<td>0.076</td>
<td>92</td>
</tr>
<tr>
<td>4.5</td>
<td>1.52</td>
<td>2.23</td>
<td>38.3</td>
<td>0.144</td>
<td>91</td>
</tr>
</tbody>
</table>

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 I⁻ was the limiting reactant. As can be seen from (Figure 4), both SO₂ absorption rates without and with reaction was 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.

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

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

Figure 4 SO₂ absorption and I⁻ 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, [I⁻]=0.4 mol L⁻¹, gas flow rate=53.57 mL min⁻¹, A: 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 I⁻-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 I⁻ 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 respective to the I⁻ conversion took the similar trend.

Assuming total consumption of SO₂, the calculated H⁺ value agreed with the measured I⁻ values. However the I⁻ 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 I$_2$ 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$_2$ 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$^{-1}$).

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Inlet I$_2$ (mmol min$^{-1}$)</th>
<th>Inlet SO$_2$ (mmol min$^{-1}$)</th>
<th>Outlet SO$_2$ (mmol min$^{-1}$)</th>
<th>Inlet I$_2$ (mmol min$^{-1}$)</th>
<th>Outlet I$_2$ (mmol min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>28.3</td>
<td>17.9</td>
<td>7.16</td>
<td>30.8</td>
<td>64.8</td>
</tr>
<tr>
<td>50</td>
<td>28.6</td>
<td>17.9</td>
<td>7.31</td>
<td>27.5</td>
<td>60.9</td>
</tr>
<tr>
<td>80</td>
<td>28.3</td>
<td>17.9</td>
<td>7.35</td>
<td>27.2</td>
<td>59.1</td>
</tr>
</tbody>
</table>

The main objective of choosing toluene as the I$_2$ 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 respective to I$_2$ disappearing.

**The effect of increasing liquid flow rate**

Runs were conducted with AFR-G1 at six liquid flow rate levels, an SO$_2$ mole fraction in gas ($y_{SO_2}$=0.50), gas flow rate (1800 mL min$^{-1}$ at STP), room temperature (22 °C), and water volumetric fraction (0.15) when SO$_2$ was excessive and I$_2$ was the limiting reactant. Table 5 shows the inlet and outlet molar flow rates of SO$_2$ and I$_2$. A nearly constant conversion of I$_2$ regardless of varying the liquid flow rate indicates that the conversion of iodine in the Bunsen reaction was controlled by equilibrium when SO$_2$ 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 SO$_2$ absorption and I$_2$ reaction rates. Increase in the liquid flow led to the linear increase of the I$_2$ reaction rate, but is did not significantly increase the SO$_2$ absorption rate.

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

<table>
<thead>
<tr>
<th>Liquid flow rate (mL min$^{-1}$)</th>
<th>Inlet I$_2$ (mmol min$^{-1}$)</th>
<th>Inlet SO$_2$ (mmol min$^{-1}$)</th>
<th>Inlet H$_2$O (mmol min$^{-1}$)</th>
<th>Outlet I$_2$ (mmol min$^{-1}$)</th>
<th>I$_2$ conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>10.3</td>
<td>40.2</td>
<td>250</td>
<td>0.68</td>
<td>93.4</td>
</tr>
<tr>
<td>40</td>
<td>13.4</td>
<td>40.2</td>
<td>333</td>
<td>0.97</td>
<td>92.7</td>
</tr>
<tr>
<td>45</td>
<td>14.6</td>
<td>40.2</td>
<td>375</td>
<td>1.16</td>
<td>92.1</td>
</tr>
<tr>
<td>55</td>
<td>18.9</td>
<td>40.2</td>
<td>458</td>
<td>1.52</td>
<td>91.9</td>
</tr>
<tr>
<td>60</td>
<td>20.5</td>
<td>40.2</td>
<td>500</td>
<td>2.19</td>
<td>89.3</td>
</tr>
<tr>
<td>90</td>
<td>30.5</td>
<td>40.2</td>
<td>750</td>
<td>3.42</td>
<td>88.8</td>
</tr>
</tbody>
</table>

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 SO$_2$ 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. In the reaction experiments, it was also observed by the color change of I$_2$ (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$_l$=0.4 mL for the AFR-LF and V$_l$=8 mL for the AFR-G1), the reaction rate values of the iodine conversion obtained with both reactors at excessive SO$_2$ and various liquid flow rates are shown in Table 6.

<table>
<thead>
<tr>
<th>Liquid flow rate in AFR-LF (mL min$^{-1}$)</th>
<th>I$_2$ reaction rate (mol m$^{-3}$s$^{-1}$)</th>
<th>I$_2$ conversion (%)</th>
<th>Liquid flow rate in AFR-G1 (mL min$^{-1}$)</th>
<th>I$_2$ reaction rate (mol m$^{-3}$s$^{-1}$)</th>
<th>I$_2$ conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>19.6</td>
<td>93</td>
<td>3</td>
<td>39.1</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>39.1</td>
<td>92</td>
<td>4.5</td>
<td>57.3</td>
<td>91</td>
</tr>
</tbody>
</table>

Now, comparing the I$_2$ conversion data and reaction rate with respective to I$_2$ 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 SO$_2$ by toluene, water, toluene-water mixture being studied with Corning AFR-LF and AFR-G1 reactors, the Bunsen reaction with I$_2$ carried by the I$_2$-toluene solution was investigated using the same reactors. From the experiments, we can withdraw the following conclusions:

i. Continuous operation of the multiphase Bunsen reaction with I$_2$ provided in the I$_2$-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.

ii. The reaction rate with respect to SO$_2$ is controlled by the SO$_2$ absorption in the toluene-water mixture. The absorption is enhanced by the reaction between dissolved SO$_2$ and I$_2$ in the solution. The reaction rate with respective to I$_2$ is controlled by equilibrium when SO$_2$ is excessive in the liquid phase. Increasing the reaction temperature higher than the room temperature decreases the SO$_2$ absorption rate but does not change much of the I$_2$ appearance rate in the excessive present of SO$_2$ in the solution.

iii. The reaction rate with respective to I$_2$ and the I$_2$ 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.

iv. The two acid products, HI and H$_2$SO$_4$, are in the aqueous phase leave the toluene to become lean of iodine for reuse. No H$_2$S is detected in gas phase and no elemental sulfur is observed in the liquid.

Nomenclatures and Abbreviations

<table>
<thead>
<tr>
<th>KL.a</th>
<th>1/sec</th>
<th>Overall mass transfer coefficient in the liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>ySO$_2$</td>
<td>---</td>
<td>mole fraction of SO$_2$ in the gas phase</td>
</tr>
<tr>
<td>TCD</td>
<td>---</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>---</td>
<td>Ultraviolet-visible spectrophotometer</td>
</tr>
<tr>
<td>AFR-LF</td>
<td>---</td>
<td>Low flow-Advanced flow reactor</td>
</tr>
<tr>
<td>AFR-G1</td>
<td>---</td>
<td>G1 Standard evaluation-Advanced flow reactor</td>
</tr>
</tbody>
</table>

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Conflicts of interest

The author declares that there are no conflicts of interest.

References


