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# Maximum production rate optimization for sulphuric acid decomposition process in tubular plug-flow reactor

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ABSTRACT

A sulphuric acid decomposition process in a tubular plug-flow reactor with fixed inlet flow rate and completely controllable exterior wall temperature profile and reactants pressure profile is studied in this paper by using finite-time thermodynamics. The maximum production rate of the aimed product $SO_2$ and the optimal exterior wall temperature profile and reactants pressure profile are obtained by using nonlinear programming method. Then the optimal reactor with the maximum production rate is compared with the reference reactor with linear exterior wall temperature profile and the optimal reactor with minimum entropy generation rate. The result shows that the production rate of $SO_2$ of optimal reactor with the maximum production rate has an increase of more than 7%. The optimization of temperature profile has little influence on the production rate while the optimization of reactants pressure profile can significantly increase the production rate. The results obtained may provide some guidelines for the design of real tubular reactors.



## 1. Introduction

Hydrogen energy has advantages such as higher combustion value and environment friendly. Hydrogen, as the secondary energy, is manufactured from processes such as steam methane reforming [1] and water electrolysis [2]. Thermochemical cycles are burgeoning method to produce hydrogen cleanly and effectively. Now there are two thermochemical cycles which are seriously considered for the hydrogen production. One is the Sulfur–Iodine cycle [3] shown in Fig. 1. The Sulfur–Iodine cycle consists of three processes: the decomposition process of gaseous hydrogen iodide, the spontaneously absorption process of gaseous sulfur dioxide in solution and the decomposition process of gaseous sulphuric acid.

The General Atomics designed a Sulfur–Iodine cycle process and its thermal efficiency is reached to 47% [4,5]. Knoche et al. [6] raised the thermal efficiency of Sulfur–Iodine cycle to 53.2% by improving the thermal efficiency of sulphuric acid system from 63.5% to 70.2%. The Japan Atomic Energy Research Institute achieved the continuously production of hydrogen by Sulfur–Iodine cycle [7], and raised the thermal efficiency of Sulfur–Iodine cycle to 56.8% [8]. Zhang et al. [9] modeled the open-loop Sulfur–Iodine thermochemical cycle and the thermal efficiency was up to 63.1%. Chen et al. [10] raised the thermal efficiency of Sulfur–Iodine cycle to 68.46% by optimizing the concentration of hydrogen iodide.

The other promising thermochemical hydrogen production process is the Hybird-Sulphur cycle [11]. As the same with the Sulfur–Iodine cycle, Hybird-Sulphur cycle also contains a sulphuric acid decomposition process. So the optimization of the sulphuric acid decomposition process is an effective way to improve the thermal efficiency of both Sulfur–Iodine cycle and Hybird-Sulphur cycle. The investigation of sulphuric acid decomposition process makes great sense to future thermochemical hydrogen production. Marshall [12] investigated the temperature of heat source that drives the sulphuric acid decomposition process. Ginosar et al. [13] and Banerjee et al. [14] studied the influence of catalysts on sulphuric acid decomposition process. Porisini [15] discovered the corrosion resistant catalyst for sulphuric acid decomposition process.

According to the theory of finite-time thermodynamics [16–31], many scholars derived the optimal paths for chemical reactions and heat transfer processes which can provide theoretical guidelines for

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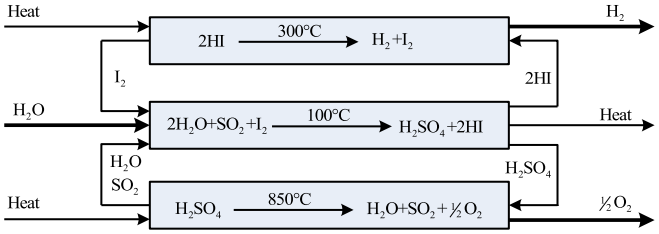


**Fig. 1.** Schematic of the Sulfur–Iodine process.

the investigation of sulphuric acid decomposition process. Mansson et al. [32] obtained the maximum production of ammonia in synthesis ammonia process with temperature as control variable. Schön and Andresen [33] derived the optimal path of chemical reaction $nA \Leftrightarrow mB$ for maximum yield of product $B$ with temperature and volume as control variables. Bak et al. [34], Wang et al. [35] and Chen et al. [36] obtained the optimal path of consecutive chemical reactions $A \rightleftharpoons B \rightleftharpoons C$ [34,35] and $xA \rightleftharpoons yB \rightleftharpoons zC$ [36] with different optimization objectives and control variables. Tsirlin et al. [37,38] derived the minimum entropy generation of chemical reaction $\sum_{i=1}^{j} \alpha_i R_i \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sum_{i=j+1}^{m} \alpha_i R_i$. Xia et al. [39–41] studied the multi-reservoir chemical engines for maximum power output with infinite or finite potential reservoir for different mass transfer laws. Hooyberghs et al. [42] obtained the efficiency bound at maximum power of a chemical engine. Ondrechen et al. [43,44] and Chen et al. [45] obtained the power characteristics of chemically driven engines based on first and second order reaction kinetic theory. Badescu and Andersen [46] and Zhang et al. [47] presented the applications of probabilistic method to the study on performance of chemically driven engines. Nummedal [48], Kjelstrup et al. [49], Nummedal et al. [50] and Wilhelmsen et al. [51] investigated the optimal configurations of various reactions in tubular reactors. Johannessen [52] and Johannessen and Kjelstrup [53] obtained the minimum entropy production rate of fixed production of sulfur trioxide in the oxidation process of sulfur dioxide with temperature as control variable. van der Ham [54] studied the sulphuric acid decomposition process and obtained the optimal reactor length and temperature profile for minimum entropy production rate with temperature of external heat source as control variable. van der Ham et al. [55] derived the optimal temperature profile of hydrogen production process in Sulphur–Iodine cycle for minimum entropy production with temperature as control variable. Based on Ref. [54], this paper will investigate the sulphuric acid decomposition process and derive the optimal exterior wall temperature profile and reactants pressure profile for maximum production rate of aimed product sulfur dioxide and compare the results with the optimization of minimum entropy generation rate in Ref. [54].

## 2. Description of system and reaction model

### 2.1. Description of the reference reactor

The sulphuric acid decomposition process $H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2}O_2$ is proceeded in two steps in tubular plug-flow reactor:

$$H_2SO_4 \rightarrow SO_3 + H_2O \quad \text{(R1)}$$

$$SO_3 \rightarrow SO_2 + \frac{1}{2}O_2 \quad \text{(R2)}$$

Reaction (R1) is the spontaneously decomposition of gaseous sulphuric acid into sulfur trioxide and water at temperatures range from 400 to 500 °C. Reaction (R2) is the catalyzed dissociation of sulfur trioxide into sulfur dioxide and oxygen at temperatures above 750 °C. Fig. 2 shows the model of tubular plug-flow reactor. All the reactants flow from the reactor inlet to the outlet. The external heat source is counter-flow one.

Several assumptions are made to simplify the reaction model. Firstly, the reactants are all near ideal gas. Secondly, no radial gradients exist in the reactor, the transport of substances is along the reactor length and only caused by convection. Lastly, the chemical reactions are only kinetically limited. Table 1 lists the main operating parameters of the reference reactor from Ref. [54].

The sulphuric acid decomposition process $H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2}O_2$ is endothermic, and according to the reaction equilibrium movement principle, the extent of the decomposition grows with the raise of the temperature. The molecules number of the process is increased and thus the lower pressure also can raise the extent of the decomposition.

### 2.2. The momentum, energy and mole balance equations

The momentum balance is given by Ergun equation, the semi-empirical formula describing the pressure change along the reactor length [54]:

$$\frac{dP}{dz} = -\left(\frac{150\eta}{D_p^2}\frac{(1-\varepsilon)^2}{\varepsilon^3} + \frac{1.75\rho_0 v_0}{D_p}\frac{1-\varepsilon}{\varepsilon^3}\right)v \quad (1)$$

where $D_p$ is the diameter of catalyst particles, $\eta$is the kinetic viscosity of reactant mixture, $\varepsilon$ is the catalyst bed void fraction, v is the gas velocity, and $\rho_0$ and $v_0$ are the density and velocity at the reactor inlet, respectively.

The heat transfer between the exterior of the reactor wall and reactants in the reactor obeys the Newtonian heat transfer law:

$$J_q = U(T_w - T) \quad (2)$$

where $U$ is the overall heat transfer coefficient, $T_w$ is the temperature of the exterior of the reactor wall, and $T$ is the temperature of the reactant mixture in the reactor.

The equation of energy conservation is [54]:

$$\frac{dT}{dz} = \frac{\pi DU(T_w - T) + A_c\rho_b\sum_j(r_{m,j}(-\Delta_r H_j))}{\sum_i(F_i C_{p,i})} \quad (3)$$

where $j = 1,2$ represents reaction (R1) and (R2), $i = 1-5$ represents the reaction components. $A_c$ is the cross-section area of the reactor, $\rho_b$ is the density of catalyst, and $C_{p,i}$ is the molar heat capacity at constant pressure of the $i$th component. For reaction $j$, $\Delta_r H_j$ and $r_{m,j}$ are the reaction enthalpy and reaction rate per catalyst weight, respectively. $F_i$ is the molar flow rate of the $i$th component [54]:

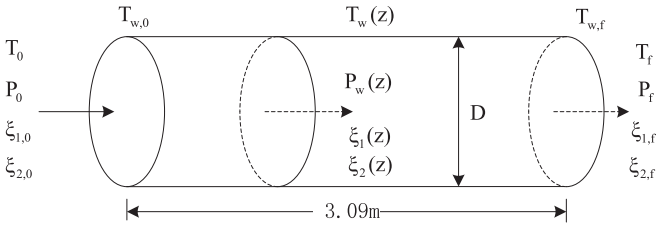


**Fig. 2.** Schematic of the tubular plug-flow reactor.