NUMERICAL ANALYSIS OF A SO_3 PACKED COLUMN DECOMPOSITION REACTOR WITH ALLOY RA 330 STRUCTURAL MATERIAL FOR NUCLEAR HYDROGEN PRODUCTION USING THE SULFUR- IODINE PROCESS

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A directly heated SO_3 decomposer for the sulfur-iodine and hybrid-sulfur processes has been introduced and analyzed using the computational fluid dynamics (CFD) code CFX 11. The use of a directly heated decomposition reactor in conjunction with a very high temperature reactor (VHTR) allows for higher decomposition reactor operating temperatures. However, the high temperatures and strongly corrosive operating conditions associated with SO_3 decomposition present challenges for the structural materials of decomposition reactors. In order to resolve these problems, we have designed a directly heated SO_3 decomposer using RA330 alloy as a structural material and have performed a CFD analysis of the design based on the finite rate chemistry model. The CFD results show the maximum temperature of the structural material could be maintained sufficiently below 1073 K, which is considered the target temperature for RA 330. The CFD simulations also indicated good performance in terms of SO_3 decomposition for the design parameters of the present study.

KEYWORDS : Direct Heating, Sulfur-iodine Process, Packed Column, Sulfur Trioxide Decomposition, Nuclear Hydrogen Production

1. INTRODUCTION

Hydrogen production technologies will vary depending on the raw materials, the adopted principles, and the quantity and purity of the hydrogen required. Many scientists and engineers are developing a wide range of processes to produce hydrogen economically and in an environmentally friendly way [1-2].

Recent developing technologies for the production of nuclear hydrogen based on the very high temperature reactor (VHTR) can be categorized into the sulfur iodine (SI) cycle, the hybrid sulfur (HyS) cycle, and others [3-4]. For SI and HyS cycle technologies, material problems with the thermo-chemical components for sulfuric acid decomposition are an issue due to the high temperature (more than 1123 K) and strongly corrosive environment of the decomposition process. Therefore, much research [5-8] is underway for the development of high performance materials for the sulfur-iodine process. On the other hand, a strategy to mitigate these material problems by reducing the temperature of the components is essential.

In this paper, a sulfur trioxide (SO_3) decomposer for the SI and HyS processes has been designed based on a direct heating concept, and is analyzed using a computational fluid dynamics (CFD) code in order to resolve the material issues surrounding the use of nuclear reactors for hydrogen production. A porous media approach has been used to model the region where chemical decomposition occurs. The finite rate chemistry model has been applied to simulate the chemical reaction in the reactor.

2. BACKGROUND AND CONCEPT OF A DIRECTLY HEATED SO_3 DECOMPOSER

The SI and HyS cycles include a sulfuric acid process that requires a sulfuric acid concentrator, a sulfuric acid evaporator, a primary decomposer that functions as a noncatalytic thermal decomposer for sulfuric acid, and a secondary decomposer for the decomposition of SO_3.

In the case of the secondary decomposer, the choice of reactor materials is limited due to severe operating conditions that include a very high temperature and pressure and a very corrosive environment. Furthermore, a heavy heatexchanging duty is required in this reactor because the primary and secondary streams are gas phases, and this situation requires more complex compact heat-exchanger configurations.

Westinghouse Advanced Energy Systems Division has performed a screening test to select structural materials for use in SO_3 decomposers, and they have recommended SiC and some other alloys for their absolute weight change [9]. One of the recommended alloys is RA330, which is an austenitic heat and corrosion resistant alloy. The chemical composition of RA330 is provided in Table 1. According to the experimental results from Westinghouse, RA330 has good corrosion-resistant properties below 1073 K. However, the effect of iodine as an impurity in a SO_3 gas stream on the corrosion of RA330 alloy is still to be determined.

Table 1. Chemical Composition of RA330 [10]

	Composition
Chromium	18.00 ~ 20.00
Nickel	34.00 ~ 37.00
Carbon	0.08 max
Silicon	1.00 ~ 1.50
Manganese	2.00 max
Phosphorus	0.030 max
Sulfur	0.030 max
Copper	1.00 max
Iron	Balance

On the other hand, membrane technologies to separate and purify a gas mixture are being developed. Both a catalytically modified mixed conducting ceramic hollow fibre membrane module, which can be used up to 1273 K, and a highly selective membrane are under development.

Under the assumptions that i) the temperature of the structural material is always maintained below 1073 K and ii) that a proper ceramic membrane for the separation of helium from a sulfur dioxide (SO_2) mixture will be developed in the near future, a directly heated SO_3 decomposition system can be established as shown in Fig. 1.

3. MODELING AND CFD METHOD OF THE DIRECTLY HEATED SO_3 DECOMPOSER

3.1 Design Modeling

A schematic of the thermo-chemical reactor modeled in this study is shown in Fig. 2. RA330 is adopted as the material of the vessel and the guide tube. RA 330 has a good oxidation resistance to a high temperature and an excellent resistance to thermal shock [10]. The decomposer has an inner dimension of 1.8(D) × 8(H) m, and is filled with Al_2O_3 catalysts with 32% porosity. Within the

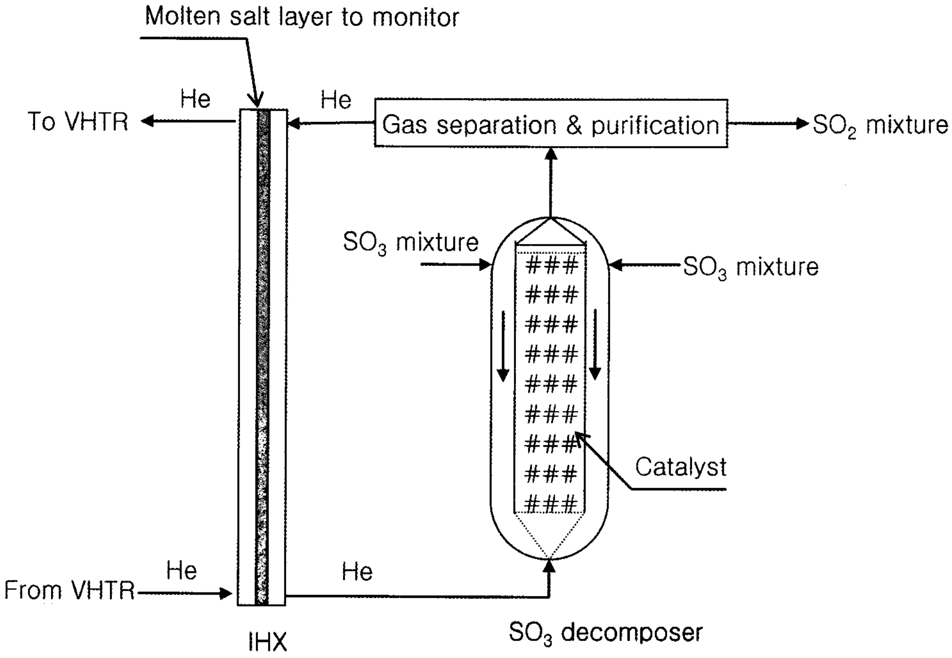


Fig. 1. Conceptual Drawing of the Directly Heated SO_3 Decomposer System

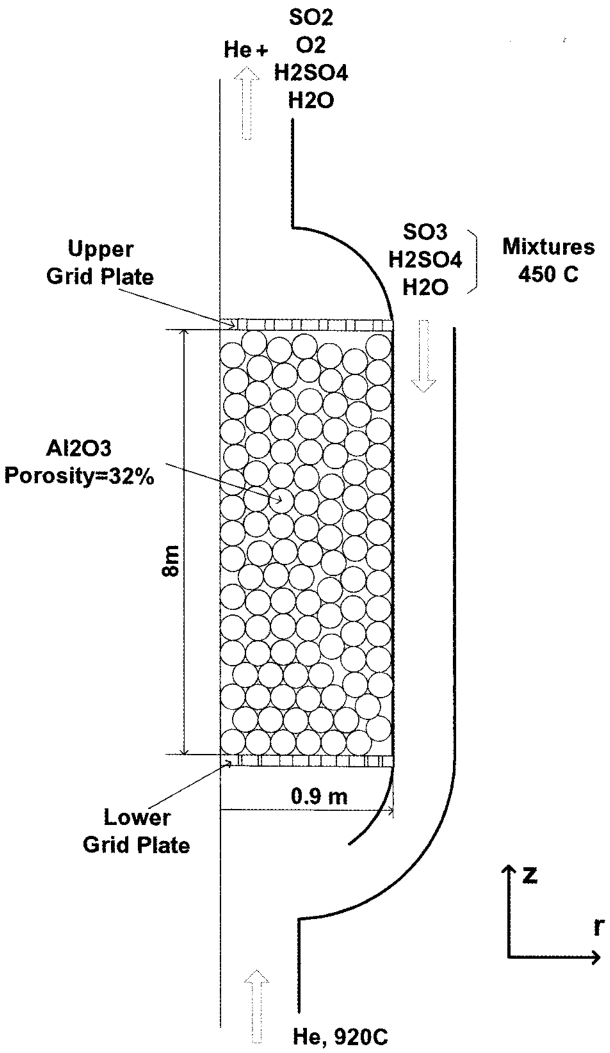


Fig. 2. A schematic of the Directly Heated SO$_3$ Decomposer

decomposer, SO$_3$ is thermally decomposed into SO$_2$ and O$_2$ in accordance with the following equation:

$$SO_3(g) \leftrightarrow SO_2(g) + \frac{1}{2}O_2(g), \quad \Delta H_{ST} = 99\,kJ/mol, \tag{1}$$

where ΔH_{ST} is the endothermic heat in standard state (298 K, 1 atm). The Al$_2$O$_3$ catalyst is used to accelerate the reaction.

A reaction rate equation for Eq. (1) can be expressed as:

$$R_{SO_3} = -k_d C_{SO_3}, \tag{2}$$

where R_{SO_3} is the reaction rate of SO$_3$ decomposition [mol/s], C_{SO_3} is the molar concentration of SO$_3$ [mol/m^3], and k_d is the reaction rate constant [1/s], respectively. Kim et al. [11] indicated that the reaction rate constant is the most important parameter in the thermal design of a SO$_3$ decomposer. However, the experimental results for the reaction rate constant are still controversial. Huang and T-Raissi [12] suggested the following expression based on the plug flow reactor packed by a WX-2 catalyst.

$$k_d = \frac{2.45 \times 10^8}{3600} \exp(-73053/RT) \tag{3}$$

In the equation above, R is the universal gas constant [J/mol K] and T is the temperature in K. On the other hand, using a hematite catalyst, Karasawa et al. [13] developed the following equation.

$$k_d = 1.31 \times 10^{15} \exp(-36299/T) \tag{4}$$

Fig. 3 shows a comparison of Eqs. (3) and (4). Equation (3) seems to be very optimistic. Equation (3) gives a good decomposition for a wide temperature range, whereas the decomposition by Eq. (4) is very small for temperatures below 1000 K.

The major design values of the decomposer are given in Table 2. The total decomposer length is 16.06 m. The decomposer height is 8 m. The inlet diameter of the helium supply pipe is assumed to be 50 cm. Tables 3 and 4 show the main thermal hydraulic data for the decomposer. The ratio of the flow rate between the SO$_3$ mixture gases and helium is 1:1, and it is assumed that the decomposer is able

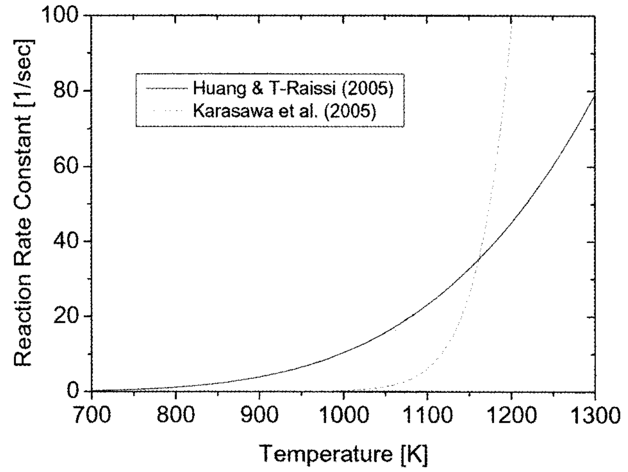


Fig. 3. Comparison of the Two Expressions for the Reaction Rate Constants

to produce hydrogen of about 1000 Nm^3/hr for the given flow conditions. The operating pressure of the helium and mixture gases is 7.09 bar. The inlet temperatures of the SO_3 mixture gases and helium are 450 ℃ and 920 ℃, respectively. The porosity of the lower grid plate is adjusted to increase the mixing of the SO_3 mixture and the helium gases.

Due to its large size (porosity of 0.32) and high conductivity (10 ~ 20 W/mK), the Al_2O_3 catalyst has to be explicitly considered in the thermo-fluid analysis. The phenomenon of heat transfer in the region of the Al_2O_3 catalyst is simply modeled with effective conductivity. A porous media model was applied to the region of the Al_2O_3 catalyst. The Ergun model [14] was used as the porous media model in the Al_2O_3 catalyst region:

$$\frac{dp}{L} = -\frac{150\mu(1-\varepsilon)^2 u}{\varepsilon^3 Dp^2} - \frac{1.75\rho(1-\varepsilon)u^2}{\varepsilon^3 D_p}, \tag{5}$$

where L is the distance between the lower grid plate and upper grid plate, μ is the viscosity [kg/ms], ρ is the density [kg/m^3], D_p is the diameter of Al_2O_3 [m], ε is the porosity [-], and u is the superficial velocity [m/s].

Fig. 4 shows the pressure drop versus gas velocity for various Al_2O_3 diameters by using Eq. (5). The viscosity and the density were adopted as the mean values in the region of the Al_2O_3 catalyst and L was set at 8 m. As shown in Fig. 4, the pressure drop increases with as the diameter of the Al_2O_3 catalyst decreases, and increases as the gas velocity increases.

Table 2. Design Values of the Directly Heated SO_3 Ecomposer

	Values
Total decomposer length	16.06m
Decomposer height	8m
Inlet diameter for mixture gases	30cm
He inlet diameter	50cm
Upper & lower Grid plate thicknesses	3cm
Al_2O_3 catalyst diameter	2cm

Table 3. Mass and Molar Fractions of the SO_3 Mixture Inlet

	H_2O	SO_3	H_2SO_4
Mass fraction	16.7%	65.5%	17.8%
Molar fraction	48.1%	42.5%	9.4%

Table 4. Operating Conditions of the Directly Heated SO_3 Ecomposer

	Flow rate	Inlet temperature	Operating pressure
He supply line	2.0 kg/s	1193 K	7.09bar
SO_3 mixture supply line	2.0 kg/s	723 K	7.09bar

3.2 Numerical Method

A detailed thermo-fluid analysis using CFD was performed with the CFX 11 code [15] to investigate steady state performance. Since the chemical reaction rate is much slower than the turbulence scale in the decomposer, the finite rate chemistry model in CFX 11 is applied based on Eqs. (1) and (3). In CFX 11, the endothermic heat in the reaction can be described by using the standard enthalpies of the considered gases. The main boundary conditions for the assessment are shown in Tables 3 and 4. The fixed flow rates of He and the SO_3 mixture gas were used as the inlet conditions. A pressure boundary condition was imposed on the outlet boundary. Adiabatic conditions were assumed to the surface of the vessel. The flow in the reactor is highly turbulent. Due to fast flow velocity and turbulence, multi-component diffusion can be neglected in the present analysis. The standard k-ε turbulence model with the scaleable wall function was used as the turbulence option. The scaleable wall function, developed by the CFX vendor, prevents the first grid point from sliding into the viscous sublayer [15]. The region packed with Al_2O_3 was modeled as an isotropic porous media. The properties of the helium gas are based on the National Institute of Standards and Technology (NIST) data base [16]. The temperature dependency of the thermo-chemical properties of the gases as well as of the structural materials are considered in the simulation.

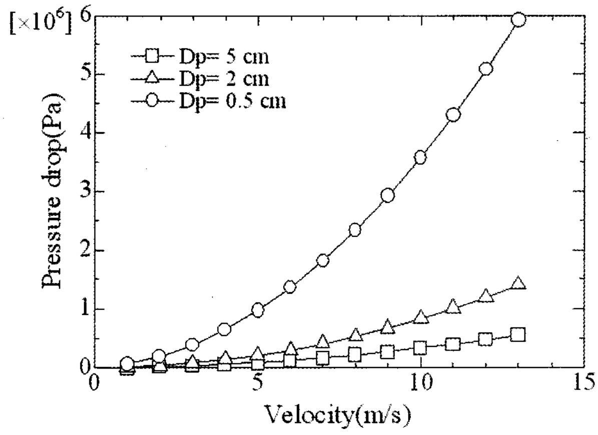


Fig. 4. Pressure Drop Versus Gas Velocity for Al_2O_3 Particle Sizes in 0.5 cm, 2 cm and 5 cm

4. CFD RESULTS

4.1 Numerical Results of the Proposed SO_3 Decomposer

Fig. 5 shows the calculated velocity vectors of the mixture gases in the decomposer. The velocity by the CFX 11 porous model is the superficial velocity. Therefore, the actual velocity in the Al_2O_3 region is about two times faster than the velocity in Fig. 5 ($1/\varepsilon^{2/3}$=2.14, ε= porosity). As shown in Fig. 5, the calculated maximum velocity is about 17 m/s below the lower grid plate and the velocity of the chemical reaction region packed with Al_2O_3 catalysts is maintained uniformly. The high speed of the mixture gases below the lower grid plate enhances the flow mixing before the chemical reaction. The calculated pressure drop of the Al_2O_3 region is 25.3 kPa. The pressure drops at the grid plates are 0.44 kPa (lower plate) and 0.41 kPa (upper

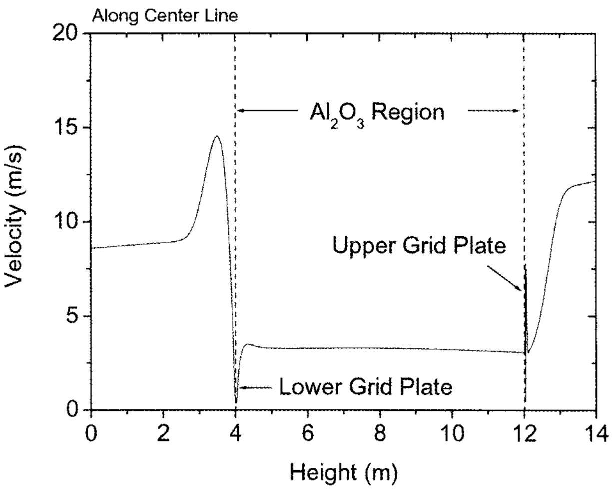


Fig. 6. Velocity Profile in the z-direction (Superficial Velocity in the Porous Region)

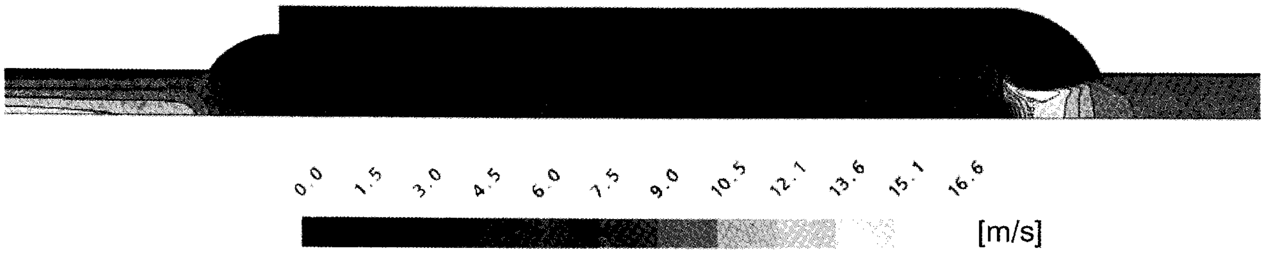


Fig. 5. Velocity Contour in SO_3 Decomposer

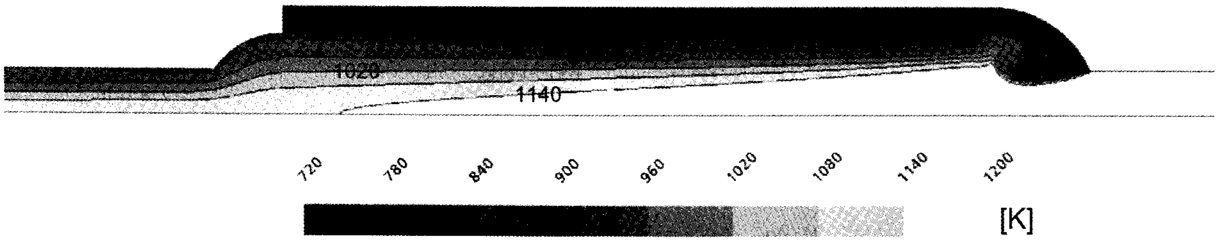


Fig. 7. Temperature Contour of SO_3 Decomposer

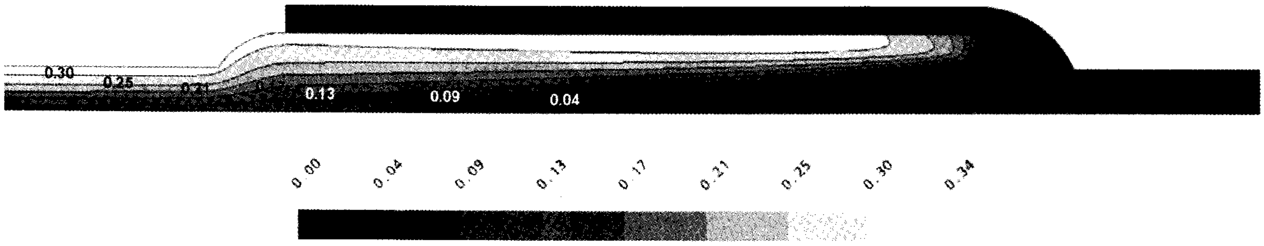


Fig. 8. SO_2 Mass Fraction Contour in the SO_3 Decomposer

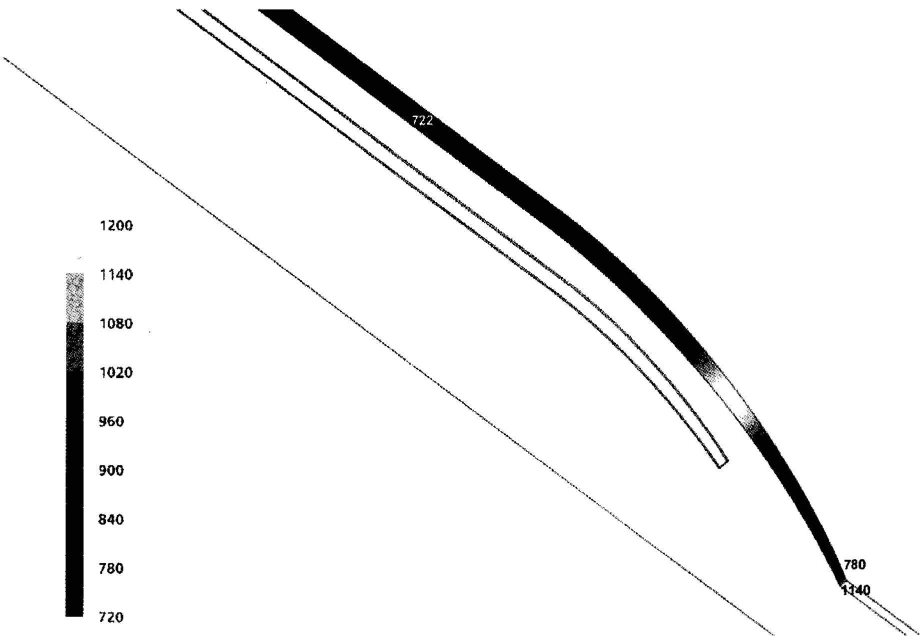


Fig. 9. Temperature Contour of Vessel Wall

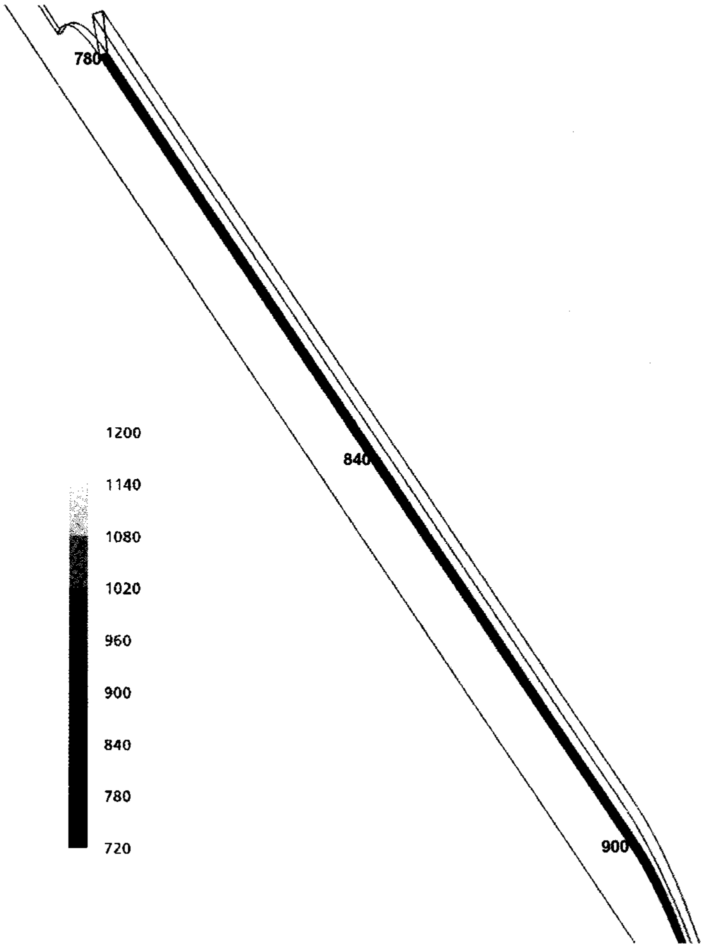


Fig. 10. Temperature Contour of Guide Tube

plate). The residence time of the mixture gases in the Al_2O_3 region is about 1.5 s.

Fig. 6 shows the calculated velocity profile along the z-direction at r= 0 m. In Fig. 6, the velocity of 9 m/s inside the inlet pipe was increased drastically below the lower grid plate due to a decrease of the flow area ($z \approx 4$ m). The flow emerges from the upper grid plate (z= 12 m) and the superficial velocity of 3 m/s in the SO_3 decomposition zone increased again to 12 m/s near the outlet of the decomposer due to a contraction of the cross section.

Fig. 7 shows the calculated temperature contours of the decomposer. It can be seen in Fig. 7 that the maximum temperature in the decomposer is 1193 K (inlet temperature of helium). The calculated average temperature in the Al_2O_3 region is 986 K. Due to the endothermic heat of the chemical reaction, a significant temperature reduction is observed near the guide tube. As shown in Fig. 8, the SO_3 decomposition mainly occurs near the guide tube (particularly the lower part). Such a chemical heat prevents the guide tube from overheating. Fig. 9 and Fig. 10 show the calculated temperature contours of the vessel wall and the guide tube. The temperatures of the vessel wall and the guide tube are sufficiently below 1073 K, which is considered the limiting temperature in this study. These results indicate that RA330 can be used as a structural material for the SO_3 decomposer.

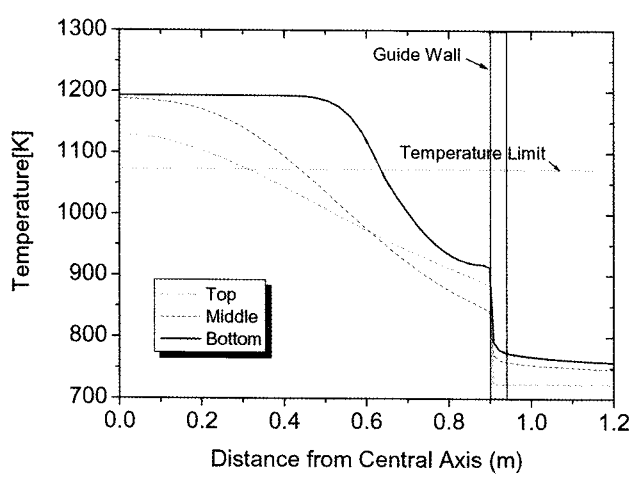
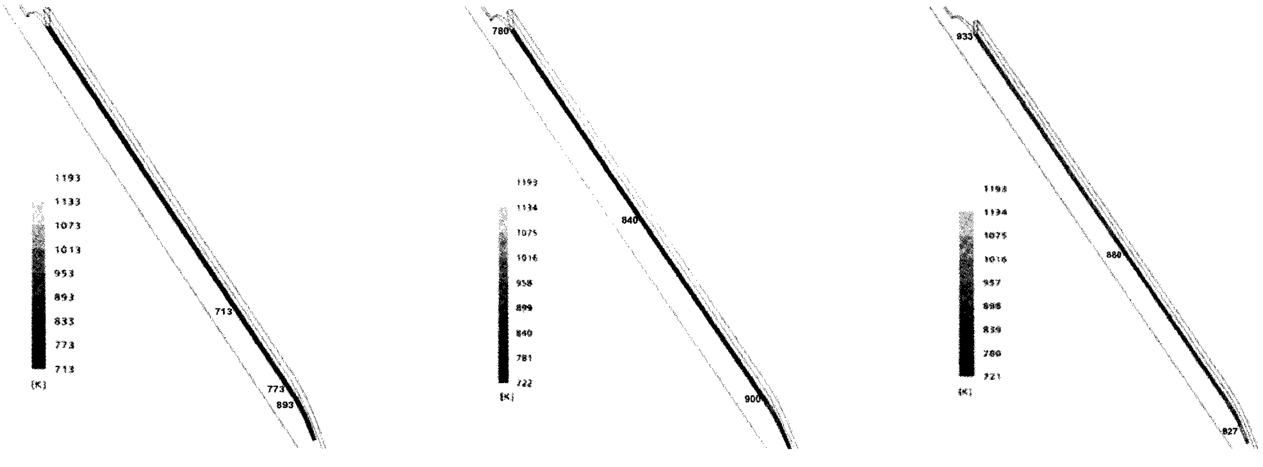


Fig. 11. Temperature Profile in the r-direction

Fig. 11 shows the temperature profile in the r-direction. In the figure, 'Bottom' represents the upside surface of the lower grid plate, and 'Top' represents the bottom surface of the upper grid plate. 'Middle' indicates the middle position of the Al_2O_3 region. It can be clearly observed that the maximum temperature of the guide tube is sufficiently below 1073 K. Most of the Al_2O_3-packed regions maintain temperatures greater than 1123 K, except the near position of the guide tube. This implies that the decomposer modelled in this study satisfies the temperature conditions for a chemical decomposition reaction. The calculated SO_3 mass fraction at the outlet is found to be nearly zero, which means the supplied SO_3 is completely decomposed at the reactor.

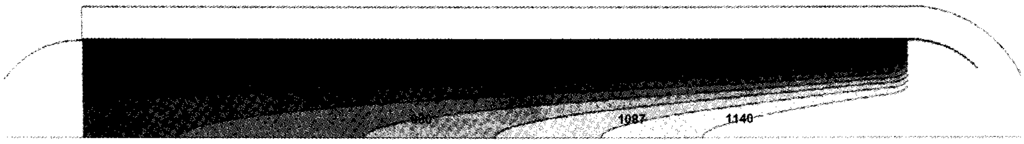
4.2 Effects of the Flow Rate of He

The temperature in the SO_3 decomposer is affected by the flow rate of the helium. Thus, we carried out numerical simulations to investigate the temperature distribution in the SO_3 decomposer for various flow rates of helium. The selected flow rates of helium are 1.0 kg/s, 2.0 kg/s (the reference value) and 3.0 kg/s. Compared with the system

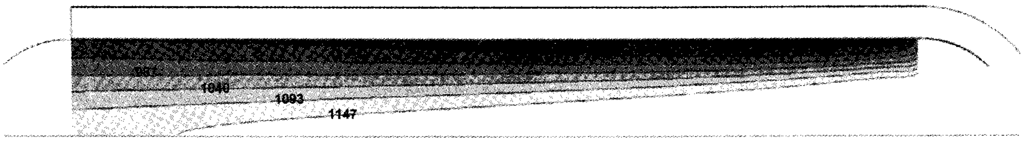


(a) He flow rate = 1.0kg/s (b) He flow rate = 2.0kg/s (reference) (c) He flow rate = 3.0kg/s

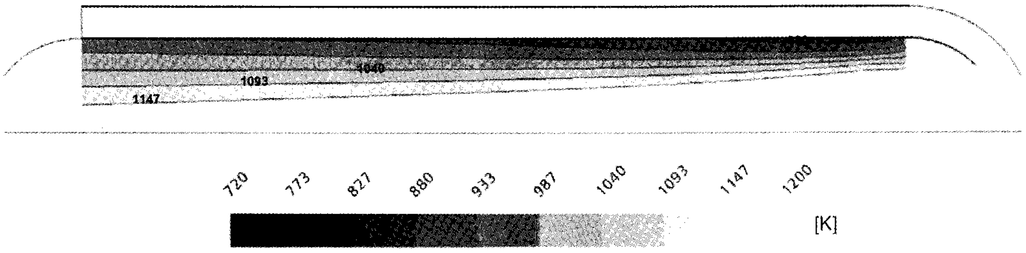
Fig. 12. Guide Tube Temperature Contour with Various He Flow Rates



(a) He flow rate = 1.0kg/s

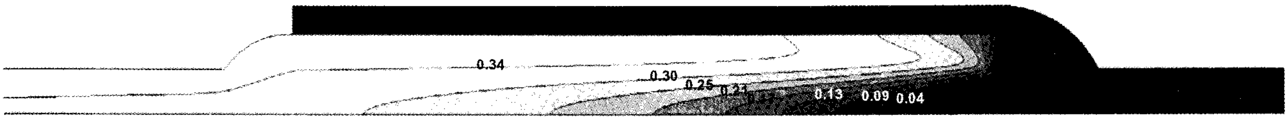


(b) He flow rate = 2.0kg/s s (reference)

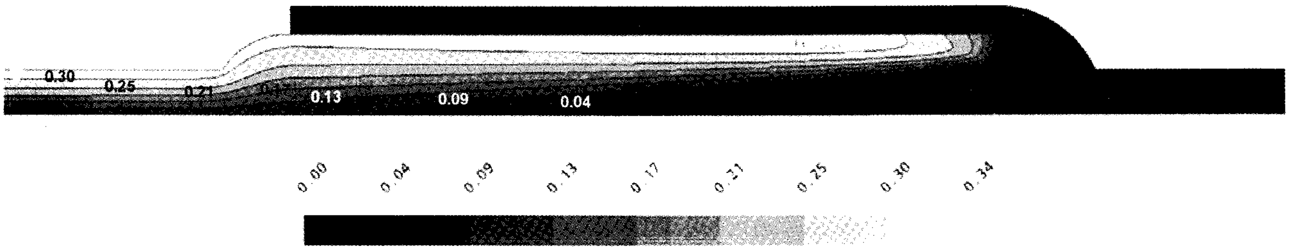


(c) He flow rate = 3.0kg/s

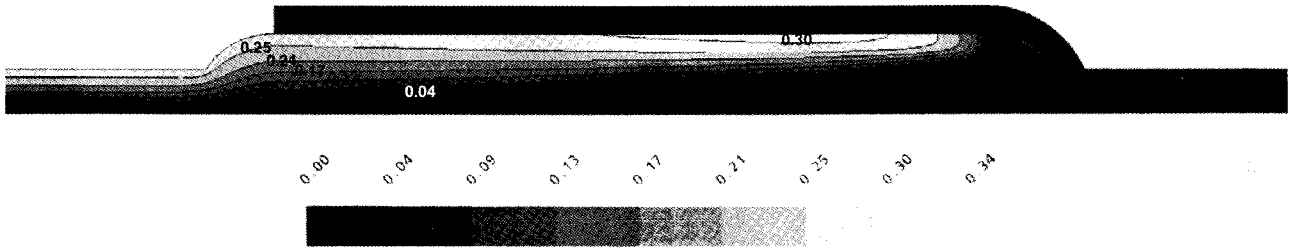
Fig. 13. Al_2O_3 Region Temperature with Various He Flow Rates



(c) He flow rate = 1.0 kg/s



(d) He flow rate = 2.0 kg/s (reference)



(c) He flow rate = 3.0 kg/s

Fig. 14. SO_2 Mass Fraction Contour with Various He Flow Rates

pressure of 7.09 bar, the pressure drop across the decomposer is very small. Therefore, the effect of the helium flow rate on the pressure distribution is not significant.

Figures 12 and 13 show the distributions of temperatures of the guide tube and the Al_2O_3-packed region for various helium flow rates. The maximum temperature of the guide tube is increased as the helium flow rate increases. However, the maximum temperature is still sufficiently below 1073 K. The mean temperature in the Al_2O_3-packed region is also increased as the helium flow rate increases. Figure 14 shows the SO_2 mass fraction contour with the three helium flow rates considered. It shows that the lower helium flow rate has a wider decomposition region of the reactor. The major calculation results for the various helium flow rates are summarized in Table 5. It is shown that the supplied SO_3 is completely decomposed at the reactor for all the considered cases. For the same decomposition capability, a lower helium flow rate is preferred since it reduces the helium separation load.

4.3 Effects of the Reaction Rate Constant

Table 5 shows that a lower helium flow rate is desirable. It should be noted here, however, that the optimistic reaction rate constant (i.e., Eq. (3)) is adopted in Table 5. Additional calculation by using Eq. (4) and the helium flow rate of 2.0 kg/s was performed. Fig. 15 shows the result of the calculation. It shows that the SO_3 decomposition occurs throughout a wider region of the reactor. The calculated average mass fraction of SO_3 at the outlet is 9.0%. This means that the supplied SO_3 is not completely decomposed at the reactor. Therefore, a helium flow rate greater than 2 kg/s is required for complete SO_3 decomposition when Eq. (4) is adopted.

5. CONCLUSIONS

A CFD analysis for a directly heated SO_3 decomposer has been conducted. When the conceptual design conditions of the decomposer presented in this study were used, the maximum temperature of the structural material (RA330) could be maintained sufficiently below the target temperature of 1073 K. The CFD results also show good performance for the proposed SO_3 decomposer. When the Huang and T-Raissi expression for the reaction rate constant is applied, the supplied SO_3 is completely decomposed at the reactor under the design parameters of the present study. The results calculated here are the first data simulating heat transfer characteristics in an SO_3 decomposer made with RA 330. These results should contribute to the optimization of chemical process heat exchanger. An improved heat transfer model should be incorporated in a future study.

Table 5. Calculation Results with the Various He Flow Rates

	He =1.0 kg/s	He =2.0 kg/s	He =3.0 kg/s
Maximum guide tube temperature	857 K	931 K	986 K
Average Al_2O_3 region temperature	845 K	986 K	1046
Average temperature at the outlet	820 K	969 K	1033 K
SO_3 mass fraction at the outlet	5.6E-2 %	1.4E-4 %	1.7E-5 %
SO_2 mass fraction at the outlet	34.9	26.2	21.0
He mass fraction at the outlet	33.3	50.0	60.0
Average sojourn time in the Al_2O_3 region	3.2 sec	1.5 sec	1.0

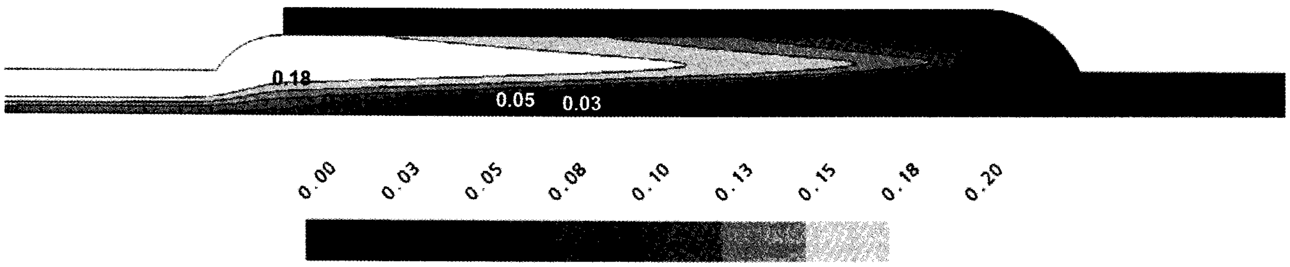


Fig. 15. SO_2 Mass Fraction Contour Based on Eq. (4) and Helium Flow Rate of 2.0 kg/s

Furthermore, thermo-mechanical design and analysis to evaluate the structural integrity of the SO_3 decomposer is intended for future work.

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