A Simulation Study of Catalytic SO_3 Decomposition in Heat Exchanger Reactor

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ABSTRACT

A SO_3 decomposition is common chemical reaction employed by thermochemical water-splitting cycles for hydrogen. This reaction proceeds endothermically in catalytic bed; in heat utilization system of the VHTR, needed heat is provided from high temperature helium gas by heat exchange. To find sizes and shapes in this reactor, a reaction rate of SO_3 decomposition was formulated by a Pt catalyst kinetic measurement experiments; besides, ordinary differential equations for this catalytic bed to produce hydrogen of 1 mol/s, in which the kinetic and heat exchange were counted, were integrated numerically. Characteristics length which represented reactor shapes and required heat transfer area were shown to attain nearly chemical equilibrium. In reference case, it was found that a required heat transfer area was 20 m^2 and very slim flow channels performed the decomposition well to attain near the chemical equilibrium.

INTRODUCTION

A huge demand for hydrogen as an energy carrier is expected for the near future. The thermochemical water-splitting IS processes(1) are due to offer massive hydrogen production methods without carbon dioxide to be supplied with heat from the high-temperature gas-cooled reactors (HTGRs), so that this process attracts broad interests to implement studies. The SO_3 decomposition reactor for oxygen production is particularly important, since large amount of heat is absorbed for the endothermic chemical reaction in a catalytic bed by receiving specific heat of high temperature helium gas. Computing heat exchange type reactor were carry out, in which the kinetics of SO_3 decomposition reaction formulated by a Pt catalyst experiments and heat exchange between the process gas and the helium take place. To investigate achieving nearly chemical equilibrium, required heat transfer area and flow channel shapes of the catalytic bed are discussed.

GOVERNING EQUATIONS

The SO_3 decomposition reaction proceeds endothermically in two stages to produce oxygen. The aqueous phase of sulfuric acid is vaporized, then, decomposed according to following reactions (1, 2):

$$\mathrm{H_2SO_4(g)} \longrightarrow \mathrm{H_2O(g)} + \mathrm{SO_3(g)} \tag{1}$$

and

$$\mathrm{SO_3(g)} \longrightarrow \mathrm{SO_2(g)} + \frac{1}{2}\mathrm{O_2(g)}, \tag{2}$$

where “g” means the gaseous phase. Firstly sulfuric acid decomposes spontaneously into sulfur trioxide and gaseous water. Secondly, in higher temperature, the sulfur trioxide decomposes into sulfur dioxide and oxygen, reaction (2), in the presence of solid catalyst.

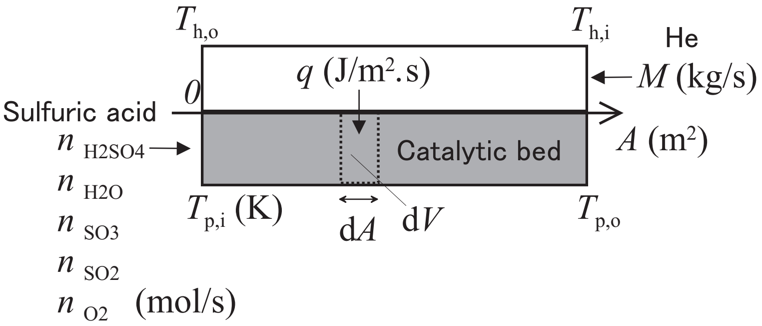

Figure 1: Calculated object of heat exchange type $\mathrm{SO_3}$ decomposition reactor. $\mathrm{SO_3}$ flows in under side channel, helium gas flows in upper side channel. Catalyst completely fills under side channel.

A calculated object of $\mathrm{SO_3}$ decomposition reactor is shown in Figure 1. Heat flux q W/m^2 through the upper side to the under side is given by

$$q = U(T_h - T_p), \tag{3}$$

where U W/m^2·K is overall heat transfer coefficients, T_h K is temperature of the helium gas, T_p is temperature of process gas. With the heat transfer area A m^2, q is expressed in

$$q = Mc_{p,h}\frac{dT_h}{dA}, \tag{4}$$

where M kg/s is flow rate of helium gas, $c_{p,h}$ J/kg·K is its specific heat. Here, a characteristic length z m was defined as

$$z = \frac{dV}{dA}, \tag{5}$$

an ordinary differential equation on temperatures:

$$n_\mathrm{total}\frac{dH}{dT}\frac{dT_p}{dA} = -\Delta H \cdot z \cdot r + q \tag{6}$$

was obtained, where V is volume of the catalytic bed, n mol/s are constituent flow rates of process gas, n_total is total molar flow rate of process gas, H J/mol is molar enthalpy of process gas, ΔH J/mol heat of reaction for reaction (2) and r mol·m^{-3}·s^{-1} is reaction rate of reaction (2). Heat of reaction for reaction (1) was considered by the term of $\mathrm{d}H/\mathrm{d}T$.

PARAMETER SETUP

The parameters in eqs.(3-6) were set up in such a way as to integrate eq. (6).

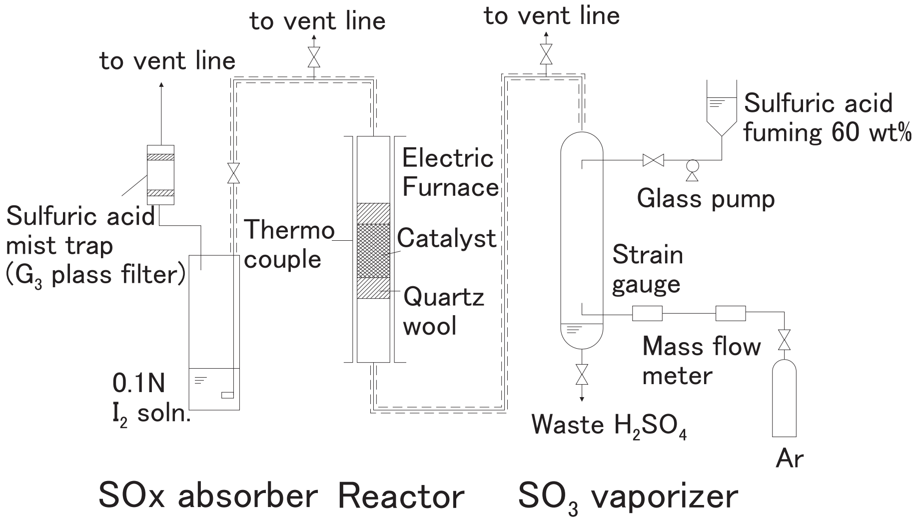

Figure 2: Experimental apparatus(3) for $\mathrm{SO_3}$ decomposition.

Overall heat transfer coefficient U is evaluated from a conceptual design(2) of advanced process heat exchangers. For the $\mathrm{SO_3}$ decomposer, a heat transfer coefficient on helium gas side of 1199 W/m^2·K was specified, another on process gas side of 130 was specified; therefore, 117.3 is employed for U in eq. (3).

A reaction rate equation was formulated from a results of a kinetic measurement experiment(3). Figure 2 shows a schematic of kinetic measurement apparatus. A 1 wt% Pt catalyst on support material of α alumina ($\mathrm{Al_2O_3}$),which bulk density was 1.12 g/cm^3, have been applyed for $\mathrm{SO_3}$ decomposition reaction.

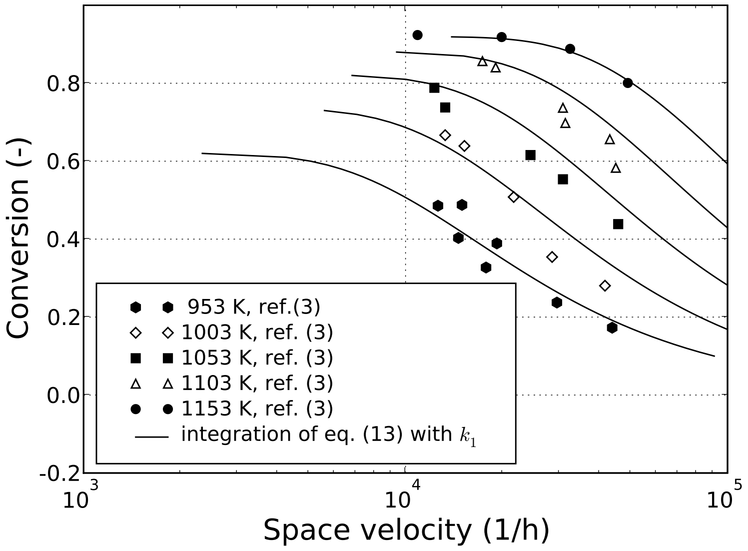

Figure 3: $\mathrm{SO_3}$ decomposition(3) over 1 wt% Pt-$\alpha\mathrm{Al_2O_3}$ catalyst. Initial $\mathrm{SO_3}$ concentration in Ar, 12 mol%.

The experiments have been conducted under atmospheric pressure. SO_3 gas produced from 60 wt% of fuming sulfuric acid was fed to a quartz reaction tube in diameter of 5 mm. The concentration of the feed SO_3 gas was 12 mol%. Space velocity of experimental parameter have been adjusted by flow rate of a carrier gas.

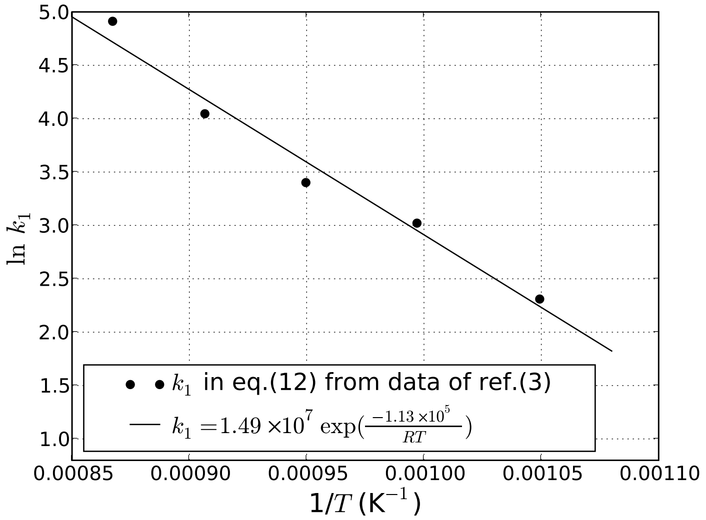

Figure 4: Arrhenius plot of SO_3 decomposition under eq. (14).

Conversion of SO_3 have been measured by chemical titration; the iodine titration was adapted for SO_2 of decomposition product and the neutralization titration was adapted for SO_3 of reactant. Figure 3 illustrates the kinetic of catalytic SO_3 decomposition. As the experimental results shows the Pt catalyst has high catalytic activity, especially in high temperature region of above 1070 K, the decomposition gas attains a chemical equilibrium state on the space velocity of 10000 h^{-1} .

In this study, a reaction rate equation of SO_3 decomposition was formulated from the experimental results of kinetic measurement. Considering that SO_3 decomposition reaction of eq. (2), to begin with, a following reaction rate equation:

$$r = -k_1 C_{\mathrm{SO_3}} + k_2 C_{\mathrm{SO_2}} C_{\mathrm{O_2}}^{0.5} \tag{7}$$

was supposed for primary simple and easy in engineering utilization, where C (mol/m^3) is molar volume concentration, r (mol/m^3 · s) is reaction rate and k is rate constant. Here, supposing a ratio of k_1 to k_2 is constant; with $r = 0$ at equilibrium sate, the ratio was given by

$$\frac{k_2}{k_1} = \frac{C_{\mathrm{SO_3}}}{C_{\mathrm{SO_2}} C_{\mathrm{O_2}}^{0.5}} = (\frac{RT}{P})^{0.5} \frac{X_{\mathrm{SO_3}}}{X_{\mathrm{SO_2}} X_{\mathrm{O_2}}^{0.5}} \,, \tag{8}$$

where X is molar fractions, P_0 (Pa) is reference pressure, T_0 (K) is reference temperature, P is total pressure, T is reaction temperature and R is the gas constant. The equilibrium constant K is

$$K = (\frac{P}{P_0})^{0.5} \frac{X_{\mathrm{SO_2}} {X_{\mathrm{O_2}}}^{0.5}}{X_{\mathrm{SO_3}}} = \exp(-\frac{\Delta G}{RT}), \tag{9}$$

where ΔG (J/mol) is change of free energy. With K, rewritten eq. (8) is obtained:

$$\frac{k_2}{k_1} = \underbrace{(\frac{RT}{P})^{0.5}(\frac{P}{P_0})^{0.5}}_{B}\frac{1}{K} = B\frac{1}{K}. \tag{10}$$

Therefore, k_2 was given by

$$k_2 = k_1 B\frac{1}{K}. \tag{11}$$

As a consequence, reaction rate r was given by

$$r = k_1(-C_{\mathrm{SO_3}} + \frac{B}{K}C_{\mathrm{SO_2}}C_{\mathrm{O_2}}^{0.5}). \tag{12}$$

Subsequently, the integration method was employed to specify reaction constant k_1. A relationship between space velocity S_v (s^{-1}) and the conversion α is given by

$$\frac{1}{S_v}\frac{PT_0}{TP_0} = \tau = C_0\int_0^{\alpha_x} -\frac{1}{r}d\alpha, \tag{13}$$

where C_0 mol/m^3 is initial molar volume concentration at reaction temperature and pressure and τ (s) is space time. With r, therefore, τ was expressed by

$$\tau = -C_0\int_0^{\alpha_x} r^{-1}d\alpha = -C_0 k_1^{-1}\int_0^{\alpha_x}(-C_{\mathrm{SO_3}} + \frac{B}{K}C_{\mathrm{SO_2}}C_{\mathrm{O_2}}^{0.5})^{-1}d\alpha. \tag{14}$$

Figure 4 shows a Arrhenius plot of the experimental data of kinetic measurement(3) using eq. (14). This figure highlights that eq. (12) can represent acceptably the experimental data. The solid curves in Figure 3 were calculated conversion by using obtained k_1.

CONDITION SETTING

For $\mathrm{H_2SO_4}$ dissociation in eq. (1), chemical equilibrium states were assumed at every location of A.

Minimum temperature difference ΔT_{min} between process side and helium side was sat at 50 K(4). Production flow rate of $\mathrm{SO_2}$, n_{SO2}, of 1 mol/s was chosen. Temperature at the outlet $T_{\mathrm{p,o}}$ was obtained as $T_{\mathrm{h,i}}$ - ΔT_{min}. Conversion at outlet was calculated using temperature of $T_{\mathrm{h,i}}$ - ΔT_{min}, the conversion was adjusted to value of 0.9 times lower than equilibrium at temperature of $T_{\mathrm{h,i}}$ - ΔT_{min} (near equilibrium state).

Following conditions of inlet sulfuric acid were adopted from flow sheet analyses(5) for $\mathrm{H_2SO_4}$ processing section: Temperature 800 K; Total pressure 1.2 MPa; Concentration of $\mathrm{H_2SO_4}$ 92.7 wt%.

Conditions of inlet helium gas were adopted from a conceptual design of HTTR-IS hydrogen production system(6). Temperature at inlet $T_{\mathrm{h,i}}$ was adapted at 880+273.15 K. Flow rate of helium gas was calculated by

$$M = n_{\mathrm{so2}}\, 285.8 \times 10^3 \frac{1}{\eta}\frac{1}{c_{p,h}(T_{\mathrm{h,i}} - T_{\mathrm{h,low}})}, \tag{15}$$

where n_{so2} is 1 mol/s, overall thermal efficiency to produce hydrogen is η=0.4 and temperature from total system outlet $T_{\mathrm{h,low}}$ is 526 K.

Data of enthalpies and free energy differences of thermodynamic tables$^{(7)}$ were used for the computations.

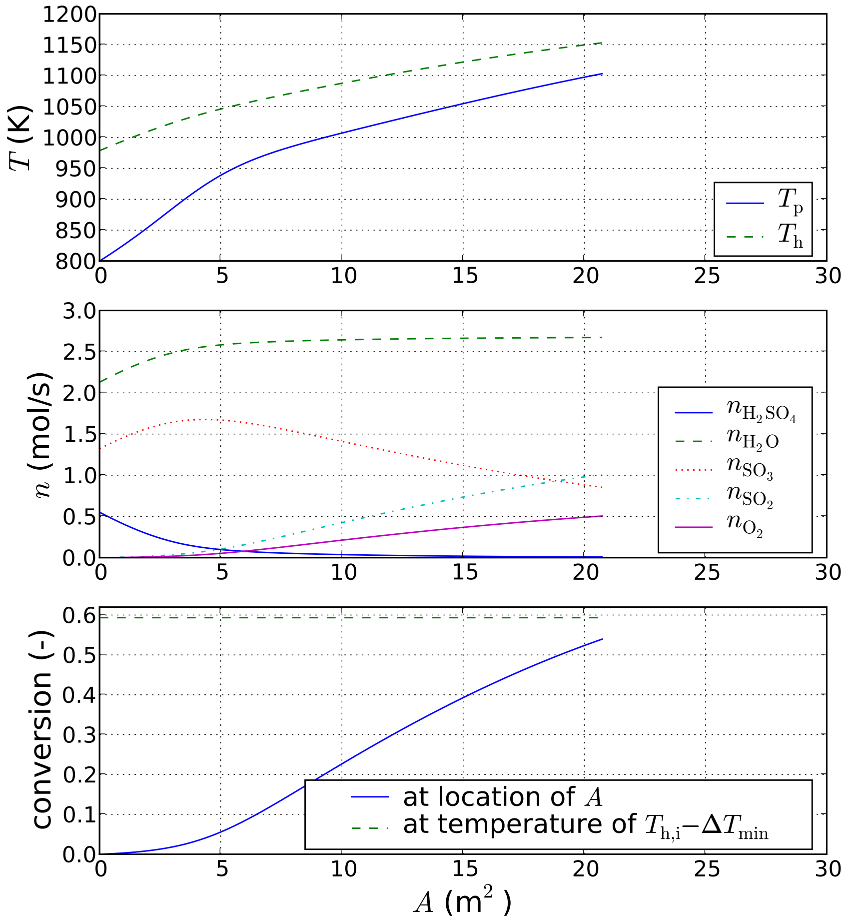

Figure 5: Integration result of eq. (6) under a_r=1.0 and a_U=1.0 on specified conditions (e.g. ΔT_{min}=50 K).

RESULTS AND DISCUSSION

Numerical integrations of eq. (6) were carried out by Euler method. On parametric calculations, following ratios a were employed:

$$r = a_r r_{\mathrm{norm}} \tag{16}$$

and

$$U = a_U U_{\mathrm{norm}}, \tag{17}$$

where r_{norm} is norm value of eq. (12) and U_{norm} is norm value of the 117.3 W/m^2·K. Figure 5 shows distributions of variables in the heat exchange type $\mathrm{SO_3}$ decomposition reactor on a_r=1.0

and a_U=1.0. This figure highlights that the specified conditions (e.g. $\Delta T_{\min}$=50 K) are satisfied in this numerical calculations.

Computations in various a_r and a_U were conducted to find A and z, at which the decomposition gas were near the chemical equilibrium state. Figure 6(a) shows contour map of required area of the reactor. The area are independent of r; in norm case, the area is in 20 - 25 m^2.

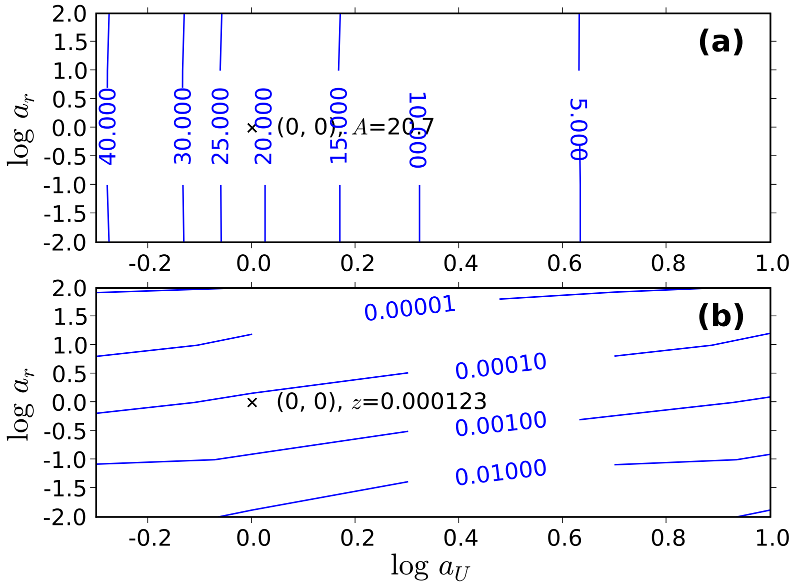

Figure 6: Required heat transfer area A and characteristics length z to attain equilibrium decomposition for heat exchange type $\mathrm{SO_3}$ decomposition reactor. (a) Contour map of required area A. (b) Contour map of characteristics length z in eq. (5). Point of (0, 0) represents norm conditions of a_r=1.0 and a_U=1.0 .

Figure 6(b) shows contour map of the characteristics length z in eq. (5). z represents shape of the catalytic bed, for example, $z = 1$ means diameter of 4 m in case of the circular tube. In case of above z, the decomposition gas could reach near the equilibrium state. In norm case, very slim flow channel even perform the decomposition reaction well to attain near the chemical equilibrium.

SUMMARY

$\mathrm{SO_3}$ decomposition is common chemical reaction employed by thermochemical water-splitting cycles for hydrogen. This reaction proceeds endothermically in catalytic bed; in heat utilization system of the VHTR, needed heat is provided from high temperature helium gas by heat exchange. To specify sizes and shape of this reactor, the kinetic of $\mathrm{SO_3}$ decomposition reaction was formulated by a Pt catalyst experiments for primary simple and easy in engineering utilization; besides, the ordinary differential equation for catalytic bed, in which the kinetic and heat exchange were considered, were computed. The characteristics length z which represented reactor shapes and the required heat transfer area were shown to attain nearly chemical equilibrium.

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