Dynamic Simulation of Hydrogen Iodide Decomposition in Catalytic Multi-Tubular Reactor

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Abstract. Sulfur-Iodine thermochemical cycle process has been considered a promising method to generate hydrogen from water. One of the main limitations of this process lies in the hydrogen iodide decomposer section, which requires substantial amount of heat at high temperature. The present study analyses the heat transfer limitation effect on the performance of hydrogen iodide decomposition in a multi-tubular catalytic reactor by means of dynamic simulation. The extensive numerical simulation shows that the inlet temperature heating medium (Helium gas) should be at least 700°C so to enable at least 90% conversion when the inlet molar fraction of hydrogen iodide is 0.6. Lowering the inlet heating medium will require the reduction in the inlet molar fraction of hydrogen iodide in order to keep the conversion at 90% and above.

1. Introduction

The water-splitting Sulfur-Iodine Thermochemical Cycle (SITC) process is one of the hydrogen production methods that has received intensive research attentions over the last two decades. This process has some advantages: (a) using abundant water supply, (b) easy separation and purification of hydrogen, (c) potential integration with nuclear reactor and other plants producing high-temperature waste heat, and (d) zero greenhouse gas emission. The SITC process has three major sections where each section corresponds to a major chemical reaction as follows [1]:

Section I: Bunsen reaction

\[ \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_4 + 2\text{HI}, \quad \Delta H_1 = -75 \pm 15 \text{ kJ/mol} \]

Section II: Sulfuric acid decomposition

\[ \frac{1}{2}\text{O}_2 + \text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_4, \quad \Delta H_2 = 186 \pm 3 \text{ kJ/mol} \]

Section III: Hydrogen iodide decomposition

\[ 2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2, \quad \Delta H_3 = 12 \text{ kJ/mol} \]

Figure 1 shows the interactions of three major sections in the SITC process. The inputs to the process is water and heat while the outputs are hydrogen (product) and oxygen (by-product). The reactants (sulfur dioxide and iodine) are fully recycled – thus no harmful waste is released to the environment. The major challenges in this process, however, arise from the need of a very high-temperature thermal energy (in Section II) and materials of construction that can cope corrosive and high-temperature environment. The
closed-cycle operation of the SITC was successfully achieved at a production rate of 32 \( \text{L/hr} \) lasting for 20 hours – the automation of the process in a stable state is considered one of the challenges \([2]\). The hydrogen iodide decomposition section is very important because it is where hydrogen is produced. One of the main concerns in the SITC process is the hydrogen iodide decomposition reactor, which is thermodynamically limited due to the reversible reaction nature. The hydrogen iodide decomposition occurs in the presence of suitable catalysts (e.g., platinum catalyst) at the temperature range of 300-500\( ^\circ \text{C} \). Due to the chromodynamics limitation, the conversion of hydrogen iodide into hydrogen is quite low.

![Sulfur-Iodine Thermochemical Process](image)

**Figure 1.** Sulfur-Iodine Thermochemical Process: Section I (dashed mix dotted area), Section II (dotted area), and Section III (dashed area) \([3]\).

2. HI decomposition reactor modelling

2.1. Process description

Figure 2 illustrate the reactor configuration for HI decomposition. The catalyst pellets are packed inside the tubes in which the reaction occurs. Since the reaction is endothermic, heating medium is required to supply for the heat of reaction. In this study, the helium (He) gas is used as the heating medium which flows in the shell side. We choose He as the heating medium because of the high-temperature condition used in this study, i.e., the heating medium should be above 400\( ^\circ \text{C} \). In this study, we choose co-current flow configuration because the reactor is thermodynamically limited especially at lower temperature. As the reaction proceeds along the reactor length, the rate of reaction becomes severely limited by the thermodynamics equilibrium at a higher temperature. Thus, reducing the temperature along the reactor helps reduce the equilibrium limitation. Consequently, with this co-current flow configuration it will be expected that the overall conversion of HI will increase but at the expense of larger reactor volume, i.e., compared to the counter-current flow configuration.
2.2. Mass and energy balance equations

In this study, the reactor is modelled as a set of ordinary differential equations (ODEs). Since the reactor is long and the spatial temperature and concentration gradients are unlikely to be constant along the reactor, it is necessary to divide the reactor into several zones. Each of the zones is then modelled using the ODEs, i.e., assumption of well mixing in each of the zones. In this case, the reactor is divided into 22 zones and each zone is 0.5 m in length. Given a zone \( j \) for \( j = 1, 2, \ldots, n \), the pseudo homogeneous mass (mole) balance equations for \( HI, I_2 \) and \( H_2 \) denoted with the subscripts \( A, B \) and \( C \) respectively are given as below:

\[
\frac{dn_{Aj}}{dt} = F_p (y_{Aj,k} - y_{Aj}) - r_{Aj}W_{cat} \tag{1}
\]

\[
\frac{dn_{Bj}}{dt} = F_p (y_{Bj,k} - y_{Bj}) + \frac{1}{2} (r_{Aj}W_{cat}) \tag{2}
\]

\[
\frac{dn_{Cj}}{dt} = F_p (y_{Cj,k} - y_{Cj}) + \frac{1}{2} (r_{Aj}W_{cat}) \tag{3}
\]

where \( n_{kj} \) denotes the number of moles of species \( k \) in the zone \( j \), \( y_{kj} \) the molar fraction of the species \( k \) in the zone \( j \), \( r_{Aj} \) the rate of consumption of \( HI \) (kmol/kg-cat.s), \( W_{cat} \) the weight of catalyst per zone (kg) and \( F_p \) the process stream flow rate (kmol/s). The energy balance in the tube-side is as follows

\[
\frac{d}{dt} \left( \frac{C_{pj}N_{T_{pj}}}{R_{pj}} \right) = F_p \bar{C}_{pj} \left( T_{pj,t} - T_{pj} \right) - \Delta H_r r_{Aj}W_{cat} + Q_{sj} \tag{4}
\]

Meanwhile, the energy balance in the shell-side is

\[
V_s \left[ \frac{d}{dt} \left( \frac{C_{pj}R_{T_{pj}}}{R_{T_{pj}}} \right) \right] = F_h \left( C_{h,j,t}T_{h,j,t} - C_{hj}T_{hj} \right) - Q_{sj} \tag{5}
\]

\[
Q_{sj} = UA_s \left( T_{hj} - T_{pj} \right) \tag{6}
\]

In the equations (4) – (6), \( \bar{C}_{pj} \) denotes the average specific heat capacity of the process fluid (kJ/kmol. K), \( C_{hj} \) the specific heat capacity of He gas (kJ/kg.K), \( T_{pj} \) the process fluid temperature (°C), \( T_{hj} \) the heating medium temperature (°C), \( \Delta H_r \) the heat of reaction (kJ/kmol-HI), \( \rho_{hj} \) the heating medium density (kg/m³), \( N_{T_{pj}} \) the total number of moles (kmol), \( U \) the overall heat transfer coefficient (W/m².K), \( V_s \) the volume of shell per zone (m³), \( A_s \) the heat transfer area per zone (m²) and \( Q_{sj} \) is the heat supply from the heating medium (kJ/s). The average specific heat capacity is calculated as follows

\[
\bar{C}_{pj} = \sum_{k=1}^{k} MW_k \bar{C}_{kj} \tag{7}
\]

where \( MW_k \) and \( \bar{C}_{kj} \) denote the molecular weight (kg/kmol) and specific heat capacity (kJ/kmol.K) of the species \( k \) respectively. The specific heat capacity (J/mol.K) of each of the species (gaseous phase) depends on the temperature and represented using empirical polynomial equation:

\[
C_k = \beta_0 + \beta_1 \bar{T} + \beta_2 \bar{T}^2 + \beta_3 \bar{T}^3 + \beta_4 \bar{T}^4 \tag{8}
\]
Here, $\tilde{T} = T/1000$ and $T$ is the absolute temperature (K). The values of parameters of the equation (8) are given in the Table 1, from the NIST Chemistry WebBook [4].

### Table 1. Parameters of specific heat capacity correlations [4].

| Parameters | HI   | $I_2$  | $H_2$ | He   |
|------------|------|--------|-------|------|
| $\beta_0$  | 26.0454 | 37.79763 | 33.066178 | 20.78603 |
| $\beta_1$  | 4.689678 | 0.225453 | -11.363417 | 4.8506E-10 |
| $\beta_2$  | 4.911765 | -0.912556 | 11.432816 | -1.5829E-10 |
| $\beta_3$  | -2.654397 | 1.034913 | -2.772874 | 1.5251E-11 |
| $\beta_4$  | 0.121419 | -0.083826 | -0.158558 | 3.1963E-11 |

2.3. Reaction kinetics

Nguyen et al. [1] studied the hydrogen iodide reaction kinetics over the Pt/γ-alumina 1 wt% in a sulfur-iodine thermochemical cycle process. The researchers involved have established new kinetic parameters of the reaction estimated from the measured data. In this work, the kinetics information from Nguyen et al. [1] is adopted. Therefore, interested readers may refer to the paper itself for the details about the reaction kinetics of hydrogen iodide over Pt-based catalyst. Table 2 shows the values of parameters used for the simulation in this study. The rate of HI decomposition is expressed as follows

$$r_A = \frac{k(1 - X) \cdot k \left(\frac{2}{3}\right)}{1 + (\sqrt{K_I}) \left(\sqrt{P_{B_0}} + \frac{P_{A_0} X^2}{2}\right)}$$

where $k = k/K_p$ and the other parameters above are defined as below:

$$K_p = \exp\left(-\frac{\Delta G^T_p}{RT}\right)$$  \hspace{1cm} (10)

$$k = 31.3\exp\left(-\frac{37.1}{RT}\right)$$  \hspace{1cm} (11)

$$K_I = 1.8 \times 10^{-9} \exp\left(\frac{75.1}{RT}\right)$$  \hspace{1cm} (12)

### Table 2. Parameters and values used in the current simulation.

| Parameters and units | Values |
|----------------------|--------|
| Number of tubes, $N_0$ | 1000 |
| Tube internal diameter, $d_t$ (m) | 0.05 |
| Tube length, $L_t$ (m) | 11.0 |
| Ratio of total tube volume to reactor shell volume, $r_v$ | 2.5 |
| Reactor shell diameter, $D_r$ (m) | 2.5 |
| Voidage factor in tube, $\varepsilon$ | 0.4 |
| Catalyst pellet (spherical shape) diameter, $d_c$ (m) | 0.005 |
| Catalyst density, $\rho_c$ (kg/m³) | 480.0 |
| Nominal feed molar fraction HI | 0.6 |
| Nominal feed molar fraction $I_2$ | 0.4 |
| Nominal feed flow rate, $F_p$ (kmol/s) | 0.02 |
| Nominal He flow rate, $F_h$ (kg/s) | 30.0 |
| Nominal inlet process temperature, $T_{p_0}$ (°C) | 350.0 |
| Nominal He inlet temperature, $T_{h_0}$ (°C) | 500.0 |
| Nominal inlet pressure of process fluid, $P_{p_0}$ (kPa) | 500.0 |
| Idea gas constant, $R$ (kJ/mol.K) | 8.3141E-3 |
| Overall heat transfer coefficient, $U$ (kW/m².K) | 0.20 |
3. Results and discussion

One of the major challenges in the operation of HI decomposition reactor is due to the limitation imposed by the thermodynamics equilibrium. A large reactor volume is required to achieve significant conversion of the hydrogen iodide. There are a number of simulation studies on HI decomposition reactor reported in the literature. Hwang and Onuki reported that 90% conversion of HI is achieved in a membrane reactor [5]. Goswami and co-workers [6] conducted simulation study on HI decomposition in a packed bed membrane reactor (PBMR) and compared the results with that in a conventional packed bed reactor. Their study showed that the parameters having high impact on conversion are the wall temperature, feed temperature, reactor diameter and packed bed porosity. They suggested that the reactor wall temperature is recommended to be in the range of 690 – 700 K, and the bed porosity is recommended to be in the range of 0.2 – 0.4. According to the simulation study of [7], the proper operating temperature of the HI thermal decomposer to satisfy the hydrogen production rate of 50 NL-H2/h and sustain the closed loop operation of the Sulfur-Iodine (SI) process is 587 °C. The simulation of SI thermochemical plant by [8], showed that the hydriodic acid (HI) decomposition step is the rate-limiting step of the entire SI cycle. In the present simulation study, the focus will be on the effects of heating medium temperature and process fluid temperature on the HI conversion.

3.1. Effect of inlet temperature of heating medium

First, an open-loop simulation is conducted where the nominal operating conditions and parameters are shown in the Table 2. Here, the effects of inlet temperature of the heating medium (He gas) on the HI percentage conversion and H2 production rate are examined. Figure 3 shows the effect of varying the inlet temperature of the heating medium from 500°C to 600°C and then to 700°C on the conversion at different inlet molar fraction of the hydrogen iodide. As the inlet temperature (Tth) increases, for a given inlet molar fraction of HI, the conversion also increases. This is accompanied by the increase in the hydrogen production rate (normal L/s). However, for a given inlet temperature of the heating medium, it can be seen that the rise of the hydrogen production rate shows rapid increase as the inlet molar fraction of HI increases up to a certain threshold value, thereafter the increase is much reduced. From the Figure 3, it can be seen that the threshold values are 0.25, 0.37 and 0.48 corresponding to the inlet temperature of heating medium at 500°C, 600°C and 700°C respectively. Increasing the inlet temperature of heating medium from 500°C to 700°C leads to about 90% increase in hydrogen production rate from 51 NL/s. This suggests that an adequate heating effect is crucial to achieve better conversion of HI. This is because the heat transfer from the heating medium to the process fluid is limited by the low overall heat transfer coefficient. To increase the heat transfer rate, it is necessary to increase the surface area for the heat transfer. This may be done by reducing the tube diameter and increasing the total number of tubes, but this has to be done with caution as not to have an excessively large pressure drop across the reactor – the smaller the tube diameter, the larger the pressure drop across the reactor. Another strategy is to increase the temperature difference between the heating medium and process fluid so to compensate for the low overall heat transfer coefficient. If molten salt is used as the heating medium, the maximum temperature for the heating medium is about 500°C. Therefore, to have a larger temperature of heating medium, helium (He) gas could be used. Note that, a higher heating medium temperature will result in a higher process fluid temperature, which will increase the reaction rate; the equilibrium constant increases with the increase in temperature because the reaction is endothermic. Thus, the decomposition reaction is favoured at higher temperature. The result of this simulation is in agreement with the previous simulation studies reported in literature, e.g., [6].

Figure 4 demonstrates the temperature profiles in the tube and shell sides of the reactor. The temperature inside the tube drops very drastically from 350°C to 275°C and 300°C when the inlet temperatures of the heating medium are 500°C and 700°C respectively. Along most of length of the reactor, the temperature inside the tube is nearly constant although a significant temperature gradient is observed in the shell side (heating medium). From this figure, it can be deduced that increasing the operating temperature of the process fluid from 275°C to 300°C will lead to about 90% increase in the hydrogen production rate, when the inlet molar fraction of HI is 0.6; equivalently, the conversion rises from 41%
to about 74%. The question is, can the conversion be raised further to above 90% for the case of inlet temperature of heating medium at 700°C, and inlet molar fraction of HI at 0.6? To answer this question, it is necessary to develop a temperature control of the reactor. Here, the temperature control maintains the exit temperature of the process fluid at a setpoint by manipulating the heating medium flow rate.

![Figure 3](image1.png)

**Figure 3.** Conversion of HI and H₂ product flow rate against inlet molar fraction of HI in the process stream under different values of inlet temperature of the heating (He gas) stream.

![Figure 4](image2.png)

**Figure 4.** Temperature profile along the reactor under different values of inlet temperature of the heating medium for inlet HI molar fraction at 0.6.

### 3.2. Closed-loop responses

The exit temperature of process stream is controlled by manipulating the heating medium flow rate. A Proportional Integral (PI) controller is adopted where the tuning is done by using the linearized model:

\[
G_p(s) = \frac{0.4\exp(-0.119s)}{1.65s + 1}
\]

(13)
Based on the linearized model (13), the PI controller is tuned using the IMC tuning method (available in the Control System Designer, MATLAB R2017b). The PI controller is given below:

\[
G_c(s) = 1.1 \left( 1 + \frac{1}{1.65s} \right)
\]  

(A4)

A series of step changes to the temperature setpoint (5°C at each step) is applied to the reactor. The impact of the setpoint changes under different inlet temperatures of the heating medium, on the conversion and heating medium flow rate are shown in Figures 5 and 6.

**Figure 5.** Conversion of HI in response to a series of temperature setpoint changes (5°C at a time) under different inlet temperatures of heating medium (inlet molar fraction of HI is 0.6).

**Figure 6.** The profiles of heating medium flow rate in response to a series of temperature setpoint changes (5°C at each step change) where the inlet molar fraction of HI at 0.6.
From Figure 5, it can be seen that the conversion increases as the exit temperature setpoint increases. The higher the temperature of the heating medium the larger is the conversion. Figure 6 shows how the heating medium flow rate varies in response to the temperature setpoint changes. When the inlet temperature of the heating medium is low, the amount of the flow rate raises dramatically with the exit temperature. Eventually, the maximum heating medium flow rate is reached (due to the physical limitation of valve that allows only up to certain range of flow) – the valve becomes saturated and it is no longer possible to raise the exit temperature any further. As a result, the maximum conversion achievable depends on the inlet temperature of the heating medium. In this case, when the inlet temperature of heating medium is 500°C, the maximum conversion achievable is only about 52%, when the inlet molar fraction of HI is 0.6. Obviously, to achieve a higher conversion the inlet temperature of the heating medium has to be increased, for examples, to 600°C and 700°C where the heating medium valve will not saturate. For the case of inlet temperature of heating medium at 700°C, the maximum achievable conversion is about 73% and the corresponding exit temperature of process fluid is 294°C. Can the conversion be raised up to 90% and above by further increasing the exit temperature? Of course, this would depend on the heating medium flow rate required, i.e., whether the valve will encounter saturation or not in order to raise the temperature to the desired value leading to 90% conversion.

A simulation is further conducted in which a series of setpoint changes is applied with a magnitude of 15°C per step change. Figure 7 shows the profile of conversion in response to the setpoint changes of exit process temperature. Obviously, an increase of the 60°C in the exit temperature from 274°C can result in about 91% conversion. Figure 8 shows the exit temperature profile in response the sequential setpoint changes. In this case, the valve does not encounter saturation as shown in Figure 9. In Figure 9, it is noticed that the percentage increase of the heating medium per step change in setpoint increases as the setpoint increases. This implies that the process gain decreases with the setpoint changes, which further implies that the process controllability decreases with the temperature setpoint increase. This decrease in process controllability can be explained by the decrease in the temperature difference between the shell and tube sides. With the decrease in this temperature difference, it is becoming more and more difficult to meet the required heat by the reaction in the face of low overall heat transfer coefficient and limited heat transfer area. As a result of that, the effect of increasing the heating medium flow rate becomes less influential at a higher setpoint of exit temperature of process fluid – leading to the reduced process controllability as process fluid temperature increases.

![Figure 7](image)

**Figure 7.** Conversion of HI in response to a series of temperature setpoint changes (15°C at a time) when the inlet temperatures of heating medium is at 700°C and inlet molar fraction of HI is 0.6.
4. Conclusion

In this study, the dynamic simulation of an industrial-scale multi-tubular catalytic reactor for HI decomposition to produce hydrogen shows that, a sufficiently high heating medium temperature is needed to achieve satisfactorily high conversion ($\geq 90\%$). This study suggests that the inlet temperature of the heating medium (He gas) should be at least 700°C to achieve over 90% conversion when the inlet molar fraction of HI is 0.6. If the inlet heating medium is reduced to 600°C, it is still possible to achieve above 90% conversion but the inlet molar fraction of HI should be less than 0.48. Please note that, at lower inlet temperature of heating medium the process controllability is low due to the near valve saturation. The main limitation for the HI reactor used as observed in this simulation is the limited heat transfer area. If the heat transfer area can be increased by 50% or more, then the process controllability can be greatly improved at a lower inlet temperature of the heating medium.
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