Minimum Entropy Generation Rate and Maximum Yield Optimization of Sulfuric Acid Decomposition Process Using NSGA-II

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Abstract: Based on the theory of finite-time thermodynamics (FTT), the effects of three design parameters, that is, inlet temperature, inlet pressure, and inlet total mole flow rate, of a tubular plug-flow sulfuric acid decomposition reactor on the total entropy generation rate (EGR) and SO\textsubscript{2} yield are analyzed firstly. One can find that when the three design parameters are taken as optimization variables, the minimum total EGR and the maximum SO\textsubscript{2} yield of the reference reactor restrict each other, i.e., the two different performance objectives cannot achieve the corresponding extremum values at the same time. Then, the second-generation non-dominated solution sequencing genetic algorithm (NSGA-II) is further used to pursue the minimum total EGR and the maximum SO\textsubscript{2} yield of the reference reactor by taking the three parameters as optimization design variables. After the multi-objective optimization, the reference reactor can be Pareto improved, and the total EGR can be reduced by 9% and the SO\textsubscript{2} yield can be increased by 14% compared to those of the reference reactor. The obtained results could provide certain theoretical guidance for the optimal design of actual sulfuric acid decomposition reactors.

Keywords: finite-time thermodynamics; sulfuric acid decomposition; tubular plug-flow reactor; entropy generation rate; SO\textsubscript{2} yield; multi-objective optimization

1. Introduction

At present, the Hybrid-Sulphur (H-S) thermochemical cycle and the Sulphur-Iodine (S-I) thermochemical cycle are considered to be the two most promising recycling methods in the preparation of hydrogen from water by thermochemical cycles [1], and the schematic diagram of S-I thermochemical cycle is shown in Figure 1. Both the H-S and the S-I cycles contain the sulfuric acid decomposition process. Therefore, it is important and necessary to improve the performance of the sulfuric acid decomposition process.

The S-I thermochemical cycle consists of three main chemical reactions: (1) the endothermic decomposition of hydrogen iodide in gas phase; (2) the spontaneous absorption of sulfur dioxide in liquid phase; (3) the sulfuric acid decomposition reaction. The corresponding reaction equations are given as follows:

\[ \text{H}_2\text{SO}_4 \xrightarrow{800\text{K}} \text{SO}_3 + \text{H}_2\text{O} \]  
\[ \text{SO}_3 \xrightarrow{1000\text{K}} \text{SO}_2 + \frac{1}{2}\text{O}_2 \]
Reaction type (I) is the spontaneous decomposition of H$_2$SO$_4$ into SO$_3$ and H$_2$O at 400–500 °C. Reaction type (II) is the reaction of SO$_3$ over 750 °C to produce SO$_2$ and O$_2$ under the action of a catalyst. In this process, a great deal of heat is consumed, which is also the main energy consumption process in the S-I and H-S thermochemical cycles.

In the aspect of thermodynamic analysis and optimization of sulfuric acid decomposition, Van der Ham et al. [1] assumed that the reaction mixture satisfies the ideal gas equation of state, established the physical model of sulfuric acid decomposition reaction, and analyzed the minimization of entropy generation rate (EGR) of a sulfuric acid decomposition reactor by using the optimal control theory. Johannessen and Kjelstrup [24] studied the EGR minimization of sulfur dioxide oxidation process. The second-generation non-dominated solution sequencing genetic algorithm (NSGA-II) has been widely used in multi-objective optimization of various engineering problems [25–30]. For example, Wang et al. [23] investigated the isotherm chemical reaction $A \Leftrightarrow B \Leftrightarrow C$ and obtained the best concentration configuration of the reaction. Johannessen and Kjelstrup [24] studied the EGR minimization of sulfur dioxide oxidation process. The second-generation non-dominated solution sequencing genetic algorithm (NSGA-II) has been widely used in multi-objective optimization of various engineering problems [25–30].

On the basis of Refs. [1,5,6], this paper will further analyze the effects of reactant inlet temperature, pressure, and total molar flow rate on total EGR and SO$_2$ yield, and perform the multi-objective optimization of the process by using the NSGA-II algorithm by applying FTT.

2. Modeling of the Sulfuric Acid Decomposition Process

A reference reactor used in the performance analysis and optimization as well as the kinetics and thermodynamics models will be introduced in this section.

2.1. Reference Reactor

The model of a tubular plug-flow reactor for sulfuric acid decomposition is shown in Figure 2. It is assumed that the temperature ($T_w$) of the outer wall of tubular plug-flow reactor does not change with time and its distribution is linear along the axial direction of the reactor. The distribution follows $T_w = 975 + 148z/L$ (K). The reaction mixture in the reactor is regarded as an ideal gas and only flows along the axial direction of the reactor. The radial concentration gradient and temperature gradient of
the reaction mixture in the reactor are ignored without both radial diffusion and back-mixing. The total molar flow rate and velocity of the reaction mixture at the cross-section of the reactor are as follows:

\[ F_{\text{tot}} = \sum_i F_i \quad (1) \]

\[ v = \frac{F_{\text{tot}} R T}{A_c \rho \times 10^5} \quad (2) \]

where \( F_i \) is the molar flow rate of reaction component \( i \), i.e., \( \text{H}_2\text{SO}_4, \text{SO}_3, \text{H}_2\text{O}, \text{SO}_2 \) and \( \text{O}_2 \); \( A_c \) is the radial cross section area of the reactor, and \( R \) is the universal gas constant.

**Figure 2.** Schematic of tubular plug-flow reactor.

The data of catalyst selection, reactor structure, and thermodynamic parameters of the reaction mixture are determined according to Ref. [1], as listed in Table 1.

| Parameter | Symbol | Value |
|-----------|--------|-------|
| Overall heat transfer coefficient/\((\text{K} \cdot \text{m}^2/\text{s})\) | \( U \) | 170 |
| Dynamic viscosity/\((\text{kg}/(\text{m} \cdot \text{s}))\) | \( \eta \) | \( 4 \times 10^{-5} \) |
| Catalyst bed porosity | \( \epsilon \) | 0.45 |
| Catalyst pellet density/\((\text{kg}/\text{m}^3)\) | \( \rho_p \) | 4200 |
| Catalyst pellet diameter/m | \( D_p \) | 0.003 |
| Inner diameter of reactor/m | \( D \) | 0.030 |
| Length of reactor/m | \( L \) | 3.090 |
| Inlet temperature/K | \( T_{\text{in}} \) | 800 |
| Inlet pressure/bar | \( P_{\text{in}} \) | 7.1 |
| Inlet total molar flow rate | \( F_{\text{tot,in}} \) | 0.034 |
| Molar fraction of inlet \( \text{H}_2\text{SO}_4 \) | \( F_{\text{H}_2\text{SO}_4,\text{in}} \) | 0.094 |
| Molar fraction of inlet \( \text{SO}_3 \) | \( F_{\text{SO}_3,\text{in}} \) | 0.425 |
| Molar fraction of inlet \( \text{H}_2\text{O} \) | \( F_{\text{H}_2\text{O},\text{in}} \) | 0.481 |
| Molar fraction of inlet \( \text{SO}_2 \) | \( F_{\text{SO}_2,\text{in}} \) | 0.000 |
| Molar fraction of inlet \( \text{O}_2 \) | \( F_{\text{O}_2,\text{in}} \) | 0.000 |

### 2.2. Models of Kinetics and Thermodynamics

The fluid flow, heat transfer, and chemical reaction of the reaction mixture in a tubular plug-flow reactor follow momentum, energy, and mass conservation equations, respectively, which are given by:

\[ \frac{dP}{dz} = -\frac{150 \eta (1 - \epsilon)^2}{D_p^2 \epsilon^3 \rho_p v} + \frac{1.75 \rho_p v}{D_p \epsilon^3} \quad \text{v} \quad (3) \]
\[
\frac{dT}{dz} = \frac{\pi DJ_q + A_c \rho_p \sum_j [r_{m,j}(-\Delta r_H)]}{\sum_j (F_j C_p,j)} \tag{4}
\]

\[
\frac{dF_{H_2SO_4}}{dz} = -A_c \rho_p r_{m,1} \tag{5}
\]

\[
\frac{dF_{H_2O}}{dz} = A_c \rho_p r_{m,1} \tag{6}
\]

\[
\frac{dF_{SO_3}}{dz} = A_c \rho_p (r_{m,1} - r_{m,2}) \tag{7}
\]

\[
\frac{dF_{SO_2}}{dz} = A_c \rho_p r_{m,2} \tag{8}
\]

\[
\frac{dF_{O_2}}{dz} = \frac{1}{2} A_c \rho_p r_{m,2} \tag{9}
\]

where $\rho_{in}$ and $v_{in}$ are the density and flow velocity of the reaction mixture on the entrance section, respectively; subscript $j = 1, 2$ represents the reaction types (I) and (II); $r_{m,j}$ is the reaction rate of mass per unit catalyst, and they are $r_{m,1} = r_1 / \rho_p$ and $r_{m,2} = r_2$; $C_p,j$ and $\Delta r_H$ are the component molar constant-pressure heat capacity and the reaction enthalpy of the reaction type $j$, and their expressions are given in the Appendix A.

The heat transfer from the heat source outside the tube to the reaction mixture inside the tube follows Newtonian heat transfer law:

\[
J_q = U (T_w - T) \tag{10}
\]

For different reaction conditions and mechanisms, the driving force in the kinetic equation could be written as different mathematical forms, and the corresponding coefficients in the kinetic equation should be determined by experiments and also be different for different choices of the driving force. According to Ref. [1], the condition that the chemical reaction occurred at the vicinity of the equilibrium is assumed to be satisfied, and all components are assumed to have stoichiometric reaction order, so the chemical reaction rates of reaction types (I) and (II) are as follows:

\[
r_1 = k_1 \left( P_{H_2SO_4} - \frac{P_{H_2O} P_{SO_3}}{K_1} \right) \tag{11}
\]

\[
r_2 = k_2 \left( P_{SO_3} - \frac{P_{SO_2} \sqrt{P_{O_2}}}{K_2} \right) \tag{12}
\]

where $k_1$ and $k_2$ are the reaction rate constants of reaction types (I) and (II), according to Ref. [1], $k_1 = 10^{-2} \text{mol} SO_3 / (\text{Pa·m}^3·\text{s})$, $k_2 = 4.7 \times 10^{-3} \exp\left(\frac{-\Delta r G_{T,j}^\circ}{R T}\right) \text{mol} SO_3 / (\text{Pa·kg·s})$; $P$ represents the partial pressure of the corresponding component; $K_j = \exp\left(\frac{\Delta r G_{T,j}^\circ}{R T}\right)$ is the equilibrium constant of the chemical reaction type $j$; $\Delta r G_{T,j}^\circ$ is the standard Gibbs free enthalpy of the reaction type $j$, and the expression is given in the Appendix A. The driving force in the kinetic Equation (12) is written as $r_2 = k_2 \left( P_{SO_3} - P_{SO_2} \sqrt{P_{O_2}} / K_2 \right)$, and effects of the different forms of the driving force on the optimization results will be considered in another paper in the future.

The SO$_2$ yield of the tubular plug-flow reactor is as follows:

\[
\Delta F_{SO_2} = F_{SO_2,\text{out}} - F_{SO_2,\text{in}} \tag{13}
\]
The local EGR of the tubular plug-flow reactor is as follows:

\[ \sigma_{\text{tot}} = \sigma_{\text{ht}} + \sigma_{\text{f}} + \sigma_{\text{cr}} = \pi DJ q \left( \frac{1}{T} - \frac{1}{T_w} \right) + A_c v \left[ -\frac{1}{T} \left( \frac{dp}{dz} \right) \right] + A_c \rho_b \sum_j r_{rj} \left( \frac{\Delta r G_j}{T} \right) \]  

(14)

where subscripts ht, f, and cr represent the local EGRs of heat transfer, fluid flow, and chemical reaction, respectively.

The total EGR is obtained by integrating the local EGR, i.e.,

\[ \Sigma_{\text{tot}} = \int_0^L \sigma_{\text{ht}} dz \]  

(15)

3. Parameter Analyses of Sulfuric Acid Decomposition Reactor

By changing the inlet parameters of the reference reactor, including the inlet temperature \( T_{\text{in}} \), pressure \( P_{\text{in}} \), and the total molar flow rate \( F_{\text{tot, in}} \), the total EGR and the \( \text{SO}_2 \) yield of the reference reactor are analyzed, and the influences of the initial inlet conditions on the two performance objectives can be obtained. The variation ranges of the initial inlet parameters are: \( 750 \text{ K} \leq T_{\text{in}} \leq 900 \text{ K}, 4 \text{ MPa} \leq P_{\text{in}} \leq 9.5 \text{ MPa}, \) and \( 0.0027 \text{ mol/s} \leq F_{\text{tot, in}} \leq 0.1 \text{ mol/s}. \)

Figure 3 shows the effects of the temperature \( T_{\text{in}} \) of the reaction mixture on the total EGR and the \( \text{SO}_2 \) yield. It can be seen that the total EGR decreases nonlinearly with the increase of the temperature \( T_{\text{in}} \), and the decreasing trend is fast firstly and then slow; when the temperature \( T_{\text{in}} \) increases from \( 750 \text{ °C} \) to \( 900 \text{ °C} \), the total EGR decreases from \( 0.331 \text{ W/K} \) to \( 0.189 \text{ W/K} \), i.e., decreases by 43%. The main reason is that with the temperature \( T_{\text{in}} \) of the reaction mixture increases, the heat transfer temperature difference between the reaction mixture and the external heat source decreases, which reduces the local EGR of heat transfer and the total EGR. The \( \text{SO}_2 \) yield increases very slowly with the increase of the temperature \( T_{\text{in}} \), and when the temperature \( T_{\text{in}} \) increases from \( 750 \text{ °C} \) to \( 900 \text{ °C} \), the \( \text{SO}_2 \) yield increases by only 0.4%. It can be seen that the total EGR can be reduced by increasing the temperature \( T_{\text{in}} \) of the reaction mixture, i.e., the irreversibility of the sulfuric acid decomposition process could be reduced by increasing the \( T_{\text{in}} \) of the reaction mixture. However, it is not significant to increase the \( \text{SO}_2 \) yield by increasing the temperature \( T_{\text{in}} \) of the reaction mixture.

Figure 4 shows the effects of the pressure \( P_{\text{in}} \) of the reaction mixture on the total EGR and the \( \text{SO}_2 \) yield. It can be seen that the total EGR decreases concave and parabolic-like with the increase of the pressure \( P_{\text{in}} \), and the minimum value is \( 0.224 \text{ W/K} \) when the pressure \( P_{\text{in}} \) is about \( 0.85 \text{ MPa}. \) The \( \text{SO}_2 \) yield decreases linearly with the increase of the pressure \( P_{\text{in}} \). When the pressure \( P_{\text{in}} \) increases from \( 0.4 \text{ MPa} \) to \( 1 \text{ MPa}, \) the \( \text{SO}_2 \) yield decreases from \( 0.0118 \text{ mol/s} \) to \( 0.0105 \text{ mol/s}, \) i.e., decreases by \( 11.02\%. \)

Figure 5 shows the effects of the molar flow rate \( F_{\text{tot, in}} \) of the reaction mixture on the total EGR and the \( \text{SO}_2 \) yield. It can be seen that the total EGR and the \( \text{SO}_2 \) yield increase with the increase of the molar flow rate \( F_{\text{tot, in}} \), and the minimum total EGR and the maximum \( \text{SO}_2 \) yield are mutually restricted. When the molar flow rate \( F_{\text{tot, in}} \) increases from \( 0.027 \text{ mol/s} \) to \( 0.10 \text{ mol/s}, \) the total EGR and the \( \text{SO}_2 \) yield increases by 4.8 times and 1.8 times, respectively.
Entropy objectives, respectively, there is no optimal solution to achieve the extremum values of the total objectives, respectively, there is no optimal solution to achieve the extremum values of the total EGR and SO₂ yield at the same time. Therefore, how to select the appropriate initial inlet conditions is a critical issue.

Temperature increasing the temperature restricted. When the molar flow rate \( F \) increasing, the SO₂ yield increases slowly and the SO₂ yield. It can be seen that the total EGR and the SO₂ yield increase with the increase of the temperature. However, the local EGR of heat transfer and the total EGR reduce the local EGR of heat transfer and the total EGR. The SO₂ yield increases very slowly and the SO₂ yield. It can be seen that the total EGR and the SO₂ yield increase with the increase of the molar flow rate \( F \) with the increase of the temperature.

The total EGR is obtained by integrating the local EGR, i.e.,

\[
\Sigma_{\text{tot}} = \Sigma_{\text{tot,in}} - \int_{\text{in}}^{\text{out}} \Delta F_{\text{SO}_{2}} \, df \]

The SO₂ yield decreases linearly with the increase of the pressure when the molar flow rate \( F \) is 0.22 mol/s.

Figure 3. The effects of \( T_{\text{in}} \) on the total EGR and the SO₂ yield.

Figure 4. Effects of \( P_{\text{in}} \) on the total EGR and the SO₂ yield.

Figure 5. Effects of \( F_{\text{tot,in}} \) on the total EGR and the SO₂ yield.
4. Multi-Objective Optimization and Result Analyses

From the analyses in Section 3, when the three inlet parameters are chosen as optimization variables, and the minimum total EGR and the maximum SO$_2$ yield are taken as optimization objectives, respectively, there is no optimal solution to achieve the extremum values of the total EGR and SO$_2$ yield at the same time. Therefore, how to select the appropriate initial inlet conditions to achieve the relative optimal total EGR and SO$_2$ yield is very important. The NSGA-II algorithm is one of the excellent algorithms to solve multi-objective optimization problems, and can give a series of non-inferior solutions (solutions that cannot be optimized for arbitrary objectives without making other objectives worse) of multi-objective problems. The corresponding improvement process is called Pareto improvement, the corresponding set of non-inferior solutions is called the Pareto-optimal solution set, and the corresponding objective function solution is called the Pareto-optimal front.

Figure 6 shows the flow chart of the NSGA-II algorithm. In this section, all of the $T_{in}$, $P_{in}$ and $F_{tot,in}$ are taken as the optimization variables to minimize the total EGR and maximize the SO$_2$ yield. The optimization intervals of the variables are consistent with the previous single-variable analysis.

![Figure 6. Basic flow chart of NSGA-II algorithm.](image)

Figure 7 is Pareto optimal frontier of a reference reactor based on the objective of minimizing total EGR and maximizing SO$_2$ yield, where points A and B represent the solution of the maximum SO$_2$ yield and the minimum total EGR, respectively. At point A, the weighting coefficient of SO$_2$ yield in multi-objective optimization is 1, and the weighting coefficient of total EGR is 0, it is also the solution of maximizing the SO$_2$ yield. Similarly, point B is the solution of minimizing the total...
EGR. From Figure 7, it can be seen that the minimum total EGR and the maximum SO$_2$ yield are mutually constrained, and they cannot achieve the extremum values at the same time. Only the relative optimal solutions of the two objectives under different weighting coefficients can be found, that is, the non-inferior solution. One can select the appropriate optimal solution from the Pareto-optimal solution set according to different needs to meet the different demands of decision-making purposes. Commonly used multi-objective decision-making methods are Shannon, LINMAP, and TOPSIS, but in the actual decision-making process, decision-making is usually based on actual engineering experience and personal preferences of decision-makers, there is no universal way to make decisions.

![Figure 7. Pareto optimal frontiers of reference reactor.](image-url)

In this paper, in order to facilitate the comparison with the reference reactor, a suitable multi-objective decision point (point C) is selected for comparison. Because the solution of the minimum specific EGRs is the solution of the total EGR and the yield under a certain ratio, the decision point of the minimum specific EGR must be on the Pareto-optimal front, which can be used as an important basis to verify the accuracy of the NSGA-II algorithm results.

Figure 8 is the bar chart of the target value of the reference reactor under optimization and non-optimization. Table 2 lists the results of each optimization target condition. It can be seen that compared with the reference reactor, the SO$_2$ yield of the reactor with the maximum yield increases by 118%, but the total EGR increases by 222%; the total EGR of the minimum EGR reactor decreases by 38%, and the corresponding SO$_2$ yield also decreased by 22%; the total EGR and the SO$_2$ yield of the reactor with the minimum specific EGR decrease by 38% and 16%, respectively. From Figure 7, it can be easily concluded that the reference reactor is not located at the Pareto optimal frontier, so the reference reactor can be optimized by Pareto improvement. A non-inferior solution (point C) is obtained by the multi-objective optimization method, in which the total EGR of the reactor decreases by 9% and the SO$_2$ yield of the reactor increases by 14% compared to the reference reactor. Also, from Figure 7, it can be seen that a series of non-inferior solutions located at the upper left of the decision point (point E) of the reactor have good properties of reducing the total EGR and increasing the SO$_2$ yield.

Figures 9–11 show the distribution of the $T_{\text{in}}$, $P_{\text{in}}$, and $F_{\text{tot, in}}$ in Pareto-optimal fronts, and the black and white dots in the figures represent the total EGR and the SO$_2$ yield, respectively, which exist in pairs. As seen from Figures 9 and 10, the $T_{\text{in}}$ and $P_{\text{in}}$ of the reaction mixture in Pareto-optimal fronts are mainly distributed in high-temperature (892–896 K) and high-pressure (9.0–9.2 bar) area, so increasing the $T_{\text{in}}$ and $P_{\text{in}}$ of the reaction mixture is an important means for Pareto improvement. Figure 11 shows that the $F_{\text{tot, in}}$ of the reaction mixture in Pareto-optimal fronts distributes uniformly in
its optimal range, which indicates that adjusting the $F_{\text{tota}l_{\text{in}}}$ of the reaction mixture in Pareto-optimal fronts is an important means to reconcile the contradiction between the minimum total EGR and the maximum SO$_2$ yield.

![Figure 8. Comparison of total EGR and the yield of optimized objectives.](image)

**Table 2. Calculation results of each target.**

| Reactor Inlet Parameters | EGR | SO$_2$ Yield |
|--------------------------|-----|--------------|
|                         | $T_{\text{in}}$ (K) | $P_{\text{in}}$ ($1 \times 10^5$ Pa) | $F_{\text{tot, in}}$ (mol s$^{-1}$) | $\Sigma_{\text{tot}} / W \cdot K^{-1}$ | $\Delta F_{\text{SO}_2}$ / mol s$^{-1}$ |
| Reference reactor       | 800 | 7.10         | 0.034 | 0.2316 | —— | 0.01100 | —— |
| Maximum yield           | 896 | 8.97         | 0.010 | 0.7450 | ↑ 222% | 0.02395 | ↑ 118% |
| Minimum EGR             | 893 | 8.69         | 0.027 | 0.1388 | ↓ 40% | 0.00862 | ↓ 22% |
| Specific EGR            | 900 | 8.62         | 0.030 | 0.1446 | ↓ 38% | 0.00930 | ↓ 16% |
| Multi-objective         | 894 | 9.18         | 0.041 | 0.2111 | ↓ 9%  | 0.01256 | ↑ 14% |

![Figure 9. Distribution of inlet temperature in Pareto-optimal fronts.](image)
5. Conclusions

In this paper, the effects of reaction mixture inlet parameters on the total EGR and SO\textsubscript{2} yield of the tubular plug-flow sulfuric acid decomposition reactor are analyzed, and the multi-objective optimization for the two performance objectives are carried out by using FTT. The results show that:

1. When the $T_{\text{in}}$ increases from 750 $^\circ$C to 900 $^\circ$C, the total EGR decreases by 43% and the SO\textsubscript{2} yield increases by 0.4%. When the $P_{\text{in}}$ increases from 0.4 MPa to 1 MPa, the curve of the total EGR versus the $P_{\text{in}}$ is a concave parabolic-like, the minimum value of the total EGR is 0.224 W/K when the $P_{\text{in}}$ equals to 0.85 MPa, and the corresponding SO\textsubscript{2} yield decreases by 11%. When the $F_{\text{tot,in}}$ increases from 0.027 mol/s to 0.10 mol/s, the total EGR and the SO\textsubscript{2} yield increase by 4.8 times and 1.8 times, respectively.

2. The reference reactor can be Pareto improvement, one of the non-inferior solutions can reduce the total EGR by 9% and increase the SO\textsubscript{2} yield by 14% compared to those of the reference reactor.

3. FTT is a powerful theoretical tool for the performance analysis and optimization of tubular plug-flow sulfuric acid decomposition reactor. The NSGA-II algorithm is an effective mathematical tool for the multi-objective optimization of tubular plug-flow sulfuric acid decomposition reactor. The Pareto-optimal fronts obtained in this paper has a certain theoretical guiding significance for the optimal designs of the actual sulfuric acid decomposition reactors.
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Nomenclature

- $A$: area $m^2$
- $C_p$: molar constant-pressure heat capacity, $kJ/(mol \cdot K)$
- $D_p$: catalyst pellet diameter, $m$
- $F$: molar flow rate, $mol/s$
- $J_q$: heat flux density, $W/m^2$
- $K$: equilibrium constant
- $L$: length, $m$
- $P$: pressure, bar
- $R$: universal gas constant, $J/(mol \cdot K)$
- $r$: reaction rate, $mol/(kg \cdot s)$
- $T$: temperature, $K$
- $v$: flow velocity, $m/s$
- $z$: length, $m$

Greek letters

- $\varepsilon$: catalyst bed porosity
- $\eta$: dynamic viscosity, $kg/(m \cdot s)$
- $\kappa$: rate constant of chemical reaction
- $\nu_i$: the stoichiometric number of reaction component $i$
- $\rho$: density, $kg \cdot m^{-3}$
- $\sigma$: local EGR, $J/K$
- $\Sigma$: total
- $\Delta G$: Gibbs free energy change of chemical reaction, $J$
- $\Delta H$: enthalpy change of chemical reaction, $J$

Subscripts

- $c$: cross section of tubular plug-flow reactor
- $cr$: chemical reaction
- $f$: fluid flow
- $ht$: heat transfer
- $i$: component
- $in$: inlet
- $j$: reaction types (I) and (II)
- $out$: outlet
- $p$: catalyst pellet
- $q$: quantity of heat
- $r$: reaction
- $tot$: total
- $w$: wall of tubular plug-flow reactor

Abbreviations

- EGR: entropy generation rate
- FTT: finite-time thermodynamics
- H-S: hybrid-Sulphur thermochemical cycle
- NSGA-II: second generation non-dominated solution sequencing genetic algorithm
- S-I: sulphur-Iodine thermochemical cycle
Appendix A

According to the Refs. [31], the component molar constant-pressure heat capacity, molar enthalpy and molar Gibbs energy can be calculated by the following formula:

\[
C_{p,i} = A_i + B_i \frac{T}{1000} + C_i \left( \frac{T}{1000} \right)^2 + D_i \left( \frac{T}{1000} \right)^3 + E_i \left( \frac{1000}{T} \right)^2 \tag{A1}
\]

\[
H_{T,i} = A_i + \frac{B_i}{2} \left( \frac{T}{1000} \right)^2 + C_i \left( \frac{T}{1000} \right)^3 + D_i \left( \frac{1}{3} \right) \left( \frac{T}{1000} \right)^3 - \frac{E_i}{4} \left( \frac{1000}{T} \right)^2 + F_i \tag{A2}
\]

\[
S_{T,i} = A_i \ln \left( \frac{T}{1000} \right) + B_i \left( \frac{T}{1000} \right) + C_i \left( \frac{T}{1000} \right)^2 + D_i \left( \frac{1}{3} \right) \left( \frac{T}{1000} \right)^3 - \frac{E_i}{2} \left( \frac{1000}{T} \right)^2 + G_i \tag{A3}
\]

\[
\Delta_r H_r = \sum_i v_i H_{T,i}
\]

\[
\Delta_r S_r = \sum_i v_i S_{T,i}
\]

\[
\Delta_r G_r = \Delta_r H_r - T \Delta_r S_r\tag{A6}
\]

where \(A_i\sim G_i\) are the thermodynamic coefficients of the formula, which are listed in Table A1; \(v_i\) is the stoichiometric number of reaction component \(i\).

| Gas         | \(M_W/\text{kg mol}^{-1}\) | \(A_i\) | \(B_i\) | \(C_i\) | \(D_i\) | \(E_i\) | \(F_i\) | \(G_i\) | \(T_{\text{min}}/K\) | \(T_{\text{max}}/K\) |
|-------------|-----------------------------|---------|---------|---------|---------|---------|---------|---------|-----------------|-----------------|
| \(\text{SO}_2\) | \(6.40 \times 10^{-2}\) | 21.430  | 74.351  | −57.752 | 16.355  | 0.087   | −305.769| 254.887 | 298             | 1200            |
| \(\text{O}_2\)  | \(3.20 \times 10^{-2}\)  | 29.659  | 6.137   | −1.187  | 0.096   | −0.220  | −9.861  | 237.948 | 298             | 6000            |
| \(\text{SO}_3\) | \(8.01 \times 10^{-2}\)  | 24.025  | 119.461 | −94.387 | 26.926  | −0.118  | −407.853| 253.51  | 298             | 1200            |
| \(\text{H}_2\text{O}\) | \(1.80 \times 10^{-2}\)  | 30.092  | 6.833   | 6.793   | −2.534  | 0.082   | −250.881| 223.397 | 500             | 1700            |
| \(\text{H}_2\text{SO}_4\) | \(9.81 \times 10^{-2}\)  | 47.289  | 190.331 | −148.123| 43.868  | −0.740  | −758.953| 301.296 | 298             | 1200            |

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